Nanotextured superhydrophobic micromesh

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Abstract

A superhydrophobic micromesh covered with nanoprotrusions has been introduced and its applicability to a waterproof mobile phone speaker has been evaluated. The nanotextured superhydrophobic micromesh showed excellent water repellency, self-cleaning and waterproofing performances. In a waterproof speaker test using the fabricated nanotextured micromesh, the micromesh did not lose its waterproof function at 2 m water depth and did not form a remnant water film after being removed from the water. The packaged speaker showed almost the same sound quality before and after dipping at a 2 m water depth. These results demonstrate that the superhydrophobic nanotextured micromesh could be directly applicable for various products that need to resist water penetration, yet allow the transmission of gases and sound/light waves.

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1. Introduction

With increasing demand in industrial applications, superhydrophobic surfaces have generated much interest in the fields of nano and micro-science and engineering. With discovery of the key to the superhydrophobic and self-cleaning characteristics of a natural lotus leaf by Barthlott and Neinhuis, numerous researchers have attempted to mimic the surface of the lotus leaf[1–9]. It is well known that the surface of the lotus leaf is covered with microprotrusions, which are in turn covered in nanoprotrusions composed of hydrophobic epicuticular wax crystalloids [1]. The maximum achievable contact angle by chemical treatment on a smooth surface has thus far been roughly 120° [10,11]. Topographical surface modification is thus thought to be indispensable to achieve a superhydrophobic surface with a contact angle greater than 150°. Most researchers have thus focused on the hydrophobic effect in terms of the geometry of nano/micropillar shapes [12–21].

Recently, a network-type microstructure covered with nanoprotrusions that maintain a superhydrophobic characteristics and a hydrophobic micromesh with a microhole array for waterproofing have been introduced [22,23]. While the network-type microstructure with nanoprotrusions has a superhydrophobic surface, the bottom of the structure is clogged. Conversely, the hydrophobic micromesh with a microhole array does not clog but its surface is not superhydrophobic. The hydrophobic micromesh showed good waterproofing ability and was successfully utilized to waterproof electronics. However, because of the formation of a water film by water wetting on the micromesh surface and the absence of self cleaning, the non-superhydrophobic characteristic of the micromesh limits its application area, including speakers. Specifically, the water film and dirt on the mesh obstructs the passage of sound waves through the micromesh, leading to sound distortion. In addition, when a water drop collides with the hydrophobic micromesh, it does not bounce on the micromesh surface, but rather adheres to the surface. An attractive solution to the aforementioned problems is to topologically modify the surface of the micromesh with nanoprotrusions.

In this study, we introduce a new micromesh covered with a nanoprotrusion array, which endows superhydrophobicity, self cleaning, and waterproofing, and evaluate its applicability for a waterproof speaker. The nanoprotrusion array decreases the contact area between water droplets and the structured surface, thereby enhancing water-repellency. The microhole array resists water penetration, yet allows the passage of gases and material waves such as sound and light. Henceforth, the micromesh covered with nanoprotrusion array is referred to as a nanotextured micromesh. To evaluate the influence of nanoprotrusions, nontextured micromeshes were also characterized.

2. Theory and design

The proposed nanotextured micromesh is illustrated in Fig. 1(a). In the proposed structure, a water drop does not wet the bottom or side faces of the nanoprotrusions; rather, it is lifted by the
structures. Therefore, this designed structure follows Cassie and Baxter's wetting model [24]. The apparent contact angle ($\theta$) based on Cassie and Baxter's model is

$$\cos \theta = -1 + f(\cos \theta_0 + 1).$$

Here, $f$ is the solid fraction defined as the ratio of the wetting area of the rough surface to the projected area and $\theta_0$ is the contact angle of a water drop on a smooth surface. The contact angle ($\theta_0$) of a smooth surface coated with a plasma polymerized fluorocarbon (PPFC) layer was measured to be $103^\circ$ and was used for the calculation. A hexagonal-shape unit cell was defined for the calculation of the ratio of the wetting area, as shown in Fig. 1(a). The solid fraction of each unit cell can be expressed as $f = [\pi \cdot (c/2)^2 \cdot n]/[2\sqrt{3} \cdot (a/2 + b)^2]$. Here, $n = [2\sqrt{3}(a + b) \cdot b]/[(c + d)^2]$ is the number of nanoprotusions that formed on the hexagonal-shape unit cell in Fig. 1(b). The design parameters $a$ and $b$ represent the hexagonal microhole width and mesh width, and $c$ and $d$ represent the diameter and spacing at the top of the nanoprotusions. The apparent contact angle can be obtained by substituting $f$ in Eq. (1). Therefore, the apparent contact angle is expressed as

$$\theta = \cos^{-1} \left[ -1 + \frac{\pi \cdot (c/2)^2 \cdot n}{2\sqrt{3}(a/2 + b)^2} (\cos \theta_0 + 1) \right].$$

The values of each parameter measured from the fabricated sample are as follows: $a = 10 \mu m$, $b = 5 \mu m$, $c = 600 nm$, and $d = 1.4 \mu m$. Therefore, $n$ is 64 and the calculated contact angle is $163^\circ$.

To evaluate the waterproof ability of the micromesh, it is necessary to understand the maximum allowable hydraulic pressure ($P_m$) that can withstand penetration of the water. As the applied hydraulic pressure ($P$) increases, the water front expands over the top surface and $\phi$ is also increased, as shown in Fig. 1(b). The equilibrium equation between the surface tension and the hydraulic pressure is expressed as

$$P = \frac{4\gamma}{a} \cdot |\sin \phi|$$

Here, $\gamma$ represents the surface tension of the water ($0.073 N/m$). When $\phi$ approaches $90^\circ$, the applied hydraulic pressure reaches its maximum value. The pressure at this moment is the maximum allowable hydraulic pressure and is concisely expressed as, $P_m = 4\gamma/a$. Here, the hexagonal microhole width ($a$) is $10 \mu m$. Therefore, the theoretical maximum allowable hydraulic pressure is calculated to be $29 kPa$.

3. Fabrication and packaging

3.1. Fabrication of nanotextured micromeshes

Fig. 2 shows schematic illustrations of the process sequence for the fabrication of a nanotextured micromesh. First, photolithography using SU-8 2002 (MICROCHEM, USA) and reactive ion etching (Oxford Instruments, UK) was sequentially carried out on a 6-in. Si wafer (LG Siltron, Korea) (Fig. 2(a)). The depth and width of the etched micropores were $1.5 \mu m$ and $1.6 \mu m$, respectively. Next, the remnant photoresist was removed via oxygen plasma ashing (Plasma finish, Germany) and a $500 nm$-thick Cr conducting seed layer was deposited by a sputtering system (A-tech, Korea) (Fig. 2(b)). A second photolithography step was then carried out using AZ9260 (AZ-Electronic Materials, USA), followed by
3.2. Packaging of the fabricated nanotextured micromeshes

3.2.1. Packaging for waterproof test to measure maximum allowable hydraulic pressure

Fig. 4 shows the packaged nanotextured micromesh for the waterproof test. The edges of the mesh were bonded on an acryl jig using epoxy (product #84101, Permatex, USA). A 10 mm hole was drilled in the center part of the acryl jig, and a urethane tube was connected to the bottom of the jig, as shown in Fig. 4(a). Water is inserted through the tube and thus the mesh directly received the hydraulic pressure. The tube has an inner diameter of 8 mm and a length of 3 m, and it is transparent and flexible. The acryl jig was then fixed in an aluminum case to minimize movement during measurements, as shown in Fig. 4(b).

3.2.2. Packaging for sound pressure tests before and after water penetration

Fig. 5(a) and (b) shows a schematic view and a photograph of a nanotextured micromesh packaged with a commercial mobile phone speaker (MPR100012, Microphone, Korea) to investigate the sound pressure difference before and after water penetration into the packaged cavity, respectively. The speaker was inserted and fixed inside of an acryl jig, which has the same shape and size as that used for the waterproof test, as shown in Fig. 4. A nanotextured micromesh was bonded on the top of the acryl jig and the bottom of the acryl jig was sealed to prevent water intrusion.

4. Measurement and discussion

The contact angles were measured using a contact angle-meter (SEO, Korea). The water used for measurement of the contact angles was deionized (DI) water and the volume of a single water droplet was 4 μl. The measured contact angle was the average obtained from five measurements. Fig. 6(a) and (b) shows captured images of water droplets on the nanotextured top surface and the nontextured bottom surface, and their contact angles were measured to be 156° and 110°, respectively. These results verify that the nanoprotrusions decrease the contact area between the water droplet and the mesh surface, and thus the surface of the nanotextured micromesh becomes superhydrophobic. This superhydrophobicity enhances the self-cleaning capability of the micromesh as well.

Fig. 6(c) and (d) are respective self-cleaning test images captured from the nanotextured surface and nontextured surface. The soils (size range: 15–88 μm) were sprinkled on the mesh samples. The meshes were set at an angle of 10° to the flat surface and a 6 μl-volume water droplet was dispensed on the mesh samples. In the case of the nanotextured surface shown in Fig. 6(c), the water droplet rolls and the area where water passes through the surface is clean. However, in the case of the nontextured surface shown in Fig. 6(d), the water droplet does not roll but instead is pinned and soil particles remain on the surface.

Fig. 7(a) and (b) are respective time lapse series of images of collisions of water droplets on the nanotextured top surface and the nontextured bottom surface. A 6 μl water droplet fell freely from a height of 30 cm. While the water droplet impinging on the nontextured bottom surface was pinned, that on the nanotextured top surface was bounced. The average bouncing height of the water droplets on the nanotextured top surface was measured to be 15 mm. Comparing respective images captured at 0.1 s of Fig. 7(a) and (b), the spreading diameter (7 mm) of the water droplet that collided with the nanotextured surface is 2 mm larger than that (5 mm) of the water droplet that collided with the nontextured surface. Nanoprotrusions lift the spreading water droplet, and thus the contact area between the spreading water and solid surface is reduced, resulting in low surface friction drag. It is well known that
Fig. 3. SEM images and photographs of the fabricated mesh samples. (a) SEM image of a fabricated nanotextured micromesh (nanotextured top surface); (b) SEM image of a fabricated nontextured micromesh (nontextured bottom surface). (c) Photograph of a fabricated nanotextured micromesh unit sample, where the overall size is 15 mm × 15 mm. Due to the through-holes, the mesh is semi-transparent and thus the PNU logo behind the mesh can be clearly seen.
a nanotextured superhydrophobic surface can effectively reduce surface friction drag [17,25–27]. Because of low surface friction on the nanotextured surface, the dynamic energy of the water droplet is less dissipated during collision compared with the case of the nontextured surface. The low energy dissipation involved in spreading and gathering during the water collision facilitates bouncing of the water droplet. In contrast, the high surface friction on the nontextured surface results in high energy dissipation. Because the dynamic energy dissipation of the water droplet and the surface energy of the nontextured surface are relatively high compared with the case of the nanotextured surface, the water droplet does not bounce on the nontextured surface. Regardless of whether the surface is nanotextured or nontextured, water penetration through the microholes was not observed in the collision experiment due to the small microhole size. This is caused by the size effect in the micro realm: at a micrometer scale, the surface tension of the water is more dominant than momentum caused by the impact. When the hole size increases, on the other hand, the surface tension effect is weakened but the momentum effect is increased. Water may thus penetrate through the holes, and the mesh thereby loses the waterproof function.

The maximum allowable hydraulic pressure of the fabricated nanotextured micromesh was measured and its waterproof ability was evaluated. Initially, water was filled inside the tube. After adjusting the height of the water surface such that it corresponded with the nanotextured micromesh, the water surface was elevated by raising the opposite end of the tube. Therefore, the applied hydraulic pressure could be determined by measuring the elevated height of the tube. A high speed charge-coupled device (CCD) camera (SR-Ultra-C, Kodak, Japan) was used to capture the penetration of water through the holes of the nanotextured micromesh. Fig. 7(c) shows high-speed camera images of the penetration of water through microholes on the nanotextured surface. The maximum allowable hydraulic pressure of the nanotextured micromeshes was measured to be 22.5 kPa. This value corresponds with 2.3 m of water. The measured maximum allowable hydraulic pressure was the average obtained from five measurements. The measured pressure value of 22.5 kPa was about 22.5% lower than the calculated pressure value, i.e., 29 kPa. The main reason for the gap is thought to be imperfect hole size and shape. Although the microfabrication method used is very precise, every hole cannot be fabricated with the exactly same size and a perfectly hexagonal shape. In the waterproof test, water first penetrates through the largest hole among all holes.

5. Application of the nanotextured micromesh: waterproof speakers

In order to evaluate the applicability of the fabricated nanotextured micromesh, sound pressure level tests for the waterproof speakers packaged with fabricated mesh sheet samples were conducted in an anechoic room. The packaged speaker with a nanotextured micromesh shown in Fig. 5(b) was dipped into water, as shown in Fig. 8(a). The maximum depth and width of water filled in the acrylic container shown in Fig. 8(a) is 2.5 m and 30 cm, respectively. Under a water depth of 2.2 m the packaged sample prevented penetration of water. To compare the sound pressures before and after water penetration into the cavity, 2 m and 2.2 m
Fig. 6. (a) and (b) Respective water droplet images to measure the contact angles (CAs) of the nanotextured top surface and nontextured bottom surface. (c) Time lapse images of self-cleaning test for nanotextured top surface. Because of superhydrophobicity (CA = 156°), the sprinkled soils (size range: 15–88 μm) were removed along the path where the water drop passes. (d) Time lapse images of self-cleaning test for nontextured bottom surface. Because of weak hydrophobicity (CA = 110°), the water droplet does not roll and the sprinkled soil particles were not removed.

Fig. 7. (a) Time lapse images of water collision on the nanotextured top surface. (b) Time lapse images of water collision on the nontextured bottom surface. A 6 μl water droplet fell freely from a height of 30 cm. While the water droplet bounced on the nanotextured top surface (bouncing height = 12 mm), that on the nontextured bottom surface did not bounce. (c) Time lapse images of water penetration through microholes. Hydraulic pressure was applied to the bottom side of the mesh.
water depths were selected for each case. Although the degree of water penetration into the cavity cannot be easily distinguished through the captured photographs shown in Fig. 8(b) and (c), we could clearly detect the water penetration into the cavity during the measurement. Fig. 8(d) shows a sound pressure level test image of the speaker packaged with a nanotextured micromesh in an anechoic room. White noise in the audible frequency band (20 Hz to 20 kHz) was input into the packaged speaker. A microphone (Free-field microphone type 4189, B&K, Denmark), which was installed 20 cm away from the packaged speaker, received the sound pressure generated from the speaker.

The mesh prevented water from penetrating under a water depth of 2.2 m fairly well. Beyond that depth, water abruptly intruded into the cavity through the microholes, and the intruded water thus wetted the speaker. The maximum waterproofing water depth (2.2 m) in the waterproof speaker test is 10 cm less than the maximum allowable water depth (2.3 m) in the waterproof test. This is thought to be attributable to damage by the relatively delicate and complicated process involved in packaging waterproof speaker.

Fig. 9 clearly shows the difference in the sound pressure levels before and after water penetration into the packaged cavity. The speaker, which was dipped in water to a depth of 2 m and was not wetted (triangles), did not show a serious sound pressure difference as compared with measurements conducted prior to dipping into the water (initial state, circles). This good sound pressure is due not only to the microhole enabling waterproofing but also the nanoprotusions enabling the absence of a water film. On the other hand, the sound pressure of the speaker, which was dipped in 2.2 m deep water and was wetted (squares), abruptly decreased beyond 2 kHz. The sound pressure of the wet speaker was on average 18.2 dB(A) lower than that of the first non-wetted speaker in a frequency range of 2–20 kHz. Water that penetrated the cavity limits movement of the speaker diaphragm, resulting in distortion and degradation of the sound pressure. This test result verifies that the proposed nanotextured micromesh is very promising for application to various waterproof products including audio speakers.

6. Conclusion

The fabricated nanotextured micromeshes provide three important functions: superhydrophobicity, self cleaning, and waterproofing. Due to the nanoprotusion array, the contact angle measured from the nanotextured surface was 156°, which was 46° higher than that measured from the nontextured surface.
This high contact angle modifies the surfaces of the nanotextured micromeshes to be superhydrophobic and endows a self-cleaning capability. Microholes resist water penetration, yet allow the passage of gases and material waves such as sound and light. The micromesh blocked the water penetration up to 2.3 m water depth. The nanotextured micromesh showed good water collision behavior. While water droplets impinging on the nontextured bottom surface were pinned, droplets on the nanotextured top surface bounced. In an application test, a mobile phone speaker was packed with the fabricated nanotextured micromesh and dipped 2 m deep water. The speaker did not become wet and not show a serious sound pressure difference with the speaker prior to dipping in the water. Through practical performance evaluations of the fabricated nanotextured micromesh, we confirmed that the micromesh could be applied various products where water penetration must be prevented while allowing passage of gases and sound/light waves.

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References


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