Adhesion Property of Vertically Aligned Carbon Nanotubes Under High Temperature

Guo Feiqian, *Li Yang* *, *Meng Guiyun*, *Sun Chengxiang*, *Dai Zhendong* *

College of Astronautics, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China

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Abstract: Because of having millions of well vertically aligned hairs on their feet, geckos can fluently walk on the vertical walls and even ceilings. Vertically aligned carbon nanotube (VACNT) array has been widely used as a bio-mimetic adhesive due to the structural and functional similarity with gecko's foot hairs. Besides, the advanced properties of VACNT make it a prominent functional adhesive. In this paper, the dry adhesion of VACNT array under the temperature range of 25—150 ℃ is studied. Because of the intrinsic excellent thermal resistance, VACNT array shows great adhesion under high temperature. When the temperature changes from 25 ℃ to 150 ℃, the shear adhesive strength of VACNT array deceases from 12.04 N/cm^2 to 6.08 N/cm^2. Though there is a 50 percent decrease, the adhesive strength of 6.08 N/cm^2 is still remarkable for dry adhesive materials. The VACNT's micro structures are analyzed by SEM and the adhesion change phenomenon is interpreted in theory. We believe that the robust high temperature adaptation of VACNT dry adhesive can be used in many extreme environments, such as aerospace application.

Key words: carbon nanotubes; adhesion; high temperature

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0 Introduction

Geckos are well-known for their fantastic wall-climbing ability. After years of researching, it has been clear that the remarkable climbing ability comes from millions of well aligned soft hairs covered on their feet[1]. Inspired by this fantastic adhesive ability, a lot of gecko foot mimic adhesive materials have been created. In general, there are two kinds of bio-mimetic dry adhesive materials: polymer-based micro-structured array[2], and the vertically aligned carbon nanotubes (VACNT) array[3].

The mushroom-capped and fibrillar structured polymer array is the first type of dry adhesive material. The pull-off and peel adhesion strengths are more than twice compared with that of the flat-topped structured polymer, and it can be reused just by water washing. At room temperature, polymer adhesive shows a robust dry adhesive ability[4]. However, when applied in extreme environment, such as high temperature, the robust adhesive ability cannot keep well[5].

Due to the structural similarity with gecko foot hairs and exceptional mechanical property, VACNT array as a gecko-inspired dry adhesive has developed rapidly in recent years[6]. Liming Dai fabricated VACNT arrays adhesive with entangled top structures and a strong shear adhesive strength of nearly 100 N/cm^2, which is 10 times that of gecko's[7].

The carbon atoms of carbon nanotube (CNT) are connected by strong covalent sp2 C-C bonds, and CNT has extraordinary thermal conductivity, mechanical, and electrical properties due to its unique chemical structure[8]. It has been proved that CNT can keep well thermal stability under the temperature range of 196 to 1 000 ℃ in atmospheric situation[9]. Thus, VACNT

* Corresponding author, E-mail address: yangli@nuaa.edu.cn, zddai@nuaa.edu.cn.

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dry adhesive may show some application potential at high temperature. In this paper, we investigated the adhesive behaviors of VACNT array in a temperature range of 25—150 ℃.

1 Experiment

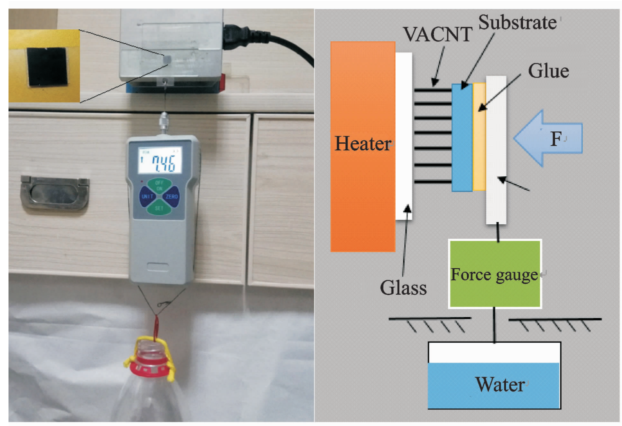
1.1 Synthesis of VACNT

The VACNT samples used for adhesion test are fabricated by low pressure chemical vapor deposition (LP-CVD). A 3-nm thicker Fe film was deposited on SiO_2/Si wafer using electron beam system as the catalyst for VACNT array growth. The growth of VACNT array took place in a quartz tube under 750 ℃, and ethylene was chosen as the carbon source. Firstly, the catalyst was pre-treated with hydrogen for several minutes, which help reduce the metallic form of the catalyst, and the catalyst film splitting into nano particles under high temperature. Then ethylene was blown into quartz tube, and decomposed into carbon atoms were in the presence of catalyst. Finally, these carbon atoms were deposited into Fe particles, and separated from the Fe particles to form the CNT when saturated [10-11]. In addition, because of the interaction between CNTs, VACNT show a uniform aligned topography [12]. The VACNT samples used for force testing have an area of about 8 mm×8 mm, and a height of about 500 μm.

1.2 Adhesive force measurement

Fig. 1 shows the measure system used for shear adhesion test. The as-grown VACNT array with the Si substrate was fixed onto a piece of plastic PET sheet through high-temperature resistant glue. An electric force gauge (270 g) was hang to the bottom of the PET sheet. A glass slide was fixed on top of a heater stage to provide a higher temperature environment.

Firstly, a pre-load F (10 N) was pressed onto the back-side of Si substrate to make sure an intimate contact between CNT and glass slide. Then, by continuously adding water into the downside plastic bottle until VACNT array was pulled off from the glass, the maximum sheer adhesive force was acquired by the force gauge. These tests were operated in the temperature range of 25—150 ℃.



(a) Schematic diagram (b) An 8 mm×8 mm VACNT hanging a bottle of water of nearly 7.46 N

Fig. 1 Sheer adhesive force measurement system

2 Results and Discussion

Table 1 is the shear pull-off force tests result of the VACNT arrays under different temperatures (respectively 25, 50, 100, 150 ℃, and each temperature point is measured for 5 times). The adhesive strength shows a downward trend as temperature increases in Fig. 2, in which the error bars represent the deviations of the forrces measured for 5 samples of the some class. The sheer adhesive strength changed from 12.04 N/cm^2 at room temperature to 6.08 N/cm^2 at 150℃, showing a 50 percent decrease of the maximum pull off force. Even though, the sheer adhesion strength of VACNT array can keep 6.08 N/cm^2 at 150 ℃, which is still remarkable for VACNT dry adhesive materials. However, the structure of thermoplastic polymer will be destroyed under high temperature like 150 ℃.

Table 1 The sheer adhesive force test results

Temperature/℃	25	50	100	150
Adhesion force /N	7.70	6.80	4.51	3.99
	7.46	6.95	4.77	3.72
	7.80	7.21	4.64	3.67
	7.66	6.72	4.35	4.21
	7.90	7.32	4.82	3.88
Adhesion strength /(N·cm^{-2})	12.04	10.94	7.22	6.08

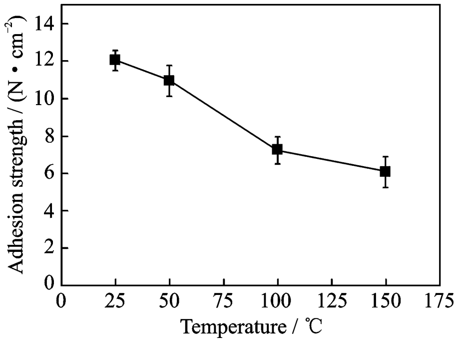
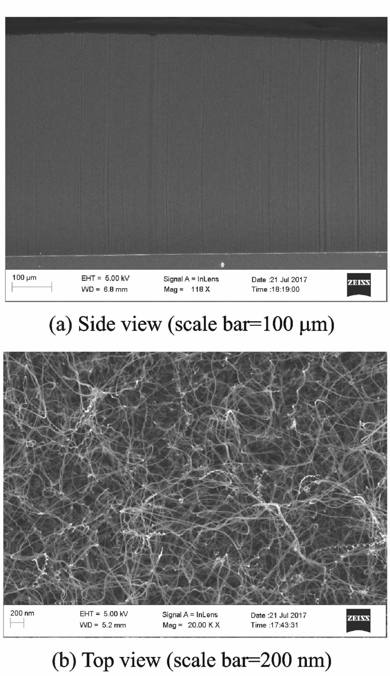


Fig. 2 Sheer adhesive strength of VACNT under different temperatures

2.1 SEM analysis

The scanning electron microscope (SEM) was used to analyze the changes of micro structures of VACNT array. Fig. 3(a) is the side view of the VACNT array, in which we see the length of VACNT array before sheer force tests is about 500 μm. The top view (Fig. 3(b)) shows that the curly CNTs entangled with each other and formed net structures. These complex structures can greatly enlarge the interaction area between VACNT array and glass surface during adhesive processes. Plenty of literatures have proved that the well aligned side walls and top curly morphologies are both important for VACNT's sheer adhesion [4].

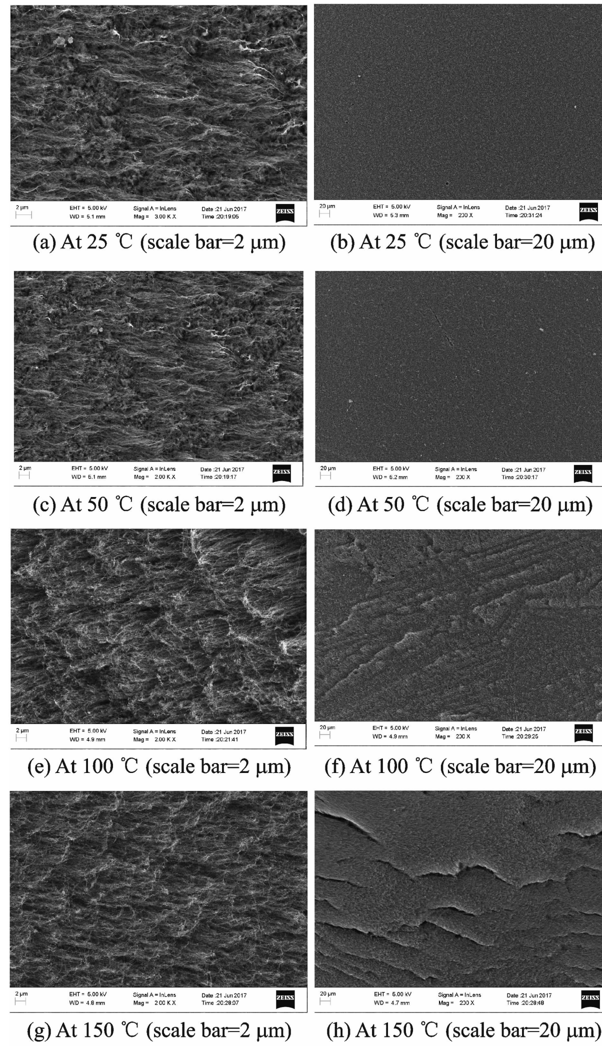
Figs. 4(a, c, e, g) are the high-magnified



(a) Side view (scale bar=100 μm)

(b) Top view (scale bar=200 nm)

Fig. 3 SEM images of VACNT before sheer adhesive force measurement



(a) At 25 ℃ (scale bar=2 μm) (b) At 25 ℃ (scale bar=20 μm)

(c) At 50 ℃ (scale bar=2 μm) (d) At 50 ℃ (scale bar=20 μm)

(e) At 100 ℃ (scale bar=2 μm) (f) At 100 ℃ (scale bar=20 μm)

(g) At 150 ℃ (scale bar=2 μm) (h) At 150 ℃ (scale bar=20 μm)

Fig. 4 SEM images of VACNT after sheer adhesive force measurement under different temperatures

top view images of VACNT arrays after sheer force tests under different temperatures. The randomly oriented top side of VACNT before shear test (Fig. 3(b)) changed to an obviously alignment (Figs. 4(a, c, e, g)) after sheer drag. The alignment of top layer CNTs further enlarges the contact area due to the side contact area increase. However, there is no big difference between top morphology of VACNT after shear test under different temperatures.

From the lower-magnified SEM images of top view of VACNT (Figs. 4 (b, d, f, h)), obvious difference appeared after shear test under different temperatures. With the increase of temperature, some aggregation and short wrinkles gradually generated (Figs. 4 (f, h)). It might because the relative movement between VACNT array and glass slide increased with an increase in the temperature. What's more, these wrinkles also change the flatness of VACNT array, which further damages the interfacial interaction between VACNT and glass slide. The wrinkles might play an important role in the decrease of VACNT's sheer adhesion (Fig. 2). Wrinkles in Fig. 4 (h) show that original vertically aligned CNTs get forked due to the shear drag and temperature increase (their side walls were divided during sheer pulling procedure). This suggested that temperature might affect the interaction between CNT's side walls.

2.2 Theoretical analysis

It has been demonstrated that van der Waals (vdW) forces play a significant role in the adhesion between CNTs and glass slides[13-14]. The vdW forces are the distance dependent interactions between atoms or molecules, and they decreased quickly at long distance. This is why we give VACNTa pre-load to make intimate interfacial contact. The vdW forces are universal, and all atoms and molecules can attract one another through this mechanism[15-16]. The vdW forces include the force between permanent dipoles (Keesom force), the force between a permanent dipole and a corresponding induced dipole (Debye force), and the force between instantaneously induced dipoles (London dispersion force). It has been proved that the vdW forces are independent of temperature except Keesom force[17]. So there is sufficient support to consider that the Keesom force is responsible for the decrease of the adhesive forces in our experiments.

The attractive vdW forces, however, become less important with an increase in temperature, because a rise in temperature increases the disordering of molecules due to increasing molecular motion[17]. In our experiments, the attractive vdW forces between the side walls of VACNTs are weaken due to the high temperature. Thus, during sheer pulling, the CNT's side walls are easily gotten forked in some weak area and forming winkles. As discussed before, these winkles play a negative role in VACNT's adhesive behaviors. On the other hand, the high temperature directly weakens the attractive vdW forces between VACNT and glass surface. Altogether, we believe one of the reason for VACNT's sheer adhesion decrease under high temperatures is the decrease of attractive vdW forces.

3 Conclusions

In this paper, we have investigated the adhesive behaviors of VACNT array under different temperatures. From the experiments, we found that higher temperature (>100 ℃) has a negative effect on VACNT's shear adhesive force. The shear adhesive force shows a 50 percent decrease from 25 to 150 ℃. Through SEM analyses, some winkles are found to emerge after sheer sliding between VACNT array and glass when temperature is over 100 ℃. These winkles play a negative role in VACNT's adhesion through damaging the interaction between VACNT and glass slide. In theory, the attractive vdW forces play a main role in VACNT array's dry adhesion, which will decrease when the temperature increases. These theoretical analyses are well consistent with our experimental results.

However, VACNT array can keep a sheer adhesion strength near 6.08 N/cm^2 even at 150 ℃, which is still remarkable for dry adhesive materials. In future, we believe that through tuning the microstructure of VACNT, it could exhibit more excellent adhesion properties and show good potential for adhesive in extreme environments, such as industrial environments and out space.

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Mr. **Guo Feiqian** is a graduate student of Nanjing University of Aeronautics and Astronautics. His research interests focus on carbon nanotube adhesive materials.

Dr. **Li Yang** is currently a postdoctor of Nanjing University of Aeronautics and Astronautics. His research interests focus on bio-inspired nano-materials.

Ms. **Meng Guiyun** received her M. S. degree in Nanjing University of Aeronautics and Astronautics in 2018. Her research interests focus on carbon nanotube adhesive materials.

Mr. **Sun Chengxiang** is a graduate student of Nanjing University of Aeronautics and Astronautics. His research interests focus on the adhesion and friction of nano-materials.

Prof. **Dai Zhendong** is professor of Nanjing University of Aeronautics. His research interests focus on biomimetic robots, friction/adhesion of bionic materials and dynamics of animal.

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