FABRICATION OF MICRO-NANO HIERARCHICAL STRUCTURES WITH MULTIWALL CARBON NANOTUBES AND POLY(DIMETHYLSILOXANE)

Hui Yun Hwang[1] and Soo Ho Han [2]

[1] Department of Mechanical Design Engineering, Andong National University, 1375, Kyeongdong-ro, Andong-si, Gyeongsangbuk-do, 36729, Republic of Korea
Email: hyhwang@andong.ac.kr (Corresponding author, Presenter)
[2] Department of Mechanical Design Engineering, Andong National University, 1375, Kyeongdong-ro, Andong-si, Gyeongsangbuk-do, 760-749, Republic of Korea
Email: asop852@naver.com

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Abstract
We proposed very easy and cost-effective method to fabricate micro-nano hierarchical structures for synthetic dry adhesives. In order to make hierarchical structures, we suggested selective etching on the micro-pillar structure reinforced with aligned nano-materials. In this study, we applied a dry etching method using plasma and a wet etching method using the solution of tetrabutylammonium fluoride (TBAF) in N-Methylpyrrolidinone (NMP) (3:1 v/v; NMP/75% TBAF in water). We investigated etching rates of each etching methods and observed etched surfaces to verify that nano-structures are well fabricated on the micro-structures.

1. Introduction

Gecko's feet have been very interesting research theme and many researchers tried to mimic them for the application of synthetic dry adhesives. Experts in biology, materials and mechanics reported the superior adhesion of Gecko's feet came from micro-nano hierarchical structures of the soles rather than their material aspects. Numerous methods were suggested for mimicking Gecko's feet and large parts of them were focused on fabricating micro-nano hierarchical structures using highly precision methods such as MEMS or NEMS. However, suggested methods have some limitations such as expensive process, small area, or low durability. Another issue is the material of synthetic dry adhesives. Thermoset or thermoplastic polymers and elastomer were considered for nano-hairy structures and nanomaterials such as nanotubes, nanofibers, and graphenes were used to enhance adhesion characteristics. Polymers and elastomers have low durability and nanomaterials have low productivities and degree of alignment [1-4].
To overcome these limitations, our group proposed the relatively easy and cost-effective method to fabricate micro-nano hierarchical structures for synthetic dry adhesives as shown in Fig. 1. As shown in Fig. 1, micro-structures with aligned nano-materials are fabricated first, and then nano-materials are exposed by etching micro-structures selectively. Finally, we can obtain micro-nano hierarchical structures. Suggested method can have both flexibility of polymeric micro-structures and durability and superior adhesion of nano-structures simultaneously. Also, this method is very cost-effective and can be used to mass production [3-4].
In this study, we used multiwall carbon nanotubes (MWCNTs) as nano-materials and poly(dimethylsiloxane) (PDMS) as elastomers. A glass plate with microholes was used to micro-patterned mold and micro-structures of PDMS with MWCNTs were fabricated. While MWCNT-

PDMS mixture flows on to microholes, MWCNTs were aligned naturally by capillary effects. The solution of tetrabutylammonium fluoride (TBAF) in N-Methylpyrrolidinone (NMP) (3:1 v/v; NMP/75% TBAF in water) removed PDMS selectively, and then aligned MWCNTs were exposed. By SEM (Scanning Electron Microscope) images, we verified that nano-structures (MWCNTs) were well fabricated on the micro-structures of PDMS.

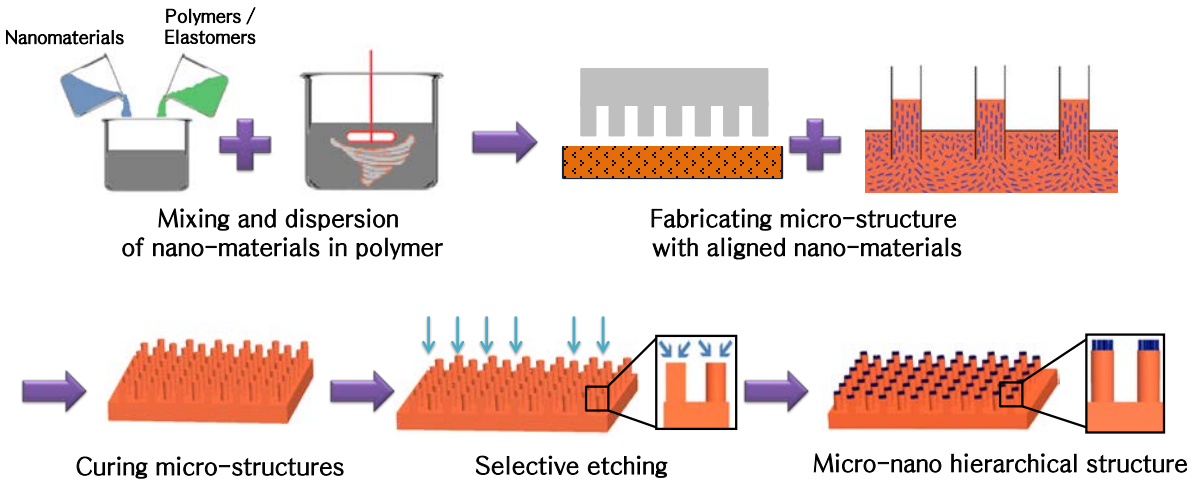


Figure 1. New fabricating method of micro-nano hierarchical structures for synthetic dry adhesives

2. Materials and Methods

2.1. Materials and Fabricating Method of Microstructures

We used PDMS (Sylgard 184) manufactured by Dow Corning and MWCNTs by Carbon Nano-Material Tech. We mixed Sylgard 184 Part A with 0, 1 and 2 wt% of MWCNTs through 3-roll mill (EXAKT, Germany) for 5 times, and then degassing under vacuum for 10 min. Sylgard 184B (Hardener) was added to the mixture of Sylgard 184A and MWCNTs using planetary centrifugal mixer (ARM-310, Thinky, USA) for 2 min, and then degassing again for 10 min.
We heated up the mixture to 60°C and held for 12 min to accomplish 0.5 of the relative degree of cure. Then micro-structure were fabricated by stamping the micro-patterned glass mold onto the mixture, and demolded after 15 min for fully cured state.

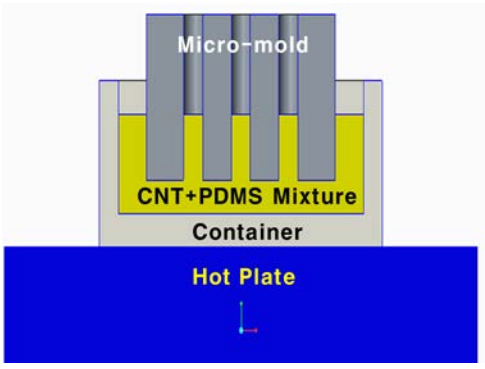


Figure 2. Fabricating microstructures of PDMS reinforced by MWCNTs

2.2. Selective Etching

We applied two different etching methods – dry etching with plasma and wet etching with etching solution [5-6].

Nitrogen and oxygen gas were used as generating plasma with 50 sccm of flow rate using plasma system (Convance, Femto Science, Korea). Plasma power and etching duration were changed.
For wet etching, the solution of tetrabutylammonium fluoride (TBAF) in N-Methylpyrrolidinone (NMP) (3:1 v/v; NMP/75% TBAF in water) was used [5]. The microstructures were immersed into the solution for 2 to 20 min under magnetic stirring, cleaned with NMP for 1 min, ethanol for 1 min and deionized water for 1 min, and then dried under the vacuum.

2.3. Surface Observation

In order to investigate the surface of microstructures, we got the surface images using Field Emission Scanning Electron Microscope (MYRA 3 XMH, Tescan, Czech).

3. Results and Discussion

3.1. Alignment of MWCNTs

First, we checked the alignment of MWCTNs within the microstructures as shown in Fig. 3. Mis-orientatin of MWCNTs was less than 12^{o} and areal density of MWCNTs was more than 80ea/μm^2.

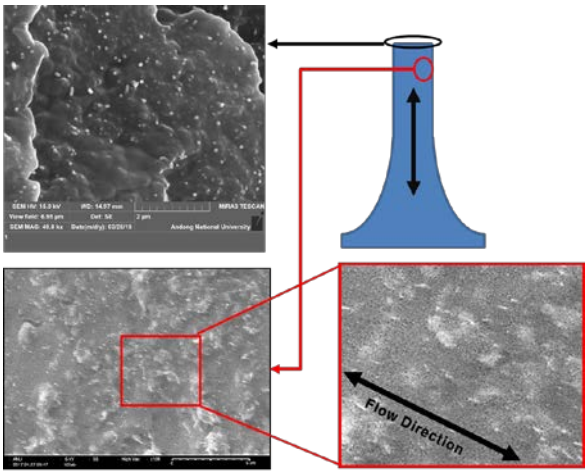
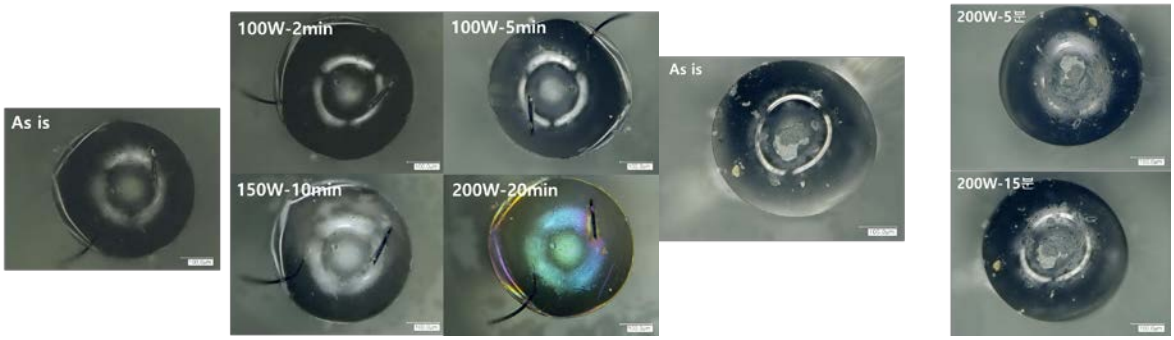


Figure 3. Alignment of MWCTNs within the microstructures

3.2. Dry Etching Results

Fig. 4 shows dry etching results with respect to the etching gas and treatment conditions. Nitrogen and Oxygen gases could not etch but deteriorate PDMS surfaces, which meant no MWCNT was not observed on the top surface of PDMS microstructures.



(a) (b)

Figure 4. Surfaces of dry-etched microstructures with (a) Nitrogen gas and (b) Oxygen gas.

3.2. Wet Etching Results

Wet etching with TBAF-NMP solution could effectively remove PDMS surfaces and exposed MWCNTs were observed as shown in Fig. 5. After 2 min treatment, MWCNTs were exposed on the surfaces but alignment and areal density were under expectation. Considering the etching rate of TBAF-NMP solution is about 5μm/min, 20 min treatment might be severe and changed the shape of microstructures as well as surface morphologies.

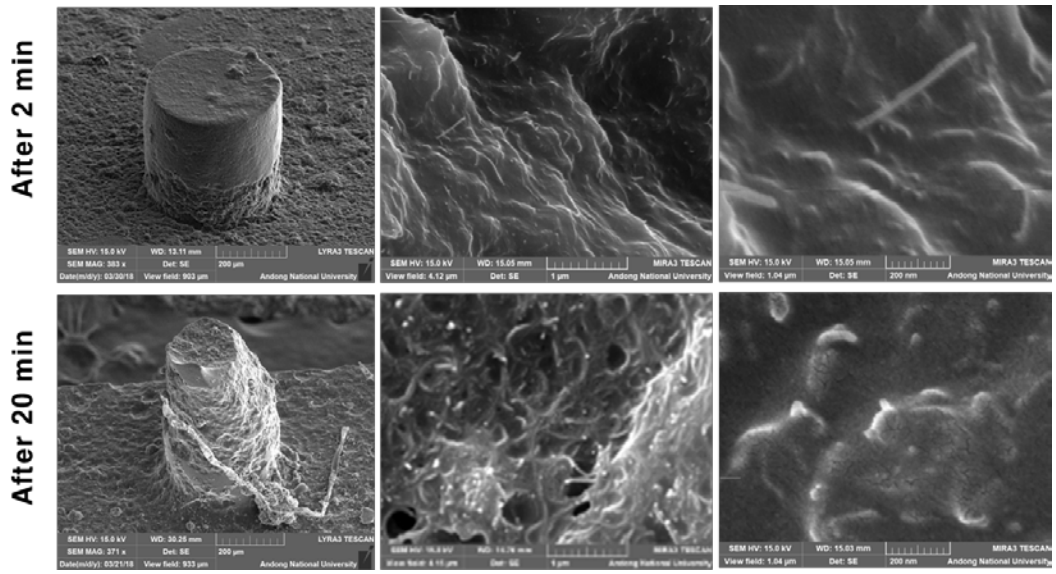


Figure 5. Surfaces of wet-etched microstructures reinforced by 1wt% of MWCNTs with respect to the treatment duration.

4. Conclusions

Presenting authors should upload the full paper on the ECCM18 submission page until May 11th, we used multiwall carbon nanotubes (MWCNTs) as nano-materials and poly(dimethylsiloxane) (PDMS) as elastomers. A glass plate with microholes was used to micro-patterned mold and micro-structures of PDMS with MWCNTs were fabricated. While MWCNT-PDMS mixture flows on to microholes, MWCNTs were aligned naturally by capillary effects. The solution of tetrabutylammonium fluoride (TBAF) in N-Methylpyrrolidinone (NMP) (3:1 v/v; NMP/75% TBAF in water) removed PDMS selectively, and then aligned MWCNTs were exposed. By SEM (Scanning Electron Microscope) images, we verified that nano-structures (MWCNTs) were well fabricated on the micro-structures of PDMS.

Acknowledgments

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