Materials Letters 213 (2018) 44–47

Contents lists available at ScienceDirect

Materials Letters

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

Porous polyamide monolith by continuous solution foaming as reusable oils and organic solvents absorbent

Liang Wang [a,*], Fangfang Ai [a], Yongsheng Liu [a,b], Yong Liu [a,*]

[a] School of Textiles, Tianjin Polytechnic University, No.399 Binshui West Road, Xiqing District, Tianjin 300387, China
[b] Key State of Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China

ARTICLE INFO

Article history:
Received 9 August 2017
Received in revised form 17 October 2017
Accepted 4 November 2017
Available online 4 November 2017

Keywords:
Porous materials
Polymers
Polyamide
Solution-foaming
Reusability
Oil spill

ABSTRACT

In this study, we prepared highly porous polyamide (PA) monolith in a continuous and scalable solution foaming process. The created materials, displaying a structure with both open and closed pores, had oils or organic solvents uptake capacities ranging from about 4.8 to 10.7 g/g. Moreover, they had sorption retention higher than 96% after 10 cycling tests because the structures of pores were not broken during the adsorption process. On the other hand, they absorbed oils and organic solvents rapidly and reached saturation in 30 s. A great promising way was provided to fabricate highly porous PA for the cleanup of large-scale oil or organic solvent spills.

1. Introduction

It has been receiving growing worldwide concern on the accidental leakage of oil and other organic liquids that caused greatly adverse impact on ecosystems and long-term environmental pollution. Current methods that were employed to treat oil spill remediation included in-situ burning, oil booms and adsorption [1,2]. Among them, oil separating by adsorption using porous materials was thought to be a more economical and efficient approach. Generally, an idea oil absorbent should have excellent buoyancy, high uptake capacity, low cost and be either reusable or biodegradable. Porous hydrophobic and oleophilic materials have recently emerged as an attractive alternative in absorbing oil due to their outstanding oil/water selectivity and excellent oil uptake capacity. Some examples of these materials included polyurethane foam [3], nanocellulose aerogel [2], carbon sponge [1,4], electrospun nanofibers [5,6] and porous metal-organic frameworks [7]. However, complicated synthesized procedure, difficult scale-up and high cost limited their practical applications. Therefore, there is an urgent need to develop novel technologies to make absorbents with inexpensive, reusable materials in a high through-put process. Fibrillar polypropylene- polytetrafluoroethylene (PP-PTFE) open-cell foam was fabricated on a large-scale in a melting extrusion process, having an oil uptake up to 25 g/g [8]. Nevertheless, to our best knowledge, there is no more study on the method that can realize large-scale production of porous absorbents. In this work, we developed an efficient and low-cost method of continuous manufacturing porous polyamide (PA) monolith on a large-scale. The structures as well as adsorption properties of created materials were investigated.

2. Experiments

PA6 with a molecular weight of 20,000 was brought from Ube Industries (Japan). Formic acid, sodium bicarbonate ($NaHCO_3$), N-hexane, N, N-dimethylformamide (DMF) and anhydrous ethanol were bought from Fengchuan chemical reagents (Tianjin). Vacuum pump oil was obtained from Sifang special oil (Beijing). Soybean oil was produced by Joyue Co., Ltd. (Tianjin). Gasoline and mineral oil were supplied by Anhui Zhongtian Petrochemical Co., Ltd. The preparation of PA foams followed the scheme illustrated in Fig. 1a. PA pellets were firstly dissolved in formic acid with a concentration of 16 wt% by magnetically stirring at room temperature for 3 h. Then 6 ml of transparent PA solution were transferred to plastic cylinder moulds with a diameter of 30 mm and a height of 20 mm. $NaHCO_3$ aqueous solutions (3 wt%) were continuously injected and reacted with formic acid, generating CO_2 that acted as a foaming agent. Finally, foam-like PA was obtained after being

---

* Corresponding authors.
E-mail addresses: liangwang@tjpu.edu.cn (L. Wang), liuyong@tjpu.edu.cn (Y. Liu).

https://doi.org/10.1016/j.matlet.2017.11.017
0167-577X/© 2017 Elsevier B.V. All rights reserved.

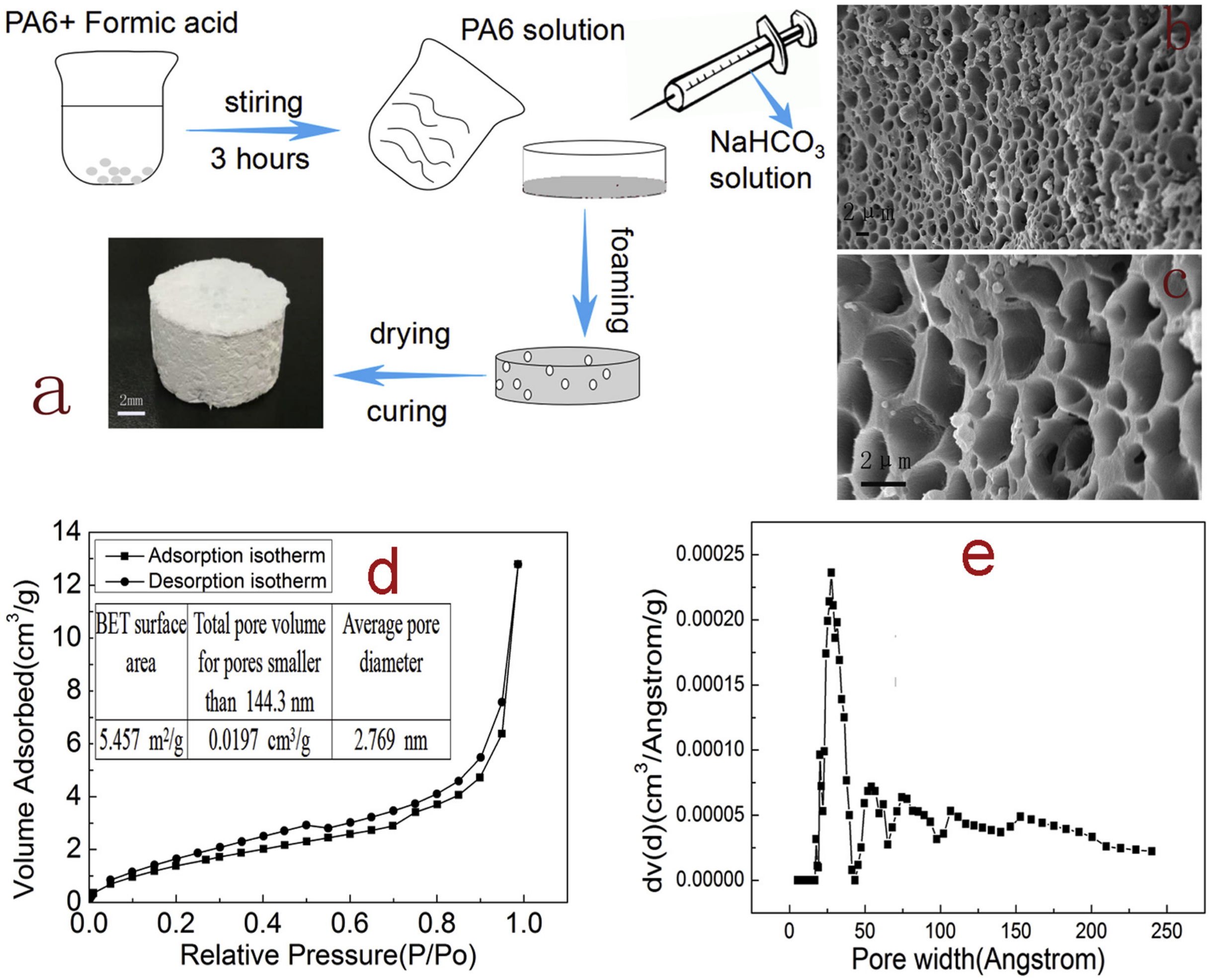

Fig. 1. (a) Scheme of preparation of porous PA monolith; (b) and (c) SEM micrographs obtained sample; (d) Nitrogen adsorption/desorption isotherms and (e) pore size distribution curve and BET analysis results of porous PA monoliths.

washed by deionized water for 4 times and dried in an oven at 60 °C for 6 h. A scanning electron microscope (SEM, Gemini500) was used to demonstrate the internal structure. The adsorption-desorption isotherm, surface area, and pore size distribution were characterized using a Quantachrome Autosorb instrument (iQ-C, Kangta) with nitrogen as the adsorbate. Mercury porosimetry was conducted using a microporous structure analyzer (Active pore IV9500, McMurray). The uptake capacity (Q) of oils and organic solvents of sample was determined by the mass before (m_0) and after (m) adsorption, $Q = (m-m_0)/m_0$, following the previous procedure [9]. To determine the reusability of PA foams, 10 times of cycling adsorption tests were conducted. The adsorption rates of samples were tested as the oil or organic uptake in term of contact time.

3. Results and discussion

The SEM micrographs of porous PA monolith are displayed in Fig. 1b and c. It had a three-dimensional (3-D) porous architecture with both closed and open cells and a mean pore size of ~2 μm. When $NaHCO_3$ aqueous solutions were injected to react with formic acid, phase separation of PA molecules from solvent occurred, forming the skeleton or cell walls of porous materials. In the mean while, large amount of CO_2 were generated. A short balance between surface tension of polymer solutions and foaming gas pressure may be realized in a mould, leading a structure with macropores. They had an apparent density of 0.074 g/cm^3 and exhibited a porosity of 93.4%. Moreover, open cell accounted for 55.6% according to mercury porosimetry. The BET surface area and the pore size distribution were also investigated. Fig. 1d shows the nitrogen adsorption-desorption isotherms of the PA monoliths. The hysteresis loop (type V) indicated the presence of mesopores. The adsorption was relatively high at P/P0 approaching 1.0, suggesting both macro and mesopores existed in the sample [8]. The corresponding pore-size distribution of the PA monoliths (Fig. 1e) revealed that they owned mesopores with a narrow size distribution ranging from 2 to 5 nm.

The obtained porous PA selectively absorbed the vacuum pump oil that floated on the water as illustrated as Fig. 2a. This suggests porous PA monoliths created in this work could be used in treating marine oil spill. The mass adsorption capacities of porous PA monolith to different substances are shown in Fig. 2b. The prepared absorbent had an uptake capacity of 10.7, 6.2, 10.0, 7.4, 8.0, 4.8 and 10.0 g/g to soy bean oil, gasoline, vacuum pump oil, mineral oil, ethanol, N-hexane and DMF, respectively. Due to the relatively low hydrophobicity of PA, the sorption performance of the PA monoliths were inferior to ones of foams modified by superhydrophobic treatment [10,11]. Among the porous polymer sorbents fabricated with simple process and low cost, the porous PA absorbed less oils or organic solvents than the open-cell PP-PTFE (5–24 g/g) [8]. However, they had a comparable sorption capacity