Chemical Engineering Journal 323 (2017) 191–202

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synthesis of lignin-based polyurethane/graphene oxide foam and its application as an absorbent for oil spill clean-ups and recovery

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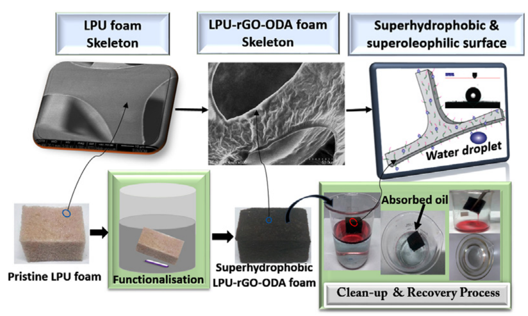
HIGHLIGHTS

- LPU-rGO-ODA foam spill clean-up sorbent was successfully fabricated.
- Hydrophobic/oleophilic molecule incorporation into pristine LPU foam was achieved.
- LPU-rGO-ODA exhibits high sorption capacity and recovery than commercial PP sorbent.
- Excellent reusability and oil/water selectivity is displayed by LPU-rGO-ODA sorbent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 January 2017
Received in revised form 7 April 2017
Accepted 9 April 2017
Available online 12 April 2017

Keywords:
Superhydrophobic
Superoleophilic
Polyurethane foam
Separation
Oil absorbent
Oil spill clean-up

ABSTRACT

Superhydrophobic and superoleophilic foam-like materials are attracting significant interest as promising absorbent for oil spill clean-up from water bodies. In this work, we report the synthesis of lignin based polyurethane (LPU) foam and its surface modification to form a superhydrophobic and superoleophilic sorbent, for use in spill clean-ups. The interior matrix of the LPU foam substrate was grafted with adhesive polydopamine-reduced graphene oxide (rGO) and octadecylamine (ODA), which reacted to transform the LPU foam skeleton to a superhydrophobic and superoleophilic 3-D structure. The resulting foam (designated as LPU-rGO-ODA) was shown to retain the interconnected porous structure, with a water contact angle of 152°. Spectroscopic and microscopic analyses were conducted to investigate the structure and morphology of the foam. Sorption experiments with crude oil, engine oil, kerosene and chloroform showed that the LPU-rGO-ODA foam was an excellent oil sorbent with a sorption capacity of 26–68 times its own weight, which was much greater than that of a commercial non-woven polypropylene sorbent. The LPU-rGO-ODA foam also exhibited a high selectivity to oil sorption and excellent reusability over repeated sorption-squeezing cycles. The absorbed oils in the sorbent could be removed and collected simply by squeezing the oil-laden sponge, and the foam sorbent became ready for reuse in next sorption cycle. As such, LPU-rGO-ODA foam is expected to be a promising oil sorbent for potential applications in oil-spill clean-ups.

1. Introduction

Clean-up of oil spill from water bodies is a worldwide challenge in view of the frequent occurrences of oil spill accidents and increasing domestic and industrial oily wastewater [1]. This has

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http://dx.doi.org/10.1016/j.cej.2017.04.054
1385-8947/

resulted in severe ecological problems, and research efforts have currently been devoted to control and rectify the catastrophic effects of oil spills on the environment through the development of effective clean-up materials for the removal and recovery of the spilled oil from the polluted water [1–6]. To address this challenge, considerable efforts have been made to clean-up oils and other organic pollutants from water using various remediation techniques (e.g., the use of absorbents, chemical dispersants and solidifiers, in-situ burning of the oil in water, mechanical clean-up, and bioremediation) [3,4,7–9]. Among these techniques, the use of porous absorbents is particularly appealing and promising because the oil pollutants are absorbed and held in place within the absorbent matrix, making subsequent recovery of the oil from its semisolid sorbent phase feasible [10–14,61]. This approach is also environmentally friendly in comparison to in-situ burning, which often causes hazardous secondary pollution to the environment.

Traditional porous absorbents for oil spill clean-ups based on natural materials include (corn stalks, vegetable fibres, cottongrass fibres, cottongrass mats, and kapok fibres etc.) and they generally exhibit a slow oil absorption rate, low oil sorption capacity and poor reusability [15–21]. Recently, chemically synthesized superhydrophobic oil absorbing materials has generated much interest because of the increasing demands for high absorption capacity, oil/water selectivity and reusability for efficient separation and recovery of oil from water surfaces [22–25]. However, the high costs of the raw materials and the sophisticated processes associated with the fabrication of such absorbents often limit their applications at commercial scales. Therefore, this calls for the development of cost-effective absorbent materials with improved characteristics for oil spill clean-ups.

Polyurethanes are a broad class of polymers having urethane moieties, and polyurethane (PU) foam represents one of its most important three-dimensional (3D) products commercially available, which has become a conventional substrate used in fabricating superhydrophobic absorbents for oil clean-up [26–33]. With a high hydrophobicity and oleophilicity, PU foam possesses the important characteristics as an absorbent for oil clean-up. However, most commercially available PU sponges exhibit hydrophilicity to some extent or even poor hydrophobicity, which compromises their practical use for oil spill clean-up and recovery. Therefore, surface modification to enhance the oil-wettability and hydrophobicity of PU is desired to make it a superhydrophobic and superoleophilic oil absorbent.

Recently, Wang et al. [30] fabricated a superhydrophobic PU absorbent by coating an ultrathin silane layer onto a polyurethane foam, and its potential use for oil spill and organic pollutant clean-up was demonstrated. The fabrication involved deposition of a Al_2O_3 transition layer onto the PU foam skeleton, followed by coupling silane molecules onto the foam skeleton through the hydroxyl groups on the surface of the Al_2O_3 layer. Although the modified PU foam sorbent obtained was reported to exhibit excellent oil-affinity and water repellence without compromising its elasticity and porosity, the scale-up of the fabrication process is likely to be rather costly. Zhou et al. [26] developed a vapour-phase deposition process to fabricate superhydrophobic and oleophilic polypyrrole-1H,1H,2H,2H-per fluorooctyltriethoxysilane (PPy-PTES) sponge sorbent from commercial PU sponges for the clean-up of oil spills and organic pollutants. The sorbent was produced by dip coating of PU in a solution of $FeCl_3$ and 1H,1H,2H,2H-perfluorooctyltriethoxysilane, followed by a second coating with polypyrrole (PPy). Their conclusions suggest that this sorbent material may find practical applications for clean-up of oil spills and removal of organic pollutants from water surfaces.

In the present study, a lignin based PU (LPU) foam substrate was synthesised and subsequently functionalized to fabricate a superhydrophobic absorbent for oil spill clean-up. Lignin is a renewable material with abundant hydroxyl groups that may be obtained from various forestry and agricultural wastes (i.e., wood, wheat straws, and corn stalks) and it has been reported that lignin can copolymerize with isocyanates in producing PU foams [34–37]. It may be pointed out that lignin is considered to be an economical substitute for polyol, which is derived from petroleum resources, and that lignin can also reduce the permeability of water across the walls of plant cells [34]. This property can be exploited to produce a hydrophobic LPU foam substrate for fabricating oil spill clean-up absorbent.

In this work, superhydrophobic and superoleophilic absorbent for oil spill clean-up was fabricated based on a hydrophobic LPU substrate coated with adhesive polydopamine-reduced graphene oxide (rGO). The idea was to synthesize LPU foam and enhance its hydrophobicity by incorporating long hydrophobic $-CH_2$ chains and alkyl groups from octadecylamine (ODA) functionalizing molecules through an adhesive coating of polydopamine rGO on the LPU foam. The $-CH_2$ long chains, which have good affinity for oil and lower surface free energy than water, were responsible for the different wettability of the resulting LPU-rGO-ODA foam sorbent to oil and water droplets. It is the wetting difference between water and oil on the porous LPU-rGO-ODA foam sorbent surface that forms the basis to separate water/oil effectively in the oil spill clean-up process. Unlike some of the previously reported superhydrophobic sorbents in which the hydrophobic coatings are attached physically onto the substrate skeletons [14,28,38] and are vulnerable to detachment by squeezing when reused repeatedly during oil spill clean-up, the hydrophobic and oleophilic coating layer of the LPU-rGO-ODA foam sorbent so prepared are covalently bonded, and they will remain un-detached by squeezing. This is made possible because of the endowed adhesive polydopamine rGO, which undergoes secondary reaction with the ODA molecules via a Michael addition or Schiff base reaction to form covalently-grafted functional layers [25,39–41]. The properties and performance of the LPU-rGO-ODA foam sorbent related to clean-up of spilled oil and organic pollutants were also investigated.

2. Experimental section

2.1. Materials

Polyphenylmethane polyisocyanate (PMDI) was purchased from Wanhua Chemical Group, China. Castor oil was purchased from Sangon Biotech (Shanghai) Co., Ltd., and polyethylene glycol (PEG-400, average molecular weight 400) was purchased from Chinasun Specialty Products Co., Ltd, China. Lignin (alkaline) was purchased from Adams Reagent Co., Ltd. Surfactant (polymethylphenylsiloxane), catalyst (dibutyltin dilaurate), graphite, oil red and methylene blue were all purchased from Energy Chemical Shanghai, China. Glycerin, sulphuric acid, cyclohexane, tetrahydrofuran (THF), 1,2-dichloromethane, chloroform, toluene, benzene, cyclohexane, acetone, ethanol, carbon tetrachloride, NaOH, 1,4-dioxiane and silicone oil were purchased from Shanghai Chemical Reagents Co. Ltd. Imidazole and phthalic anhydride were purchased from Sigma Aldrich. Commercial nonwoven-polypropylene sorbent (PPS) was purchased from Suzhou YJ Environmental Protection Co. Ltd, and SJ MA 10 W-50 engine oil was purchased from Sinopec, China. Crude oil was provided by Dondying HAIKE Group, Shandong, China. All chemicals were used as received without further purification. Water used in this study was deionized.