



Doctor of Philosophy

Fabrication of durable polymer-based

superhydrophobic surface with silica nanoparticles

The Graduate School of the University of Ulsan School of Mechanical Engineering

Oyunchimeg Erdene-Ochir

Fabrication of durable polymer-based superhydrophobic surface with silica nanoparticles

Supervisor: Professor Doo-Man Chun

A Dissertation Submitted to the Graduate School of the University of Ulsan in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

by

Oyunchimeg Erdene-Ochir

School of Mechanical Engineering University of Ulsan, South Korea February 2022

Fabrication of durable polymer-based

superhydrophobic surface with silica nanoparticles

This certifies that the thesis of Oyunchimeg Erdene-Ochir is

approved

Committee Chairman:

Professor Chung, Koo-Hyun

Committee Member:

Professor Chun, Doo-Man

Professor Kim, Dong-Kyu Committee Member: Professor Lee, Yoon Ho Committee Member:

Committee Member:

Professor Kim, Chung-Soo

School of Mechanical Engineering University of Ulsan, South Korea February 2022

Acknowledgments

First and foremost, I am extremely grateful to my supervisor, Prof. Doo-Man Chun, for his invaluable advice, support, and patience during my Ph.D. study. His immense knowledge and plentiful experience have encouraged me in all the time of my academic research and my daily life.

Besides my advisor, I would like to thank the rest of my thesis committee: Professors Koo-Hyun Chung, Dong-Kyu Kim, Yoon Ho Lee, and Chung-Soo Kim for their encouragement, insightful comments that helped me to further improve my dissertation.

I would like to thank all the members of the Hybrid Manufacturing Technology Lab. It is their kind help and support that made my study and life in Korea a wonderful time.

Finally, I would like to express my gratitude to my wife, my children, and my family. Without their tremendous understanding and encouragement in the past few years, it would be impossible for me to complete my study.

Abstract

The superhydrophobic surface is generally made by controlling the surface chemistry and surface roughness, also it has a water contact angle of at least 150 degrees, and a sliding angle (usually) less than 10°. Therefore, researchers have confirmed that the superhydrophobic surface is produced by this combination of nano/microscale surface structures and materials with low surface energy. In recent years, a rapid number of research works have been focused on developing low-cost, simple, and green manufacturing processes for superhydrophobic surfaces fabrication. However, a common drawback of these modern studies is related to the fabrication process, which consists of uses of chemicals process and complex equipment with post process. In other words, it is limited to apply in real-world industrial applications because of their high fabrication cost, toxic materials. To address these problems, we proposed a fabrication method in this dissertation. In order to do it, we developed the durable superhydrophobic coated surface on the thermoplastic materials with nano-scale hydrophobic silica by rough surface using the simple, low-cost, and without chemical methods in this dissertation. Moreover, simple, and green techniques are used for improving superhydrophobic coated surface mechanical durability.

As result, hydrophobic silica nanoparticles have been widely used to generate nano-microscale structures on hydrophobic surfaces with low surface energy by various coating processes with binders for the realization of a superhydrophobic surface. Here, the hydrophobic polypropylene surface and flexible hydrophobic polyethylene terephthalate/polydimethylsiloxane surface were coated with a thick-coated layer of hydrophobic silica nanoparticles using a simple method such as compression molding process, hot-roll lamination and peeling assisted by heat treatment. The important barrier for the wide usage of these superhydrophobic coatings with hydrophobic silica nanoparticles is poor mechanical durability. Mechanical contact or abrasion causes the gradual loss of superhydrophobic coating, and a thin coating layer can be easily destroyed thus limiting the superhydrophobicity function. We prepared the superhydrophobic coated films having a thick coating layer with hydrophobic silica nanoparticles that can overcome.

The obtained results, the mechanical durability of the superhydrophobic surface was evaluated by the scotch tape test, scratch test with sandpaper, and bending test. The chemical stability of the superhydrophobic surface was tested by the chemical test with medium solutions and, stability in ambient air. Finally, some potential applications were reported as water droplet bouncing, and selfcleaning.

Contents

Ackno	wledgmentsi
Abstra	actii
Conte	ntsiv
List of	f Figures vii
List of	f Tables xi
List of	f Abbreviationsxii
Chapt	er 1: Introduction of superhydrophobicity1
1.1.	Superhydrophobic surface
1.2.	Fabrication of polymer-based superhydrophobic coated surface
1.2	2.1 Compression molding process
1.2	2.2 Hot-roll lamination and peeling process
1.3.	Research motivations and objectives7
1.4.	Thesis organization9
Chapt	er 2: Robust superhydrophobic surface on polypropylene with thick
hydro	phobic silica nanoparticle coated films prepared by facile
compr	ession molding
2.1.	Background12
2.2.	Experimental14
2.2	2.1. Materials and methods14
2.2	2.2. Fabrication of superhydrophobic PP/SNPs coated films
2.2	2.3. Characterization of surface morphology and wettability
2.2	2.4. Mechanical durability17
2.2	2.5. Chemical stability and aging stability

2.3. Results	18
2.3.1. Wettability	18
2.3.2. Surface morphology	19
2.3.3. Mechanical durability	22
2.3.4. Stability in ambient air and chemical stability	25
2.4. Discussion	27
2.5. Summary	29
Chapter 3: Facile fabrication of mechanical durable and flexible	
superhydrophobic surface PDMS/SNPs coated on polyethylene	
terephthalate film by a hot-roll lamination and peeling process	
3.1. Background	
3.2. Experimental methods	
3.2.1. Materials and equipment	34
3.2.2. Fabrication of flexible superhydrophobic PDMS/SNPs coated	1
films	35
3.2.3. Surface characterizations of coated films morphology and we	ttability
investigation	
3.2.4. The mechanical durability	
3.2.5. The aging stability and chemical stability	
3.3. Results	40
3.3.1. Wettability of fabricated superhydrophobic PDMS/SNPs coa	ted films
	40
3.3.2. Surface characterization	41
3.3.3. Mechanical durability tests	43
3.3.4. Stability in ambient air and chemical stability with pH effect	48

3.4. Discussion	51
3.5. Summary	
Chapter 4: Conclusion	
REFERENCES	
Appendices	72
Appendix A: Credits & Copyright Permissions	
Appendix B: The wettability and image of the fabricated superhydr	ophobic
PA6/SNPs coated films using the compression molding process	72

List of Figures

Figure 1. Superhydrophobicity in nature
Figure 2. The contact angle on the (a) smooth surface, (b), and (c) rough surfaces.
Figure 3. The applications of superhydrophobic coatings surface5
Figure 4. Many papers were published in the last ten years under the topic
superhydrophobic polymer surface taken from the Web of Science7
Figure 5. Schematic diagram of the compression molding processes for the
superhydrophobic surface15
Figure 6. Images of materials and the fabricated PP/SNPs coated films16
Figure 7. Wettability results of the fabricated PP/SNPs coated films for (a) CA
and (b) SA19
Figure 8. FE-SEM images of the fabricated PP/SNPs coated films at different
magnifications (a-d)
Figure 9. FE-SEM images of the cross-section of the fabricated superhydrophobic
coated films with relative SNPs weight ratios of (a) 100%, (b) 33%, and (c) 11
%
Figure 10. EDS result for chemical composition on the fabricated
superhydrophobic coated films with a relative SNPs weight ratio of 100 %21
Figure 11. Schematic diagram of the scotch tape test for the fabricated
superhydrophobic coated films and the five wettability measurement
positions
Figure 12. Results of the scotch tape test of the fabricated superhydrophobic
coated films with different relative SNP weight ratios of 100%, 33%, and 11%:
(a) CA and (b) SA23
Figure 13. Schematic diagram of the scratch test with sandpaper for the fabricated
superhydrophobic coated films and the five wettability measurement
positions

Figure 14. Results of the sandpaper scratch test on the fabricated
superhydrophobic coated films with relative SNP weight ratios of 100%: (a) CA
and (b) SA
Figure 15. Images of sample surfaces during the scratch test with sandpaper25
Figure 16. Results of the chemical stability test upon immersion in acidic, neutral,
and alkaline solutions for the fabricated superhydrophobic coated films with a
relative SNP weight ratio of 100 %: (a) CA and (b) SA27
Figure 17. Time sequential images of self-cleaning on the fabricated
superhydrophobic PP/SNPs coated films
Figure 18. Time sequential images of the water droplet bounce on the fabricated
superhydrophobic PP/SNPs coated films
Figure 19. A schematic diagram of hot-roll lamination and peeling assisted by
heat treatment for the superhydrophobic coated films
Figure 20. Images of the fabricated superhydrophobic PDMS/SNPs coated films
and materials
Figure 21. Wettability images of the fabricated flexible superhydrophobic
PDMS/SNPs coated films41
Figure 22. The surface structure of the fabricated superhydrophobic PDMS/SNPs
coated films for (a) FE-SEM images of surface morphology and (b) confocal laser
scanning microscopy results of roughness profile and surface roughness
value
Figure 23. Results of the fabricated PDMS/SNPs coated films for (a) FE-SEM
image of cross-section and (b) EDS line for chemical composition43
Figure 24. A schematic diagram of the scotch tape test of flexible superhydropho-
bic coated films and the five different positions of wettability44
Figure 25. Results of the scotch tape test of the fabricated flexible PDMS/SNPs

Figure 26. A schematic diagram of the scratch with sandpaper test of the flexible superhydrophobic coated films and the measurement position of wettability.....46

Figure 27. CA and SA results of the scratch with sandpaper test of the fabricated
flexible PDMS/SNPs coated films46
Figure 28. The function of a bending times of fabricated flexible superhydropho-
bic PDMS/SNPs coated films47
Figure 29. CA and SA results of a bending test of the fabricated flexible superhy- drophobic PDMS/SNPs coated films
Figure 30. Results of stability in the air for the fabricated superhydrophobic PDMS/SNPs coated films
Figure 31. A schematic diagram of the chemical stability test of the fabricated flexible superhydrophobic coated films and the three measurement positions of wettability
Figure 32. Results of the chemical stability test using acidic, neutral, and alkaline
solutions for the fabricated superhydrophobic PDMS/SNPs coated films for (a)
CA and (b) SA51
Figure 33. Effect of a process procedure for the fabricated flexible superhydro- phobic PDMS/SNPs coated films
Figure 34. FE-SEM and cross-section images of the fabricated superhydrophobic
PDMS/SNPs coated films using after mechanical durability tests for (a) scotch
tape test and (b) scratch with sandpaper test53
Figure 35. Mechanism of mechanical durability of the fabricated superhydropho- bic PDMS/SNPs coated films
Figure 36. The fabricated flexible superhydrophobic PDMS/SNPs coated films

for (a) large size image and (b) deformability	57
Figure 37. Time sequential images of self-cleaning on the fabricated flexible s	su-
perhydrophobic PDMS/SNPs coated films	.58
Figure 38. Time sequential image of the water droplet bouncing on the fabrica	ited
superhydrophobic PDMS/SNPs films	58
Figure A 1. Image and wettability of the fabricated superhydrophobic PA6/SN	Ps
coated films using the compression molding process	.73

List of Tables

Table 1: Process parameters for the compression molding with hydrophobic SNPs
on PP16
Table 2: Parameters of the fabrication process for superhydrophobic surface of
PDMS/SNPs coated films
Table 3: Summarization results of after mechanical durability tests for the fabri-
cated superhydrophobic PDMS/SNPs coated films54
Table 4: Comparison of mechanical durability of coating layer for the fabricated
flexible superhydrophobic coated films56

List of Abbreviations

Nº	Short name	Full name
1	СА	Contact angle
2	ТА	Tilting angle
3	SA	Sliding angle
4	PP	Polypropylene
5	SNPs	Hydrophobic silica nanoparticles
6	PET film	Polyethylene terephthalate film
7	PDMS	Polydimethylsiloxane
8	FESEM	Field Emission Scanning Electron Microscopy
9	EDS	Energy-dispersive X-ray spectroscopy
10	CLSM	Confocal laser scanning microscopy

Chapter 1: Introduction of superhydrophobicity

1.1. Superhydrophobic surface

The superhydrophobic surface can be found in nature [1] such as lotus leaf, butterfly wings, rice leaf, rose petal, and desert beetle as shown in Figure 1.



Figure 1. Superhydrophobicity in nature [1].

In discrete, the superhydrophobic surface was explained by the angle between liquid, solid, and air. This angle was divided into two types of angles as a high contact angle (CA $>150^{\circ}$) and a small sliding angle (SA $<10^{\circ}$). Superhydrophobic surfaces are commonly divided into two classes: low adhesion to water ("lotus effect") with a low sliding angle (SA), typically smaller than 10°, and high adhesion to water ("petal effect" or "pinned effect") with a high SA or even no SA. In normal cases, the superhydrophobic surface is created by the rough surface and low surface energy with surface materials is required.



Figure 2. The contact angle on the (a) smooth surface, (b), and (c) rough surfaces.

Several wetting models have been proposed to calculate contact angle on the surface included Young's model, Wenzel model, and Cassie-Baxter model as shown in Figure 2. With a rough surface, the Cassie-Baxter model (partial wetting) and the Wenzel model (full wetting) can be used for explanation of the wetting states while the Young's model [2][3][4] can be used for smooth (or flat) surface. The wettability on a smooth surface that follows Young's model can be described by using equation (1). While equations (2), and (3) were used to describe the wettability of the rough surface follow Wenzel [3][4] and Cassie-Baxter's [3][4] model, respectively.

$$\cos\theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \tag{1}$$

$$\cos\theta_w = r\cos\theta_e \tag{2}$$

$$\cos\theta_c = \varphi_1 \cos\theta_e - \varphi_2 \tag{3}$$

where θ_e is the equilibrium water droplet contact angle on a flat surface, r is a roughness factor equal to the actual surface divided by the geometric surface, θ_w is the water droplet contact angle in the full wetting state on a rough surface, θ_c

is the water droplet contact angle in the partial wetting state on a rough surface, φ_1 is the area fraction of the water-solid area to the projected area, and φ_2 is the area fraction of the water-air area to the projected area, θ is the water droplet contact angle in the smooth surface, $\gamma_{SA}, \gamma_{SL}, \gamma_{LA}$ are the surface energies of the solid against air, solid against liquid, and liquid against air, respectively.

Inspired by nature, artificial superhydrophobic surfaces have been developed by arranging periodically the unitary random micro-structures and combination of micro-structures with surface energy or special shape of structure. Artificial superhydrophobic coating surfaces have been created using polymer materials. Polymer materials have significantly lower surface free energy than metallic materials. Moreover, they demonstrate excellent workability and a high modulus of elasticity [5]. Consequently, fabricating polymeric superhydrophobic surfaces has drawn the attention of many researchers.

The superhydrophobic coated surface can be used for a wide range of potential applications such as self-cleaning, drag reduction anti-frosting, anti-icing, anti-corrosion, oil/water separation, and so on as shown in Figure 3. There are many applications for superhydrophobic surface exits, however, the way to create this kind of surface is still attractive and alluring for researchers. And a new process to generate a superhydrophobic surface should be green and low-cost manufacturing, be more stable, and more durable than the old one, and it can apply widely in the industry, these requirements are always a challenge for researchers.





Recently, numerous studies on superhydrophobic surfaces have been reported. A superhydrophobic surface was achieved by the fabrication of micro/nanometer-scale rough structures [7] by different methods, such as electrochemical deposition [8], chemical vapor deposition [9], layer-by-layer deposition [10], solgel [11], compression molding [12], lamination based process [13] and so on. All of these techniques required elaborated procedures and a high cost of fabrication. Among these techniques, compression molding, lamination and peeling processes were simple and without chemicals because they could be and friendly to the environment, low-cost fabrication, it can easily apply to the industry.

1.2. Fabrication of polymer-based superhydrophobic coated surface1.2.1 Compression molding process

Fabricating polymeric superhydrophobic surfaces have been drawn the attention of many researchers. Because polymer materials have lower surface free energy than metallic materials, they have outstanding workability and a high modulus of elasticity. Techniques such as injection molding, compression molding, hot embossing, and polymer casting play an important role in the mass production of superhydrophobic polymer surfaces. Among these techniques, compression molding is one of the commonly used manufacturing processes in industry and the fabricated micro-nano structures on thermoplastic polymer materials make the surface more durable than a coated surface [14–16].

1.2.2 Hot-roll lamination and peeling process

Recently, transparent superhydrophobic coatings have been prepared on different substrates by using methods such as spray coating, spin coating, dip coating, blade-coating, photopolymerization, and so on. However, the suitability for practical applications of these methods is limited by numerous factors but especially by cost and durability. Hence, some researchers' superhydrophobic coatings have been prepared on polymer materials by using a lamination-based process with other methods. These methods were created the micron and submicron structures superhydrophobic coated films. These methods superhydrophobic surfaces will be activated only by peeling off the laminated polymer film. In addition, we report a simple method such as a hot-roll lamination and peeling assisted by heat treatment process by fabrication of flexible superhydrophobic coated films. The number of papers published under the topic superhydrophobic polymer surface in the last ten years has been increased as shown in Figure 4.



Figure 4. Many papers were published in the last ten years under the topic superhydrophobic polymer surface taken from the Web of Science.

1.3. Research motivations and objectives

As a member of a Hybrid Manufacturing Technology Lab, in the past, we already developed a simple and post-treatment process method for making polymer-based superhydrophobic surfaces by hydrophobic silica nanoparticles (SNPs) without chemicals, no complicated equipment, and high contact angle (CA > 170°).

First, this simple method included the compression molding process and hydrophobic silica nanoparticles materials, which meant, the polypropylene samples with hydrophobic surface were fabricated by a simple method, then the fabricated sample was modified by hydrophobic silica nanoparticles using the compression molding process to become a superhydrophobic coated films with micro/nanostructure will appear on the coated surface. With this simple process, several work-related polymer materials as polyvinylidene fluoride, polystyrene, polypropylene, and silicon rubber have been conducted and published. However, in these publications, the researchers focused on the uses of harmful chemicals and the fabrication process in several and separate consecutive steps.

Second, this facile method and post-treatment process included the hot-roll lamination and peeling process assisted by heat treatment and hydrophobic silica nanoparticles materials, which meant, the PET film with PDMS polymers samples with flexible hydrophobic surface were fabricated by a facile method, then the fabricated coated sample was modified by hydrophobic silica nanoparticles using a hot-roll lamination and peeling process assisted by heat treatment process to become a flexible superhydrophobic coated films with micro/nanostructure will appear on the hydrophobic surface. With this facile method and post-process, some research on many kinds of polymer materials as polypropylene, high-density polyethylene, linear lower density polyethylene, lower density polyethylene, and ultrahigh molecular weight polyethylene has been conducted and published. However, in these publications, the researchers focused on relatively high fabrication costs and requires harmful chemicals.

Furthermore, some applications such as self-cleaning, large size for mass production were proposed in this study.

The simple techniques using compression molding or hot-roll lamination and peeling assisted by heat treatment processes can be a good candidate to apply in manufacturing and industry due to the following reasons:

- To fabricate the superhydrophobic surface (low surface energy and surface structure).
- High durability (thick functional film).
 - 8

- Green and low-cost manufacturing process (compression molding, hot-roll lamination and peeling process without toxic chemicals).

Additionally, the results could provide a useful guide to select the proper method, structures, and thickness of the coating for adjusting wettability, surface morphology on the polymer substrates with hydrophobic silica nanoparticles.

1.4. Thesis organization

The thesis's structure will be divided into 4 chapters as below:

Chapter 1 focuses on the literature review including the definition of superhydrophobic surface, some applications, and how to generate a polymer-based superhydrophobic surface by hydrophobic silica nanoparticles. Next, a review about using compression molding, hot-roll lamination and peeling assisted by heat treatment processes for the fabrication of polymer-based superhydrophobic coated films will be mentioned. The final part will describe the motivation, and the objectives, and the thesis organization.

Chapter 2 describes the robust superhydrophobic surface on polypropylene with thick hydrophobic silica nanoparticle-coated films prepared by facile compression molding. Besides, the surface analysis with chemical composition on fabricated coated films was investigated. Then, the coating thickness on fabricated coated films with different weight ratios of SNPs was studied. In addition, it was measured the mechanical durability of fabricated coated films by scratch with sandpaper and scotch tape test. And the chemical stability of the prepared samples was measured by medium solutions with a pH effect. Final some potential applications also are mentioned in this chapter.

Chapter 3 describes the facile fabrication of mechanical durable and flexible superhydrophobic PDMS/SNPs surface coated on polyethylene terephthalate film by a hot-roll lamination and peeling assisted by heat treatment. The chapter indicated coating thickness and surface morphology with the chemical composition of the fabricated PDMS/SNPs coated films. And the chemical stability and robustness of the prepared surface were also investigated. In addition, it was shown the folding and flexibility of coated films. Finally, some potential applications were shown in this chapter.

Chapter 4 summarizes several outstanding results from the compression molding process with hydrophobic silica nanoparticles and a hot-roll lamination and peeling assisted by heat treatment with SNPs were mentioned in this chapter. Chapter 2: Robust superhydrophobic surface on polypropylene with thick hydrophobic silica nanoparticle coated films prepared by facile compression molding

2.1. Background

Superhydrophobic surfaces have been extensively studied for their unique interfacial interaction between water and solid surface, and the superhydrophobic surface was defined by a water contact angle (CA) greater than 150°, and sliding angle (SA) less than 10° [17, 18] with numerous special properties, such as selfcleaning[19–21], anti-icing [18, 22], water-proofing [23] and anti-fouling [20, 21, 23]. These properties may come from the minimum contact area of the watersolid interface as well as the trapped air at the interface, and they can control the material and energy transport at the interface. Researchers have confirmed that the superhydrophobic surface is produced by this combination of nano/microscale surface structures and surface materials with low surface energy [24]. The superhydrophobic surface is an evolutionary adaptation in nature and these surfaces can be easily observed from nature such as lotus leaves and butterfly wings, wherein superior non-wetting is achieved [25]. T. Onda et al. [26] reported the first artificial superhydrophobic surfaces in 1995. Since 1995, many researchers have reported many creative ways to make rough surfaces with low surface energy.

Many scientists have focused on the fabrication of superhydrophobic coated surfaces with polymers and low surface energy organic materials that help to improve the surface roughness and durability [23]. Various different techniques were used for fabrication of superhydrophobic surfaces such as etching [17], dip-coating [19], spray-coating [28, 29], spin-coating [30], sol-gel [20], electrodeposition [31], anodization [32], electrochemical deposition [33], phase separation [34], casting [18], and nanocomposite coatings [23]. However, some techniques are complex while others use toxic materials. Therefore, a simple and green manufacturing process for superhydrophobic surfaces is required.

Compression molding is one of the commonly used manufacturing processes in the industry, and the fabricated micro-nano structures on thermoplastic polymer materials make the surface more durable than a coated surface [14, 15, 35]. There are several polymer materials used in the compression molding process such as polyvinylidene fluoride [23], polystyrene [36], polypropylene [12], and silicone rubber [35]. Thermoplastic polypropylene (PP) is widely used due to its lightweight and non-toxicity properties. Additionally, the superhydrophobic surface on PP can be easily achieved by softening upon heating and hardening by cooling or using a solvent due to its hydrophobicity [23, 37, 38].

Hydrophobic silica/polymer composites were used to fabricate a superhydrophobic coated surface. Several studies have been reported on the preparation of superhydrophobic coated surfaces with polymer materials, such as SiO_2 /polystyrene [30, 33] and SiO₂/polyvinyl chloride [30]. This SiO₂/polymer composite coating exhibits a strong potential for industrial applications. Silica nanoparticle/polymer composite coated surfaces were prepared by spin-coating [30] and radiation polymerization [33] techniques. In addition, PP and silica nanoparticles (SNPs) have been used for superhydrophobic surfaces. Hydrophobic silicacoated superhydrophobic PP membrane fabricated by dip-coating was used for oil-water separation [39]. Superhydrophobic PP/silica coating using drop-casting of PP and silica solution was used for cell adhesion control [40]. The practical use of superhydrophobic nanoparticle/polymer composite surfaces is severely limited by poor mechanical durability. All-organic coatings have good chemical stability but poor mechanical durability. Recently, researchers have focused on the durability improvement of superhydrophobic surfaces [25]. Some researchers have reported mechanical durability by using scratch tests on sandpaper. Metal polymer composites [41, 42], etched metal substrates with low surface energy [43, 44], and hydrophobic nanoparticles with polymer [45–47] have been studied for robust superhydrophobic surfaces, and they showed good superhydrophobicity after scratch testing. However, the usage of toxic chemicals [41–43, 47] and relatively long process time [44] were limitations.

In this research, a facile compression molding was used for the fabrication of superhydrophobic surfaces on PP with silica nanoparticles to overcome the poor durability of superhydrophobic coated surfaces. Then, the surface morphology of the fabricated coated films was evaluated by field emission scanning electron microscopes (FE-SEM), and the coating thickness was analyzed using energy-dispersive spectrometry (EDS) lines. Meanwhile, the durability of the fabricated PP/SNPs coated films by scotch tape test and sandpaper test were investigated. The chemical stability of the fabricated superhydrophobic coated surface was tested with medium solutions having different pH values [48, 49]. The results showed robust superhydrophobic coated films with the merits of self-cleaning and water droplet bouncing.

2.2. Experimental

2.2.1. Materials and methods

For sample preparation and chemical stability test, commercially available homopolymer polypropylene (Hopelen, SJ-170T, Lotte Chemical Corporation, Korea), hydrophobic silica nanoparticles (specific surface area 120 m²/gm, fumed silica K-D15, OCI Company, Korea), and medium solutions (buffer solutions with pH 2, pH 7, and pH 13., Daejung Chemicals & Metals CO.LTD., Korea) were purchased and used as received. The pH 2 solution, pH 7 solution, and pH 13 solution were produced by hydrochloric acid, water, and sodium hydroxide, respectively. Superhydrophobic coated films were prepared by a compression molding process with a heating press, and the sample size was 40 × 40 mm. A heating press machine (D1P-25J, Dae Heung Science., Korea) was used in the compression molding process to fabricate the superhydrophobic coated surface. A mold with a cavity size of $40 \times 40 \times 10$ (L × W × H) mm was used for molding of the pellet and powder materials.

2.2.2. Fabrication of superhydrophobic PP/SNPs coated films

A schematic diagram of the fabrication processes is shown in Figure 5. The superhydrophobic surface was fabricated by polypropylene and hydrophobic

silica using the compression molding process. The flat hydrophobic surface was prepared by PP pellets with an average size of about 2 to 3 mm. The flat PP plate was prepared via a compression molding process using the heating machine. The PP pellet was put into the cavity of the mold. The material was placed in the mold cavity; the mold was installed on the lower platen of the heating press machine at 180°C for five minutes. Subsequently, the mold was pressed using a hydraulic pump until the required pressure (from 7.5 to 8 MPa) was achieved. The upper and lower platens were kept closed to allow the pellet PP to completely cure. When the compression molding was finished, the mold was taken out and was cooled at ambient temperature for 30 min.



Figure 5. Schematic diagram of the compression molding processes for the superhydrophobic surface.

The superhydrophobic PP/SNPs films were prepared using the heating press machine under pressure via a compression molding process. The fabricated polypropylene plate was placed inside the mold cavity. The hydrophobic silica powder was put into the cavity on the PP plate; the mold was placed on the lower platen of the heating press machine at 160°C for five minutes. Subsequently, the two platens were pressed closer together using a hydraulic pump until the desired pressure (from 7.5 to 8 MPa) was reached. This pressure was repeated one time. The platens were kept closed to allow the PP/SNPs films to achieve complete compression. When the cycle was complete (13 min), the platens were opened

and allowed to cool at ambient temperature. After 40 min of cooling, the fabricated samples were detached from the mold. Figure 6 shows the fabricated PP/SNPs films and images of original materials. To study the effect of hydrophobic silica nanoparticles, three relative weight ratios of SNPs such as the maximum weight for full mold cavity, a third, and a ninth were used. The detailed process parameters for the compression molding process of the hydrophobic silica nanoparticles are summarized in Table 1.



Polypropylene pellet

Polypropylene plate

Hydrophobic silica

PP/SNPs coated films

Figure 6. Images of materials and the fabricated PP/SNPs coated films.

Table 1: Process parameters for the compression molding with hydrophobicSNPs on PP.

Parameter	Unit	Value
Compression molding pressure	MPa	7.5–8
Compression heating time	min	5
Compression pressure time	min	5
Molding temperature	°C	160
Mold cavity size	mm	$40 \times 40 \times 10$
Cooling time	min	40
Polypropylene weight	g	3.6
The relative weight ratio of hydrophobic silica		100%
(Maximum weight for molding cavity:	0.53 g)	33%
	0,	11%

2.2.3. Characterization of surface morphology and wettability

The surface morphologies of the fabricated superhydrophobic PP/SNPs coated films were evaluated with field emission scanning electron microscopy (JEOL, JSM-6500F, Tokyo, Japan). The chemical composition of the fabricated superhydrophobic coated films was determined by energy-dispersive spectrometry using the same instrument. Three different positions were observed to evaluate the elemental composition of three samples with different weights of SNPs.

The CA and SA of the prepared PP/SNPs coated films were measured with a contact angle meter (SDL200TEZD, FEMTOFAB, Seoul, Korea) at room temperature. The measurement of CA and SA for all samples was carried out five times to obtain reliable results. The volume of a water droplet was 10 microliters for the CA and SA.

2.2.4. Mechanical durability

The scotch tape test and scratch test with sandpaper were carried out for the mechanical durability of the superhydrophobic surface with PP/SNPs coated films. The tape test was conducted along the test method B of ASTM D 3359-09. The scotch tape (Scotch-550; 3M; Seoul; Korea) was attached to the superhydrophobic PP/SNPs coated films, and then the tape was removed. A thin eraser was applied with a pressure of 6.1 kPa (1 kg weight on 40×40 mm of area) to ensure good contact was made between the composite coated films and scotch tape [22]. The second mechanical durability test of the fabricated samples was evaluated via a sandpaper abrasion method [50]. The superhydrophobic surface was placed on the 1000 grit sandpaper (CC-1000 Cw; Daesung Abrasive Co., Seoul, LTD; Korea) with a pressure of 3.1 kPa (500 g weight on 40×40 mm of area). The fabricated PP/SNPs coated films were moved by 10 cm followed by 90° rotations, and the procedure was repeated. The CAs and SAs were measured every cycle of the scratch test.

2.2.5. Chemical stability and aging stability

Chemical and aging stabilities were studied on the fabricated superhydrophobic surface after about 300 days. First, the surface wettability of the fabricated PP/SNPs coated films was observed after 300 days of storage at ambient conditions. Consequently, a chemical stability test was carried out to evaluate the durability of the superhydrophobic PP/SNPs coated films at room temperature using acidic, neutral, and alkaline medium solutions. The prepared superhydrophobic PP/SNPs coated films were placed with the medium solutions, and the CAs and SAs were measured at different time intervals. Each sample was tested with the medium solutions for 0, 1, 3, 6, 9, 12, and 24 h immersion. At the time intervals, the fabricated PP/SNPs coated films were taken out from the medium solutions, the surface was dried at room temperature for one hour, and the CAs and SAs were measured.

2.3. Results

2.3.1. Wettability

The wettability of the fabricated PP/SNPs coated films was examined by CA and SA measurements, as shown in Figure 7 (Video S1). The coated films exhibited good superhydrophobicity when the compression pressure was between 7.5 and 8 MPa with a heating temperature from 160 to 180°C. The CA was about 175° (Figure 7a) and the SA was about 3°.

The rough surface structures and surface energy determined by chemical compositions are important for extreme wettability. Herein, the addition of the hydrophobic silica nanoparticles could increase the surface roughness by making nano/microscale structures, and the hydrophobic coating on silica could reduce the surface energy. Consequently, superhydrophobic PP/SNPs coated films with a high CA have been obtained [30].



Figure 7. Wettability results of the fabricated PP/SNPs coated films for (a) CA and (b) SA.

2.3.2. Surface morphology

The surface morphology of the coated films was analyzed using FE-SEM. The coated films with SNPs having a 100% weight ratio during the compression molding process were used. As shown in Figure 8, nanoscale silica particles covered the entire surface, and random microscale rough structures were observed. The surface morphology was not changed with different relative weight ratios of SNPs. These nano-micro hierarchical structures with hydrophobicity may make the surface superhydrophobic.



Figure 8. FE-SEM images of the fabricated PP/SNPs coated films at different magnifications (a-d).

Additionally, the cross-section of the fabricated superhydrophobic PP/SNPs coated films was observed to evaluate the thickness of the films. To determine the effect of SNP weight difference, the PP/SNPs coated films with different relative weight ratios of SNPs, such as 11%, 33%, and 100%, were evaluated. The result showed that different thicknesses of fabricated superhydrophobic coated films were obtained according to the different relative weight ratios of SNPs, as shown in Figure 9. The results showed that the thickness of the coated film with relative SNP weight ratios of 11%, 33%, and 100% was from 13 to 25 μ m, 13 to 29 μ m, and 15 to 34 μ m, respectively. As the weight of SNPs increased, the overall thickness of the coated film increased.


Figure 9. FE-SEM images of the cross-section of the fabricated superhydrophobic coated films with relative SNPs weight ratios of (a) 100%, (b) 33%, and (c) 11 %.

Additionally, the line EDS was used for the chemical composition on the PP/SNPs coated film. As shown in Figure 10, the PP/SNPs coated film with 100% relative weight ratio of SNPs is composed of carbon, oxygen, and silicon elements, and the chemical compositions of the film were different from the base PP layer and the mounting material layer. All the samples with different weight ratios showed similar results.



Figure 10. EDS result for chemical composition on the fabricated superhydrophobic coated films with a relative SNPs weight ratio of 100 %.

2.3.3. Mechanical durability

The durability of the superhydrophobic surface is a very crucial feature for practical usage. Mechanical durability is the major challenge for superhydrophobic surfaces. In this study, the mechanical durability of the fabricated superhydrophobic PP/SNPs coated films was characterized using the scotch tape test and scratch test with sandpaper.

First, the scotch tape test was carried out with samples with different relative SNP weight ratios of 11%, 33%, and 100%. After the scotch tape test, the CA and SA were observed. The test schematic diagram and five different positions for the CA and SA measurements are shown in Figure 11. The scotch tape test of the fabricated PP/SNPs coated films is shown in Video S2. Adhesion and peeling of tape were repeated for the coating degradation. The first scotch tape test did not affect the CA and SA, and this result showed the film's robustness. The CA and SA results after the tape test for the fabricated superhydrophobic coated films with different relative SNP weight ratios of 11%, 33%, and 100% were summarized in Figure 12. The average values were used, and the error bars in Figure 12 indicate the minimum and maximum values, and a 90 degrees value in SA means that the water droplet was attached to the surface even with tilting of 90 degrees. The scotch tape test results showed that the coated films could resist scotch tape peeling with results of 25 repetitions for 100%, 20 repetitions for 33%, and 10 repetitions for 11% for superhydrophobicity with the average CAs greater than 150° and average SAs less than 10°. From the scotch tape-peeling test, the fabricated superhydrophobic surface with the PP/SNPs coated films showed good mechanical durability, and the durability could be increased by increasing the thickness of PP/SNPs film.



Figure 11. Schematic diagram of the scotch tape test for the fabricated superhydrophobic coated films and the five wettability measurement positions.



Figure 12. Results of the scotch tape test of the fabricated superhydrophobic coated films with different relative SNP weight ratios of 100%, 33%, and 11%: (a) CA and (b) SA.

Second, a scratch test was performed on the superhydrophobic surface of PP/SNPs coated films. Figure 13 displays the schematic diagram of the scratch test with sandpaper and five positions of CA and SA measurements after the scratch test. The scratch test with sandpaper was performed up to the travel distance of 460 cm, and the surface did not show any sliding angle after the travel distance. The scratch test of the PP/SNPs coated film with a 100% relative weight ratio of SNPs was demonstrated (Video S3), and Figure 14 shows the CA and SA

results after the scratch test with a 20 cm travel distance. The average CA was less than 150° after a travel distance of 380 cm and the average SA became greater than 10° after a travel distance of 120 cm. Additionally, the scratch test with sandpaper proved that the fabricated superhydrophobic PP/SNPs coated film exhibited good mechanical durability. The change of wettability and the film surface under scratch test was also observed, as shown in Figure 15. The surface of the as-prepared sample was white, and there was almost no damage for the first scratch test cycle (10 cm distance). From the second scratch test cycle (20 cm distance), the color change was observed because of the gradual wear of PP/SNPs film. Until 100 cm distance in the scratch test, the sample showed a high CA of about 170° and SA less than 10°; even the sample surface showed a clear non-white area. As the distance in scratch tests increased, the CA decreased, and the SA increased. Finally, the SA was not measured after 250 cm in the abrasion test because the PP/SNPs film was severely damaged.



Figure 13. Schematic diagram of the scratch test with sandpaper for the fabricated superhydrophobic coated films and the five wettability measurement positions.



Figure 14. Results of the sandpaper scratch test on the fabricated superhydrophobic coated films with relative SNP weight ratios of 100%: (a) CA and (b) SA.



Figure 15. Images of sample surfaces during the scratch test with sandpaper.

2.3.4. Stability in ambient air and chemical stability

The fabricated superhydrophobic PP/SNPs coated films were stored under ambient conditions for 10 months. Then, the surface wettability was evaluated with the CA and SA for stability in ambient air. The results showed that the average CA and SA for five samples after 10 months in ambient air were 176.9° and 3.2°, respectively. The CA and SA were not degraded after storage, which indicated that the fabricated PP/SNPs coated films have long-term stability in air.

The pH effect on the chemical stability of the fabricated superhydrophobic PP/SNPs coated films was evaluated by immersion in medium solutions with pH 2, pH 7, and pH 13. This experiment was carried out as a function of immersion time such as 0, 1, 3, 6, 12, and 24 h under three different medium solutions: acidic, neutral, and alkaline conditions. Then, the CAs and SAs were measured. Figure 16 showed the average CAs and SAs of the three samples with three different measurement positions for each sample. For all solutions, the CA of the fabricated films gradually decreased concerning the immersion time. Similarly, the SA gradually increased concerning the immersion time. The CA decreased in the ranges of $176 \pm 1^{\circ}$ and the SA increased in the ranges of $3 \pm 1^{\circ}$ to $13 \pm 3^{\circ}$ within 1, 3, 6, and 12 h after immersion in acidic and neutral solutions. The results showed a small change in wettability. However, the CA decreased to 43.0° and there was no SA after 12 h immersion in the alkaline solution. The average CAs of the fabricated superhydrophobic PP/SNPs coated surface of PP/SNPs coated films after immersion in acidic, neutral, and alkaline solutions for 24 h were 166.3°, 167.6°, and 74.6°, respectively. Additionally, the average SAs of the PP/SNPs coated films after immersion in acidic, neutral, and alkaline solutions for 24 h were estimated to be 12.9°, 12.7°, and no sliding angle, respectively. These results indicate that the fabricated superhydrophobic PP/SNPs coated films have good chemical stability for acidic and neutral solutions. However, the fabricated surface can be damaged by an alkaline solution. The reason why the alkaline solution changed the wettability of the fabricated samples may be attributed to the chemical degradation of hydrophobic coating on silica nanoparticles. The dimethyldichlorosilane or polydimethylsiloxane was used in surface treatment for hydrophobicity of the silica nanoparticles [36]. This chemical structure can be degraded by hydrolysis, and hydrolysis can generate a hydroxyl group that can attack the silicon atom. The presence of hydroxyl groups makes the surface more

hydrophilic. The dimethyldichlorosilane or polydimethylsiloxane can be degraded rapidly with high alkaline conditions [51].



Figure 16. Results of the chemical stability test upon immersion in acidic, neutral, and alkaline solutions for the fabricated superhydrophobic coated films with a relative SNP weight ratio of 100 %: (a) CA and (b) SA.

2.4. Discussion

Hydrophobic silica nanoparticles have been widely used to produce nanomicroscale structures on surfaces with low surface energy by various coating processes with binders for the realization of a superhydrophobic surface. The important barrier for the wide usage of these superhydrophobic coatings with SNPs is poor mechanical durability. Mechanical durability is the main issue limiting the application of superhydrophobic coatings [52]. Mechanical contact or abrasion causes the gradual loss of superhydrophobic coating, and a thin coating layer can be easily destroyed, thus limiting the superhydrophobic coated films that had a thick coating layer with hydrophobic silica nanoparticles using compression molding. The obtained results from the mechanical durability tests revealed that the presence of thick PP/SNPs coated films successfully resisted adhesion and abrasion. The thick superhydrophobic PP/SNPs coated film with a thickness thicker than 10 μ m exhibited good mechanical durability and good resistance in scotch tape and scratch tests using sandpaper. However, most superhydrophobic coatings with thin films are not suitable for resisting mechanical contact or abrasion. Therefore, contact or abrasion with small pressure could damage the surface structures and the surface lost superhydrophobicity [22]. In addition, the fabrication process is simple and uses commercially available compression molding without using toxic chemicals. All materials are commercially available and nontoxic. Moreover, there were no additional pre- or post-treatments. Therefore, the proposed fabrication method can be used widely without new equipment or materials.

To show the superhydrophobic performance, self-cleaning and water droplet bouncing was demonstrated. The self-cleaning performance of the PP/SNPs coated films was demonstrated with the sugar powder, as shown in Figure 17 (Video S4). As water droplets slide on the superhydrophobic coated surfaces, the sugar powders can be trapped by the water droplets [53].



Figure 17. Time sequential images of self-cleaning on the fabricated superhydrophobic PP/SNPs coated films.

The water droplet bounce on the fabricated superhydrophobic PP/SNPs

coated films is demonstrated in Figure 18 (Video S5). The fabricated film showed good superhydrophobicity to repel the water droplets [54, 55].



Figure 18. Time sequential images of the water droplet bounce on the fabricated superhydrophobic PP/SNPs coated films.

2.5. Summary

We developed a simple compression molding process for the fabrication of superhydrophobic PP/SNPs coated films. The obtained PP-coated films with different SNP weight ratios exhibited superhydrophobic behavior with a high CA of about 170° and SA less than 5°. The scotch tape test and scratch test were used to check the mechanical durability of our fabricated PP/SNPs coated films. The results showed that PP/SNPs coated films could maintain the superhydrophobic tendency after several repetitions of tape tests and long-distance scratch tests. Moreover, increasing the SNP weight ratio in the coated films resulted in the overall improvement of mechanical durability. The surface morphology and corresponding EDS linear scan for elemental analysis showed the successful fabrication of thick superhydrophobic PP/SNPs films with nano-microscale structures having hydrophobic SNPs via a facile compression molding process. The chemical stability of the fabricated superhydrophobic coated surface was elucidated for using acidic, neutral, and alkaline solutions. The PP/SNPs coated films showed high chemical stability in acidic and neutral solutions. However, the chemical stability of the fabricated superhydrophobic coated surfaces in the alkaline solution was not sufficient. In this research, nanoscale silica particles covered the entire surface, and random rough nano-microscale structures were formed. These nano-micro hierarchical structures with hydrophobicity could

make the surface superhydrophobic. The practical meaning is to confirm the feasibility of the mass-production of robust superhydrophobic surfaces with the widely used facile compression molding process using commercially available materials as purchased without the additional treatment or usage of toxic chemicals. We believe that the proposed fabrication method of superhydrophobic coated surfaces would be effective for realizing a robust superhydrophobic surface in real applications.

Chapter 3: Facile fabrication of mechanical durable and flexible superhydrophobic surface PDMS/SNPs coated on polyethylene terephthalate film by a hot-roll lamination and peeling process

3.1. Background

The surface of Lotus leaf and dragonfly wings cannot wetted by water droplets in rain, researchers called these interesting phenomena as superhydrophobic surfaces [56]. Since reporting of lotus effect, the superhydrophobic surfaces have attracted much attention due to their excellent properties as self-cleaning and water repellency [56–58]. Basically, the superhydrophobic surface is defined as the surface that verify water contact angle (CA) greater than 150° and sliding angle (SA) less than 10° [57, 58]. To improve the superhydrophobic tendency of surface several parameters can be modified as: a) surface roughness formation of micro/nano patterns; b) using hydrophobic materials with low energy surface [59]. The superhydrophobic surface coatings have potential applications in many fields such as self-cleaning [56–58], drag-reduction [56] [60], anti-icing, etc.

Various superhydrophobic surfaces were created by different methods with appropriate materials. The fabrication of superhydrophobic coated films could improve the surface properties of material and extending its application [61]. Polymer materials have lower surface free energy than metallic materials, they have outstanding workability and a high modulus of elasticity [62]. Polyethylene terephthalate (PET) film is an engineering polymer that has a wide application range in industry, electronic, and automotive application. The wide use of PET film is attributed to its superior properties such as low-temperature durability, high mechanical strength, high heat resistance, high electrical insulation, and high transparency [63]. As well as the PET film is widely used in lamination process owing to the low-cost flexibility [63][64][65]. Also, Polydimethylsiloxane (PDMS) is a common low surface energy materials, which is non-toxic, inexpensive, and is a simple fabrication to process [66], so it is widely used in lab-on-a-chip and inflexible devices applications [67]. When used the hot lamination process, PDMS material most important function, it adhered to the substrate between coating. In addition, the hydrophobic silica nanoparticles usually use the coating of the

superhydrophobic surface because is inexpensive and environmentally.

Some researchers' superhydrophobic coated films were created the micron and sub-micron structures on polymer materials by lamination process with other methods. Superhydrophobic surfaces have been fabricated by the polymer film using the methods such as hot-press lamination and peeling [13], [68], [69], and peeling process [70]. The method is cost-effective, facile [68], non-toxic [69] and has the potential for mass production [13], [68]. These methods superhydrophobic surfaces will be activated only by peeling off the laminated polymer film. Additionally, the superhydrophobic coated film on PET film is suitable for rapid large-area production [59].

PDMS layer bonding to hydrophobic silica nanoparticles was used to fabricate superhydrophobic coated films on by various substrates. Several studies have been reported on the preparation of superhydrophobic coated films by hydrophobic silica compressed to the PDMS layer, such as on the shrink film [45], the glass surface [71], the magnesium alloys [72], the wood [73] and aluminum surface [60]. These PDMS/SiO2 composite coated films exhibit high flexibility and mechanical robustness applicable to large-scale sizes on any substrate. The PDMS layer with silica nanoparticle-coated films was prepared by combined with anodic oxidation and dipping method spin-coating [60], casting [45], a thermal evaporation method [71], painting-rapping method [72], and dip-coating [73] techniques.

Recently, researchers have focused on the robust development of superhydrophobic coated films on any substrate [61]. The number of researchers has described mechanical robustness by using abrasion test on sandpaper. PDMS layer with silica NPs superhydrophobic coated film on the polymer, ceramic, and organic material have been studied for robust superhydrophobic surfaces, and they showed good superhydrophobic tendency after scratch testing. However, the usage of toxic chemicals and the long fabrication process time were limitations.

33

In this study, we demonstrated a facile fabrication of mechanical durable and flexible superhydrophobic coated films by PET/PDMS polymer with hydrophobic silica NPs were carried out hot-roll lamination and peeling assisted by the heat treatment process. Then, the morphology of surface and surface roughness average values of fabricated superhydrophobic coated films were estimated by field emission scanning electron microscopes (FE-SEM) and confocal laser scanning microscopy (CLSM), respectively. And the chemical compositions and coating thickness were analyzed by energy-dispersive spectrometry (EDS) line. In addition, the mechanically robust and chemical stability of prepared SH coated films were considered. The obtained coated films mechanical robust excellent superhydrophobic surface with the good of performance such as water droplet bouncing, and self-cleaning.

3.2. Experimental methods

3.2.1. Materials and equipment

The Polyethylene Terephthalate (PET) film purchased with thickness of 100 μ m was purchased from Film Bank CO.LTD., Korea. The Polydimethylsiloxane (PDMS) polymer (Silicone Elastomer Base with a Curing Agent, SYLGARDTM 184) was bought from Dow Silicone Corporation, United States. Hydrophobic silica nanoparticles (SNPs) (specific surface area of 120 m²·gm⁻¹, fumed silica K-D15) was purchased from OCI company, Korea. The buffer solutions with different pH (2, 7, and 13) was bought from Daejung Chemicals & Metals CO.LTD., Korea. The used double-sided foam tape in mechanical durability test (18 mm x 2.5 m x 1 mm) was purchased from OKONG company, Korea. A laminator machine (Coating machine, LamiPlus-360G, Copier Land CO.LTD., Korea) was used in the hot-roll lamination process to generate flexible superhydrophobic coated films.

3.2.2. Fabrication of flexible superhydrophobic PDMS/SNPs coated films

A schematic diagram describing the fabrication processes of flexible superhydrophobic coated films using a spray method, a hot-roll lamination and peeling assisted by heat treatment are shown in Figure 19. The flexible superhydrophobic coated films were fabricated by hydrophobic PET/PDMS surface and silica NPs in two steps. The hydrophobic coating was created on the PET film using the spray gun with a solution of PDMS. The hydrophobic coating was fabricated in two processes. Herein, the flexible hydrophilic substrate was prepared by the PET film with double-sided foam tape. Then, the double tape was adhered with dimensions by 50 mm x 50 mm on the PET film. After that, the PDMS was mixed with 10:3 weight ratios of silicone elastomer base and curing agent. To obtain a uniform dispersion of PDMS in the solution, the solution was ultrasonicated for 15 minutes. Then, a solution of PDMS was sprayed inside the squares (made the area of 50 mm x 50 mm by double tape) of the PET film using an air gun at 280 kPa with a distance between about 10 cm the from an air gun to the PET film. A solution of PDMS was sprayed on the PET film and repeated for 3 and 4 times. One spray cycle takes 14 seconds with an interval of 4 minutes between successive cycles. Finally, the substrate of the PDMS layer with a hydrophobic surface was kept at ambient temperature for 10 minutes.



Figure 19. A schematic diagram of hot-roll lamination and peeling assisted by heat treatment for the superhydrophobic coated films.

Subsequently, the hydrophobic surface with a PDMS layer was modified by the hydrophobic silica NPs using a hot-roll lamination process followed by thermal annealing. Firstly, 0.2 g fumed silica powder was dispersed into the fabricated hydrophobic PET/PDMS surface with an area of 50 mm x 50 mm by double tape. Then, the fumed silica powders were covered on the fabricated PDMS layer with hydrophobic coated film. Secondly, another PET film was covered on the fabricated PDMS/SNPs coated films using one-step lamination processing by a laboratory hot-roll laminator machine at 135°C for 1 time. After that, the laminated coated films were exposed to the thermal annealing process by the oven at 135°C for 16 minutes.

The PDMS layer increased the bonding between the silica NPs and PET film through post heat treatment. After post-heating, the lamination sample was taken out from the oven, which cooled was at room temperature. The cooled prepared lamination sample was cut an area of 50 mm x 50 mm. When cut the prepared lamination sample was removed a double-sided foam tape. Next, another PET film was anti-adhered to with fabrication PDMS/SNPs coated film that was peeled off manually from prepared the lamination sample with an area of 50 mm x 50 mm. The resulting, fabricated hydrophobic PET/PDMS with hydrophobic silica NPs coated films were cleaned by an ultrasonic cleaner at 5 minutes inside into the ethanol and dried at ambient temperature.

Lastly, the flexible superhydrophobic surface was generated by the fabrication of hydrophobic PET/PDMS coated film with hydrophobic SNPs. Figure 20 shows the fabrication flexible superhydrophobic PDMS/SNPs coated films and the corresponding images of raw materials. Here, we study the effect of hydrophobic silica NPs on the PDMS layer with hydrophilic PET film.



Figure 20. Images of the fabricated superhydrophobic PDMS/SNPs coated films and materials.

(SNPs)

(PET film)

The characteristic parameters of the fabrication process of flexible superhydrophobic PDMS/SNPs coated films are recorded in Table 2.

Table 2: Parameters of the fabrication process for superhydrophobic surface ofPDMS/SNPs coated films.

Process	Parameter	Value	
	Spray time * (sec)	55	
Spray method	Pressure (kPa)	280	
	Distance (cm)	10 - 15	

Hot roll lamination _	Temperature (°C)	135	
	Lamination speed (mm/sec)	1.2	
Oven _	Temperature (°C)	135	
	Time (min)	16	

* Spray times required to spray the plate surface with an area of 50x50 mm².

3.2.3. Surface characterizations of coated films morphology and wettability investigation

The surface morphology of the fabricated flexible superhydrophobic PDMS/SNPs coated films was examined by field emission scanning electron microscopy (HITACHI, SU8220, Tokyo, Japan). The chemical composition of the fabricated flexible superhydrophobic coated films was analyzed using energy-dispersive x-ray spectroscopy using the FE-SEM.

Confocal laser scanning microscopy (KEYENCE, VK-X200 series) was used to analyze the surface roughness of the fabricated flexible superhydrophobic coated films.

The CA, SA, and tilting angle (TA) of the fabricated coated surface were observed by a contact angle meter (SDL200TEZD, FEMTOFAB, Seoul, Korea) at ambient temperature with a 10 microliters water droplet. The average value of the CA, and SA were measured five times for each sample.

3.2.4. The mechanical durability

The mechanical durability of the fabricated flexible superhydrophobic PDMS/SNPs coated films were carried out by scotch tape, abrasion with sandpaper, and bending tests. A standard method B of ASTM D 3359-09 was used to evaluate the mechanical durability of coated film using the adhesion test with scotch tape. The scotch tape (Scotch-550; 3M; Seoul; Korea) was attached to the fabricated flexible PDMS/SNPs coated films at an applied pressure of 3.9 kPa (1 kg weight on 50 \times 50 mm of area), and then the scotch tape was detached [74]. The CAs and SAs of every cycle were measured on the prepared 3 samples. The

second mechanical durability test of the fabricated flexible superhydrophobic coated films was estimated by abrasion test with sandpaper [45]. The prepared flexible coated films were placed on the 240 grit sandpaper (CC-240 Cw; Daesung Abrasive Co., Seoul, LTD; Korea) with the rough side was connected. The fabricated flexible PDMS/SNPs coated films were moved by 10 cm followed by 90° rotations with a pressure of 1.2 kPa (25 g weight on 15×15 mm of area) and the procedure was replicated. The CAs and SAs were measured on each sample every cycle of the abrasion test. The last mechanical durability test of the prepared flexible PDMS/SNPs coated films was assessed by a bending test [75]. The bending test was folded forwards and backward, from - 90° to 90° for one time, this repeated process was defined as one cycle on the fabricated flexible superhydrophobic surface.

3.2.5. The aging stability and chemical stability

The chemical and aging stabilities were investigated on the fabricated flexible superhydrophobic PDMS/SNPs coated films after about 150 days. First, the surface wettability of the fabricated flexible PDMS/SNPs coated films was observed after 150 days of storage at ambient conditions. Second, a chemical stability test was used to evaluate the durability of the prepared flexible PDMS/SNPs coated films at ambient temperature using the medium solutions such as at different pH ranges (2, 7, and 13). The chemical stability test was carried out to immerse each sample at different times (1, 3, 6, 9, 12, and 24 h) for medium solutions with each pH value. The during a time, the fabricated flexible superhydrophobic coated film was removed from the medium solutions, then the sample was dried at ambient conditions for one hour, and the wettability was measured by CAs and SAs.

3.3. Results

3.3.1. Wettability of fabricated superhydrophobic PDMS/SNPs coated films

Figure 21a shows the wetting image of fabricated superhydrophobic PDMS/SNPs coated films. The surface wettability of the prepared superhydrophobic coated films was investigated by CA, TA, and SA measurements as shown in Figure 21b-d (Video S6). The fabricated coated films displayed excellent superhydrophobic tendency when the hot-roll lamination temperature was 135°C with a treatment heating temperature was in the oven the 135°C at 16 minutes. Figure 21b show the CA was about 176.3°, in Figure, 21c the TA was about 2.1° and, in Figure, 21d the SA was about 2.3°.

It is known that the wettability of the surface is governed by chemical compositions that determine the surface energy and the rough surface structure. Herein, the main function of silica NPs in the hydrophobic coating is to generate nano/micro-scale roughness, and hydrophobic PDMS to make low surface energy. Meanwhile, the combination of roughness and low surface energy on the fabricated coatings results in higher contact angle [76].



Figure 21. Wettability images of the fabricated flexible superhydrophobic PDMS/SNPs coated films.

3.3.2. Surface characterization

The surface morphology plays the main character in the development of superhydrophobic surfaces. The surface morphology of flexible superhydrophobic bic PDMS/SNPs coated films is shown in Figure 22, in which the coated films with hydrophobic silica NPs are compressed to the PDMS layer during the hot-roll lamination and peeling assisted by the heat treatment process was utilized. When we use heat treatment processes the hydrophobic PDMS layer was bonded to the hydrophobic silica NPs. The fabricated PDMS/SNPs coated films exhibit a rough surface with a wide dispersion of nano/microstructures surface. The fabricated superhydrophobic PDMS/SNPs surface consists of the nano/micro hierarchical structures that help to improve the superhydrophobic tendency of the coated films [71], [76].



Figure 22. The surface structure of the fabricated superhydrophobic PDMS/SNPs coated films for (a) FE-SEM images of surface morphology and (b) confocal laser scanning microscopy results of roughness profile and surface roughness value.

The average surface roughness of the fabricated flexible PDMS/SNPs coated films was measured using confocal laser scanning microscopy Figure 22b displays the micro-scale structure via the roughness profile and surface roughness of the prepared films that measured as 5.29 μ m for the R_a , and 6.58 μ m for R_q .

The thickness of the coated film was determined using the cross-section FE-SEM image of the fabricated superhydrophobic PDMS/SNPs surface with PET film. The thickness for fabricated superhydrophobic coated films was shown in Figure 23a, which was found to be around 100 μ m above PET film.



Figure 23. Results of the fabricated PDMS/SNPs coated films for (a) FE-SEM image of cross-section and (b) EDS line for chemical composition.

The line EDS was used to determine the chemical composition of prepared PDMS/SNPs coated with PET film. The recorded EDS spectrum of the coated superhydrophobic films is shown in Figure 23b that illustrates that the PDMS/SNPs coated film with PET film is composed of carbon, oxygen, and silicon elements.

3.3.3. Mechanical durability tests

The combined micro/nanostructures superhydrophobic are generally subject to mechanical damage, which deficit the practical application. Herein, the mechanical robustness of the fabricated flexible superhydrophobic PDMS/SNPs coated films was studied using mechanical tests such as the adhesion scotch tape test, abrasion test with sandpaper, and bending test with folding.

Firstly, the scotch tape test was carried out on the fabricated superhydrophobic PDMS/SNPs coated films. The CA and SA were evaluated after the scotch tape test. A schematic diagram of the test and five different positions for the CA and SA measurements are shown in Figure 24. In Video S7 shown is the scotch tape test of the fabricated superhydrophobic coated films. Adhesion and peeling of scotch tape were replicated for the prepared coating breakdown. In Figure 25 shows the results of the CA and SA after the scotch tape test for the fabricated PDMS/SNPs coated films was condensed. The error bars with the average values in Figure 25 were designated the minimum and maximum values, and a 90 degrees value in SA means that the water droplet was attached to the surface even with tilting of 90 degrees. The resulting prepared coated films could resist scotch tape peeling with results of 20 replicating for superhydrophobic tendency with the average CAs about 170° and average SAs less than 10°. From the scotch tapepeeling test, the fabricated flexible superhydrophobic PDMS/SNPs coated films appear good mechanical durability.



Figure 24. A schematic diagram of the scotch tape test of flexible superhydrophobic coated films and the five different positions of wettability.



Figure 25. Results of the scotch tape test of the fabricated flexible PDMS/SNPs coated films for CA, and SA.

Then, an abrasion test was performed on the fabricated flexible superhydrophobic surface of PDMS/SNPs coated films. Figure 26 presents the schematic diagram of the abrasion test with sandpaper and the CA and SA measurements position of wettability. The abrasion test with sandpaper was conducted to the move distance of 500 cm. This during the distance on the fabricated coated surface after the abrasion tests did not show any sliding angle. The abrasion test of the prepared flexible superhydrophobic PDMS/SNPs coated films were displayed (Video S8), and Figure 27 shows the CA and SA results after the sandpaper test with a 10 cm move distance. The average CA was higher than 160° after a move distance of 500 cm and the average SA became less than 10° after a move distance of 400 cm. Additionally, the abrasion test with sandpaper proved that the fabricated flexible superhydrophobic coated film exhibited good mechanical durability.



Figure 26. A schematic diagram of the scratch with sandpaper test of the flexible superhydrophobic coated films and the measurement position of wettability.



Figure 27. CA and SA results of the scratch with sandpaper test of the fabricated

flexible PDMS/SNPs coated films.

Lastly, the flexibility of the superhydrophobic surface is related to water repellency. A bending test was examined on the prepared superhydrophobic coated film still exhibited extreme water repellency one folding cycle shown in Figure 28 (for details, Video S9). CA and SA average values measured after 100 folding cycles shown in Figure 29 that the fabricated surface did not undergo crucial changes compared with the one before during the experiment cycles, indicating that the coating could resist severe mechanical bending. The fabricated superhydrophobic coated films by micro/nanostructure of silica nanoparticles, together with the PDMS layer, have achieved both mechanically durable and flexible abilities.



Figure 28. The function of bending times of the fabricated flexible superhydrophobic PDMS/SNPs coated films.



Figure 29. CA and SA results of a bending test of the fabricated flexible superhydrophobic PDMS/SNPs coated films.

3.3.4. Stability in ambient air and chemical stability with pH effect

The fabricated flexible superhydrophobic PDMS/SNPs coated films were stored at room temperature for 5 months. Then, the surface wettability was evaluated with the CA and SA for stability in ambient air are shown in Figure 30. The results showed that the average CA and SA for five samples after 5 months in ambient air were 176.3° and 3.5°, respectively. The CA and SA were not degraded after storage, which indicated that the fabricated flexible superhydrophobic PDMS/SNPs coated films have long-term stability in air.



Figure 30. Results of stability in the air for the fabricated superhydrophobic PDMS/SNPs coated films.

The chemical stability of the fabricated flexible superhydrophobic PDMS/SNPs coated films was estimated in medium solution with different pH ranges (2, 7, and 13). This chemical test was performed as a function of immersion time such as 1, 3, 6, 12, and 24 h. Then, the CA and SA were measured. A schematic diagram of the chemical test and three different positions for the CA and SA measurements are shown in Figure 31.



Figure 31. A schematic diagram of the chemical stability test of the fabricated flexible superhydrophobic coated films and the three measurement positions of wettability.

The results of the average values of the CA and SA after the chemical test for the fabricated PDMS/SNPs coated films are shown in Figure 32. The CA of the fabricated coated films is gradually decreased with respect to the immersion time for all solutions. In contrast, the SA gradually increased with respect to the immersion time. The CA decreased in the range of $176 \pm 4^{\circ}$ and the SA increased in the ranges of $2.3 \pm 0.1^{\circ}$ to $9 \pm 2.2^{\circ}$ within 1, 3, 6, 12, and 24 h after immersion in acidic and neutral solutions. The wettability of the surface exhibited a small change after 12 in both acidic and neutral solutions. In contrast, in the alkaline solution, the CA decreased to 134.3° and there was no SA. These results showed, the average CAs on the fabricated flexible superhydrophobic PDMS/SNPs coated films after immersion in acidic, neutral, and alkaline solutions for 24 h are 172.7°, 172.3°, and 128°, respectively. In addition, the average SAs of the PDMS/SNPs coated films after immersion in acidic, neutral, and alkaline solutions for 24 h are approximated to be 9.5°, 9.8°, and no sliding angle, respectively. These results indicated that the fabricated superhydrophobic PDMS/SNPs coated films have strong chemical stability for acidic and neutral solutions. However, the prepared coated surface can be harmed by alkaline solution. The observed low stability

may be attributed to the chemical degradation of the PDMS used in the surface treatment of hydrophobic silica nanoparticles [51, 77]. The chemical structure of the PDMS can be degraded by hydrolysis, and hydrolysis can create a hydroxyl group that can attack the silicon atom. The presence of hydroxyl groups expands damage to the wettability of the surface [78]. In addition, the polydimethylsilox-ane (dimethyldichlorosilane) structure is observed can be degraded rapidly in al-kaline condition [51].



Figure 32. Results of the chemical stability test using acidic, neutral, and alkaline solutions for the fabricated superhydrophobic PDMS/SNPs coated films for (a) CA and (b) SA.

3.4. Discussion

PDMS as low surface energy material is used to create a relatively smooth and continuous structure with a certain degree of hydrophobicity by spraying with chemical reagents on hydrophilic surfaces [45]. The superhydrophobic surface has realized through the formation of micro/nano rough heterostructure surface involving low surface energy hydrophobic silica NPs using various coating processes [77]. Herein, the hydrophobic silica NPs is compressed to the hydrophobic PDMS layer that generates thick PDMS/SNPs layers and resulting in the improvement of superhydrophobic tendency as shown in Figure 33.



Figure 33. Effect of a process procedure for the fabricated flexible superhydrophobic PDMS/SNPs coated films.

The fabricated superhydrophobic PDMS layer with hydrophobic silica NPs is badly off for mechanical durability, which restrict the wide usage in commercial applications. The mechanical durability is an important point that restrict the application of fabricated superhydrophobic coating films [45].

Gradual loss of the superhydrophobic coating due to mechanical contact or wear that thin coating layer and surface roughness can be easily destroyed. To overcome this problem, we prepare the flexible superhydrophobic coated films with high thickness and high roughness coating layer of hydrophobic silica NPs using hot-roll lamination and peeling assisted by heat treatment. The acquired results from the mechanical durability tests disclosed that the presence of thick flexible PDMS/SNPs coated films successfully resisted adhesion and abrasion tests. The thick flexible superhydrophobic coated film with a thickness thicker higher than 100 μ m exhibited excellent mechanical robustness and good resistance in scotch tape and, scratch with sandpaper tests. Results showed that after mechanical durability tests using the sandpaper and scotch tape tests, where loss of coated film thickness, are illustrated in Figures 34a and b FE-SEM image show that after the scotch tape test the fabricated coated films keep a micro-nanostructure structure. However, after the sandpaper test there is variation on the fabricated coated films thickness.



Figure 34. FE-SEM and cross-section images of the fabricated superhydrophobic PDMS/SNPs coated films using after mechanical durability tests for (a) scotch tape test and (b) scratch with sandpaper test.

The detailed results after mechanical durability tests of the fabricated superhydrophobic PDMS/ silica NPs layer are summarized in Table 3. To show the results of aggregation, the wettability is changed of the fabricated superhydrophobic coated films, where the average CAs are decreased in the range from 15 to 20 degrees and the average SAs are increased from 18 to 23 degrees. The surface roughness of the micro/nano rough surface is damaged by about 1 micrometer of the fabricated coated films. The thickness loss of the fabricated superhydrophobic surface with silica NPs coated films ranging from 30 to 40 micrometers.

Table 3. Summarization results of after mechanical durability tests for the fabricated superhydrophobic PDMS/SNPs coated films.

	Fabricated	After the scotch	After the sandpa-			
	PDMS/SNPs	tape test (100	per test (500 cm)			
	coated film	times)				
	Average values					
Wettability (°)	CA= 176.3	CA=154.5	CA=161.6			
	SA= 2.4	SA= 20.5	SA= 26.1			
Surface rough-	$R_a = 5.29$	$R_a = 4.21$	$R_a = 3.98$			
ness (µm)	$R_q = 6.58$	$R_q = 5.31$	$R_q = 5.33$			
Thickness of						
fabricated coated	More than 100	About 70	About 60			
film (µm)						

The fabricated superhydrophobic coated thick films are inappropriate for mechanical wear resisting because mechanical wear with small force could harm the structure of coatings and the coatings lost superhydrophobicity [79]. In terms of the mechanical durability of the fabricated coated films, the mechanical durability test gradually destroys the coated layer resulting in the decrease of layer thickness along with the loss of nano-microstructures with low surface energy for superhydrophobicity, as shown in Figure 35.



Figure 35. Mechanism of mechanical durability of the fabricated superhydrophobic PDMS/SNPs coated films.

The mechanical durability of the coated layer depends on the thickness of the superhydrophobic surface with coating films. Herein, the fabricated flexible superhydrophobic PDMS/SNPs coated films have become thick for the coating layer. The mechanical durability of the coated layer with fabricated flexible superhydrophobic PDMS/SNPs surface compared to some reference papers is illustrated in Table 4. In addition, a thin coating layer of the superhydrophobic surface is easily damaged is shown in Table 4. However, the fabricated superhydrophobic surface with a thick coating layer is keep superhydrophobicity.

Methods	Materials	Thickness of	Wettability	Abrasion test	Adhesion test	Ref
		coating (µm)				
Hot-roll lamination and peeling assisted by heat treatment	PET film, PDMS and silica nanoparticles	103	CA: 176.3° SA: 2.3°	CA: 167.4° SA: 8.54° <i>after 350 cm</i> (CC-240 and P=1.2 kPa)	CA: 170.8° SA: 9.6° after 20 times (P=3.9 kPa)	This work
Electro-deposition	PDMS, silica nano- particle and mid steel	15	CA = 156.° SA=7°	CA: >150° SA: < 10° <i>after 112 cm</i> (CC-1200 and P= 0.9 kPa)	Didn't used	[80]
Spray coating	Epoxy resin, acetone, and ethanol	lower than 10	CA = 153.6° No mention SA	Didn't used	CA = 115° No data for SA <i>after 7 times</i>	[81]
Electrospray deposition	Fumed silica nano- particles, epoxy resin, and ceramic	about 2	CA = 155° No mention SA	CA =150° No data for SA <i>after 100 cm</i> (CC-600 and P= 0.5 kPa)	CA = 152° No data for SA <i>after 9 times</i>	[82]

Table 4. Comparison of mechanical durability of coating layer for the fabricated flexible superhydrophobic coated films.
The fabrication process is simple and uses a commercially available hotroll lamination and peeling process without using toxic chemicals. However, there applied the easy post-treatments process. All materials are commercially available and non-toxic. Therefore, the proposed fabrication method can be used low-cost equipment and materials. All these things are important components to apply the proposed fabrication method to mass production.

The large sizes and deformability of coated films for the fabricated flexible superhydrophobic PDMS/SNPs coated films were demonstrated in Figures 36a and b. (Video S10).



Figure 36. The fabricated flexible superhydrophobic PDMS/SNPs coated films for (a) large size image and (b) deformability.

The superhydrophobic performance was appeared on the fabricated coated films by the self-cleaning and water droplet bouncing was displayed. The selfcleaning performance of the flexible PDMS/SNPs coated films was demonstrated with the sugar powder as shown in Figure 37 (Video S11). As displayed in Figure 37, water droplets slide on the fabricated superhydrophobic coated films, the sugar powders can be trapped by the water droplets.



Figure 37. Time sequential images of the self-cleaning on the fabricated flexible superhydrophobic PDMS/SNPs coated films.

The water droplet bounce on the fabricated flexible superhydrophobic coated films is demonstrated in Figure 38 (Video S12). The fabricated film exhibited excellent superhydrophobicity to repulse the drop of water.



Figure 38. Time sequential image of the water droplet bouncing on the fabricated superhydrophobic PDMS/SNPs films.

3.5. Summary

In summary, we developed a simple and low-cost hot-roll lamination and peeling process assisted by thermal annealing to fabricate a robust superhydrophobic surface consisting of the PDMS layer and silica NPs. The results showed that the fabricated flexible superhydrophobic coated film exhibit a very large CA of 176.3° and a very small SA of 2.3° at room temperature. The surface morphology was analyzed using FE-SEM images, which revealed the formation of nano/micro-structure rough surface of flexible superhydrophobic PDMS/SNPs. The fabricated superhydrophobic flexible coated films showed very strong mechanical durability and excellent chemical stability in acidic and neutral medium solutions. However, the fabricated film exhibited very low chemical stability in a strongly alkaline medium. The practical meaning is the suitability of the large size for mass-production of mechanical durable and flexible superhydrophobic coated films using a simple and low-cost hot-roll lamination and peeling assisted by thermal annealing process using environmentally friendly and commercially available materials.

Chapter 4: Conclusion

This thesis is started with facile and low-cost methods for generating superhydrophobic coating surfaces by the hydrophobic silica nanoparticles on thermoplastic materials. These methods and polymer materials were chosen because it is simple, does not require complicated equipment, does not require chemicals, and are commercially available. The superhydrophobic surface created by these micro/nanostructures and surface materials with low surface energy was confirmed by researchers. Hydrophobic silica nanoparticles have been widely used to create combined structures on surfaces of low surface energy by various coating methods with binders for the realization of a superhydrophobic surface. Many scientists have focused on the fabrication of superhydrophobic coated surfaces with polymers and low surface energy organic materials that help to improve the surface roughness and durability. Moreover, nanoscale silica particles covered the entire surface, and random nano-microscale rough structures were formed. These nano-micro hierarchical structures with hydrophobicity could make the surface superhydrophobic. The key findings in each chapter were summarized below:

(1) A superhydrophobic surface on PP with hydrophobic silica nanoparticles was fabricated by using a compression molding process without chemical or complex equipment. The surface analyzes and robustness by CA and SA measurement on the fabricated coated films were investigated. The results showed that the surface morphology and corresponding EDS linear scan for elemental analysis showed the successful fabrication of thick superhydrophobic PP/SNPs films with nano-microscale structures having hydrophobic silica nanoparticles. Furthermore, that PP/SNPs coated films could maintain the superhydrophobic tendency after several repetitions of tape tests and long-distance scratch tests. Moreover, increasing the SNPs weight ratio in the coated films resulted in the overall improvement of mechanical durability. Mechanical robustness is of prime importance in many applications using superhydrophobic coated surfaces. Additionally, the chemical stability of the fabricated superhydrophobic coated surface was elucidated for using acidic, neutral, and alkaline solutions. The PP/SNPs coated films showed high chemical stability in acidic and neutral solutions however, the chemical stability of the fabricated superhydrophobic coated surfaces in the alkaline solution was not sufficient.

(2) Using hot-roll lamination and peeling assisted by heat treatment process for fabricating superhydrophobicity on PDMS/PET film with hydrophobic silica nanoparticles was reported. The results showed that fabricated flexible coated film was shown a large than CA of 170° and lower a SA less than 3° at ambient temperature. Moreover, the surface morphology, roughness average values, and elemental analysis with EDS line appeared the successful fabrication of flexible superhydrophobic PDMS/SNPs films with nano-microscale structures. The fabricated flexible superhydrophobic coated films were shown forceful mechanical durability with flexible and excellent chemical stability for not sufficient alkaline solution and high resistance to an acidic solution. The practical meaning is the suitability of the large size for mass production of mechanical durable and flexible superhydrophobic coated films.

REFERENCES

- Fei L, He Z, LaCoste JD, Nguyen TH, Sun Y (2020) A Mini Review on Superhydrophobic and Transparent Surfaces. Chem Rec 20:1257–1268
- Kim W, Kim D, Park S, Lee D, Hyun H, Kim J (2018) Engineering lotus leaf-inspired micro-and nanostructures for the manipulation of functional engineering platforms. J Ind Eng Chem 61:39–52
- 3. Parvate S, Dixit P, Chattopadhyay S (2020) Superhydrophobic surfaces: insights from theory and experiment. J Phys Chem B 124:1323–1360
- Manoharan K, Bhattacharya S (2019) Superhydrophobic surfaces review: Functional application, fabrication techniques and limitations. J Micromanufacturing 2:59–78
- Zhou M, Xiong X, Jiang B, Weng C (2018) Fabrication of high aspect ratio nanopillars and micro/nano combined structures with hydrophobic surface characteristics by injection molding. Appl Surf Sci 427:854–860
- Hooda A, Goyat MS, Pandey JK, Kumar A, Gupta R (2020) A review on fundamentals, constraints and fabrication techniques of superhydrophobic coatings. Prog Org Coatings 142:105557
- 7. Deeksha P, Deepika G, Nishanthini J, Hikku GS, Jeyasubramanian K, Murugesan R (2020) Super-hydrophobicity: Mechanism, fabrication and its application in medical implants to prevent biomaterial associated infections. J Ind Eng Chem
- Zhang B, Zhao X, Li Y, Hou B (2016) Fabrication of durable anticorrosion superhydrophobic surfaces on aluminum substrates via a facile one-step electrodeposition approach. Rsc Adv 6:35455–35465
- Hozumi A, Cheng DF, Yagihashi M (2011) Hydrophobic/superhydrophobic oxidized metal surfaces showing negligible contact angle hysteresis. J Colloid Interface Sci 353:582–587
- 10. Syed JA, Tang S, Meng X (2017) Super-hydrophobic multilayer coatings with layer number tuned swapping in surface wettability and redox catalytic

anti-corrosion application. Sci Rep 7:1-17

- 11. Zhang X, Zheng F, Ye L, Xiong P, Yan L, Yang W, Jiang B (2014) A onepot sol-gel process to prepare a superhydrophobic and environmentresistant thin film from ORMOSIL nanoparticles. RSC Adv 4:9838–9841
- Lee K-M, Ngo C-V, Jeong J-Y, Jeon E, Je T-J, Chun D-M (2017) Fabrication of an anisotropic superhydrophobic polymer surface using compression molding and dip coating. Coatings 7:194
- Zhang Z-X, Zhang T, Zhang X, Xin Z, Deng X, Prakashan K (2016) Mechanically stable superhydrophobic polymer films by a simple hot press lamination and peeling process. RSC Adv 6:12530–12536
- Maghsoudi K, Momen G, Jafari R, Farzaneh M, Carreira T (2018) Micronanostructured silicone rubber surfaces using compression molding. Mater Sci Forum 941 MSF:1802–1807 . https://doi.org/10.4028/www.scientific.net/MSF.941.1802
- Lee KM, Ngo CV, Jeong JY, Jeon E chae, Je TJ, Chun DM (2017) Fabrication of an anisotropic superhydrophobic polymer surface using compression molding and dip coating. Coatings 7: . https://doi.org/10.3390/coatings7110194
- Maghsoudi K, Momen G, Jafari R, Farzaneh M, Carreira T (2018) Micronanostructured silicone rubber surfaces using compression molding. In: Materials Science Forum. Trans Tech Publ, pp 1802–1807
- Zhi J-H, Zhang L-Z, Yan Y, Zhu J (2017) Mechanical durability of superhydrophobic surfaces: The role of surface modification technologies. Appl Surf Sci 392:286–296
- Chen K, Gu K, Qiang S, Wang C (2017) Environmental stimuli-responsive self-repairing waterbased superhydrophobic coatings. RSC Adv 7:543–550
- Latthe SS, Sutar RS, Kodag VS, Bhosale AK, Kumar AM, Sadasivuni KK, Xing R, Liu S (2019) Self–cleaning superhydrophobic coatings: Potential industrial applications. Prog Org Coatings 128:52–58

- 20. Zhang X, Liu Z, Li Y, Cui Y, Wang H, Wang J (2020) Durable superhydrophobic surface prepared by designing "micro-eggshell" and "web-like" structures. Chem Eng J 392:123741
- Sun R, Zhao J, Li Z, Mo J, Pan Y, Luo D (2019) Preparation of mechanically durable superhydrophobic aluminum surface by sandblasting and chemical modification. Prog Org Coatings 133:77–84
- 22. Wang N, Xiong D, Deng Y, Shi Y, Wang K (2015) Mechanically robust superhydrophobic steel surface with anti-icing, UV-durability, and corrosion resistance properties. ACS Appl Mater Interfaces 7:6260–6272
- 23. Wu B, Lyu J, Peng C, Liu J, Xing S, Jiang D, Ju S, Tiwari MK (2020) Compression molding processed superhydrophobic CB/CeO2/PVDF/CF nanocomposites with highly robustness, reusability and multifunction. Colloids Surfaces A Physicochem Eng Asp 590:124533
- Sun R, Zhao J, Li Z, Mo J, Pan Y, Luo D (2019) Preparation of mechanically durable superhydrophobic aluminum surface by sandblasting and chemical modification. Prog Org Coatings 133:77–84 . https://doi.org/10.1016/j.porgcoat.2019.04.020
- Peng C, Chen Z, Tiwari MK (2018) All-organic superhydrophobic coatings with mechanochemical robustness and liquid impalement resistance. Nat Mater 17:355–360
- Onda T, Shibuichi S, Satoh N, Tsujii K (1996) Super-water-repellent fractal surfaces. Langmuir 12:2125–2127
- Zhi JH, Zhang LZ, Yan Y, Zhu J (2017) Mechanical durability of superhydrophobic surfaces: The role of surface modification technologies. Appl Surf Sci 392:286–296 . https://doi.org/10.1016/j.apsusc.2016.09.049
- 28. Zhang X, Wang H, Liu Z, Zhu Y, Wu S, Wang C, Zhu Y (2017) Fabrication of durable fluorine-free superhydrophobic polyethersulfone (PES) composite coating enhanced by assembled MMT-SiO 2 nanoparticles. Appl Surf Sci 396:1580–1588 . https://doi.org/10.1016/j.apsusc.2016.11.217

- Gong X, He S (2020) Highly durable superhydrophobic polydimethylsiloxane/silica nanocomposite surfaces with good selfcleaning ability. ACS omega 5:4100–4108
- Chen H, Zhang X, Zhang P, Zhang Z (2012) Facile approach in fabricating superhydrophobic SiO2/polymer nanocomposite coating. Appl Surf Sci 261:628–632 . https://doi.org/https://doi.org/10.1016/j.apsusc.2012.08.071
- 31. Jain R, Pitchumani R (2018) Fabrication and characterization of zinc-based superhydrophobic coatings. Surf Coatings Technol 337:223–231
- Liu W, Luo Y, Sun L, Wu R, Jiang H, Liu Y (2013) Fabrication of the superhydrophobic surface on aluminum alloy by anodizing and polymeric coating. Appl Surf Sci 264:872–878
- 33. Xu D, Wang M, Ge X, Lam MH-W, Ge X (2012) Fabrication of raspberry SiO 2/polystyrene particles and superhydrophobic particulate film with high adhesive force. J Mater Chem 22:5784–5791
- Liu M, Jia Z, Liu F, Jia D, Guo B (2010) Tailoring the wettability of polypropylene surfaces with halloysite nanotubes. J Colloid Interface Sci 350:186–193
- 35. Maghsoudi K, Momen G, Jafari R, Farzaneh M (2018) Direct replication of micro-nanostructures in the fabrication of superhydrophobic silicone rubber surfaces by compression molding. Appl Surf Sci 458:619–628
- 36. Chun D-M, Davaasuren G, Ngo C-V, Kim C-S, Lee G-Y, Ahn S-H (2014) Fabrication of transparent superhydrophobic surface on thermoplastic polymer using laser beam machining and compression molding for mass production. CIRP Ann 63:525–528
- Erbil HY, Demirel AL, Avcı Y, Mert O (2003) Transformation of a simple plastic into a superhydrophobic surface. Science (80-) 299:1377–1380
- Contreras CB, Chagas G, Strumia MC, Weibel DE (2014) Permanent superhydrophobic polypropylene nanocomposite coatings by a simple onestep dipping process. Appl Surf Sci 307:234–240

- Kansara AM, Chaudhri SG, Singh PS (2016) A facile one-step preparation method of recyclable superhydrophobic polypropylene membrane for oil– water separation. RSC Adv 6:61129–61136
- 40. Hejazi I, Seyfi J, Hejazi E, Sadeghi GMM, Jafari SH, Khonakdar HA (2015) Investigating the role of surface micro/nano structure in cell adhesion behavior of superhydrophobic polypropylene/nanosilica surfaces. Colloids Surfaces B Biointerfaces 127:233–240
- Zhu X, Zhang Z, Men X, Yang J, Wang K, Xu X, Zhou X, Xue Q (2011) Robust superhydrophobic surfaces with mechanical durability and easy repairability. J Mater Chem 21:15793–15797
- Kumar A, Gogoi B (2018) Development of durable self-cleaning superhydrophobic coatings for aluminium surfaces via chemical etching method. Tribol Int 122:114–118
- 43. She Z, Li Q, Wang Z, Li L, Chen F, Zhou J (2013) Researching the fabrication of anticorrosion superhydrophobic surface on magnesium alloy and its mechanical stability and durability. Chem Eng J 228:415–424
- 44. Wang H, He M, Liu H, Guan Y (2019) One-step fabrication of robust superhydrophobic steel surfaces with mechanical durability, thermal stability, and anti-icing function. ACS Appl Mater Interfaces 11:25586– 25594
- Xue C-H, Tian Q-Q, Jia S-T, Zhao L-L, Ding Y-R, Li H-G, An Q-F (2020) The fabrication of mechanically durable and stretchable superhydrophobic PDMS/SiO 2 composite film. RSC Adv 10:19466–19473
- 46. Liu M, Luo Y, Jia D (2020) Synthesis of mechanically durable superhydrophobic polymer materials with roughness-regeneration performance. Compos Part A Appl Sci Manuf 133:105861
- Zhang X, Zhi D, Sun L, Zhao Y, Tiwari MK, Carmalt CJ, Parkin IP, Lu Y (2018) Super-durable, non-fluorinated superhydrophobic free-standing items. J Mater Chem A 6:357–362

- Zimmermann J, Artus GRJ, Seeger S (2007) Long term studies on the chemical stability of a superhydrophobic silicone nanofilament coating. Appl Surf Sci 253:5972–5979
- 49. Liu Y, Xi N, Fu S, Yang G, Fu H, Chen H, Zhang X, Liu N, Gao W (2018) Mechanical and chemical stability of super-hydrophobic coatings on SMA490BW substrate prepared by HVOF spraying. Mater Res Express 5:115030
- Yin L, Yang J, Tang Y, Chen L, Liu C, Tang H, Li C (2014) Mechanical durability of superhydrophobic and oleophobic copper meshes. Appl Surf Sci 316:259–263 . https://doi.org/10.1016/j.apsusc.2014.08.002
- Ducom G, Laubie B, Ohannessian A, Chottier C, Germain P, Chatain V (2013) Hydrolysis of polydimethylsiloxane fluids in controlled aqueous solutions. Water Sci Technol 68:813–820
- 52. Gong X, He S (2020) Highly Durable Superhydrophobic Polydimethylsiloxane/Silica Nanocomposite Surfaces with Good Self-Cleaning Ability. ACS omega 5:4100–4108
- 53. Zhi J, Zhang L-Z (2018) Durable superhydrophobic surface with highly antireflective and self-cleaning properties for the glass covers of solar cells. Appl Surf Sci 454:239–248
- Jung YC, Bhushan B (2008) Dynamic effects of bouncing water droplets on superhydrophobic surfaces. Langmuir 24:6262–6269
- Crick CR, Parkin IP (2011) Water droplet bouncing—a definition for superhydrophobic surfaces. Chem Commun 47:12059–12061
- 56. Wu Y, Shen Y, Tao J, He Z, Xie Y, Chen H, Jin M, Hou W (2018) Facile spraying fabrication of highly flexible and mechanically robust superhydrophobic F-SiO 2@ PDMS coatings for self-cleaning and dragreduction applications. New J Chem 42:18208–18216
- 57. Celik N, Torun I, Ruzi M, Esidir A, Onses MS (2020) Fabrication of robust superhydrophobic surfaces by one-step spray coating: evaporation driven

self-assembly of wax and nanoparticles into hierarchical structures. Chem Eng J 396:125230

- 58. Zhang X, Zhu W, He G, Zhang P, Zhang Z, Parkin IP (2016) Flexible and mechanically robust superhydrophobic silicone surfaces with stable Cassie–Baxter state. J Mater Chem A 4:14180–14186
- 59. Wang J, Chen H, Wang X, Yuan Z (2016) Facile method to prepare a transparent superhydrophobic PET film. Appl Phys A 122:1–7
- Li S, Liu X, Li L, Zhang H, Qiu C (2019) Drag-reductive and anti-corrosive superhydrophobic surface fabricated on aluminum with thin PDMS/SiO2 coating. Mater Res Express 6:1065a8
- Li D-W, Wang H-Y, Liu Y, Wei D-S, Zhao Z-X (2019) Large-scale fabrication of durable and robust super-hydrophobic spray coatings with excellent repairable and anti-corrosion performance. Chem Eng J 367:169– 179
- Maghsoudi K, Vazirinasab E, Momen G, Jafari R (2020) Advances in the fabrication of superhydrophobic polymeric surfaces by polymer molding processes. Ind Eng Chem Res 59:9343–9363
- Endo T, Reddy L, Nishikawa H, Kaneko S, Nakamura Y, Endo K (2017) Composite engineering–direct bonding of plastic PET films by plasma irradiation. Procedia Eng 171:88–103
- Goh CS, Tan SC, Ngoh SL, Wei J (2012) Surface treatment of polyethylene terephthalate (PET) film for lamination of flexible photovoltaic devices. Energy Procedia 15:428–435
- 65. Han MH, Jegal JP, Park KW, Choi JH, Baik HK, Noh JH, Song KM, Lim YS (2007) Surface modification for adhesion enhancement of PETlaminated steel using atmospheric pressure plasma. Surf coatings Technol 201:4948–4952
- 66. Ye X, Cai D, Ruan X, Cai A (2018) Research on the selective adhesion characteristics of polydimethylsiloxane layer. AIP Adv 8:95004

- Kim D, Yun K-S (2013) Patterning of carbon nanotube films on PDMS using SU-8 microstructures. Microsyst Technol 19:743–748
- Zhang Z-X, Zhao X, Li Y-N, Ma Z-G, Xin ZX, Prakashan K (2016) Fabrication of a superhydrophobic LLDPE film by thermal lamination and peeling. J Polym Eng 36:635–640
- Zhang Z-X, Li Y, Ye M, Boonkerd K, Xin Z, Vollmer D, Kim JK, Deng X (2014) Fabrication of superhydrophobic surface by a laminating exfoliation method. J Mater Chem A 2:1268–1271
- Zhang ZX, Li YN, Xia L, Ma ZG, Xin ZX, Kim JK (2014) Fabrication of superhydrophobic film by microcellular plastic foaming method. Appl Phys A 117:755–759
- Park EJ, Sim JK, Jeong M-G, Seo HO, Kim YD (2013) Transparent and superhydrophobic films prepared with polydimethylsiloxane-coated silica nanoparticles. RSC Adv 3:12571–12576
- 72. Xie J, Hu J, Lin X, Fang L, Wu F, Liao X, Luo H, Shi L (2018) Robust and anti-corrosive PDMS/SiO2 superhydrophobic coatings fabricated on magnesium alloys with different-sized SiO2 nanoparticles. Appl Surf Sci 457:870–880 . https://doi.org/10.1016/j.apsusc.2018.06.250
- 73. Chang H, Tu K, Wang X, Liu J (2015) Fabrication of mechanically durable superhydrophobic wood surfaces using polydimethylsiloxane and silica nanoparticles. RSC Adv 5:30647–30653 . https://doi.org/10.1039/c5ra03070f
- 74. Cao C, Yi B, Zhang J, Hou C, Wang Z, Lu G, Huang X, Yao X (2020) Sprayable superhydrophobic coating with high processibility and rapid damage-healing nature. Chem Eng J 392:124834
- 75. Wang N, Lu Y, Xiong D, Carmalt CJ, Parkin IP (2016) Designing durable and flexible superhydrophobic coatings and its application in oil purification. J Mater Chem A 4:4107–4116
- 76. Tang X, Wang T, Yu F, Zhang X, Zhu Q, Pang L, Zhang G, Pei M (2013)

Simple, robust and large-scale fabrication of superhydrophobic surfaces based on silica/polymer composites. RSC Adv 3:25670–25673

- 77. Erdene-Ochir O, Chun D-M (2021) Robust Superhydrophobic Surface on Polypropylene with Thick Hydrophobic Silica Nanoparticle-Coated Films Prepared by Facile Compression Molding. Energies 14:3155
- Zhong L, Gong X (2019) Phase separation-induced superhydrophobic polylactic acid films. Soft Matter 15:9500–9506
- 79. Zhang X, Liu Z, Li Y, Cui Y, Wang H, Wang J (2020) Durable superhydrophobic surface prepared by designing "micro-eggshell" and "web-like" structures. Chem Eng J 392:123741. https://doi.org/10.1016/j.cej.2019.123741
- Zhang X-F, Chen Y-Q, Hu J-M (2020) Robust superhydrophobic SiO2/polydimethylsiloxane films coated on mild steel for corrosion protection. Corros Sci 166:108452
- 81. Cai C, Sang N, Teng S, Shen Z, Guo J, Zhao X, Guo Z (2016) Superhydrophobic surface fabricated by spraying hydrophobic R974 nanoparticles and the drag reduction in water. Surf Coatings Technol 307:366–373
- Rahman MK, Phung TH, Oh S, Kim SH, Ng TN, Kwon K-S (2021) High-Efficiency Electrospray Deposition Method for Nonconductive Substrates: Applications of Superhydrophobic Coatings. ACS Appl Mater Interfaces 13:18227–18236

Appendices

Appendix A: Credits & Copyright Permissions

Notes on Copyright Licenses for Reproduction of Text and Figures in this Thesis

Chapter 1:

For reproducing those figures that have appeared in the following publication with credit to other sources, permission has also been sought from the respective sources.

Chapter 2:

The text excerpts and the figures presented in Chapter Two are reproduced with permission from the following article:

Oyunchimeg Erdene-Ochir, and Doo-Man Chun, "*Robust Superhydrophobic Surface on Polypropylene with Thick Hydrophobic Silica Nanoparticle-Coated Films Prepared by Facile Compression molding*", Energies 2021, 14, 3155.

Appendix B: The wettability and image of fabricated superhydrophobic PA6/SNPs coated films using the compression molding process.

In addition, we are studying the fabrication of robust superhydrophobic surfaces with different thermoplastic polymer materials. Figure A 1 shows the wettability by measuring CA and SA of the fabricated superhydrophobic surface on polyamide 6 (PA6) with hydrophobic silica nanoparticles (SNPs) coated films using the compression molding process.



Figure A 1. Image and wettability of the fabricated superhydrophobic PA6/SNPs coated films using the compression molding process.