

Surface Functionalization of Polyurethane Foams for Enhanced Hydrophobicity

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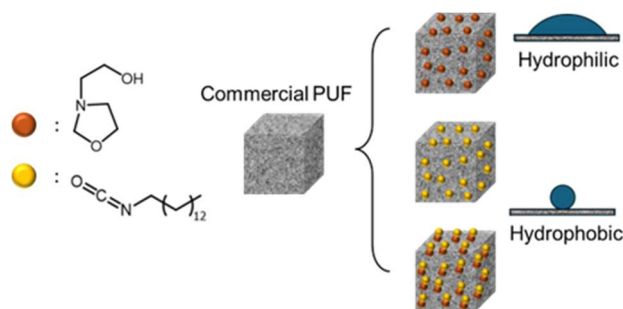
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Abstract

Oil contamination in water resources remains a significant concern for human and environmental health, and organic sorbents are among the prominent technologies developed for remediation. Meanwhile, the growing appetite for polyurethane foams (PUF) has produced challenges in the recycling and management of post-consumer PUFs. This study explores a novel approach to enhance the oleophilicity of commercial PUFs through surface modification. Introducing new pathways to functionalize commercial PUFs with facile processing routes may simultaneously enable PUF waste management and oil spill remediation. Surface modification with 2-(oxazolidin-3-yl)ethanol and tetradecyl isocyanate on commercial PUFs provides significant enhancements of oil/water uptake with high selectivity, as well as providing thermal and chemical stability. Various characterization methods, including TGA, SEM, and XPS, collectively reveal the chemical and physical properties of surface-functionalized PUFs. This research potentially enables cost-effective and scalable surface modification of PUFs for their application in controlling oil contamination. Surface functionalized PUFs present a promising opportunity for various applications, including oil spill remediation and oil/water separation processes to tackle water resources contamination.



Introduction

For centuries, different human activities have polluted water resources. Marine transportation and industrial waste streams have significantly contributed to oil contamination of clean waters.¹ Exxon Valdez in 1989 (11 million gallons) and Deep Horizon in 2010 (4.9 million barrels) were

two of the greatest oil spill disasters that heavily affected the marine environment.^{2,3} Natural water movement, alongside weather and climate change, increases the oil transportation on the water surface far beyond its original location, harming marine and terrestrial organisms.⁴ Researchers are developing various technologies to control and remediate oil spills, including physical/mechanical, chemical, and biological methods.⁵⁻⁸ Cost efficiency and rapid absorption rates of organic sorbents have made them a suitable recovery method for oil spill scenarios. Polyurethane foams (PUFs) are among the most popular organic sorbents.⁹

Due to their tunable properties for different commercial applications, polyurethanes (PU) have gained popularity in recent decades, and PU-containing products play a crucial role in our daily lives.¹⁰ The global market for PU, primarily available as covalently crosslinked PUFs, is expected to exceed \$90.3B in 2032 and currently represents a market share of 23% among foamed polymers.¹¹ The growing demand for microcellular materials and metamaterials in rapidly emerging technologies, ranging from lightweight materials for construction and infrastructure to ubiquitous foam mattresses and energy-saving insulations, continues to contribute to the large volumes of solid waste that must be managed. With over 50,000 mattresses discarded in the U.S. daily that contain more than 75% recyclable components, the low recycling rate of 5-10% diverts the majority of valuable resources to local landfills.¹² A major barrier preventing broader adoption of mattress recycling is economics. While steel and wood are relatively easily recycled, the market for recovered PU foam is limited to one main low-value application – carpet padding (or re-bond). Therefore, there is a need to drive broader recycling and higher recycling rates and develop additional, higher-value markets for recycled PUF.^{13, 14}

Existing studies have demonstrated successful surface oleophilic enhancement of polymeric materials for various applications, such as membranes,¹⁵⁻¹⁷ hydrogels,^{18, 19} aerogels and sponges,^{20, 21} and nanowires and nanotubes.^{22, 23} Surface modifications such as spray coating,²⁴ chemical vapor deposition (CVD),²⁵ grafting,²⁶⁻²⁹ and hydrothermal processing³⁰ enhance PUF performance. Barry *et al.* at Argonne National Laboratory utilized sequential infiltration synthesis (SIS) to activate post-consumer foams to create oleophilic products.³¹ Despite exhibiting enhanced oil sorption properties, these early advances lacked facile processing routes. In addition, Ng *et al.* implemented a CVD method to functionalize PU foam surfaces with hydrophobic monomers. While the aforementioned method deposits ultra-thin layers with versatile chemistry, the complex and high-cost equipment, slow deposition rates, and size limitations hindered potential commercial impact.²⁵

Herein, this research proposes a novel route toward PUF surface functionalization utilizing reactive groups in existing carbamate linkages within the foam matrix. This synthetic method may present a cost-effective and scalable approach with facile processing, leveraging commercially available PUF. 2-(oxazolidin-3-yl) ethanol and tetradecyl isocyanate were used to functionalize the PUF surface. The modified PUFs were investigated for absorption capacities, particularly for oil absorption processes. The foam surface functionalization and oleophilicity/hydrophilicity were characterized using x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and a series of oil/water absorption tests.

Experimental

Materials

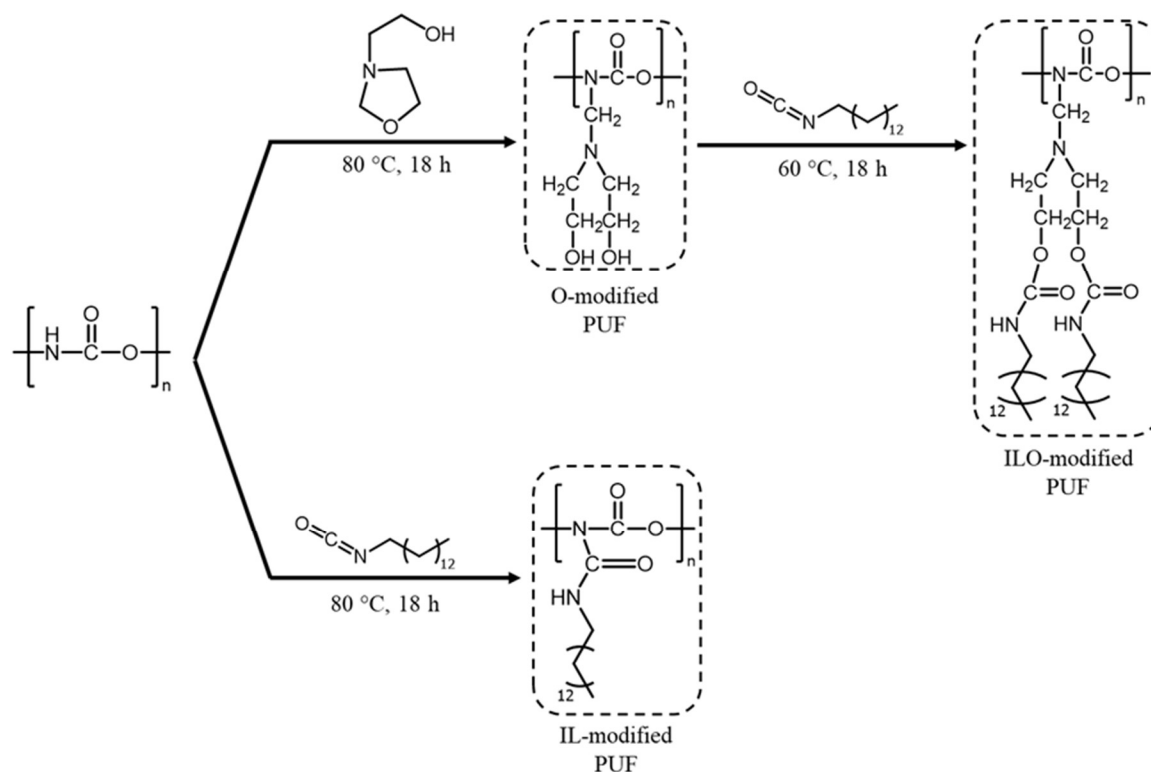
PUF was kindly supplied by Covestro AG. Tetradecyl isocyanate, tert-butyldimethylsilyl chloride, chloroform-d (CDCl_3 , 99.8%), diethanolamine (DEA), and paraformaldehyde were obtained from Sigma-Aldrich and used as received.

Synthesis of 2-(oxazolidin-3-yl)ethanol

The reaction was performed as described in the earlier literature.³² A solution of diethanolamine (105 g, 1.00 mol) in isopropanol (200 ml) was added to a suspension of paraformaldehyde (30.0 g, 1.00 mol) in toluene (200 mL). The mixture was heated to 80 °C under reflux for 18 h. The solvents were removed under reduced pressure for 12 h to yield the product 2-(oxazolidin-3-yl)ethanol (89.2 g, 85.0%). The final chemical structure was verified with ^1H NMR spectroscopy in CDCl_3 as shown in Figure S1.

Surface functionalization of PUF

Each PU foam was cut into 1 cm cubes. PU foam pieces were washed with methanol and dried in an oven under reduced pressure at 60 °C for 12 h. The following process was used for surface modification; each PUF piece was submerged in 3.0 mL of modifying agent to ensure complete exposure; detailed reaction conditions are illustrated in the supporting information Scheme S2-4. 2-(Oxazolidin-3-yl)ethanol, tetradecyl isocyanate, and a combination of both were utilized to modify the surface of PUFs. As shown in Scheme 1, surface-modified PUFs are referred to as O-modified, IL-modified, and ILO-modified PUFs, respectively. Ultimately, surface-modified PUF pieces were washed with methanol and dried under reduced pressure at 90 °C for 12 h.



Scheme 1. Surface modification of PUF using 2-(oxazolidin-3-yl)ethanol, tetradecyl isocyanate, and a combination as modifying agents.

Characterization

Prior to analysis, all samples were dried in an oven for 16 h at 90 °C. Scanning electron microscopy (SEM) was performed on a ThermoScientific Phenom XL G2 desktop SEM under backscattering detector, 0.1 Pa vacuum, and 10kV accelerating voltage. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 5500 under N₂ at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was conducted on Kratos Axis Supra + with survey mode. A thin layer of finely cut PUF was adhered to glass slides for XPS measurements.

The method to measure the oil/water absorption capacity of PUF samples is illustrated in Figure 1. 100 mL of pure mineral oil and pure water were separately poured into glass jars. The initial dry weight of PUF samples was measured and recorded. Dry PUF samples were immersed in liquid-containing jars. Subsequently, the jars were placed on a shaker table at 150 rpm for 30 min. After 30 min, the samples were removed from the shaker table and allowed to settle for 2 min. Following this step, the samples were removed and held for 30 s to drain off the excess liquid. The PUF samples' saturated weight was measured and recorded. The following equation calculates oil/water uptake:

$$\text{oil/water uptake (g/g)} = (S_f - S_i)/S_i \quad (1)$$

where S_i is the initial dry weight of the PUF sample and S_f is the final saturated weight.

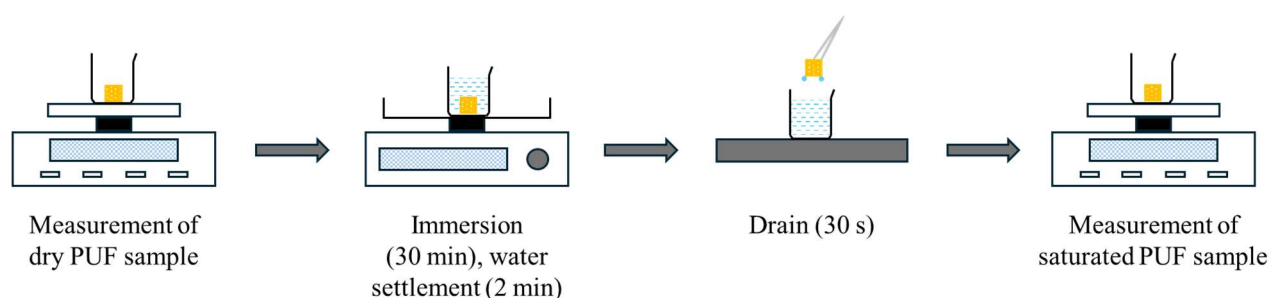


Figure 1. Graphical illustration of PUF sample oil/water absorption test.

Results and Discussion

Oil and water uptake of the pristine and surface-modified PUF cubes were measured as described above. The results, illustrated in Figure 2(a), revealed a significant change in the oleophilic/hydrophilic properties, depending on the modification type.-

The unmodified pristine PUF exhibited an oil uptake of 14.4 g/g and a water uptake of 11.8 g/g. O-modified PUF demonstrated a notable increase in both oil and water uptake, reaching 28.1 g/g for oil, and 25.3 g/g for water, reflecting improved overall sorption properties. Hydroxyl groups form hydrogen bonds with water molecules, encouraging higher hydrophilicity in an aqueous environment, which likely contributes to the higher water absorption. In a non-polar environment, the two hydroxyl groups of the O-modified PUF likely participate in intramolecular hydrogen bonding, decreasing the hydrophilic properties of the foam. This, along with the more open celled nature of the O-modified foam (see below), may explain the increase in oil absorption observed.

IL-modified PUF displayed superior performance with an oil uptake of 21.4 g/g and a markedly reduced water uptake of 2.7 g/g. As summarized in Figure 2(b), this modification achieved an oil:water selectivity of 7.93, representing an approximately 7-fold improvement compared to the unmodified foam or O-modified PUF. This finding aligns with the expected enhancement in oleophilicity and reduction in hydrophilicity resulting from the hydrophobic, non-polar long-chain alkyl isocyanate attached to the foam surface.

The ILO modified foam showed a marked additional increase in oil absorption (45.1 g/g) and a small decrease in water absorption (21.3 g/g) compared to the O-modified foam. This is consistent with an increase in oleophilicity resulting from reaction of the hydroxyl groups of the O-modified foam with the very oleophilic long chain aliphatic isocyanate.

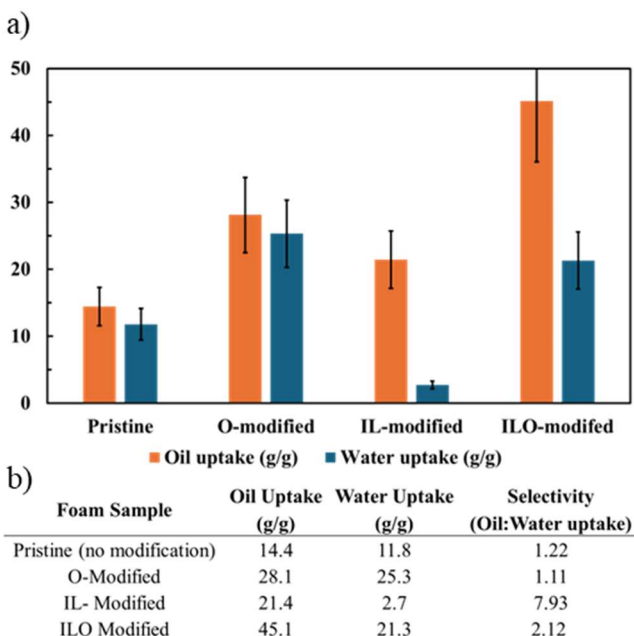


Figure 2. (a) Oil/water absorption capacities of PUF samples demonstrate surface-modification, **(b)** oil and water uptake properties of surface-modified PUFs.

The surface-modified PUFs exhibited oil uptakes ranging from 21 to 45 g/g, significantly higher than reported for two different polypropylene-based commercial oil-absorbing products, which show oil uptake values of ~8 to 12 g/g.^{33, 34}

As illustrated in Figure 3, the IL-modified PUF effectively absorbed mineral oil floating on the surface of water, leaving no visible separate layer of mineral oil after collection. Furthermore, the liquid retrieved from the IL-modified PUF, as depicted in Figure 3, did not show evidence of major layer separation, indicating high selectivity of the modified PUF for oil absorption.

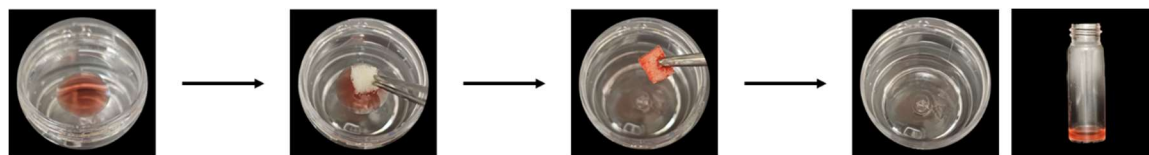


Figure 3. The mineral oil/water separation process with the IL-modified PUF demonstrates its oleophilic properties. Red ink was added to the oil for clear observation.

The modified surface functionalities of the PUF samples significantly impacted their oil and water uptake capacities, but we also carried out analysis of the surface to collect further evidence for the chemical modification of the surface. Scanning electron microscopy (SEM) imaging, presented in Figure 4, highlighted structural changes in the foam surfaces following modification. Figure 4(a) illustrates the pristine PUF's three-dimensional porous structure. In contrast, post-modification SEM images revealed a more open-cell structure compared to the smooth surface of the unmodified sample. Additionally, SEM images of the modified PUF samples, shown in Figure

4(b)-(d), displayed more irregular three-dimensional structures on their surfaces. Notably, the modification using 2-(oxazolidin-3-yl)ethanol caused a more significant impact on the foam's cellular structure compared to the isocyanate lipid modification route.

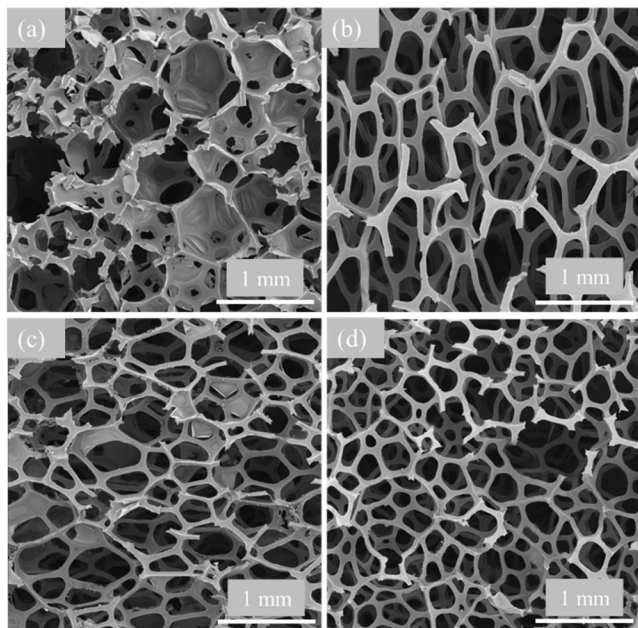


Figure 4. SEM images of the pristine PUF (a), O-modified PUF (b), IL-modified PUF (c), and ILO-modified PUF (d).

XPS analysis provided a detailed method for investigating the surface composition of PUF samples. The XPS survey scans of the PUF samples, before and after surface modification, as shown in Figure 5, demonstrated significant changes in the O1s signal at ~ 530 eV, the C1s signal at ~ 285 eV, and the N1s signal at ~ 395 eV, corresponding to the introduction of surface functionalities absent in the pristine PUF samples. Carbon, nitrogen, and oxygen atoms were measured on the surface of the PUF both before and after modification, and atom concentration % is summarized in Table 1. After the surface modification with 2-(oxazolidin-3-yl) ethanol, an increase in oxygen content to (18.50%) and carbon content to (73.32%) indicated the addition of these groups to the surface of the foam. Further analysis of IL-modified PUFs revealed a significant increase in carbon content (82.61%) and a decrease in oxygen (8.83%). PUFs modified with both 2-(oxazolidin-3-yl)ethanol and isocyanate lipids demonstrated a further increase in carbon (88.06%) and nitrogen (4.68%) concentrations while reducing oxygen content to (6.14%). This elemental composition aligned with the expected addition of non-polar lipid groups to the already modified foam surface, resulting in enhanced oleophilicity compared to 2-(oxazolidin-3-yl)ethanol-only modification.

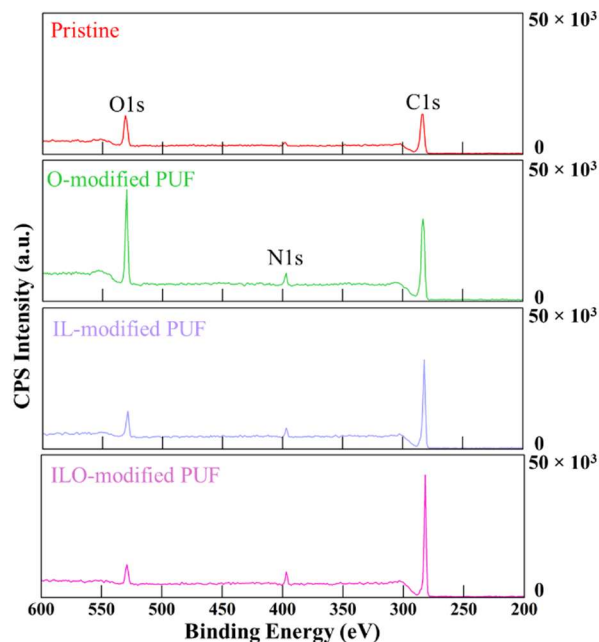


Figure 5. Elemental analysis with XPS indicates the change in the presence of different elements with different surface modification routes.

The IL-modified PUF, which demonstrated the highest oil selectivity, exhibited N/C and N/O ratios of 0.05 and 0.48, respectively, indicating a significant increase in carbon content, resulting in a more hydrophobic surface structure. This analysis was consistent with the ILO-modified PUFs, which showed the highest oil absorption capacity. In contrast, the O-modified PUF presented an O/C ratio of 0.25 and an N/C ratio of 0.03. Compared to the pristine PUF, these values reflected a higher oxygen content on the foam's surface, aligning with the anticipated presence of the 2-(oxazolidin-3-yl)ethanol modifying group.

Table 1. Elemental atom concentration% of pristine and surface-modified PUFs

PUF sample	Atom concentration%					
	C	N	O	O/C	N/C	N/O
Pristine	72.38	2.51	16.03	0.22	0.03	0.16
O-modified	73.32	2.44	18.50	0.25	0.03	0.13
IL-modified	82.61	4.21	8.83	0.11	0.05	0.48
ILO-modified	88.06	4.68	6.14	0.07	0.05	0.76

To further investigate the surface properties and confirm the presence of expected functional groups (i.e., hydroxyl groups introduced through modification with 2-(oxazolidin-3-yl)ethanol), silylation of O-modified PUFs was conducted (Scheme S5). XPS analysis verified the successful silylation of the O-modified PUFs. The Si content on the PUF surface increased from 5.75% to 8.10% following silylation, confirming the addition of silyl groups (Figure S2). The ratio of added silicon to nitrogen (Si/N \sim 2) indicated that the surface effectively reacted during the silylation

process. Furthermore, the introduction of non-polar groups reduced the hydrophilicity of the PUF samples, as demonstrated by the results of oil/water absorption tests (Figure S3).

In addition to the high selectivity of IL-modified PUF, the increase in both oleophilicity and hydrophilicity observed in O-modified PUFs is noteworthy. The previously discussed results indicated that hydroxyl groups on the surface of O-modified PUF formed intramolecular hydrogen bonds, which provided a shielding effect on the foam in the presence of oil. However, in the presence of water, the hydroxyl groups preferentially formed hydrogen bonds with water, rendering the surface more hydrophilic.³⁵ Based on SEM images of surface-modified PUFs, the O-modified samples exhibited rougher surfaces and higher surface area compared to the pristine foam. According to *Wenzel*, surface roughness significantly influences wettability, which explains the concurrent increase in oil and water uptake observed alongside the chemical modifications.³⁶ These findings strongly suggest that the proposed surface modification routes substantially impacted the hydrophilicity and oleophilicity of PUFs by altering the cellular structures and surface area of the foam while preserving overall structural integrity. Moreover, the increased surface area plays a partial role in increasing the liquid uptake of the O-modified PUFs, enabling the foam surface to encounter more liquid.

Finally, TGA as depicted in Figure 6 revealed that the degradation of pristine PUF occurred in two distinct steps. In contrast, the PUFs exhibited three separate weight-loss steps after surface modification. The initial weight loss of the modified foams resulted in a mass loss of approximately 2 wt.%. The second weight loss step, occurring at approximately 275–300 °C, corresponded to the degradation of the (–CO–NH–) hard segment. The final weight loss, which was observed at approximately 375–400 °C, was attributed to the combined degradation of both hard and soft segments.³⁷ Furthermore, TGA analysis indicated an earlier onset of surface functionality degradation compared to the decomposition steps of the hard and soft segments of the PUF.

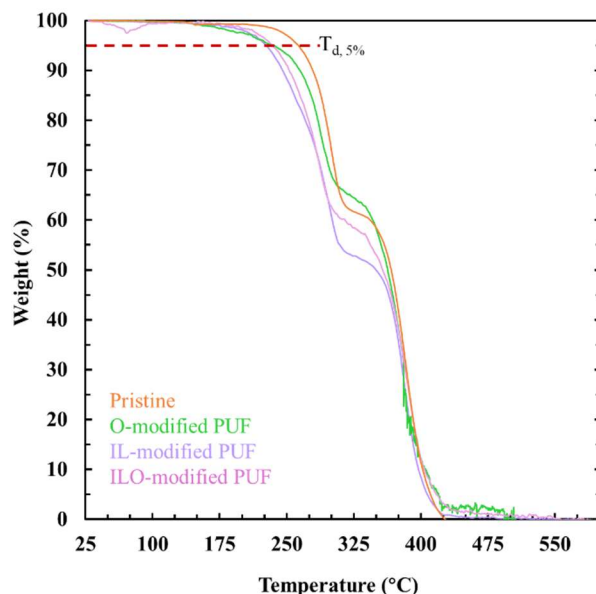


Figure 6. TGA results of the pristine and surface-modified PUFs.

Conclusions

This manuscript describes a facile approach to surface modification of PUFs. The preceding literature describes modification methods with extensive and complicated processing of PUFs for various applications. Post-consumer applications for PUFs have gained attraction due to the growing production and low recycling rates. However, high cost, complex methodology, and scalability have hindered the current recycling methods. This work reports a facile, potentially cost-effective alternative to expand the scope of post-consumer PUF applications to answer prevalent environmental problems.

Surface-modified PUFs demonstrated enhanced oil/water absorbency factors using the described procedures to attach different modifying groups. Oil/water uptake results indicated the tailored surface functionality of the modified PUFs provided excellent control over oil and water uptake enhancements with high selectivity. TGA and XPS highlighted the successful surface modification of commercial PUFs with alterations from the pristine PUF, while SEM imaging provided insight into the structural alterations of the samples. IL-modified PUF exhibited the highest absorption selectivity, while ILO-modified PUF showed the highest oil uptake.

Various chemical and physical characterization techniques collectively confirmed a pathway to tune the surface properties of PUFs for specific applications. Thus, these synthetic methodologies for functionalizing the surface of PUF could be extended to areas such as water-wicking foams and filtration media tailored for the selective capture of contaminants. This research provides a pathway to address the need for alternative uses for PUF at the end of its lifetime to reduce its diversion to landfills. We believe future work focusing on optimization for commercial adaptation

and broader implementation is warranted. Ultimately, the resulting upcycled materials suggest a strategy for sustainability and circularity of polyurethane foams.

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Conflicts of interest

The authors declare no conflicts of interest.

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Supporting information

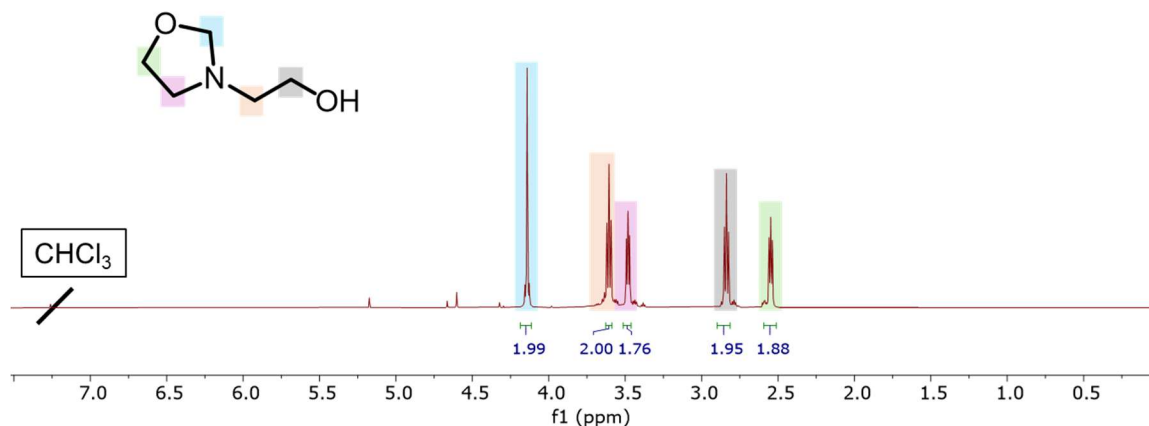
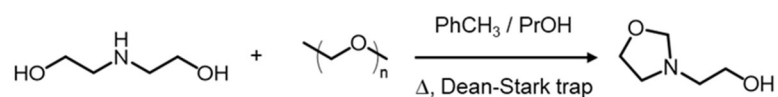
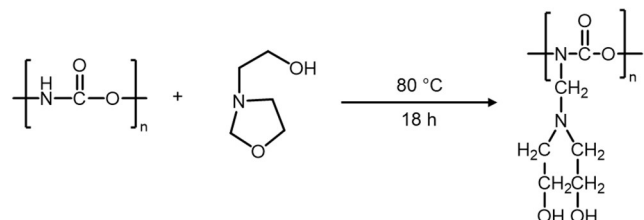


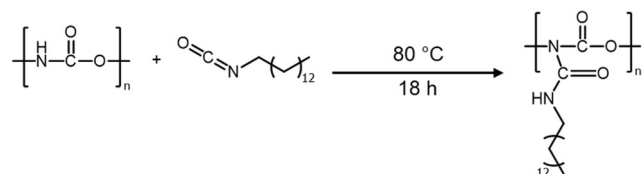
Figure S1. ¹H NMR confirms the successful synthesis of 2-(oxazolidin-3-yl)ethanol.



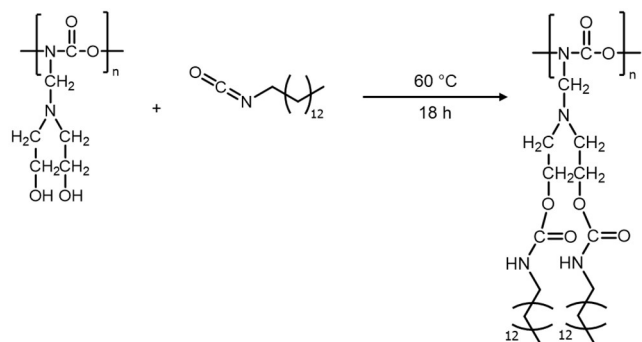
Scheme S1. 2-(Oxazolidin-3-yl)ethanol synthesis from formaldehyde and diethanolamine is cost-effective and scalable.



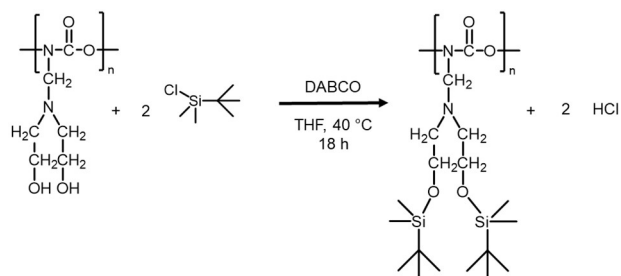
Scheme S2. Functionalization of Covestro pristine PUF using 2-(oxazolidin-3-yl)ethanol was successfully performed by submerging the foam in 2-(oxazolidin-3-yl)ethanol and heating it to 80 °C overnight.



Scheme S3. Foam functionalization using tetradecyl isocyanate involved immersing the foam pieces in the isocyanate solution and heating them to 80 °C overnight, followed by washing and drying.



Scheme S4. O-modified PUF was reacted with the isocyanate lipid at 60 °C overnight to further modify.



Scheme S5. Silylation of O-modified PUF was performed using a silylation reaction in tetrahydrofuran (THF) at 40°C for 18 hours overnight. Post-reaction, the samples were washed with methanol and dried under vacuum.

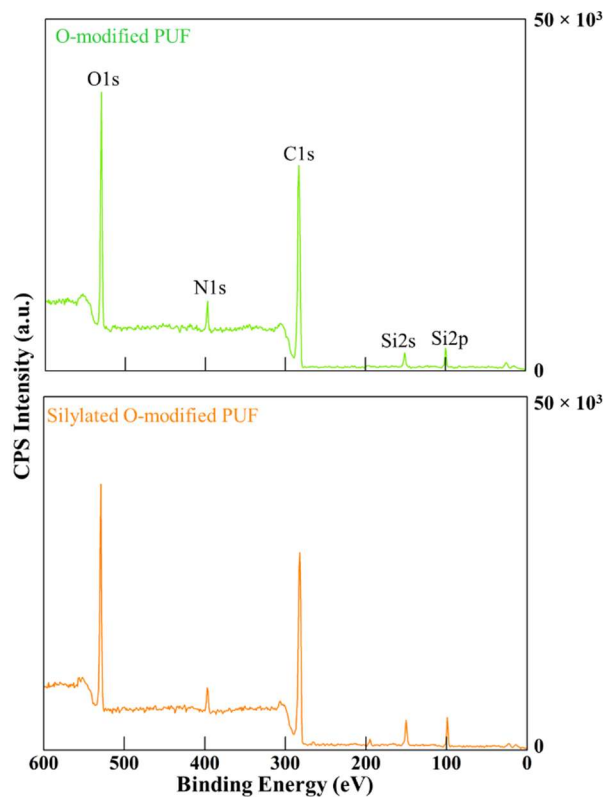


Figure S2. XPS analysis confirmed successful silylation of the O-modified PUFs. The silicon (Si) content on the PUF surface increased from 5.75% to 8.10% after the silylation process, indicating the addition of silyl groups.

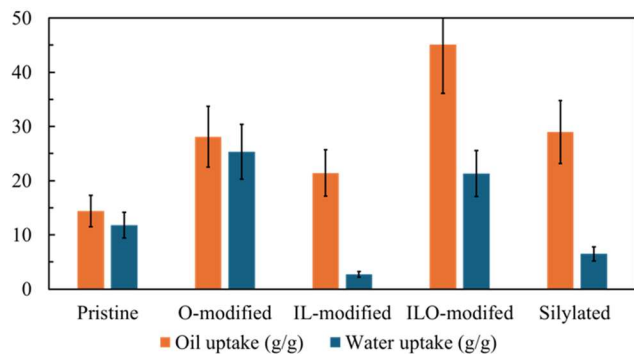


Figure S3. Oil/water uptake tests on the silylated O-modified PUFs showed lower hydrophilicity compared to O-modified samples due to the presence of non-polar groups on the surface of the foam.