Article **Journal of Technology and Innovation**
June 2022, Vol.9 No.24 29-35

SiO_2-PDMS as oil removal system

SiO_2-PDMS como sistema de eliminación de aceite

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DOI: 10.35429/JTI.2022.24.9.29.35 Received January 30, 2022; Accepted June 30, 2022

Abstract

En este trabajo se presenta un diseño de sistema de remoción de aceite basado en el uso de sílice hidrofóbica (SiO_2/PDMS) obtenida por la co-condensación de sílice con polidimetilsiloxano (PDMS) empleando DBTL como catalizador de policondensación. La cantidad de PDMS en la estructura de la SiO_2/PDMS varió del 10 hasta el 40%w. La SiO_2/PDMS se impregnó en un sistema de esponja y se evaluó la cantidad de sílice hidrofóbica atrapada en la misma por gravimetría; además, la espectroscopia de infrarrojo permitirá identificar a la sílice hidrofóbica en la esponja y los principales grupos funcionales de la misma. El carácter hidrofóbico se determinó a través de la modificación en la capacidad de absorción de agua de la esponja y mediante la medición del ángulo de contacto. Por otra parte, La microscopia óptica permitió identificar cambios en la superficie de la esponja debido a la presencia de la SiO_2/PDMS. Finalmente se determinó el efecto de la cantidad de PDMS sobre la capacidad de remoción de aceite en agua.

SiO_2-PDMS, Hydrophobicity, Oil removal, Hybrid materials, Hydrophobic sponge, Hydrophobic sponge

Resumen

En este trabajo se presenta un diseño de sistema de remoción de aceite basado en el uso de sílice hidrofóbica (SiO_2/PDMS) obtenida por la co-condensación de sílice con polidimetilsiloxano (PDMS) empleando DBTL como catalizador de policondensación. La cantidad de PDMS en la estructura de la SiO_2/PDMS varió del 10 hasta el 40%w. La SiO_2/PDMS se impregnó en un sistema de esponja y se evaluó la cantidad de sílice hidrofóbica atrapada en la misma por gravimetría; además, la espectroscopia de infrarrojo permitirá identificar a la sílice hidrofóbica en la esponja y los principales grupos funcionales de la misma. El carácter hidrofóbico se determinó a través de la modificación en la capacidad de absorción de agua de la esponja y mediante la medición del ángulo de contacto. Por otra parte, La microscopia óptica permitió identificar cambios en la superficie de la esponja debido a la presencia de la SiO_2/PDMS. Finalmente se determinó el efecto de la cantidad de PDMS sobre la capacidad de remoción de aceite en agua.

SiO_2–PDMS, Hidrofobicidad, Remoción de aceite, Materiales híbridos, Esponja hidrofóbica

Citation: GÓMEZ-LÓPEZ, Rosa Viridiana, SALAZAR-HERNÁNDEZ, Mercedes, MORENO-PALMERIN, Joel and SALAZAR-HERNÁNDEZ, Carmen. SiO_2-PDMS as oil removal system. Journal of Technology and Innovation. 2022. 9-24:29-35.

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Introduction

A hydrophilic substance is one that readily takes up water molecules, i.e., it is soluble in water. This is due to the polar groups that interact with the water molecule as shown in Figure 1a; where NaCl dissociates into Na^+ and Cl^-, then, the positively charged sodium interacts with the oxygen of water that has a negative partial charge density (δ^-); while Cl^- will interact with the hydrogens of water since they have a positive partial charge δ^+. On the other hand, a hydrophobic substance is one that is insoluble in water, such as fats, hydrocarbons, among others, since they do not have polar groups that allow their interaction with H_2O (Figure b) (Ahmad D, 2018).

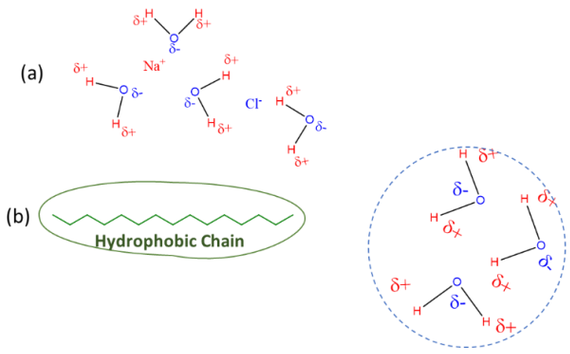

Figure 1 (a) hydrophilic behavior (b) hydrophobic behavior phase separation with water

Hydrophobic silica and surface modification by co-condensation

As shown in Figure 2a, on the surface of a silica are found the functional groups "silanols, Si–OH" which on dissociation generate an H^+ and a negative charge on oxygen forming a hydrophilic character on the silica. However, silanols are reactive groups that can be used to react with organosilanes, $R–Si(OR)_4$ (Figure 3b) and modify the silica surface to obtain hydrophobic surfaces (Yokogawa H,1995; Daoud W.A, 2006; Anderson A.M, 2011; Liu J; 2022; Ariati R.M, 2022). Among the widely used methods for the modification of a silica surface, highlights the method of co-condensation, which consists of carrying out the co-polymerization of TEOS in the presence of an organosilane ($R\text{-}Si(OR)_4$) resulting in the formation of the three-dimensional silica network trapping the hydrophobic R groups inside and outside of the silica surface (Putz A.M, 2019; Costa M.B, 2018).

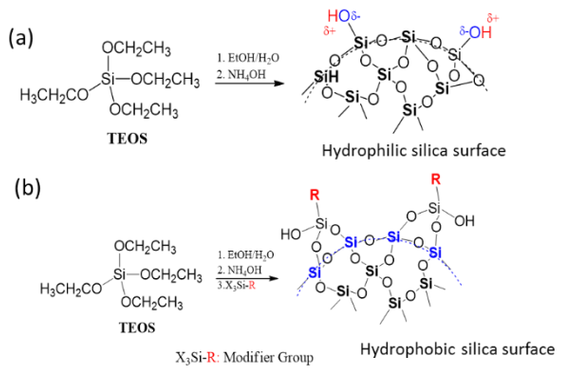

Figure 2 (a) Production of hydrophilic silica (b) Production of hydrophobic silica

Hydrophobic silica as an oil contaminant removal system

Nowadays, water quality is a relevant issue of high environmental concern, since water is exposed to many pollutants, including oily substances that cause serious environmental damage (Gupta R.K, 2017). To remove this type of substances, the use of hydrophobic surfaces has been proposed (Xue Z, 2014; Chu Z, 2014; Chen CH, 2019; Kumari P, 2022). For example, Baing N et al, 2021 propose the use of hydrophobic silver nanoparticles modified with dopamine and incorporated into a cellulose foam as an oil removal system, obtaining a removal efficiency higher than 95%. The authors attribute this result to the hydrophobic behavior of the material.

On the other hand, hydrophobic silica has been employed in oil removal through oil gelation and thereby causing water separation (Wang J, 2019; Sert Çok S, 2021; Syed S, 2011; Dai X, 2022). Cho Y.K et al., modify silica nanoparticles with PDMS (polydimethylsiloxane) using chemical vapor deposition obtaining hydrophobic silica with contact angle around 163.55º that enhance the oil gelation for its separation (Cho Y.K,2014).

This paper presents the modification of a silica using PDMS through the sol-gel method and the use of a polycondensation catalyst to obtain a sol solution containing the structure shown in Figure 3; the SiO_2-PDMS is impregnated in polyurethane foam to determine its effect as an oil-in-water removal system.

ISSN: 2410-3993

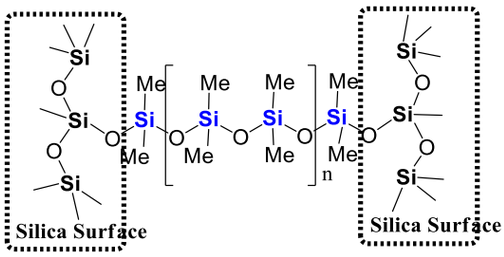

Figure 3 Structure for SiO_2/PDMS-functionalized

Methodology

SiO_2/PDMS Synthesis

The silica modification was conducted by Co-condensation; as reported by Salazar-Hernandez et al (Salazar-Hernández C, 2019; Salazar-Hernández C, 2021). The polymerization of TEOS (Aldrich; 99%) adding PDMS (Gelest) and DBTL as polycondensation catalyst is performed by magnetic stirring for 30 min at 50 ºC. Table 1 specifies the concentrations of PDMS used in the silica modification.

	TEOS	PDMS
SiO_2-10PDMS	10 g	1 g
SiO_2-20PDMS	10 g	2 g
SiO_2-40PDMS	10 g	4 g

Table 1 Amounts of TEOS/PDMS used for silica modification.

SiO2-PDMS-functionalized SiO_2-PDMS-Sponge Impregnation

Polyurethane foam samples with dimensions of $5 \times 3 \times 2$mm are obtained and these are immersed in the sol solution prepared with TEOS/PDMS/DBTL to achieve its total impregnation. Subsequently, they are dried at 50ºC for 24 h.

SiO_2-PDMS characterization

The chemical structure of the foam and SiO2-PDMS were observed by ATR-FT using a Nicolet-iS10 Thermoscientific analyzer, obtaining an average of 16 scans, with 4 cm^{-1} resolution and spectral window from 4000 to 600 cm^{-1}. On the other hand, gravimetry analysis is used to quantify the weight percentage of SiO_2-PDMS gained in the foam (1).

$$\%M_{SiO2-PDMS} = \frac{(M_{sponge/SiO2-PDMS}) - M_{sponge}}{M_{sponge}} X100 \quad (1)$$

The hydrophobic property is quantified through the change in water accessible porosity ($\%P_{H2O}$); using Equation 2. In addition, the contact angle for the modified sponge is measured by performing hydrophobicity tests using 1 μL water droplets and measuring the contact angle with IC-Measure software.

$$\%P_{H2O} = \frac{M_{wet} - M_{dry}}{M_{dry}} X100 \quad (2)$$

On the other hand, the change in the foam structure caused by the SiO_2/PDMS deposition was observed through a stereoscope.

Oil Removal Capacity Measurement

To measure the oil removal capacity of the modified silica, 2 g of vegetable oil was added to a beaker and then the modified foam was passed with SiO_2-PDMS. After removal, the foam/SiO_2-PDMS is placed at 100°C for 24 h to evaporate the absorbed water and subsequently quantify the amount of oil removed by weight gain of the modified foam.

Results

Infrared Spectroscopy Characterization of R-SiO_2

Figure 4 shows the infrared spectra of the polyurethane foam, SiO_2-PDMS and P.F/SiO_2–10PDMS. For the polyurethane foam (Figure 4a) the characteristic bands of a urethane were observed. At 3293 cm^{-1} the N-H group is observed; while in the range of 2969-2865 cm^{-1} the C–H stretching bands were observed, while at 1704 cm^{-1} the carbonyl group (–C=O) is present and at 1639 cm^{-1} the C–O–C deformation.

On the other hand, the spectrum corresponding to SiO_2-PDMS (Figure 4b) indicates the chemical bonding of PDMS with the silica structure. It is observed that at 1100 cm^{-1} the siloxane groups (Si–O–Si) that form the inorganic matrix are found and at 1200 cm^{-1} the intense signal of the C–Si group of PDMS is observed and, finally, at 773 cm^{-1} the siloxanes corresponding to the PDMS chain are observed as an intense signal. The C–H stretching band corresponding to the $–CH_3$, of PDMS was found as a single band of low intensity at 2961 cm^{-1}.

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The spectrum of the foam impregnated with SiO_2-PDMS is presented in Figure 4c. It is observed the integration of the signals corresponding to the foam (3293 cm^{-1}, N-H; 1704 cm^{-1}, –C=O and 1639 cm^{-1} C–O–C) as medium intensity signals. On the other hand, the signals corresponding to SiO_2–PDMS are maintained as intense signals.

The amount of modified silica deposited on the sponge specimens varies according to the PDMS modifier percentage, as observed in Figure 5. The higher the PDMS content in the SiO_2–modified SiO_2 increases the mass deposited inside the foam specimens; having as a minimum mass of 4.53±0.25g SiO_2–PDMS/g P.Foam and as a maximum 7.36±0.71 g SiO_2–PDMS/g P.Foam.

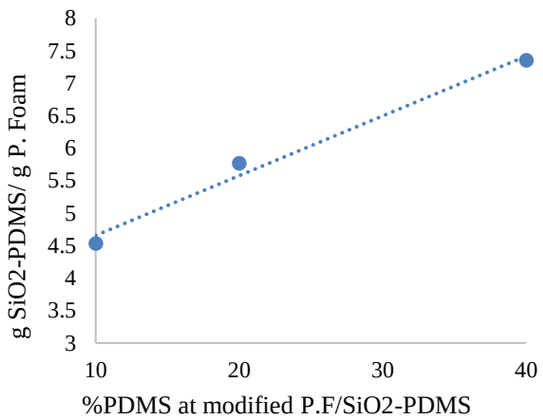

Figure 5 SiO_2-PDMS deposited into polyurethane foam

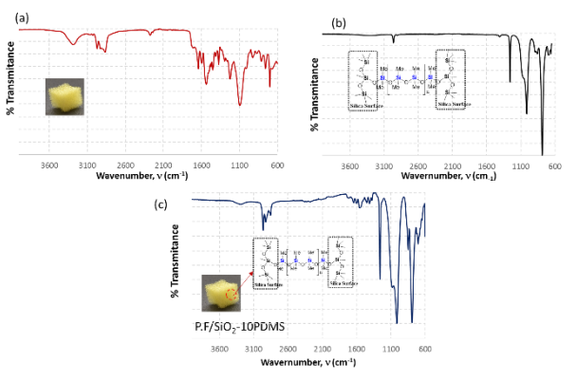

Figure 4 FT-IR (a) polyurethane foam (b) SiO_2-PDMS (c) P.F/SiO_2-PDMS

Figure 6 shows the change in the pore network present in the P.Foam due to the SiO_2-PDMS deposit; where it can be seen that, according to the PDMS content, there is an increase in the amount of pores filled with the modified silica. With 10% PDMS the pore structure is preserved reducing only the pore size, while at 20% a higher pore filling is observed with a higher number of pores filled with 40% PDMS.

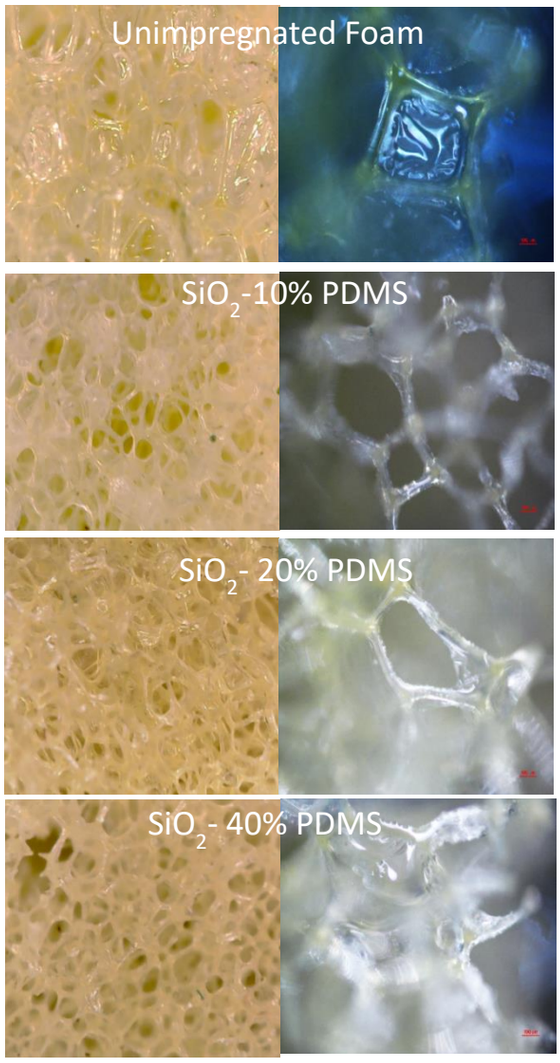

Figure 6 Porosity changes into P. Foam due to SiO_2-PDMS deposited

ISSN: 2410-3993

Hydrophobic assessment

The hydrophobicity of P. foam and modified silica was evaluated through the change in porosity accessible to water (Figure 7). It is observed that P. Foam has a high-water absorption capacity, reaching 19 gH_2O/g P.Foam. When P. Foam is modified with SiO_2–PDMS the adsorption capacity is drastically reduced to 1.619±0.45 $gH_2O/gP.F/SiO_2$–PDMS when modified with SiO_2–40PDMS; while for P.Foam modified with SiO_2–10PDMS an adsorption capacity of 2.08±0.71 $gH_2O/gP.F/SiO_2$–PDMS is observed.

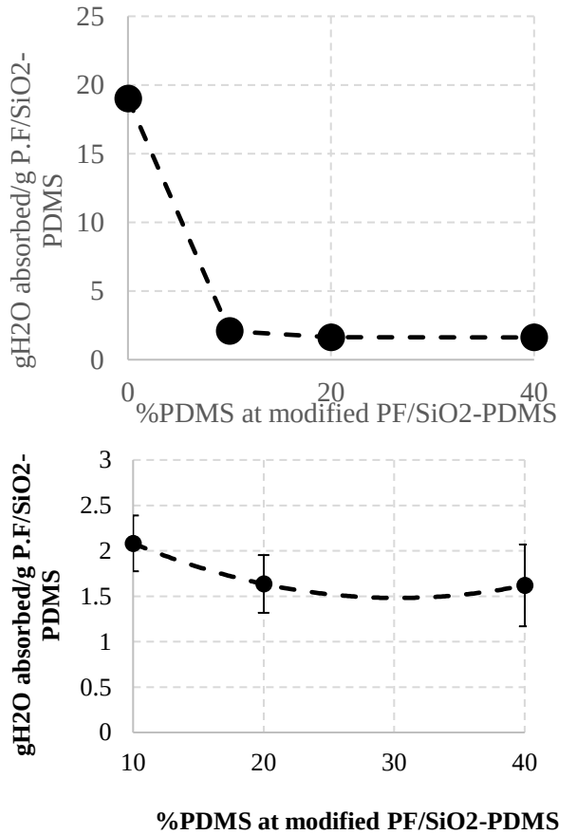

Figure 7 Water absorption capacity for P.F/SiO_2-PDMS

The decrease in water absorption capacity is due to the change from hydrophilic to hydrophobic behavior in P.foam, in addition to a decrease in porosity due to the deposition of SiO_2–PDMS within the pores of the foam in the silica modified with 20 and 40% PDMS, respectively.

On the other hand, the contact angle θ was measured for the different samples tested with the modified silica (Figure 8a) if the angle value is greater than 10º and less than 90º the material is hydrophilic; while if the angle value is between 90º and 120º it is a hydrophobic material and greater than 120º corresponds to a superhydrophobic material (Zhang X.F, 2020). According to the results obtained, the unmodified foam is a hydrophilic material with a contact angle θ=57.505±1.54º (Figure 8b and c).

According to the modification of P. Foam with SiO_2–PDMS changes the behavior from hydrophilic to hydrophobic presenting contact angles between 107.8±2.46º for P.F/SiO_2–10PDMS, 116.67±2.46º for P.F/SiO_2–20PDMS and 118.2±1.28º for PF/SiO_2–40PDMS. The increase in contact angle occurs linearly as the PDMS content in the modified silica increases. Therefore, the hydrophobic behavior in these materials is due to the PDMS content in the modified silica and the effect of foam roughness does not generate a significant contribution in the hydrophobicity of the material.

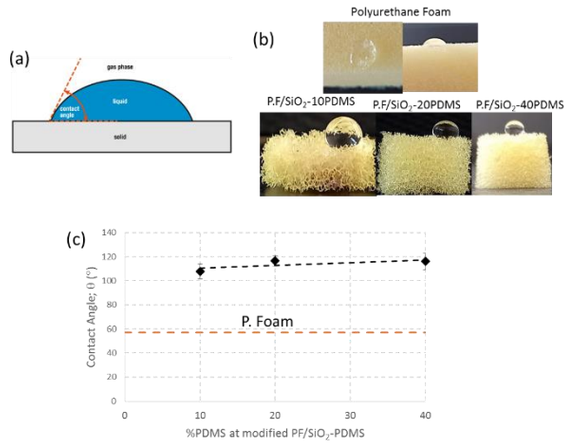

Figure 8 (a) Contact angle (b) water drop on surface foam and surface foam modified (c) contact angle according to PDMS

Oil removal capacity

The removal capacity for SiO_2–PDMS-modified P.Foam increased linearly with PDMS content. For PF/SiO_2-10PDMS a removal capacity of 14.69 g oil/m^2 PF/SiO_2–PDMS was determined, while PF/SiO_2–40PDMS presented a removal capacity of 21.22 g oil/m^2 PF/SiO_2–PDMS. The unmodified sponge has a low removal capacity, having a removal capacity of 10 g oil/m^2 PF (Figure 9).

ISSN: 2410-3993

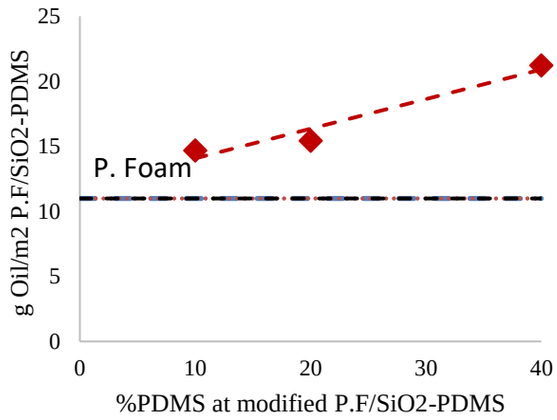

Figure 9 Oil removal capacity

Acknowledgments

The authors are grateful for the financial support granted by the Secretaria de Investigación y Posgrado of the Instituto Politécnico Nacional through project **SIP 1172/2022.**

Conclusions

According to the results, the SiO_2–PDMS was impregnated in the macroporosity of the Polyurethane Foam; modifying its physical properties such as contact angle and water absorption capacity. The P. foam presents a contact angle of 57.50º, corresponding to a hydrophilic material, however, the oil removal capacity was 10 g oil/m^2 P. Foam. On the other hand, Polyurethane Foam impregnated with modified silica is a hydrophobic material with a higher oil removal capacity.

The increase in oil removal capacity in the P.F/SiO_2–PDMs is due to the integration of hydrophobic groups (PDMS) in the foam which improves the compatibility with the hydrocarbon increasing the removal capacity up to 21.22 oil/m^2 PF/SiO_2–PDMS.

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