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Preparation of superhydrophobic coating films using silica nanoparticles and trimethylethoxysilane

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Abstract−Superhydrophobic coating solutions were prepared using fumed silica nanoparticles and trimethylethoxysilane (TMES) as precursors. At this time, the surface of silica nanoparticles was modified by TMES from hydrophilic to hydrophobic in various types of catalysts and organic solvents. The prepared coating solutions were coated on a cold rolled steel sheet by using a spin coater, and then superhydrophobic coating films were prepared by thermal curing. In this process, the effects of the amount of silica nanoparticles added, the type of catalysts, and the type of organic solvents were observed on the hydrophobicity of the coating films. As the content of silica nanoparticles added increased from 0 g to 0.08 g, the contact angle of the coating films increased from 93° to 151°, and when 0.08 g of silica nanoparticle was added, it showed superhydrophobicity of 151°. On the other hand, when nitric acid and hydrochloric acid, strong acids, were used as catalysts, the coating films showed low hydrophobicity of 73° and 86°, respectively. However, when oxalic acid, a weak acid, was used, the coating film showed superhydrophobicity of 151°. In addition, with methanol as an organic solvent, the coating film showed superhydrophobicity of 151°, while when i-propanol and n-butanol were used, the coating films exhibited low hydrophobicity of 97° and 91°.

Keywords: Silica Nanoparticles, Trimethylethoxysilane, Superhydrophobic, Coating Films, Surface Modification

INTRODUCTION

Recently, superhydrophobic surfaces with water contact angles of 150° or more have attracted great interest due to their importance for applications such as self-cleaning, anticorrosion coatings, oil/water separation, and fluid drag reduction [1]. In 1997, Barthlott and Neinhuis discovered that the self-cleaning properties of lotus leaves were due to their specialized surface morphology and hydrophobicity [2]. The specialized surface morphology prevents dirt from forming intimate contact with the surface, while its high hydrophobicity makes the leaves water-repellent. Lotus leaves show that a combination of micro and nano-hierarchical structures and low surface energy components is required to form superhydrophobic surfaces [3]. This can be achieved by depositing a layer with surface-modified silica nanoparticles on the substrates.

Silica nanoparticles can be used to form micro and nano-hierarchical structures with superhydrophobicity through surface modification. Since silica nanoparticles are hydrophilic due to hydroxyl groups on the outer surfaces of particles, some hydrophobic materials with low surface energy, such as fluorine compounds or silicon compounds, are used to modify the surface of silica nanoparticles. Since fluorine atoms can form very stable covalent pairs when combined with carbon to form low surface energy, fluorine compounds have been most frequently used to make superhydrophobic coating films [4,5].

However, fluorine compounds are limited because they are expensive and hazardous to humans and the environment. Substitutes for fluorine compounds with low surface energy include wax, paraffin, polyurethane, dendrimer, and silicone. Among them, silicon compounds have the lowest surface energy after the fluorine compounds, so a siloxane (Si-O-Si) structure is introduced on the substrate surface to make the surface water-repellent [6,7]. More specifically, silicone compounds have a very stable chemical structure and are considered the most stable water-repellent compounds after fluorine compounds [7].

Trimethylethoxysilane (TMES), a type of silicon compound, can be used as a capping material to modify the surface of hydrophilic silica nanoparticles. Because TMES has a single ethoxy ($-OC_2H_5$) group, it effectively reduces the amount of OH groups on the surface of silica nanoparticles.

Recently, we prepared water-repellent coating solutions using TMES and methyltrimethoxysilane (MTMS) by the sol-gel method [8,9]. The solutions were coated on a cold rolled steel sheet by using a spin coater, and non-fluorine water-repellent coating films were prepared by thermal curing. However, the water repellency of the coating films was limited, and the water contact angle did not exceed 120° because no specific structure was given to the coating films. From this observation, we concluded that the chemical composition of the coating solutions just turned the substrate surface from hydrophilic to hydrophobic, but not superhydrophobic.

In this study, the surface of hydrophilic silica nanoparticles was modified by TMES using various types of catalysts and organic solvents in a colloidal solution to make a superhydrophobic coating film. To the best of our knowledge, no studies have been conducted on the effects of different types of catalysts and organic solvents used during the surface-modification of silica nanoparticles on the

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superhydrophobicity of coating films. The purpose of this study is to prepare a superhydrophobic coating film using silica nanoparticles whose surfaces have been modified by TMES with various types of catalysts and organic solvents. In this process, the effects of the amount of silica nanoparticles added, the type of catalysts, and the type of organic solvents on the superhydrophobicity of the coating film were studied.

EXPERIMENTAL

1. Materials

Hydrophilic fumed silica nanoparticles (nanopowder, 10-20 nm, 99.5%) and trimethylethoxysilane [TMES, $C_2H_5OSi(CH_3)_3$, 98%] were purchased from Sigma Aldrich. Methanol (MeOH, CH_3OH, 99.5%, Samchun Chemical), ethanol (EtOH, C_2H_5OH, 95%, Samchun Chemical), i-propanol (i-PrOH, i-C_3H_7OH, 99%, Sigma Aldrich), n-butanol (n-BuOH, n-C_4H_9OH, 99%, Sigma Aldrich), ethyl acetate (EA, $CH_3COOC_2H_5$, 99%, Sigma Aldrich), and methyl ethyl ketone (MEK, $C_2H_5COCH_3$, 99%, Sigma Aldrich) were used as organic solvents for the dispersion of silica nanoparticles. In addition, oxalic acid ($C_2H_2O_4$, 99.5%, Jin Chemical), hydrochloric acid (HCl, 99%, Sigma Aldrich), nitric acid (HNO_3, 99%, Sigma Aldrich), and ammonia water (NH_4OH, 95%, Sigma Aldrich) were used as catalysts for the hydrolysis and condensation reactions of TMES. The reagents were used without purification or chemical treatment.

2. Preparation of Coating Films

Several solutions were prepared by dissolving TMES in various types of organic solvents and then stirring these at room temperature (RT) for 5 min. After H_2O and various types of catalysts were added to the prepared TMES solutions, the solutions were stirred at RT for 12 h to perform hydrolysis and condensation. Finally, fumed silica nanoparticles were added and stirred at RT for 24 h to prepare hydrophobic coating solutions. After a certain amount of the hydrophobic coating solutions was dropped on a cold rolled steel sheet, spin-coating was performed at 1,000 rpm for 1 min. Then, hydrophobic coating films were prepared through thermal curing at 120 °C for 2 h. The preparation process is illustrated in Fig. 1.

3. Characterization

3-1. SEM Analysis

High resolution FE-SEM (MIRA3-LM, Tescan) was used to observe the surface morphology of the coating films. The acceleration voltage was set to 10 kV and the surface of the coating film was magnified to 15,000 times to observe the morphology.

3-2. Contact Angle Measurement

The contact angle to water on the coating films was observed using a contact angle meter (Phoenix 10, Surface Electro Optics). A zoom microscope was used to enlarge the surface image to the optimal magnification. Next, water droplets were added to the surface of the coating films, and the contact angle was measured by quantitative analysis using a monitor and a SurfaceWare9 program. The average value of five measurements of the samples was recorded as the contact angle value.

3-3. FR-IR Analysis

The bond vibration of C-H, O-H and Si-C in silica nanoparticle and TMES was observed by Fourier transform infrared spectroscopy (FT-IR, Cary 630, Agilent Technologies).

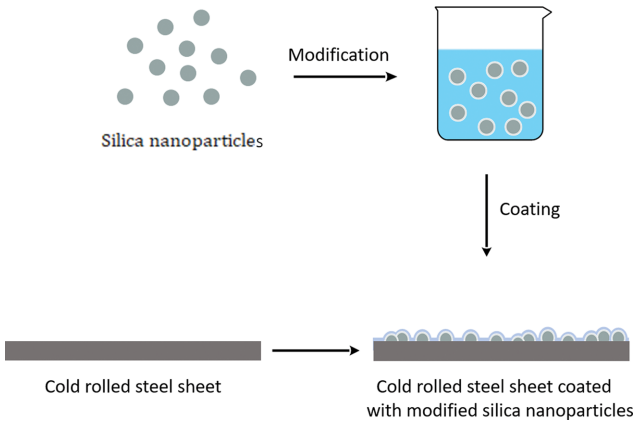

Fig. 1. Schematic illustration of the preparation of superhydrophobic coating films by doping TMES-modified silica nanoparticles on the cold rolled steel sheet.

RESULTS AND DISCUSSION

1. Effect of the amount of Silica Nanoparticles Added on the Hydrophobicity of Coating Films

Fig. 2 shows a schematic illustration of TMES modification on hydrophilic silica nanoparticles dispersed in methanol solvent. TMES

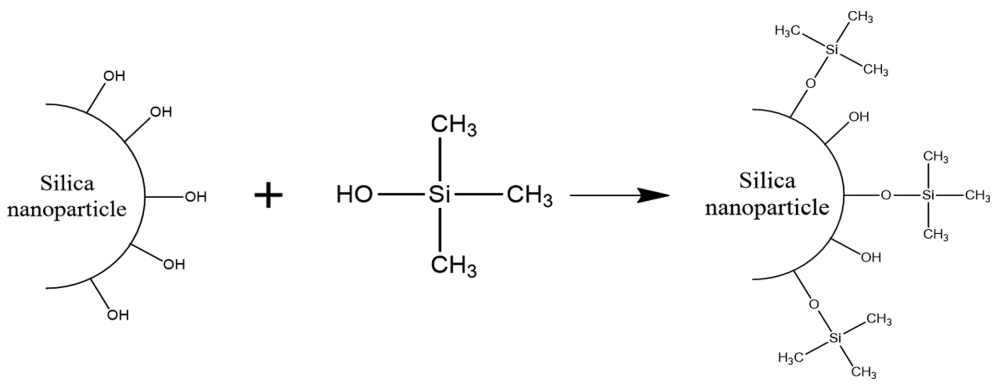

Fig. 2. Schematic illustration of the preparation of TMES-modified silica nanoparticles.

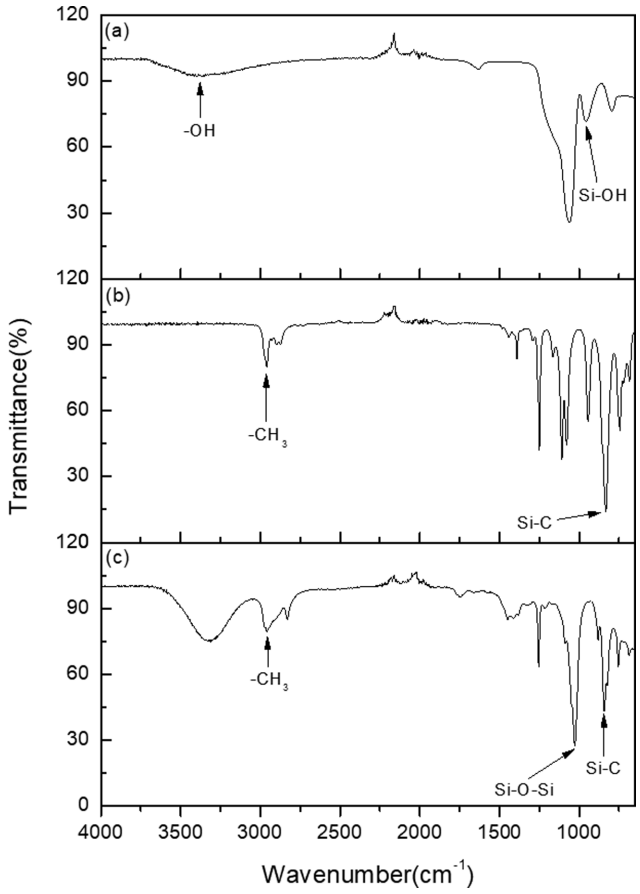

Fig. 3. The FT-IR spectra of (a) silica nanoparticles, (b) TMES, and (c) TMES-modified silica nanoparticles.

can be immobilized on the surface of the silica nanoparticles through dehydration of water molecules with an oxalic acid catalyst. The modification was investigated by FT-IR measurement.

Fig. 3 shows the FT-IR spectra of silica nanoparticles, TMES, and TMES-modified silica nanoparticles, which were obtained after surface modification of silica nanoparticles by TMES. The broad band of silica nanoparticles around 3,438 cm^{-1} in Fig. 3(a) is due to the stretching of various hydroxyl (-OH) groups, e.g., those on silica nanoparticles or water [10]. The absorption band at 946 cm^{-1} is assigned to the stretching vibration of Si-OH groups on surfaces of silica nanoparticles [11]. The -CH_3 and Si-C stretching vibrations of TMES in Fig. 3(b) are shown at 2,956 and 847 cm^{-1}, respectively [12]. The absorption band at 1,077 cm^{-1} is due to the asymmetric stretching of the Si-O-Si bond [12]. For the TMES-modified silica nanoparticles in Fig. 3(c), the Si-O-Si absorption band at 1,077 cm^{-1} and the -CH_3 and Si-C stretching vibration bands at 2,956 and 847 cm^{-1}, respectively, appear, but the stretching vibration of Si-OH groups at 946 cm^{-1} disappears. This suggests that the reaction between TMES and the hydroxyl groups of silica nanoparticles has occurred to form ≡Si-O-Si$(CH_3)_3$ species on the silica nanoparticle surface, and the surface of silica nanoparticles was successfully modified with TMES.

Table 1 shows the composition of the coating solutions prepared as a function of the amount of silica nanoparticles added to the methanol solvent with an oxalic acid catalyst. Fig. 4 shows the SEM surface morphology of coating films prepared by changing the amount of silica nanoparticles added from 0 g to 0.12 g in Table 1. As shown in Fig. 4(a), when silica nanoparticles were not added, the smooth surface could be obtained because there was no silica nanoparticle present on the surface of coating films. As the loading of silica nanoparticles increased in the coating solutions, the surface of the coating films was gradually covered with a layer of silica nanoparticles, resulting in uneven clusters on the surface. When a small amount of 0.03 g of silica nanoparticles was added, a small amount of nanoparticles was formed on the surface of the coating films, as seen in Fig. 4(b). However, when the amounts of added nanoparticles were 0.06 g and 0.08 g, as seen in Figs. 4(c) and (d), the coating films showed a rough surface with randomly distributed particles over the entire coating surface and a closely packed structure. On the other hand, the coating film with an excess of 0.12 g of nanoparticles added showed a loosely packed structure with grooves due to significant aggregation between silica nanoparticles, as seen in Fig. 4(e).

Fig. 5 shows the water contact angles of the coating films as a function of the amount of silica nanoparticles added. The coating films, in which the amount of silica nanoparticles was changed to 0 g, 0.03 g, 0.06 g, 0.08 g, and 0.12 g, showed contact angles of 93°, 108°, 143°, 151°, and 150°, respectively. When the silica nanoparticles were not added, the contact angle of the coating film was as low as 93°. The reason for this low contact angle is that the hydrophobicity was only affected by the methyl group of TMES that existed on coating films, since there was no surface roughness due to the absence of nanoparticles in the coating film, as shown in Fig. 4(a). As the amount of silica nanoparticles added increased, the contact angles of coating films also increased. When a small amount of 0.03 g of nanoparticles was added, the contact angle in Fig. 5(b) was 108°, which was an increase compared to 93° without the addition of nanoparticles. This seems to be due to the surface rough-

Table 1. The composition of the coating solutions prepared as a function of the amount of added silica nanoparticles

Sample code	TMES (mole)	H_2O (mole)	MeOH (mole)	Oxalic acid (mole)	Silica nanoparticle (g)
S1					0
S2					0.03
S3	0.02	0.01	0.06	0.0008	0.06
S4					0.08
S5					0.12

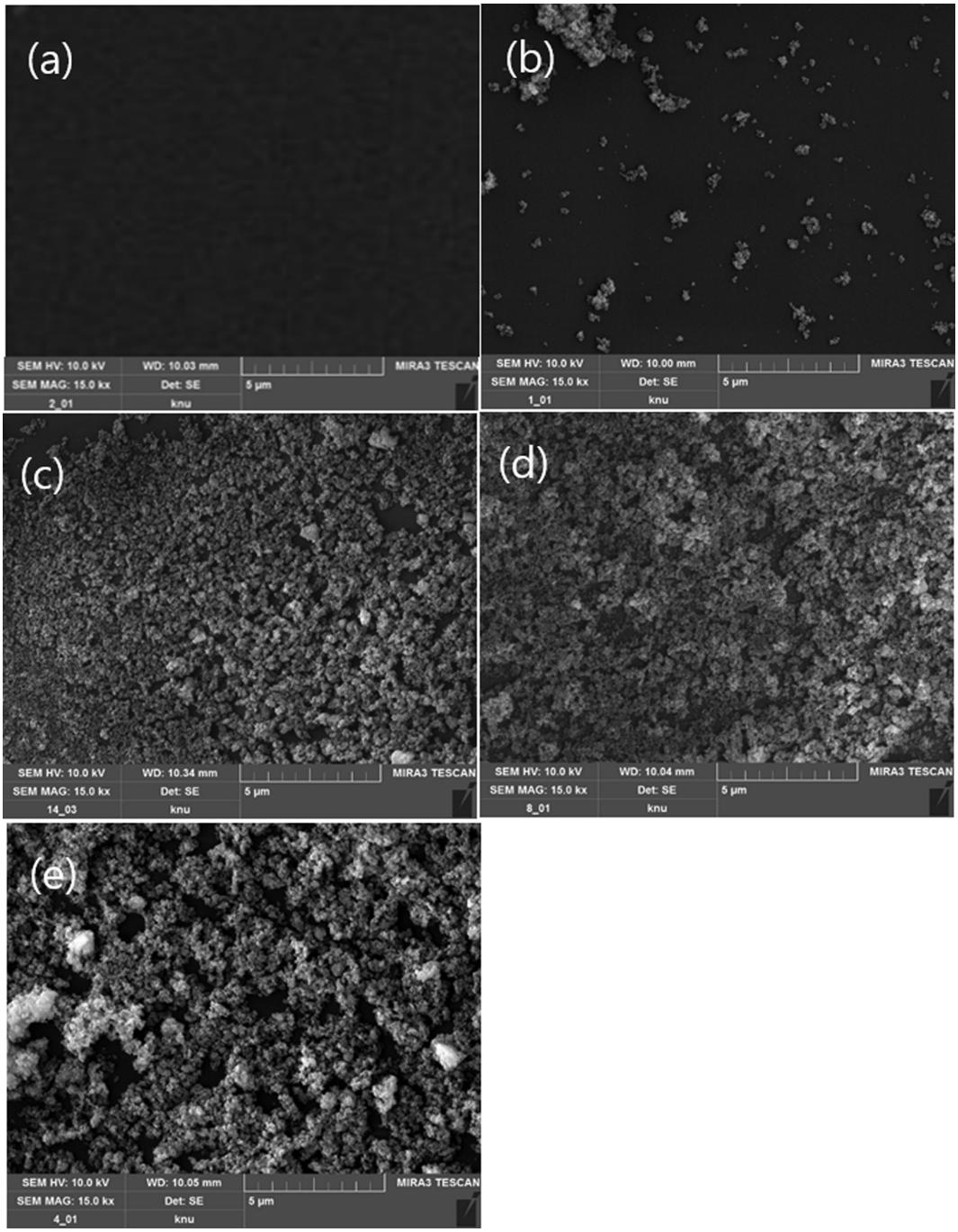

Fig. 4. The SEM surface morphology of coating films prepared by varying the amount of added silica nanoparticles. (a) 0 g, (b) 0.03 g, (c) 0.06 g, (d) 0.08 g, and (e) 0.12 g.

ness formed by the addition of silica nanoparticles. However, since the amount of nanoparticles added was small, it was not distributed over the entire surface, so the contact angle of the surface did not increase significantly. When the amount of added nanoparticles was 0.06 g and 0.08 g, the modified nanoparticles were uniformly distributed over the entire surface, resulting in high contact angles of 143° and 151°, respectively, as seen in Figs. 5(c) and (d). Especially, in the case of 0.08 g, the coating film showed a contact angle of 151°, which showed the superhydrophobicity. It seems that the superhydrophobicity is due to the surface roughness formed by the addition of modified silica nanoparticles. However, it was remarkable that when an excess amount of 0.12 g of nanoparticles was added, the contact angle of the coating film in Fig. 5(f) was 150° and was not improved due to significant aggregation between nanoparticles despite the increase in the amount of nanoparticles added. This result is consistent with Toh et al., who did not observe an improvement in the contact angle despite an increase in the amount of silica nanoparticles added due to significant aggrega-

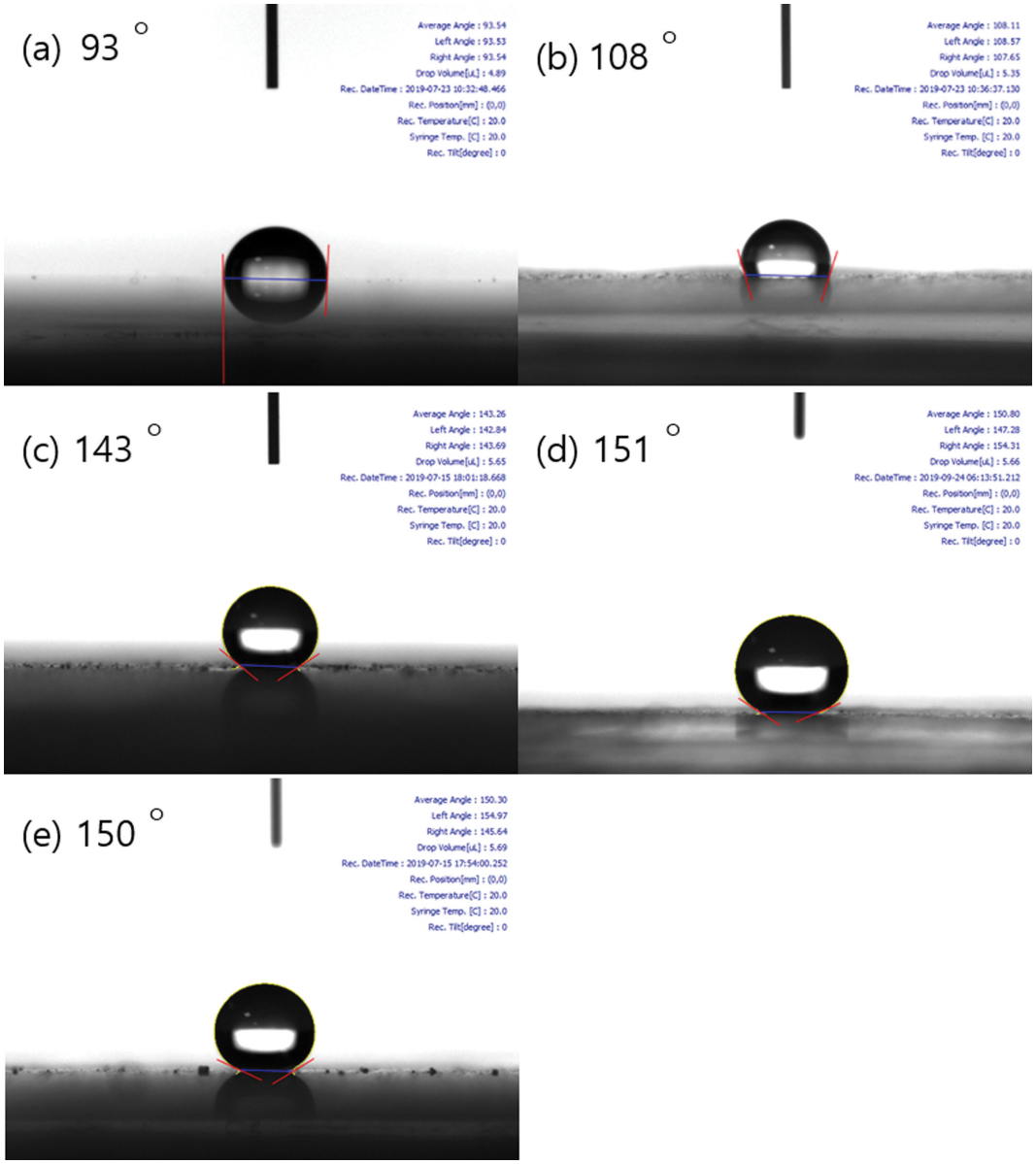

Fig. 5. Water contact angle of the coating films as a function of the amount of added silica nanoparticles on the hydrophobicity. (a) 0 g, (b) 0.03 g, (c) 0.06 g, (d) 0.08 g, and (e) 0.12 g.

tion between nanoparticles [13]. From these observations, it can be concluded that superhydrophobic coating could be successfully fabricated on a cold rolled steel sheet via the addition of TMES-modified silica nanoparticles. However, when the amount of silica nanoparticles exceeded 0.08 g, significant aggregation occurred between silica nanoparticles and the contact angle was rather reduced.

2. Effect of Type of Catalyst on the Hydrophobicity of Coating Films

When TMES is added to silica nanoparticles dispersed in methanol, the ethoxy group (Si-OC_2H_5) of TMES hydrolyzes with water in methanol to form a silanol group (Si-OH), as shown in Eq. (1).

$$(CH_3)_3\text{-Si-}OC_2H_5+H_2O\rightarrow(CH_3)_3\text{-Si-OH}+C_2H_5OH \quad (1)$$

Then, the silanol group in the hydrolyzed TMES tends to undergo a condensation reaction to yield a dimer called hexamethyldisiloxane (HMDS), as shown in Eq. (2).

$$(CH_3)_3\text{-Si-OH}+\text{HO-Si-}(CH_3)_3\rightarrow(CH_3)_3\text{-Si-O-Si-}(CH_3)_{3+}+H_2O \quad (2)$$

In the case of surface modification of silica nanoparticles, it is well known that hydrolyzed TMES adsorbs more on the surface of silica nanoparticles than HDMS dimer [14].

Chang et al. studied the hydrolysis and condensation reactions of TMES at different pH values [11]. They reported that the hydrolyzed TMES monomers combined with each other to form a dimer (HMDS) through a condensation reaction. They also found that little conversion to form HMDS occurred when the pH value was higher than 1.3. However, when the pH value was lowered to 0.8 or less, the hydrolysis and condensation reactions occurred rapidly and the product was mainly composed of HMDS.

Table 2. The composition of coating solutions prepared with different types of catalysts in methanol

Catalyst types	TMES (mole)	H_2O (mole)	MeOH (mole)	Catalyst (mole)	Silica nanoparticle (g)
Oxalic acid Hydrochloric acid Nitric acid Ammonia	0.02	0.01	0.06	0.0008	0.08

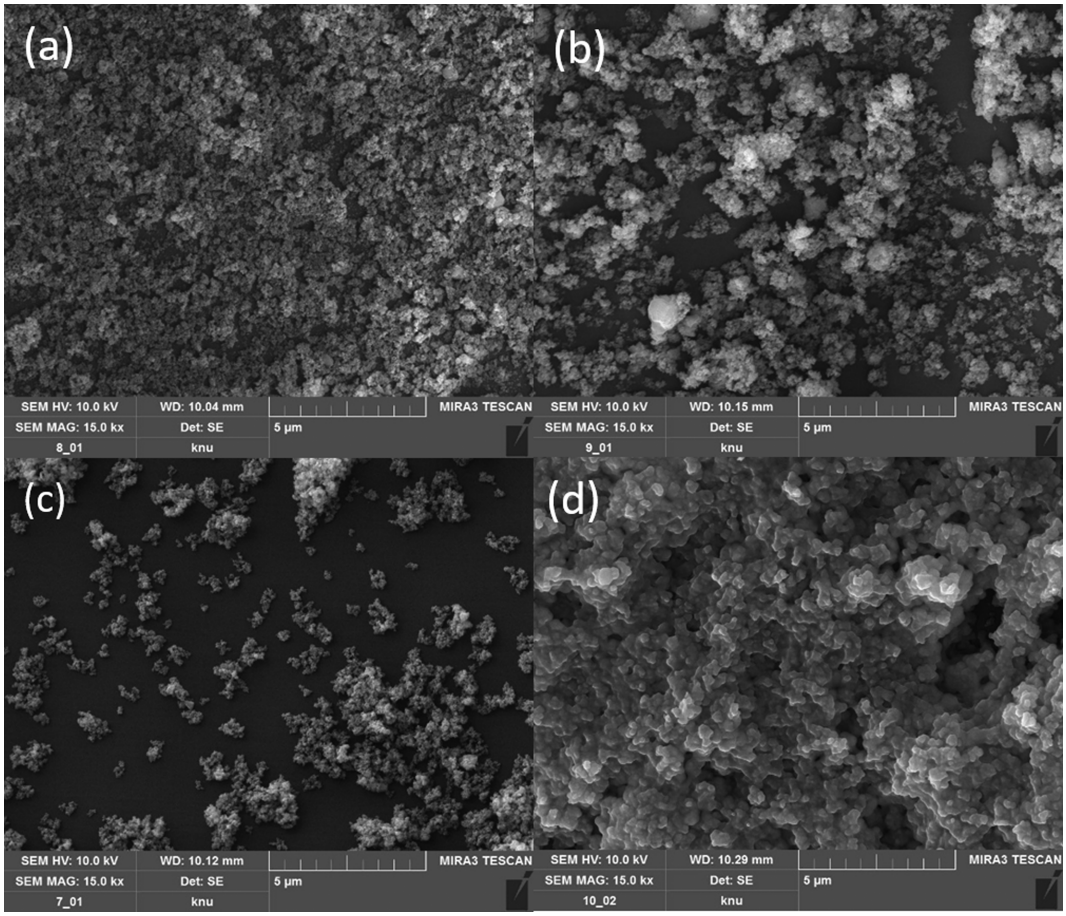

Fig. 6. The SEM surface morphology of the coating films prepared by using different catalysts of (a) oxalic acid, (b) hydrochloric acid, (c) nitric acid, and (d) ammonia.

Table 2 shows the composition of coating solutions to reveal the effect of various types of catalysts in methanol solvent on the hydrophobicity of the coating films. Fig. 6 shows the SEM surface morphology of the coating films prepared using different catalysts of (a) oxalic acid, (b) hydrochloric acid, (c) nitric acid, and (d) ammonia. When oxalic acid, a weak acid, was used as a catalyst, silica nanoparticles were evenly distributed and coated on the entire substrate. However, when hydrochloric acid and nitric acid, strong acids, were used as catalysts, wide uncoated areas without nanoparticles appeared on the surface. On the other hand, when ammonia, a base, was used as a catalyst, silica nanoparticles were uniformly distributed on the coating films, but the particles were larger than that of oxalic acid and severe aggregation between nanoparticles was observed.

Fig. 7 shows the effect of type of catalysts on the contact angles of the coating films. The coating films prepared with different catalysts of oxalic acid, hydrochloric acid, nitric acid, and ammonia show contact angles of 151°, 86°, 73°, and 143°, respectively. As observed by Cheng et al. [11], when oxalic acid, a weak acid catalyst, was used, there was almost no condensation reaction between the hydrolyzed TMES monomers, so the solution was composed of hydrolyzed TMES monomers, showing preferred adsorption on the surface of silica nanoparticles. Therefore, the modified silica nanoparticles were evenly distributed on the substrate surface, showing a superhydrophobicity of 151°. However, when hydrochloric acid and nitric acid, strong acid catalysts, were used, the coating films showed low hydrophobicity of 86° and 73°, respectively. In this case, the hydrolysis and condensation reactions of

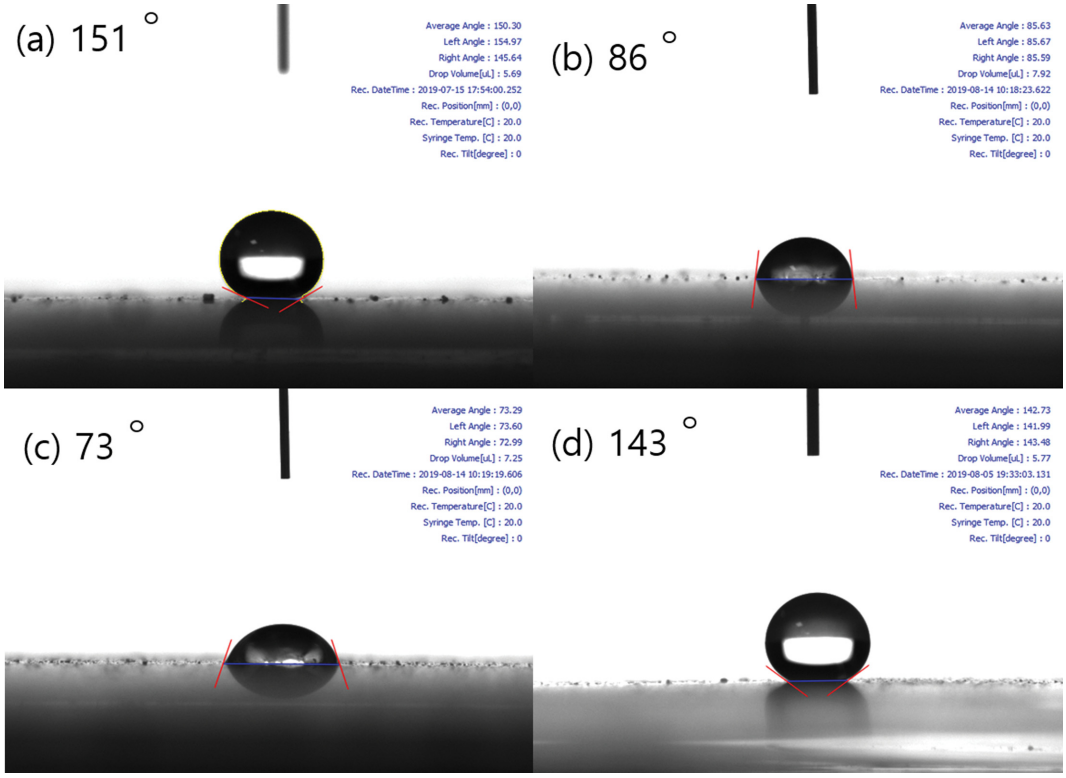

Fig. 7. Water contact angles of the coating films prepared by using different catalysts of (a) oxalic acid, (b) hydrochloric acid, (c) nitric acid, and (d) ammonia.

TMES occurred rapidly, as mentioned by Cheng et al. [11]. The solution was composed of HMDS dimer, so it was less adsorbed on the surface of silica nanoparticles. Therefore, the silica nanoparticles with less surface modification were not well coated on the surface, as shown in Figs. 6(b) and (c), resulting in low contact angles of 86° and 73°. In the case of ammonia, which is a base catalyst, the contact angle of the coating film was 143°, which was slightly lower than that of oxalic acid of 151°. It is presumed that the aggregation between the nanoparticles was severe in ammonia catalyst and the surface roughness was less than that of oxalic acid, resulting in a lower contact angle of the coating film.

3. Effect of Type of Organic Solvents on the Hydrophobicity of the Coating Films

When hydrophilic silica nanoparticles are dispersed in polar organic solvents with hydroxyl groups such as alcohols, polypropylene glycol, and acetone, they form a stable, low viscosity sol with no aggregation between nanoparticles [15]. It is known that the hydrogen bonding between silanol group (Si-OH) on the surface of silica nanoparticles and the polar organic solvent contributes to the formation of this stable sol [16]. However, hydrophilic silica nanoparticles, dispersed in non-polar organic solvents without hydroxyl groups, undergo gelation due to direct bonding between silanol groups on the surface of silica nanoparticles [15]. On the other hand, when the surface of hydrophilic silica nanoparticles is modified by TMES as the capping agent, the TMES moiety [-Si(CH_3)$_3$] on the surface of nanoparticles effectively prevents the formation of bonds between the silica nanoparticles. As a result, the modified nanoparticles can be dispersible in various types of organic solvents, including polar and non-polar solvents [11]. Chang et al. prepared hydrophilic silica nanoparticles from tetra-

Table 3. The composition of coating solutions prepared with different types of organic solvents under oxalic acid along with the solubility parameters of organic solvents in this study

Solvent types	Solubility parameter δ (MPa$^{1/2}$)	TMES (mole)	H_2O (mole)	Solvent amount (mole)	Oxalic acid (mole)	Silica nanoparticle (g)
Methanol	29.6	0.02	0.01	0.06	0.0008	0.08
Ethanol	26.5					
i-Propanol	23.6					
n-Butanol	23.1					
Methyl ethyl ketone	19.1					
Ethyl acetate	18.1					

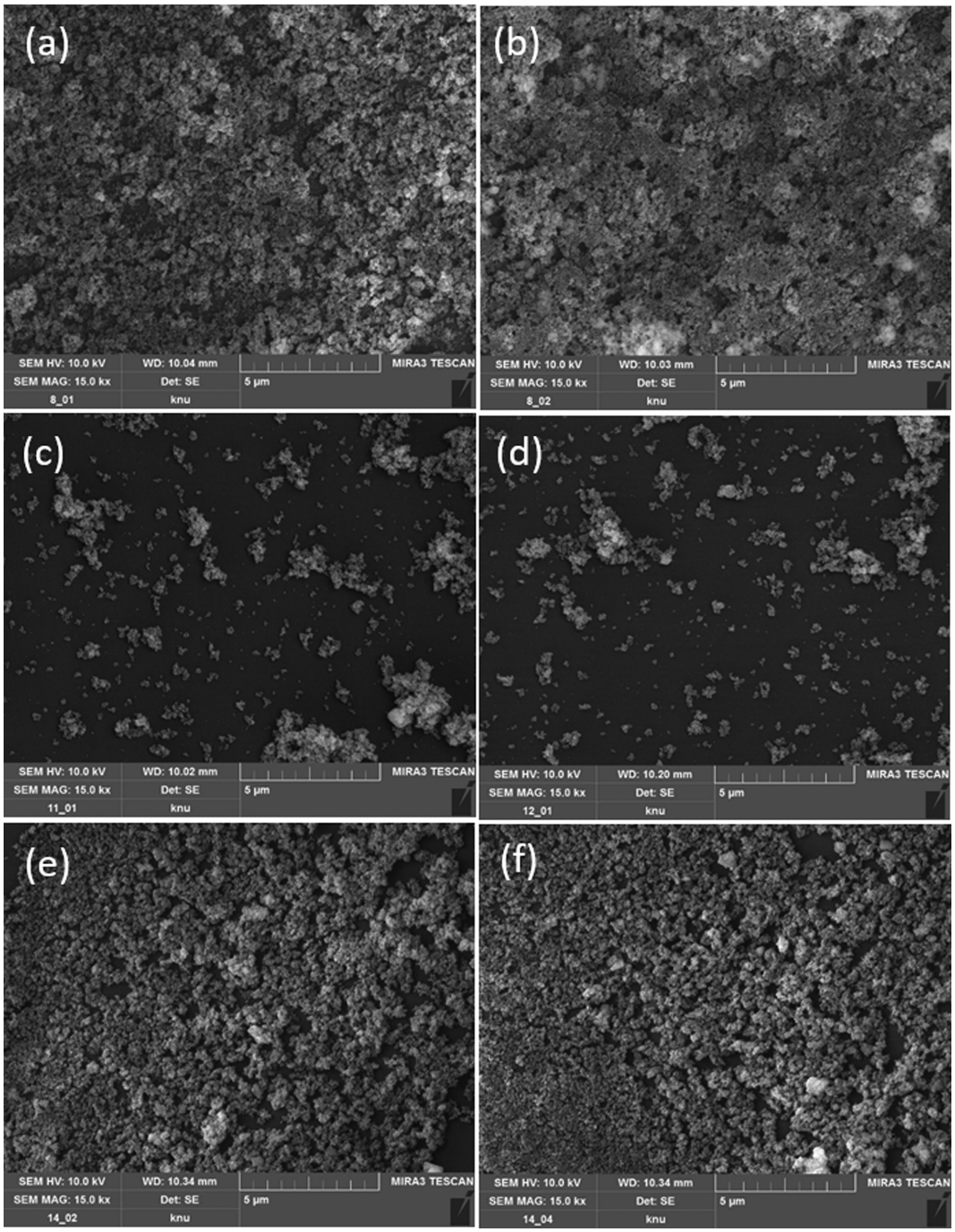

Fig. 8. The SEM results of surface microstructure of the coating films prepared with (a) methanol, (b) ethanol, (c) i-propanol, (d) n-butanol, (e) methyl ethyl ketone, and (f) ethyl acetate.

ethylorthosilicate by the sol-gel method, after modifying the surface of silica nanoparticles using TMES, a capping agent [11]. They found that the TMES-modified silica nanoparticles could be dispersible in a variety of organic solvents (polar and non-polar solvents), with the dispersibility depending on the amount of TMES bound to the silica nanoparticles. They also observed that the size of the silica nanoparticles, dispersed in various organic solvents, decreased as the solubility parameter of organic solvents increased [11].

Table 3 shows the composition of coating solutions prepared with various types of organic solvents with an oxalic acid catalyst, and the solubility parameters of organic solvents used in this study [17]. Fig. 8 shows the SEM results of surface microstructures of the coating films prepared with (a) methanol, (b) ethanol, (c) i-propanol, (d) n-butanol, (e) methyl ethyl ketone, and (f) ethyl acetate. In the case of coating films prepared with methanol and ethanol, as shown in Figs. 8(a) and (b), the silica nanoparticles are evenly coated over the whole substrate to form a rough surface. How-

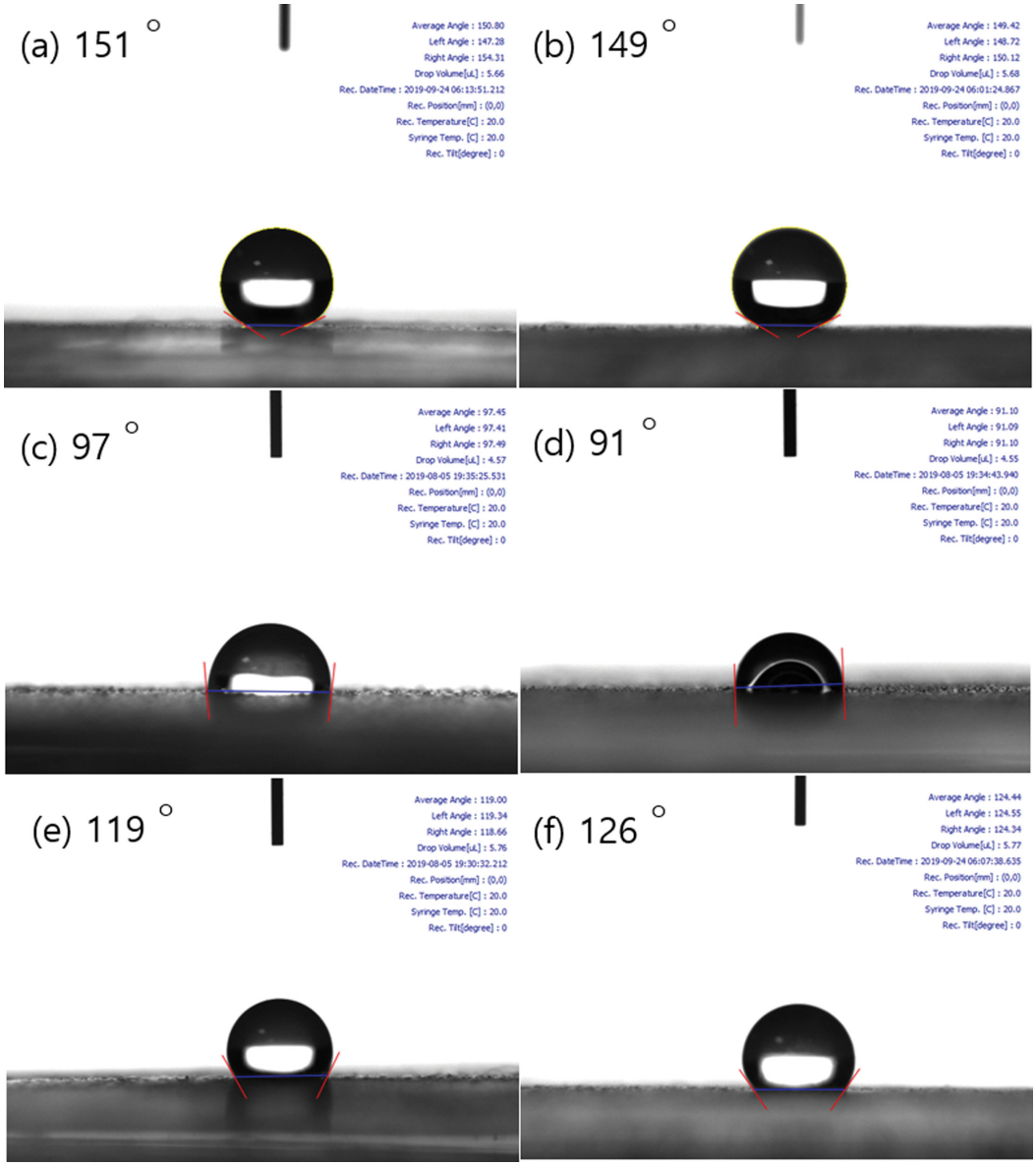

Fig. 9. Water contact angles of the coating films prepared with (a) methanol, (b) ethanol, (c) i-propanol, (d) n-butanol, (e) methyl ethyl ketone, and (f) ethyl acetate.

ever, the coating films prepared with i-propanol and n-butanol in Figs. 8(c) and (d) shows regions that were not extensively coated with nanoparticles on the substrates. In addition, in the coating films, prepared with methyl ethyl ketone and ethyl acetate, ketone solvents in Figs. 8(e) and (f), the nanoparticles are evenly coated on the entire substrate.

Fig. 9 shows the effect of different types of organic solvents on the contact angles of coating films. The coating films prepared with methanol and ethanol exhibit high contact angles of 151° and 149°, respectively, as the nanoparticles are evenly distributed on the surfaces, as shown in Figs. 8(a) and (b). However, i-propanol and n-butanol show low contact angles of 97° and 91°, respectively, due to the broad areas not covered with silica nanoparticles, as shown in Figs. 8(c) and (d). On the other hand, when methyl ethyl ketone and ethyl acetate, ketone solvents were used, the coating films show that silica nanoparticles are evenly coated on the entire substrate, as shown in Figs. 8(e) and (f). Therefore, the coating films prepared with methyl ethyl ketone and ethyl acetate exhibit relatively high contact angles of 119° and 126°, respectively. However, as shown in Table 3, the solubility parameters of the ketone solvents are lower than those of methanol and ethanol, and the nanoparticles in the solutions are larger than those of methanol and ethanol, resulting in a less rough structure on the coating films. For this reason, unlike methanol and ethanol, high hydrophobicity above 149° was not observed in the coating films of methyl ethyl ketone and ethyl acetate.

CONCLUSION

A superhydrophobic coating film was successfully prepared by

forming a rough structure of silica nanoparticles modified with TMES on the surface of the cold rolled steel sheet. The surface characteristics of the coating film were studied by SEM, FT-IR, and static contact angle measurements. FT-IR analysis confirmed that the reaction between TMES and the hydroxyl groups of silica nanoparticles occurred to form ≡Si-O-Si$(CH_3)_3$ species on the silica nanoparticle surface, and the surface of silica nanoparticles was modified by TMES. The coating film, prepared without silica nanoparticles, showed a low contact angle of 93°, whereas when 0.08 g of silica nanoparticles was added, the coating film exhibited a contact angle of 151°, showing superhydrophobicity.

Hydrophobic coating solutions were prepared in methanol solvent with various catalysts: oxalic acid, hydrochloric acid, nitric acid, and ammonia. In the case of oxalic acid, a weak acid, nanoparticles coated on the surface of substrates were evenly distributed. On the other hand, in the case of hydrochloric acid and nitric acid, strong acids, a large area without nanoparticles was observed. When an oxalic acid was used, the solution consisted of hydrolyzed TMES, showing preferred adsorption on the surface of silica nanoparticles. Therefore, the modified silica nanoparticles were evenly distributed on the substrate surface, resulting in a superhydrophobicity of 151°. However, when hydrochloric acid and nitric acid, strong acid catalysts, were used, the hydrolysis and condensation reactions of TMES occurred rapidly and the solution was composed of HMDS dimer, so that less adsorption occurred on the surface of silica nanoparticles. Therefore, silica nanoparticles with less surface-modification were not well coated on the surface of substrates, resulting in low contact angles of 85° and 73°.

Hydrophobic coating films were prepared with various types of organic solvents, such as methanol, ethanol, i-propanol, n-butanol, methyl ethyl ketone, and ethyl acetate. The type of organic solvents had a great influence on the morphology and contact angles of coating films. High contact angles above 149° were obtained for methanol and ethanol solvents. However, i-propanol and n-butanol showed low contact angles of 97° and 91°, respectively. On the other hand, in the case of methyl ethyl ketone and ethyl acetate, ketone solvents, the nanoparticles in the solutions were larger than those of methanol and ethanol, and the roughness of the coating films was smaller than that of methanol and ethanol. This is the reason why high hydrophobicity above 149° was not observed in the coating films of methyl ethyl ketone and ethyl acetate.

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REFERENCES

1. H. Gu, Q. Zhang, J. Gu, N. Li and J. Xiong, *J. Sol-Gel Sci. Technol.*, **87**, 478 (2018).
2. W. Barthlott and C. Neinhuis, *Planta*, **202**, 1 (1997).
3. S. S. Latthe, H. Imai, V. Ganesan and A. V. Rao, *Appl. Surf. Sci.*, **256**, 217 (2009).
4. X. M. Liu and J. H. He, *Langmuir*, **25**, 11822 (2009).
5. R. G. Wang and J. Kaneko, *Surf. Eng.*, **29**, 255 (2013).
6. S. A. Mahadik, F. Pedraza and R. S. Vhatkar, *J. Alloys Compd.*, **663**, 487 (2016).
7. Q. Q. Shang, Y. H. Zhou and G. M. Xiao, *J. Coat. Technol. Res.*, **11**, 509 (2014).
8. D. G. Kim, B. H. Lee and K. C. Song, *Korean Chem. Eng. Res.*, **57**, 177 (2019).
9. D. G. Kim, B. W. Lee and K. C. Song, *Korean Chem. Eng. Res.*, **57**, 749 (2019).
10. Z. Wang, W. Yang, F. Sun, P. Zhang, Y. He, X. Wang, D. Luo, W. Ma and G. C. Sergio, *Sur. Eng.*, **35**, 418 (2019).
11. C. C. Chang, J. H. Lin and L. P. Cheng, *J. Appl. Sci. Eng.*, **19**, 401 (2016).
12. F. H. Huang, C. C. Chang, T. Y. Oyang, C. C. Chen and L. P. Cheng, *J. Nanopart. Res.*, **13**, 3885 (2011).
13. M. J. Toh, P. C. Oh, A. L. Ahmad and J. Caille, *Korean J. Chem. Eng.*, **36**, 1854 (2019).
14. K. C. Song, J. K. Park, H. U. Kang and S. H. Kim, *J. Sol-Gel Sci. Technol.*, **27**, 53 (2003).
15. S. R. Raghavan, H. J. Walls and S. A. Khan, *Langmuir*, **16**, 7920 (2000).
16. S. R. Raghavan, and S. A. Khan, *J. Colloid Interface Sci.*, **185**, 57 (1997).
17. C. A. Saiz, S. Darvishmanesh, A. Buekenhoudt and B. V. Bruggen, *J. Membr. Sci.*, **546**, 120 (2018).