

# Preparation of Antifog Hard Coatings Based on Carboxy-Functionalized Polyhedral Oligomeric Silsesquioxane Cross-Linked with Oligo(ethylene glycol)s

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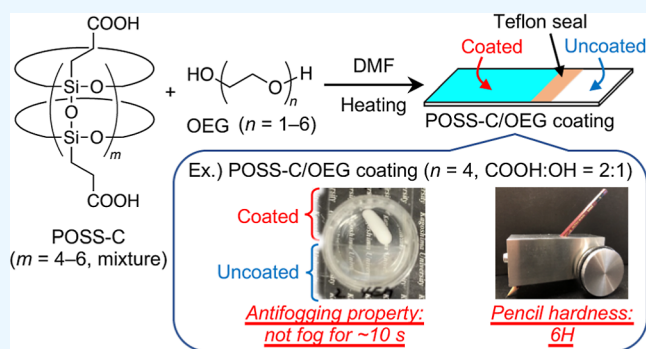
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**ABSTRACT:** In this study, we prepared antifog hard coatings by heating a mixture of carboxy-functionalized polyhedral oligomeric silsesquioxane (POSS-C) and oligo(ethylene glycol)s (OEGs,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ,  $n = 1-6$ ) in *N,N*-dimethylformamide, applying the mixture onto a glass substrate, and subsequently removing the solvent via heating. In addition, we evaluated the water resistance, hardness, and antifogging performance of the coatings. In particular, the coating produced at a 2:1 functional group ratio of POSS-C to tetraethylene glycol (OEG,  $n = 4$ ) coating exhibited high surface hardness (6H), as determined using pencil scratch testing. The coating remained clear after exposure to the vapor of warm water at 40 °C at a height of 2 cm for 10 s, demonstrating its antifogging property. Furthermore, no dissolution or cracking was observed when the POSS-C/OEG coating ( $n = 4$ ,  $\text{COOH}/\text{OH} = 2:1$ ) was immersed in water at room temperature for 1 h, confirming its water resistance. The Fourier transform infrared/attenuated total reflectance results showed the formation of ester bonds, indicating the construction of a network structure that enhanced the water resistance and hardness of the coating.



## INTRODUCTION

Fogging occurs when light is diffusely scattered by small water droplets formed via the condensation of water vapor on cool surfaces upon rapid changes in environmental factors, such as temperature, humidity, and air circulation. Antifogging technologies have been widely utilized in automobile windshields, eyeglasses/goggles, bathroom mirrors, solar panels, and analytical/medical devices.

Various antifogging materials have been developed based on rendering surface hydrophobicity (water repellency) to minimize water droplet adhesion or inducing hydrophilicity to promote the formation of a thin continuous water layer.<sup>1-3</sup> Coating the substrate surface with hydrophobic materials typically involves lowering the surface free energy using low-energy materials.<sup>4-7</sup> However, the generation of intricate surface morphologies over a wide range is challenging. Moreover, poor adhesion to the substrate and the opacity of the coating further restrict the applicability of such coatings for antifogging purposes.

Therefore, surface coating using hydrophilic/water-absorbing materials has become the mainstream approach for the preparation of antifogging materials. Hydrophilic/water-absorbing materials can be classified into two categories: inorganic materials, such as titanium dioxide and silica,<sup>8-16</sup> and hydrophilic organic polymers. Titanium dioxide exhibits

superhydrophilicity upon UV irradiation, making it suitable for antifog coatings. Silica-based coatings prepared under high-temperature conditions provide hydrophilic surfaces, enabling antifogging properties. However, the reliance on UV irradiation and high-temperature treatment limits indoor use and hinders applications on resin substrates. Meanwhile, hydrophilic organic polymer coatings can be utilized as versatile antifog coatings owing to their excellent formability.<sup>17-31</sup> They incorporate hydrophilic groups, such as hydroxy, carboxy, ammonium, and sulfo groups. For example, polyacrylate coatings with various hydrophilic groups exhibit antifogging properties.<sup>32</sup> Nonetheless, their hardnesses are generally lower than those of inorganic materials. Consequently, the transparency and antifogging properties gradually deteriorate because of scratching and abrasion. Therefore, the development of antifog hard coatings utilizing organic-inorganic hybrid materials is highly desired.<sup>33-38</sup> For instance, organic-inorganic hybrid coatings obtained by

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incorporating 3-trimethoxysilylpropyl methacrylate into silica and subsequently performing the radical polymerization of acrylate monomers have been reported.<sup>39</sup>

Recently, antifog hard coatings utilizing silsesquioxane (SQ) have been increasingly employed. Based on the number of organic substituents (R) and oxygen atoms bonded to the silicon atom, siloxanes are classified into M (3 organic substituents and 1 oxygen atom), D (2 organic substituents and 2 oxygen atoms), T (1 organic substituent and 3 oxygen atoms), and Q units (only oxygen atoms). SQ comprises only T unit, and its unit composition is denoted as  $\text{RSiO}_{1.5}$ .<sup>40</sup> Representative SQ structures include a ladder-like structure, fully condensed cage structure, incompletely condensed cage structure, and double-decker structure. Fully condensed cage oligomers are referred to as polyhedral oligomeric SQs (POSSs), which find extensive applications across various fields.<sup>41–43</sup> Furthermore, various side chain functional groups exist for SQs. In particular, our research group developed ladder-like polySQs with ammonium,<sup>44,45</sup> carboxy,<sup>46</sup> sulfo,<sup>47</sup> and phosphonic acid<sup>48</sup> groups, and POSSs with ammonium,<sup>49–55</sup> carboxy,<sup>56,57</sup> and imidazolium<sup>58–61</sup> groups. In addition to these regularly structured SQs, polySQs that possess hydrophilic functional groups can be used to prepare antifog hard coatings owing to the combination of the rigid framework derived from T structures of siloxane bonds and hydrophilic side chains.

For example, coatings based on polySQs obtained via the hydrolytic polycondensation (sol–gel reaction) of silane coupling agents bearing amino or glycidyl groups have been investigated.<sup>62–64</sup> In addition, we have developed antifog hard coatings based on polyamides obtained via the polycondensation of POSS possessing amino and carboxy groups on side chains. This preparation involved the use of a condensation agent, 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS), and heating at 80 °C in dehydrated dimethyl sulfoxide (DMSO) for 12 h.<sup>65</sup> Although this coating exhibited excellent antifogging properties and hardness, it tends to delaminate upon water immersion. The development of coatings with superior antifogging performance, hardness, and water resistance holds significant potential to realize their practical applications.

In this study, we developed water-resistant antifog hard coatings by combining carboxy-functionalized POSS (POSS-C) with mechanical robustness and hydrophilicity and oligo(ethylene glycol)s (OEGs) with film-formability, slight flexibility, and hydrophilicity.

## EXPERIMENTAL SECTION

**Materials.** 2-Cyanoethyltriethoxysilane (CETES, 98%), ethylene glycol (99.5%), diethylene glycol (99.5%), triethylene glycol (99%), tetraethylene glycol (95%), pentaethylene glycol (95%), and hexaethylene glycol (98%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Trifluoromethanesulfonic acid (HOTf, 99%) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Sodium hydroxide (NaOH, 97%) and polyethylene glycol with an average molecular weight of 1000 (PEG1000) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Ethanol (99%) was purchased from Nippon Alcohol Hanbai Co., Ltd. (Tokyo, Japan). Amylene-stabilized chloroform (99%), *N,N*-dimethylformamide (DMF, 99.5%), acetonitrile (99.5%), acetone (99%), and hydrochloric acid (HCl, 35–37%) were purchased

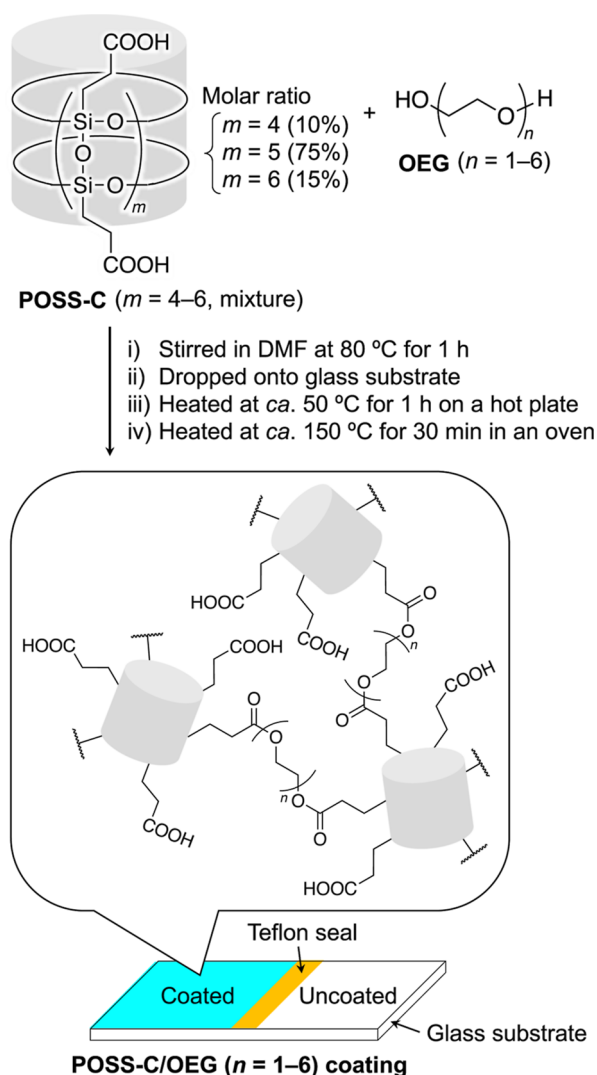
from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan). All reagents and solvents were used without further purification.

**Preparation of Carboxy-Functionalized Rod-like PolySQ and POSS-C.** Carboxy-functionalized rod-like polySQ was prepared as a precursor for POSS-C as described previously, with minor adjustments.<sup>46</sup> After adding a 2.0 mol  $\text{L}^{-1}$  NaOH aqueous solution (60 mL, 120 mmol) to CETES (8.871 g, 40 mmol) while stirring at room temperature, the resulting solution was continuously stirred for 15 h. Subsequently, the mixture was heated at ca. 50 °C in an open system until the solvent completely evaporated. After the crude product was maintained at 100 °C in an oven for 2 h, 1.0 mol  $\text{L}^{-1}$  HCl aqueous solution (120 mL, 120 mmol) was added at room temperature (ca. 25 °C). This solution was further heated at ca. 50 °C in an open system until the solvent completely evaporated (ca. 6 h). Water (25 mL) was added to the resulting solid product, and the mixture was promptly stirred using a spatula for 1 min. Immediate suction filtration was performed to eliminate sodium chloride generated from the reaction of NaOH and HCl. In this operation, it is important to stir and filter quickly as prolonged stirring causes all the products to dissolve in water. This operation was repeated three times. The resulting solid was dried under reduced pressure at room temperature, yielding a white powdered product (5.304 g, quantitative yield).

POSS-C was prepared with slight adjustments to the method reported in the literature.<sup>57</sup> First, 0.50 mol  $\text{L}^{-1}$  HOTf aqueous solution (100 mL, 50 mmol) was added to carboxy-functionalized rod-like polySQ (4.171 g, 33.33 mmol unit). Subsequently, the solution was heated at ca. 60 °C for 20 min, and the resulting solution was stirred at room temperature for 2 h. Then, the solution was heated at ca. 50 °C in an open system until the solvent completely evaporated (ca. 5.5 h). At this stage, the solution remained in a liquid state owing to the presence of HOTf. The resulting liquid was subsequently held in an oven at 100 °C for 2 h. After cooling to room temperature, acetone (8.4 mL) was added. This solution was poured into a mixed solvent of acetone and chloroform (1:9 v/v, 416 mL) and stirred at room temperature for ca. 15 h. The insoluble part was separated by filtration and washed with acetonitrile (ca. 25 mL, 5 times). Then, the insoluble part was dissolved in acetone (ca. 25 mL), and the acetone-soluble part was separated using filtration. Finally, acetone was evaporated, and the resulting solid product was dried under reduced pressure at room temperature, yielding a white powdered product (0.707 g, yield 17%). The structure of POSS-C was confirmed by <sup>1</sup>H and <sup>29</sup>Si NMR spectra (Figures S1 and S2). In this study, a mixture of octamer, decamer, and dodecamer POSS in a molar ratio of 10:75:15 was used for the coating preparation as described below (Scheme 1).

**Preparation of POSS-C/OEG Coatings.** The glass substrate (48 mm × 28 mm, thickness: 1.3 mm) was ultrasonically cleaned in ethanol (ca. 3 min) and hydrophilized using plasma equipment (Plasma Modifier PM100, Yamato Scientific Co., Ltd., Tokyo, Japan). This plasma treatment of the glass substrate was performed by flowing oxygen at a flow rate of 100 mL  $\text{min}^{-1}$  for 30 s and then irradiating the plasma for 3 min. To ensure a consistent coating area for the applied solution on the glass substrate, a Teflon seal was affixed to the glass substrate, resulting in an area of 840  $\text{mm}^2$  (30 mm × 28 mm). The weights and molar quantities of POSS-C and OEG in the reaction described below are provided as an example of

### Scheme 1. Preparation of Antifog Hard Coatings with Water Resistance (POSS-C/OEG ( $n = 1-6$ ) Coatings)



the reaction involving tetraethylene glycol (OEG,  $n = 4$ ). POSS-C [0.0125 g, 0.1 mmol based on repeating units (carboxy groups)] and tetraethylene glycol (0.0051 g, 0.025 mmol, 0.05 mmol based on hydroxy groups) were dissolved in DMF (0.3 mL). The mixture was stirred at 80 °C for 1 h, resulting in a homogeneous solution. This solution was then applied onto the glass substrate 840 mm<sup>2</sup> (30 mm × 28 mm). The coated substrate was heated in an open system on a hot plate (setting temperature: 50 °C) for 1 h to remove DMF. Subsequently, the substrate was treated in an oven at 150 °C for 30 min to prepare POSS-C/OEG coatings ( $n = 4$ , COOH/OH = 2:1). COOH/OH = 2:1 means the molar ratio of carboxy groups in POSS-C to hydroxy groups in OEG. Other POSS-C/OEG coatings were also prepared similarly, where “ $n$ ” represents the degree of polymerization of OEG, and “COOH/OH” indicates the molar ratio of carboxy groups in POSS-C to hydroxy groups in OEG.

**Measurements.** The UV–vis spectra were measured using a JASCO V-630 spectrophotometer (JASCO Corporation, Tokyo, Japan). The surface morphology of the coatings was observed via scanning electron microscopy (SEM) using the FEI Quanta 250 instrument (FEI Company Japan Ltd., Tokyo, Japan). The chemical compositions of the coatings were

analyzed using energy-dispersive X-ray spectroscopy (EDX) embedded into the FEI Quanta 250 device. The Fourier transform infrared/attenuated total reflectance (FTIR/ATR) spectra were recorded using an IRSprit-T (SHIMADZU CORPORATION, Kyoto, Japan). The pencil hardness was measured using a pencil scratch tester (TP GIKEN Co., Osaka, Japan) at an angle of 45° under a loading of 750 g. The pencil used was made by Mitsubishi Pencil Co., Ltd. (Tokyo, Japan). The lead of the pencils was ground perpendicularly to make an angle of 90° before each pencil hardness measurement. The water contact angles of the coatings were evaluated using a water-drop contact-angle meter (SIimage Entry 6, Excimer, Inc., Kanagawa, Japan). The amount of water droplet was 3.6 μL, and the contact angle of the water droplet was measured with a charge-coupled device camera using the half angle method. The antifogging performance of the coatings was evaluated by placing the coating surface facing down at a distance of 2 cm from warm water at 40 °C and exposing it to water vapor. The water resistance of the coatings was evaluated by immersing them in water at room temperature for 1 h, wiping off water droplets on the surface, and observing the state of the coatings.

## RESULTS AND DISCUSSION

**Preparation of POSS-C/OEG Coatings.** The preparation of the water-resistant antifog hard coatings, POSS-C/OEG coatings, was performed as follows. A DMF solution of POSS-C and OEG was heated and stirred under a closed system and then applied on glass substrates. Subsequently, the coated substrates were heated for 1 h in an open system to remove DMF. The coatings were further heated in an oven at 150 °C for 30 min to promote esterification (Scheme 1). All coatings prepared in this study were colorless and transparent (Figure S3). As a representative example, UV–vis measurement was performed on the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1), which showed over 98% transmittance in the visible wavelength region (Figure S4). From the SEM image of this coating, a smooth surface at the micrometer scale was observed (Figure S5a), and a peak corresponding to silicon atom was detected in the EDX pattern (Figure S5b), indicating the presence of POSS-C components on the surface.

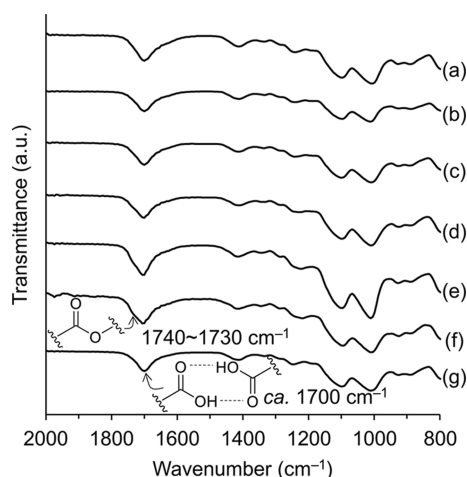
**Water Resistance of POSS-C/OEG Coatings.** To evaluate water resistance, the coated glass substrates were immersed in water at room temperature for 1 h and then taken out to observe the appearance of the coatings. POSS-C/OEG coatings ( $n = 1$ , COOH/OH = 5:1, 2:1, and 1:1) and POSS-C/OEG coatings ( $n = 2$ , COOH/OH = 5:1 and 2:1) were dissolved upon immersion in water (runs 1–5 in Table 1), suggesting the absence of the cross-linked network structure. This was verified by the FTIR/ATR results (Figures 1a,b, 2a,b, and 3a), which showed the absence of absorption peaks at ca. 1730 cm<sup>-1</sup> attributed to ester bonds. When the coatings were prepared on glass substrates using ethylene glycol and diethylene glycol alone, respectively, and heated in an oven at 150 °C, they disappeared in ca. 5–10 min. This implies that ethylene glycol and diethylene glycol evaporated before the formation of ester bonds with POSS-C, resulting in a coating of POSS-C alone that dissolved in water.

In the POSS-C/OEG coating ( $n = 2$ , COOH/OH = 1:1), POSS-C/OEG coatings ( $n = 3$ , COOH/OH = 5:1, 2:1, and 1:1), and POSS-C/OEG coating ( $n = 4$ , COOH/OH = 5:1), numerous fine cracks were observed (runs 6–10 in Table 1). In the FTIR spectra, although the absorption peaks attributed

**Table 1. Summary of Water Resistance, Surface Hardness, Antifogging Performance, and Water Contact Angle of POSS-C/OEG Coatings**

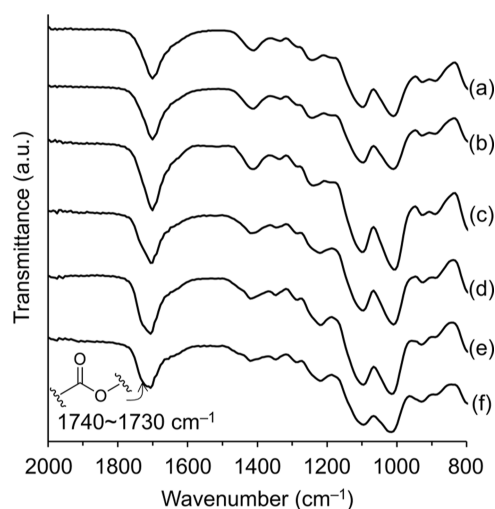
run	coating	feed molar ratio <sup>a</sup> COOH/OH	water resistance <sup>b</sup>	surface hardness <sup>c</sup>	time to keep antifogging <sup>d</sup> (s)	water contact angle
1	POSS-C/OEG ( <i>n</i> = 1)	5:1	dissolved	4H	20	80°
2	POSS-C/OEG ( <i>n</i> = 1)	2:1	dissolved	4H	14	76°
3	POSS-C/OEG ( <i>n</i> = 1)	1:1	dissolved	5H	13	76°
4	POSS-C/OEG ( <i>n</i> = 2)	5:1	dissolved	5H	5	76°
5	POSS-C/OEG ( <i>n</i> = 2)	2:1	dissolved	4H	15	76°
6	POSS-C/OEG ( <i>n</i> = 2)	1:1	cracked	6H	8	93°
7	POSS-C/OEG ( <i>n</i> = 3)	5:1	cracked	6H	10	82°
8	POSS-C/OEG ( <i>n</i> = 3)	2:1	cracked	6H	5	83°
9	POSS-C/OEG ( <i>n</i> = 3)	1:1	cracked	7H	5	83°
10	POSS-C/OEG ( <i>n</i> = 4)	5:1	cracked	5H	17	83°
11	POSS-C/OEG ( <i>n</i> = 4)	2:1	not dissolved not cracked	6H	10	79°
12	POSS-C/OEG ( <i>n</i> = 4)	1:1	not dissolved not cracked	3H	9	67°
13	POSS-C/OEG ( <i>n</i> = 5)	5:1	not dissolved not cracked	3H	6	98°
14	POSS-C/OEG ( <i>n</i> = 5)	2:1	not dissolved not cracked	HB	8	80°
15	POSS-C/OEG ( <i>n</i> = 5)	1:1	not dissolved not cracked	less than 2B	12	78°
16	POSS-C/OEG ( <i>n</i> = 5)	5:1	not dissolved not cracked	less than 2B	6	72°
17	POSS-C/OEG ( <i>n</i> = 6)	2:1	not dissolved not cracked	less than 2B	9	73°
18	POSS-C/OEG ( <i>n</i> = 6)	1:1	not dissolved not cracked	less than 2B	40	40°
19	POSS-C		dissolved	5H	40	73°
20	PEG1000		dissolved	less than 2B	120	5°

<sup>a</sup>Feed molar ratio of the COOH group in POSS-C to the OH group in OEG. <sup>b</sup>The coated glass substrate was immersed in water at room temperature for 1 h and then taken out to observe the appearance of the coating. <sup>c</sup>The surface hardness of coatings was evaluated using pencil scratch testing. <sup>d</sup>The evaluation of antifogging properties was performed by placing the coated glass substrate with the coated side facing down 2 cm above warm water at 40 °C to for water vapor exposure and observing the antifogging behavior.



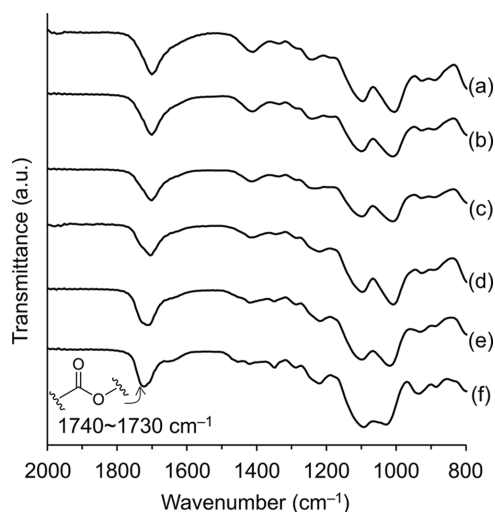
**Figure 1.** FTIR/ATR spectra of POSS-C/OEG coatings [(a) *n* = 1, (b) *n* = 2, (c) *n* = 3, (d) *n* = 4, (e) *n* = 5, and (f) *n* = 6] (the feed molar ratio of the COOH group in POSS-C to the OH group in OEG was 5:1) and (g) POSS-C coating.

to the ester bond (ca. 1730 cm<sup>-1</sup>) were not clearly observed (Figures 1c,d, 2c, and 3b,c), their partial insolubility led to the expectation of the presence of partial cross-linking between the carboxy groups in POSS-C and the hydroxy groups in OEG. However, some un-cross-linked components dissolved as soluble components, leading to vacant spaces and the emergence of cracks due to contraction during drying. When the coating was prepared via triethylene glycol alone using the same procedure and heated in an oven at 150 °C, it disappeared in ca. 15 min, suggesting the partial evaporation of triethylene glycol during the coating preparation process and the subsequent insufficient cross-linking.



**Figure 2.** FTIR/ATR spectra of POSS-C/OEG coatings [(a) *n* = 1, (b) *n* = 2, (c) *n* = 3, (d) *n* = 4, (e) *n* = 5, and (f) *n* = 6] (the feed molar ratio of the COOH group in POSS-C to the OH group in OEG was 2:1).

Meanwhile, POSS-C/OEG coatings (*n* = 4, COOH/OH = 2:1 and 1:1), POSS-C/OEG coatings (*n* = 5, COOH/OH = 5:1, 2:1, and 1:1), and POSS-C/OEG coatings (*n* = 6, COOH/OH = 5:1, 2:1, and 1:1) did not dissolve or crack (runs 11–18 in Table 1). Based on the FTIR/ATR results, absorption peaks at ca. 1730 cm<sup>-1</sup> attributed to ester bonds were observed in the coatings that did not dissolve or crack, in addition to the absorption peaks at ca. 1700 cm<sup>-1</sup> due to carboxy groups dimerized through hydrogen bonding (Figures 1e,f, 2d–f, and 3d–f). These results suggest the construction of a three-dimensional cross-linked network structure.

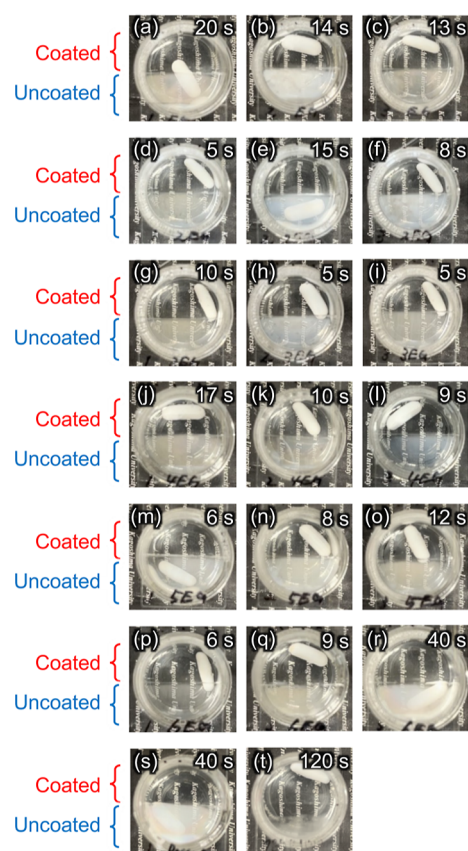


**Figure 3.** FTIR/ATR spectra of POSS-C/OEG coatings [(a)  $n = 1$ , (b)  $n = 2$ , (c)  $n = 3$ , (d)  $n = 4$ , (e)  $n = 5$ , and (f)  $n = 6$ ] (the feed molar ratio of the COOH group in POSS-C to the OH group in OEG was 1:1).

**Hardness of POSS-C/OEG Coatings.** The surface hardness of the POSS-C/OEG coatings was evaluated using a pencil scratch testing. The pencil hardness of POSS-C/OEG coatings ( $n = 1$ –4) prepared using OEG with lower molecular weights ranged from 3H to 7H, demonstrating a considerably high surface hardness (runs 1–12 in Table 1). Conversely, the pencil hardness of POSS-C/OEG coatings ( $n = 5$  and 6) was found to be less than 2B to 3H, revealing a decrease in surface hardness with increasing molecular weight of OEG (runs 14–18 in Table 1). This is due to the higher proportion of organic components within the coating as the molecular weight of OEG increased. Among these coatings, only the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) exhibited a lack of dissolution or cracking in the water resistance tests and demonstrated high surface hardness (6H) in the pencil scratch test (run 11 in Table 1).

The POSS-C/OEG coating ( $n = 4$ , COOH/OH = 1:1) and POSS-C/OEG coating ( $n = 5$ , COOH/OH = 5:1) also showed reasonably good performance in the evaluation of water resistance and surface hardness (runs 12 and 13 in Table 1); however, their surface hardness (3H) was lower than that of the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) (6H). We assume that the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 1:1) has a higher proportion of organic components compared to the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) because of the higher molar ratio of OEG, resulting in decreased surface hardness. Meanwhile, for the POSS-C/OEG coating ( $n = 5$ , COOH/OH = 5:1), OEG with a higher molecular weight leads to the lower surface hardness as described above.

**Antifogging Property of POSS-C/OEG Coatings.** The evaluation of antifogging properties was performed by placing the coated glass substrate with the coated side facing down 2 cm above warm water (40 °C) for water vapor exposure and observing the antifogging behavior (Figure S6). Figure 4 shows the antifogging behavior of all coatings performed in this study. In particular, the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) maintained its antifogging state for 10 s after exposure to water vapor (Figure 4k and run 11 in Table 1), which, along

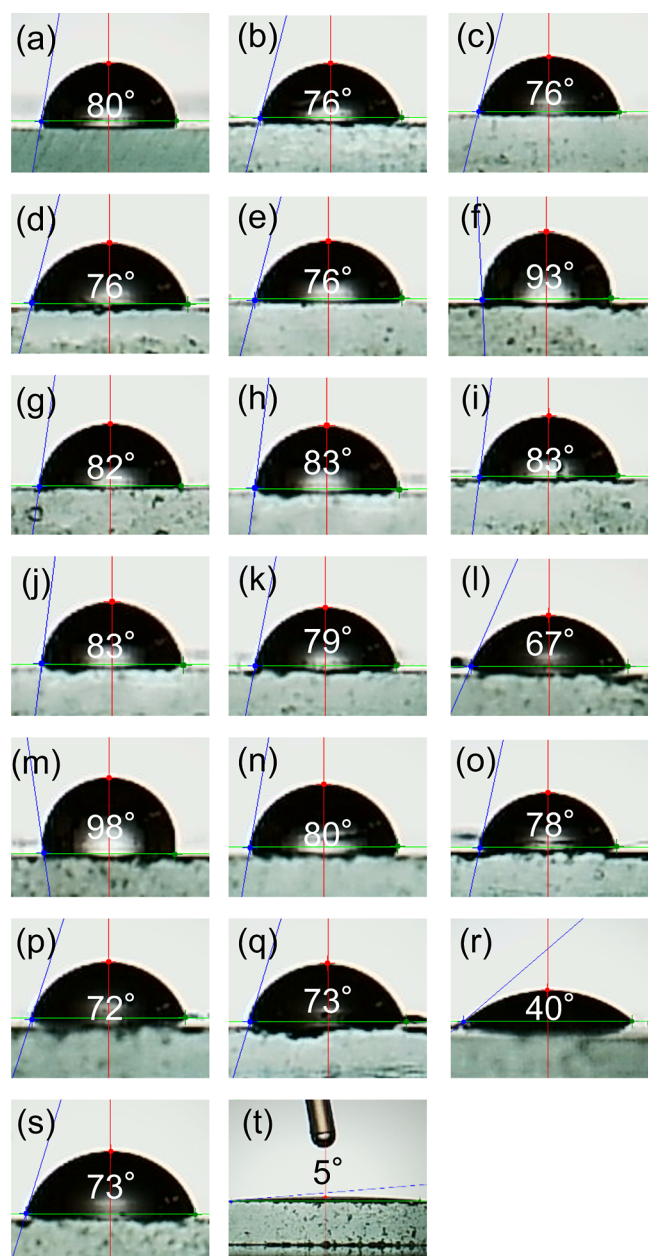


**Figure 4.** Antifogging behavior of POSS-C/OEG coatings [ $n = 1$ , COOH/OH = (a) 5:1, (b) 2:1, and (c) 1:1], POSS-C/OEG coatings [ $n = 2$ , COOH/OH = (d) 5:1, (e) 2:1, and (f) 1:1], POSS-C/OEG coatings [ $n = 3$ , COOH/OH = (g) 5:1, (h) 2:1, and (i) 1:1], POSS-C/OEG coatings [ $n = 4$ , COOH/OH = (j) 5:1, (k) 2:1, and (l) 1:1], POSS-C/OEG coatings [ $n = 5$ , COOH/OH = (m) 5:1, (n) 2:1, and (o) 1:1], POSS-C/OEG coatings [ $n = 6$ , COOH/OH = (p) 5:1, (q) 2:1, and (r) 1:1], (s) POSS-C coating, and (t) PEG1000 coating upon exposure to water vapor.

with excellent water resistance and surface hardness (6H), proved its potential as an antifog hard coating.

**Water Contact Angles of POSS-C/OEG Coatings.** The water contact angles of the POSS-C/OEG coatings were measured to comprehend their antifogging mechanism (Figure Sa–r). For comparison, the coatings of POSS-C and PEG1000 were prepared using the same method (Figure Ss,t). Because the OEGs used as the starting materials were liquid, the coatings could not be produced using them alone. As an alternative, PEG1000 was chosen as a compound containing ether bonds for comparison.

The water contact angles of the POSS-C and PEG1000 coatings were 73 and 5°, respectively (Figure Ss,t, and runs 19 and 20 in Table 1). In contrast, the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) exhibited a water contact angle of 79° (Figure 5k and run 11 in Table 1), surpassing those of the POSS-C and PEG1000 coatings. Presumably, the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) with a network structure formed by ester bonds possesses small pores, resulting in a slight lotus leaf effect, which leads to a higher water contact angle compared to the coatings of POSS-C or PEG1000 alone. Alternatively, when the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) with small pores is exposed to water vapor, water molecules enter the pores as



**Figure 5.** Water contact angles of POSS-C/OEG coatings [ $n = 1$ , COOH/OH = (a) 5:1, (b) 2:1, and (c) 1:1], POSS-C/OEG coatings [ $n = 2$ , COOH/OH = (d) 5:1, (e) 2:1, and (f) 1:1], POSS-C/OEG coatings [ $n = 3$ , COOH/OH = (g) 5:1, (h) 2:1, and (i) 1:1], POSS-C/OEG coatings [ $n = 4$ , COOH/OH = (j) 5:1, (k) 2:1, and (l) 1:1], POSS-C/OEG coatings [ $n = 5$ , COOH/OH = (m) 5:1, (n) 2:1, and (o) 1:1], POSS-C/OEG coatings [ $n = 6$ , COOH/OH = (p) 5:1, (q) 2:1, and (r) 1:1], (s) POSS-C coating, and (t) PEG1000 coating.

vapor. Then, they cool down, and the resulting water fills the pores of the coating uniformly, suppressing light scattering.

**Mechanism of Water-Resistant Antifog Hard Coating Formation.** First, the antifogging mechanism during water vapor exposure is discussed. It is believed that the carboxy groups in POSS-C and the ether chains in OEG, which are hydrophilic components, contribute to the antifogging properties of the coatings. Furthermore, small pores exist within the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) with a network structure. When exposed to water vapor, water molecules enter these pores, where they cool down, and the

resulting water fills the pores of the coating uniformly. This is expected to suppress light scattering, ultimately resulting in the manifestation of antifogging properties.

Next, we describe the mechanism of the observed hard-coating property through pencil scratch testing. The surface hardness of the coating composed solely of POSS-C was determined to be 5H. Based on this observation, it is considered that the robust hardness (6H) of the developed POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) stems from the sturdy framework inherent to POSS-C. In addition, the construction of a network structure upon the formation of ester bonds contributes to the enhanced hardness. Moreover, this network structure provides insolubility to the coating; thus, it can be regarded as the mechanism underlying water resistance.

## CONCLUSIONS

In this study, a water-resistant antifog hard coating, POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1), was obtained by mixing POSS-C and tetraethylene glycol in a 2:1 feed molar ratio based on their functional groups (COOH and OH groups) and heating the mixture in DMF, followed by its application onto a glass substrate and evaporating the solvent via heating. When the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1) was exposed to water vapor at a height of 2 cm above warm water at 40 °C, the coated surface remained clear for ca. 10 s, and it demonstrated a surface hardness of 6H. Even after immersion in water at room temperature for 1 h, the coating did not dissolve or crack, exhibiting excellent water resistance. The antifog hard coatings developed in this study may evolve into applications for antifogging in resin window glass, which is expected in future automobile lightweighting efforts, due to their significantly high surface hardness.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c03563>.

$^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra of POSS-C, appearance of POSS-C/OEG coatings, UV-vis spectrum and SEM and EDX of the POSS-C/OEG coating ( $n = 4$ , COOH/OH = 2:1), and photos of the equipment used for antifogging evaluation (PDF)

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## Author Contributions

Individual author contributions are as follows: J.N. contributed to almost all of the experimental work and wrote the paper. S.M. contributed to UV-vis, SEM, EDX and water contact angle measurements after water vapor exposure. Y.K. designed the research, directed this study, and edited the paper.

## Notes

The authors declare no competing financial interest.

## ABBREVIATIONS

SO, silsesquioxane; POSS, polyhedral oligomeric silsesquioxane; POSS-C, carboxy-functionalized polyhedral oligomeric silsesquioxane; OEG, oligo(ethylene glycol); UV-vis, UV-visible; SEM, scanning electron microscopy; EDX, energy-dispersive X-ray spectroscopy; FTIR/ATR, Fourier-transform infrared spectroscopy/attenuated total reflection; EDC, 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride; NHS, *N*-hydroxysuccinimide; DMSO, dimethyl sulfoxide; CETES, 2-cyanoethyltriethoxysilane; HOTf, trifluoromethanesulfonic acid; PEG1000, polyethylene glycol with an average molecular weight of 1000; DMF, *N,N*-dimethylformamide

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