

SiO₂/PDMS functionalized hybrid ceramics: effect of functional group on hydrophobic behavior

Cerámicos híbridos SiO₂/PDMS-funcionalizado: efecto del grupo funcional sobre el carácter hidrofóbico

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Abstract

In this paper, the hydrophobic effect of the functional group in a hybrid ceramic synthesized from tetraethyl orthosilicate (TEOS) and polydimethylsiloxane (PDMS) is investigated. The hybrid ceramics were synthesized using di-butyl-di-di-tin laurate (DBTL) as a polycondensation catalyst and different concentrations of the polysiloxane chain varying from 20-40%w. Infrared spectroscopy confirmed the formation of the hybrid material, observing the corresponding signals for the siloxane bond (Si–O–Si) corresponding to the silica network, inorganic fragment (1100 cm⁻¹) and those corresponding to the polymer chain (785 cm⁻¹) besides, the Si–C bond of the polymer is presented at 1250 cm⁻¹. The amino functional group was identified as a low intensity signal at 1300 cm⁻¹ (N–C) and 1204 cm⁻¹ (Si–N); on the other hand, the phenyl group was present at 3080 cm⁻¹ for the C–H group of the aromatic ring and with the C=C bond of the ring at 1429, 794 and 845 cm⁻¹. While the hydrophobic character was evaluated with the contact angle θ , obtaining a hydrophobic to superhydrophobic behavior with θ de 110-130°.

Resumen

En este trabajo se estudia el efecto hidrofóbico del grupo funcional en un cerámico híbrido sintetizado a partir del Tetraetil-ortosilicato (TEOS) y el polidimetilsiloxano (PDMS). Los cerámicos híbridos fueron sintetizados empleando al di-butil-di-laurato de estaño (DBTL) como catalizador de policondensación y diferentes concentraciones de la cadena de polisiloxano variando desde el 20-40%w. La espectroscopia de infrarrojo corroboró la formación del material híbrido, observando las señales correspondientes para el enlace siloxano (Si–O–Si) correspondientes para la red de sílice, fragmento inorgánico (1100 cm⁻¹) y los correspondientes a la cadena polimérica (785 cm⁻¹); además de presentarse el enlace Si–C, del polímero a 1250 cm⁻¹. El grupo funcional amino se identificó como señal de intensidad baja a 1300 cm⁻¹ (N–C) y 1204 cm⁻¹ (Si–N); por su parte el grupo fenilo se hizo presente a 3080 cm⁻¹ para el grupo C–H del anillo aromático y con el enlace C=C del anillo a 1429, 794 y 845 cm⁻¹. Mientras que el carácter hidrofóbico se evaluó con el ángulo de contacto, θ , obteniendo un comportamiento de hidrofóbico a superhidrofóbico con θ de 110-130°.

Hybrid ceramic, TEOS, PDMS, Hydrophobic

Cerámico híbrido, TEOS, PDMS, Hidrofóbico

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Introduction

In nature there are several materials that are hydrophobic (water repellent), one of them is the lotus flower, which contains on its surface non-polar substances (fats and waxes) that repel water. On the other hand, they produce roughness, which is the physical factor that causes this behavior. Figure 1 shows some examples of hydrophobic surfaces in nature; Figure 1a shows the hydrophobic behavior of the lotus flower, where, in addition to having a waxy surface, it is observed that the surface is formed by a roughness with controlled morphology (surface formed by agglomeration of spherical particles).

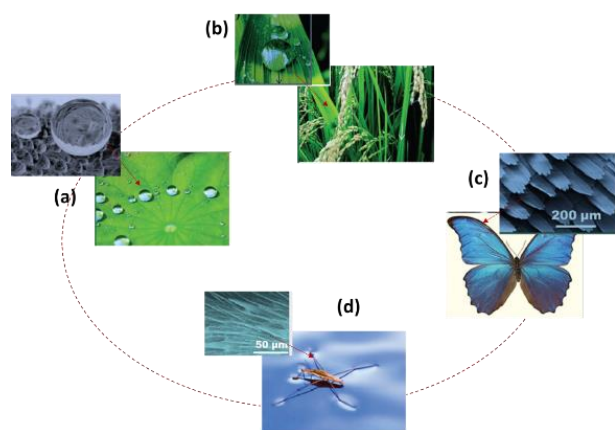


Figure 1 Examples of hydrophobicity in nature (a) lotus flower (b) rice leaf (c) butterfly wings (d) mosquito legs
Source: [1, 2]

Another hydrophobic surface in nature is the leaf of the rice plant, where the hydrophobicity is generated by the trough arrangement of the leaf (Figure 1b). Butterfly wings are another example of this type of materials, where the trough structure is the originator of this behavior (Figure 1c), the legs of the mosquito (Figure 1d) is another example of hydrophobicity in nature, similar to butterfly wings these surfaces have a specific arrangement in the surface roughness, needle-like that allow repelling water [1-3].

Hydrophobic properties in materials can be created by two different techniques: Chemical modification of the surface or physical modification of the surface (roughness modification). In the first one, as shown in Figure 2, the surface is chemically modified by adding organic groups that give the material the hydrophobic character. This modification is carried out in thin layers that homogeneously cover the entire surface.

To achieve this, the functional groups present in the material must be taken into account to add a modifying agent (crosslinked) that allows adherence to the surface of the material and to the R-modifying group, which is the one that will generate the hydrophobicity.

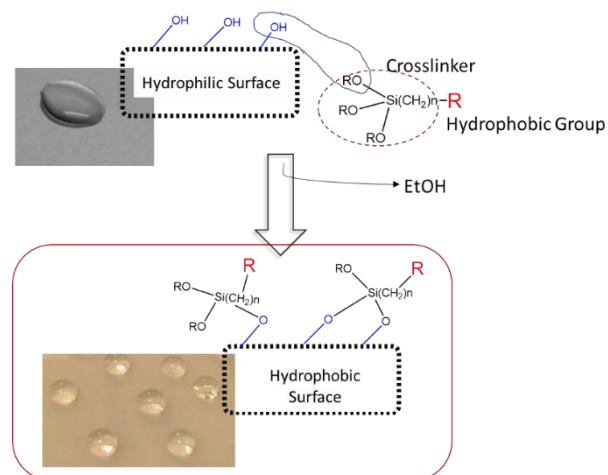


Figure 2 Methods for obtaining hydrophobic surfaces by chemical modification
Source: [4]

The aim of this work is to obtain a hybrid ceramic (inorganic/organic) with hydrophobic properties that can be used as an adsorbent for oil pollutants.

Methodology

Hybrid ceramic synthesis

The ceramic was synthesized according to the method reported by C. Salazar-Hernández et al [5,6]. Where the polymerization of TEOS (Aldrich, 99%) is carried out by co-condensation using different amounts of PDMS; according to the amounts indicated in Table 1. The PDMS functionalized were hydroxyl-terminated polydimethylsiloxane (DMS-12; Gelest 16-32 cSt), amino-terminated polydimethylsiloxane (DMS-N12; Gelest 15-30 cSt) and hydroxyl-terminated diphenylsiloxane-dimethylsiloxane copolymer (PDS-1615; Gelest 50-60 cSt; 14-18% diphenylsiloxane). To obtain the sol solution, the 10 g of TEOS were mixed with the PDMS, adding 0.1 g of dibutyl dilaurate tin (DBTL; ALdirch 99%), which acts as a polycondensation catalyst [7]; according to the reaction shown in Figure 4.2b; the mixture was kept under constant magnetic stirring for 30 min at a temperature of 40°C; until the ceramic was obtained.

	DMS-12 (g)	DMS-N12 (g)	PDS-1615 (g)
SiO ₂ /DMS-CH ₃ -10	1	–	–
SiO ₂ /DMS-CH ₃ -20	2	–	–
SiO ₂ /DMS-CH ₃ -40	4	–	–
SiO ₂ /DMS-N(CH ₃) ₂ -10	–	1	–
SiO ₂ /DMS-N(CH ₃) ₂ -20	–	2	–
SiO ₂ /DMS-N(CH ₃) ₂ -40	–	4	–
SiO ₂ /PDS-10	–	–	1
SiO ₂ /PDS-20	–	–	2
SiO ₂ /PDS-40	–	–	4

Table 1 TEOS and PDMS functionalized ratios used to modify porous systems

Characterization

INFRARED SPECTROSCOPY. The chemical structure of the sponge and the SiO₂-PDM has been observed by ATR-FT using a Nicolet-iS10 ThermoScientific equipment, obtaining the average of 16 scans, with 4 cm⁻¹ resolution and spectral window from 4000 to 600 cm⁻¹.

CONTACT ANGLE - The contact angle for the sponge and sponge-modified was determined using a drop of distilled water from L. The image was taken with a conventional cell camera and the contact angle was measured with the free software IC-Measure using the horizontal base as a reference.

Results

Functionalized SiO₂/PDMS Ceramics

Figure 3 shows the corresponding spectrum for the SiO₂/PDMS-CH₃-10 modified ceramic. Where the signals corresponding to TEOS are not present; the corresponding spectrum for the starting reagent DMS-12. However, in the structure of the ceramic, the siloxane chain is observed in the structure of the modified ceramic; as well as the signals indicating the presence of the silica network. The main signals identifying the formation of the silica network from TEOS are the Si-O-Si bond observed as a broad band with a shoulder at 1004 cm⁻¹, □□; as well as two broad signals of moderate intensity at 855 cm⁻¹ and 695 cm⁻¹; □□. In addition, the -CH₂CH₃ group of the unreacted alkoxides is observed as bands of moderate intensity at 2922 cm⁻¹ and 2851 cm⁻¹, □□.

For SiO₂/DMS-N(CH₃)₂; the N-C bond of the functional group was identified at 1300 cm⁻¹ (signal G) as a broad band of low intensity, while the Si-N bond was identified at 1204 cm⁻¹ (signal F). For the SiO₂/PDS, the C-H bond of the aromatic group was identified with a multiplet at 3084-3000 cm⁻¹ (C signals). Likewise, the C=C bond of the aromatic ring was identified at 1429 cm⁻¹ □; while at 794 cm⁻¹ and 845 cm⁻¹ □□□ the C-H of the phenyl group was identified (C signals).

Figure 4a shows the drops used to measure the contact angle in the unmodified sponge and those modified with the different ceramics. The sponge shows a hydrophilic behavior with θ of 46.2°. When the ceramics were added inside the sponge structure, the angle increased to a value greater than 100°, behaving as hydrophobic surfaces. The highest hydrophobicity was observed with the methyl functional group and with the 40%w concentration; with a θ =132°; reaching a superhydrophobic behavior

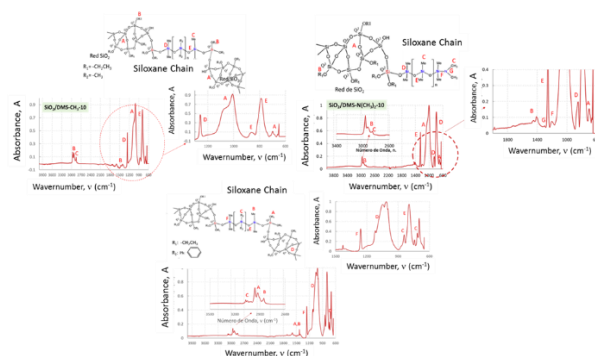


Figure 3 Infrared spectra of the functionalized ceramics

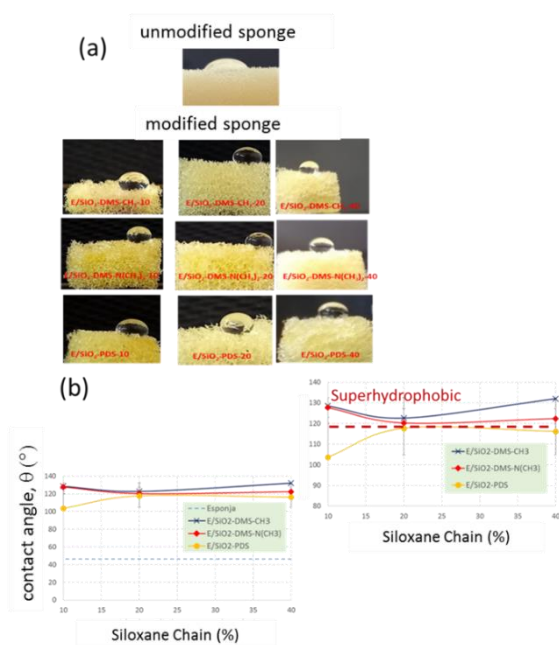


Figure 4 Hydrophobic behavior of hybrid ceramics

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Conclusions

PDMS allows to generate the hydrophobic property in the silica structure and by modifying the chain with amino and phenyl groups, hybrid ceramics with hydrophobic and superhydrophobic character are obtained; reaching values of $\theta = 132^\circ$ when the siloxane concentration in the silica network is 40%w.

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