

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**FABRICATION OF MICROPORES ON
POLYDIMETHYLSILOXANE SURFACE VIA STEAM ANNEALING
PROCESS**

SEVDE ÖMEROĞLU
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
CHEMICAL ENGINEERING DEPARTMENT

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THESIS SUPERVISOR
ASST. PROF. MUHAMMED ENES ORUÇ

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

POLİDİMETİLSİLOKSAN YÜZEY
ÜZERİNDE BUHAR TAVLAMA PROSESİ
İLE MİKRO GÖZENEKLERİN
OLUŞTURULMASI

SEVDE ÖMEROĞLU
YÜKSEK LİSANS TEZİ
KİMYA MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
DR. ÖĞR. ÜYESİ MUHAMMED ENES ORUÇ

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2022



YÜKSEK LİSANS JÜRİ ONAY FORMU

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SUMMARY

The development of superhydrophobic surfaces (SHS) with water-repellent properties is a very important area for industries such as construction, automotive, aerospace, and food processing due to their corrosion protection, pollution reduction, and self-cleaning properties. For this purpose, it is aimed to develop an alternative method to impart superhydrophobic properties to polydimethylsiloxane (PDMS) surfaces that can be produced with a simple methodology, biocompatible, fast, and easy to manufacture.

In this study, microporous structures have been created by applying hot water steam at high pressure to PDMS surfaces prepared with three different mixing ratios. The surfaces have been coated with silica nanoparticles with hydrophobic properties by the spray coating method. In addition, the properties of silica nanoparticle-coated microporous PDMS superhydrophobic surfaces and the durability of nanoparticles have been investigated. The surfaces have been characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and contact angle measurement.

Morphological analysis results on SEM images show that PDMS surfaces prepared with different mixing ratios change the pore size and hydrophobic properties formed on the surfaces. In the study, 5:1, 10:1 and 20:1 (w/w) prepolymer and curing agent mixture ratios were studied. The maximum microporous surface area was formed on the PDMS surface prepared with a ratio of 20:1 (w/w). The water contact angles of the microporous surfaces prepared at mixing ratios of 5:1, 10:1 and 20:1 (w/w) are 125°, 134° and 148°, respectively. The water contact angles of the surfaces covered with silica nanoparticles have as 158°, 172° and 176°, respectively. To examine the SHS strength, water spray impact test was applied and PDMS surface with 20:1 (w/w) ratio showed the best durability.

Key Words: Superhydrophobicity, Polydimethylsiloxane (PDMS), Steam Annealing.

ÖZET

Su itici özelliğe sahip süperhidrofobik yüzeylerin geliştirilmesi, korozyona karşı koruma, kirlenmeyi azaltma ve kendi kendini temizleme özellikleri nedeniyle inşaat, otomotiv, havacılık ve gıda işleme gibi sektörler için oldukça önemli bir alandır. Bu amaçla, biyo uyumlu, hızlı ve kolay imal edilebilen, basit bir metodoloji ile üretilen polidimetilsiloksan (PDMS) yüzeylere süperhidrofobik özellik kazandırmak için alternatif bir yöntemin geliştirilmesi hedeflenmiştir.

Bu çalışmada, üç farklı karışım oranları ile hazırlanan PDMS yüzeylere, yüksek basınçta sıcak su buharı uygulanarak mikro gözenekli yapılar oluşturulmuştur. Yüzeyler, sprey kaplama yöntemi ile hidrofobik özelliğe sahip silica nanopartiküller ile kaplanmıştır. Ayrıca silica nanopartikül kaplı mikro gözenekli PDMS süperhidrofobik yüzeylerin özellikleri ve nanopartiküllerin dayanımları incelenmiştir. Yüzeyler, taramalı elektron mikroskobu (SEM), X-ışını fotoelektron spektroskopisi (XPS), Fourier dönüşümü kızılötesi spektroskopisi (FTIR) ve temas açısı ölçümü ile karakterize edilmiştir.

SEM görüntüleri üzerinde yapılan morfolojik analiz sonuçları, farklı karışım oranları ile hazırlanan PDMS yüzeylerin, yüzeyler üzerinde oluşan gözenek boyutunu ve hidrofobik özelliklerini değiştirdiğini göstermektedir. Çalışmada 5:1, 10:1 ve 20:1 (w/w) prepolimer ve kütleme ajanı karışım oranları ile çalışılmıştır. En fazla mikro-gözenek yüzey alanı, 20:1 (w/w) oranıyla hazırlanan PDMS yüzey üzerinde oluşturulmuştur. 5:1, 10:1 ve 20:1 (w/w) karışım oranlarında hazırlanan mikro gözenekli yüzeylerin su temas açıları sırasıyla 125°, 134° ve 148°' dir ve silica nanopartiküller ile kaplı yüzeylerin su temas açıları ise sırasıyla 158°, 172° ve 176° olarak ölçülmüştür. Süperhidrofobik yüzey dayanımını incelemek için su sprey darbe testi uygulanmıştır ve en iyi dayanımı 20:1 (w/w) karışım oranına sahip PDMS yüzey göstermiştir.

Anahtar Kelimeler: Süperhidrofobiklik, Polidimetilsiloksan, Buhar Tavlama.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations</u> <u>and Acronyms</u>	<u>Explanations</u>
~	: Approximately
<	: Less than
>	: Greater than
°	: Degree
°C	: The degree Celsius
θ	: Contact angle
γ_{SL}	: Interfacial tension of solid-liquid interfaces
γ_{SV}	: Interfacial tension of solid-vapor interfaces
γ_{LV}	: Interfacial tension of liquid-vapor interfaces
θ_Y	: Young's contact angle
C	: Carbon
C4F8	: Octafluorocyclobutane
CPS	: Counts per second
DMF	: Dimethylformamide
eV	: Electrovolt
Fe ₃ O ₄	: Iron (II, III) oxide
FTIR	: Fourier Transform Infrared Spectroscopy
kV	: Kilovolt
LBL	: Layer-by-layer
MC	: Microcapsules
NPs	: Nanoparticles
O	: Oxygen
OH	: Hydroxyl
PDMS	: Polydimethylsiloxane
SEM	: Scanning Electron Microscopy
SHS	: Superhydrophobic surfaces
Si	: Silicon
THF	: Tetrahydrofuran
w/w	: weight per weight

WCA : Water contact angle
XPS : X-ray Photoelectron Spectroscopy



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1. INTRODUCTION

1.1. Motivation

The advancements in micro and nanofabrication techniques and nanomaterials allow simulating nature's unique properties to practical applications. For example, the fabrication of superhydrophobic surfaces (SHS) is of great interest for oil-water separation, anti-corrosion, and self-cleaning. We define SHS as static contact angles higher than 150° and sliding angles less than 5° . For superhydrophobicity, two factors surface chemistry and surface roughness, play a vital role. Therefore, it is required to increase surface roughness and reduce the surface energy to accomplish SHS [1]. In order to provide these two characteristics, the sol-gel method, electrospinning, electrochemical methods, plasma techniques, a layer-by-layer method, and spray coating of nanoparticles are primarily used [2].

Coating surfaces with nanoparticles is a practical approach to achieving SHS [3]. The coated nanoparticles reduce the surface energy and create roughness, minimizing contact between the solid surface and the liquid [4]. However, when the liquid surface is exposed to mechanical load, the nano-based coating can be easily discharged, and the superhydrophobic property cannot be protected [5]. It has been proved that robust superhydrophobicity can be achieved by utilizing an appropriate microstructure design as shielding pockets for nanostructures which provides mechanical durability [6].

Polydimethylsiloxane (PDMS) elastomer with microscale structures can be used as an ideal reservoir for nanoparticles (NPs) for its simple manufacturing [7]. Lithographic techniques are complicated procedures making them challenging to implement at the industrial scale. Therefore, the methods such as direct templating, emulsion templating, gas foaming, and phase separation techniques have been used to fabricate porous microstructures [8]. However, these methods require using different solvents or inorganic additives, additional steps of curing and etching, and suffer from the pores with broad size distribution and random arrangement. Therefore, for practical applications, they are not useful fabricating techniques for PDMS, and a straightforward methodology that is fast and easy to manufacture is essential.

A cost-effective and straightforward PDMS porous structure production, called steam annealing, has been developed for flexible electronic applications [9], [10]. In

principle, in a pressurized chamber, an uncured PDMS layer is exposed to hot water vapor resulting in hole formation on the surface. Rapid curing occurs, and around ten μm pores are formed quickly.

1.2. The Objective of the Thesis

This thesis aims to fabricate micro-holes on the PDMS surface via the steam annealing process and deposit nanoparticles within these microstructures. We hypothesized that these micro-holes could act as a reservoir for nanoparticles. In this way, the mechanical durability of the superhydrophobic surface resistance against abrasion will be provided. The objectives of the thesis are to:

- investigate the micro-hole size by varying the PDMS base and curing ratio,
- deposit the nanoparticles via spray coating on the PDMS surface,
- perform tests against abrasion and water impact.

1.3. The Scope of the Thesis

In this study, we fabricated PDMS substrates with micro holes via the steam annealing process. The holes' size was analyzed by the ImageJ software to investigate the effect of PDMS base and curing ratio on morphology. Then we used the spray coating method to deposit the nanoparticles on these surfaces. Finally, we tested the wettability of the surfaces after exposure to mechanical abrasion and water impact.

2. BACKGROUND

2.1. Superhydrophobicity

Wettability is a phenomenon that any surface exhibits when it comes into contact with water; for example, some surfaces are readily wetted by water, while others repel water droplets [11]. The contact angle between any surface and a liquid determines the degree of liquid repulsion of the surfaces. Surface tension and surface energy play an essential role in predicting the behavior of a liquid on the surface. Thomas Young pioneered the determination of the effects of surface tension and surface energy on wettability [12]. Young's studies demonstrated that the contact angle of liquid dropped onto flat solid surface changes as a function of the surface free energy of the solid surface. Thus, the surface's wettability depends on both the surface tension of the liquid and the energy of the solid surface. Mathematically, Young's equation, as shown in Equation (2.1), describes the wetting of a liquid on an ideal surface [13].

$$\cos\theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \quad (2.1)$$

Where θ is the contact angle of the liquid on a surface, γ is the surface tension, γ_{SV} , γ_{SL} , and γ_{LV} are the surface tension of the solid-vapor interface, solid-liquid interface, and liquid-vapor interface, respectively (Figure 2.1a). In general, the surface wetting behavior is divided into three groups based on the water contact angle (WCA) obtained from Young's model. WCA values in the range of $0^\circ < \theta \leq 90^\circ$, $90^\circ < \theta \leq 150^\circ$, and $150^\circ < \theta \leq 180^\circ$ are categorized as hydrophilic, hydrophobic, and superhydrophobic surfaces, respectively (Figure 2.1b) [14].

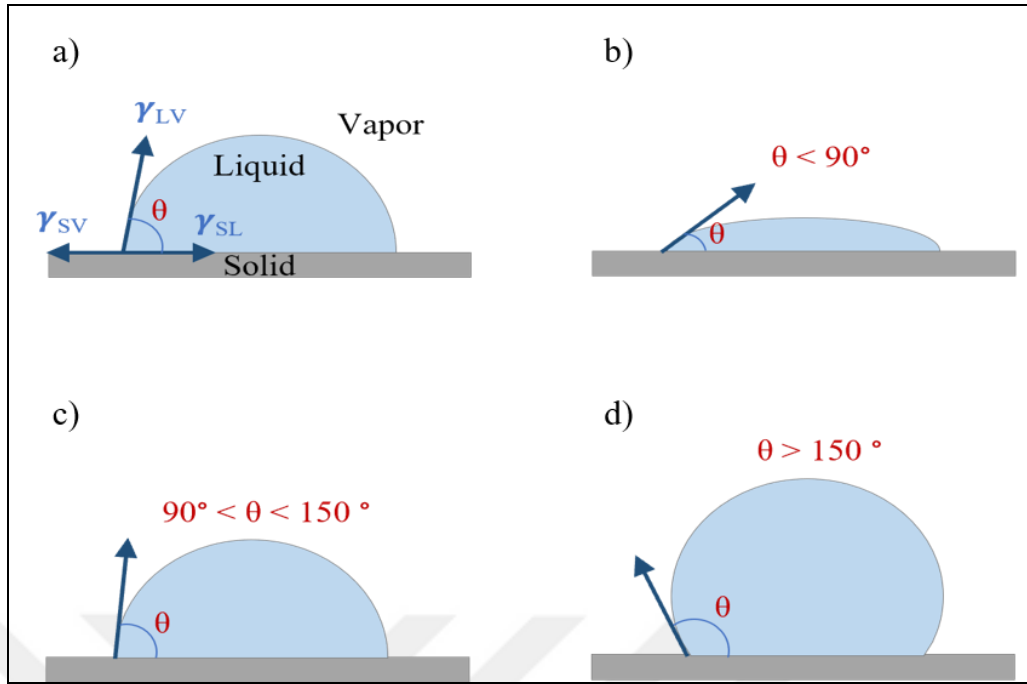


Figure 2.1: a) Illustration of the three-phase contact line of a droplet on a smooth surface in Young's model. b) Hydrophilic, c) hydrophobic, and d) superhydrophobic states of water droplets on surfaces.

In addition to low surface energy, surface roughness also allows for the formation of superhydrophobic surfaces. Surfaces without roughness do not show superhydrophobic properties. Wenzel and Cassie-Baxter models describe the effect of rough surfaces on superhydrophobic surfaces [15], [16].

According to the Wenzel method, as the roughness of a hydrophilic surface increases, the contact angle of the surface decreases and the surface wetting behavior of the liquid increases. On the other hand, it is observed that there is an increase in the water contact angle on the hydrophobic surface. Due to the gravitational effect on hydrophilic surfaces, it infiltrates into the rough surface.

Cassie-Baxter method, when the surface roughness is in the nano and micron size, the water repellency of the surface increases thanks to the air trapped between the rough surfaces. In other words, the hydrophobicity of the surface increases when air is trapped between the rough surfaces. Since the distance between the rough structures is large in the Wenzel method, it is not possible to compress air on the rough surface. A schematic of the Wenzel and Cassie-Baxter wetting model on a roughness surface is given in Figure 2.2 [16].

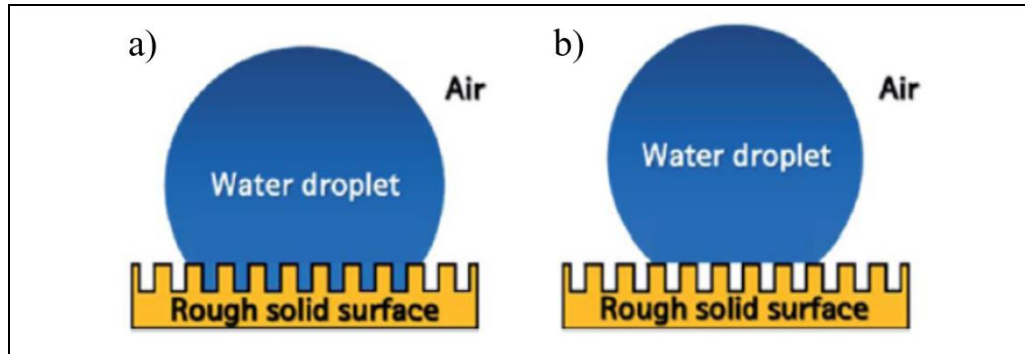


Figure 2.2: A schematic illustration of a) Wenzel model and b) Cassie-Baxter model.

2.2. Fabrication Methods of Superhydrophobic Surfaces

To obtain superhydrophobic surfaces, the surface roughness must be increased and the surface energy reduced. The production of superhydrophobic surfaces can be achieved by roughening the surface of a material with low surface energy or by reducing the surface energy of a rough material [17]-[19]. This section briefly describes the methods used to produce superhydrophobic surfaces.

2.2.1. Sol-Gel Method

More desirable are single-step and simple applications where high roughness and low surface energy are achieved simultaneously. The sol-gel method is a frequently preferred method for producing superhydrophobic surfaces because it is technically simple to apply, inexpensive, and easy to control in the process. Luo et al. [20] prepared microcapsules (MCs) with durable superhydrophobic/superoleophilic properties so that oil droplets could be easily separated from the emulsion. The surfaces were coated with a sol-gel surface treatment consisting of (3-aminopropyl), triethoxysilane (APTES), and tetraethylorthosilicate (TEOS) materials (Figure 2.3). The resulting MCs were superhydrophobic, and after the UV aging test and the solvent immersion test was performed at specific times, water contact angles of more than 160° and shear angles (SAs) of less than 3° were observed. In another study, Latthe et al. [21] observed durable superhydrophobic coating on glass with the silica-polymethylmethacrylate (PMMA) polymer they prepared by the sol-gel method. The

surface microstructure and wettability were not affected under the water jet test, and the water contact angle of the surface was measured at 159°.

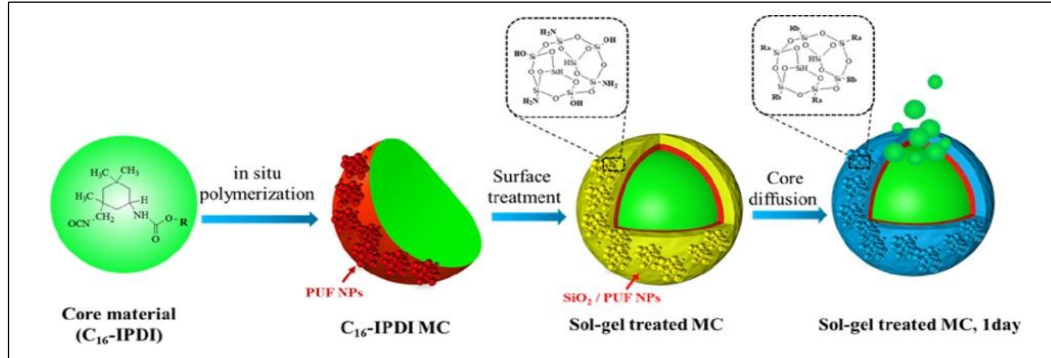


Figure 2.3: Preparation of superhydrophobic sol-gel treated MCs.

2.2.2. Electrospinning

Electrospinning is a method of producing micro-and nanofibers by applying a voltage to polymer solutions. This method, which is very suitable for creating rough surfaces, is a prevalent method for obtaining superhydrophobic surfaces. Ma et al. focused on electrospinning polystyrene-polydimethylsiloxane copolymers and polystyrene homopolymers to develop low surface energy surfaces. Thus, they fabricated siloxane polymer fibers with low surface energy and a water contact angle of 163° [22]. Miyauchi et al. created biomimetic superhydrophobic surfaces (Figure 2.4) with the microfiber surfaces they fabricated with microfibrillar polystyrene mats (PS) [23]. Micro and nanostructures on microfiber structures increased hydrophobicity. By changing the solvent mixture dimethylformamide (DMF) / tetrahydrofuran (THF) ratios, the best contact angle value was measured as 159,5°. Zhu et al. used the electrospinning method and carbonization to create magnetic Fe₃O₄-filled CNFs with superhydrophobic characteristics [24]. The contact angle value was measured as 152.3° in CNF films filled with 50% Fe₃O₄ by weight.

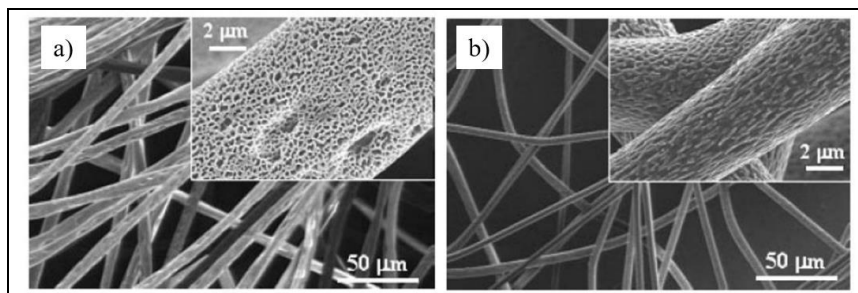


Figure 2.4: SEM images of the PS fibers by electrospinning method with different weight ratios of THF/DMF; a) 3/1, b) 2/2.

2.2.3. Electrochemical Methods

Electrochemical processes are a highly preferred method as they can be applied to extensive surfaces as well as create various surface morphologies. This method is easy to implement and is faster than many methods. Furthermore, this approach creates surfaces with multiple morphologies, such as dendrites, fibers, and tubes. Ye et al. obtained a porous surface in the form of a honeycomb by applying anodic oxidation on anodic aluminum oxide (AAO) films [25]. Oikawa et al. achieved microcones surfaces with 10 nm pores and a wetting angle of 158° on anodic niobium layers by anodizing niobium in glycerol electrolyte [26]. Song et al. used sodium chloride (NaCl) solution containing fluoroalkylsilane on aluminum surfaces as electrolytes (Figure 2.5) and obtained superhydrophobic surfaces by getting rough structures with a one-step electrochemical process [27].

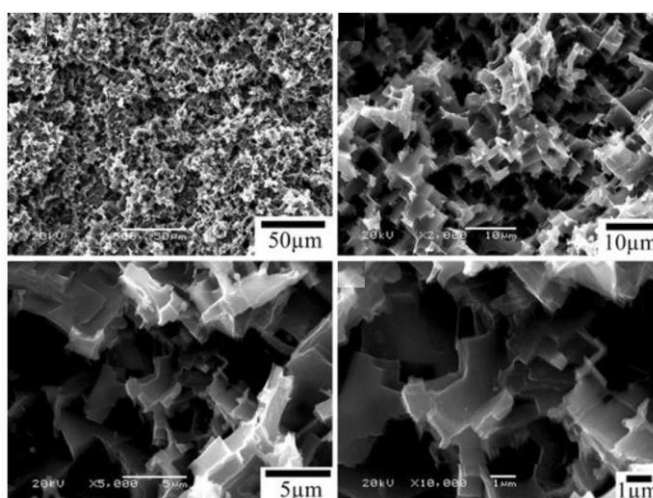


Figure 2.5: SEM images of the aluminum surfaces obtained by NaCl electrolyte.

2.2.4. Layer-by-Layer Method

Layer-by-layer (LbL) technique is defined as a method consisting of oppositely charged layers based on adsorption of negatively and positively charged species by immersion in a solution [28], [29]. These surfaces, which can also be used for nanoparticle coatings, reduce the surface's wettability by making the top layer hydrophobic [30].

Broderik et al. formed covalent multilayer materials by adding an amine-reactive polymer with azlactone functionality (PVMDA) and polyethyleneimine (PEI) to polar aprotic solvents. As a result, the water contact angle is 160° [31]. In the study by Kim et al. reduced Ag nanoparticles were deposited on thin polyelectrolyte multilayers (PEM) prepared from polyethyleneimine (LPEI) and poly(acrylic acid) (PAA) and crosslinked with the surfaces (Figure 2.6) [32]. The formed PEM films were fabricated using the layer-by-layer technique. Metallic Ag nanoparticles created stress on the surfaces, causing the surface to fold. The surface folds modified with a fluorine compound exhibited a water contact angle of 170° , resulting in the formation of superhydrophobic surfaces.

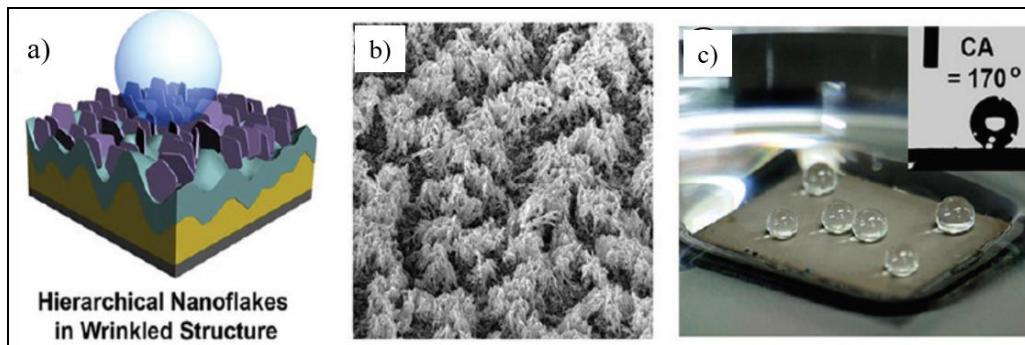


Figure 2.6: a) Schematic illustration of the thin films, b) SEM images of PEM film surface, c) Superhydrophobic feature of the surface and the water contact angle is 170° .

2.2.5. Plasma Techniques

Plasma etching, an effective and easy-to-use method for forming superhydrophobic surfaces, reduces surface energy and increases surface roughness. It also allows the formation of optically desirable superhydrophobic materials.

contact angle value of the PDMS surfaces as approximately 170° thanks to the regular structures on the surface [36].

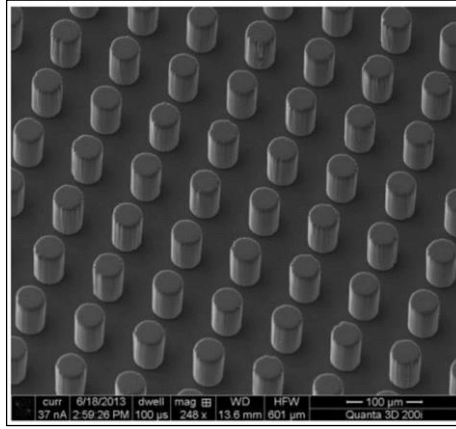


Figure 2.8: PDMS micropillar produced from SU-8 mold by a soft lithography method.

2.3. PDMS Steam Annealing Process

The PDMS material is generally prepared by mixing the base silicone elastomer and the curing agent with a 10:1 (wt/wt). After that, the air bubbles formed during the mixing are degassed. Then, the degassed prepolymer is cured at different temperatures.

The steam annealing process, a curing method, has been used in some studies to obtain porous micro-holed PDMS surfaces [37]–[41]. This simple and low-cost method depends on exposing the hot water vapor to PDMS prepolymer inside a pressurized chamber such as an autoclave chamber [42]. The elevated temperature, pressure, and moisture lead to accelerated curing and form holes on the PDMS surfaces. Figure 2.9 shows the steam annealing mechanism [41].

To our knowledge, the first study using this method on PDMS curing was performed by Jeong et al. [37]. After obtaining porous steam annealed PDMS surface, they have produced a flexible and stretchable microelectronic device by coating it with Ti and Au via the e-beam method.

Jang et al. [39] steam annealed the PDMS and investigated the effect of polymer thickness on the porosity. They have reported that the number of micro-holes on the top and bottom PDMS increased as polymer thickness decreased. Mariello et al. have fabricated a flexible triboelectric device by utilizing steam annealed PDMS surface [40].

Baek et al. [41] have investigated the effect of different viscosities (1:1 wt/wt, 2:1 wt/wt, 5:1 w/w, and 10:1 wt/wt ratios of base silicone elastomer and curing agent) on steam annealed PDMS surface morphology. They have concluded that PDMS surfaces with different elastomer and curing agent ratios have approximately the same average hole size. However, the density of the holes differed.

The schematic comparison of the PDMS produced by the conventional method and the microporous PDMS surfaces created by the steam annealing method is given in Figure 2.10 [42].

Also, Yun et al. [38] have used the steam annealing process and obtained a porous PDMS surface with an average hole size of 21 μm (Figure 2.11) to fabricate an epidermal graphene-based sensor.

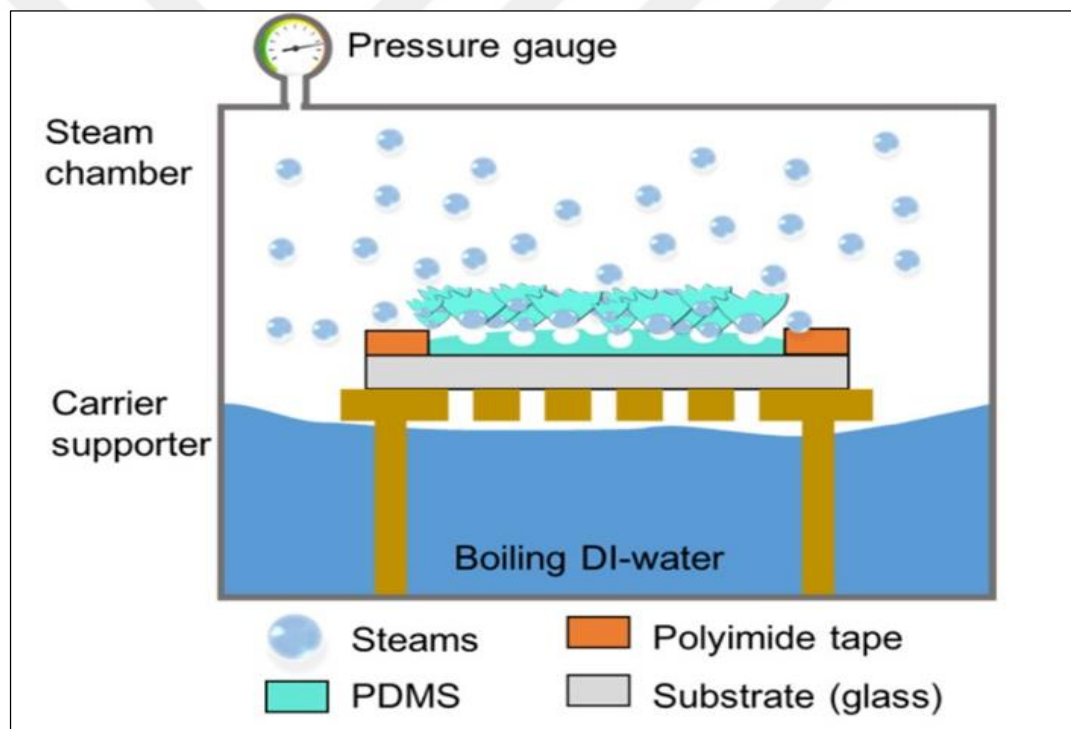


Figure 2.9: Schematic illustration of the steam annealing mechanism.

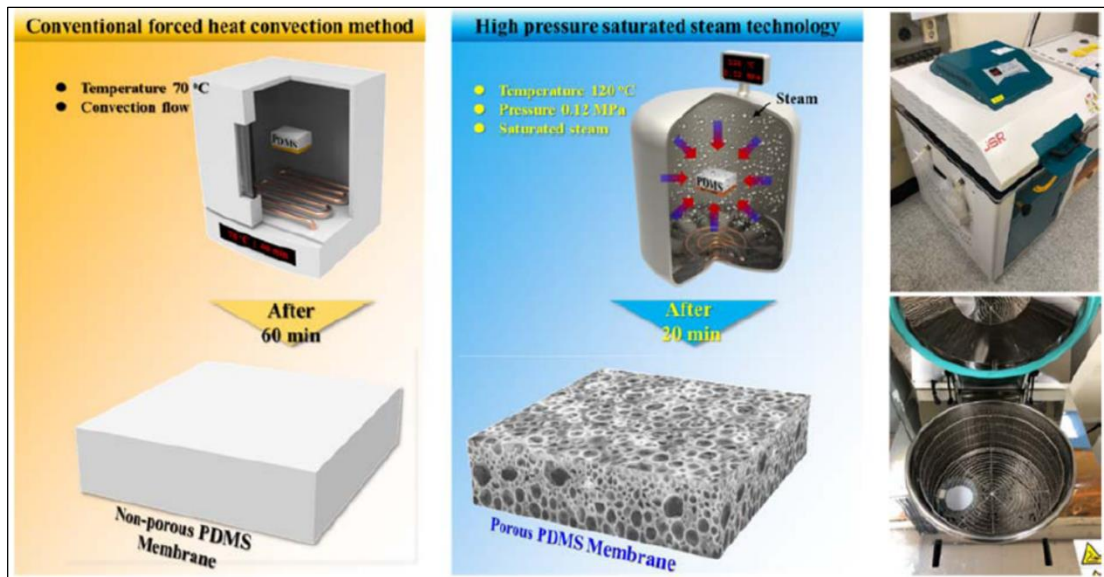


Figure 2.10: Schematic comparison of conventional and steam annealing methods in PDMS production.

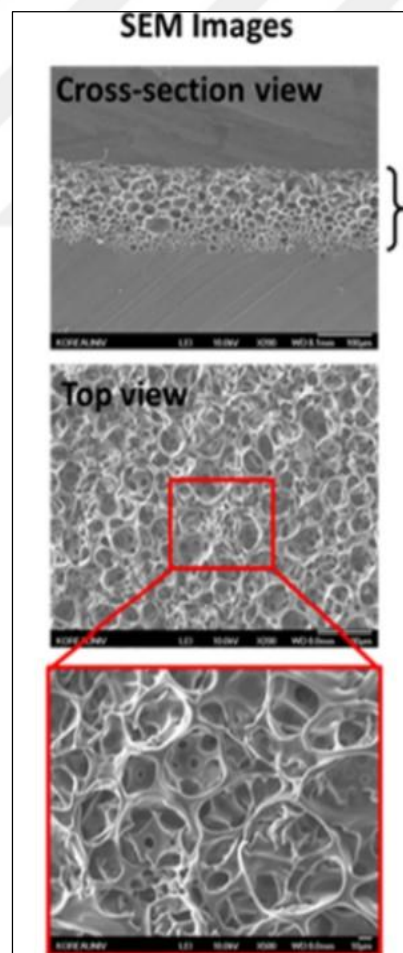


Figure 2.11: Steam annealed porous PDMS surface with 21 μm of average hole size.

3. MATERIALS AND METHODS

3.1. Materials

The chemicals and materials used throughout this study are listed in Table 3.1.

Table 3.1: The used chemicals/products during the experimental study and their suppliers.

Chemicals/Products	Chemical Formula	Supplier
Polydimethylsiloxane (PDMS, Sylgard 184) Containing silicon elastomer base and curing agent	$(C_2H_6OSi)_n$	Dow Corning
Silica Nanoparticles (SiO_2) Nanopowder, 10-20 nm particle size (BET), 99.5% trace metals basis	SiO_2	Sigma Aldrich
Dodecyltrichlorosilane $\geq 95.0\%$ (GC)	$C_{12}H_{25}Cl_3Si$	Sigma Aldrich
Ethanol Anhydrous, 99.8%	C_2H_5OH	Merck
Toluene Anhydrous, 99.8%	CH_3OH	Merck

3.2. Methods

3.2.1. Preparation of Plain and Micro-Porous PDMS Layers

The first step for preparing plain and micro-porous PDMS layers, silicone elastomer base, and curing agent were thoroughly mixed at 5:1, 10:1, and 20:1 (w/w) ratios. 5 gr of silicone elastomer base and 1 gr of curing agent were mixed in a beaker to prepare PDMS layers at a ratio of 5:1 (w/w). Likewise, to prepare 10:1 (w/w) and 20:1 (w/w) PDMS samples, 10 and 20 gr of silicone elastomer base were cast into

separate beakers, and 1 and 2 gr of curing agent were added into the beakers, respectively. All samples were mixed thoroughly for 5 minutes. The mixtures formed at each ratio were cast on glass Petri dishes around 1 mm thickness. Then, all the pieces were kept in a vacuum desiccator for 30 minutes to remove the air bubbles formed in the polymer with the effect of the mixture. Different curing methods were used to prepare plain and microporous PDMS samples. Plain PDMS layers (micro-pores free) prepared at three ratios were cured on a hot plate at 75 °C for 3 hours. Other Petri dishes containing PDMS polymer mixtures in 3 different proportions were placed in the steam chamber (Hirayama HVE-50 Upright Autoclave) for steam annealing, as shown in Figure 3.1, and pressurized to steam water for 30 minutes at 120 °C, 01 MPa. In the last step, the samples were kept on a hot plate at 70 °C to evaporate the water droplets within the porous.

The microporous and plain PDMS samples' names were expressed with abbreviations throughout this work as shown in Table 3.2. P5, P10, and P20 denote plain PDMS surfaces at 5:1, 10:1 and 20:1 (w/w), respectively, while M5, M10 and M20 represent microporous PDMS surfaces at 5:1, 10:1 and 20:1 (w/w), respectively. Figure 3.2 shows the plain PDMS and microporous PDMS samples prepared in the experiment.



Figure 3.1: Hirayama HVE-50 autoclave device used in the experiments.

Table 3.2: The contents and preferred abbreviation of samples.

Abbreviation of Sample	Explanation
P5	Plain PDMS sample at 5:1 (w/w) mixture containing silicone elastomer base and curing agent
P10	Plain PDMS sample at 10:1 (w/w) mixture containing silicone elastomer base and curing agent
P20	Plain PDMS sample at 20:1 (w/w) mixture containing silicone elastomer base and curing agent
M5	Micro-porous PDMS sample at 5:1 (w/w) mixture containing silicone elastomer base and curing agent
M10	Micro-porous PDMS sample at 10:1 (w/w) mixture containing silicone elastomer base and curing agent
M20	Micro-porous PDMS sample at 20:1 (w/w) mixture containing silicone elastomer base and curing agent

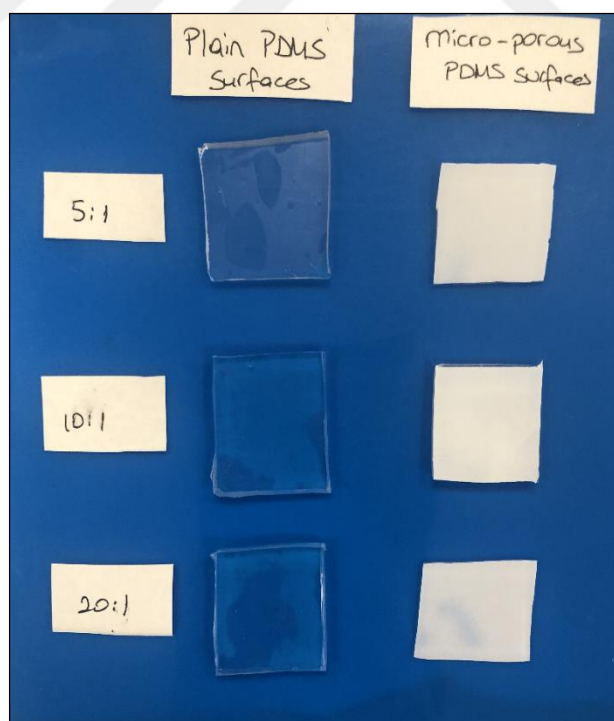


Figure 3.2: The prepared PDMS plains and micro-porous PDMS samples.

3.2.2. Preparation of Superhydrophobic Nanoparticles and Their Coating on Micro-Porous PDMS Surfaces

Silica nanoparticles were dehydrated to remove water adsorbed at 100 °C for 2 h in an oven. Firstly, 3.0 g of silica nanoparticles were dispersed in 60 mL toluene solvent and stirred with a magnetic mixer for half an hour. 1 mL of dodecyltrichlorosilane, a silane coupling agent, was slowly dropped into the solution containing silica nanoparticles to coat the surface silica particle with the polymer chains. The mixture was then stirred for 2 h at room temperature and centrifuged at 4000 rpm for 20 min to remove unreacted dodecyltrichlorosilane. Then the functionalized nanoparticles were dried in an oven at 100 °C for 8 h. The hydrophobic silica nanoparticles formed are shown in Figure 3.3. The functionalized silica nanoparticles were added to ethanol to prepare a 2 wt% spray-coating suspension solution for PDMS layers. PDMS samples were cut into pieces with sizes of 10 cm×2 cm and cleaned with ethanol before drying with nitrogen. For the final step, functionalized nanoparticles scattered in ethanol were sprayed using a spray-coater with a 0.35 mm inner diameter nozzle at ~ 4 bars pressure. The resulting coated PDMS layers were dried at room temperature for 24 h.



Figure 3.3: Hydrophobic silica nanoparticles.

The hydrophobic nanoparticles (HNPs) and the hydrophobic nanoparticle-coated M5, M10, and M20 micro-porous PDMS surfaces were named HNPs-M5, HNPs-M10, and HNPs-M20, respectively, as shown in Table 3.3. Silica nanoparticle-coated micro-porous PDMS surfaces are shown in Figure 3.4.

Table 3.3 Abbreviation names of hydrophobic nanoparticles and micro-porous PDMS surfaces coated with them.

Abbreviation of Sample	Explanation
HNP_s	Hydrophobic silica nanoparticles
HNP_s-M5	Hydrophobic silica nanoparticle-coated of M5 sample
HNP_s-M10	Hydrophobic silica nanoparticle-coated of M10 sample
HNP_s-M20	Hydrophobic silica nanoparticle-coated of M20 sample

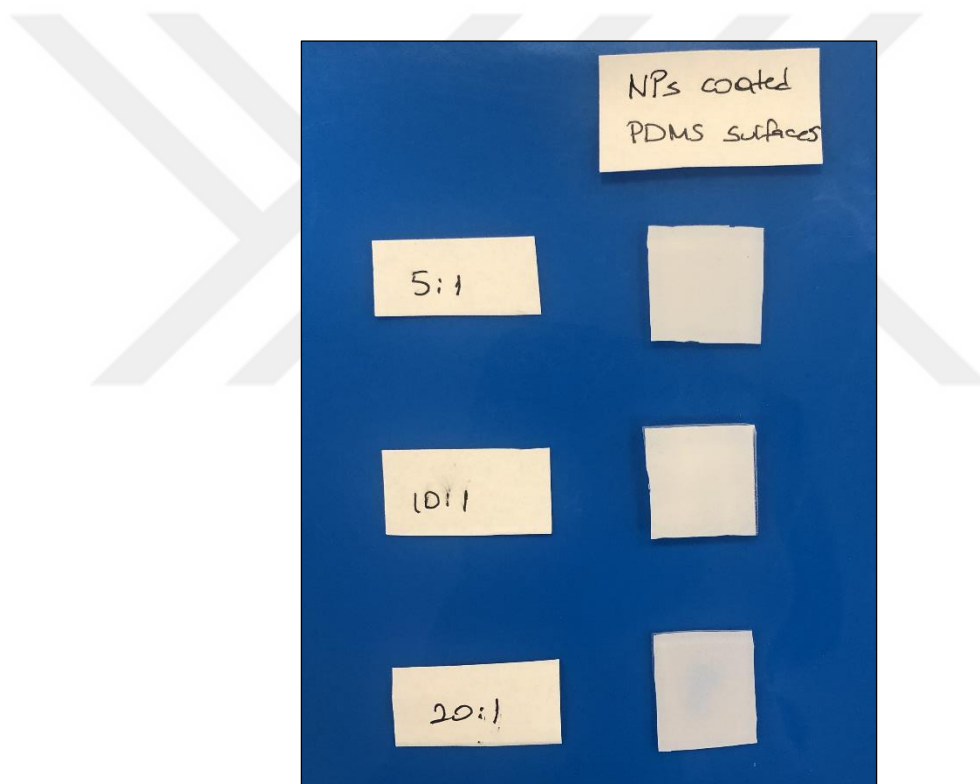


Figure 3.4 Silica nanoparticle-coated micro-porous PDMS samples.

3.3. Characterization Methods

3.3.1. Scanning Electron Microscopy (SEM)

The morphologies of the microporous PDMS layers before and after nanoparticle coating and the smooth PDMS surface were investigated using scanning

electron microscope SEM, Philips XL 30 SFEG at Gebze Technical University. The surfaces were observed at 500x magnification and 30 kV. The areas of microporous on the PDMS surfaces were calculated with the ImageJ program using SEM images.

3.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopic characterization method confirmed the coating of the PDMS porous surfaces with superhydrophobic silica nanoparticles. FTIR analysis (Perkin Elmer model) was used at Gebze Technical University between 600 cm^{-1} and 3100 cm^{-1} infrared spectra. The surfaces were characterized by two-step measurements before and after coating with superhydrophobic nanoparticles. The presence of functional groups was examined with the obtained peaks' assistance.

3.3.3. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was also performed for the elemental composition characterization of the surfaces. All samples' surface chemistry was analyzed with XPS using an Al $K\alpha$ X-ray source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH, Berlin, Germany) at Gebze Technical University. Via this instrument, O 1s, C 1s, Si 2s, and Si 2P spectra binding energies were analyzed, and peak fitting was made using Casa XPS software.

3.3.4. Water Contact Angle Measurement

Water contact angle measurements were performed with the KSV CAM200 contact angle meter (Figure 3.5) at Gebze Technical University. This measurement was taken for each step of the produced HNPs- PDMS surfaces, and the hydrophobic properties of the surfaces were verified. 5 μl of water was dropped on each surface using an automatic dispenser. The wettability of the surfaces was analyzed with the help of the angles formed by the droplets on the surfaces.



Figure 3.5: KSV CAM200 Contact angle meter.

4. RESULTS AND DISCUSSION

4.1 Morphological Analysis

4.1.1 The Effect of PDMS Mixing Ratios on Microporous Created via Steam Annealing Process

The porous structures polymerized rapidly when hot steam provided by boiling water was applied to the PDMS pre-polymer surface via the steam annealing method, eliminating the need for an additional thermal curing process. Steam etching was exposed for 30 min, and the high-pressure-saturated steam polymerized the PDMS to create solid porous structures inside a steam chamber. The process in the steam chamber was completed in three stages. In the first step, the uncured PDMS mixtures were placed in the chamber at 100 °C and reached 120 °C within 3 minutes. In this step, air bubbles were formed on the PDMS surfaces by increasing the pressure until saturation. In the second step, the bubbles that had advanced from the surface to the depth of the PDMS were pressurized by saturation steam. The PDMS samples, which were cross-linked by the effect of temperature, became solid. Then the chamber temperature was lowered to the cooling temperature (60 °C) for 20 minutes, and the curing was completed. The high-pressure steam that penetrated the uncured PDMS surfaces created asymmetric microporous on the PDMS surfaces.

In the traditional PDMS curing process, the PDMS mixture, which is removed from air bubbles, is formed by self-curing on a hot plate at a specific temperature and time.

To investigate the effect of porous structures on surface wettability, plain PDMS surfaces were prepared and compared with them. In addition, surface wettability was also investigated by studying the effect of the PDMS mixing ratio on the density and size of microporous.

Figures 4.1 and 4.2 show a top view of SEM images of microporous M5, M10, and M20 surfaces and plain P10 surface morphology. The areas of the microporous formed on the surfaces and the number of porous were calculated with the ImageJ software. In Figure 4.3, the representations of the regions of microporous formed on the surfaces in the ImageJ software are given. The number of microporous, total area,

and average pore size of the M5, M10, and M20 surfaces calculated using the ImageJ program are shown in Table 4.1.

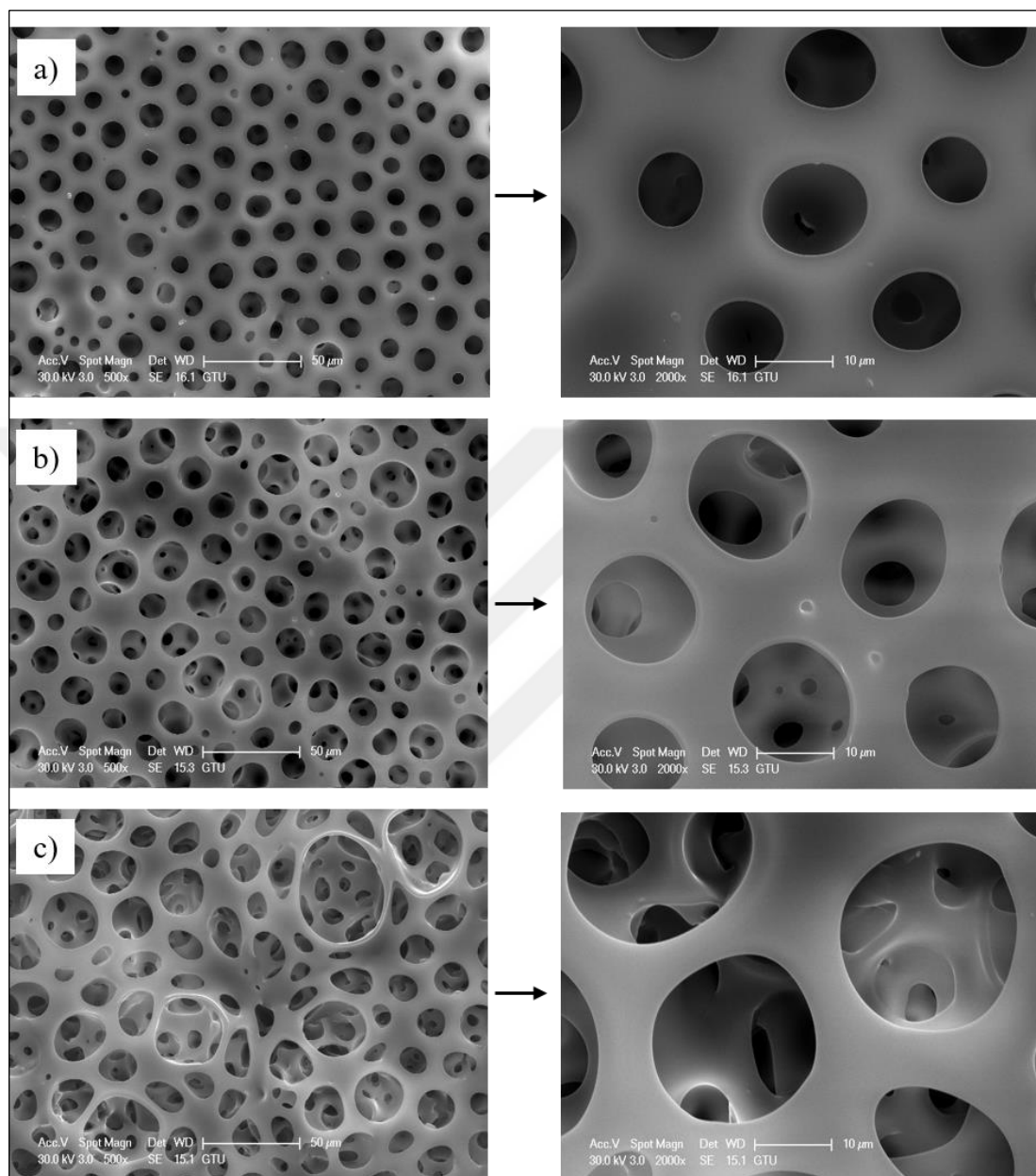


Figure 4.1: A top-view of SEM images of a) M5 b) M10 c) M20 samples.

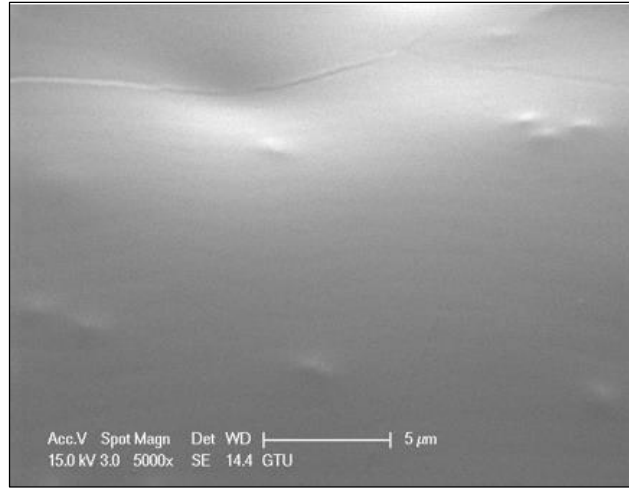


Figure 4.2: A top-view of SEM images of P10 samples.

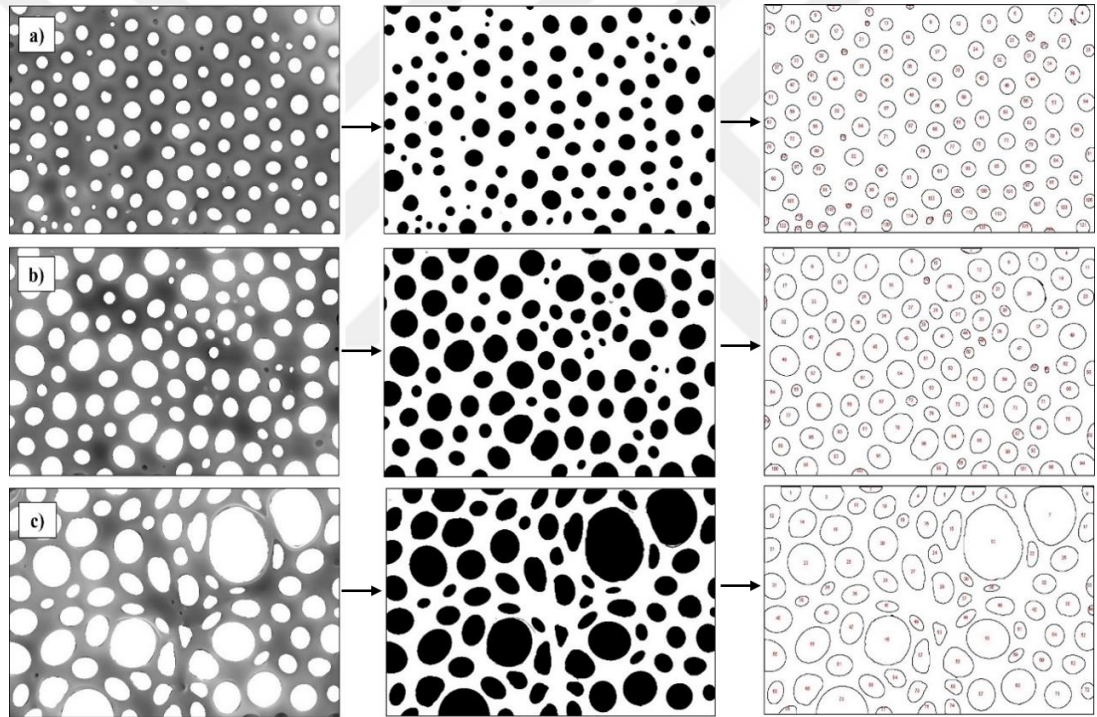


Figure 4.3: The appearance of the micropores formed on the a) M5 b) M10 c) M20 surfaces in ImageJ software used to calculate the areas.

Thanks to the ImageJ program, the borders of microporous can be determined, and the area and number of porous can be calculated. According to the calculations made with the help of SEM images, the microporous on the PDMS surfaces prepared with different mixing ratios have different sizes and areas. M5, M10, and M20 samples have 128, 102, and 77 microporous in the same area, respectively, and have an average

of 23.52%, 38.84%, and 48.92% micropore area. PDMS surfaces prepared at different mixing ratios and exposed to steam annealing have different pore sizes and densities.

In addition, more microporous were formed deeper into the PDMS surfaces, as seen in the SEM images in Figure 4.1. The number of microporous in the depths is seen at least in M5 and at most in M20.

Table 4.1: The number of micropores, total area, and average pore size of the M5, M10, and M20 surfaces calculated using the ImageJ program.

Sample	Count	Total Area	Average Size	% Area
M5	128	9763.82	76.28	23.52
M10	102	16167.36	158.50	38.84
M20	77	20413.81	265.11	48.92

According to the literature, the resistance of materials to deformation is defined by Young's modulus of elasticity (E) [39]. When Young's elastic modulus decreases, surface deformation increases. This defines the hardness of the material. In the study by Park et al. the modulus of elasticity for PDMS surfaces was measured to be 1,090 kPa, 580 kPa, and 280 kPa for a 5:1, 10:1, and 20:1 (w/w) mixing containing a silicone elastomer base and a curing agent (crosslinking agent), respectively [43]. Thus, the fact that the P5 sample prepared in this work is softer and the P20 sample is harder supports the literature data reported. In this context, PDMS becomes softer when the amount of curing agents (crosslinking agents) in the PDMS content is low. Conversely, PDMS is harder when the proportion of curing agents is high.

In this study, the water vapor molecule that accumulated on the uncured M5 surface during steam annealing had a shorter adhesion time on the surface due to the faster curing of the PDMS. In addition, the penetration time of the molecule deeper than the surface was also short. The smaller and fewer pores in M5 confirm this situation. As the curing agent ratio decreases (M20), the steam annealing process of PDMS takes longer and the water vapor molecule accumulated on the surface takes longer to penetrate the surface. Thus, wider, and deeper pores were obtained.

4.1.2 Coating of PDMS Surfaces with Silica Nanoparticles

In this part, hydrophobicity was imparted to silica nanoparticles by modifying the surfaces of commercial SiO_2 nanoparticles with the chemical dodecyltrichlorosilane. In this study, long-chain dodecyltrichlorosilane with low surface energy was preferred. It is known for its weak decomposition property and is not as hazardous as fluoroalkyl-containing silane chemicals for modification agents [44]. Silica nanoparticles are hydrophilic due to the silanol groups on the surface. Therefore, the surface was hydrophobically modified using the silane coupling agent dissolved in an organic solvent such as toluene using dodecyltrichlorosilane. The silane coupling agent converts the hydroxyl groups on the surface of the silica nanoparticles into hydrocarbon chains and provides the chemical transformation of the nanoparticle surfaces [45]. The chemical reaction is shown in Figure 4.4. Wang et al. showed that unmodified silica nanoparticles, which are hydrophilic due to their hydroxyl groups, become hydrophobic when modified with a silane-containing bipolar chemical [46].

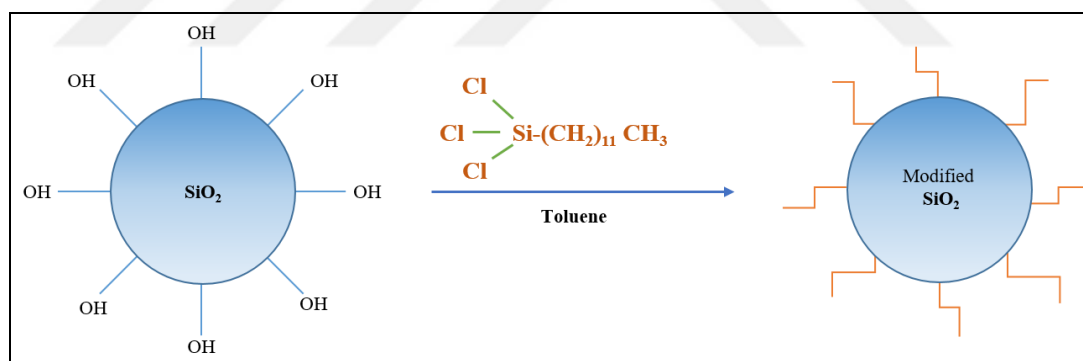


Figure 4.4: Illustration of the preparation of hydrophobic silica nanoparticles.

In their study, Ogihara et al. focused on the effects of alcohol type on HNPS (modified silica nanoparticles) coatings [47]. It was observed that the surface wettability depends on the type of alcohol in which the HNPs were dispersed. The dispersion of HNPs in alcohols affects the uniformity and durability of the surface coatings. In the studies, HNPs were dispersed in an ethanol solution, and PDMS surfaces were coated using the spray coating method, which is a simple and inexpensive method that proceeds in one step. In addition, silica nanoparticles tend to

agglomerate on the surfaces on which they are coated. HNPs showed distribution and adhesion without agglomeration on the surfaces when dispensed in ethanol.

The HNPs were added to the ethanol solution to form a 2% (weight) suspension. To make the coating thicker, two rounds of the coating were performed. SEM Images of P20 and HNPs-M5, HNPs-M10, and HNPs-M20 surfaces because of evaporation of ethanol at room conditions are shown in Figure 4.5.

Based on the surface morphologies, it is seen that nanoparticles can be coated on both surfaces and can also be coated inside micropores.

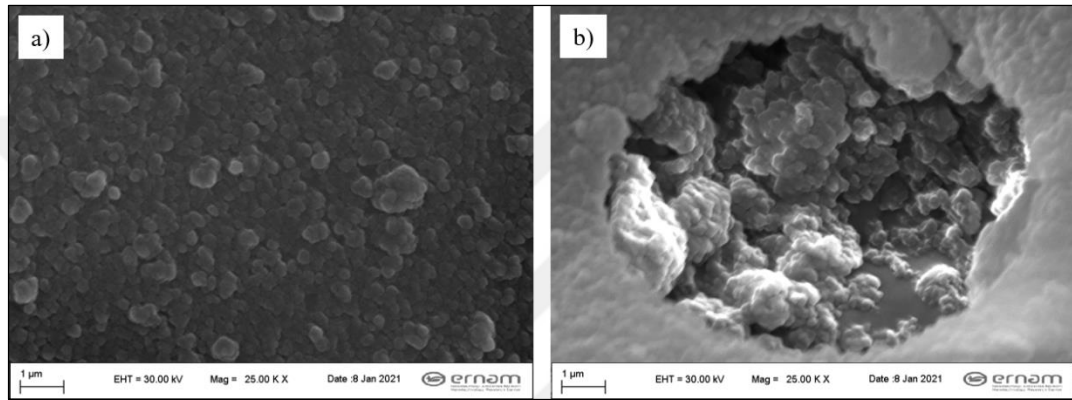


Figure 4.5: SEM analysis images of a) silica-coated P20 b) HNPs-M20 surfaces.

4.1.3 Investigation of Nanoparticle Coated PDMS Microporous Surfaces After Water Spray Impact Test

The durability of superhydrophobic coatings has become very important in recent years. No matter how good the production properties of the obtained surfaces are, if the coatings are not durable, the surface wettability will lose its effect in long-term applications, and the process will not work. In recent years, many studies have focused on the mechanical robustness of SHS. The mechanical strength of the surface has been tested by methods such as abrasion test [48]–[50], sandblasting test [51], tape peeling test [52], [53], and water impact test [54].

In this study, 50 spray water tests were performed on the HNPs-M5 surface, and 200 spray water tests were performed on the HNPs-M10 and HNPs-M20 surfaces. Fewer water spray tests are applied to the HNPs-M5 surface than to the other surfaces because the nanoparticles on the surfaces lose their surface properties after 50 cycles

of water spraying. SEM Images of the HNPs-M5, HNPs-M10, and HNPs-M20 surfaces after the water hammer test are shown in Figure 4.6.

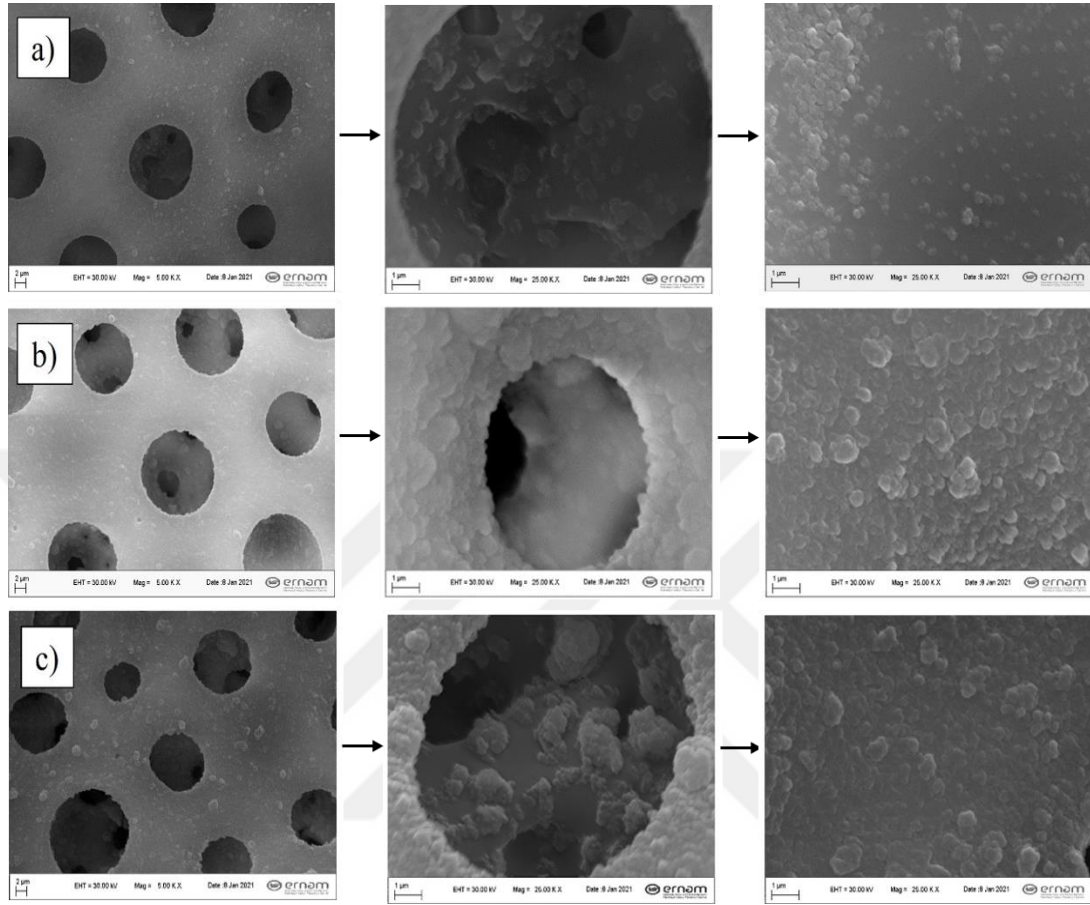


Figure 4.6: SEM images of a) HNPs-M5 b) HNPs-M10 c) HNPs-M520 surfaces after the water spray test.

From the images of SEM, it can be seen that the existence of nanoparticles decreases after the water spray test on the HNPs-M5 surface compared to other surfaces. The nanoparticles in the micropores deep in the HNPs-M20 surface keep their stability, and it can be seen that their resistance to the water impact test is high. Due to the high number of micropores, the HNPs-M20 sample contains more nanoparticles on its surface. The density of micropores formed on the surfaces increases the mechanical strength of the coating.

4.2 Contact Angle Measurement Results

4.2.1 Contact Angle Measurements of Plain and Steam Annealed Micro-Porous PDMS Surfaces

The wettability of a solid surface by a drop of liquid can be quantitatively determined by contact angle measurements (CA). The most critical parameters affecting the wettability of a solid surface are surface-free energy and roughness. In this section, the relationship between the PDMS mixing ratios of prepolymer and curing agent and their surface wettability is investigated by contact angle analysis. The water contact angles of plain PDMS surfaces and microporous PDMS surfaces are shown in Figure 4.7.

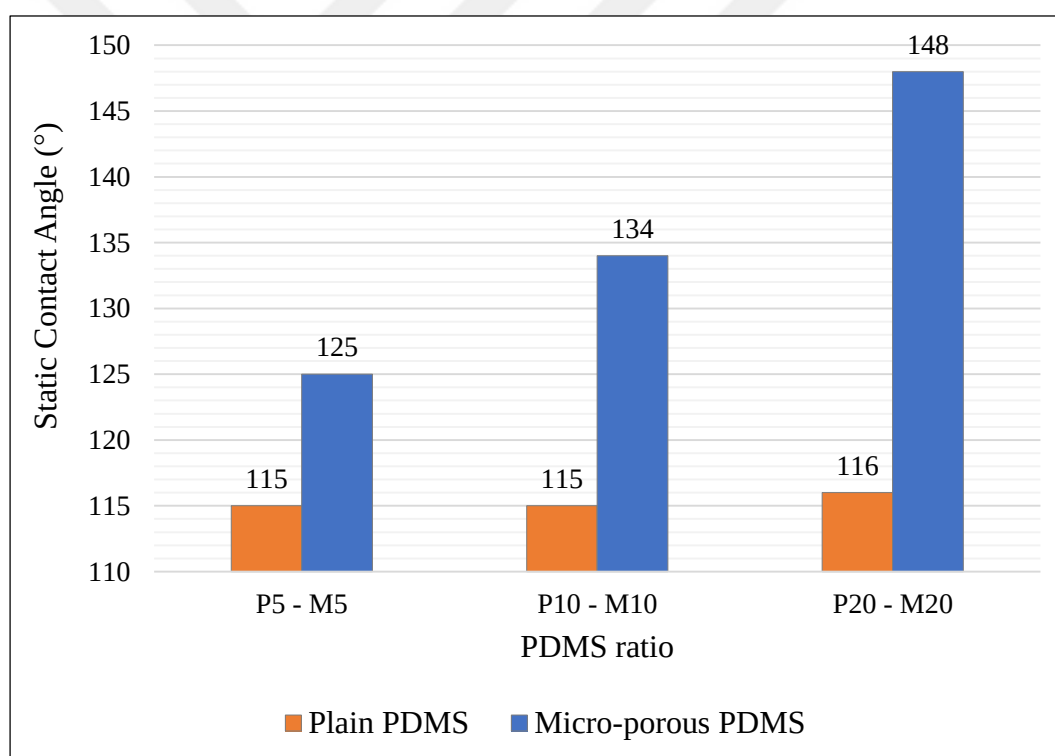


Figure 4.7: The WCA of plain and micro-porous PDMS surfaces.

According to the results of the analysis, the WCA measurements of the P5, P10 and P20 surfaces are about 115°. This result proves that the PDMS mixing ratios do not affect the wettability of the PDMS surfaces. WCA of 125°, 134°, and 148° was obtained for the M5, M10, and M20 surfaces, respectively.

The contact angle values of the microporous surfaces are higher than those of the plain PDMS surfaces. According to the results obtained; The surface roughness achieved by the micropores increases the superhydrophobic properties of the surface. This confirms studies showing that rough structures increase surface hydrophobicity [55], [56].

Looking at the contact angle values of M5, M10 and M20, it was confirmed by the analysis of SEM in the previous section that the number of microporous increases with decreasing curing ratio. M20 has the highest number of microporous and thus the highest surface roughness. For this reason, the contact angle value of the M20 sample was higher than the other surfaces.

4.2.2 Contact Angle Measurements of Nanoparticle Coated Plain and Micro-Porous PDMS Surfaces

WCA measurements of plain and microporous PDMS surfaces coated with silica nanoparticles are given in Figure 4.8. According to the measurements, the contact angles of the hydrophobic silica nanoparticle-coated P5, P10 and P20 plain surfaces are approximately 142° . The contact angle measurements of HNPs-M5, HNPs-M10 and HNPs-M20 microporous surfaces are 158° , 172° , and 176° , respectively.

Silica nanoparticle-coated flat PDMS surfaces show hydrophobic properties. This is because silica nanoparticles modified with a silane coupling agent show hydrophobic properties. In the study of Xu et al., the contact angle values measured because of the modification of silica nanoparticles with a silane coupling agent support our results [57].

Coating plain PDMS surfaces with nanoparticles only make them hydrophobic. Increasing contact angle values indicate that the hydrophobic nanoparticles applied to microporous surfaces impart superhydrophobic properties to the surfaces. Comparing the measurements in Figures 4.7 and 4.8 shows that both silica nanoparticle coating and microporous surfaces are required to obtain superhydrophobic surfaces.

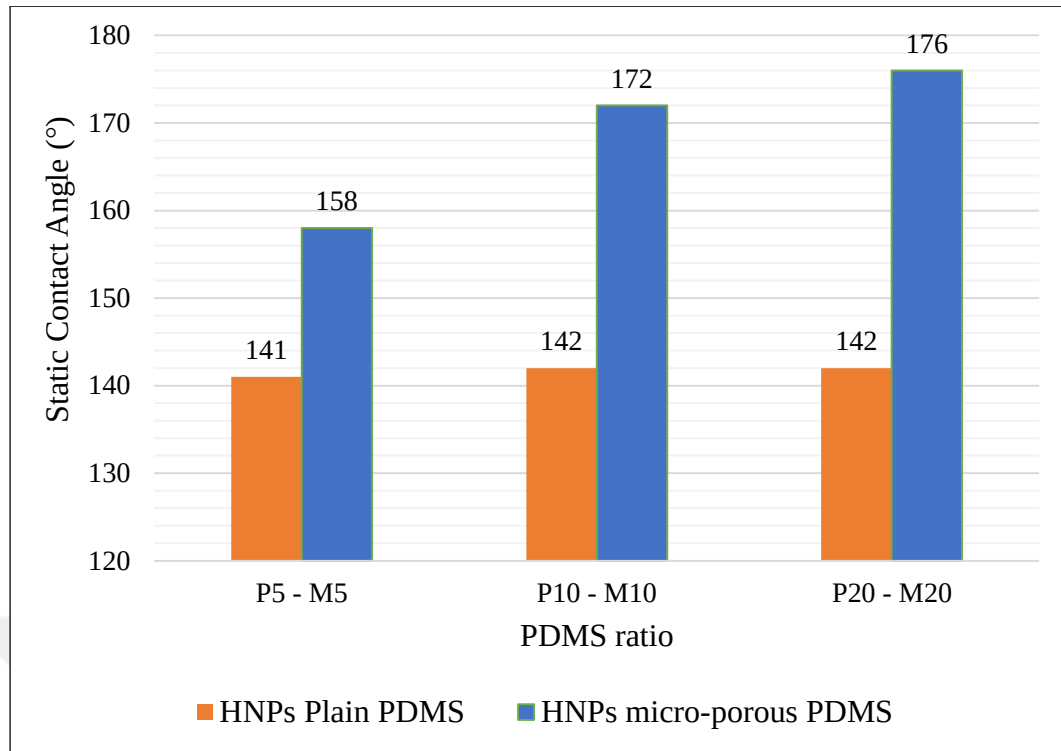


Figure 4.8: WCA measurements of plain and microporous PDMS surfaces coated with silica nanoparticles.

4.2.3 Contact Angle Measurements After Water Spray Impact Tests

The WCA measurements of each surface after the water spray impact test are shown in Figure 4.9. After the water hammer test, the WCA values of the plain PDMS surfaces coated with nanoparticles are 130°, 132°, 133°. The WCA of the HNPs-M5, HNPs-M10, and HNPs-M20 are 142°, 168°, and 176°, respectively, after the water impact test.

As a result of the contact angle measurements, it was found that HNPs-M5 lost its superhydrophobic property when 50 cycle spray water impact tests were performed. After 200 spray impacts were applied to the HNPs-M10 surface, the contact angle was decreased to 168°. The loss of superhydrophobicity of HNPs-M5 and the slight decrease in contact angle of HNPs-M10 are related to the number and width of microporous on the surface. It was expected that the HNPs-M5 surface would lose its water repellent property with the smallest microporous size. On the other hand, the contact angle value of HNPs-M20 did not change after 200 cycles of the water impact test. The high durability and high strength of the nanoparticles coated on these surfaces were achieved relative to other surfaces.

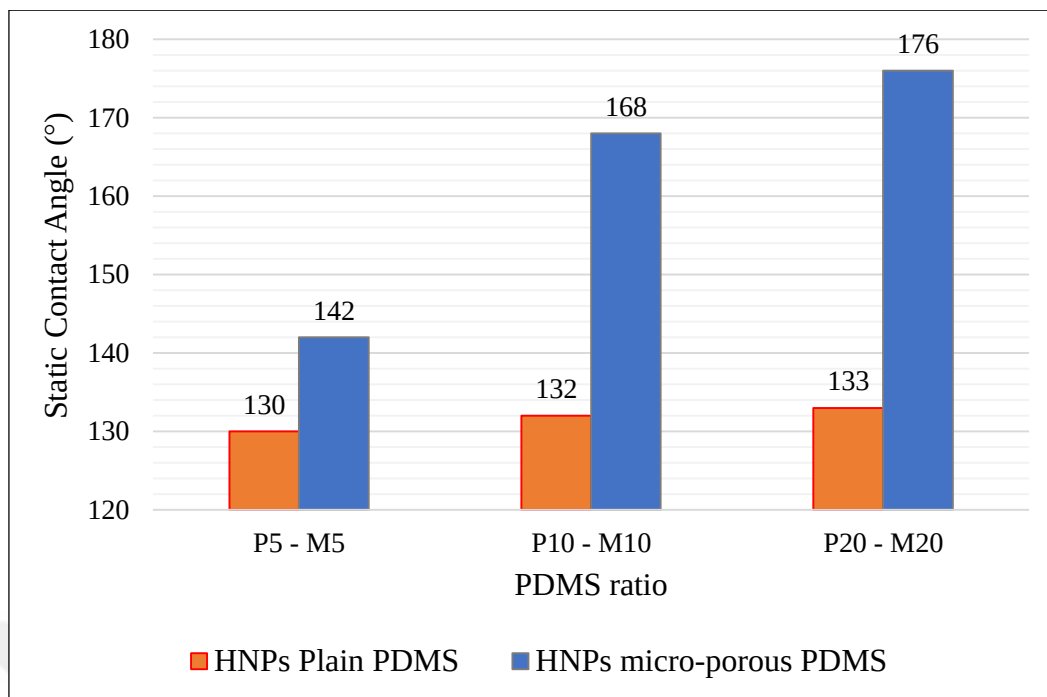


Figure 4.9: WCA measurements of samples after the water spray impact test.

4.3 FTIR and XPS Analyses of the Samples

Spectroscopic characterization of the surface structures confirmed the presence of nanoparticles on the surfaces. FTIR characterization of the fabricated microporous M20 sample and the HNPs-M20 sample coated with silica nanoparticles was performed (Figure 4.10). In addition, when the FTIR analysis of the produced nanoparticles is referenced, it has been proven that the HNPs-M20 surfaces are coated with nanoparticles.

In FTIR measurements of samples containing PDMS surfaces, asymmetric and symmetric stretching vibrations of PDMS-specific CH_3 methyl groups are observed at 2961 cm^{-1} and 1409 cm^{-1} , respectively. Peaks at 798 cm^{-1} and 699 cm^{-1} indicate asymmetric CH_3 vibrations and C-Si stretching, respectively. Peaks at 1054 cm^{-1} and 1010 cm^{-1} correspond to the stretching vibrations of asymmetric and symmetric Si-O-Si stretching, respectively [58]. The FTIR spectrum of the silica nanoparticles is dominated by strong and broad symmetric Si-O-Si stretching peaks at about 1055 cm^{-1} . The weak peaks at 2923 cm^{-1} are caused by the asymmetric stretching of the CH_3 groups of the alkylsilane added during silanization [7]. According to the FTIR spectrum analysis graph, micro-porous PDMS surfaces, nanoparticle coated PDMS

surfaces, and silica nanoparticles have characteristic peak values. This confirms that no new chemical composition has occurred.

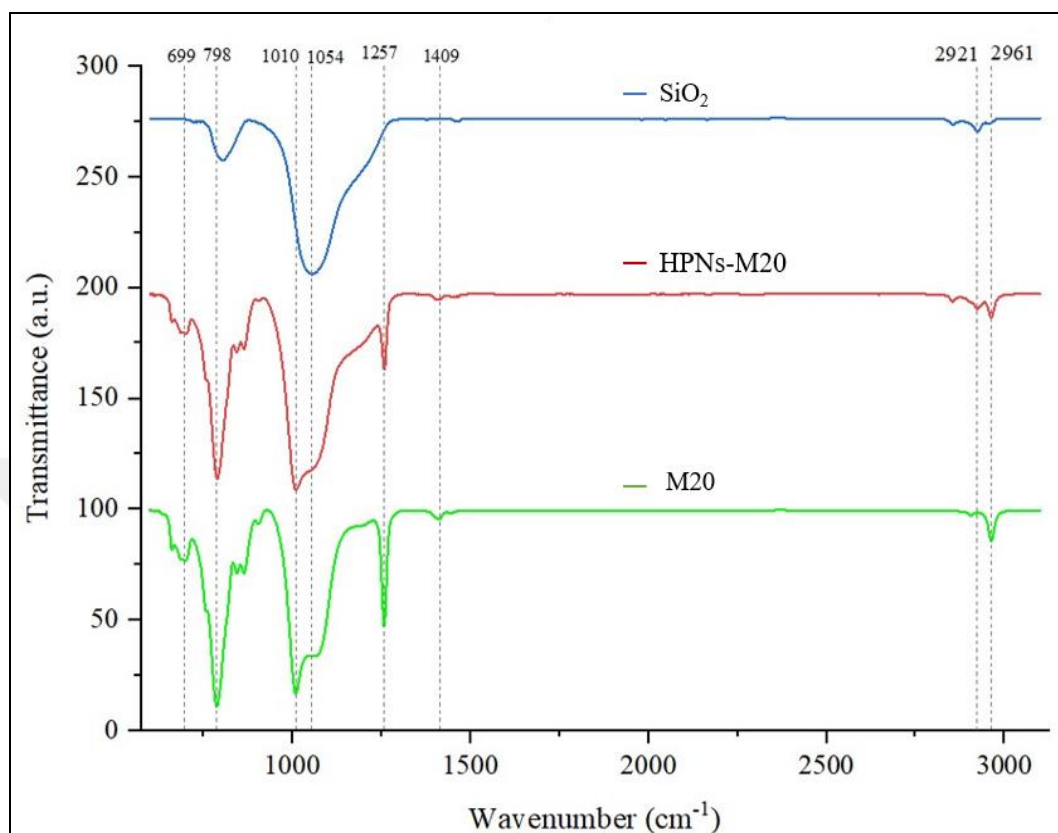


Figure 4.10: FTIR spectra of M20 (green), N20 (red), and silica nanoparticles (blue).

The graph of the XPS study to obtain the chemical compositions of HNPs-M20 and M20 surfaces is given in Figure 4.11. The O 1s (532 eV), C 1s (285 eV), Si 2p, and Si 2s (155 eV) (103 eV) peaks can be seen clearly in the spectra of surfaces. Looking at the atomic percentage table (Table 4.2); oxygen concentration on the surface decreased due to the bonding of naturally occurring -OH groups on the PDMS surface with silane-modified silica nanoparticles under room conditions. This proves the existence of silica nanoparticles on the surfaces.

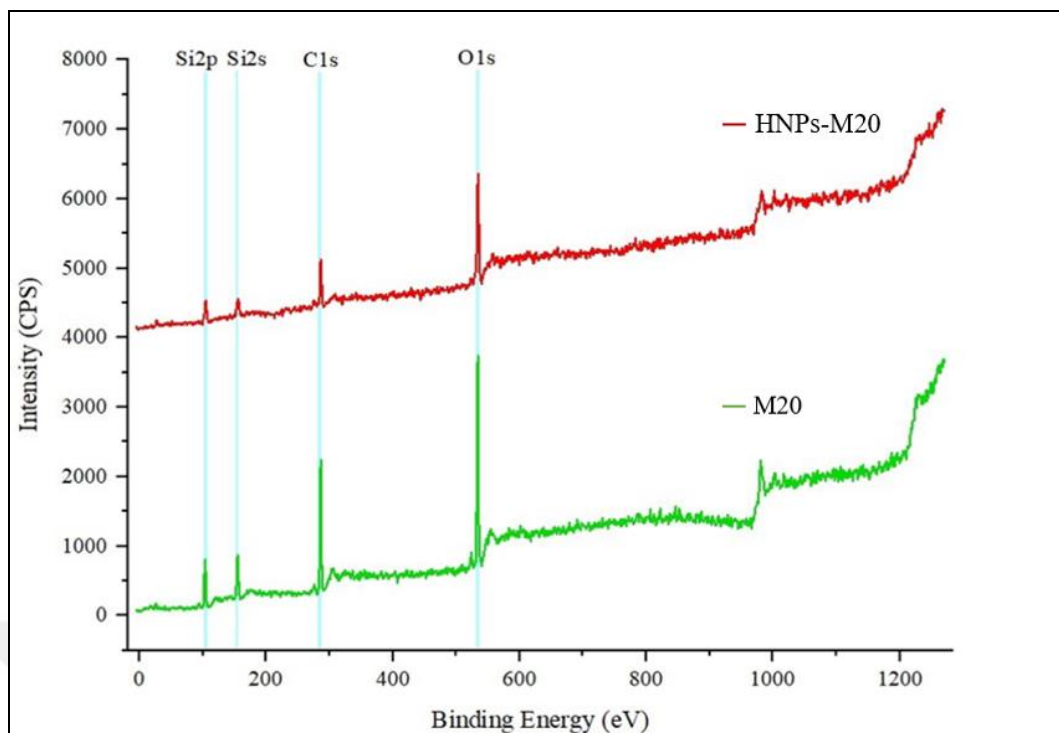


Figure 4.11: Wide-scan or survey spectrum of the M20 and HNPs-M20 surfaces, showing all elements present.

Table 4.2: Quantification table indicating the atomic species and atomic percentages of the HNPs-M20 and M20 surfaces.

Sample	O 1s %	C 1s %	Si 2s %	Si 2P %
HNPs-M20	20.35	38.78	21.33	19.54
M20	26.04	31.94	18.88	23.14

5. CONCLUSIONS

Superhydrophobic surfaces, which are exceptionally water repellent, can be used in various industries, including automotive, aerospace, construction, textiles, and food packaging. According to the present literature, the structure is critical to creating superhydrophobic surfaces. Deposition of porous structures with nanoparticles functionalized with organic molecules to minimize surface energy is one of the simplest ways to create micro- and nanoscale structures. Since the coating can be easily applied without complicated and expensive methods, this technology has high commercialization potential. Structures with porous texture at the micro-nano scale allow strong superhydrophobic surfaces, according to various studies inspired by superhydrophobic structures in nature. Due to porous structures, water-repellent surfaces with low contact angle hysteresis and facile droplet sliding are also possible. The mechanical ability of these surfaces to protect from impact and abrasion significantly increases the preferability of superhydrophobic surfaces.

In this current study, a highly effective method is presented to produce mechanically durable superhydrophobic coatings by deposition of hydrophobic nanoparticles in the solution phase of microporous structures formed on PDMS surfaces using high-pressure water steam. The other goal of this investigation was to see how changing base silicone elastomer prepolymer and curing agent ratios affected the morphologies of the steam annealed master mold and microporous.

The obtained results are listed below:

- The microporous PDMS surfaces with 5:1, 10:1, and 20:1 (w/w) of prepolymer and curing agent ratio have an average microporous area of 76,28 μm^2 , 158.50 μm^2 , and 265.11 μm^2 , respectively. It is concluded that the microporous PDMS surfaces prepared at different mixing ratios have different micropore sizes. This result shows that microporous sizes increase as the curing agent ratio decreases.
- In the obtained SEM images, it is seen that as the curing agent ratio decreases, a higher number of micropores are formed in the depths of the microporous surface. It has been observed that this reduces the surface wettability.
- The flat PDMS surfaces with 5:1, 10:1, and 20:1 (w/w) of base silicone elastomer and curing agent ratio have a water contact angle value of 115°, 115°, and 116°, respectively. On the other hand, the microporous PDMS surfaces with 5:1, 10:1,

and 20:1 (w/w) ratios have a water contact angle value of 125°, 134°, and 148°, respectively. While these results show that flat PDMS surfaces prepared at different ratios do not affect the surface wettability, contact angle measurements of microporous PDMS surfaces prove that the surfaces gain hydrophobic properties.

- According to the contact angle measurements of the hydrophobic silica nanoparticle-coated flat surfaces with 5:1, 10:1, and 20:1 (w/w) ratios are approximately 142°. The hydrophobic silica nanoparticle coated microporous PDMS surfaces with 5:1, 10:1, and 20:1 (w/w) ratios have 158°, 172°, and 176°, respectively. These results indicate that the contact angle measurements of plain PDMS surfaces coated with nanoparticles are insufficient to obtain superhydrophobic surfaces. To acquire an effective superhydrophobic surface, it is necessary to obtain both silica nanoparticle coating and porous surfaces.

- After the water spray impact test of nanoparticle coated flat PDMS surfaces with 5:1, 10:1, and 20:1 (w/w) ratios of the contact angles are 130° 132° 133°, respectively. Moreover, silica nanoparticle-coated microporous surfaces have 142°, 168°, and 176°, respectively. In this situation, the 5:1 ratio PDMS surface loses its superhydrophobic feature after applying 50 rounds of water spray impact test. On the other hand, there is no change in contact angle measurement in the 1:20 ratio PDMS surface after 200 cycles of the water spray impact test. The stability and strength of the nanoparticles coated on these surfaces are quite successful compared to the surfaces prepared with other mixing ratios.

- According to the FTIR spectrum analysis graph, micro-porous PDMS surfaces, nanoparticle coated PDMS surfaces, and silica nanoparticles have characteristic peak values. This confirms that no new chemical composition has occurred.

- XPS analysis has been performed to analyze chemical states. When the composition of the elements on the PDMS surface was calculated in percent, it was observed that different chemical components have not occurred for both microporous PDMS surface and nanoparticle coated microporous surfaces.

- The fact that the nanoparticle-coated microporous 20:1 mixing ratio PDMS surface shows superhydrophobic properties and due to the fact it has resistant to abrasion tests, we achieved the goal of this thesis study.

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BIOGRAPHY

I received my bachelor's degree from Yildiz Technical University in the department of chemical engineering in 2017. I started my master's degree at Gebze Technical University in the department of chemical engineering in 2018. During this period, I took part in the TUBITAK 116E743 project "Holographic single cell imaging technique that measures the change in mechanical stiffness (cell stiffness) structure of circulating cancerous cells (CTCs) using quantitative phase imaging method" as a scholar for 4 years. My academic background and experience have shaped my overall professional objective, which is to make a solid contribution to clean-room technology. After the TUBITAK project, I have been working as a researcher in the Semiconductor Technologies Research Laboratory (YITAL) at TUBITAK BILGEM since March 2020.

APPENDICES

Appendix A: Publications from the Thesis

Omeroglu S., Celik N., Onses M. S., Oruc M. E., (2022), “Investigation of the effectiveness of microporous PDMS structures for superhydrophobic coatings”, 3rd International Conference on Scientific Research, Adana, Turkey, 4-5 January.

