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The effects of incorporating fluorinated polyhedral oligomeric silsesquioxane, $[F_3C(CH_2)_2SiO_{1.5}]_n$ on the properties of the silicones

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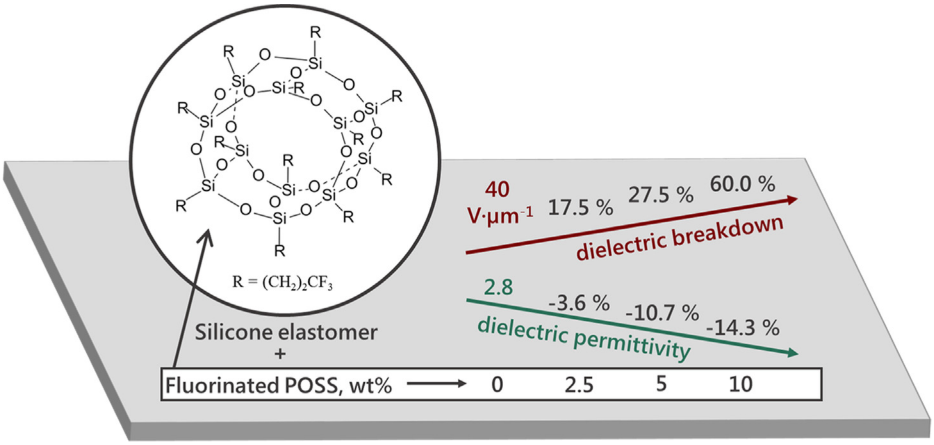
HIGHLIGHTS

- Fluorinated POSS was prepared and dispersed as filler within silicone matrix.
- Low polarizability of the fluorocarbon groups leads to decreasing of dielectric permittivity.
- POSS cage acts as electron scavengers leading to increased dielectric strength.
- POSS acts as reinforcing filler for silicone.
- The presence of fluorinated POSS does not affect significantly hydrophobicity of the silicone.

GRAPHICAL ABSTRACT



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ABSTRACT

A hydrophobic filler with the siloxane skeleton, fluorinated polyhedral oligomeric silsesquioxane (F-POSS), was incorporated in varying percentages (2.5, 5, and 10 wt%) in a polydimethylsiloxane-α,ω-diol (PDMS) of molecular weight 230,000 g/mol, in solution. Some structural characteristics and properties derived from F-POSS (low polarizability, weak intermolecular force, low surface energy), similar to those of polydimethylsiloxane, create prerequisites for good compatibility of these two components and enrichment of some of their features: better mechanical parameters, increased hydrophobicity and lower dielectric constant useful for practical applications such as insulators. The composites processed as films and stabilized by condensative crosslinking of OH ends of PDMS with a tetrafunctional silane were studied in terms of morphology, mechanical properties, hydrophobicity of the surface, and water vapor sorption capacity, optical properties, dielectric behavior, conductivity, and dielectric strength. Results showed that, although the mixing of the two components was made in solution, it did not occur at the molecular level. However, the expected results are achieved except the hydrophobicity which is not affected noticeable.

1. Introduction

Silicone elastomers, which mostly consists in crosslinked polydiorganosiloxane (mainly polydimethylsiloxane), are a known

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class of materials that are distinguished by a combination of properties that make them useful in almost all areas, from biomedical to aerospatial. However, due to very weak intermolecular interactions, silicone elastomers have relatively weak mechanical properties, which limit their applicability in some areas. One easily approachable way to remove this shortcoming is the incorporation of reinforcing fillers, often inorganic compounds, which, depending on their nature, can also influence other properties of silicones such as the thermal, electrical, optical, surface, etc. The effectiveness of the chosen filler depends, in addition to its nature, on the dispersion degree, size and shape of the particles and the strength of the interaction with the polymer matrix [1,2].

The reinforcing filler often used for silicones is fumed silica (particle size of 5–50 nm and surface area of 50–600 m^2/g). Because the silicone matrix is hydrophobic, while the silica particles possess Si–OH groups on their surface, a hydrophobization treatment is required in order to ensure the matrix-filler compatibility and to maximize the performance of resulting nanocomposites [3]. One form of nanoscopic silica is polyhedral oligomeric silsesquioxane (POSS), an organic–inorganic hybrid nanomaterial with formula $(RSiO_{3/2})_n$, where n is the number of the silicon atoms of the cage, $n = 8$, 10 or 12, while R is H or a variety of organic groups) [4]. When POSS structure contains eight silicon and ten oxygen atoms, such well-defined, highly symmetric molecule has a diameter around 1.5 nm including vertex R group being effectively the smallest possible silica nanoparticles [1,4–6]. The presence of organic groups to silicon atoms ensures interface of POSS's inorganic core with the polymer matrix thus creating the prerequisites for their good compatibility without the necessary surface treatment of filler [7]. In general, POSSs are soluble and thus in optimal conditions, they could be dispersed in the polymer matrix at the molecular level [1]. The presence of nanometric cage in POSS leads to composites with very low dielectric constant, the lower as the POSS content of the material is higher [7,8]. It is assumed that the POSS nanoparticles act as electron scavengers in the polymer matrix, the electrons being impeded by the POSS molecule surfaces. This effect is further enhanced by a better dispersion of POSS within the matrix increasing the active surface of particles [9]. Furthermore, the high insulation properties of POSS provide a better insulating barrier for quantum tunneling, prevents leakage current, and show lower dielectric loss in POSS-based percolative nanocomposites [7].

In general, there are addressed two ways to incorporate POSS in polymer matrices: physical incorporation by melt mixing or solvent casting methods (e.g., in polypropylene, polystyrene, polyamide, polyoxymethylene, high-density polyethylene, poly[(ε-caprolactone)-*block*-(4-vinyl pyridine)], polyimides, polyepoxide, etc.) [9–11] and chemical binding when POSS moieties are bonded covalently within copolymer structures (styrene, methacrylate, norbornyl, vinyl, epoxy, phenolic, benzoxazine, amine, polyurethane, poly(ethylene-oxide), etc.) [10,12,13]. The resulting systems could show some improvements in polymer properties such as glass transition temperature, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen permeability [14]. The literature survey reveals that the preparation of organic–inorganic hybrid structures by chemical incorporating of mono- di- or multifunctional POSS in organic polymer (in the main chain, pendant or as a crosslinker) is preferable to the first approach [7] because in such an up approach, individual POSS molecules are covalently attached to the host polymer, while in nanocomposite, the self-assembly aggregation or crystallization could occur with negative impact on the macroscopic physical properties of the resulted materials [5,15].

There are only few reports about incorporation of POSS within siloxane matrix [15,16] aiming to prepare coatings with resistance to atomic oxygen erosion [16] or to study the compatibility of the two components [15] but none relating to fluorinated POSSs. Therefore, in the present work we plan to incorporate a POSS full-substituted with (3,3,3-trifluoropropyl) groups to the silicon atom (F-POSS) in a matrix consisting of a PDMS of molecular weight 230,000 $g\,mol^{-1}$ crosslinked by chain ends condensation with a tetrafunctional agent. The resulted materials were investigated from the point of view of morphology, mechanical surface, optical and dielectric properties and hydrophobicity. In literature there are also fewer reports about incorporation of the F-POSS within polymer matrices and these are mainly based on poly(vinylidene fluoride), emphasizing the effects related to improving the mechanical properties [17].

2. Experimental

2.1. Materials

Polydimethylsiloxane-α,ω-diol (PDMS) with average number molecular weight $M_n = 230{,}000\,g\,mol^{-1}$ was synthetized through acid catalyzed ring-opening polymerization of octamethylcyclotetrasiloxane, according to reference [18]. Tetraethylorthosilicate, $Si(OC_2H_5)_4$, with purity >99.0%, trimethoxy(3,3,3-trifluoropropyl)silane, $F_3C(CH_2)_2Si(OCH_3)_3$, of purity ≥97.0% (GC), and dibutyltin dilaurate (DBTDL) were purchased from Sigma–Aldrich, while potassium hydroxide, ACS reagent, ≥85%, pellets, was acquired from Fluka.

2.2. Measurements

Fourier transform infrared spectrometer (FTIR), type Bruker Vertex 70 FT-IR instrument, equipped with a Golden Gate single reflection ATR accessory was used to measure spectrum in range 600–4000 cm^{-1}, at ambient temperature. The NMR spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer, operating at 400.1, 100.16 and 79.4 MHz for ^1H, ^{13}C and ^{29}Si, respectively, using a four nuclei direct detection probe (^1H, ^{13}C, ^{19}F and ^{29}Si). The solvent used for the NMR analysis was THF-d_8. The chemical shifts are referenced to internal TMS (tetramethylsilane) for both ^1H and ^{29}Si. Morphology of sample was conducted on Hitachi High-Tech HT7700 transmission electron microscopy (TEM), operated at a 100 kV accelerating voltage in high-contrast mode. In order to prepare for measurement, the dispersion of sample in toluene was placed on carbon-coated copper grids with 200-mesh size and then the solvent was removed under vacuum. Scanning electron microscope (ESEM) Quanta 200 operating at 20 kV with secondary and backscattering electrons in low vacuum mode was used to study morphology of composite. An energy-dispersive X-ray spectroscopy (EDX) available on ESEM Quanta 200 was used in order to determine elemental composition. The mechanical tensile tests were performed on dumbbell-shaped cut samples with a TIRA test 2161 apparatus (Maschinenbau GmbH Ravenstein, Germany) with an extension rate of 20 mm/min, at room temperature. Three measurements were made for each sample taking into account the average of the values obtained. An SPM Solver Pro-M platform (NT-MDT, Russia) instrument was used for atomic force microscopy (AFM) measurements, using a rectangular NSG10/Au cantilever and a nominal elasticity constant of $KN = 11.5\,nm^{-1}$. Water contact angle measurements were performed at room temperature by the sessile-drop technique with a KSV CAM 101 goniometer equipped with a CCD camera connected to a computer. The average value of three measurements was considered. Moisture sorption–desorption isotherms of the film samples within 0–90% relative humidity (RH) were recorded at room temperature on the fully automated gravimetric analyzer IGAsorp supplied by Hiden Analytical, Warrington (UK). UV–vis transmittance measurements on the composite films were performed on a SPECORD 210 PLUS

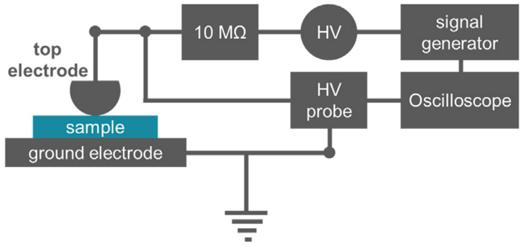


Fig. 1. Scheme for electrical breakdown setup used [20,21].

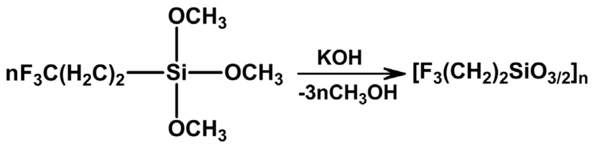
spectrophotometer (Analytik Jena) at room temperature. Novocontrol "Concept 40" broadband dielectric spectrometer (Hundsangen, Germany) was used to record the dielectric spectra of samples (mounted between gold platens). The measurements (conductivity, dielectric constant and losses) were performed at room temperature (25 °C) for the frequency ranging between 1 and 100,000 Hz. The breakdown voltage was determined on a home-built setup (Fig. 1) [20,21], applying a ramp signal of 500 V s^{-1}. The samples were placed between two unequal electrodes, 150 mm planar ground electrode and a 5 mm high voltage electrode.

2.3. Synthesis of fluorinated polyhedral silsesquioxane, F-POSS

Polyhedral oligomeric 3,3,3-trifluoropropylsilsesquioxane, $[F_3C(CH_2)_2SiO_{1.5}]_n$, F-POSS, was prepared according to procedure described in [19]. To the solution of trimethoxy(3,3,3-trifluoropropyl)silane (1.91 ml) dissolved in 10 ml ethanol, a solution of KOH (2 mg) in deionized water (0.27 ml) was added. The mixture was stirred at room temperature for 24 h. The resulting white precipitate was decanted and washed several time with ethanol. Yield: 60%, m.p. 230–232 °C (from THF); Anal. wt% Calcd for $C_3H_4F_3O_{1.5}Si$: C, 24.16; H, 2.70. Found: C, 23.40; H, 2.33. IR spectrum (KBr pellet), selected bands, ν_{max}: 425m, 462m, 554w, 706w, 802m, 837m, 902m, 1028s, 1069vs, 1127vs, 1224vs, 1273s, 1318m, 1376m, 1422w, 1449m, 1632vw, 2920vw, 2957vw, 2980vw, 3436vw. ^{1}H NMR (THF-d$_8$, 400.1 MHz): δ 2.17–2.30 (m, **CH**$_2$–CF$_3$), 0.95–1.00 (m, **CH**$_2$-Si); ^{13}C NMR (THF-d$_8$, 79.4 MHz): 128.50 ppm (q, *J* = 276 Hz) and 128.54 ppm (q, *J* = 275.96 Hz) for –Si–CH$_2$–CH$_2$–**CF**$_3$**;** 28.36 ppm (q, *J* = 30.60 Hz) and 28.17 ppm (q, *J* = 30.47 Hz) for **–**Si–CH$_2$–**CH**$_2$; 5.06 ppm (q, *J* = 2.14 Hz) and 5.48 ppm (q, *J* = 1.74 Hz) –Si–**C**H$_2$–; ^{29}Si NMR (THF-d$_8$), 79.4 MHz): δ 69.24 and 72.05 ppm.

2.4. Preparation of nanocomposites

To 0.75 g of PDMS dissolved in 10 ml of toluene were added 2.5, 5, and 10 wt% F-POSS to prepare composites NC2.5, NC5, and NC10, respectively, the sample without addition of filler being as a reference NC0. After 60 min of stirring, 0.07 ml of tetraethylorthosilicate as crosslinking agent were added to the reaction mixture and stirred for another 30 min, after that 10 μl of DBTDL as a catalyst were added, stirred for 5 min and quickly poured as film on a Teflon substrate and left in ambient conditions to stabilize by crosslinking. This occurs by the condensation of PDMS chain OH-ends with tetraethylorthosilicate. To ensure completion of reaction and aging, the films were kept in the laboratory environment about two weeks before characterization by different techniques. The morphology and mechanical behavior of the aged films were studied to emphasize the dispersion of the filler within polymeric matrix and its reinforcing effect. The films were also investigated in terms of visible transparency, hydrophobicity and electrical insulation capacity that is expected to be improved from those of simple silicones.



Scheme 1. Reaction leading to $[F_3C(CH_2)_2SiO_{1.5}]_n$, F-POSS (*n* presumed to be 12).

3. Results and discussions

3.1. Synthesis and characterization of fluorinated polyhedral silsesquioxane, F-POSS

F-POSS was prepared by hydrolysis-condensation of 3,3,3-trifluoropropyltrimethoxysilane catalyzed by KOH in ethanol (Scheme 1), by adapting procedure described in reference [19] for the synthesis of nonafluorohexil, tridecyfluorooctyl and heptadecafluorodecyl octahedral silsesquioxanes. The structure and purity of the product were checked by elemental analysis and spectral (IR, ^{1}H, ^{13}C and ^{29}Si NMR), the results of which correspond to the $[F_3(CH_2)_2SiO_{3/2}]_n$ formula.

According to literature [22], in the chosen conditions, T10 isomer is formed as major component, with minor amounts of T8 and T12 isomers. Unfortunately, X-ray diffraction experiments on single crystals separated from tetrahydrofuran or toluene-tetrahydrofuran mixture to identify the size of the polyhedron failed. The contoured structural model based on records seems to be the species with 12 silicon atoms. This is supported by ^{29}Si NMR data. Thus, in this spectrum (Fig. 2) there are present the two singlets at −69.24 and −72.05 ppm, corresponding to the two different types of silicon atoms (eight of a kind and four of another kind) due to the distorsion of the dodecasilsesquioxane cage [23,24].

Since their first getting, fluorinated POSSs were distinguished by unique properties derived from the fluorine particularity. The fluorinated alkyl groups are known to be basically inert. Because the electrons of fluorine are kept very tight and close to the nucleus this has low polarizability leading to very weak intermolecular forces [25], that are reflected in their behavior. Thus, they tend to volatilize at 300 K prior to decomposition [19], and have low surface energy. Due to steric and electronic repulsion, fluoroalkyl chains are rigid, thus creating a large shell that prevents van der Waals attraction between POSS cores [26]. TEM images (Fig. 3a and b) of the F-POSS deposited from toluene solution on grid, in similar conditions to those in which the composites were also prepared, reveal submicrometer aggregates.

This product was used as filler for the high molecular weight PDMS (230,000 g mol^{-1}) in that was incorporated in various proportions, 2.5, 5 and 10 wt%. Given its solubility in toluene and the hydrophobic nature of F-POSS, it was incorporated as solution in polydimethylsiloxane hydrophobic matrix thus without requiring any preliminary treatment.

3.2. Study of F-POSS incorporation as filler in silicone matrix

3.2.1. Morphology

TEM images taken on the F-POSS/PDMS film (Fig. 3c) poured as toluene solution on grid followed by crosslinking reveal presence of submicrometer aggregates similar with those formed by single F-POSS solution in toluene. Morphology of the composite films was investigated by SEM in cross-section obtained by fracture in liquid nitrogen (Fig. 4). Thus, although the incorporation of the filler was done in solution when the mixing at the molecular level would have been expected, in reality this does not happen but there is a clustering of the filler (aggregates around 0.5 μm in diameter), as well as a structuration of the material, which makes the surface formed

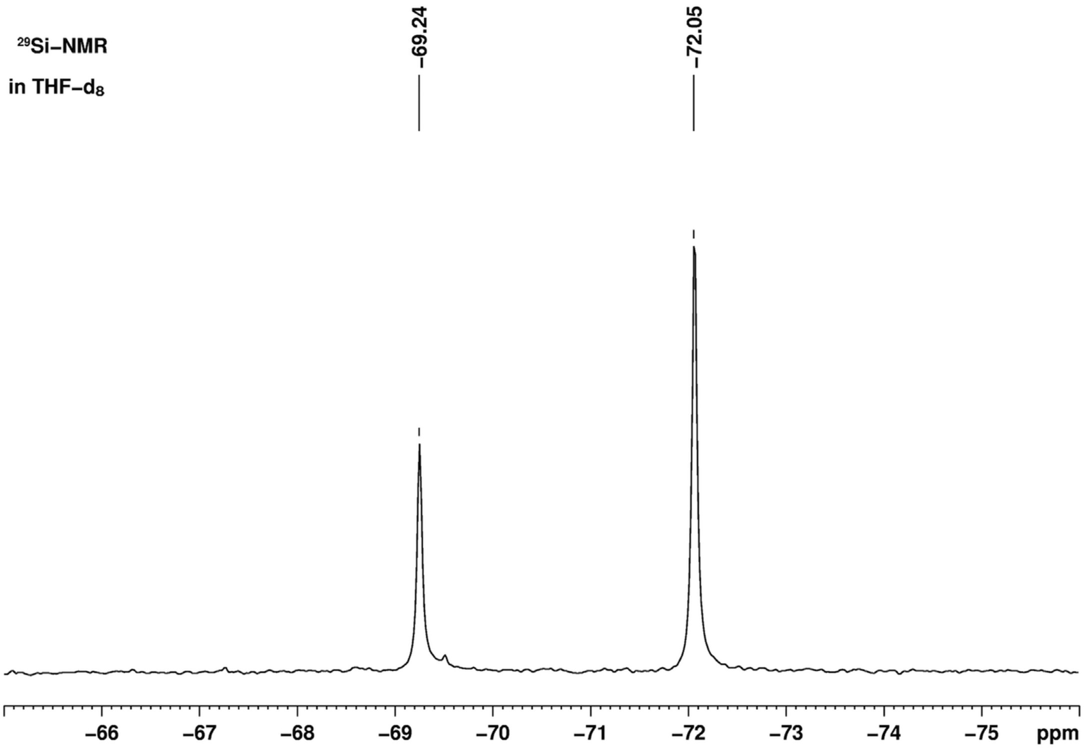


Fig. 2. ^{29}Si spectrum for fluorinated polyhedral silsesquioxane, F-POSS.

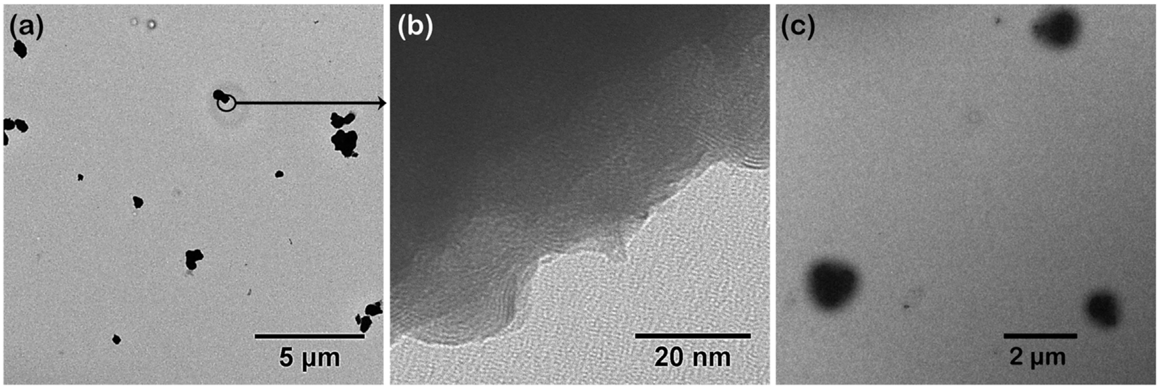


Fig. 3. TEM images of F-POSS deposed from toluene solution (a, b) and F-POSS incorporated in toluene solution of PDMS subsequently crosslinked (c).

Table 1
Mechanical parameters estimated on the basis of stress-strain curves.

Sample	Stress at break, σ (MPa)	Young modulus, Pa,[a] E (MPa)	Strain at break, ε (%)
NC0	0.18	0.03	1019
NC2.5	0.20	0.055	700
NC5	0.22	0.15	628
NC10	0.20	0.20	446

[a] Young's modulus calculated at 10% strain.

by cryo-fracturing to be very irregular (Fig. 4b–d) as compared with reference NC0 sample (Fig. 4a).

3.2.2. *Mechanical behavior*

Stress-strain curves were recorded for the composite films (Fig. 5), the main parameters of these being summarized in Table 1. As can be seen, by incorporating increasing amounts of F-POSS, the mechanical behavior of the materials changes in that the strength and modulus increase, while elongation decreases significantly.

3.2.3. *Surface and optical properties*

It is well known that methyl groups are the organic groups with the lowest surface energy, which, when are attached to the highly flexible siloxane backbone, present their highest level of efficiency thus making the polydimethylsiloxane to have a surface energy of about 20 mN/m. Because of this fact, polydimethylsiloxane easily form water-repellent films with good release properties [27,28]. Hydrophobic nature proves primarily through high water contact angle and low levels of moisture sorption. In our case, the reference sample consisting in pure crosslinked PDMS shows water contact angle of 114.2° and 0.88 wt% moisture sorption at 90% RH. On the other hand, POSSs containing fluorocarbon groups are hydrophobic, the series member FD_8T_8 having a water contact angle of 154° (with about 40° higher than the water contact angle of polytetrafluoroethylene) [19] and, to some extents, it is inert to organic solvents [29]. Therefore, fluorinated silsesquioxanes have many potential

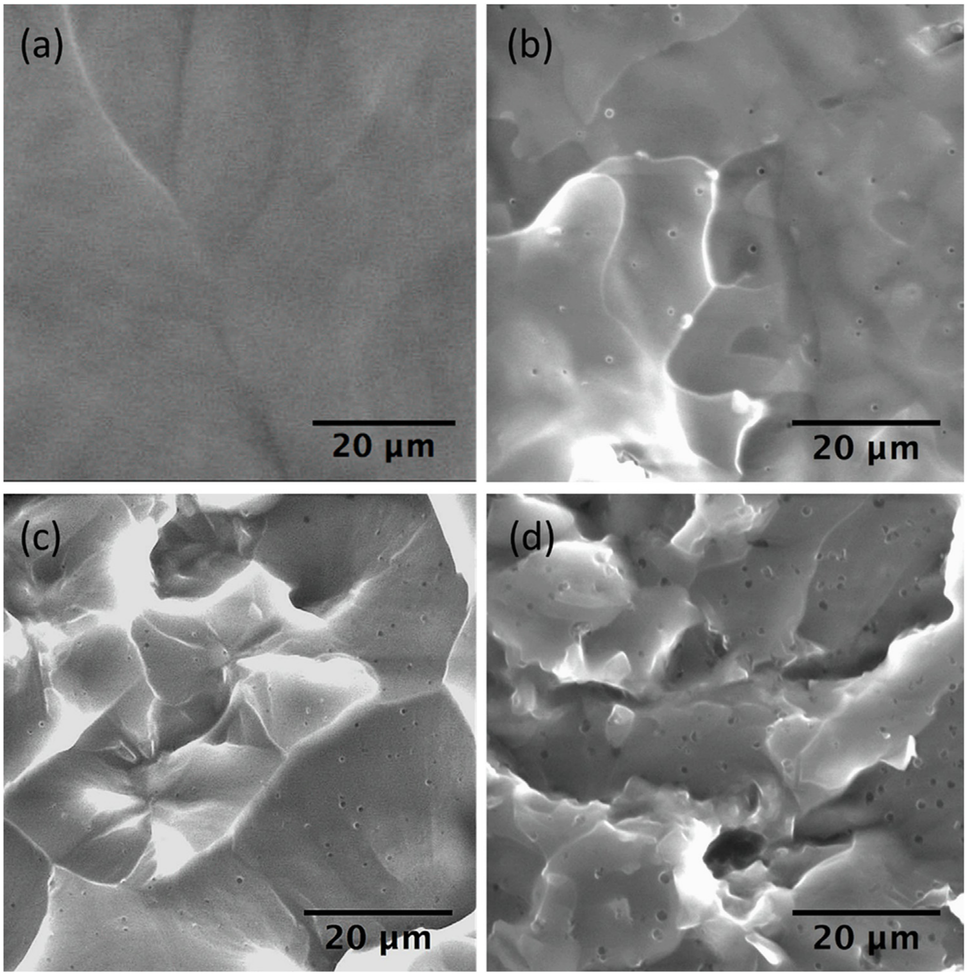


Fig. 4. SEM images on cryo-fractured section of the NC0 (a), NC2.5 (b), NC5 (c), NC10 (d) films.

Table 2
Some surface and optical features and of composite films.

Sample	WCA (°)	Moisture sorption (wt% d.b.)	Root mean square (10×10 µm) (nm)	*Fluorine content* (at%)	Transmittance at 600 nm (%)	Thickness (µm)
NC0	114.2	0.88	32.4	0	88.4	171
NC2.5	114.4	0.35	45.8	0.13	87.0	150
NC5	114.0	0.59	50.2	0.25	83.9	170
NC10	114.3	0.98	75.1	0.56	74.5	186
F-POSS[a]	–	0.76	–	–	–	–

[a] Measured on F-POSS processed in pill form.

applications as modifiers for wetting-resistant surfaces [30]. Due to the low surface energy features of F-POSS, research efforts have focused on exploiting these properties for applications related to icephobicity, antiwetting coatings, and oil–water separation capabilities [31]. So it was expected that by incorporating F-POSS in PDMS, the latter will become even more hydrophobic as the amount of filler is higher. However, in our case no occurs any change in water contact angle value as a result of incorporation of increasing amounts of F-POSS within PDMS, and its value remains around 114° (Table 2).

This could be explained by the fact that the main factors that determine the surface wettability (surface chemistry and roughness) [32,33] does not change significantly by incorporating filler. Thus fluorine content varies in the range 0–0.56 at% and root mean square between 32.4 and 75.1, as estimated by EDX and AFM, respectively (Table 2), variations which are not able to determine a trend change in contact angle values. The low surface energy coupled with high flexibility of polydimethylsiloxane chain makes its segments between crosslinks to migrate to the material–air interface to form a smooth hydrophobic surface characteristic to silicones. On the other hand, literature has shown in the case of polymethyltrifluoropropylsiloxane that the presence of trifluoropropyl group confers resistance to solvents (little swelling in alkane or aromatic solvents [28]) but does not lead to a significant decrease in surface energy of PDMS, this effect being obtained only in the case of long pendant fluorocarbon chains, such as heptadecafluorodecyl. The uncompensated dipole between the fluorocarbon and hydrocarbon segments has an unfavorable impact on surface tension [34].

Moisture sorption isotherms were recorded in the 0–90% humidity range. All isotherms show similar shape, specific for hydrophobic materials (Fig. 6). The maximum sorption values extracted on the isotherms are in the range 0.35–0.98 wt% (Table 2). At first glance, unexpectedly, the sorption capacity

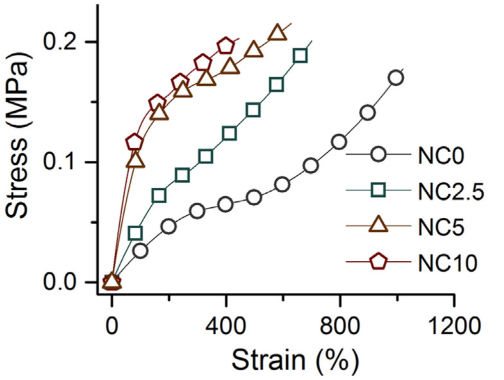


Fig. 5. Stress-strain curves for the composite films.

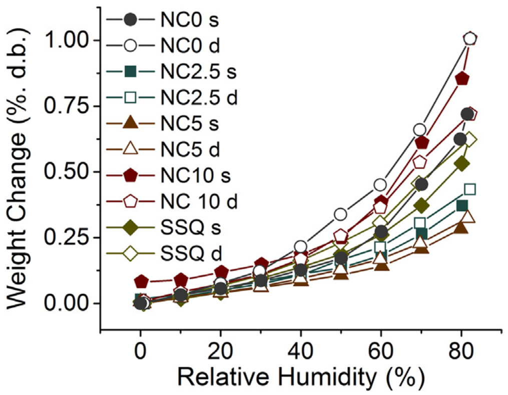


Fig. 6. Water vapor sorption–desorption isotherms.

slightly increases as a result of the incorporation of F-POSS within the silicone matrix. This behavior could be explained by the presence of filler that, when is dispersed within matrix, creates some porosity, while the filler's itself contribution to increased hydrophobicity is insignificant.

The optical properties of the studied silicone films were analyzed by UV–vis absorption spectroscopy. Fig. 7 shows the optical transmission spectra of PDMS films with different contents of F-POSS. The neat silicone film and the sample containing 2.5 wt% F-POSS are highly transparent having an average transmittance around 87%. The transmittance level decreases as the amount of filler increases. By incorporating up 10 wt% F-POSS in the silicone matrix, the transmittance is affected falling to about 74% (Table 2). In the low energy range ($\lambda > 700$ nm), the transmission was almost constant at 80% (Fig. 7).

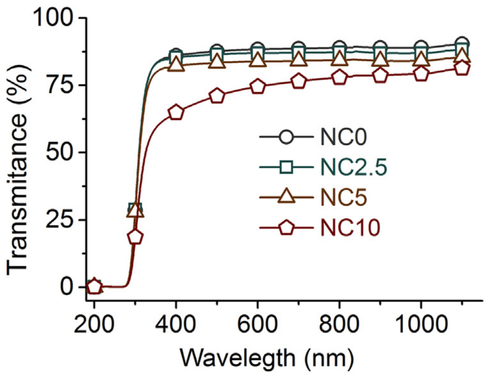


Fig. 7. UV–vis transmittance curves for the composite films.

3.2.4. *Dielectric measurements*

Some of the fundamental electrical properties of interest for insulators are dielectric constant (ε'), dielectric loss (ε''), dielectric strength and volume resistivity [35]. The dielectric permittivity indicates the ability of a material to store electrical energy in response to an electric field. In general, a low value ($\varepsilon' = 2–5$) is needed for materials that can be used as electrical insulators [35]. As the size of electronic devices is reduced, the need for lower dielectric constant materials becomes more stringent [36,37]. It was found that the presence of fluorine increases the free volume in F-POSS (due to the relatively large volume of fluorine compared with hydrogen) thus reducing the number of polarizable groups per volume unit [25]. This, along with low polarization, creates conditions for getting materials with low dielectric constant, but it depends if substitution is symmetrical or not [38]. Low moisture sorption along with other consecrated properties of silicones such as weathering resistance or large window of working temperature, constitute a guarantee for constancy of certain properties, including electrical, when the environmental conditions change. In our case, it can be noticed a slight decrease in dielectric permittivity by adding F-POSS and increasing its content (Fig. 8). For example, a decrease of approximately 15% in the dielectric permittivity by adding 10 wt% filler was obtained.

It can also be seen that the permittivity values remain almost constant throughout the frequency range in which the measurements were made. The losses are extremely low but an interesting pattern was observed in conductivity variation (Fig. 8.c). Thus, while at low frequencies the conductivity decreases with two order of magnitude (from 2.1×10^{-13} to 9.1×10^{-15} S cm^{-1} at 1 Hz) by incorporating 10 wt% filler, at high frequencies this trend is reversed (from 6.7×10^{-10} to 5.5×10^{-8} S cm^{-1} at 10^6 Hz) (Table 3).

An explanation would be based on that at low frequencies DC conductivity prevails and thus for a certain time, the dipoles remain orientated and an approximately independent frequency domain is

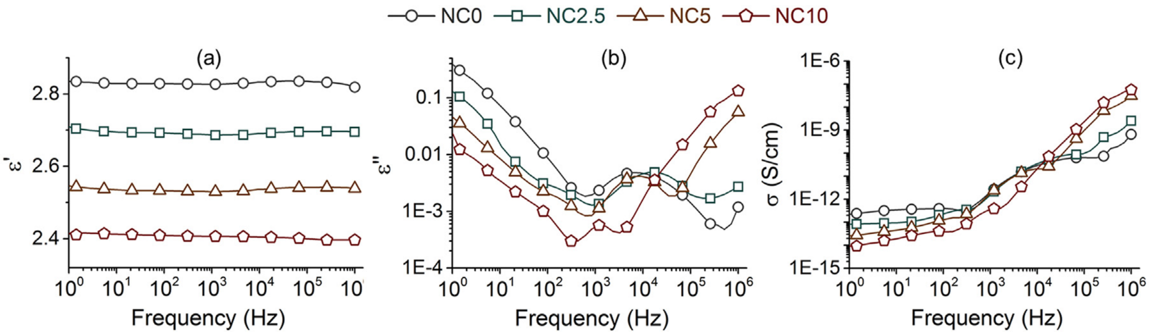


Fig. 8. The frequency dependence of: (a) the dielectric permittivity; (b) dielectric loss; (c) electrical conductivity for the prepared composites.

Table 3
Dielectric parameters for the prepared composites.

Sample	ε'		ε''		Conductivity (S cm^{-1})		Breakdown (V µm^{-1})
	1 (Hz)	10^6 (Hz)	1 (Hz)	10^6 (Hz)	1 (Hz)	10^6 (Hz)	
NC0	2.8	2.8	3.8×10^{-1}	1.2×10^{-3}	2.1×10^{-13}	6.7×10^{-10}	40
NC2.5	2.7	2.7	1.2×10^{-1}	2.7×10^{-3}	8.3×10^{-14}	2.6×10^{-9}	47
NC5	2.5	2.5	4.5×10^{-2}	5.6×10^{-2}	2.6×10^{-14}	3.1×10^{-8}	51
NC10	2.4	2.4	2.3×10^{-2}	1.3×10^{-1}	9.1×10^{-15}	5.5×10^{-8}	64

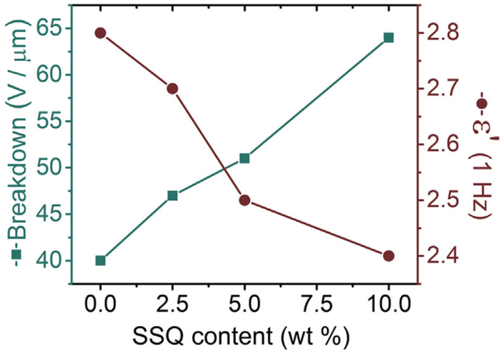


Fig. 9. Comparison between variations of dielectric breakdown and permittivity values with the addition of filler in silicone matrix.

observed, along with a decrease due to the ability of the F-POSS to withhold electrons. In the frequency domain 10^2–10^4 Hz, a relaxation behavior was observed, characteristic for composites and describes the accumulation of charges at the filler–matrix interface. At high frequencies, the dipoles oscillate and with the increased free volume achieved by F-POSS addition, as described above, the mobility is increased leading to a higher conductivity. Dielectric strength, another parameter useful in assessing isolation capacity of a material, is defined as maximum voltage that can be applied across this without causing dielectric breakdown (during which the material would become conductor) [35]. Literature reported POSS impregnated polymers showing enhanced high voltage properties [9]. Significant increases were also recorded in our case in the breakdown values, for example an increasing with 60% when 10 wt% filler was incorporated (sample NC10). It should be noted that breakdown variation with the filler content is reverse than the dielectric permittivity as otherwise expected (Fig. 9).

4. Conclusions

By incorporating fluorinated polyhedral oligomeric silsesquioxane within a silicone matrix, some of its properties slightly change in the sense that mechanical strength increases, while elongation at break and dielectric permittivity decrease. The conductivity decreases at low frequency, while at high frequency this increases as the F-POSS content is higher. The most significant changes occur in the breakdown field value, which significantly increases at 10 wt% F-POSS content. The trifluoropropyl group proved ineffective to confer hydrophobicity as both moisture sorption and especially wettability remained unchanged as a result of F-POSS incorporation within silicone. When 10 wt% F-POSS was incorporated within PDMS, the resulting composite films become slightly opaque, in special in the high energy range (λ < 700 nm), when visible transmittance falls to about 74%.

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