ANALYZE THE SHAPING CHARACTERISTICS OF MICRO-CYLINDRICAL-POST IN MANUFACTURING PROCESS OF A SUPERHYDROPHOBICITY FILM

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Abstract - Superhydrophobic films (SHF) have recently increased in routine due to their non-wettable capacity. Superhydrophobicity can be occurred by making a micro-structural-post on materials with the surface having a low energy level. Thus, the shaping characteristics of the micro-structural-post should be considered. This paper analyzes the influence and evaluates the characteristics of micro-cylindrical-post having different parameters to the superhydrophobicity of PUA film. Firstly, the structure and characteristics of Polyurethane Acrylate (PUA) material are introduced. Moreover, the manufacturing process to create the microcylindrical-post on PUA film is illustrated. Finally, the influence of the different shaping parameters of micro-cylindrical-post on the superhydrophobicity of PUA film is evaluated and analyzed.

Key words - Superhydrophobicity material; manufacturing process; Shape optimization

1. Introduction

Superhydrophobic films (SHF) have recently increased in routine due to their non-wettable capacity [1]. In material science, the superhydrophobicity (or ultra-hydrophobicity) is a phenomenon to help the surface immensely difficult to wet or having a non-wettable capacity [2]. Moreover, the superhydrophobic capacity is defined by contact angle between water-droplets and the surface which should be more than 150° angle, as shown in Figure 1. The superhydrophobicity can be easily seen in nature by the features of the lotus leaves (called by name "Lotus effect"). When the water drops down on the Lotus leaf, it cannot remain on the leaf surface due to the needle-shaped wax tubes covering all the leaf surface [3]. Furthermore, some dirty particles or dusts can be also removed by water droplets because of mircro/nano tubes on the leaf surface, which retrict the adhesion of droplet on the leaf surface [3], [4]. Nowadays, the hydrophobic phenomenon can be seen widely due to fabricating artificial surfaces with superhydrophobic ability. They can be appeared normally in our house with anti-sticking fan, antibiofouling paint, and dust-free glass; or in vehicle with windshield and solar-cell panel [4]. Sometimes the superhydrophobic surface can be seen on shoes because the material surface of shoes has shark-texture-skin in microstructure [5].

Superhydrophobicity can be occurred by making a microstructural-post on materials with the surface having a low energy level. There are several methods to fabricate the superhydrophobic surface, such as: electrospinning, wet chemical reation, chemical etching, photolithography, lithography... [3] However, all these methods can be classified into two mainly purposes: making micro/nanostructures on superhydrophobic subtracted; and/or modifying by chemistry to create hydrophobic surfaces with a low surface energy. For making micro/nanostructures on superhydrophobic subtracted, lithography, electrospining and photolithography methods are usually used to create micro/nano patterns on the material for surface roughness with micro-posts [1], [3]. Whereas, to modify by chemical methods, the superhydrophobic surfaces is created by some wet chemical reactions to control dimensional micro/nano structures by nanofibers or nanoparticles [2], [4].



Figure 1. Water contact angle

For some applications which we meet usual on daily (such as: windshields of vehicles, solar-cell panels, door glasses...), the synthesizing approaches by coating the material with low surface energy on a micro/ nanostructures surface can be used much more than the others [6]. One of common materials for superhydrophoic film using for solar panels or windshields which required properties of transparent and flexible is PDMS/PUA material [7]. The PDMS layer having high hydrophobic capacity but hard to make a thin form is coated to microstructure of a thin PUA layer [8], [9]. Similarity, nanosilica can also by sprayed on microstructure of a thin PUA layer to preceduce the coating process for the superhydrophobic film [10]. Depends on the diffence in approaches [11-13], the manufacturing system for those superhydrophobic films can be economical and multiscale manufacturing process.

This paper analyzes the influence and evaluates the characteristics of micro-cylindrical-post having different parameters to the superhydrophobicity of PUA film. First of all, the structure and characteristics of PUA material are introduced. Moreover, the manufacturing process to create the micro-cylindrical-post on PUA film is illustrated. Finally, the influence of the different shaping parameters of micro-cylindrical-post on the superhydrophobicity of PUA film is evaluated and analyzed.

2. Characteristics of PUA material

Polyurethane Acrylate (PUA) material is widely applied due to its authentic characteristics, such as: low viscoscity, high solution, 3D architectures and easily making a thin film [9]. In daily, PUA material can be seen in some applications such as painting, adhesives, membranes, foams, packing overcoat films... The PUA material can be created by combining Polyurethane (PU) and Polyacrylate (PA) emulsion, some commercial products of PUA material are introduced in Table 1 [14]. There are two main types of PUAs: UV-curable PUA and waterborne PUA. Obviously, waterborne PUA can be especially applied to industrial painting process;whereas UV-curable PUA is major spreadly used due to its advantages (low environmental impact and energy consumption [15].

Trade name	Provider	Using purposes
EB280; EB265	SK-Cytec	Prepolymer
M3130	Miwon Specialty Chemical Co.,Ltd	Modulator for hard mold
M3160		Modulator for normal grade
M3150		Modulator for soft mold
Rad2200N	TEGO Che.Service	Releasing agent
Irgacure 184; Darocur 1173	Ciba Spec. Chem. Inc.	Photoinitiator

Table 1. Some commercial product of Pre-PUA materials

The UV-Curable PUA is usually used as mold or base for the others attached on [7], [9]. In general, the PUA mold material comprises Urethane for a functionalized prepolymer, photonitiator and UV-curable releasing agent to modify the surface energy. Furthermore, the prepolymers with urethane acrylate plays a role as adhesives to support the completed films having flexibility, durability, abrasion resistance and good hardness. Thus, UV-Curable PUA is commonly used as a base material or the mold material. However, PUA is one type of hydrophilic material (WCA is lower than 90⁰); hence, to make a superhydophobic film, PUA is combined with the other materials having hydrophobic capacity (PDMS, nanosilica...) [16].

3. Manufacturing process PUA/PDMS film

Firstly, the micro-cylindrical-post is fabricated on the surface of PUA film. In general, as shown in Figure 2, the size of a microcylindrical-post is determined by its diameter 'd' and height 'h'; whereas pitch distance 'a' between posts can be defined by a parameter to create an equal array on the surface of PUA film. Also, a mold with negative patterns is used to make the positive patterns on the surface of PUA film. This process is called by 'Copy and Paste' process when PUA film is transferred all the designed pattern from a mole to its surface with the support of UV light. Furthermore, for purposes of making very thin PUA film and multiscale manufacturing process, a roll-toroll system (R2R) can be used as illustrated in Figure 3 [17]. The mold and PUA film are superimposed on each other and pressed by two or three rollers of machine to make a thin film. In this research, various parameters of microcylindrical-posts are used, consisting of 10(µm) or $20(\mu m)$ for diameter 'd', and $20(\mu m)$ or $27(\mu m)$ for height '*h*', respectively. Furthermore, the pitch distance '*a*' between micro-posts is varied from 40 to $120(\mu m)$ [14].

7



Figure 2. Schematic of different designs for structure of micro-post array: (a) 3-D View; (b) Top-view



Figure 3. Multiscale manufacturing process with R2R system [17] (Open access)



Figure 4. Illustration for fabrication process of PUA/PDMS film

Furthermore, the fabrication process of PUA/PDMS film is illustrated in Figure 4. For beginning, the PDMS prepolymer layer is placed on the PUA film with positive pattern. Some solvents (such as Toluence, or some green solvents...) can be use to dilute the PDMS prepolymer. Then, the diluted PDMS is spray-coated on PUA surface; this process helps the PDMS layer can uniformly wet on rough surface of the initial PUA film by the spray pressure [18]. In the following, the spray-coated PDMS on PUA film is replaced on the Teflon film and heated with temperature 100°C-150°C [19] to reduce curing time and forming the PDMS/PUA film as soon as possible.

4. Results and discussion

4.1. Various shapes of micro-cylindrical-post

The rough surfaces of PDMS/PUA film with various shapes of micro-cylindrical-post arrays are shown by scanning electron microscope (SEM) images in Figure $5 \div 7$. Based on the SEM images, the fidelity of micro-post corresponding the different parameters of its shape is revealed. As be seen in Figure 5 and Figure 6, when the pitch distance 'a' is increased, the denisity of micro-post in same

square unit is reduced. Besides, the quality of micro-post having a small diameter (such as 10μ m) is also guaranteed to fabricate on PUA film. Furthermore, the SEM images of the fabricated surfaces with various pitch distances of microcylindrical-post are illustrated in Figure 7. During the coating process, the thin PDMS layer is covered on the surface of PUA film and the PUA/PDMS film is created. To evaluate the hydrophobic capacity of the fabricated films with various parameters of micro-cylindrical-post arrays, the WCA testing process can be applied by using the optical images for a water droplet on the fabricated surfaces.



Figure 5. The SEM images before coating process of 10 (μm) of diameter 'd' and 20(μm) of height 'h' of micro-cyclindrical-post with 120 (μm) of pitch distance 'a'



Figure 6. The SEM images of $20(\mu m)$ of diameter 'd' and $27(\mu m)$ of height 'h' of micro-cyclindrical-post with $40(\mu m)$ of pitch distance 'a'



Figure 7. The SEM images with various pitch distances of micro-cylindrical-post

4.2. Water contact angle

Figure 8 shows a checking result of water contact angle (WCA) for water droplet on the the 10- μ m diameter and 20 μ m-height post array with 120 μ m pitch distance. In general, WCA, surface tension and interfacical tension of this test can be measured by the optical tensiometer (or called by the name "goniometers"). Based on this optical image as shown in Figure 8, the WCA for a droplet on a surface can be determined.



Figure 8. The optical image of water droplet on the 10-µm diameter and 20µm-height post array with 120 µm pitch distance

The results of WCA for a droplet on fabricated films with various parameters of micro-cylindrical-post arrays are illustrated in Figure 9. As the figure shows, the surfaces with a more considerable pitch distance for micro-posts have a higher value of WCA than those with a smaller pitch distance for micro-posts. Furthermore, diameter of micro-cylindrical-post also affects the WCA. At the same value of pitch distance, the micro-cylindrical-post having a smaller diameter has higher WCA than the one with a larger diameter. This can be due to reducing contact area fraction when the pitch distance between micro-posts is increased. It points that at the wetting state there is an air pocket trapped between the contact surface and droplet which supports the droplet existing between the microcylindrical-post. The size of this airpocket is determined by value of diameter and pitch distance of micro-cylindrical-post. When diameter is decreased and pitch distance is increased, the size of airpocket is increased then the WCA is also raised in the following. However, when pitch distance of micro-post array is increased over 90(µm), the value of WCA cannot be increased. The air pocket trapped can be not enough stable to support the water droplet if pitch distance is increased more than 90(µm). Whereby, the transition between Cassier Baxter state to Wenzel state can be occurred when the water is allowed to intrude into space between micro-posts and decreased the value of WCA from its maximum value. On the other hand, the superhydrophobic performance is easily occurred for micro-cylindrical-post with 10µm of diameter without considering to pitch distance between micro-posts and height of micro-post. However, contact angle of micro-post arrays with $20(\mu m)$ height can be more than 150° when their pitch distance between micro-posts is more than 70(µm). Obviously, the hydrophobic capacity is only happened with the fabricated films having 20µm of micro-post's diameter and lower than 70(µm) between micro-posts, Finally, the height of microclyndrical-post does not much influence to the superhydrophobicity of the fabricated films between microposts with 20µm of height and 27µm of height (WCA~156° with 20µm of height and WCA~158° with 27µm of height).



Figure 9. The static contact angles of different arrays of micro cylindrical post fabricated on PUA/PDMS film

5. Conclusions

The paper presents the influence and evaluates the characteristics of micro-cylindrical-post having different parameters to the superhydrophobicity of PUA film. In coating process, PUA film is cover by a PDMS prepplymer layer to make the superhydrophobiciy.

Some opinions can be concluded from this paper in the following:

- Pitch distance between micro-posts and diameter of micro-cylindrical-post influence much to the superhydrophobicity of the fabricated. The microcylindrical-post having a smaller diameter has higher WCA than the one with a smaller diameter. Whereas, the surfaces with a more considerable pitch distance for microposts have a higher value of WCA than those with a smaller pitch distance for micro-posts. This can be due to reducing contact area fraction when the pitch distance between micro-posts is increased. However, when pitch distance of micro-post array is increased over 90(µm), the value of WCA cannot be increased.

- The superhydrophobicity is easily occurred for microcylindrical-post with $10\mu m$ of diameter without considering to pitch distance between micro-posts and height of micro-post.

- The height of micro-clyndrical-post does not much influence to the superhydrophobicity of the fabricated films between micro-posts with 20 μ m of height and 27 μ m of height (WCA~156° with 20 μ m of height and WCA~158° with 27 μ m of height).

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