HYBRID SOL-GEL THIN FILMS WITH ALUMINA NANOPARTICLES WITH HYDROPHOBIC PROPERTIES

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Abstract
We have prepared hybrid silica-alkylsiloxane thin films which include alumina nanoparticles to be used as passive hydrophobic surfaces. Polydimethylsiloxane (PDMS) and Hexamethyldisilazane (HMDZ), together with tetraethyl orthosilicate (TEOS) have been used as silica-silicone hybrid precursors. Samples have been characterized by scanning electron microscopy and water contact angle measurements. Despite nanoparticle aggregation, which prevents water dropplets to achieve a Cassie-Baxter wetting mode, the results show a 130º water contact angle for the 'up to date' best set of parameters.

1. Introduction

Ice formation is a major problem in a variety of industries world wide: energy generation, power distribution or aviation and telecommunication networks, among others [1 – 5]. Many studies are being carried out in order to combat these ice-shields due to their severe consequences (economic costs and safety risks) [1, 6].

Partly inspired by the properties of the lotus leaf, we have prepared new formulations of the thin films aimimng the prevention of ice-formation by the modification of superficial properties. In this way, we would avoid droplet freezing on top of the surface and thus it would be possible to develop an anti-ice device.

The formation of ice-shields occurs when super-cooled droplets (or snow particles) come into contact with an exposed surface, freezing on them. Actually, there are some devices designed to combat these ice-shields, but most of them try to melt or remove the ice after it has been formed. In this sense, they are de-icing devices. Some examples are electro-thermal resistances located inside the wings of an aircraft or the use of deicing fluids like ethylene glycol. [4 – 6]

These procedures are effective, but they require reapplication, an economical extra cost and they may cause undesired effects like corrosion and often have detrimental environment consecuences. A more attractive approach is the use of passive methods which do not need external energy for deicing while preventing ice accumulation. These technologies usually involves surface modifications or coatings with materials capable to disrupt or avoid ice formation.

The understanding of the mechanisms behind ice adhesion is a necessary but still unsolved task, although there isn't a teory to explain the relationship between ice adhesion and water wettability, superhydrophobity has been demonstrated to be useful property to achieve this goal[1, 7, 8].

Superhydrophobic surfaces are those presenting a static water contact angle (WCA) above 150º with a low water contact angle histeresys (CAH) and a dropplet sliding angle (SA) lower than 5º [1, 9]. Based in the properties of the lotus leaf [9], we have tried to prevent ice-formation, by modifying the surface properties in two ways:

- By means of a very high interfacial energy with water (or a surface with low interaction with water molecules).
- By means of a very high specific area (with a very high microroughness).

We have tried to fulfill these two requierements preparing hybrid coatings which include funcionaliced nanosized particles.

2. Materials and Methods

2.1. Materials

For coatings preparation we have used tetraethylorthosilicate (TEOS), polydimethylsiloxane (PDMS), hexamethyldisilazane (HMDZ), isopropanol, ammonia purchased from Sigma-Aldrich and used without further modification. Alumina (Al_2O_3) nanoparticles (medium size 160 nm, verified by scanning electron microscopy) from EVONIK were also used.

2.2. Preparation of hydrophobic coatings

Samples were prepared via the following procedure: Alumina nanoparticles were put in a beaker with the selected amount of TEOS, 50 µL of ammonia and 10 mL of isopropanol. The mixture was magnetically stirred for 3 h to allow the hydrolysis reaction of the alcoxy groups (Figure 1) and the beginning of the polycondensation that will form a silica layer over the particles (Figure 2).
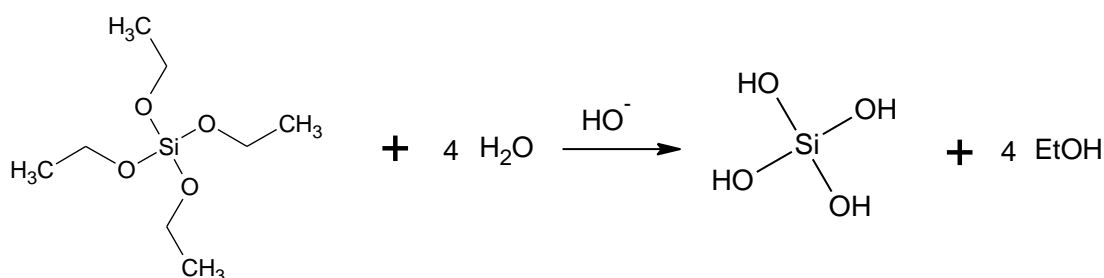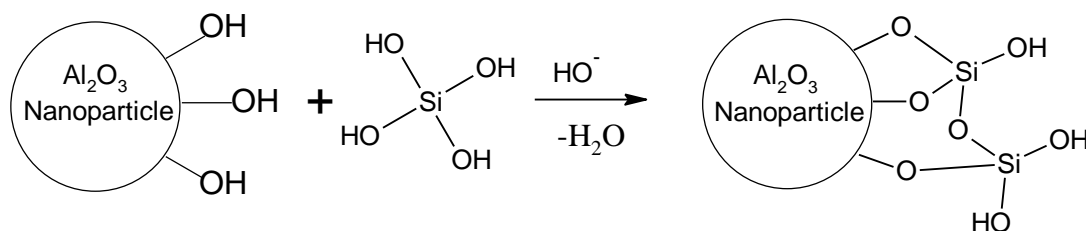
Figure 1. Scheme of the hydrolysis reaction of TEOS.

Figure 2. Scheme of the polycondensation reaction of silicon hydroxide around an alumina nanoparticle.

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Simultaneously, another beaker was prepared containing one alkylsilane, 10 mL of isopropanol and the same amount of catalyst. This beaker is also stirred during 3 h. Afterwards, the beaker containing no particles was slowly poured over the first one while stirring and the mixture was left reacting during 6 h, 24 h, 72 h and 1 week. The presence of an alkylsiloxane hydrolizated will interfere in the formation of the silica net, producing an hybrid silica / silicone, also known as creamer (Figure 3).
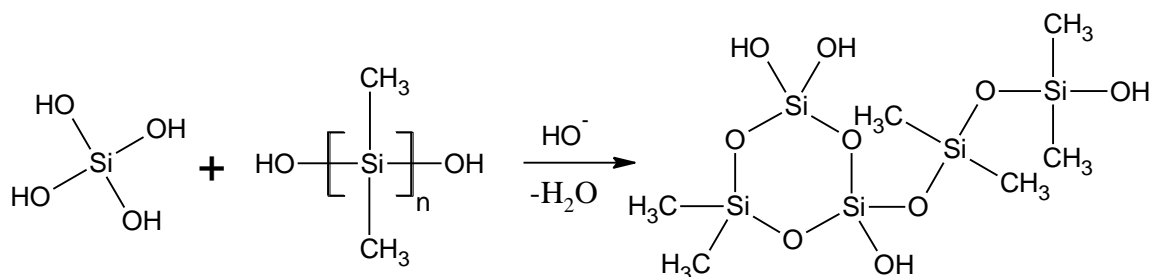

Figure 3. Scheme of the polycondensation reaction of hydrolizated TEOS and PDMS

Once the reaction time was completed, some microscope glass slides, gently cleansed with isopropanol, were dip-coated into the solution at 0.4cm/s and dried in an oven at 110ºC during 24h.

The effect of several parameters like the type of hybrid alkoxide, molar relation TEOS / alkylsilane, concentration of alumina nanoparticles, reaction time and catalyst have been considered.

2.3. Characterization

The WCA of the coatings were determined from silhouettes the static 7 µL distilled water droplets using an elliptical best-fit model carried out with a goniometer Krüss Easy Drop DO4010. The study of the surface morphology was done with a scanning electron microscope JEOL JSM 6335F at the Centro Nacional de Microscopía Electrónica of the Universidad Complutense de Madrid.

3. Results and discussion

The main features of the prepared samples with TEOS and PDMS or HMDZ are summarized in tables 1 and 2 respectively. As can be seen in table 1, the best WCA result, 130 °, is obtained with sample 12 TPA. Comparing samples 7 TPA, 8 TPA and 9 TPA we can deduce that adding 50g/L (5% p/v) of Al_2O_3 nanoparticles the WCA improves around 30 degrees, so is the best concentration to be used in order to increase the WCA value. In addition, comparing samples 8 TPA and 12 TPA, it can be seen that higher concentrations of alkylsiloxane need higher reation times, because of the need to hydrolyze completely.

Table 2 shows samples prepared with HMDZ as alkysiloxane. For short reaction times, e.g. samples 1 THA and 2 THA, the WCA value obtained was lower than the one obtained with the corresponding PDMS samples 4 TPA and 12 TPA (Table 1). This behaviour could be explained through a reduction of the speed reaction due to a decrease of linking groups: HMDZ only has one, while PDMS has two. Or due to steric impediments from the methyl groups. It can be also observed that, if the synthesis takes enough time, the WCA value approaches to the values of the PDMS (samples 4 THA and 5 THA).

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Table 1. TEOS/PDMS prepared coatings with their WCA value.

Sample name	TEOS (mol/L)	PDMS (mol/L)	Al₂O₃ (g/L)	Reaction Time (h)	Water Contact Angle (degrees)
1 TPA	0.5	0.03	10	24	95
2 TPA	0.5	0.06	10	24	91
3 TPA	0.2	0.1	50	6	124
4 TPA	0.2	0.15	50	6	124
5 TPA	0.2	0.15	25	168	97
6 TPA	0.2	0.15	0	6	93
7 TPA	0.15	0.2	25	6	99
8 TPA	0.15	0.2	50	6	118
9 TPA	0.15	0.2	75	6	118
10 TPA	0.1	0.075	50	6	111
11 TPA	0.05	0.037	50	6	125
12 TPA	0.15	0.2	50	72	130
13 TPA	0.075	0.1	50	168	128

Table 2. TEOS/HMDZ prepared coatings with their WCA value.

Sample name	TEOS (mol/L)	HMDZ (mol/L)	Al₂O₃ (g/L)	Reaction Time (h)	Water Contact Angle (degrees)
1 THA	0.2	0.15	50	6	104
2 THA	0.15	0.2	50	72	120
3 THA	0.075	0.1	50	72	100
4 THA	0.15	0.2	50	168	129
5 THA	0.075	0.25	50	168	130

Figure 4 a and b show the SEM image of the surface of sample 12 PTA where Al_2O_3 nanoparticles appear agglomerated forming an interconnected three dimensional network with numerous holes on the substrates surface. On figure 5 the TEOS/PDMS hybrid matrix of the sample 10 PTA hides the particles and also smooths the surfaces of particle agglomerates. This reduces the specific area and the capability to trap air bubbles provoking a interaction increase between the surface and the drops as the surface.

WCA values of both series of samples prepared are below the superhydrophobic characteristic value of 150˚ and the droplets are pinned to the surface in all samples, either PDMS or HMDZ. As in the Leidenfrost effect, the reason why the drops can slide freely on the surface is the existence of an air cushion on which they can "levitate" and move with a low friction [10]. In the case of superhydrophobic materials, this cushion appears as a result of small air bubbles being trapped in the surface roughness between the drops and the surface, also known as the Cassie-Baxter wetting mode[11], which requires a very high roughness to occur.

These results suggest that the coatings haven't reached the Cassie-Baxter state, necessary to achieve superhydrophobicity. Instead, the drops are in the Wenzel wetting state [11, 12] fully contacting the surface, which causes a huge interaction between them and avoids the sliding of the water droplet.
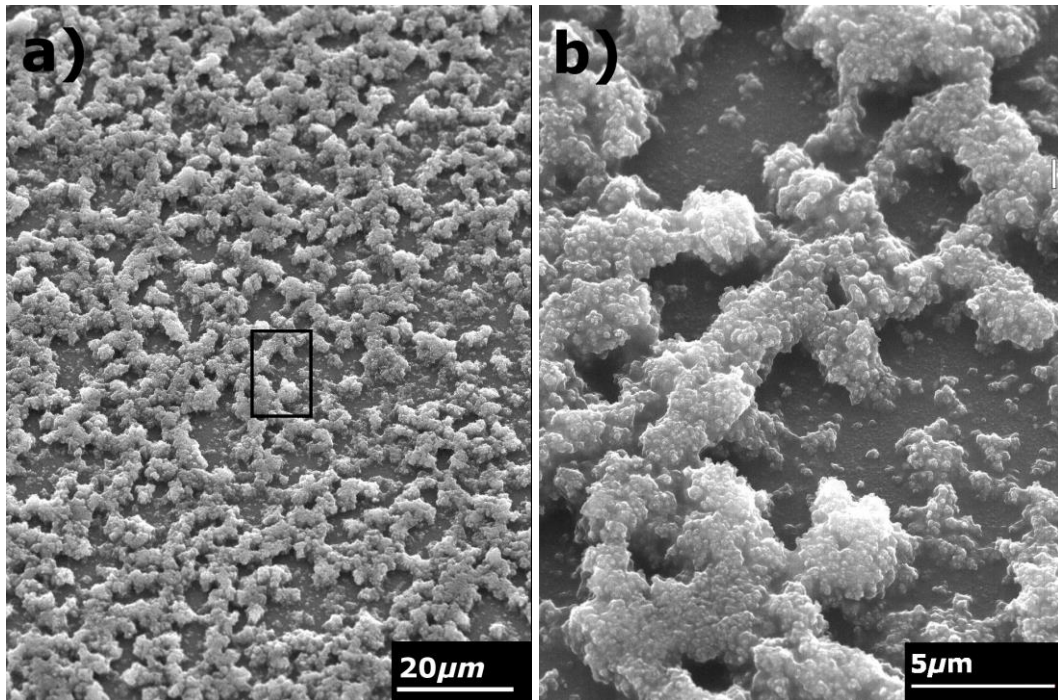
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Figure 4. a) SE-SEM image of sample 12 TPA tilted 30º and b) detail at higher magnification.
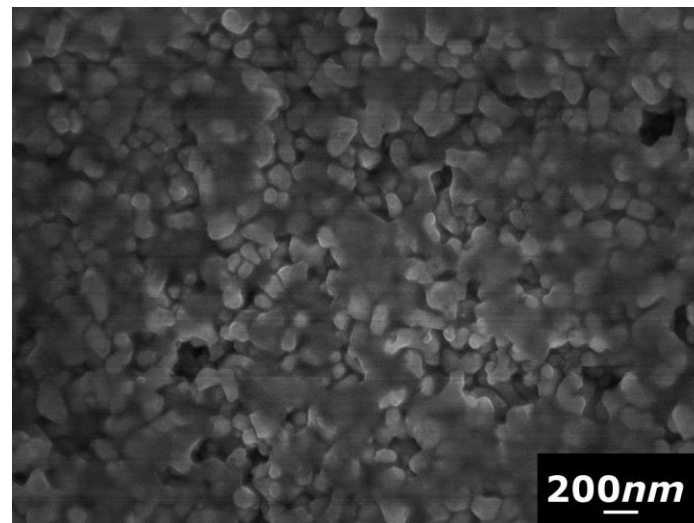

Figure 5. SE-SEM image of sample 10 TPA

4. Conclusions

We have prepared hybrid fluorine-free silica-alkysilane thin films which include alumina nanoparticles and present a remarked hydrophobic behavior, as it is shown by water contact angle measurements. Our first results show a 130º water contact angle for the 'up to date' best set of parameters. Scanning electron microscopy images show a lower roughness than expected, caused by nanoparticles aggregation, that prevents water dropplets to achieve a Cassie-Baxter wetting mode. Futher optimization of the synthesis is required in order to avoid nanoparticles agglomeration, which would lead to higher water contact angle values, reaching a superhydrophobic behavior and probably also reducing the amount of particles used.

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5. Acknowledgements

6. References

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