


Post-Consumer Polyurethane Foams Hydrophobization Through Surface Modifications for Oil Spill Sorption

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To increase oil sorption, polyurethane foams were modified with MoS₂, ZnO grafting and/or hexadecanoic acid coating. The foams were characterized by Scanning Electron Microscopy + Energy Dispersive X-ray Spectroscopy and Contact Angle techniques. Three sorption tests were performed. In tests with 100% water, the ZnO-PC modification showed a reduction of 35.7% in the seawater sorption when compared to Un-PC. In tests with 100% oil, there was a 29-fold increase in sorption (more than 2803%) of S46 lubricant oil when Un-PC performance was compared with ZnO-PC. In tests on the multicomponent systems, the lowest seawater sorption was 0.01 ± 0.00 g.g⁻¹ (HA-PC), 0.08 ± 0.01 g.g⁻¹ (Un-PC), and 1.39 ± 0.02 g.g⁻¹ (Un-PC) for 20W40 engine oil, S46 lubricating oil, and diesel, respectively. The highest oil sorption in the systems was 41.34 ± 1.02 g.g⁻¹ (HA-PC), 32.81 ± 0.31 g.g⁻¹ (MoS₂-PC), and 14.78 ± 0.27 g.g⁻¹ (ZnO-PC) for diesel, S46 lubricating oil, and 20W40 engine oil, respectively. The reuse tests indicated that even after 10 cycles, the ZnO-PC foam kept its sorption capacity unchanged. Post-consumer foams proved to be effective in the sorption of different oils spilled into seawater, especially those grafted with ZnO rods or impregnated with MoS₂.

Keywords: Oil pollution, Oil spills, Polyurethane foams, Reduce, reuse, recycle.

1. Introduction

Offshore oil exploration is fundamental to maintaining and developing the global economy. Advanced technology is present from exploration to the transport of extracted oil. However, as in all major industrial processes, accidents might happen. In recent decades Brazil¹ and other countries² have faced oil spill catastrophes into the sea, which causes irreparable damage to different biomes.

Different methods can be used to contain and capture the spilled oil depending on its type, quantity, and weather conditions, among other factors. Some methods use surface collectors to separate the oil from seawater, and other more extreme methods consist of burning oil under proper conditions³. More recent studies have focused on materials capable of absorbing the oil in their own structure, such as cotton fibers⁴, or even in porous structures, such as polymeric foams⁵, for example.

Using porous structures to recover oil in water has chemical affinity as the main challenge. Foams, for example, may have an affinity for both water and oil. However, it is possible to change this behaviour through techniques such as grafting or coating, for example. Grafting foams with ZnO nano and micro rods might improve the attraction for non-polar structures due to Van Der Waals forces, as well as coating foams with long-chain carboxylic acids, such as hexadecanoic acid, might increase oil selectivity⁶.

Brazil faces serious problems related to recycling and waste treatment. Post-consumer polyurethane foams, mainly from mattresses, can be seen discarded in vacant properties throughout all major cities due to the lack of public action, inspection, and punishment. Since 2014, Brazil has produced

more than 1 million m³ of new polyurethane foam per day, which increases the need for studies on its recycling and reuse after its commercial life⁷. Although research on alternative applicability for new polyurethane is common^{8,9}, there are still few viable proposals for using post-consumer foam. The use of post-consumer polyurethane foams as sorbents has not been reported so far.

This work presents innovation and originality by using polyurethane foam obtained from discarded mattresses as sorbent for oils spilled in seawater. Here, post-consumer polyurethane foams are removed from the environment, recycled through simple and inexpensive surface modifications, and reused to separate oils in seawater. In this way, two apparently unrelated problems are addressed: one residue is used to remove another.

2. Material and Methods

2.1. Materials

A 100% polyurethane mattress with a density of 18 kg.m⁻³ was purchased from a national supplier. A post-consumer mattress with the same characteristics as the new one was obtained from an irregular disposal area. There was no visible damage or compaction, but there were characteristic time-of-use stains, likely from urine and/or sweat, as well as dust and hairs. Samples of both foams were cut into 1 cm x 1 cm x 1 cm cubes and washed multiple times with distilled water and 70% ethanol. Seawater was obtained directly from the Atlantic Ocean (5° 52' 52" S, 35° 10' 16" W) in Natal, Brazil, and filtered on blue band filter paper to remove suspended solids. Diesel, S46 lubricating oil, and 20W40 engine oil were

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purchased from a national fuel chain. Turpentine solvent was purchased at a local supermarket. Anhydrous ethanol, methanol, zinc acetate dihydrate, zinc nitrate hexahydrate, hexamethylene-tetramine, hexadecanoic acid (HA), hexane, molybdenum disulfide (MoS_2), and potassium hydroxide were purchased from Dinâmica Química Contemporânea, Brazil. All analytical reagents were used as received.

2.2. ZnO grafting

Zinc oxide (ZnO) rods were synthesised in two steps adapting the classic sol-gel route⁶. For the first, the pH of a 100 mL solution of $0.1 \text{ mol}\cdot\text{L}^{-1}$ zinc acetate dihydrate in methanol was raised to a range between 10 and 11 with a $1 \text{ mol}\cdot\text{L}^{-1}$ potassium hydroxide solution in methanol, monitored with a pH meter (PH009, B-MAX, China). The resulting solution was stirred at 510 rpm for 80 min in a mechanical stirrer (TE-139, Tecnal, Brazil). At 65 min, 15 mL of distilled water were added to the system still under agitation. The contents were centrifuged (Sorvall ST 16/16R, Thermo Scientific, Germany) at 3500 rpm for 10 min. The supernatant was discarded, and the precipitate was resuspended with distilled water and methanol for purification. The centrifugation and cleaning process was carried out thrice. The precipitate was resuspended in 200 mL of distilled water at the end of the washing. The foam cubes were submerged for 5 min. After light compression, the foams were cured in an oven (E099EV, FANEM, Brazil) at 170°C under a vacuum of $9.14\cdot 10^4 \text{ Pa}$. The submersion and curing process was repeated thrice.

In the second step, 100 mL of $0.03 \text{ mol}\cdot\text{L}^{-1}$ zinc nitrate hexahydrate solution were mixed with 100 mL of $0.03 \text{ mol}\cdot\text{L}^{-1}$ hexamethylenetetramine solution. The foams from the first stage were immersed in the resulting solution, and the system was kept in a water bath (TE-184, Tecnal, Brazil) at 85°C for 3 h. At the end of the process, the foams were washed with distilled water and dried in an oven at 60°C .

2.3. HA coating and ZnO grafting/HA coating

In a beaker, 200 mL of a $1\cdot 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ solution of HA in ethanol was prepared. The foams cubes were submerged for 48 h in the solution inside a sealed flask to avoid solvent evaporation. Afterwards, the foams were washed with 70% ethanol and oven-dried at 60°C .

Foams grafted with ZnO were submitted to the coating proceeding above with HA resulting in a combination of modifications.

2.4. MoS_2 deposition

In a 500 mL Erlenmeyer flask capped, 200 mg of molybdenum disulfide was dissolved in 200 mL of anhydrous ethanol. The solution was stirred at 1550 rpm in a magnetic stirrer (QUIMIS, model Q261A21, Brazil) for 48 hrs. The resulting solution was poured into a 250 mL beaker and the foams were inserted and kept submerged for 5 min. Then, they were dried in a vacuum oven (FANEM, model E099EV, Brazil) for 12 min at 170°C under a vacuum of $9.14\cdot 10^4 \text{ Pa}$. The entire process from foam insertion was repeated 3 times to improve MoS_2 fixation, according to methodology adapted from Gao et al.¹⁰.

2.5. Sorption capacity test

The sorption tests were adapted from ASTM F726-12: Standard Test Method for Sorbent Performance of Adsorbents¹¹. The test for determining the amount of water/oil sorbed was adapted from ASTM D95-13: Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation¹².

2.5.1. Water sorption

In this test, new and post-consumer polyurethane foam cubes were pre-weighed (S_{PU}) and then individually inserted into 100 mL Erlenmeyer flasks filled with 50 mL of water. In triplicate, the Erlenmeyer flasks were shaken for 15 min at 150 rpm in a Kline-type shaker (KLA-210, Satra, Brazil). At the end of the agitation, the system was left to rest for 2 min. The PU cubes were removed from the Erlenmeyer flasks with metallic tweezers and allowed to drain for 30 s before being weighed ($S_{\text{PU+W}}$) on a tared analytical scale (2104N, Marconi, Brazil). The amount of water sorbed was calculated according to the following equation:

$$\text{Water sorption} (\text{g}\cdot\text{g}^{-1}) = \frac{S_{\text{PU+W}} - S_{\text{PU}}}{S_{\text{PU}}} \quad (1)$$

where S_{PU} is the initial PU cube dry weight and $S_{\text{PU+W}}$ is the weight of PU cube + water sorbed.

2.5.2. Oil sorption

Pre-weighed PU foams (S_{PU}) were added in 100 mL beakers with half of their capacity filled with the oil to be tested. The foams were allowed to float freely in the oil for 30 min before being removed with metal tweezers. The foams were kept suspended for 30 s to drain the excess of oil before being weighed ($S_{\text{PU+O}}$). Diesel, S46 lubricant oil, and 20W40 engine oil were tested. The tests were performed in triplicate. The amount of oil sorbed was calculated according to the following equation:

$$\text{Oil sorption} (\text{g}\cdot\text{g}^{-1}) = \frac{S_{\text{PU+O}} - S_{\text{PU}}}{S_{\text{PU}}} \quad (2)$$

where S_{PU} is the initial PU cube dry weight and $S_{\text{PU+O}}$ is the weight of PU cube + oil sorbed.

2.5.3. Water–oil system sorption

In this test, new and old PU foam cubes were pre-weighed (S_{PU}) and then individually inserted into 100 mL Erlenmeyer flasks filled with 4 g of oil and 46 g of water (a 2 mm layer of oil). In triplicate, the Erlenmeyer flasks were shaken for 15 min at 150 rpm in a Kline-type shaker (KLA-210, Satra, Brazil). At the end of the agitation, the system was left to rest for 2 min. The PU cubes were removed from the Erlenmeyer flasks with metallic tweezers and allowed to drain for 30 s before being weighed ($S_{\text{PU+W+O}}$).

Each PU cube was transferred to a respective distillation flask connected to a condenser and a trap (Dean-Stark), according to ASTM D95¹². 100 mL of turpentine were added to the distillation flask. The boiling continued until there was no change in the distillation trap's graduated scale. The volume of water sorbed was read directly on the graduated scale and converted to base mass through density (S_{W}). Diesel, S46 lubricant oil, and 20W40 engine oil were tested.

The oil sorption in water–oil system (S_o) was calculated according to the following equation:

$$S_o = S_{PU+W+O} - S_{PU} - S_w \quad (3)$$

where S_{PU} is the initial PU cube dry weight; S_w is the weight of water sorbed; S_{PU+W+O} is the entire system weight, and S_o is the weight of oil sorbed.

2.6. Desorption and reusability

After sorption tests on water–oil systems, the desorption and reuse capacity of the foams were analyzed. The foams were pressed through a vise tool (BVV3, Vertex, Taiwan) with a pressing force of 1300 kgf to desorb the water/oil. After pressing, the foams were resubmitted to the water–oil sorption test repeatedly. The foam volume was also monitored to evaluate deformation that might happen after several cycles.

2.7. Characterization

The morphology of new and post-consumer, modified and unmodified PU foams was analyzed by Scanning Electron Microscopy (SEM) after previous gold coating and the chemical elements were semi-quantified by Energy Dispersive X-ray Spectroscopy (EDS) (JSM - 6610LV, Jeol, Japan). Hydrophobic and oleophilic characteristics were analyzed in a Drop Shape Analyzer (DSA 100, Kruss, Germany).

The bulk density for new and post-consumer foam before modifications was determined according to the following equation¹³. The weight was determined on an analytical scale and the measurements were taken using a caliper. The test was conducted in triplicate.

$$\text{Density} = \frac{m}{l \cdot w \cdot h} \quad (4)$$

where m , l , w , and h are the weight, length, width, and height of the samples, respectively.

All data from this work were processed using Statistica 7.0 statistical software. The effects caused by the treatments were analyzed using Analysis of Variance (ANOVA). All assumptions of the statistical model were verified in advance (independence, normality and homoscedasticity).

3. Results and Discussion

3.1. Modifications

The graft allowed the ZnO rods to interact with the polyurethane structure. During growth, hydrogen bonds were formed between the polyurethane molecule and ZnO rods, as shown in Figure 1. The connection between ZnO and H reduces the strength of the hydrogen bond between H–N in the polyurethane. A powerful bond forms when H is chemically connected with F, O, and N. Since the modification goal is to reduce the polarity of polyurethane foam, decreasing the H–N straight is essential. Dorraji et al.¹⁴ and Rahman¹⁵ also associated the preference for ZnO to bond with the N–H groups in different polyurethanes, either during the synthesis process or as a graft.

The modification order interferes with the interaction for the combined modification ZnO/HA. As the graft with ZnO occurs first, followed by the coating with hexadecanoic acid (HA), the second interacts preferentially with the first. Segovia et al.¹⁶ studied the ability of ZnO to form sheets with organic compounds, especially with carboxylic acids. There is believed to be an induced-dipole attraction between the carboxyl radical of organic acids and the metallic part of inorganic structures. The same observation was made by Trino et al.¹⁷, who identified the preference of groups with greater intermolecular strength in organic molecules (carboxyl) for interactions with ZnO. The theoretical model of these connections is illustrated in Figure 1.

In the coating modification, interactions between HA and polyurethane are direct and controlled by dipole-induced forces. The polyurethane coating process with HA allowed adequate fixation of this acid, which will be responsible for promoting interactions with the oils to be absorbed.

Pore impregnation with molybdenum disulfide has a simple mechanism, as shown in Figure 1. The laminar structure of MoS₂ interacts with the covalent bonds of the polyurethane, weakening its polarity. This attraction is purely by intermolecular forces of the Van Der Waals type. Once fixed in the foam pores, the MoS₂ sheets, connected and attracted to each other by dipole-induced force, are simultaneously able to repel water while attracting non-polar substances, such as oils, for example. The same behavior was observed in a study by Gao et al.¹⁰

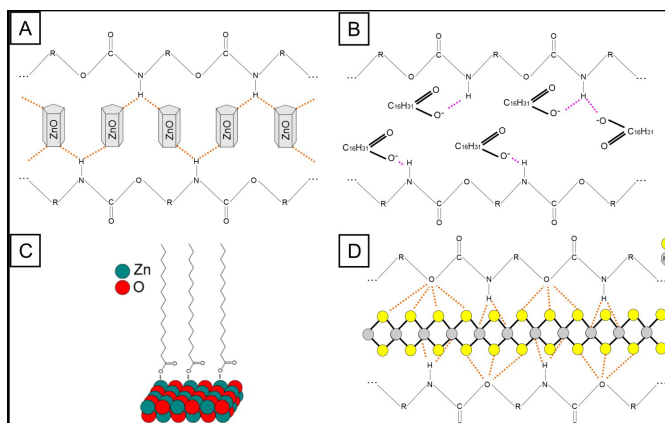


Figure 1. Illustration of the mechanism for polyurethane modification with: ZnO grafting (A), coating with HA (B), ZnO grafting followed by coating with HA (C), and deposition with MoS₂ (D).

3.2. SEM + EDS

The SEM images in Figure 2 show that both new (Un-N) and post-consumer unmodified foams (Un-PC) have similar structures with well-defined pores and channels. As expected, the HA coating process on new (HA-N) and post-consumer (HA-PC) foams did not change its structure. The ZnO graft slightly altered the surface of both new (ZnO-N) and post-consumer (ZnO-PC) foams, a fact evidenced by the presence of ZnO crystals and rods (zoomed-in Figure 2). The rods have variable sizes, from nanometers to measures greater than 1 micrometer.

The combined process of coating and grafting on new (ZnO/HA-N) and post-consumer (ZnO/HA-PC) foams produced less surface alteration if compared to the grafting process alone. There is less exposure of the rods, probably caused by the HA coating that covered the ZnO rods (which might interfere with its hydrophobic/oleophilic action). As seen for ZnO-N and ZnO-PC, MoS₂-N and MoS₂-PC also changed the PU structure from smooth to rough after the deposition of transition metal dichalcogenide particles. It was possible to observe the presence of molybdenum crystals fixed on the surface of the foams with an average size of 3 micrometers (zoomed-in Figure 2).

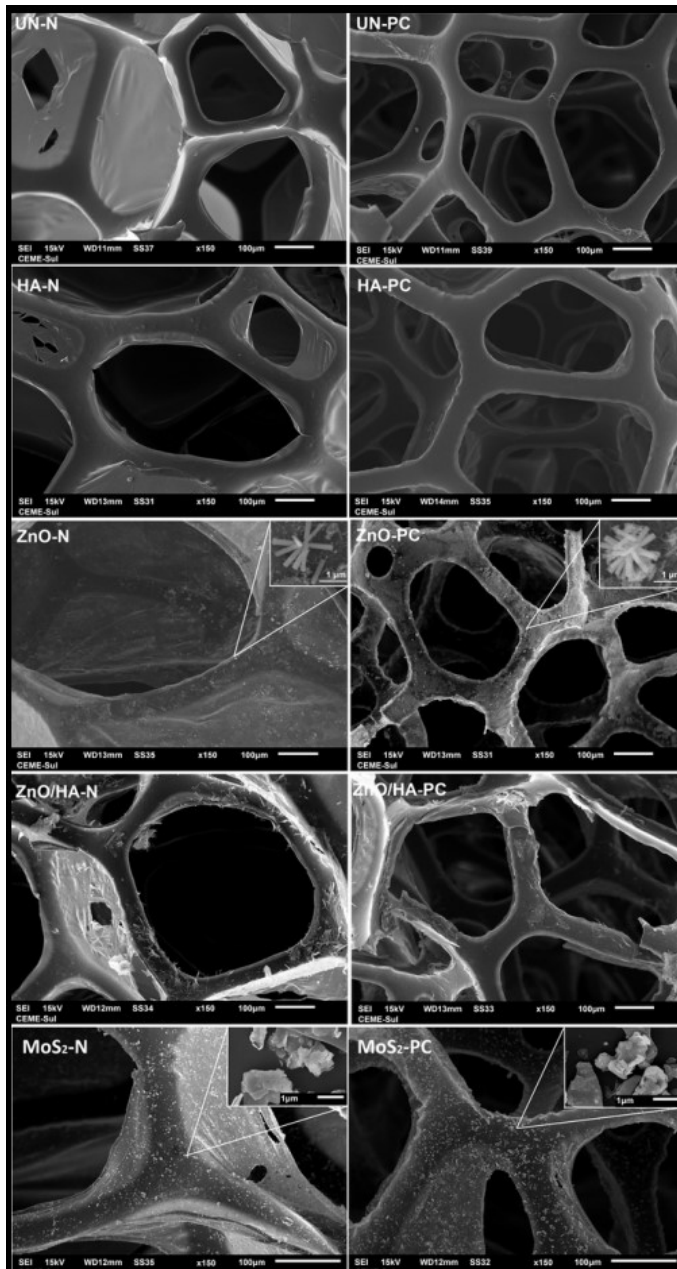


Figure 2. SEM images of the PU foams: unmodified (Un) new (N) and post-consumer (PC); coated with HA; grafted with ZnO (highlight for ZnO rods); with combined modification of grafting ZnO + coating HA; with deposition of MoS₂ (highlight for Mo particles).

The EDS analysis transcribed in Table 1 identified the presence of C, N, and O in all situations, which was expected since the molecules present in polyurethane have several chemical bonds with these basic elements, in addition to H, which is not identifiable due to limitation of the technique employed. Although not part of the reagents used in the PU synthesis, Ca was detected in all foams. This is due to the use of CaCO_3 during synthesis as a “filler” to increase foam density. As expected, the modifications that used ZnO graft showed a strong presence of Zn, while not even a trace of Zn was identified in the others. The same occurred for foams modified with MoS_2 , which were the only ones where S and Mo were detected.

3.3. Surface Tension Analyzer

The seawater contact angle shown in Figure 3 was calculated to determine the hydrophobicity of modified and unmodified foams. The same was performed using S46 lubricating oil to evaluate the oil affinity. The contact angle calculation was done after 5 s of contact between the 5 μL of liquid and the foam's surface.

For the S46 lubricating oil, Un-N presented an angle of 77.3° and Un-PC 82.2°, while for seawater the angles were 90.1° and 104.4°, respectively. This suggests that both new and post-consumer unmodified foam should be poorly attracted to oil but too attractive to seawater since the closer to 180°, the lower the seawater sorption and the closer to 0°, the greater the oil sorption¹⁸. All modified foams in contact with lubricant oil showed a contact angle of 0° after 5 s, which means that all the oil deposited on the foam surface was sorbed due to the success in increasing the oil affinity.

If compared with unmodified foams, the modification with HA was practically irrelevant in terms of hydrophobization/contact angle: from 90.1° (Un-N) to 92.5° (HA-N) and from 104.4° (Un-PC) to 107.7° (HA-PC).

For the modification with zinc rods, the results showed a considerable increase in hydrophobization if compared to the unmodified foams, reaching up to 124.6° (ZnO-N) and 121.3° (ZnO-PC). The difference in seawater and S46 lubricating oil drops' sphericity is notable in the highlights of Figure 3. While ZnO-PC foam showed oil affinity by absorbing the S46 lubricating oil drops and hydrophobicity by repelling the spherical-shaped seawater drops, Un-PC showed the opposite behavior. The increase in oil affinity and hydrophobicity of the foams obtained from grafting with Zn rods was caused by the increase in the roughness of the polyurethane surface. Li et al.⁶, using a similar mechanism of grafting Zn rods to new polyurethane foams, were able to improve the contact angle from 98° (Un-N) to 143.3° (ZnO-N), an increase of 45.3° (against 34.5° of this present work).

For the combination of modifications, the new foam achieved an angle of 125.5°, which was very close to that observed for the single modification with Zn rods. In the post-consumer foam, the combination of modifications produced an angle of 114.9°, which was significantly lower than that observed for the single modification with Zn rods. As for MoS_2 modification, the increase in hydrophobicity was more significant for MoS_2 -N than MoS_2 -PC (30.1° and 8°, respectively).

Table 1. EDS for the main elements identified in the foams.

Weight %	C	N	O	Ca	Zn	S	Mo
Un-N	31.03	22.41	40.56	6.00	-	-	-
Un-PC	37.80	16.40	43.11	2.70	-	-	-
HA-N	38.26	17.55	36.59	7.60	-	-	-
HA-PC	42.56	18.86	36.11	2.46	-	-	-
ZnO-N	13.46	1.88	4.47	1.80	78.39	-	-
ZnO-PC	5.15	0.60	1.85	0.60	91.80	-	-
ZnO/HA-N	32.50	9.36	16.15	2.17	39.82	-	-
ZnO/HA-PC	19.17	2.91	4.04	6.21	67.67	-	-
MoS_2 -N	43.61	7.71	12.94	2.04	-	24.24	9.46
MoS_2 -PC	23.00	5.90	6.97	1.74	-	34.44	27.95
Atom %	C	N	O	Ca	Zn	S	Mo
Un-N	37.61	23.30	36.91	2.18	-	-	-
Un-PC	44.45	16.54	38.06	0.95	-	-	-
HA-N	46.04	18.11	33.06	2.80	-	-	-
HA-PC	49.16	18.68	31.31	0.85	-	-	-
ZnO-N	40.58	4.87	10.11	1.01	43.43	-	-
ZnO-PC	21.44	2.13	5.79	0.46	70.18	-	-
ZnO/HA-N	53.61	13.24	20.00	1.07	12.07	-	-
ZnO/HA-PC	49.16	6.41	7.78	4.77	31.88	-	-
MoS_2 -N	61.46	9.31	13.69	1.07	-	12.80	1.67
MoS_2 -PC	45.69	10.05	10.39	1.30	-	25.62	6.95

3.4. Foams density

According to Vilar¹⁹, polyurethane foams with density ranging from 14 to 50 kg·m⁻³ are classified as flexible. These foams are produced from the reaction between polyol (triols with molecular weight between 3000-4000 and hydroxyl number between 40-56 mg KOH/g) and isocyanate (TDI - toluene diisocyanate). The reaction also contemplates the use of catalyst (tin octoate and amines), surfactant (silicone) and blowing agents (water and auxiliary agents).

Labels on both new and post-consumer foam confirm the density (18 kg·m⁻³) and composition (100% polyurethane - polyol x isocyanate), meeting the definition of flexible foam.

The new and post-consumer foams presented a bulk density of 17.72 ± 1.18 kg·m⁻³ and 18.97 ± 0.96 kg·m⁻³, respectively, with values close to those stated on the industrial label. Bulk density is directly linked to the volume of empty pores and can significantly vary between samples, as the pores in the foams are not uniform.

3.5. Water sorption capacity

The hydrophobization process is based on reducing the sorption capacity of water. In this way, the lower the water sorption, the more efficient the hydrophobization process is.

New modified and unmodified PU foams did not present a statistical difference for the sorption of distilled water, as shown in Figure 4. The same behavior was observed when using seawater. For the old foams, when compared to Un-PC, the ZnO/HA-PC modification showed a reduction of 28.5% in the sorption capacity of distilled water (from 9.98 ± 0.77 g·g⁻¹ to 7.13 ± 0.23 g·g⁻¹, respectively). For seawater, ZnO-PC (6.42 ± 0.33 g·g⁻¹) showed the best result with a 35.7% reduction in sorption when compared with Un-PC (9.98 ± 0.53 g·g⁻¹).

If the type of water used in the test is compared, in all cases the distilled water sorption was higher than the seawater sorption.

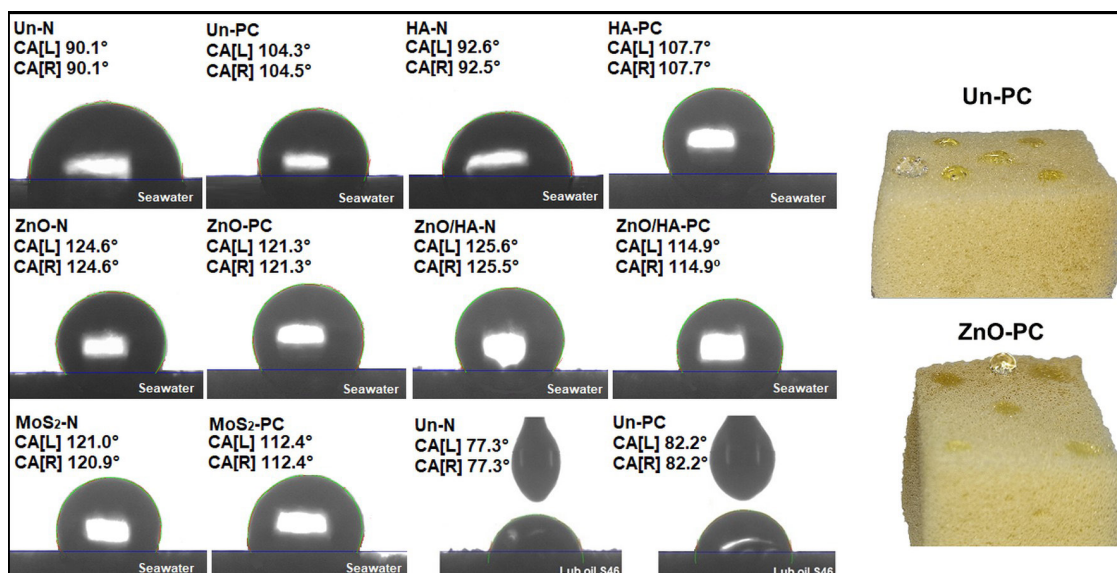


Figure 3. Contact Angle measurement between seawater's (or lubricant oil's) drops and the surface of the PU foams: unmodified (Un) new (N) and post-consumer (PC); coated with HA; grafted with ZnO; with combined modification of grafting ZnO + coating HA; with deposition of MoS₂. Highlighted Un-PC and ZnO-PC with drops of seawater and S46 lubricating oil on their surfaces.

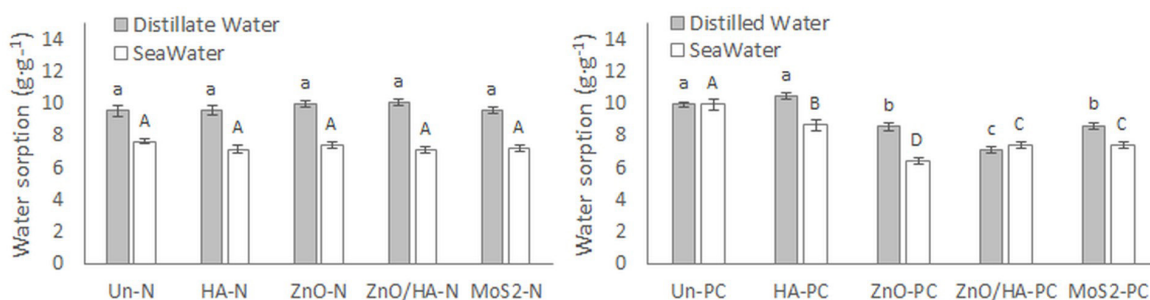


Figure 4. Distilled water and seawater sorption capacities (g·g⁻¹) in PU foams: unmodified (Un) new (N) and post-consumer (PC); coated with HA; grafted with ZnO; with combined modification of grafting ZnO + coating HA; with deposition of MoS₂. Identical lowercase (distilled water) and uppercase (seawater) letters at the top of the bars indicate no statistical difference in the Tukey test (p -value > 0.05) for each type of water among all foams.

3.6. Oil sorption capacity

In a system composed only of oil, the foams had different behaviors in terms of sorption capacity, as shown in Figure 5. Although the modifications applied to the foams proved to be relevant, the oil viscosity proved to be even more.

For both new and post-consumer foams, the coating with HA provided the best results for diesel sorption if compared to the other foams. The bond between the carboxyl radical from the hexadecanoic acid and the hydrogen atoms present in the polyurethane structure fixed the acid's long carbonic chain on the foam's surface (Figure 1). This chain is formed only by nonpolar C-H bonds and increases the oil affinity while decreasing the hydro affinity of the foams. Consequently, there was an improvement in the amount of diesel absorbed by the foam. Compared to the respective unaltered foams, the increase in diesel sorption was 3.64% and 15.96% for HA-N and HA-PC, respectively. Another factor that justifies the result for foams coated with HA lies in the low viscosity of diesel, which favored flow into the foam with very little resistance compared to other oils with higher viscosity and, consequently, greater resistance to flow.

In the system 100% S46 lubricating oil (~46 cSt), the sorption capacity ranged from $2.38 \pm 0.12 \text{ g}\cdot\text{g}^{-1}$ (Un-N) to $43.59 \pm 0.89 \text{ g}\cdot\text{g}^{-1}$ (ZnO-N) for new foams and from $1.46 \pm 0.02 \text{ g}\cdot\text{g}^{-1}$ (Un-PC) to $42.39 \pm 0.69 \text{ g}\cdot\text{g}^{-1}$ (ZnO-PC) for post-consumer foams.

In the 100% 20W40 engine oil system (~120 cSt), the sorption capacity ranged from $2.18 \pm 0.10 \text{ g}\cdot\text{g}^{-1}$ (Un-N) to $41.28 \pm 1.00 \text{ g}\cdot\text{g}^{-1}$ (ZnO-N) for the new foams and from $1.92 \pm 0.07 \text{ g}\cdot\text{g}^{-1}$ (Un-PC) to $41.36 \pm 0.91 \text{ g}\cdot\text{g}^{-1}$ (ZnO-PC) for post-consumer foams.

Among the types of foams and oils tested, the most significant increase in sorption capacity was for S46 lubricating oil sorbed into the post-consumer foam. Between Un-PC and ZnO-PC, there was a 29-fold increase in sorption (an increase of approximately 2803%).

Jamsaz and Goharshadi²⁰ evaluated the oil sorption capacity of unaltered PU. Among the oils tested, the PU foam was able to sorb about $4 \text{ g}\cdot\text{g}^{-1}$ of hydraulic oil and about $6 \text{ g}\cdot\text{g}^{-1}$ of crude oil. Considering that both oils have a viscosity between 10 ~ 100 cSt, the results are compatible with those determined in this work for lubricating oil S46 and engine oil 20W40.

3.7. Water–oil system sorption

Preliminary tests on water-oil systems were conducted to assess the influence of the type of water used: distilled or seawater. In the distilled water-oil system (data not shown), the behavior was statistically similar to that observed for the seawater-oil system (Figure 6). This indicated that the presence of salts and minerals in seawater did not cause a statistically significant difference in the sorption capacity of foams when compared to distilled water.

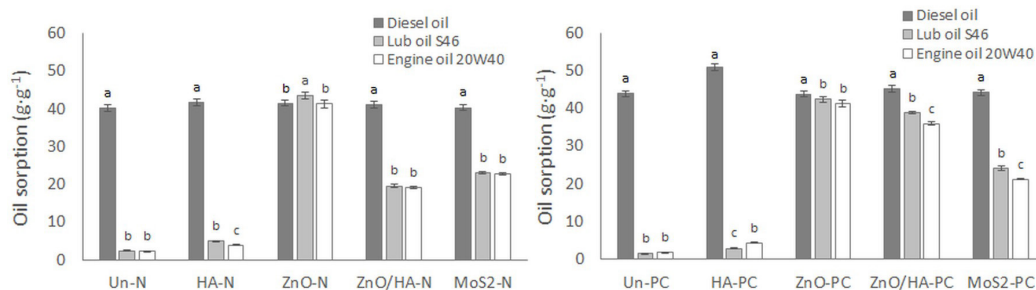


Figure 5. Oil sorption capacities ($\text{g}\cdot\text{g}^{-1}$) in PU foams: unmodified (Un) new (N) and post-consumer (PC); coated with HA; grafted with ZnO; with combined modification of grafting ZnO + coating HA; with deposition of MoS_2 . Identical lowercase letters at the top of the bars indicate no statistical difference in the Tukey test (p -value > 0.05) for the oils tested in each type of foam.

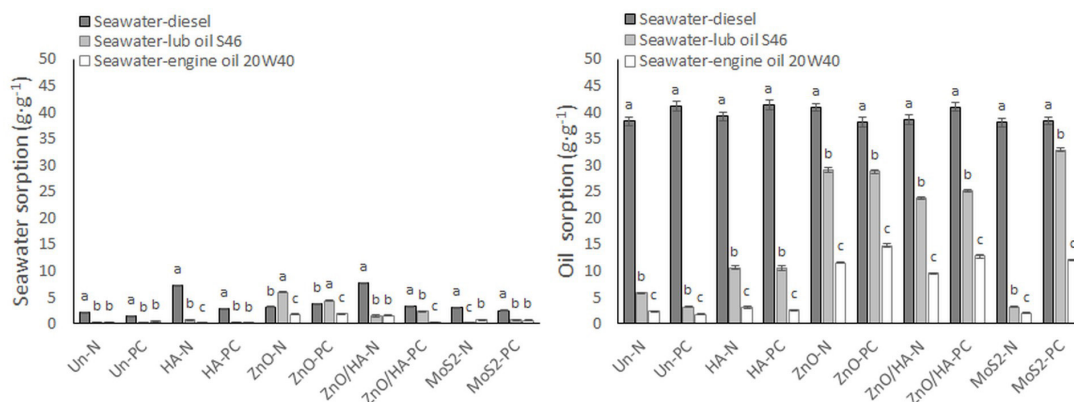


Figure 6. Seawater and oil sorption ($\text{g}\cdot\text{g}^{-1}$) for each seawater-oil system in PU foams: unmodified (Un) new (N) and post-consumer (PC); coated with HA; grafted with ZnO; with combined modification of grafting ZnO + coating HA; with deposition of MoS_2 . Identical lowercase letters at the top of the bars indicate no statistical difference in the Tukey test (p -value > 0.05) for the seawater/oils tested in each type of foam.

Among the new foams, the lowest and highest seawater sorption was $0.08 \pm 0.01 \text{ g}\cdot\text{g}^{-1}$ (HA-N in the seawater-engine oil system) and $7.64 \pm 0.12 \text{ g}\cdot\text{g}^{-1}$ (ZnO/HA-N in the seawater-diesel system), respectively. As for the post-consumer foams, $0.01 \pm 0.00 \text{ g}\cdot\text{g}^{-1}$ (HA-PC) and $1.93 \pm 0.07 \text{ g}\cdot\text{g}^{-1}$ (ZnO-PC), respectively, both in the seawater-20W40 engine oil system.

Oil sorption ranged from $1.81 \pm 0.10 \text{ g}\cdot\text{g}^{-1}$ (Un-PC) to $14.78 \pm 0.27 \text{ g}\cdot\text{g}^{-1}$ (ZnO-PC) in the seawater-20W40 engine oil and from $3.20 \pm 0.12 \text{ g}\cdot\text{g}^{-1}$ (Un-PC) to $32.81 \pm 0.31 \text{ g}\cdot\text{g}^{-1}$ (MoS₂-PC) in the S46 lubricant oil system, both for post-consumer foams. For diesel, the sorption was statistically uniform for both new and post-consumer foams, reaching up to $41.34 \pm 1.02 \text{ g}\cdot\text{g}^{-1}$ (HA-PC).

Regarding the type of oil used, viscosity played an essential role in the sorption capacity of the foams. Diesel oil has a low kinematic viscosity (4~5 cSt) and was sorbed by the foams in statistically identical amounts regardless of whether they were modified or not. The diesel oil penetrated the pores and channels of the foams facing no resistance.

When S46 lubricating oil was used, its viscosity (46 cSt), which is about 10 times higher than diesel oil, showed relative difficulty penetrating the foam pores and channels. Both new and post-consumer foams modified with ZnO rods obtained relevant results in the sorption of S46 lubricating oil. If compared with the Un-PC results, there was an increase of approximately 800% in the sorption capacity of S46 lubricating oil by ZnO-PC.

Similar behavior was observed for 20W40 motor oil with viscosity (120 cSt) about 25 times higher than diesel oil and about 3 times higher than S46 lubricating oil. This system's best results were observed for the modification with ZnO rods. If compared to Un-PC, there was an increase of approximately 716% in the sorption capacity of 20W40 motor oil by the ZnO-PC foam.

As seen in the SEM image (Figure 2), the nano and micro rods of Zn modified the surface of the polyurethane from smooth to rough. This added to the Van Der Waals forces present were able to "pull, attract" the oil with more significant viscosities into the foam pores and channels. This result highlights the effectiveness of the modification.

Regardless of viscosity, all modified post-consumer foams showed greater sorption capacity when compared to Un-PC. The increases observed for the ZnO-PC foam, for example, are linked to an increase in oil affinity but also to a reduction in hydro affinity. As observed in Figure 3, ZnO-PC experienced a 16.9° increase in the contact angle between the seawater droplet and the modified foam surface compared to Un-PC. At the same time, the contact angle between the oil droplet and the surface of the ZnO-PC foam was zero, representing a drop of 82.2° when compared to Un-PC. The contact angles indicate that the graft with ZnO was able to modify the surface structure of the polyurethane, significantly increasing its selectivity for oil over seawater.

The combined modification slightly reduced the sorption capacity of the S46 lubricating oil. The increase in lubricating oil sorption for ZnO/HA-PC was about 683% compared to Un-PC, which is about 115% less than that observed for ZnO-PC. The same effect was observed in the 20W40 engine oil sorption. If ZnO/HA-PC is compared with Un-PC, the increase in the sorption of motor oil was approximately 602%. However, if compared with the observed sorption for ZnO-PC, there was a reduction of approximately 113%.

Microscopy (Figure 2) of the combined modification showed a reduction in roughness caused by the ZnO graft after HA coating. As the treatment order was graft \rightarrow coating, it is believed that HA acted as a film that coated the ZnO rods, partially inhibiting its oleophilic action.

Molybdenum disulfide has a structure that resembles graphite. Each Mo (IV) occupies a prismatic trigonal coordination sphere linked to six sulfide ligands. The trigonal prisms are connected by the edges, producing two-dimensional units known as lamellae. Each sulfur is pyramidal and it is linked to three Mo centers. In this way, the trigonal prisms are interconnected to give a layered structure. These layers exhibit intermolecular forces of the dipole-induced type, typically Van Der Waals. In the highlights of Figure 2, it is possible to see the MoS₂ particles deposited on the surface of the polyurethane. The non-polar forces present in the MoS₂ layer and the increase in roughness on the PU surface made this modification the one with the best result in the sorption of S46 lubricating oil, increasing the sorption by about 925% compared to Un-PC, reaching up to $32.81 \pm 0.31 \text{ g}\cdot\text{g}^{-1}$ (MoS₂-PC).

It is interesting to observe that the increase in viscosity decreased the sorption capacity. For the ZnO-PC modification, for example, the sorption dropped from $38.07 \pm 0.87 \text{ g}\cdot\text{g}^{-1}$ of diesel to $28.74 \pm 0.37 \text{ g}\cdot\text{g}^{-1}$ of S46 lubricating oil (drop of 24.5%) and $14.78 \pm 0.27 \text{ g}\cdot\text{g}^{-1}$ of 20W40 engine oil (a 61.2% drop). This is due to the increase in resistance that the flow faces with the increase in viscosity, which outweighs the gains in intermolecular forces generated by the chemical modifications.

The capillarity effect is also essential to provide continuity of fluid flow through the PU pores and channels. If the fluid stops in the initial portion of the pore, there will be an obstruction and consequent flow blockage. However, if the intermolecular forces caused by the modifications attract the fluid beyond the initial portion of the pores and channels, the flow will continue until it completes the total volume of the pores.

Wu et al.²¹ used a lignin-based multifunctional polyurethane foam with SiO₂ nanoparticles to achieve 99% recovery of both n-hexane and chloroform spilled in distilled water. Zhang et al.²² modified polyurethane through the deposition of ferric oxide nanoparticles, graphene oxide, and phytic acid. A 98.9% recovery was obtained in the water-n-hexane system. These values are higher than the maximum recoveries obtained for S46 lubricating oil (95%) and 20W40 engine oil (82%). However, the difference between viscosities is a factor that must be considered. In Table 2 are shown comparisons of polyurethane sorption tests available in the literature with the data obtained in this study.

3.8. Reusability

In general, the ZnO-PC modification showed the best results in the sorption tests performed. Especially in the seawater-S46 lubricating oil multicomponent test, where the modification was responsible for the highest proportional oil sorption among the different systems studied. Therefore, a reuse test was applied to this modification.

The ZnO-PC foam was subjected to 10 cycles of sorption/desorption in the multi-component system seawater-S46 lubricating oil. There were no signs of compaction, surface, or structural characteristics changes after the cycles, as seen in Figure 7.

Table 2. Oil sorption capacities for polyurethane reported in literature.

Modification applied to PU	Oil studied	Sorption capacity ($\text{g}\cdot\text{g}^{-1}$)*	Reference
None	Diesel	39.75	6
	Kerosene	39.90	
Lauryl methacrylate coating	Diesel	46.98	6
	Kerosene	41.42	
None	Hydraulic oil	4.00	20
	Crude oil	6.00	
Seashell powder + epoxy resin	Hydraulic oil	32.00	20
	Crude oil	27.50	
Graphene-meso + Iron Oxide	Diesel	200.00	23
	Tetrahydrofuran	150.00	
Textile sludge derived biochar + polydimethylsiloxane	Diesel	26.88	24
None	Gasoline	16.55	25
Chitosan and nano-montmorillonite	Gasoline	25.24	25
None ¹	Diesel	41.18	This study
Hexadecanoic acid coating ¹	Diesel	41.34	This study

*Maximum reported values. ¹Post-consumer polyurethane foam tested in a seawater-oil system.

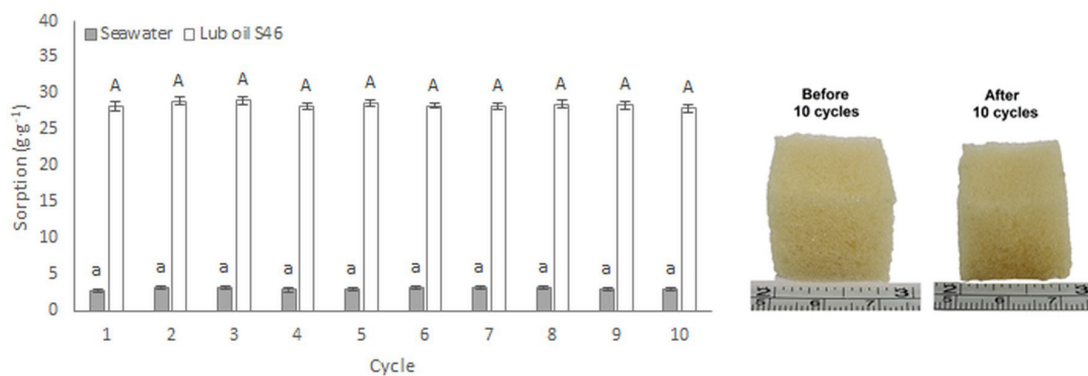


Figure 7. Seawater and S46 lubricant oil sorption behavior throughout the 10 cycles of sorption/desorption using ZnO-PC foam. On the right, images of the foam before and after 10 cycles. Identical lowercase (seawater sorption) and uppercase (lub oil S46 sorption) letters at the top of the bars indicate no statistical difference in the Tukey test (p -value > 0.05) for each fluid compared.

The amount of seawater and oil sorbed suffered minor variations between cycles ($28.28 \pm 0.60 \text{ g}\cdot\text{g}^{-1}$ of oil sorbed in cycle 1 and $27.98 \pm 0.51 \text{ g}\cdot\text{g}^{-1}$ in cycle 10).

These results confirm the possibility of reuse this foam, which reduces costs while increasing its industrial attractiveness²⁶.

4. Conclusions

In this study, one residue was used to remove another. After the modifications and tests, the results showed that for a low viscosity oil such as diesel, the chemical modifications contributed little to the increase in the PU selectivity for oil over water. In this situation, Un-PC was statistically similar to the others. For more viscous oils, the foams modified with ZnO showed gains of nearly 716% (20W40 motor oil) and 800% (S46 lubricating oil) in oil sorption capacity when compared to the foams without the modification.

Post-consumer foams performed statistically similarly to new foams. This indicates that the time of use did not directly influence the sorption capacity or retention of modifications.

After at least 10 cycles of sorption/desorption, the ZnO-PC foam kept the sorption capacity statistically unchanged. Therefore, post-consumer polyurethane foams proved to be susceptible to surface modification and presented a high selectivity capacity for the sorption of oil in seawater.

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