ELSEVIER

2013 International Symposium on Environmental Science and Technology (2013 ISEST)

Oleophilic polyurethane foams for oil spill cleanup

Hua Li[a], Lifen Liu[a,*], Fenglin Yang[a]

[a]MOE, Key lab of Industrial Ecology and Environmental Engineering, School of Environmental Science & Technology, Dalian University of Technology, Dalian 116024, China

Abstract

To improve the oleophilic and hydrophobic properties of polyurethane (PU) for oil spill cleanup, graft copolymerization of oleophilic monomer was performed using divinylbenzene (DVB) as the cross-linker, benzoyl peroxide (BPO) as the initiator, toluene as the solvent. The grafting reaction was carried out by placing the PU foams in toluene solutions of monomer at constant temperatures. The effects of the monomer ratio, cross-linker, initiator, polymerization time, and different grafting monomers were studied. The optimum monomer, polymerization time, initiator, cross-linker and monomer weight ratios were found to be Lauryl methacrylate (LMA), 6 h, 5 % and 1.5 % of PU, and the ratio of LMA to PU at 1.5, respectively. The maximum sorption obtained was 46.98g diesel and 41.42g kerosene per gram of modified PU. The water sorption of the modified PU decreased 50%, compared with the blank PU.

Keywords: Raft copolymerization; Polyurethane foam; Lauryl methacrylate; Oil sorption

1. Introduction

Recently, the ocean pollution by oil spillage has been noted as a big environmental problem for the world. As the adverse impacts of spilt oil to ecosystems and the long-term effects of environmental pollution, it calls for an urgent need to develop a wide range of materials for cleaning up oil from oil impacted areas effectively, as the treatment should vary with time, the type of oil and spill scale, the location and weather conditions [1]. Representative treatments of spilt oil include usages of oil dispersant, oil gelling agent, and oil sorbent [2]. Each method has its own advantages and disadvantages. The use of sorbents is considered the most ideal solution because it can remove oil from the sea. Oil sorbents can be divided into three basic types: natural inorganic, natural organic, and synthetic.

The natural inorganic sorbents such as clay [3], perlite [4], and glass wool [5] are inexpensive and available in large quantities. Natural organic sorbents consist of hay, feather, straw, peat moss [6], and

---

* Corresponding author. Tel.: +86-411-84706173; fax: +86-411-84708083.
E-mail address: yuzhe25521@yahoo.com.cn.

other carbon-based products. The disadvantage of natural sorbents is that they are dusty, difficult to use under windy conditions, and have little oil absorbency. In addition, some natural organic sorbents absorb not only oil but also water, causing the sorbents to sink. Synthetic organic sorbents such as polymeric foams(polyurethane, polypropylene, polyethylene, and cross-linked polymers including rubber), are the most commonly used commercial sorbents in oil spill cleanup, due to their oleophilic and hydrophobic properties [7].

The ultralight, open-cell polyurethane foams (PU) have low density and high porosity, it is considered to be a good oil-sorbent. However, since it is formed by the reaction of Di- /poly- functional hydroxyl (polyol) or amino-containing compounds with di-/poly-isocyanates, it has lots of ether- ester-, carbamate- and amide- groups, which make PU absorb not only oil but also water. In this study, in order to develop the oleophilic/hydrophobic properties of PU foams, PU foams were grafting copolymerization with some oleophilic monomers. Lauryl methacrylate (LMA), Butyl Methacrylate (BMA) and Styrene (St) were selected as monomers; divinylbenzene (DVB) was the cross-linker, benzoyl peroxide (BPO) was the initiator and toluene was used as the solvent. The effects of the monomer ratio, amount of cross-linker and initiator, polymerization time and different grafting monomers were studied.

2. Experiment

2.1. Materials

PU (15kg/cm^3 Dalian Lida Co., Dalian, China, cut to 1cm×1cm×1cm before being used). LMA (Shanghai aoke Co., Shanghai, China). BMA (AR; FuChen Chemical Reagent Co., Tianjin, China). St (AR; FuChen Chemical Reagent Co., Tianjin, China). Divinylbenzene(DVB) (AR; TCI Co., Japan). Benzoyl peroxide (BPO) (AR; Damao Chemical Reagent Co., Tianjin, China), Toluene (AR; FuChen Chemical Reagent Co., Tianjin, China), Ethanol (AR; FuChen Chemical Reagent Co., Tianjin, China), diesel (Tech; Dalian, China) and kerosene (Tech; Dalian, China) .They were all used as received.

2.2. Synthesis

The reaction was run in a 100 ml three-necked reaction flask equipped with thermometer, nitrogen gas inlet and reflux condenser. A given weight of initiator benzoyl peroxide (BPO) was dissolved in 50ml toluene. The PU cubes were totally immersed into the stirred reactive solution for 20 min at 80℃. The mixture of LMA with DVB cross-linker was then added to the flask. After 6h of reaction at a stirring speed of 500 rpm under a nitrogen atmosphere at 80℃. The cubes were washed with ethanol and deionized water for several times, then dried at 60℃under vacuum for 48h.

2.3. Sorption capacity test

The method developed for the measurement of oil sorption capacity of the sorbent was based on ASTMF726–99: Standard Test Method for Sorbent Performance of Adsorbents.

For oil sorption tests, diesel or kerosene (50ml) was poured into a 100ml beaker. The sorbent was weighed and the value recorded, then it was immersed into the oil. In general, after 20 min±20 s of immersion, the sorbent was removed and allowed to drain for 30 s±3 s. The saturated sorbent was then immediately transferred to a pre-weighed weighing bottle and weighed. The oil sorption of sorbent on a weight basis was calculated as follows:

$$\text{Oil sorption (g/g)} = (S_t - S_0)/S_0 \tag{1}$$

where S_0 is the initial dry weight of a sorbent, S_t is the weight of sorbent with oil absorbed.

For water sorption tests, the sorbent was first weighed then placed in a 100ml Erlenmeyer flask which was filled with 50ml water. The sealed container was then placed in a shaker (150 rpm) and shaken for 15

min. The contents of the flask were allowed to settle for a period of 2 min. The sorbent was removed and allowed to drain for 30 s±3 s, then immediately transferred to a pre-weighed weighing bottle and weighed. The water sorption on a weight basis was calculated as follows:

$$\text{Water sorption (g/g)} = (S_t - S_0)/S_0 \qquad (2)$$

where S_0 is the initial dry weight of sorbent, S_t is the weight of sorbent (after water sorption).

All tests performed at $23\,°C \pm 4\,°C$ and were carried out in triplicate with the mean of the three runs used for calculations. If the value of any run (g/g) deviated by more than 15% from the mean of the three runs, then the sample was rejected and the test repeated with three new specimens.

3. Results and discussion

3.1. Effect of the ratio of LMA to PU on oil and water sorption

The effect of monomer concentration on oil and water sorption was studied by changing the ratio of LMA to PU from 0.0 to 2.0, at constant grafting polymerization conditions: at temperature (80 °C), polymerization time (6 h) and added initiator was 5%wt of PU, added cross-linker was 1%wt of PU.

It can be seen from the Fig. 1, the oil absorbency was initially increased with the increase of monomer concentration, reached a maximum value (44.96g/g for diesel sorption, 40.73g/g for kerosene sorption) and then decreased. As the monomer concentration increased, the diffusion of monomer molecules into the PU structure increased, leading to higher oil sorption. However, the oil sorption was decreased when the ratio of monomer to the PU mass was over 1.5. This may be caused by the enhanced homo-polymer formation at high monomer concentrations, that increased gel-formation and shielded the active sites, eventually affected the further grafting reaction[8]. On the other hand, the grafted PU foam had decreased water sorption with the increase of monomer concentration. When the oil sorption reached the maximum value, the water sorption was 6.51g/g, a decrease of 54%, compared with the blank PU. Grafting LMA made the PU more hydrophobic and oleophilic, and the ratio of LMA to PU was 1.5 the optimum value
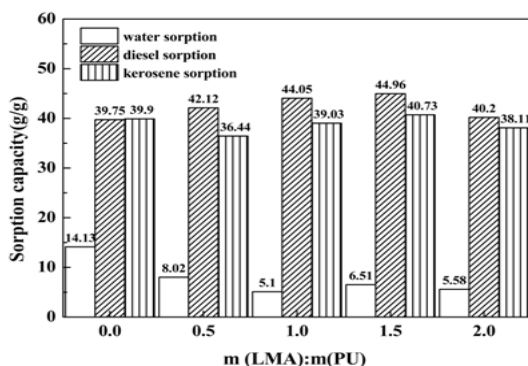

Fig. 1. Effect of the ratio of LMA to PU on oil and water sorption.

3.2. Effect of the initiator concentration on oil and water sorption

In Fig. 2, the effect of initiator concentration on oil and water sorption was shown. The oil sorption of the grafted PU foam increased as the BPO concentration increased from 1% to 5%. Further increases in BPO concentration decreased the oil sorption. Free radicals occurred as a result of the decomposition of BPO in various reactions in the polymerization media. An increase in the concentration of BPO increased

the chance of hydrogen abstraction from the PU backbone and chain transfer reactions of LMA homo-polymer with PU. However, the excess increase in the concentration of BPO caused termination reactions of PU macro-radicals or growth of polymer chains or combined reactions between them, consequently, the graft yield decreases [9] and the oil sorption decreases. Initiator addition at 5%wt of PU was the optimum value.
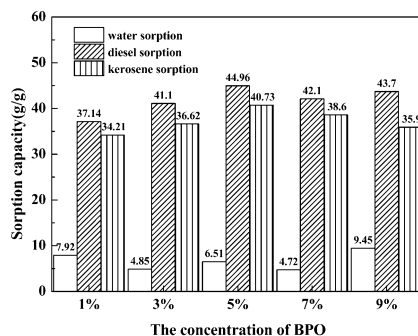

Fig. 2. Effect of the concentration of BPO on oil and water sorption. Reaction temperature 80℃, reaction time 6 h , m (LMA): m (PU)=1.5 and cross-linker concentration(1%wt of PU).

3.3. Effect of the cross-linker concentration on oil and water sorption

For oil-absorbing materials, a cross-linked network structure on the surface of PU was a key factor, if a network structure did not form, even if the grafting rate was high, the grafted polymer may be dissolved in the oil that lowers the oil sorption. In Fig. 3, the effect of cross-linker concentration on oil and water sorption was shown. The oil sorption was initially increased, and later decreased with the increase of cross-linker concentration. When the cross-linker concentration was not enough, it couldn't form a network structure, the grafted polymer may get dissolved in the oil. When the cross-linker concentration was excessive, the network surface of the PU was too dense to adsorb more oil, which reduced oil sorption [10]. The optimal cross-linker added was 1.5% of the amount of PU. The maximum oil sorption of this grafted PU foam was 46.98g/g for diesel and 41.42g/g for kerosene, and the water sorption was reduced to 7.03g/g.

3.4. Effect of the polymerization time on oil and water sorption

The effect of polymerization time on oil and water sorption was investigated by changing the polymerization time (from 4 to 8h) at constant polymerization conditions (temperature 80℃, monomer ratio of LMA to PU=1.5, initiator and cross-linker was 5% and 1.5%wt of PU, respectively). As shown in Fig. 4, oil sorption first increased with an increase in polymerization time and then reached a saturation value at 6h for LMA. The maximum oil sorption was obtained 46.98g/g for diesel and 41.42g/g for kerosene. As the polymerization time increased, the polymer network on the PU surface was getting too dense, which resulted in a lower oil sorption [11]. So, the best polymerization time was 6 h.

3.5. Effect of the different grafting monomers on oil and water sorption

The effect of different grafting monomers on oil and water sorption was studied, using Lauryl methacrylate, short-chain butyl methacrylate monomer(BMA) and styrene monomer(St), at constant

conditions (grafting temperature 80℃, 6 h polymerization time and 5%wt PU initiator, 1.5%wt PU cross-linker, and constant ratio of monomer to PU 1.5). In Fig. 5, the result showed that PU grafted with the long-chain LMA monomer had the maximal oil sorption, 46.98g/g for diesel and 41.42g/g for kerosene. According to the principle of similar polarity and similar solubility parameters, the solubility parameters of Lauryl methacrylate was most closed to the oil solubility parameters, so grafting Lauryl methacrylate on PU had increased the sorbent oil sorption to higher level [12].
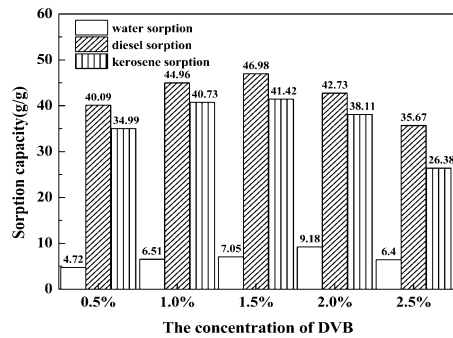

Fig. 3. Effect of DVB on oil and water sorption. Reaction temperature 80℃, reaction time 6 h, m (LMA): m (PU)=1.5 and initiator concentration (5%wt of PU).
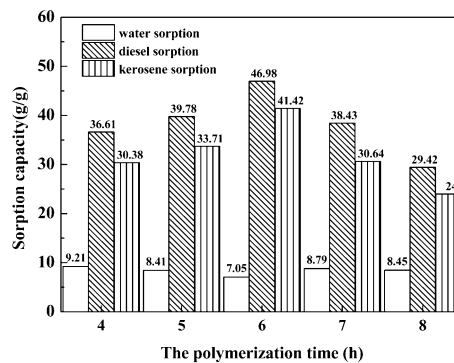

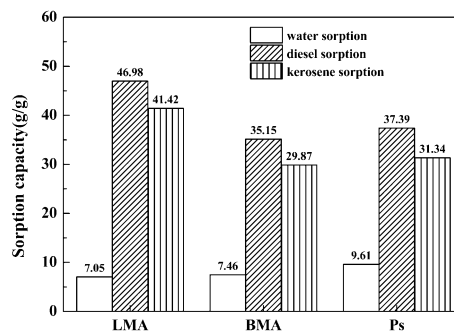Fig. 4. Effect of the polymerization time on oil and water sorption.

Fig. 5. Effect of the grafting different monomers on oil and water sorption.

3. Conclusions

In this study, copolymer-grafting PU foams with different oleophilic monomer was carried out using divinylbenzene (DVB) as the cross-linker, benzoyl peroxide (BPO) as the initiator, toluene as the solvent. The determined optimal polymerization conditions for obtaining a sorbent with higher oil removal capacity were as follows: ratio of LMA to PU 1.5, amount of cross-linker DVB=1.5 %wt PU, amount of BPO =5.0 % wt PU, polymerization time 6h. The maximum oil sorption of the grafted PU foams was 46.98g/g for diesel and 41.42g/g for kerosene. The grafting treatment reduced PU foams water sorption by 50%, to 7.03g/g.

References

[1] ADEBAJO M.O., FROST R.L., KLOPROGGE J.T., CARMODY O. and KOKOT S.. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties, *J. Porous Mater*. vol.10, pp. 159–170, 2003.

[2] SHIMIZU TOSHIKI, KOSHIRO SATORU, YAMADA YOSHIO and TADA KOICHI. Effect of Cell Structure on Oil of Highly Oil Absorptive Polyurethane Foam for On-Site Use. *J. Appl. Polym. Sci.* vol.65, pp. 179–186, July 1997.

[3] Carmody Onuma, Frost Ray, Xi Yunfei, Kokot Serge. Adsorption of hydrocarbons on organo-clays-Implications for oil spill remediation. *J. Colloid Interface Sci.*, vol. 305, pp. 17–24, 2007.

[4] Bastani D. , Safekordi A.A. , Alihosseini A., Taghikhani V.. Study of oil sorption by expanded perlite at 298.15K. *Sep. Purif. Technol.*, vol.52, pp.295–306, 2006.

[5] Annunciado T.R., Sydenstricker T.H.D., Amico S.C.. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *Mar. Pollut. Bull.*, vol.50,pp.1340–1346,2005.

[6] Suni S., Kosunen A.-L., Hautala M., Pasila A., Romantschuk M.. Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills. *Mar. Pollut. Bull*, vol.49, pp. 916–921, 2004.

[7] Duong Hien T. T., Burford Robert P.. Effect of Foam Density, Oil Viscosity, and Temperature on Oil Sorption Behavior of Polyurethane. *J. Appl. Polym. Sci.* vol.99, pp. 360–367, 2006.

[8] Sanli O., Pulat.E. Solvent assisted graft copolymerization of AAm on PET films using benzoyl peroxide initiator. *J. Appl. Polym. Sci.* vol.47, pp. 1–6, 1993.

[9] Pulat Mehlika, Babayigit Dogan. Surface modification of PU membranes by graft copolymerization with acrylamide and itaconic acid monomers. *Polym. Test*, vol.20, pp. 209–216, 2001.

[10]Ha lidanM ama t, Kurbanjian Rouz, Ab lim it, Aynnur. Synthesis of AlkylMethacrylate Modified Cellulose Based Oil Material. *Petrol Chem. Techno.*, vol.39, pp. 664–668, 2010.

[11] Zhou Xiao-Ming, Chuai Cheng-Zhi. Synthesis and Characterization of a Novel High-Oil-Absorbing Resin. *J. Appl. Polym. Sci.* vol.115, pp. 3321–3325, 2010.

[12] Ding Lei, Li Yi, Jia Di, Deng Jianping, Yang Wantai. β-Cyclodextrin-based oil-absorbents:Preparation, high oil absorbency and reusability. *Carbohydr. Polym.*, vol.83, pp. 1990–1996, 2011.