

Evaluation of Flexible Postconsumed Polyurethane Foams Modified by Polystyrene Grafting as Sorbent Material for Oil Spills

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ABSTRACT: This work studies the possibility of reusing flexible postconsumed polyurethane foams modified by grafting with polystyrene as a sorbent material for the mitigation of oil spills. Different foams were evaluated via crude oil sorption and retention experiments, density, and morphological analyses. The foams with the best performance were chemically modified by grafting with polystyrene under different conditions (initiator concentration, styrene volume, and reaction time) in a system initiated by oxo-reduction of Ce(IV) from an amoniacal ceric nitrate

solution. A three-level factorial design was used to study the influence of the variables. The foams were characterized via spectroscopy (XPS/ESCA and infrared) and water and oil sorption. Foam modification via grafting with polystyrene showed to be a viable alternative to increase its oil sorption ability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1842–1849, 2009

Key words: polyurethanes; foams; macroporous polymers; grafting; oil spill clean-up

INTRODUCTION

The adverse impacts to ecosystems and the long-term effects of environmental pollution caused by oil spills are a major global concern. Accidents or oil release during transportation and storage often occur in the sea, although sometimes rivers and lakes may also be affected.

The effectiveness of oil spill remediation varies with the type of oil, the amount of spill, the period of time since the spill has occurred, the location, and the weather conditions, among other aspects. Although the spills have been occurring for many decades, there is still an urge for the development of materials for the cleaning up of impacted areas.¹

Large-scale oil spills at sea are usually cleaned up through the use of booms that confine the oil within a specific area (called containment) or prevent the oil from spreading over a certain area (diversion). Skimmers have been used to recover the oil from the water surface,^{1,2} but the processing of the resulting oily water is also a challenge. Oil washed upon shores is usually collected via suction and shovels are used to remove oil-covered sand and gravel. Sorbents, on

the other hand, are usually used to remove residual oil from water and also, in small-scale spills,^{3,4} whereas biosurfactants are used for soil washing and oil removal from contaminated areas and from sorbents, when they are intended to be reused.⁵

Oil sorbent materials can be grouped into inorganic mineral, synthetic organic and organic vegetable products. Good sorbent materials must present characteristics, such as hydrophobicity, oleophilicity, high uptake ability and sorption rate, retention over time, reusability, and biodegradability. It is clearly difficult to obtain all properties in a single material, although some organic vegetable products, such as *Salvinia* and other types of peat-moss together with silk-floss⁶ are being recently described as very efficient sorbent materials.^{7,8}

Postconsumed polyurethane (PU) foams are of environmental concern because of its polluting nature. Flexible or rigid PU foams, once their life-cycle is over, are normally buried in specific locations, or incinerated under controlled conditions, to minimize environmental problems related to the production of highly toxic fumes. Thus, postconsumed PU foams cannot be treated as an ordinary polymeric residue and, because of that, much is to be gained if another use is to be found for this material after its first life cycle.

PU foams,⁹ similarly to natural porous materials, such as saw-dust and *Salvinia* tend to present higher oil sorption at lower temperatures or when less

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TABLE I
Factors and Levels Analyzed in the 2³ Factorial Design

Factor	Level (-)	Level (+)
Volume of styrene monomer—STY (mL)	25	50
Concentration of the reaction initiator—ACN (mol/L)	0.01	0.25
Reaction duration— <i>t</i> (h)	13	21

viscous oils and derivatives are used. When the oil is more viscous, pores may become obstructed and therefore, sorption capacity decreases. The opposite is found for sorbents with fibrous morphologies, such as silk-floss and cotton,¹⁰ because in these fibers thin oil films develop among fiber filaments, favoring higher oil uptake for more viscous oils.

In this work, flexible PU foams, originally used as mattresses, were evaluated as sorbent materials for oil spills. The foams were used before and after chemical modification via polystyrene grafting, which was used to increase their oleophilic character and hence to improve their performance as sorbents of heavy oil in aqueous conditions. Water uptake, apparent density, and crude oil sorption uptake experiments at different conditions (sorption period, temperature, using salty, or deionized water) were also carried out and the foams were further characterized through infrared analysis (FTIR-ATR), X-ray spectroscopy (XPS), and scanning electronic microscopy (SEM).

EXPERIMENTAL

Materials

Crude heavy oil from offshore wells of the basin Campos/Rio de Janeiro, Brazil, was supplied by Repar/

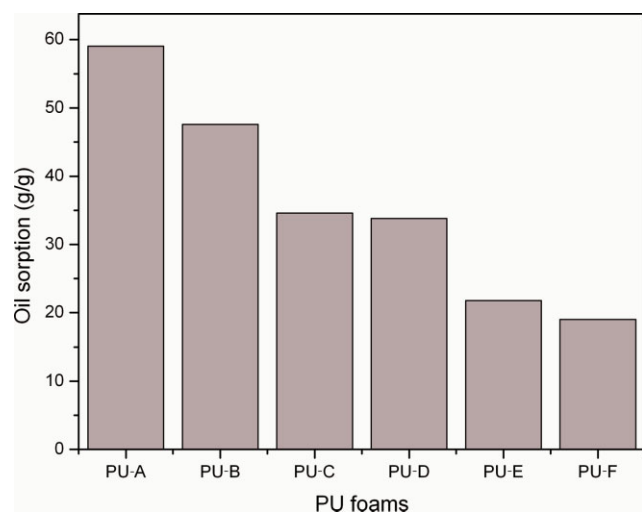


Figure 1 Oil sorption for the different PU foams (oil 27°API, room temperature, static system, 80 min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

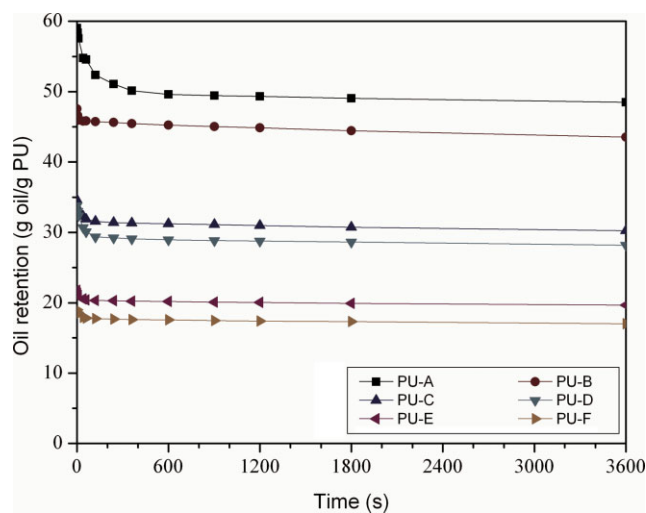


Figure 2 Oil retention capacity of the different PU foams (oil 27°API, room temperature, static system). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

Petrobras and used in oil sorption experiments. The density of the used oil varied between 0.9012 and 0.8890 g/cm³ (25–27°API, respectively) at 20°C, with a viscosity variation between 204.1 and 35.2 cSt.

The different flexible PU foams, originally used as mattresses, were of the polyether type, being supplied by Ronconi (Curitiba, Brazil). Apparent density of the foams was determined according to ASTM D792, and an optical microscopy technique with image analysis (software Image-Pro) was used to quantify the number of pores/cm² and the pore size distribution.

Sorption experiments

For each sorption experiment, 0.25–0.35 g of PU was used. A certain amount of crude oil (15, 25, 35, or 45 mL) was poured into a 250 mL beaker containing 150 mL of either deionized or salty (i.e., marine) water, produced according to ASTM D1141-90, and kept under constant stirring of approximately 500 rpm (to favor oil dispersion in the water) according to ASTM F716-93 and ASTM F726-93; this was called the dynamic system. In the static system, the followed procedure was the same except that stirring was not used.

For each different foam, three independent sorption experiments were carried out. The oil uptake of the

TABLE II
Apparent Densities of Different PU Flexible Foams

PU foam	Apparent density (kg/m ³)
PU-A	13.2 (±0.4)
PU-B	17.3 (±0.6)
PU-C	21.8 (±0.8)
PU-D	19.3 (±0.2)
PU-E	25.5 (±0.8)
PU-F	25.9 (±0.8)

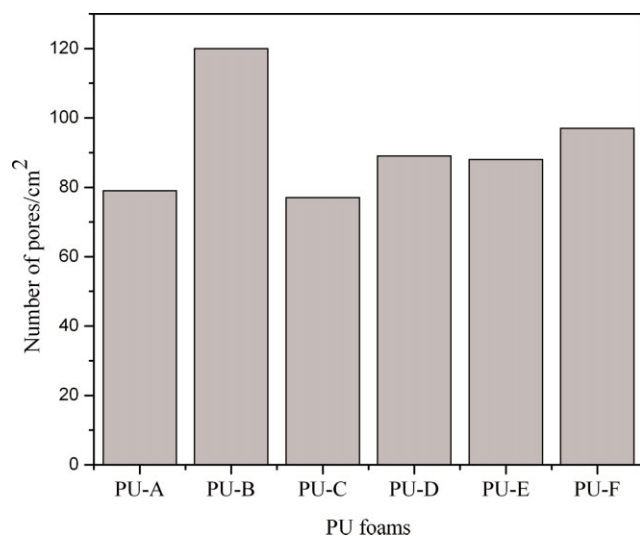


Figure 3 Number of pores/cm² of the different PU foams. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

foam (S) was evaluated as the ratio between sorbed oil and original sorbent mass (S_0) according to eq. (1):

$$S(\text{g/g}) = \frac{S_t - S_w - S_0}{S_0} \quad (1)$$

where S_t is the total weight, S_w , the weight of sorbed water and S_0 , the weight of dry sorbent.

The water uptake of the foams was evaluated by distilling the material after sorption, according to ASTM D95-83. Furthermore, after oil sorption, some foams were manually compressed between sorption papers to remove residual oil and underwent another sorption procedure, in up to three sorption cycles, to evaluate their capability of being reused.

Oil retention was evaluated by using PU samples (0.25–0.35 g, dimensions: 40 mm × 40 mm × 10 mm) that were forced to submerge into 75 mL of crude oil in a beaker (API 27) for 2 h at 24 ± 2°C. After that, the oil-soaked foams were removed and drained for 2 h until constant weight, being the weight monitored throughout the experiment.

Grafting procedure

Distinct routes may be found in the literature for the grafting of PU with polystyrene in a system initiated by oxi-reduction of Ce(IV) (e.g., Coutinho and Martins¹¹). The route followed in this work is described below.

Styrene was washed with NaOH and vacuum distilled to remove the polymerization inhibitor 4-terc-butyl catecol. The polystyrene grafting reactions were carried out in acid medium (pH around 1–2) with the use of a 1M amoniacal ceric nitrate (ACN) solution and in nitrogen atmosphere. The nitrogen was purified for oxygen removal with the use of three Fieser columns.¹²

To perform the reactions, nitrogen gas was fed into the acid solution in a 1-L flask containing the foam samples (dimensions: 40 mm × 40 mm × 10 mm). Styrene, the initiator, was then added to the 0.1M solution of amoniacal ferrous sulfate and later, the methanol was added to the system as a reaction terminator. All grafted samples, called here PU-g-PS, were thoroughly washed with methanol. Each reaction was carried out about eight times.

The reaction conditions (initiator concentration, ACN; styrene volume, STY; and reaction time, t) were studied through a 2³ factorial design procedure. Table I shows the factors and levels analyzed.

X-ray diffractograms were recorded on a Rigaku/Philips x-ray diffractometer with Ni-filtered Co K α radiation at 40 kV and 20 mA. A software was used for the deconvolution of the spectra to evaluate the degree of crystallinity of the samples by an area method using $2\theta = 21^\circ$.¹⁰

XPS/ESCA of the surface of the foams was carried out with a Multilab ESCA 3000 VG Microtech (Mg K α) operating with 0.8 eV, vacuum of 10⁻⁹ mbar, 15 kV, 20 mA (ASF atomic sensitivity factors for X-ray sources at 90°C—C 1s = 0.711, O 1s = 0.296, and N 1s = 0.477). Calculation of the atomic percentage was carried out using the area of the spectra related

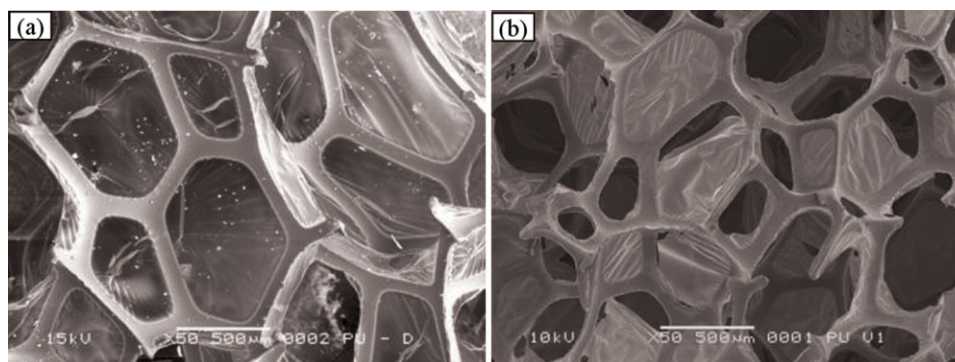


Figure 4 SEM micrographs of PU-A and PU-B foams [(a) and (b), respectively]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

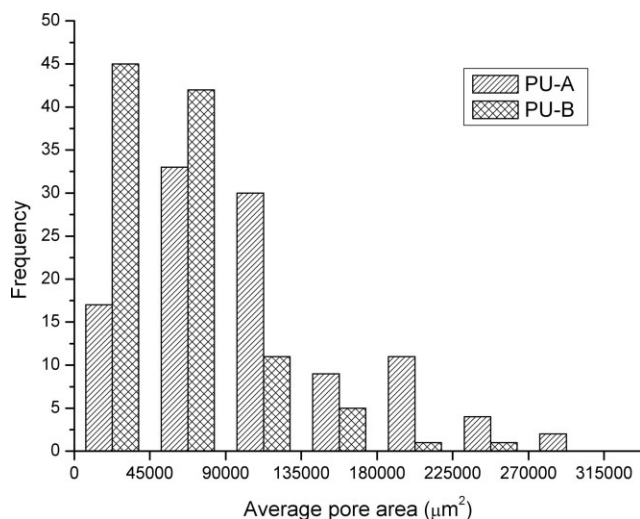


Figure 5 Histogram of pore areas of PU-A and PU-B foams.

to each element found on the sample surface, with the aid of the SDP32-XPS International software.

Foams were also analyzed with a Biorad Excalibur Series infrared spectroscopy (ATR) equipment with Fourier transform to identify chemical changes after grafting with polystyrene.

A Phillips SEM XL-30 was used to study foam surface topography. Before examination, the foams were sputter-coated with a thin layer of gold.

RESULTS AND DISCUSSION

Figures 1 and 2 present oil sorption and retention, respectively, of the different PU flexible foams. The apparent densities and number of pores/cm² of

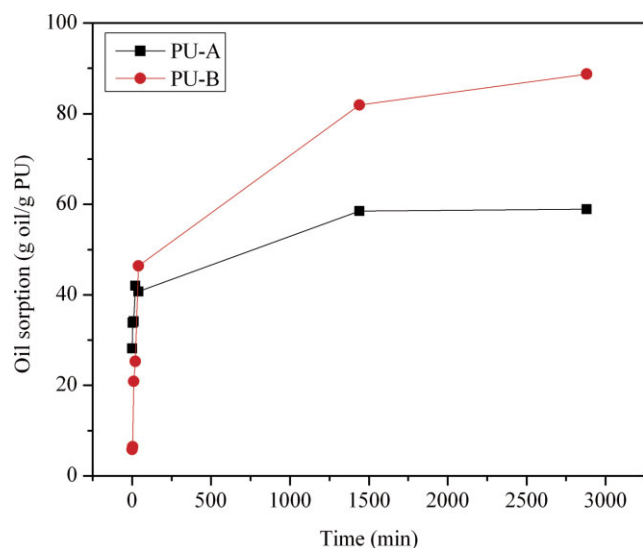


Figure 6 Crude oil sorption capacities of foams PU-A and PU-B (oil 27°API, room temperature, static system). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

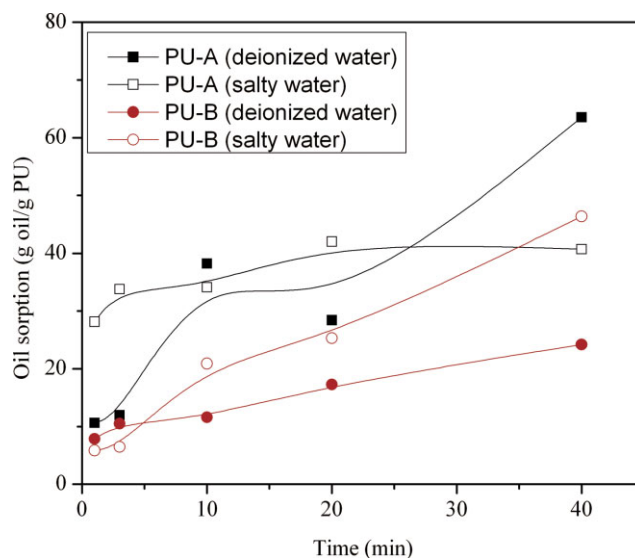


Figure 7 Oil sorption capacities of foams PU-A and PU-B in deionized water (oil 25°API, dynamic system—148 g/L). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

these foams are shown in Table II and Figure 3, respectively.

It can be seen that foam samples A and B presented the lowest density values, i.e., they have more open spaces and therefore, the oil may occupy a larger volume within. However, Figure 3 shows that PU-B has many more pores per cm² than PU-A, which PU-A partially compensates by having larger pores, which can be seen in the SEM micrographs of these foams [Figs. 4(a,b)]. The micrographs also show the presence of thin cellular wall films within the foams, which may enhance its surface area, possibly further aiding oil sorption.

Figure 5 shows the histograms of the distribution of pore areas of foams PU-A and PU-B. Foam A presents a wider pore distribution with fewer small pores and less pores/cm² and showed higher oil sorption than foam B, which has a smaller mean

TABLE III
Combination Matrix of Polymerization Reaction Conditions and Oil and Water Sorption in 80 min for Modified PU Foam A

Reaction	STY	ACN	<i>t</i>	Oil sorption (g oil/g PU)	Water content (%)
1	—	—	—	54.77 (±0.48)	23.52 (±1.56)
2	+	—	—	49.47 (±5.45)	24.50 (±6.40)
3	—	+	—	52.85 (±0.68)	12.59 (±1.38)
4	+	+	—	48.32 (±4.94)	22.64 (±1.95)
5	—	—	+	58.25 (±2.81)	28.57 (±1.99)
6	+	—	+	52.54 (±1.82)	27.75 (±5.36)
7	—	+	+	46.87 (±1.17)	11.96 (±0.38)
8	+	+	+	51.65 (±2.57)	6.10 (±2.75)

TABLE IV
Effects of the Parameters Used in the Factorial Design on Oil Uptake

I (mean)	51.017(± 1.485)
Principal effect	
STY	-4.275 (± 2.970)
ACN	-3.780 (± 2.970)
T	4.720 (± 3.970)
Two factors interaction	
STY \times ACN	3.430 (± 2.970)
STY \times t	6.770(± 2.970)
ACN \times t	-2.835 (± 2.970)
Three factors interaction	
STY \times ACN \times t	3.155 (± 2.970)

pore area (0.105 mm^2 for PU-A and 0.063 mm^2 for PU-B) but a higher number of pores.

Because of the higher oil uptake, PU foams A and B were chosen for the subsequent studies. Figures 6 and 7 present oil sorption results for foams A and B, the former figure shows oil sorption in the static system, whereas the latter shows oil sorption in salty or deionized water (dynamic system). For short sorption times, PU-A exhibited higher sorption rate than PU-B, probably due to the larger pores of the for-

mer. However, for longer experiments, PU-B showed higher sorption probably because it presents a higher amount of smaller pores, which may promote diffusion and pore filling. The type of water, i.e., deionized or salty water, also influenced the sorption behavior, maybe as a consequence of changes in oil viscosity. Salty water shows higher viscosity because the ions present in the water promote water sorption, which affects viscosity.¹³ It is also interesting to notice that both foams showed very distinct sorption kinetics, PU-A reached a plateau in 25 h (1500 min), whereas PU-B is still far from it for the same sorption time.

As these preliminary results with the untreated PU foams showed not so high sorption capacity, PU-A samples were submitted to chemical modification via polystyrene grafting to improve their efficiency regarding oil sorption. After the different grafting reactions, the PU-A foam samples, originally white and very smooth, became yellowish and more rigid. In fact, the higher initiator concentration the stronger the yellow color of the treated foams, suggesting a more pronounced material degradation through oxidation.

During the grafting of the polystyrene, the following possibilities may be envisaged:

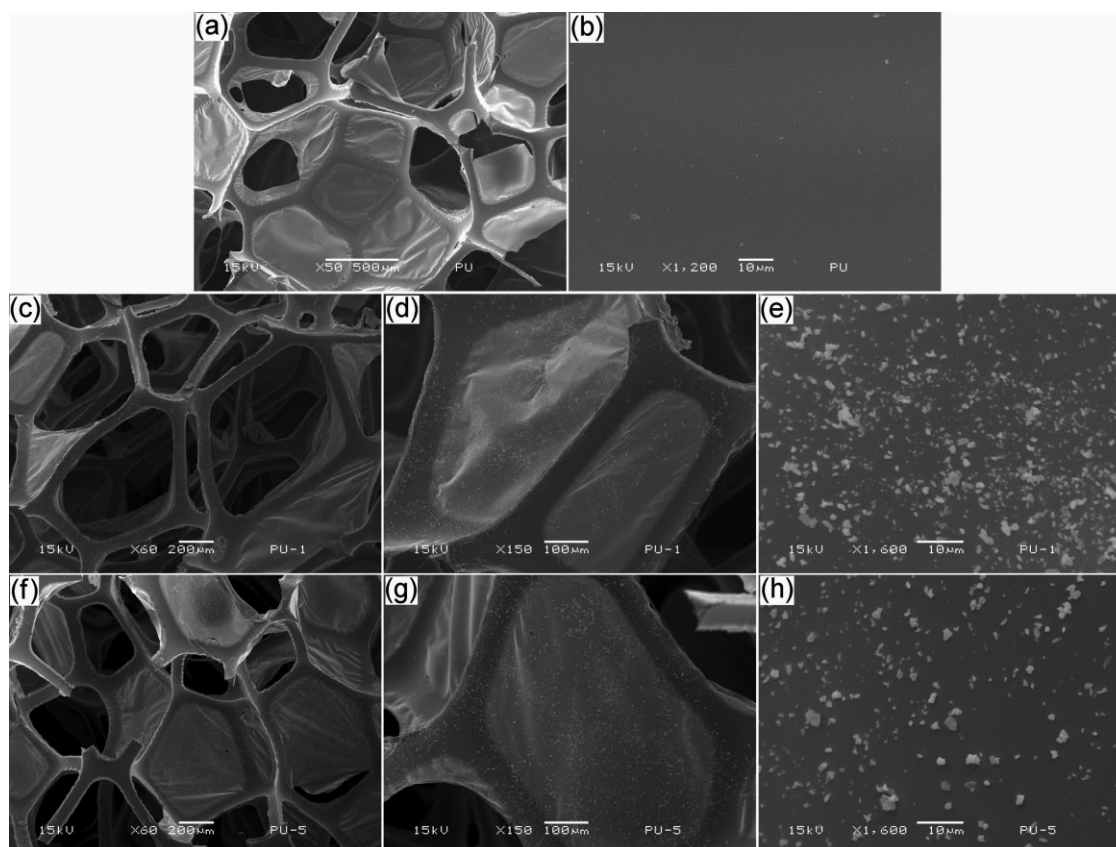


Figure 8 SEM foams micrographs of untreated PU (a,b); PU-g-PS-1 after immersion in toluene (c-e); PU-g-PS-5 after immersion in toluene for 24 h (f-h).

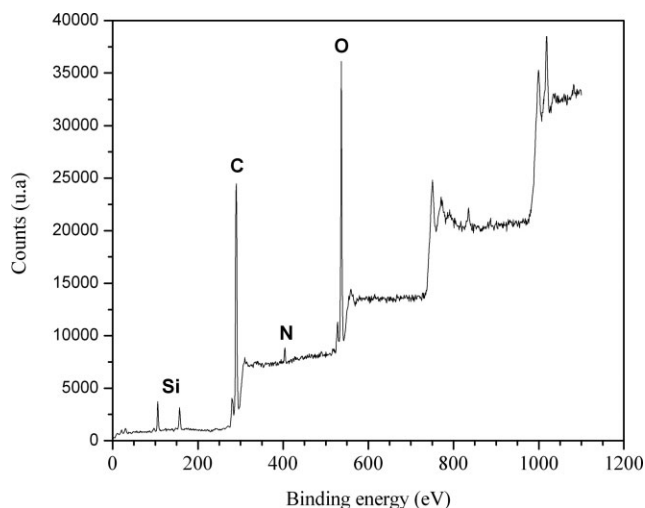


Figure 9 XPS spectrum of PU-A showing the peaks corresponding to oxygen, nitrogen, carbon, and silicon.

- i. The ACN may produce few radicals in the PU chain, and when PS bonds to these radicals, the formation of a grafted PS chain with low molecular weight occur¹¹;
- ii. The ACN may produce various radical sites in the PU chain and incorporate grafted PS with a higher molecular weight, and
- iii. The production of homopolymer may occur, competing, during its growth, with the grafted PS chain.

The first two possibilities are controlled by the degree of crosslinking of the PU. In the PU foams studied here, the material exhibits nonrigid characteristics, in other words, the degree of crosslinking is not too high, so, the occurrence of situations (i) and (ii) will determine the grafting degree that will be obtained in the final material.

Table III presents the combination matrix of the eight different reaction (polymerization initiated by Ce^{4+}) conditions carried out and the respective oil and water sorption in salty water for each condition after 80 min of sorption. The untreated A foam presented a sorption capacity of 27.60 (± 1.12) g oil/g PU and a salty water uptake of 17.0% (± 5.33), whereas some of the modified foams showed lower water uptake. The water uptake increases for longer sorption periods, that is justified by the prolonged contact of the water with the oil which allows the water to get inside the oil phase. It can also be seen in Table III that the best grafting conditions regarding oil sorption (58.25 ± 2.81 g oil/g PU in salty water) were those shown under reaction number 5.

The oil sorption capacities of foams reacted in conditions 1 (called PU-g-PS-1) and 5 (called PU-g-PS-5) in deionized water were 41.65 (± 1.82) and 47.80 (± 5.72) g/g oil, respectively, whereas the water uptake was 26.04% ± 1.19 and 28.90% ± 6.38 , respectively. Again, the oil uptake of the untreated PU (PU-A) in deionized water was much lower, 25.20 g oil/g PU, with a water uptake of 2.54% ± 0.16 .

Regarding the statistical analysis (Table IV), all parameters were found to be significant except the interaction between the ACN concentration and the reaction time (t). Because a shorter polymerization time favors production and decreases costs, reaction conditions named reaction 1, with the second highest oil sorption capacity, may be chosen as the most adequate polymerization conditions for the grafting reaction of PU with polystyrene.

Figure 8 shows SEM foams micrographs of untreated and modified PU-g-PS-1 and PU-g-PS-5 foams. It can be seen that the foams presented heterogeneous characteristics, with open cells and some closed cells. The grafted foams presented a rougher surface than that of the untreated foam, possibly with a higher surface area. It was also observed a two-phase

TABLE V
Elemental Surface Constitution (%-Atomic Concentration) and Surface Bonds (Below) Found via XPS in the PU Foams

Sample	C 1s	O 1s	N 1s	Si 2p	O/C	N/C	N/O
PU-A	68.15	22.39	1.71	7.75	0.33	0.025	0.076
PU-g-PS-1	66.08	22.04	1.76	10.12	0.33	0.027	0.080
PU-g-PS-5	68.77	20.76	2.86	7.61	0.30	0.042	0.138

C-C/C-H	C 1s			O 1s				N 1s		
	C-O-C	N-C=O	N-C/C-O	N-C=O	C-O-C	O=C-O	C-O/Si-O	N-C=O	N-H	
284.82	286.41	289.04	287.50	531.74	532.88	533.90	532.51	400.20	399.50	
PU-A	52.7	42.7	1.8	2.8	26.4	50.7	20.5	2.4	45.0	25.0
PU-g-PS-1	59.9	34.9	2.1	3.1	40.0	38.7	19.0	2.3	68.0	32.0
PU-g-PS-5	57.3	36.4	1.6	4.7	36.0	44.5	17.8	1.7	69.5	30.5

morphology—a homogeneous matrix composed of PU and small domains of grafted PS [Fig. 8(e)].

The modified foams were immersed in toluene to check if there was a permanent foam grafting or if the observed morphology was due to the presence of residual polystyrene. After a 1-day immersion in toluene, the grafted foams kept the same structure, ratifying that the polystyrene was chemically bonded to the PU phase. The micrographs ratified the presence of two phases, which had been observed before the swelling experiments [Fig. 8(h)].

Figure 9 shows a XPS spectrum of PU-A (untreated). The presence of silicon was noted in all analyzed samples, originated from residues of surfactant used in the PU formulation. The relative contents of C, N, O, and Si in the PU foams are listed in Table V. Carbon and oxygen were the prevalent elements on the surface of all samples, and a small amount of nitrogen from the rigid segment phase (i.e., the urethane group) was also detected.

Table V also shows the surface bonds of PU-A, PU-g-PS-1, and PU-g-PS-5 obtained with XPS. It can be seen that there was an increase in C—C/C—H bond content for PU-g-PS-1 and PU-g-PS-5 along with a decrease in the C—O—C bond, suggesting that a more hydrophobic material was obtained. Examination of Table V reveals that there are different O/C, N/C, N/O, C—C/C—H and C—O—C ratios in the samples. The O/C ratio was higher than that of N/C, suggesting that the soft segment (polyether) is preferably located on the surface of the modified samples.^{14,15}

The PU-g-PS-5, which showed the best sorption performance, presented O/C = 0.0, N/C = 0.04, and N/O = 0.14. With the grafting reaction, the PS por-

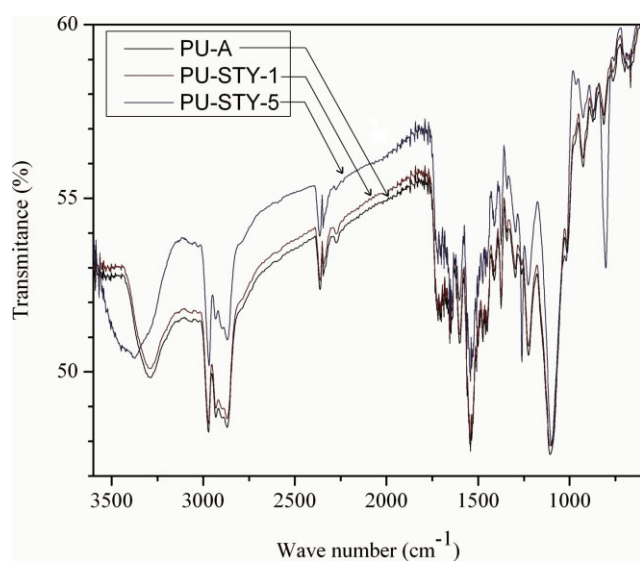


Figure 10 FTIR spectra of untreated (PU-A) and grafted (modified) foams (PU-g-PS-1 and PU-g-PS-5). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

TABLE VI
Description of Absorption Bands Found for the PU Foams in This Work, Based on the Literature^{20,21}

Absorption (cm ⁻¹)	Description
3446–3140	N—H stretching
2976–2800	C—H stretching: antisymmetric and symmetric vibration of methylene groups
2870	O—CH ₂ stretching
1600–1800	Amide I: C=O stretching vibration
1540	Amide II: ($\delta_{N-H} + \nu_{C-N} + \nu_{C-C}$)
1459	C—H stretching vibration
1455	CH ₂ scissoring and CH ₃ deformation
1373–1377	Amide II: (ν_{C-N})
1261–1296	Amide III: (ν_{C-N})
1100–1388	C—O—C stretching vibration, ether group
1067	O—C=O stretching in the hard urethane segment and steric CO vibration
1012	CH ₂ : stretching and rocking vibrations
1002	C—C: stretching and rocking vibrations
800	Amide IV, V and VI: mixed modes including N—H out-of-plane deformation
806	Si—O: stretching vibrations
766	Amide IV: out-of-plane deformations modes
700–600	N—H out-of-plane bend
695	Amide V: stretching vibrations
669	C=C (out-of-plane ring)

tion is inserted into the rigid segment, bonded to the nitrogen atom.¹⁶ Then, if N/C = 0.04 and N/O = 0.14, the C increment is much higher, suggesting the formation of a more hydrophobic structure¹⁴ and justifying the sorption results for this sample. Besides, nitrogen is only present at the rigid segment.^{17–19} In short, these findings suggest that the polystyrene grafting of the PU contributes to the enhancement of the C—C/C—H bonds and for the improvement of the oleophilic character of the sample.

The degree of crystallinity obtained through X-ray diffraction patterns for the untreated and modified (PU-g-PS-1 and PU-g-PS-5) samples were, respectively, 7.1%, 18.5%, and 19.2% showing the untreated foam to be a more amorphous material. This small variation may have occurred because of some reorganization of chains during the grafting of polystyrene. This molecular reorganization may be

TABLE VII
Reutilization Capability of the PU-A, PU-g-PS-1, and PU-g-PS-5 Foams, Using the Oil (25°API)/Salty Water System—Dynamic System for 80 min

Sample	First cycle (g oil/ g PU)	Second cycle (g oil/ g PU)	Third cycle (g oil/ g PU)
PU-A	27.60 (±1.12)	27.50 (±1.81)	25.65 (±2.05)
PU-g-PS-1	54.77 (±0.48)	57.22 (±4.16)	57.07 (±2.93)
PU-g-PS-5	58.25 (±2.81)	50.48 (±1.51)	56.99 (±2.37)

attributed to the presence of some PS (which is slightly more crystalline—10.35%) or to the influence of the STY monomer and the NCA solution on the original PU foam during grafting.

Figure 10 presents FTIR spectra of PU-A, PU-g-PS-1, and PU-g-PS-5. A description of the main absorption bands of the spectra may be found in Table VI. It was observed that the amide III bands ($1261\text{--}1296\text{ cm}^{-1}$) of PU-g-PS-1 and PU-g-PS-5 are stronger than that for the PU-A suggesting that grafting may have occurred in the nitrogen element.¹⁶

Reusability is another desired characteristic of oil sorbents because the life cycle of materials may be extended.^{22,23} Therefore, two extra sorption cycles were carried out for the PU-A, PU-g-PS-1, and PU-g-PS-5 samples in salty water. It was observed that the modified samples were able to maintain their high sorption capacity and physical integrity (Table VII).

CONCLUSIONS

In this work, the possibility of using flexible PU postconsumed foams modified by grafting with polystyrene as a sorbent material for the mitigation of oil spills was investigated. Oil sorption was found to be dependent on the morphological and physical–chemical characteristics of the foams, such as density, distribution of pore sizes, interface between sorbent-sorbate, and hydrophobicity of the surface.

The modification of the original foams via grafting with polystyrene showed to be an alternative way to increase their oil sorption ability. XPS analyses have confirmed the increase in hydrophobicity of the surface of the foams. The sorption values found indicate that the foams show very interesting characteristics for the targeted application, such as considerable oil uptake and high sorption rates (fast sorption kinetics), with the supplementary possibility of being reutilized in subsequent sorption cycles, without compromising their sorption ability.

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