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SUPERHYDROPHOBIC MATERIALS AND COATINGS

RESEARCH ARTICLE

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Effect of reinforcement ratio on contact angle in hydrophobic/ superhydrophobic AA5754/SiCp composite materials

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ABSTRACT

Functional surfaces are defined as smart surfaces with properties different from the material's own properties. These surfaces increase energy efficiency in various applications, reduce costs by extending the lifetime of materials, and contribute to environmental sustainability. Superhydrophobic surfaces, a type of functional surfaces, are water-repellent surfaces where water droplets that contact the surface slide off the surface. The high water repellency and anti-corrosion properties of these surfaces are obtained by coating their micro- and nano-structured surfaces with low surface energy materials. In this study, the surface roughness of AA5754/SiCp composite materials with different reinforcement ratios was changed in a controlled manner by chemical etching for 5, 15, 25, and 35 minutes. After chemical etching, stearic acid (STA) modification was applied to the samples. Thus, hydrophobic and superhydrophobic structures were formed on the composite material surfaces. The effects of increasing the reinforcement ratio and chemical etching time on surface roughness and contact angle value in composite materials were investigated. It was found that the contact angle value increased with increasing reinforcement ratio in composite materials, while the surface roughness value tended to increase with increasing chemical etching time. These results show that the application areas of metal-based composite materials can be further increased.

1. Introduction

Functional surfaces are defined as surfaces that provide various functional properties to material surfaces in addition to their own properties (Wulf et al. 2002). Nowadays, functional surfaces have an important place in sectors such as medicine, electronics, and energy production due to their new properties in line with technological advances and increasing needs. Examples of such surfaces are hydrophilic, hydrophobic, self-cleaning (Wang et al. 2025), anti-bacterial (Zhu et al. 2024), anti-fog (Zeng et al. 2025), and corrosion resistant surfaces (Zhou et al. 2023).

Hydrophobic surfaces, a type of functional surfaces, are defined as water-repellent surfaces. Surfaces with a contact angle value of 90–150° are called hydrophobic surfaces, and functional surfaces with an angle greater than 150° are called superhydrophobic surfaces. Inspired by some superhydrophobic surfaces found in nature, many different methods have been developed to obtain these surfaces (Guo and Liu 2007). Some of these methods include electrochemical etching (Sun et al. 2022), laser etching (Emelyanenko et al. 2015), chemical deposition (Wang et al. 2019), and chemical etching (Attar et al. 2020). Among these methods, chemical etching is one of the oldest and relatively inexpensive methods. The most important advantages of the method are that it can be applied to almost all engineering materials, the processed material is not exposed to any thermal and dynamic effects, and precise processing can be performed at the micrometer scale. However, increasing the surface roughness of materials by chemical etching alone is not sufficient to obtain a superhydrophobic surface. In addition, material surfaces with increased surface roughness should be modified using a chemical with low surface energy. In studies using this method, hydrophobic or superhydrophobic structures were obtained on aluminum material surfaces, and various contact angle values were measured.

Yin et al (2012) chemically etched aluminum sample surfaces in hydrochloric acid (HCl) and hydrofluoric acid (HF). They were then modified using a 2.0 wt% SC-1060 F ethanol solution. After the modification process, the surface contact angle of the samples was measured as 161.2 ± 1.7°. Thus, a superhydrophobic-coated aluminum material was obtained. Li et al. (2014) modified the sample surfaces with stearic acid (STA) after chemically etching aluminum materials in HCl. The contact angle was measured as 164.2°. Deng et al. (2017) etched aluminum sheets in a chemical solution containing copper sulfate ($CuSO_4$) and sodium chloride (NaCl). It was then modified in a 1.0 wt% PFDTS ethanol solution. The result of the contact angle measurement with water was determined as 162°. Zhang et al. (2019) etched aluminum plates by droplet etching with an HCl solution. It was then modified in 0.01 M perfluorooctanoic acid (PFOA) aqueous solution. The contact angle was measured as 156 ± 2°.

In the literature, studies on obtaining superhydrophobic structures on aluminum matrix composite material surfaces are very limited. In this study, the formation of superhydrophobic structures on the surfaces of AA5754 composite materials and AA5754 alloy matrices reinforced with SiC particles at different rates (5, 10, 15, and 20 vol%) is discussed. The effect of varying reinforcement ratios on the contact angle on hydrophobic or superhydrophobic coated composite material surfaces was investigated.

2. Experimental section

2.1. Materials

The aluminum composite plates used in the study were produced by compression casting after a semi-solid mixing process (Urkmez 2004). The composite plates with an AA5754 matrix were cut with an abrasive water jet cutting machine (20 × 20 × 10 mm). The chemical composition of the AA5754 alloy used as the matrix material is given in Table 1. Ethanol (C_2H_6O), purified water (H_2O), HCl, HF, nitric acid (HNO_3), N,N'-Dicyclohexylcarbodiimide (DCC), STA, and hexane (C_6H_{14}) were purchased from Interlab Laboratory Products Industry and Trade Inc. AA5754/SiCp composites specimens were prepared using direct semi-solid stirring and squeeze casting by adding 5–20 vol% of SiCp (about 10 μm). This method is described in a patent held by Urkmez Taskin and Taskin (2015). The scanning electron microscopy (SEM) image of sample AA5754 is given in Fig. 1.

2.2. Preparation of hydrophobic/superhydrophobic aluminum and aluminum matrix composite material surfaces

Each sample was sanded with a 180, 400, 800, and 1200 mesh sandpaper. The samples were first soaked in ethanol for 20 minutes, then in pure water for 10 minutes, and then dried in an oven at 80 °C after cleaning. The samples were chemically etched in an etching solution containing HF, HCl, HNO_3, and distilled water for 5, 15, 25, and 35 minutes. After chemical etching, the samples were kept in a modification solution containing DCC, STA and hexane for 24 hours. The chemical compositions of the etching solution and the modification solution are given in Table 2.

Table 1. Chemical composition of AA5754 matrix material (%)

Al	Mg	Si	Fe	Mn	Others (total)
96.38	2.94	0.11	0.31	0.14	0.12

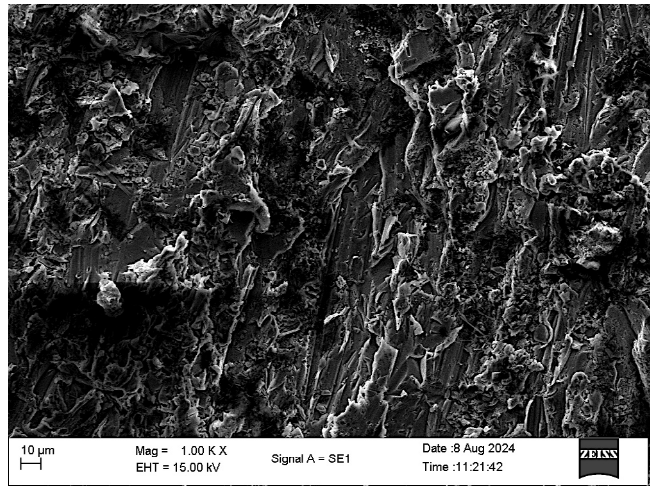

Fig. 1. SEM image of AA5754 (x1000 magnification).

Table 2. Chemical compositions of the etching and modification solutions

Etching solution		Modification solution	
HCl	7.5 ml	DCC	0.51 mg
HF	5 ml	STA	0.71 mg
HNO_3	12.5 ml	n-Hexane	500 ml
Dist. water	475 ml		

2.3. Characterization

The surface morphology of the samples was observed with a SEM (Zeiss EVO LS 10) at ×1000 magnification. The surface roughness measurements were made with a surface roughness measuring device (Taylor Hobson Precision) on a fixed surface. The Ra (average absolute roughness value) parameter was used in the measurements. The contact angle measurements were made using an optical contact angle measuring device (Attension Theta Lite) with the still drop method. Contact angles were measured at two different points for each sample, and average values were calculated.

3. Results and discussion

The samples with different reinforcement ratios by weight (0%, 5%, 10%, 15%, and 20%) that were chemically etched for different durations (5, 15, 25, and 35 min) were coded based on their weight ratios and etching times, respectively. For example, a 15-minute chemically etched 5% reinforced sample is coded as "R5/15".

The surface roughness of the AA5754 and AA5754 matrix composite material samples was increased by chemical etching. The pits formed on the surface of the material were observed by SEM. The images obtained are given in Fig. 2.

The values obtained as a result of the contact angle and surface roughness measurements are given in Fig. 3. It was observed that the surface roughness did not change significantly during the chemical etching time, but the contact angle increased. The highest Ra values were observed as follows:

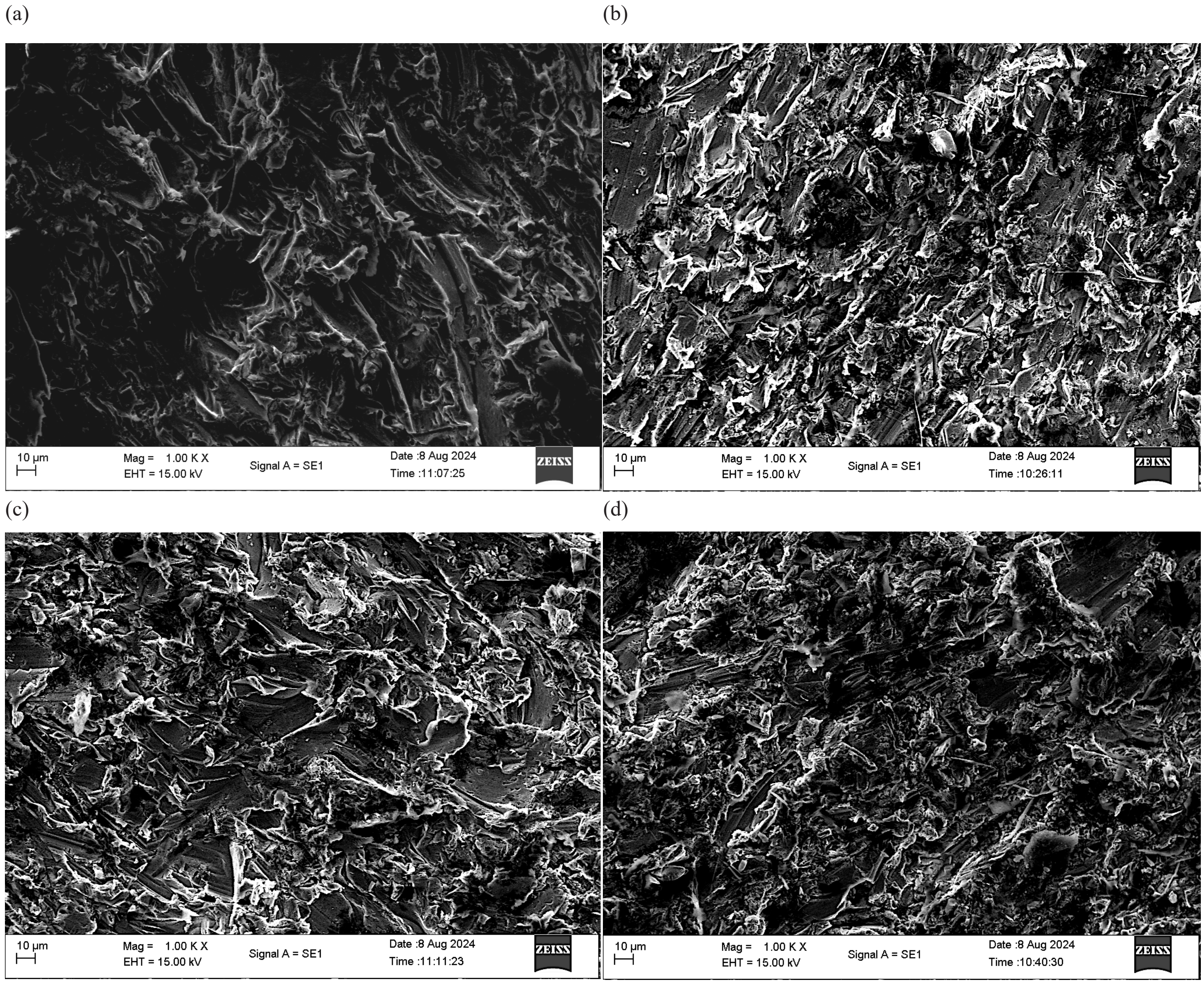

Fig. 2. SEM images of the rough surfaces of the AA5754 matrix composite material treated with a 5-minute chemical etching process at reinforcement ratios of (a) 5 vol%, (b) 10 vol%, (c) 15 vol%, and (d) 20 vol% (x1000 magnification).

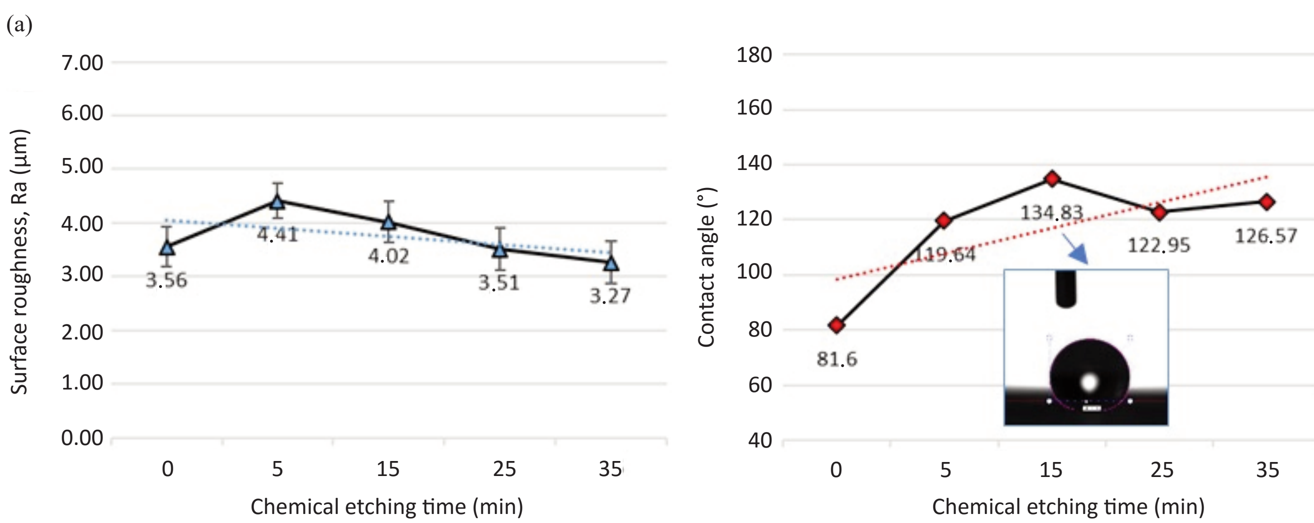

Fig. 3. Change of surface roughness and contact angle values based on chemical etching time for AA5754 and AA5754 matrix composite materials with reinforcement ratios of (a) 5 vol%, (b) 10 vol%, (c) 15 vol%, and (d) 20 vol%. *Continued on the next page*.

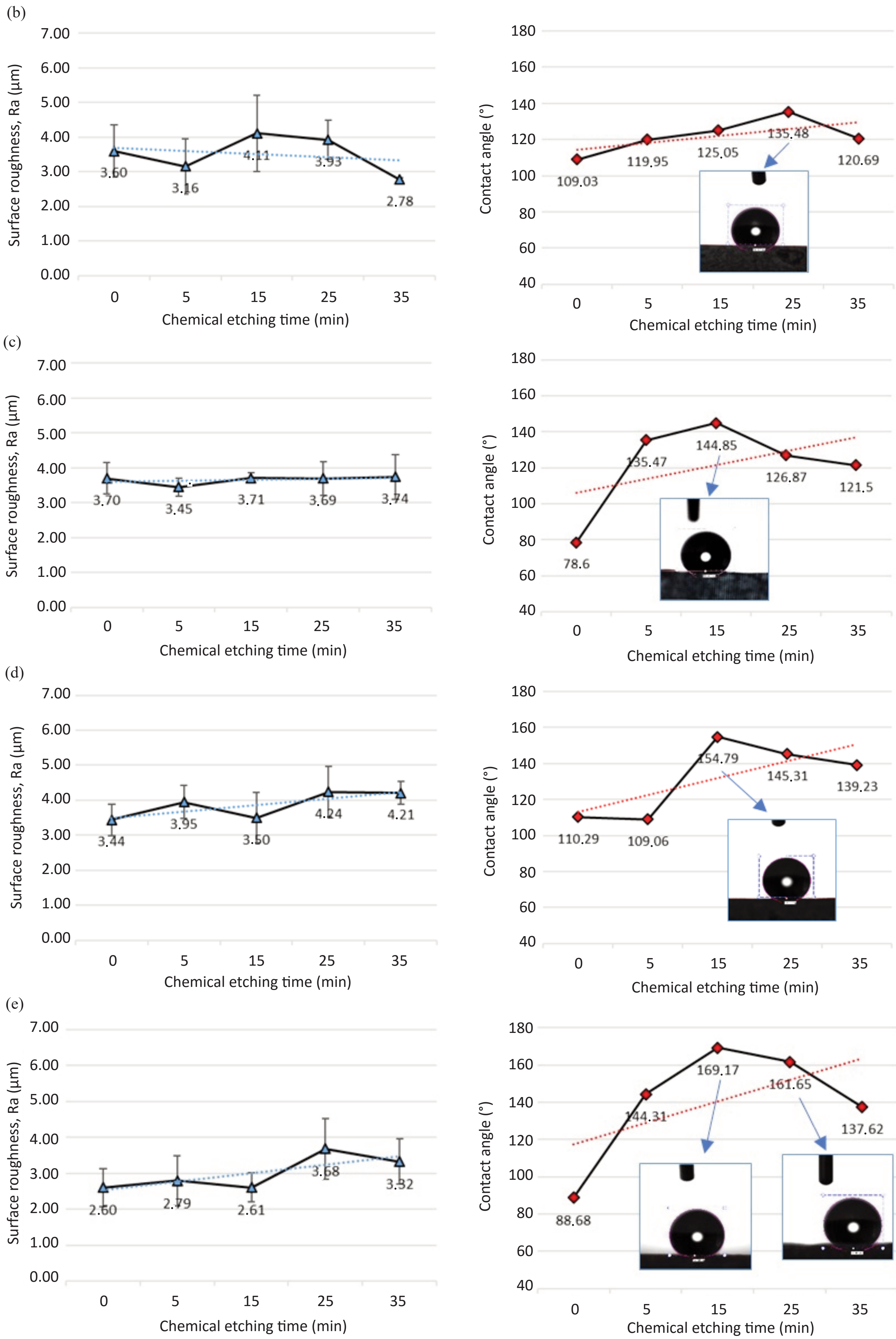

Fig. 3. *Continued.*

4.41 ± 0.33 µm in the unreinforced sample at the 5th minute of chemical etching (R0/5), 4.11 ± 1.10 µm in the 5% reinforced sample at the 15th minute (R5/15), 3.74 ± 0.65 µm in the 10% reinforced sample at the 35th minute (R10/35), 4.24 ± 0.72 µm in the 15% reinforced sample at the 25th minute (R15/25), and 3.68 ± 0.84 µm in the 20% reinforced sample at the 25th minute (R20/25).

Waterdrop contact angle is an important parameter for identifying the wetting behavior of surfaces (Urkmez Taskin and Ordu 2021). The highest contact angle values were 134.83 ± 6.04° for the unreinforced sample with 15 minutes of chemical etching (R0/15), 135.48 ± 7.78° for the R5/25 sample, 144.85 ± 3.30° for the R10/15 sample, 154.79 ± 5.93° for the R15/15 sample, and 169.17 ± 2.95° for the R20/15 sample. Thus, while hydrophobic structure was formed on the surfaces of unreinforced, 5% and 10% reinforced samples, superhydrophobic structure was formed on the surfaces of 15% and 20% reinforced samples. Although the surface roughness does not change significantly, the change in the contact angle suggests the formation of nanoscale pits (smaller than a micrometer) on the surface. It reveals the necessity of examining the surface roughness with more sensitive surface characterization devices in future studies.

4. Conclusions

AA5754 and AA5754 matrix composite materials were subjected to chemical etching in a controlled manner for 5, 15, 25, and 35 minutes and then kept in the modification solution for 24 hours. The surface roughness and contact angle values of all samples were measured before and after the chemical treatments. The measured values were analyzed, and the following conclusions were reached:

1. It was observed that the surface roughness of composite materials with AA5754 and AA5754 matrices can be controlled as a function of time.
2. Hydrophobic and superhydrophobic structures were successfully formed on the surfaces of AA5754 and AA5754 matrix composite materials by chemical etching and a subsequent modification process.
3. Higher contact angle values were obtained with an increasing reinforcement ratio in composite materials.

Data availability statement

All data are available in the article.

Acknowledgments

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Tugevdussuhte mõju kontaktnurgale hüdrofoobsetes/superhüdrofoobsetes AA5754/SiCp komposiitmaterjalides

Tunahan Pamukcu ja Nilhan Urkmez Taskin

Funktsionaalsed pinnad on defineeritud kui nutikad pinnad, mille omadused erinevad materjali enda omadustest. Need pinnad suurendavad energiatõhusust erinevates rakendustes, vähendavad kulusid, pikendavad materjalide eluiga ja toetavad keskkonnasäästlikkust. Superhüdrofoobsed pinnad, mis on üks funktsionaalsete pindade rakendusvaldkond, on vetthülgavad pinnad, millelt veepiisad pinnaga kokkupuutel hõlpsalt eemalduvad. Nende pindade suur vetthülgavus ja korrosioonikindlus saavutatakse mikro- ja nanostruktuursete pindade katmisel väikese pinnaenergiaga materjalidega. Uuringus muudeti erineva tugevdussuhtega AA5754/SiCp komposiitmaterjalide pinnakaredust kontrollitult keemilise söövitamise abil (5, 15, 25 ja 35 minutit). Pärast söövitamist rakendati proovidele steariinhappe (STA) modifikatsiooni. Selle tulemusel moodustusid komposiitmaterjali pindadel hüdrofoobsed ja superhüdrofoobsed struktuurid. Uuriti tugevdussuhte ja keemilise söövitusaja mõju komposiitmaterjalide pinnakaredusele ja kontaktnurgale. Leiti, et kontaktnurga väärtus suurenes koos tugevdussuhte kasvuga, samas kui pinnakaredus suurenes söövitusaja pikenemisel. Tulemused näitavad, et metallipõhiste komposiitmaterjalide rakendusvõimalusi saab veelgi laiendada.