Sorbent system based on organosilane-coated polyurethane foam for oil spill clean up

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Abstract

In this study, flexible and open cell polyurethane foams were formulated and chemically modified with organosilane to be used as a sorbent system for oil spill cleanup. Six polyurethane foams with different densities and three oil types with different viscosities were investigated. Moreover, sorbents were characterized based on their surface modification and sorption capacities. The main results indicated that the surface treatment on the solid fraction of the foam was effective, observing by the contact angle, thereby increasing the hydrophobicity of the samples. Cell morphology and foam density directly affect the sorption capacity of foams. Foams with high densities are indicated for oils with low viscosity, and foams with low densities are indicated for viscous oils. The oil sorption capacity also depends on oil viscosity (and temperature).

Keywords PU foams · Sorbents · Organosilane · Oil spill

Introduction

In recent years, oil spill contamination has been frequently reported with the expansion of oil exploration in marine environments and the transportation of oil products. Massive pipeline networks, ships and vehicles are used for the distribution and transportation of oil and its by-products. The pipelines and risers, which carry tens of cubic meters of oil per day, run the risk of rupture, thereby leading to oil spills.

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Accidents involving tankers and vessels, and leakages in storage tanks at petrochemical plants, terminals, distribution points and fuel stations can release significant amounts of oil and its derivatives, such as naphtha, gasoline, kerosene, LPG, diesel oil and fuel oil, into the environment, which could lead to the contamination of soil, water and air [1–4]. Oil and its by-products form an insoluble layer on the water surface and hinder the aeration and the natural illumination of water bodies, thereby causing harm to the fauna and flora of the exposed environment [5–9].

In the past few years, the sorption process has shown great potential for the treatment of industrial effluents and as an efficient and economical alternative in the remediation of areas degraded by oil spill. In the sorption process, absorption, adsorption and desorption processes take place simultaneously, that is, the oil is retained on the surface of the solid fraction of the sorbent during adsorption, the oil is trapped inside the system during absorption, and the sorbed oil is withdrawn from the system during desorption [5–7, 10].

In this context, several materials have been tested to study their use as sorbents materials for the removal and recovery of oils in marine environments and to minimize the environmental impacts caused by them [5, 11–14]. Duong and Burford (2006) [15] reported that for a high efficiency of an oleophilic sorbent, the rate of diffusion of oil into the sorbent must be rapid, in great quantity, and without the system dissolution (rupture and disintegration of sorbent solid medium). Furthermore, the desorption process of oil when removing the sorbent from the marine medium must be low, that is, the oil must be retained inside the system until its removal from the environment. Liu et al. (2013) [16] describe an ideal sorbent as a material that has high sorption capacity of the oil, selectivity to oil and not to water, low density and recyclability and is non-aggressive to the environment.

Oleophilic sorbents are materials that float on the surface of water that is contaminated with oil, and selectively remove only the oil from the water by moving the oil to the interior of the sorbent, thus forming a semisolid phase, following which the whole system can be mechanically removed [17]. Sorbents are materials that have significant oil removal capacity and are able to absorb 3 to 100 times their original mass [9]. The selectivity of the sorbent to the oil (the material needs to be predominantly hydrophobic and oleophilic) is one of the most important properties with respect to the efficiency of a sorbent in removing nonpolar oils, especially when this is the removal of these oils in aquatic environments [18].

Flexible polyurethane (PU) foams are promising materials for absorbing liquids. They can be defined as a class of porous polymers, where the dispersion of a gas during the polymerization process gives rise to the formation of small air bubbles or cells interconnected in a three-dimensional structure. PU foams can be produced with high concentration of open cells, and their viscoelastic properties allow for an efficient sorption and desorption of oil, thus allowing the collection, transportation and recovery of the oil and the subsequent reuse of the foam [3, 19]. In addition, PU foams are materials that can be produced with low energy consumption and low investment equipment [20, 21]. In general, the variation and manipulation of the PU foam formulation in processing allows for the production of different cell morphologies that directly impact the sample density, which can vary from 8 to 50 kg.m^{-3}. Consequently, a wide variation in

mechanical properties and sorption capacity can be obtained [22, 23]. However, PU foams are materials whose chemical structure is composed of both polar and nonpolar segments [24], which may impact oil selectivity (sorption of both aqueous and oleophilic phases). Thus, to maximize the efficiency of PU foam as an oleophilic sorbent, it is necessary to chemically modify the polymeric surface of the foam, thereby increasing its hydrophobicity [11].

The chemical modification of the foam's hydrophilic surfaces with hydrophobic rendering treatments may be a potential way to increase the selectivity of PU foam without compromising the porous foam structure [12, 19, 25–29]. One of the hydrophobic surface treatments that has gained prominence in recent years is the process of silanization, which is the reaction of hydroxyls present on the surface of a sample with alkoxy groups present in the silane. Organosilanes are used in the treatment of surfaces to diminish the effect of groups present on the surface of a substrate and replace them with specific functional groups. The mechanism of silane reaction on a surface that contains exposed hydroxyl is shown in Fig. 1. This reaction is based on the bifunctionality of silanes, which means that it has two distinct reactive groups in the molecule. In the presence of water, the silane tends to hydrolyze, forming silanol. The silanol then reacts with the functional groups of the substrate (such as hydroxyls) (a) forming covalent bonds and/or (b) strong interaction via secondary bonds with the surface of the substrate [30, 31].

In this sense, the application of chemical treatments on the surface of the solid fraction of a PU foam can contribute to one of the biggest challenges in the development of sorbents, which is the development of a system with high sorption capacity (and oil collection), low cost of production, possibility of large-scale production, storage time without system deterioration, high selectivity to oil and recyclability. In this sense, the objective of this study was the development of PU foams, evaluation of different cellular morphologies of PU foams and the accomplishment of a chemical treatment to modify the selectivity of PU foams, aiming to increase the sorption capacity of oils in aqueous mediums.
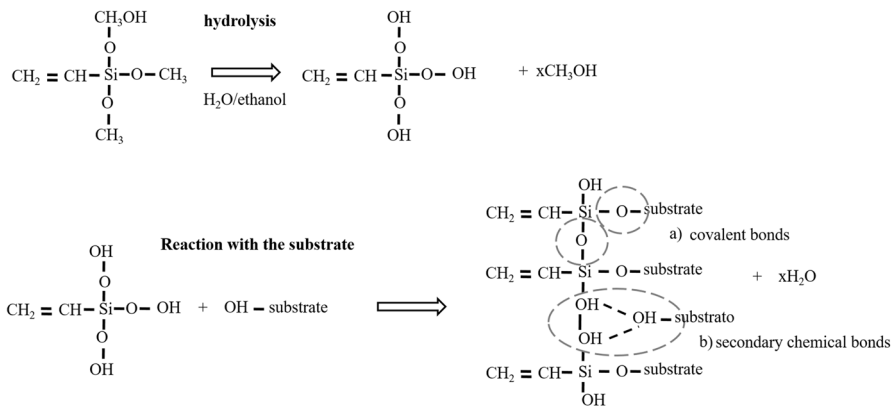

Fig. 1 Mechanism of reaction on a substrate coated with organosilane (adapted from Lu 2013) [31]

Materials and methods

Materials

For the development of PU foams, Voranol WL 4010 polyol and Voranate ™ T-80 TDI toluene diisocyanate (TDI), supplied by Dow Brasil Sudeste Industrial Ltda., were used. The amine catalyst (Dabco® 2033 Catalyst) was supplied by Air Products, and the organometallic tin octanoate catalyst (Kosmos® 29) was supplied by Evonik Industries. The surfactant, commercially known as Niax silicone L-595, was supplied by Momentive Performance Materials Inc. Methylene chloride, a deionizing agent supplied by Brasil Sudeste Industrial Ltda, and deionized water were used. For the hydrophobic coating of PU foams, triethoxyvinylsilane (TEVS) (supplier code: 175560) and tetraethoxysilane (TEOS) (supplier code: 13190) were used, both were supplied by Sigma-Aldrich.

The oils used for the sorption tests were as follows: Ipiranga SAE 5W30 oil (lubricating motor oil) with a density of 0.86 g.cm^{-3} at 20 °C and a kinematic viscosity of 70 cSt at 40 °C, soybean oil (vegetable oil–cooking oil) with a density of 0.91 g.cm^{-3} at 20 °C and a kinematic viscosity of 32 cSt at 40 °C and kerosene (fuel oil) with a density of 0.78 g.cm^{-3} at 20 °C and kinematic viscosity of 2.2 (max) cSt at 40 °C.

Polyurethane foams production

The first step of this study was the development of flexible PU foams. Table 1 shows the PU foams formulated with varying densities expressed in parts per hundred polyol (pphp).

PU foams were produced by the batch method using a Fisaton 715 propeller mixer having a rotational speed of 2500 rpm. Initially, water, amine and silicone were added to the polyol and stirred for 80 s. Then, tin octanoate was added and mixed for 40 to 50 s. Thereafter, TDI and methylene chloride were added to the blend with vigorous stirring for approximately 10 to 15 s, and then, the mixture was poured into a mold for free expansion, to form the foam. The foam was cured for 48 h in an environment having a controlled temperature of 23 °C. After this, the

Table 1 Polyurethane foams formulations (pphp)

Reagents	PU 1	PU 2	PU 3	PU 4	PU 5	PU 6
Polyol	100	100	100	100	100	100
Diisocyanate	95	85	80	73	67	51
Water	7.3	6.5	6	5.4	4.9	4.2
Amine	0.5	0.4	0.30	0.2	0.18	0.12
Silicone	5	4	3.3	2.2	1.7	0.8
Octoate	0.9	0.7	0.50	0.4	0.3	0.18
Chloride	43	30	22	11	6	12

specimens were cut (25×25×25 mm), cleaned with acetone and dried in an oven at 80 °C for 2 h.

Chemical treatment of PU foams with organosilane-based coating

Silane hydrolysis was carried out for which a solution of water/alcohol (70:30) with 1% (mass) of organosilane TEVS and 1% (mass) of organosilane TEOS was used. Acetic acid (approximately 10 mL for each liter of solution) was added dropwise to stabilize the pH of the solution to 4.5. The solution was stirred for 2 h. After this, foam samples (25×25 × 25 mm) were immersed in the solution and the solution was stirred slowly with a magnetic bar stirrer for 4 h. Later, the foams were removed from the solution, the excess liquid was drained, and the samples were dried (with the occurrence of concomitant organosilane curing) at 120 °C for 4 h.

Characterization

Five specimens, each sized 25 × 25 × 25 mm, were used per sample, and the densities of the foams were calculated using Eq. 1 as described in ASTM D3574-11.

$$\rho_f = \frac{m_f}{v_f} \times 10^6 \tag{1}$$

where ρ_f is the foam density (kg.m^{-3}), m_f is the mass (g) and v_f is the volume (mm^3) of the specimen.

Sample morphology was evaluated by field emission scanning electron microscopy (FEG-SEM) using a Shimadzu device (Superscan SS-550 model) and a Tescan microscope (model Mira3). All samples were precoated with gold (Au), and 15 kV voltage was used. The foam area was observed vertically, in the direction of expansion of the samples.

Chemical properties were evaluated using the Nicolet iS10 Fourier transform infrared (FTIR) spectrometer (Thermo Scientific) by attenuated total reflectance (ATR). The samples were scanned in the region of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Thermal properties of the foams were evaluated by thermogravimetric analyzer (TGA) (Shimadzu model TGA-50) with a heating ramp of 23 to 800 °C at a rate of 10 °C.min^{-1}, under nitrogen atmosphere (50 mL.min^{-1}). Approximately, 10 mg of the sample was used for each assay.

To evaluate the hydrophobic characteristics of the coated foam, three specimens measuring approximately 25 × 25 × 25 mm were conditioned in an environment with a temperature of 23 ± 2 °C and a relative humidity of 60 ± 5%. Samples were then placed under a glass slide, and a drop of deionized water was added to it with a glass syringe at five different points under the same conditions of packaging. Images were taken with a Lumix FZ40 digital camera as soon as

the drop touched the surface of the sample and after five minutes and were analyzed using the Surftens 3.0 software.

The static sorption test was performed based on the methodology proposed by ASTM F726-12, in which the sorbent is added to the oil for a period of 15 to 30 min (sorption time increases with increasing oil viscosity) until the samples are completely submerged in the oil. Later, the samples are withdrawn and suspended for 30 s to drain the excess oil (desorption) and are re-weighed. The dimensions of the samples used in the test were $25 \times 25 \times 25$ mm. All samples were evaluated in triplicate, and the tests were performed at 23 °C.

Two methods were used to calculate the sorption capacity of PU foams: (1) the usual method, which evaluates the sorption capacity as a function of the mass of the sorbent before and after the test, as represented in Eq. 2, and (2) sample collection capacity. With respect to the collection of oil per sample, the test specimens, having a constant volume ($25 \times 25 \times 25$ mm) and being exposed to the different types of oils according to the methodology described previously, were compressed (crushed) for maximum oil removal from the body of the foam. The oil that was collected from the test specimens (with constant volume) was then weighed (measured unit) in grams, and all the tests were performed in triplicate.

$$SC = \frac{M_1 - M_0}{M_0} \tag{2}$$

where SC is the sorption capacity (g.g^{-1}), M_0 is the mass (g) of the dry sorbent and M_1 refers to the mass (g) of the sorbent added the sorbate, that is, the mass after the sorption test.

The reusability test was also based on the methodology proposed by ASTM F726-12, in which the sorbent measuring $25 \times 25 \times 25$ mm was exposed to 100 sorption cycles. After measurement of sorbents sorption capacity, a compression process was used to remove the oil in each cycle. This process was performed with the aid of two smooth rollers rotating in complementary direction with 1.5 mm distance between them, thus suffering a compression effort. This analysis was performed only on the PU3 sample coated with organosilane, using SAE 5W30 oil.

The dynamic sorption test was performed with a heterogeneous mixture of 300 mL of deionized water and 12 g of SAE 5W30 oil. The mixture was stirred continuously for 1 min with a magnetic plate mixer. Moreover, the specimen (volume $25 \times 25 \times 25$ mm) was added to the system for a period of 1 min. The stirring was discontinued, and the sorbent was withdrawn from the system. A desorption time of 30 s was allowed. The sample was weighed before and after exposure to the dynamic water/oil system, as well as after the specimen was mechanically compressed to extract the oil collected by the sorbent to evaluate the amount of water sorbed together into the system. In all the samples, the amount of water collected by the sorbent was less than 0.5 g.

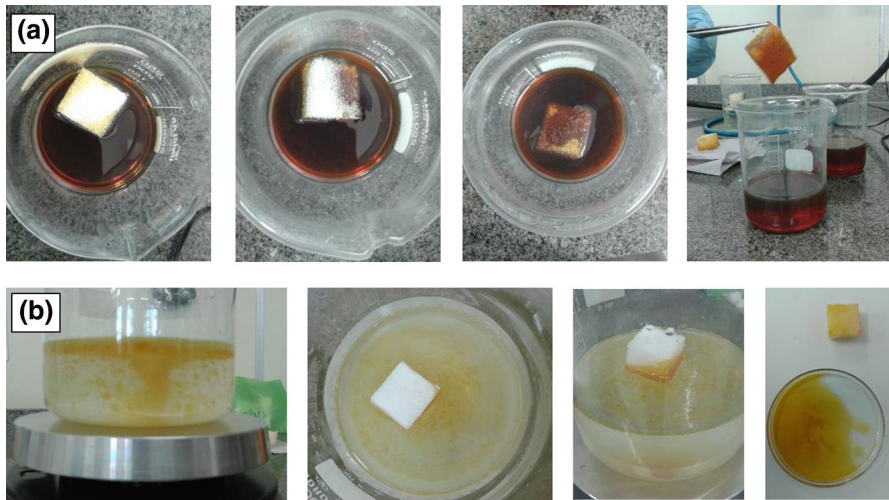Figure 2 represents the stepwise procedure used in the static and dynamic sorption tests.

Fig. 2 Photographic images of the methodology used for **a** static sorption and **b** dynamic sorption

Results and discussion

Table 2 shows the density of PU foams, as formulated in Table 1, and the influence of the chemical treatment on this property.

A gradual increase in the density of PU foams from formulation PU1 to PU6 is observed. With a reduction in the additives used in the formulation in relation to the polyol, especially water and methylene chloride (which are the blowing agents used), there is a reduction in the foam expansion capacity and a consequent increase in the density of the foam (decrease in the capacity of expansion). One of the most important functions of water in the formulation of flexible PU foams is to control the density of the foam. In general, larger the amount of water used in the formulation, lower the density of the foam. Methylene chloride, a physical blowing agent, is a low-boiling liquid, which uses the heat released during the formation of the foam to convert into the gaseous state and, thus aids in the formation of gases, which further decreases the density of the foam. After the chemical treatment, there is an increase of 15 to 25% in foam density due to the deposition of the coating on the solid surface of the PU foam.

The morphological analysis of the different compositions of the PU (PU1 to PU6) that are already silanized is obtained by MEV-FEG and is presented in Fig. 3. It can

Table 2 PU foam densities (kg m^{-3}) according to the formulation, before and after the silane coating

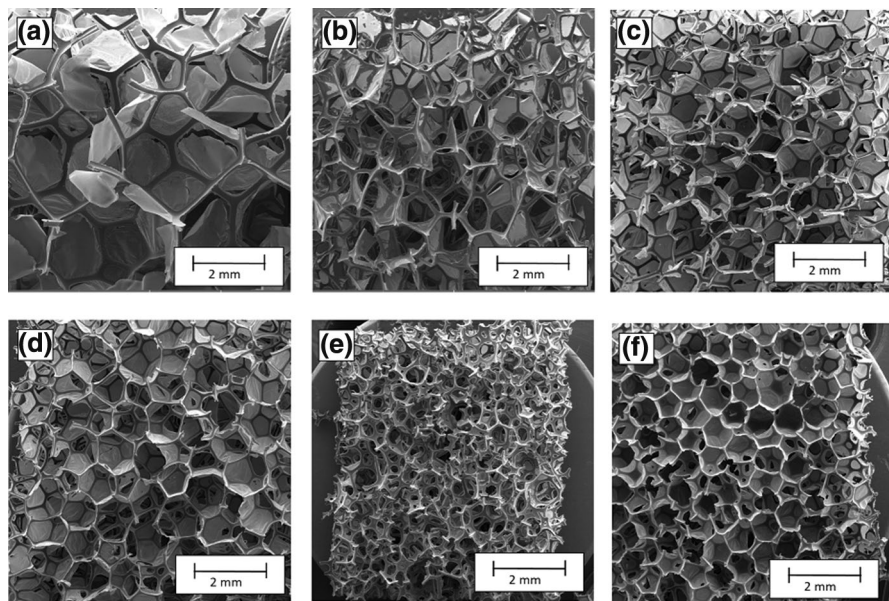| Silanization	PU1	PU2	PU 3	PU4	PU5	PU6
Before	7.5 ± 1.0	9.2 ± 0.4	10.1 ± 0.4	18 ± 0.9	22.4 ± 1	32.5 ± 1.5
After	9.3 ± 0.5	10.7 ± 1.3	11.7 ± 0.7	22.5 ± 1.6	26.5 ± 2	36.6 ± 2.3

Fig. 3 Micrographs obtained from MEV of PU foams with different densities: **a** PU1; **b** PU2; **c** PU3; **d** PU4; **e** PU5; and **f** PU6

be observed from the micrographic images that with an increase in the foam density, there is a decrease in the cell size of the foam, as well as an increase in the amount of cells per unit area. In all formulations, there were some cells with unopened pores (thin polyurethane film). The presence of this film on cell pores can influence the oil retention capacity, as the oil can adhere to the surface of this film and aid in the adsorption, but can also affect the speed of migration of the oil into the cell, as it restricts the passage of oil.

Figure 4 shows the SEM micrographs of the surface of the foam polymer matrix (PU3) in the cell boundary, before and after the organosilane coating. Other samples also presented similar characteristics. The layer of organosilane that the samples are coated with is fragmented during the cutting of the samples, thereby exposing more clearly the coating layer of the organosilane. In general, organosilanes, after curing, have rigid vitreous characteristics, which corroborate with the images presented. The PU foam exhibited smooth surface on the solid fraction. It was clearly seen that the introduction of organosilane on the foam increased the surface roughness of the foam. This introduced roughness to the foam affects its interaction with the oil, due to an amplification or enlargement of the solid–liquid interactions [3].

Figure 5 shows the FTIR spectra (Fig. 5a) and the TGA thermograms (Fig. 5b) of the PU3 sample foams before and after the organosilane coating. The PU foam samples, among the different compositions, do not differ in the materials used for the synthesis but in the amount of the formulation, so there are no significant compositional differences between the chemical groups present in the samples. Figure 5a shows that there are characteristic chemical groups of the PU in the foam sample
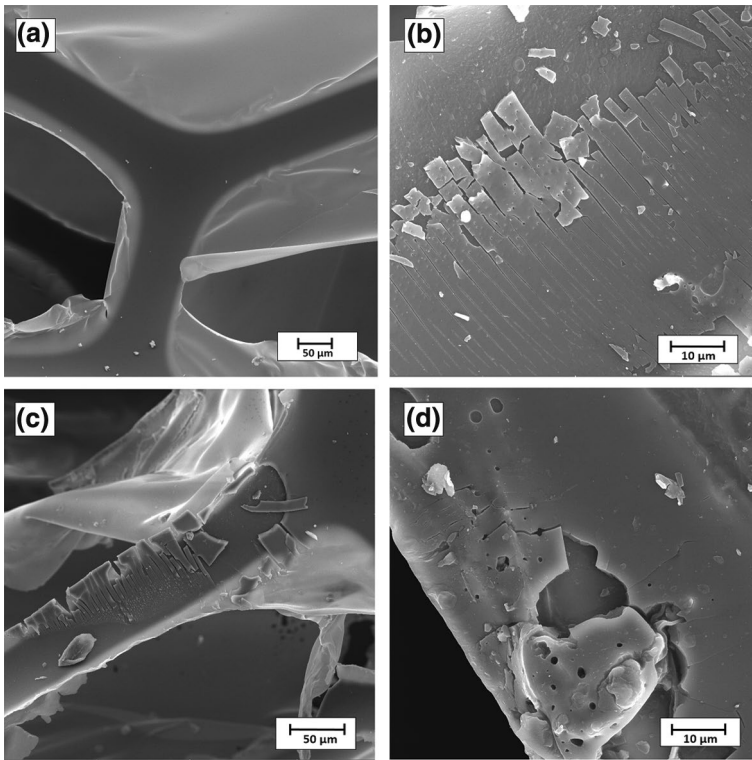
Fig. 4 Micrographs obtained by SEM of PU3 foam: **a** uncoated and (**b, c, d**) after coated with organosilane

that are not treated with the chemical, that is, a band at 3320 cm^{-1} of the group NH (urethane), a peak at 2272 cm^{-1}, attributed to NCO group present in the isocyanate, absorption bands at 1224 cm^{-1} and 1513 cm^{-1} due to the presence of NH and NC, respectively, and a band at 1725 cm^{-1} which is attributed to the presence of the carbonyl (C=O). The bands between 1075 and 1115 cm^{-1} are attributed to COC, bands between 2880 and 2890 cm^{-1} are attributed to CH groups, bands at 1605, 1540 and 870 cm^{-1} are due to aromatic structures, such as C=C of the benzene ring [19]. In the sample coated with the organosilane TEVS, a band is observed at 765 cm^{-1} and is related to Si–C [32]; there is an increase in the band intensity near 3500 cm^{-1}, which may be due to the presence of terminal OH groups of the hydrolyzed organosilane. After the chemical treatment, several characteristic bands of the PU disappear, which may be attributed to the test method used (FTIR-ATR), where the depth of penetration of the beam interferes with the reading of the chemical composition of the PU with hydrophobic coating.

In Fig. 5b, two stages of mass loss are observed in the polyurethane, that is, between 280 and 318 °C and between 364 and 400 °C. According to Gu and Sain (2013) [33], the first stage of PU degradation occurs with the breakdown
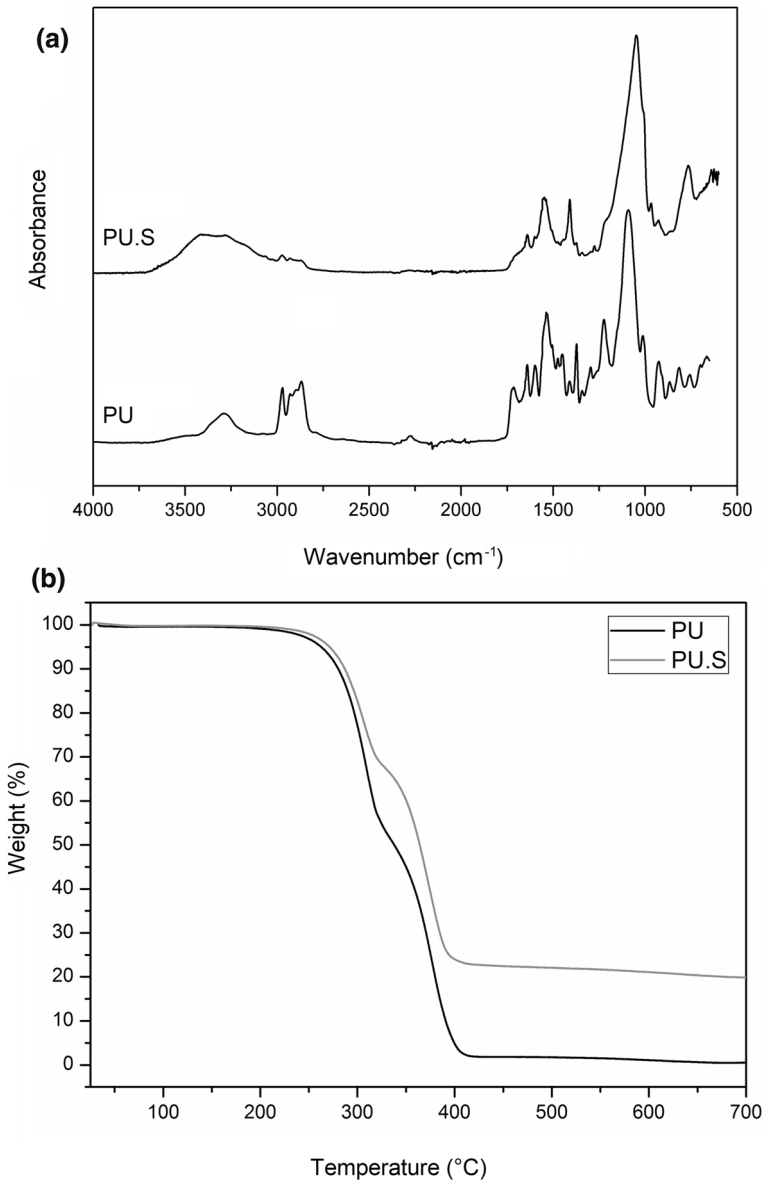
Fig. 5 Analyses of PU foams before and after organosilane coating on: **a** FTIR spectrum and **b** TGA
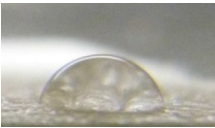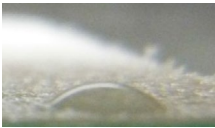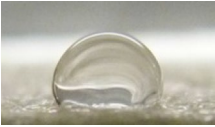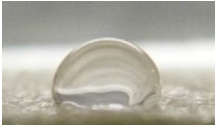
of the isocyanate and alcohols bonds. In the second stage, the flexible segments of polyol are degraded. After coating the PU foam with organosilane, there is an increase in ash content after exposure to the thermal degradation test. This is due to the coating layer composed of silicate groups that do not completely degrade at the temperature at which the material is exposed.

The hydrophobic characteristics of the PU foams were determined by measuring the contact angle of their sample surfaces with water (polar liquid), which is defined as the angle between the solid surface and the tangent line of the liquid phase at the interface of the solid phase. Table 3 shows the contact angle values of PU3 foams. In the PU that is not treated with organosilane, the contact angle at time zero ($t=0$) was 77.8°. The contact angle obtained in the silanized PU sample was 110.2° at time $t=0$. After the 5 min of the test, the water droplets in the silanized PU foam demonstrated a slight decrease in the contact angle in relation to $t=0$, probably due to the migration of water into the porous structure [34]. Chemically untreated foam showed a greater movement of water into the foam's core after 5 min. When a water droplet placed on the PU foam substrate, the water immersed into its matrix quickly, while for PU foam coated with organosilane, the water droplet did not penetrate into its matrix completely because the organosilane increased the hydrophobicity of the foam. According to Cunha et al. (2010) [35], the hydrophobicity of a material can be evaluated when the contact angle of the water droplet on the material surface is greater than 90°, so that it can be defined as hydrophobic. Assuming that water is a fluid, higher the contact angle, greater is the hydrophobicity. Consequently, a higher contact angle increases the selectivity and the interaction of the foam with oil, allowing for greater efficiency in the removal of oil in a heterogeneous water–oil system and for performing important steps in the beginning of the sorption process of the same [34].

Figure 6 shows the graph of the static sorption capacity of silanized PU foams with varying densities with respect to different types of oil (without water). The sorption capacity of foams without the organosilane coating was not quantified because of the difficulty in infiltrating the oil into the foam structure and submerging it in the oily medium. This phenomenon is associated with the surface tension of the oil and with the chemical affinity of the foam, and it can be observed in Fig. 7.

Tanobe (2007) [11] mentions that the surface tension of a liquid is directly related to the wettability of different substrates. In a porous medium, the greatest wettability will be of the liquid whose surface tension quotient and viscosity is higher, for the same temperature. With an increase in the degree of hydrophobicity of the

Table 3 PU foam surface contact angle before and after chemical treatment with organosilane

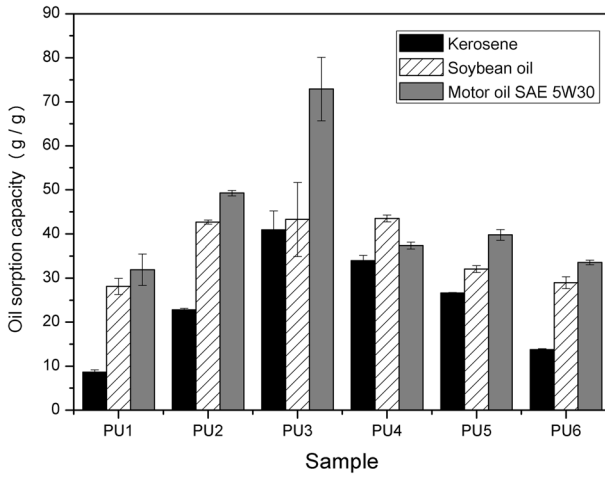| Sample	Contact angle (t=0 min)		Contact angle (t=5 min)	
PU		77.8°		49.5°
PU/silane		110.2°		105.7°

Fig. 6 Static sorption capacity of PU foams with different types of oils
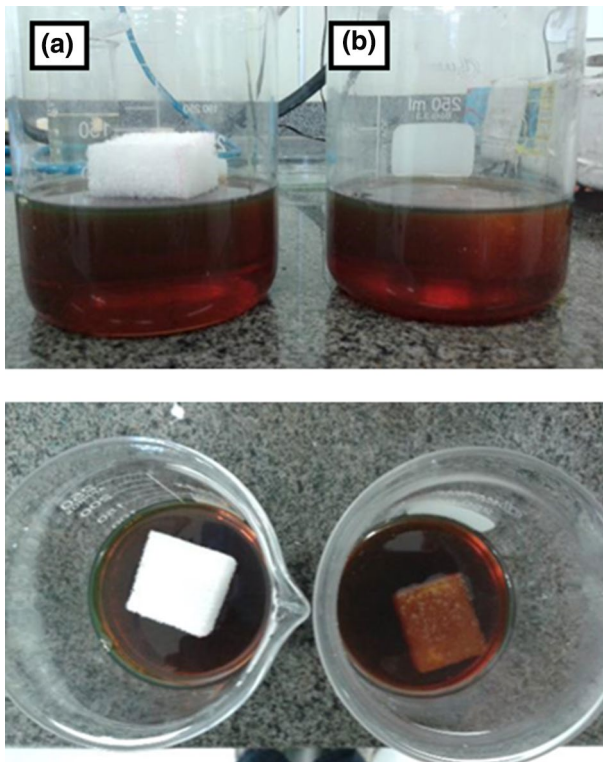

Fig. 7 Sorption test of PU3 foams in SAE 5W30 oil using **a** foam without chemical treatment and **b** with chemical treatment

foam after the chemical treatment with organosilane, the effect of the surface tension is reduced. Since both phases have greater chemical interactions, coating the foam with the organosilane allows for faster infiltration capacity of the oil, when compared to uncoated foam. The same effect was reported by Liu et al. (2013) [16] in which they observed that graphene-coated PU foams have a faster infiltration capacity when compared to conventional PU foams. Conventional PU foams (with no external force) were not completely submerged in oil even after 24 h of exposure, whereas hydrophobic coating PU foams took only 20 to 40 s for total immersion in oil. This phenomenon was attributed to the higher oleophilicity of the graphene-coated foam, which have more chemical affinity with the oils.

By analyzing the data from Fig. 6, it is observed that more viscous oils lead to a higher sorption capacity of PU foams. This phenomenon is mainly attributed to the desorption capacity of oil after the withdrawal of the system. Highly viscous oils are more difficult to drain out of the foam and require more time for desorption, so a greater amount of oil is trapped inside the foam. As the desorption time in the experiment was set at 30 s for all samples, it was expected that the foams would demonstrate a higher sorption capacity for more viscous oils. Tanobe (2007) [11] pointed out that the sorption process efficiency is directly influenced by the viscosity of the oil, that is oils with high viscosity have greater anchorage and retention in porous polymer systems compared to less viscous oils. However, it must be considered that more viscous oils may require more time to migrate into the porous structure. Figure 6 shows that the sorption capacity of the lower viscosity oil (kerosene) and higher viscosity oil (SAE 5W30) is attributed to the PU3 sample. Oils with intermediate viscosity, as in the case of soybean oil, samples PU2, PU3 and PU4 presented similar results.

Lower the density of the foam, greater is the fraction of the volume available to fill with oil. However, it is necessary to consider that a smaller contact area between the solid fraction of the foam and the oil may impact the efficiency of the adsorption phenomenon of the oil on the polymeric surface of the foam. The distribution and cell size and porosity of foams are fundamental parameters in choosing an ideal sorbent that is suited to the type of oil that needs to be collected. Variation in oil viscosities (high and low viscosity) can impact the efficiency of the sorbent during the oil desorption process.

Low-density foams have a lower solid fraction by volume, that is, larger cells and a small number of cells, leading to a lower contact area. These characteristics could favor their use as sorbents for high viscosity oils, as they facilitate the migration of oil into the foam interior and favor its absorption in the sorbent system. Owing to a more closed porous network (larger numbers of cells that are smaller in size), high-density foams will require a longer sorption time for the total migration of more viscous oils into the foam interior. Therefore, high-density foams are best suited for the collection of low-viscosity oils, such as fuels, kerosene, among others. The greater contact area promoted by the higher fraction of solids by volume in high-density foams favors the phenomenon of adsorption and retention of the low-viscosity oil inside the foam.

In order to determine the sorbent efficiency, there is a need to calculate the maximum theoretical sorption capacity (MTSC)—Eq. 3, which corresponds to the total

available volume inside the foam core for filling the porous structure (solid fraction) of the foam with oil. Thus, the volume available in the fraction of voids inside the foams with different densities was considered. However, it is necessary to emphasize that some other phenomena with respect to oil collection were disregarded in this equation, such as the desorption time of the oil after the removal of the foam from the system, the oil on the surface of the foam, and the viscosity of the oil. In this sense, Eq. 3 proposes to determine the foam void content and the maximum theoretical sorption capacity.

$$\text{MTSC} = \frac{\left[v_f \times \rho_o \times \left(1 - \frac{\rho_f}{\rho_{sp}} \right) \right] - m_f}{m_f} \tag{3}$$

where MTSC is the maximum theoretical sorption capacity ($g.g^{-1}$), V_f is the foam volume (cm^3), ρ_o is the density of the oil ($g.cm^{-3}$), ρ_f is the foam density and ρ_{sp} is the density of the solid polymer ($g.cm^{-3}$). The density of the solid polymer was previously measured, assuming that a value of 1.05 $g.cm^{-3}$ for solid PU and m_f is the theoretical mass of the foam.

Based on this, Table 4 presents the data of the theoretical sorption capacity of the foam, the mean value of sorption obtained experimentally and the calculation of the sorption efficiency with respect to theory and experiment. As expected, the lower-density samples showed low sorption efficiency, mainly as a function of their cellular structures. A larger cell size and a low contact area of the solid fraction, which may affect the adsorption phenomenon, increased the desorption rate after removal of the sorbent of the oily medium. In some cases, such as the PU3 to PU6 samples, the sorption efficiency exceeded the limit of 100% of the volume available for oil occupancy within the void fraction of the foam because the oil adhered to the outer surface of the foam proof body. This phenomenon became more pronounced with oils of higher viscosity.

Table 4 Efficiency of theoretical and experimental sorption capacity

	PU1	PU2	PU3	PU4	PU5	PU6
Kerosene						
MTSC (g/g)	82.1	71.1	64.9	32.9	27.7	19.5
SC (g/g)	8.6	22.8	40.9	33.9	26.6	13.7
Efficiency (%)	10.5	32.1	63.0	103.0	96.0	70.2
Soybean oil						
MTSC (g/g)	95.9	83.1	75.9	38.5	32.4	23.0
SC (g/g)	28.1	42.6	43.3	43.4	32.0	29.0
Efficiency (%)	29.3	51.2	57.7	112.7	98.8%	126.0
SAE 5W30						
MTSC (g/g)	90.6	78.5	71.6	36.4	30.6	21.7
SC (g/g)	31.9	49.2	72.9	37.6	39.7	33.5
Efficiency (%)	35.2	62.7	101.8	103.2	129.7	154.4

Figure 8 shows sorption capacity per cycle (reusability) for PU3 sample. It was observed that, at the beginning of the test (cycle 1), sorption capacity is similar to the static sorption capacity, as shown in Fig. 6. In cycle 3, the sample has an increase in the sorption capacity. According to Fenner et al. (2018) [36], this phenomenon is due to foam structure having mixture of open and closed cells, and by forcing the oil removal by compression, the film in the pore of the cell split, increasing the number of connected cells, thus favoring the passage of oil through the structure as well as filling it with oil. After 50 cycles, the sample begins to show a decrease in the sorption capacity, probably due to the deterioration of the PU foam skeleton structure. At the end of 100 cycles, the sample showed a reduction of 17.6% of oil sorption capacity compared to the initial measurement.

The data presented in Fig. 7 and Table 4 express the sorption capacity in gram of oil per gram of sorbent, that is, with an increase in foam density, the sorption capacity tends to decrease. This is due to an increase in the mass of the sample (specimens with constant volume) that is directly related to the sorption capacity of the foam. Thus, the oil collection capacity per unit volume of the sorbent (specimen) is shown in Fig. 9, with the amount of oil collected measured in grams per specimen, having the same dimensions ($25 \times 25 \times 25$ mm).

It is observed that the highest oil collection capacity of the PU foam is for the oil of higher viscosity (SAE 5W30), and in this analysis the sample that presented the highest collection capacity is PU5. For kerosene, the highest oil retention was observed in the PU4 sample, and for the soybean oil, the highest oil collection capacity was also observed in the PU4 and PU5 samples. In the PU1 sample, the kerosene sorption and collection capacity were lower than the other samples.

Figure 10 presents the oil collection capacity (SAE 5W30) in the dynamic sorption test (water and oil). Higher oil collection capacity was observed in the PU3 sample, probably due to the ease of migration of the oil into the system due to the low exposure time (1 min) of the foam in the agitated water and oil
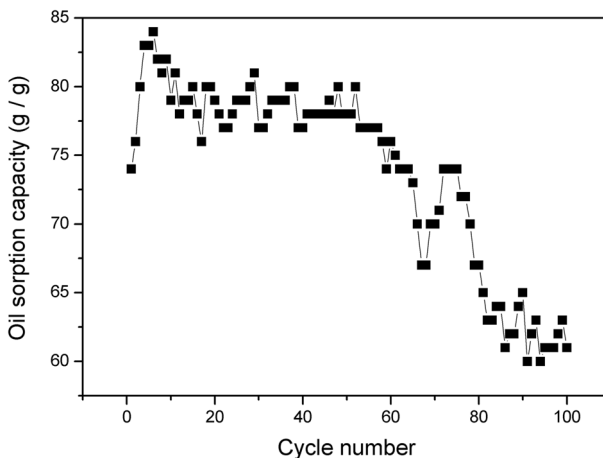

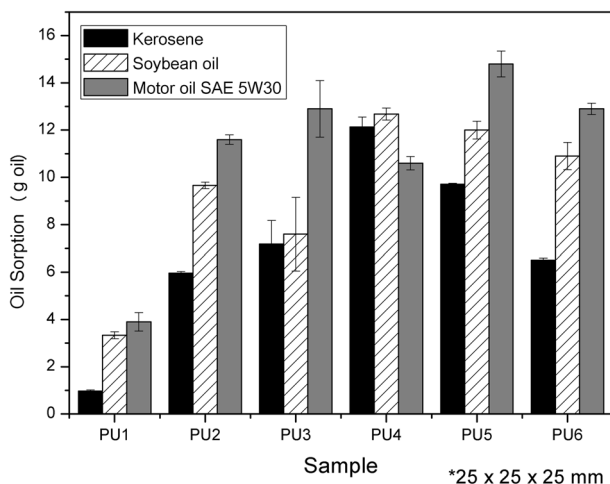**Fig. 8** Reusability of PU3 sample with SAE 5W30 oil

Fig. 9 Quantity (g) of oil collected by sample of PU foam after sorption test
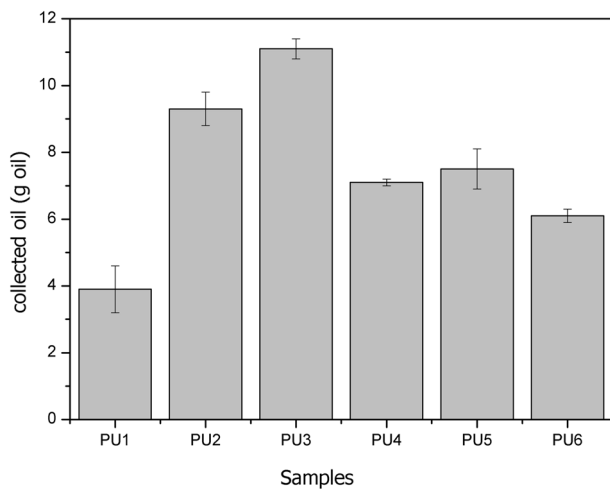

Fig. 10 Quantity of oil collected in the dynamic sorption test

system. In all the samples, the amount of water withdrawn together with the sorbent oil was less than 0.5 g. It was not possible to observe the total oil collection capacity in any of the PU samples, that is, the collection of 12 g (100%) of oil, because small fractions of the oil adhered to the wall of the beaker during the test and a fraction of the oil was retained in the solid structure of the PU foam after the removal of the oil from the foam by compression.

Conclusions

The efficiency of the oil sorption capacity of the foam is directly associated with its density and cell structure, as well as with the viscosity of oil. In general, higher the PU foam density (as a function of the smaller fraction of voids within the porous structure of the foam), lower is the sorption capacity. However, low-density foams usually have larger cells resulting in lower sorption capacity and poor oil collection due to the ease of desorption and flow of the oil after the removal of the foam from the oily medium. Chemical treatment increases the selectivity of the foam to the oil, thereby facilitating the immersion of the PU foam in the oleophilic medium, as compared to the non-coated organosilane PU foam. The foam composition with the highest sorption capacity (g oil/g sample) was PU3, while the samples with the highest oil collection capacity (oil collected by test specimen) were PU4 and PU5 samples. In the dynamic sorption test, all samples demonstrated low sorption of water and the sample with higher sorption efficiency was PU3.

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