Improving superhydrophobicity of polydimethylsiloxanes using embedding fluorinated polyhedral oligomeric silsesquioxanes cages

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Received: 14 April 2020 / Accepted: 14 October 2020 / Published online: 5 November 2020
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Abstract

Improving the superhydrophobicity of polydimethylsiloxane (PDMS) is a current interest in a wide range of applications from biomedical to aerospace. Although many fabrication techniques are available to improve the superhydrophobicity of PDMS, a significant problem occurs when the fabrication technique applies as a scalable but simple one. Here, we have described simple methods to achieve superhydrophobicity of PDMS using short-chained fluorinated polyhedral oligomeric silsesquioxanes (FPOSS). Two species of FPOSS were incorporated into PDMS using four different methods; non-solvent blending, solvent blending, spraying FPOSS/PDMS solution onto a partially cured PDMS matrix and spraying only FPOSS solution onto partially cured PDMS surfaces. Among two FPOSS species, spraying FPOSS onto partially cured PDMS produced a superhydrophobic surface with a static water contact angle of $167^\circ \pm 1^\circ$. Trifluoropropylisobutyl POSS (TFP) resulted in a higher hydrophobicity than trifluoropropyl POSS cages (CM). The multi-scale structured surface morphology, compatibility of functional groups attached to FPOSS and the fluorine content have shown a significant contribution on the superhydrophobicity in FPOSS/PDMS systems. Amorphous nature of the PDMS has improved upon incorporating FPOSS. Hence, this work presents a detailed study on the effect of the preparation method of FPOSS/PDMS composite on its superhydrophobicity.

Keywords PDMS · Fluorinated POSS · Superhydrophobic · Spray-coating · Partially curing

1 Introduction

Polydimethylsiloxane (PDMS)-based materials have been used in a wide range of applications from biomedical to aerospace [1, 2], considering their specific properties such as low toxicity, high flexibility, physiological inertness, optical transparency and hydrophobic nature [3–5]. In the recent past, attempts have been made to engineer the enhanced properties of PDMS using various technological

approaches including nanotechnology-based approaches [6]. One such value addition process is engineering superhydrophobic PDMS by increasing the surface roughness and by introducing fluorine-containing fillers [2, 7–9].

In many applications, nanostructured particles have been used to enhance nano/microscale surface roughness of polymers [8–11]. Polyhedral oligomeric silsesquioxane (POSS), one of the nanostructurally well-defined class of synthetic molecules represented by the chemical formula

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-03721-y>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2020) 2:1944 | <https://doi.org/10.1007/s42452-020-03721-y>

(RSiO_{1.5})_n has been commonly used to fabricate such surfaces since the monodispersion of POSS molecules ranged from 1 to 3 nm creates the multi-scale surface roughness [8, 12]. Further, improved hydrophobicity has been introduced to the POSS molecule by connecting fluorinated hydrocarbon functional groups to silicon atoms of POSS cages [13–15]. Here, both the cage-like structure and the fluorination collectively cause a dramatic reduction in surface energy up to the solid–liquid interfacial tension (γ_{sv}) of 10 mN m^{−1} for fluorinated POSS fabricated surfaces [16]. Though longer fluorocarbon chains with a chain length of C₈ or more tend to further decrease the surface energy, the literature suggests that those molecules consist of higher persist in bioaccumulation leading to potential toxicity [15]. However, short fluorocarbon chains with a chain length of C₄ or fewer have not been reported to exhibit bioaccumulation [17]. Only few studies have been reported the importance of the incorporation of fluorinated POSS with PDMS chemically grafting via hydrosilation [9], physically blending, dip coating and spray-coating of fluorinated POSS on cured PDMS [18–20]. Although the chemical methods have recently served as novel strategies for incorporation, researches are still in favour of the physical ones as they provide simple, inexpensive and easy control over the surface energy [20].

This study suggests a new method to achieve superhydrophobicity of PDMS using short-chained fluorinated POSS via a simple physical fabricating route. Here, we demonstrate a comparative study on the effect of the preparation method of FPOSS/PDMS composite on its superhydrophobicity using different physical incorporation methods. Here, we used four incorporation methods; (1) non-solvent blending (M1), (2) solvent blending (M2), (3) spraying FPOSS/PDMS solution onto partially cured PDMS (M3) and (4) spraying only FPOSS solution onto partially cured PDMS surfaces (M4). We identified that the fourth method was the most effective one to achieve superhydrophobicity of PDMS using short-chained fluorinated POSS. Therefore, curing time of PDMS and concentration of FPOSS were further studied to obtain a most superhydrophobic and robust surface from M4 method.

2 Materials and methods

2.1 Materials

PDMS Sylgard 184 Kit with components of base and curing agent was purchased from Dow Corning, USA. Trifluoropropyl POSS (TFP, FL0583) and Trifluoropropyl POSS Cage Mixture (CM, FL0578) were purchased from Hybrid Plastics, USA. Tetrahydrofuran (THF), chloroform, ethanol

and iodomethane (99%) from Sigma Aldrich, USA were obtained and used without any further purification.

2.2 Incorporation of FPOSS to PDMS matrix

The two FPOSS species of CM and TFP were incorporated into PDMS using four different methods; non-solvent blending, solvent blending, spraying FPOSS/PDMS solution onto partially cured PDMS and spraying only FPOSS solution onto partially cured PDMS surfaces. The incorporation methods are summarized in Fig. 1. Just after the fabrication, all the samples were washed with 10 mL of distilled water, dried at 37 °C and stored in closed Petri dishes for further usage.

2.2.1 Method 1—non-solvent blending (M1)

PDMS base and curing agent were mixed at a 10:1 weight ratio according to the manufacturer's instructions. A percentage of 5–30 wt% of FPOSS was added to the PDMS base/catalyst mixture and stirred at 400 rpm for 5 min until an even dispersion was obtained. Then, the mixture was degassed for 5 min until the entrapped air bubbles disappeared. The blend was cured initially at 80 °C for 1 h and followed by at 100 °C for 2 h.

2.2.2 Method 2—solvent blending (M2)

FPOSS (30 wt%) was added to the 10:1 PDMS base/catalyst (w/w) mixture. Tetrahydrofuran (THF) was added until the concentration reached 10 mg mL^{−1}. The mixture was stirred at 400 rpm for 5 min. Initially, the mixture was heated to 60 °C, which is lower than the boiling point of the solvent (boiling point of THF = 66 °C), to promote migration of FPOSS towards the surface. After the solvent was evaporated, the film was cured at 80 °C for 1 h and followed by curing at 100 °C for 2 h to further strengthen.

2.2.3 Method 3—spray-coating of FPOSS/PDMS solution on partially cured PDMS (M3)

PDMS prepolymer was mixed in a 10:1 (w/w) base/catalyst ratio, stirred at 400 rpm for 5 min, degassed for 5 min and subsequently, cured at 80 °C for 1 h. The solution for the spray was prepared as reported by Golovin et al. [13] with modifications. A concentration of 30 mg mL^{−1} of FPOSS solution in THF was added to PDMS prepolymer (base/catalyst = 10:1) to prepare 25 wt% of FPOSS in PDMS and stirred vigorously at 400 rpm for 5 min. The FPOSS/PDMS solution was sprayed on the half-cured PDMS sheet (40*40*2 mm³) using a spray gun (Model 130, 0.3 mm dual action airbrush kit) while continuously heating the PDMS sheet at 105 °C. The spraying was continued for 100 s over

Fig. 1 Schematic diagram of FPOSS/PDMS incorporation methods. M1: Non-solvent blended; M2: Solvent blended; M3: FPOSS with PDMS spray-coated on half-cured PDMS; M4: FPOSS spray-coated on half-cured PDMS

10 cm from the sample with an approximate N_2 pressure of 0.35 MPa. The spray-coated samples were further cured at 100 °C for 2 h.

2.2.4 Method 4—spray-coating of FPOSS solution on partially cured PDMS (M4)

Partially cured PDMS sheets were prepared and heated to the gel point of PDMS at 80 °C. PDMS prepolymer was mixed in a 10:1 (w/w) base/catalyst ratio, stirred at

400 rpm for 5 min, degassed for 5 min. The mixture was cured at 80 °C. The time to reach the half-cured state was optimized. A concentration of 30 mg mL⁻¹ of FPOSS was prepared in THF and sprayed for 100 s on the half-cured PDMS sheet using a spray gun (over 10 cm from the sample with an approximate N_2 pressure of 0.35 MPa) with continuous heating at 105 °C until the gel point of PDMS. The spray-coated samples were further cured at 80 °C for 1 h and followed by curing at 100 °C for 2 h [21].

2.3 Characterization

The hydrophobicity and the oleophobicity of the surfaces were determined using deionized water and ethanol, respectively.

All contact angles of single liquid droplets (5 μL) on the surfaces were measured using the sessile drop method (ImageJ, version 1.50). Five independent measurements across the sample surface were taken at room temperature (27 $^{\circ}\text{C}$) and atmospheric pressure and then averaged.

Contact angle hysteresis was calculated using the advancing contact angle (θ_a) and receding contact angles (θ_r) of water. Sliding angles were measured by rotating the stage together with the camera and the lamp as a whole unit. The total surface energy of the prepared surface (γ_s) was calculated using the contact angle hysteresis method. Here, γ_l is the surface energy of deionized water.

$$\text{Contact angle hysteresis} = \theta_a - \theta_r \quad (1)$$

$$\gamma_s = \gamma_l (\cos \theta_r - \cos \theta_a) \{ (1 + \cos \theta_a)^2 / ((1 + \cos \theta_r)^2 - (1 + \cos \theta_a)^2) \} \quad (2)$$

Surface morphologies together with the elemental analysis of the coatings were imaged on a scanning electron microscope (Hitachi SU 6600, 15.0 kV) equipped with an energy-dispersive X-ray detector after gold sputtering. All measurements were carried out in the secondary electron mode. Surface topographies of FPOSS/PDMS were measured using a non-contact mode atomic force microscope (AFM, PARK System $\times 100$). Fourier transform infrared (FTIR) spectra were recorded between 4000 and 600 cm^{-1} averaging 32 scans using Nicolet IS 10 in ATR mode.

X-ray diffraction (XRD) analysis was conducted using Rigaku, Ultima IV instrument focus X-ray diffractometer using Cu K α radiation ($\lambda = 1.540 \text{ \AA}$) over a 2θ angle of 2° to 40° with a step size of 0.02° . Diffractograms were analysed using Peakfit (v4.12) software. The peak area fractions from deconvoluted peaks were determined to obtain the crystalline to the amorphous percentage of FPOSS/PDMS materials.

3 Results and discussion

3.1 Methods of incorporating FOSS with PDMS

Contact angles of water (CA_{water}) and ethanol ($\text{CA}_{\text{ethanol}}$) were measured to understand the wetting behaviour of the prepared composites materials (Table 1). As for the first method (M1), the properties of the FPOSS/PDMS blends were similar to those of unmodified PDMS. Because the absence of a solvent at low temperatures of about 80 $^{\circ}\text{C}$ tends to result in poor dispersion of FPOSS in PDMS matrix, most of the POSS cages form large crystallite aggregates [22]. Cured PDMS network may trap the POSS cages within the bulk of the matrix and hinders the POSS contribution to the surface. Thus, non-solvent blending has produced a flat surface without any defects or scratches as shown in Fig. 2 (i) which have further been confirmed by the roughness studies. The surface roughness varied only from $\pm 5 \text{ nm}$ according to AFM results shown in Fig. 2 (ii). Also, the cross sections of non-solvent blended FPOSS/PDMS show that aggregated FPOSS has dispersed in the middle of the PDMS layer but not on the surface (Fig. 3). These results may have been prominent factors in the inability to change in the hydrophobicity of PDMS. This evidence is similar to the study done by Liu et al. [22] who showed

Table 1 Contact angle data and the resulted hydrophobic/oleophobic nature of composited preparation by different methods

Method	Chemical species	Advancing/receding angle (water)	Contact angle hysteresis	Static contact angle (water)	Sliding angle (water)	Static contact angle (ethanol)	Total surface free surface energy (mJ/m^2)	Hydrophobicity	Oleophobicity
M1	TFP	106 $^{\circ}$ /90 $^{\circ}$	16 $^{\circ}$	104 $^{\circ} \pm 0^{\circ}$	90 $^{\circ} \pm 1^{\circ}$	35 $^{\circ} \pm 0^{\circ}$	21.9	H/O	O/I
	CM	108 $^{\circ}$ /88 $^{\circ}$	20 $^{\circ}$	104 $^{\circ} \pm 0^{\circ}$	90 $^{\circ} \pm 0^{\circ}$	35 $^{\circ} \pm 0^{\circ}$	19.9	H/O	O/I
M2	TFP	135 $^{\circ}$ /32 $^{\circ}$	101 $^{\circ}$	129 $^{\circ} \pm 2^{\circ}$	> 90 $^{\circ}$	40 $^{\circ} \pm 1^{\circ}$	5.0	H/O	O/I
	CM	106 $^{\circ}$ /32 $^{\circ}$	74 $^{\circ}$	103 $^{\circ} \pm 1^{\circ}$	> 90 $^{\circ}$	42 $^{\circ} \pm 1^{\circ}$	20.9	H/O	O/I
M3	TFP	143 $^{\circ}$ /100 $^{\circ}$	43 $^{\circ}$	143 $^{\circ} \pm 2^{\circ}$	25 $^{\circ} \pm 2^{\circ}$	33 $^{\circ} \pm 2^{\circ}$	2.4	H/O	O/I
	CM	112 $^{\circ}$ /30 $^{\circ}$	82 $^{\circ}$	105 $^{\circ} \pm 1^{\circ}$	> 90 $^{\circ}$	37 $^{\circ} \pm 1^{\circ}$	17.3	H/O	O/I
M4	TFP	167 $^{\circ}$ /144 $^{\circ}$	12 $^{\circ}$	167 $^{\circ} \pm 1^{\circ}$	2 $^{\circ} \pm 0^{\circ}$	17 $^{\circ} \pm 2^{\circ}$	1.9	SH/O	O/I
	CM	125 $^{\circ}$ /53 $^{\circ}$	72 $^{\circ}$	112 $^{\circ} \pm 1^{\circ}$	> 90 $^{\circ}$	34 $^{\circ} \pm 2^{\circ}$	9.2	H/O	O/I
–	Flat PDMS	108 $^{\circ}$ /86 $^{\circ}$	22 $^{\circ}$	104 $^{\circ} \pm 0^{\circ}$	90 $^{\circ} \pm 0^{\circ}$	35 $^{\circ} \pm 1^{\circ}$	19.5	H/O	O/I

H/O, hydrophobic; SH/O, superhydrophobic; H/I, hydrophilic; SH/I, superhydrophilic; O/O, oleophobic; SO/O, superoleophobic; O/I, oleophilic; SO/I, superoleophilic

that such phenomenon is affected by the agglomeration of FPOSS in PDMS. However, the agglomeration varied with the nature of the FPOSS species since similar surface properties including surface energy and solubility parameter of both filler and the polymer lead to a better dispersion. Also, a considerable variation results in a higher driving force for agglomeration of nanoparticles [23]. More descriptively, TFP has a better distribution in PDMS matrix than CM since TFP/PDMS consists of dipole–dipole interactions due to the presence of iso-butyl groups in TFP, which are compatible with methyl groups in PDMS. The structures of TFP and CM are shown in Fig. 4.

In the second method, M2, a solvent blending technique was used to increase the migration of FPOSS within the composite surface during the PDMS curing process. Solvent blending resulted in a higher hydrophobic TFP/PDMS surface than M1 method with CA_{water} of 129 °C, while there was no difference of CA_{water} of the CM/PDMS blends prepared by M1 and M2 methods. Here, the observed higher hydrophobic surface than pure PDMS was due to the presence of multi-scale 3D blocks of FPOSS as shown in Fig. 2 (i). However, M2 method is neither suitable to obtain the surface superhydrophobicity nor self-cleaning as these properties form when static CA_{water} on a surface is above 150° with a low sliding angle. The failure to achieve the expected level of superhydrophobicity ($CA_{\text{water}} > 150^\circ$) may be due to the absence of nanoscale roughness associated with nano-fillers on the surface. The other defect associated with this solvent blended method is that the surfaces consist of macroscale surface defects since the evenness in macroscale of hydrophobicity could not be maintained.

To retain FPOSS on the uppermost area of PDMS surface, we focused on the spray-coating technique as the third incorporation method (M3) by adopting a procedure described by Golovin et al. [13] with a simple modification. A solution of PDMS and FPOSS mixture was sprayed on partially cured PDMS surfaces instead of spraying on fully cured PDMS to improve the adherence of FPOSS on the PDMS surface. According to previous studies, M3 method has led to the formation of superhydrophobic surface for POSS species with long fluorinated chains (e.g. 1H,1H,2H,2H-heptadecafluorodecyl) those have surface energy around 10 mN m⁻¹. However, the incorporation of TFP and CM has shown lower CA_{water} of 143° and 105°, respectively, compared to the contact angle of long-chain fluorinated POSS obtained by M3 method. It could be due to two reasons. Firstly, it is possible to be less hydrophobic than long-chained fluorinated POSS because both TFP and CM consist of specific surface energies less than long-chain fluorinated POSS [13, 24]. But, M3 technique could improve the hydrophobicity of TFP/PDMS surface up to CA_{water} of 143° although the hydrophobicity of

CM/PDMS remained unchanged. Secondly, the average nanoscale surface roughness (< 100 nm) contributes to minor effects on contact angle and hysteresis [14]. AFM studies revealed that the surface roughness of TFP/PDMS obtained by M3 method fluctuates within ± 200 nm [Fig. 2 (ii)]. FPOSS agglomerates with a narrow size distribution which are deeply embedded in PDMS were clearly shown in SEM images [Fig. 2 (i)].

In M4 method, a solution of FPOSS was sprayed on partially cured PDMS to disperse almost all FPOSS on the surface of PDMS. Among the four incorporation methods, M4 method caused for the highest hydrophobicity with a CA_{water} of 167° for TFP/PDMS surface while exhibiting a less sliding angle of 2° that resulted in a self-cleaning surface. In terms of CM/PDMS, CA_{water} increased up to 112° but did not achieve superhydrophobicity. However, notable low surface energy could be assigned for both TFP-M4 and CM-M4 methods. This behaviour is described by together with Cassie–Baxter state for TFP/PDMS and Wenzel state for CM/PDMS which describes the non-wetting and the wetting behaviour of surfaces, respectively, even with the presence of higher contact angles [25]. Moreover, a surface with a considerable multi-scale roughness was obtained only from TFP-M4 method, which was caused by nano/microscale FPOSS agglomerates [Fig. 2 (ii)] resulted in ± 500 nm surface roughness variation. TFP incorporation produced square shape aggregates via M4 method, while CM incorporation showed plate-like aggregates with lower surface inhomogeneity [Fig. 2 (i)]. The higher hydrophobicity over other methods may be due to the predominant contribution of microscale surface roughness other than the amount of fluorination itself. These findings thus suggested that the microscale surface roughness contributes predominantly to obtaining superhydrophobicity other than the amount of fluorination itself. The so-called phenomenon is further confirmed from the comparative EDX data in Table 2 since TFP spray-coated PDMS surfaces consist of less weight percentage of fluorine than that of CM spray-coated PDMS surfaces allowing more FPOSS molecules exposing to the air–solid interface.

Figure 2 (iii) presents a summary of the results obtained for the static water contact angle and static ethanol contact angle measurements on the composite surfaces. It is apparent from this table that liquids with lower surface energy, such as ethanol, exhibit the opposite trend with respect to the contact angles for water ($\gamma_{\text{sv,water}} = 72.7$ mN m⁻¹ at 30 °C). When considering the definition of oleophilic surfaces (water contact angle less than 90°) [26], all the produced surfaces are oleophilic and TFP-M4 method exhibited the highest oleophobicity.

FTIR spectra were analysed to further confirm the presence of individual functional groups of both PDMS and fluorinated POSS cages. Neither new peak appearance

Fig. 2 Surface characterization of FPOSS/PDMS; (i) SEM images of the surface of TFP/PDMS (left) and CM/PDMS (right) composites prepared from different incorporation methods; **a, b** M1; **c, d** M2; **e, f** M3; **g, h** M4; (ii) AFM images of TFP/PDMS produced by different methods; (iii) Dependency of static contact angles for water and ethanol with respect to the method of FPOSS incorporation; (iv) FTIR spectra of **a** TFP incorporated PDMS; **b** CM incorporated PDMS. M1: Non-solvent blended; M2: Solvent blended; M3: FPOSS with PDMS spray-coated on half-cured PDMS; M4: FPOSS spray-coated on half-cured PDMS

nor the disappearance of existing peaks was observed in TFP/PDMS FTIR spectra [Fig. 2 (iv)]. However, FTIR spectra related to TFP-M1 and TFP-M2 methods show higher peak shifts related to C–H and C–F bonds (Supplementary material S1). These shifts are caused by the intermolecular interactions during the formation of large agglomerates of TFP between trifluoropropyl group and iso-butyl groups, and/or formation of dipole–dipole interactions between methyl group in PDMS and iso-butyl group in TFP molecule. Either TFP-M3 or TFP-M4 methods had not contributed to a higher peak shifting possibly contributing to Van der Waals forces which facilitates the surface migration of TFP. In CM/PDMS spectra, the peaks related to C–F and Si–O–Si bonds had shifted. This might be caused by the interactions between POSS cage and fluorinated functional groups of nearby CM molecules possibly resulting in CM agglomeration. This indicates that the ability to forming interactions between the PDMS and CM was poor and as a result of that, the dispersion of CM in PDMS matrix could not be observed.

3.2 Condition optimization for FPOSS spray-coated PDMS

So far, this paper has focused on selecting the physical incorporation method to gain improved superhydrophobicity of PDMS using FPOSS. These experiments confirmed that the highest superhydrophobicity has been achieved via TFP-M4 method. Therefore, the following section will discuss the conditions to produce the most superhydrophobic TFP-M4.

The heating time of PDMS to reach the optimum static CA_{water} was 7 min for 10 mg mL^{-1} of TFP concentration at 80°C followed by 24 h room temperature curing [Fig. 5 (i)]. During the first 4 min period, the static CA_{water} was constant because the gel point of the composite had not reached until 4 min. Consequently, when TFP sprayed, the slow post-curing process at room temperature resulted in maintaining less viscosity of the PDMS matrix for a long time. This phenomenon facilitated the penetration of TFP to the bulk of the PDMS matrix to some extent. As the partially curing process of PDMS initiated at 4 min, the viscosity of PDMS began to increase and limited the time for

penetration of TFP in PDMS. Thus, most of TFP entrapped on the uppermost surfaces as embedded particles. After 7 min of heating, PDMS was eventually fully cured. The extra TFP amount has been washed away during the washing step. The SEM images in Fig. 5 (ii) depict the embedding nature of TFP in PDMS confirming embedding decrement with increasing curing time. After 4 mg mL^{-1} of TFP loading on the PDMS surface, TFP begins to agglomerate via self-assembling. Therefore, a multi-scale roughness is generated on PDMS surface causing an increment of hydrophobicity as shown in Fig. 5 (i). However, static water contact angle became plateau after 25 mg mL^{-1} , since no more TFP loading was allowed after the completion of surface coverage.

The results in this section indicate that the most superhydrophobic TFP-M4 surface can be achieved through the curing time of 7 min together with the FPOSS concentration of 25 mg mL^{-1} . The next section, therefore, moves on to discuss the EDX spectroscopic data of the TFP-M4 surface with enhanced superhydrophobicity.

3.3 Effect of FPOSS incorporation on the crystallinity of PDMS

The addition of POSS nanoparticles into polymers results in changes in the polymer's physical, chemical and mechanical properties including crystallinity [27, 28]. Neat FPOSS comprises high crystalline nature with distinct diffraction peaks. Their corresponding lattice spacing is depicted in Fig. 6. The incorporation of FPOSS in PDMS has subjected to a decrease in the characteristic peak area of those peaks while retaining the diffraction pattern constant. This observation indicates any of the incorporation methods had not resulted in any distortion of FPOSS crystalline structure implying that the FPOSS and PDMS form a two-phase crystalline structure. The incorporation has affected not only on the crystallinity of FPOSS but also on the PDMS crystallinity. Table 3 presents the ratios of crystallinity to amorphous derived from each XRD spectra. Overall, the incorporation of FPOSS has resulted in an increment of the amorphous nature of PDMS (two characteristics peaks of neat PDMS: the crystalline peak at a degree of 11.82° and the amorphous peak at a degree of 20.45°).

The method of incorporation is one of the ways that changes the crystallinity of PDMS. Introducing fillers and liquids affects the potential to the crystalline arrangement of PDMS. This phenomenon becomes severe if the solvent and filler are introduced during the PDMS curing process with pressure arisen by the spraying process. In the M1 method, we have introduced only FPOSS fillers. The low dispersal of FPOSS cages resulted from FPOSS agglomeration in M1 process retards the molecular motion of the PDMS chains and hence, decreases crystal growth of

Fig. 3 SEM images of cross sections of non-solvent blended FPOSS/PDMS produced by M1 method; **a** TFP with 1% concentration, **b** TFP with 5% concentration, **c** TFP with 30% concentration, **d** CM

with 1% concentration, **e** CM with 5% concentration and **f** CM with 30% concentration

PDMS [27]. In the solvent blending method, M2, both filler and liquid were introduced which was expected to have less crystallinity than non-solvent blending, M1 process. But, due to the better dispersion and the adequate time to slowly evaporate the liquid facilitates enough time to arrange more PDMS chains into crystalline domains. In both M3 and M4 methods, not only the effects of filler and the liquid but also the spraying process makes more disturbance to the PDMS chain arrangement during the curing process limiting the crystalline arrangement of PDMS.

The chemistry of filler is another factor that influences the PDMS crystallinity [29]. Although the two types of incorporated fillers contain fluorinated groups, iso-butyl groups in TFP facilitate a better distribution in the PDMS matrix than CM that is compatible with methyl groups in PDMS. Thus, when comparing the two FPOSS species incorporated with PDMS, the crystallinity of CM has reduced even in the non-solvent system (16%) confirming its higher affinity to agglomerate than TFP (25%).

Although the same incorporation method is used, the PDMS crystallinity can be changed with incorporation

Fig. 4 Fluorinated POSS species used in this study (TFP has one short fluorinated chain while CM has eight short fluorinated chains)

Table 2 EDX data for FPOSS spray-coated PDMS surfaces produced by M4 method

Element	TFP-M4		CM-M4	
	(wt%)	Error (%σ)	(wt%)	Error (%σ)
C	46.5	0.5	31.0	0.4
O	28.0	0.4	23.5	0.2
Si	19.2	0.2	16.5	0.1
F	6.4	0.2	29.1	0.2

conditions such as the percentage of cured PDMS before the disturbance and the degree of disturbances [30]. When the heating time of PDMS before spraying the FPOSS and THF is changing, the percentage of cured PDMS also changes. In 5 min of heating, PDMS has not reached to the partially curing state. Therefore, it behaves like the M2 method that PDMS crystallinity is more like pure PDMS. In 10 min of heating, PDMS has passed its optimal partially curing state but not yet fully cured where FPOSS can do a less effect to the PDMS chain arrangement than in 7 min. The amount of disturbance of M4 method is considered as the percentage of FPOSS when the amount of THF and spraying conditions is similar. With an increase in FPOSS fraction, FPOSS molecules tend to agglomerate and as a result, the crystallinity of PDMS has reduced.

However, the affinity to agglomerate is higher in CM than in TFP. It facilitates CM agglomeration at a concentration of CM below TFP. Therefore, at FPOSS concentration of 15, PDMS crystallinity is less in CM than in TFP due to the early agglomeration.

It is possible to reduce the mechanical strength and transparency due to the decrease in the crystallinity caused by the agglomeration of FPOSS. But, the same property together with the topological structure of the surface has resulted in the superhydrophobicity of the FPOSS/PDMS. Some studies attempt to overcome this problem by developing low superomniphobic surfaces and highly transparent surfaces [13]. However, tailoring the material crystallinity and morphology according to biomedical applications is in further studies for TFP/PDMS combination.

4 Conclusion

Short-chained FPOSS incorporated PDMS has been less reported in achieving superhydrophobicity. This study suggests that the method of incorporation and the nature of the FPOSS molecule drive hydrophobicity of PDMS until superhydrophobicity. To study the most

Fig. 5 Improving hydrophobicity of TFP/PDMS; (i) Dependency of the static water contact angle of samples prepared by TFP-M4 method with respect to; **a** curing time of PDMS; **b** concentration of TFP; (ii) SEM images of TFP/PDMS surfaces produced by TFP-M4

method a with a different curing time of PDMS; **a** 5 min; **b** 7 min; **c** 9 min; (iii) EDX data for TFP/PDMS surface produced by TFP-M4 method with the optimized curing time of 7 min and the optimized concentration of 25 mg mL⁻¹

suitable incorporation method, we tested four different ways; non-solvent blending, solvent blending, spraying FPOSS/PDMS solution onto partially cured PDMS surface and spraying only FPOSS solution onto partially cured PDMS surfaces. Among them, a simple physical fabricating method that is spray-coating of FPOSS on partially cured PDMS resulted in a superhydrophobic surface with

the oleophilic properties. The outcomes are summarized as follows.

- TFP is a short-chained FPOSS which is a suitable candidate for obtaining superhydrophobic/oleophilic PDMS surfaces. The hydrophobicity can be improved up to a static water contact angle of $167^\circ \pm 1^\circ$

Fig. 6 Comparison of XRD patterns of neat and PDMS blends of; **a** TFP/PDMS; **b** CM/PDMS

Table 3 Crystalline percentage of FPOSS/PDMS composites

Method	Description	Crystalline percentage (%)	
		TFP	CM
M1	Non-solvent blending	25	16
M2	Solvent blending (30 wt%)	37	38
M3	Spray-coating of FPOSS/PDMS solution on partially cured PDMS	19	39
M4	Spray-coating of FPOSS solution on partially cured PDMS		
4.1	Effect of the time allowed to cure PDMS before spraying FPOSS		
	5 min	31	
	7 min	20	
	10 min	26	
4.2	Effect of concentration		
	5 mg mL ⁻¹	33	36
	15 mg mL ⁻¹	29	13
	30 mg mL ⁻¹	19	19
5	Pure PDMS	36	

under conditions of PDMS curing time of 7 min for 25 mg mL⁻¹ of TFP concentration at 80 °C.

- The surface roughness together with the fluorine content on the surface influenced the superhydrophobic characteristics.
- However, CM has not made significant changes on either hydrophobicity or oleophobicity with any of the four incorporation methods.

- The surface functional groups of FPOSS have influenced the hydrophobicity difference between TFP and CM.
- The incorporation of FPOSS has influenced the decrease in crystallinity of PDMS.

These findings have provided better insight into the importance of the preparation method on FPOSS/PDMS composite and its superhydrophobic properties.

Acknowledgements Authors acknowledge Thusitha Etampawala and Asitha Cooray for kind discussion and access for Instrument Centre in this institution.

Authors' contributions DRR, NK, MMW and BG developed the concept. BG and DRR designed the study. BG prepared the samples. BG and DS characterized the samples. BG and DRR analysed the data. BG and DS draughted the article. DRR, NK and MMW revised the article critically. All the authors gave the final approval for the publication.

Funding This work was completely granted by the Centre for Advanced Materials Research of University of Sri Jayewardenepura, Sri Lanka under Grant AMRC/RE/2016/Mphil-05

Compliance with ethical standards

Conflict of interest We have no competing interests.

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