



Biodegradable polylactic acid porous monoliths as effective oil sorbents



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ABSTRACT

The ecological and environmental damage resulting from oil pollution is an area of great concern. Biocompatible porous monoliths based on polylactic acid (PLA) modified with reduced graphene oxide (rGPLA) as effective oil sorbent were prepared by freeze-drying. The porous monoliths were characterized by scanning electron microscopy and X-ray diffraction. Their physical properties including water contact angles, compressive strengths and moisture absorption were investigated. The incorporation of reduced graphene oxide (rGO) increased the hydrophobicity of the rGPLA porous monoliths resulting in highly selective absorption for oil. In addition, the use of rGO increased the compressive strength of the porous monoliths so they could be recycled. These porous rGPLA monoliths are green biodegradable efficient absorbents that should be useful for the treatment of oil spills.

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1. Introduction

The ecological and environmental damage resulting from oil pollution is an area of great concern [1–4]. Various approaches are being studied to deal oil spills including booms, skimmers, absorbents, in-situ burning, hydrocarbon-degrading microorganisms, dispersants and solidifiers [5,6]. Among these methods low cost absorbents are considered the most efficient and economical. In addition absorbents are considered to be ecologically friendly since do not generate by-products that may cause further pollution [7,8]. Commonly used absorbent materials include inorganic mineral materials [9,10], composite materials [5,11] and nature fibers [12,13].

Although absorbents are widely used in practical applications, some limitations of these materials are needed to be overcome, such as environmental incompatibilities and poor recyclability [14–16]. In particular, some of these materials absorb water and oil simultaneously which reduces the separation selectivity and efficiency [17]. Therefore, there is a pressing need to develop absorbent materials with high oil absorption capacities, high selectivity, excellent recyclability and that are environmentally benign [18].

Recently, porous materials with superhydrophobicity and superoleophilicity have received extensive attention due to their potential applications for oil-water separation. This is because these materials only absorb oils [19,20]. For example, Hu et al. prepared carbon nanotube-graphene hybrid aerogels with superhydrophobicity and superoleophilicity for oil sorption [21], and Bi and co-workers prepared sponge graphene which was a highly efficient and recyclable sorbent for oils and organic solvents [22]. However, these materials were limited by cost and complex preparation processes for practical applications high.

Poly(lactic acid) (PLA) is a promising biodegradable polymer material because it has good biocompatibility, good physical and mechanical properties, and excellent permeability [23–25]. PLA has been used as an alternative to conventional synthetic polymers [24]. However, the water contact angle of PLA is about 85°, which is not suitable for oil-water separations [26]. Therefore, in order for PLA to be useful in oil-water separations, it would need to be modified to make it more hydrophobic. Reduced graphene oxide (rGO) is the reduction product of graphene oxide (an oxygen-abundant material produced by the controlled oxidation of graphite [27]). Reduced graphene oxide has some excellent properties like high mechanical strength and a large surface area [28], but most importantly, rGO is oleophilic [29], which makes it a good material for hydrophobic modification.

Herein, porous monoliths based on PLA modified with rGO (rGPLA) were prepared by freeze-drying. The rGO modification

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caused the porous rGPLA monoliths to become more oleophobic and stronger. Therefore, the porous rGPLA monoliths should be cost effective, highly efficient, selective, reusable and biodegradable absorbents for oil spills.

2. Materials and experimental

2.1. Materials

Graphite was obtained from Qingdao Graphite Co. and polylactic acid was from Shenzhen BrightChina Industry Co. Corn oil and olive oil were from Wal-Mart. Diesel oil was from China Petroleum & Chemical Co. Vacuum lubricant oil, mineral oil, 1,4-dioxane and hydrazine were from Tianjin Chemical Reagent Co. All the chemicals were used as received.

2.2. Preparation of rGO

Graphene oxide (GO) was prepared from purified natural graphite by a modified Hummer's method [30] and then was reduced with hydrazine as showing in [supplementary information \[29,31\]](#).

2.3. Preparation of porous rGPLA monoliths

A weighed amount of PLA was added to 1,4-dioxane and stirred to form a PLA solution. Next rGO powder was added to the PLA solution with stirring, followed by ultrasonic treatment (200 W) for about 1 h. This resulted in a rGPLA suspension. Two series of samples were prepared as follows: series 1 was PLA suspensions with different PLA weight percentages (1.0%, 1.5%, 2.0%, 2.5% and 3.0%); series 2 contained different weight percentages of rGO (1.0%, 1.5%, 2.0%, 3.0%, 4.0% and 5.0%) relative to the weight of PLA.

The rGPLA suspensions were poured into plastic tubes (20-mm in diameter and 50-mm in length) that were placed in insulated Styrofoam containers. The tubes were then frozen with liquid nitrogen. Next the solidified mixtures were transferred to a freeze-drying vessel (Alpha1-2, Christ, Germany) and freeze-dried at $-50\text{ }^{\circ}\text{C}$ for 48 h under vacuum (less than 20 Pa) to obtain porous rGPLA monoliths. Similarly, porous PLA monoliths with no rGO were prepared. The porous monoliths were stored in a desiccator prior to analysis.

2.4. Characterization

2.4.1. Scanning electron microscopy (SEM) observation

The morphology of the porous PLA and rGPLA monoliths were observed with a scanning electron microscope (SEM, JEOL-6700F ESEM, Japan). Before observation, the samples were coated with gold using a sputtering coater (Desk-II; Denton Vacuum, Japan).

2.4.2. Fourier transform infrared (FT-IR) spectra

A Fourier transform infrared spectrometer (Paragon-1000, Perkin-Elmer, USA) was used to characterize the rGPLA monoliths. The powders of rGO, PLA and rGPLA monoliths were pulverized with KBr and pressed into pellets. The spectra were obtained in the range of $500\text{--}4000\text{ cm}^{-1}$ by averaging 16 scans at 1 min intervals to minimize the effects of dynamic scanning. The resolution was 4 cm^{-1} .

2.4.3. X-ray diffraction (XRD) analysis

The X-ray diffraction diagrams of the porous PLA and rGPLA monoliths were measured by step scanning on a X'pert, PANalytical X-ray diffractometer with $\text{Cu K}\alpha$ tube ($\lambda = 1.73\text{ \AA}$) at a scanning rate of $4^{\circ}/\text{min}$ at a voltage of 45 kV and a current of 30 mA. The data

were collected from 10 to 30° (2θ).

2.4.4. Physical properties

The compressive strengths of the porous PLA and rGPLA monoliths were measured by first placing the samples into a programmable temperature and humidity chamber with a temperature of $25 \pm 2\text{ }^{\circ}\text{C}$ and a relative humidity of $65 \pm 2\%$ for about 24 h. Then the compressive strengths of the samples were measured with a dynamic mechanical analyzer at a compressing rate of 1 mm/min.

The hydrophobicities of the porous PLA and rGPLA monoliths were measured with an optical contact angle measuring device (OCA20110524; Dataphysics Instruments, Germany) using a droplet ($4.8\text{ }\mu\text{L}$) of water or lubricant oil as the indicator.

The density (ρ) of the monoliths was calculated using the equation: $\rho = m/V$, where, m is the weight of the monolith and V is the volume of the monolith. The porosity (ϕ) of the sponge was calculated using the relationship: $\phi = V - V_a/V \times 100\%$, where, V (cm^3) is the total volume of the porous rGPLA monoliths, V_a (cm^3) is the actual volume of the material.

2.5. Moisture sorption

The moisture absorbed by the porous PLA and rGPLA monoliths was measured in an environment that contained a $\text{Mg}(\text{NO}_3)_2$ solution to give a relative humidity (RH) of 55%. The samples were placed in the incubators at $25\text{ }^{\circ}\text{C}$ and they were weighed at intervals until their weights became constant. The moisture absorbability (MA) was calculated as follows: $MA = (m_t - m_0)/m_0$, where, m_0 and m_t are the dry weight of the monolith and its weight at a given time, t , respectively. The tests were performed in triplicate and the average value is reported.

2.6. Absorption measurement for oils

2.6.1. Oil absorption capacities of the porous PLA and rGPLA monoliths

The absorption capacities (Q) of the porous PLA and rGPLA monoliths for various organic liquids were measured. All tests were performed at $20\text{ }^{\circ}\text{C}$. A weighed amount of the monolith was immersed in 40 mL of oil or organic solution in a 200-mL conical flask for 5 min. Then the soaked monolith was removed from the solution, held for 10 s to allow the residual surface liquid to drip off, and then the monolith was weighed. The sorption capacity of the monolith was expressed as grams of oil absorbed per gram of monolith (g g^{-1}) and was calculated from the equation: $Q_t = (m_t - m_0)/m_0$, where, Q_t is the sorption capacity of the monolith at a certain time t (s), and m_t (g) and m_0 (g) are the monolith weights before and after the absorption test, respectively. The sorption kinetics of the monolith was investigated by placing a monolith onto the surface of the oil and then measuring the weight of the monolith as a function of the sorption time.

2.6.2. Reusability of the porous PLA and rGPLA monoliths

The porous PLA and rGPLA monoliths were regenerated by simple centrifugation. Centrifuging (5000 r min^{-1} for 1 min) the monolith removed the absorbed oil. Each sample was used for six cycles of absorption and centrifugation.

3. Results and discussion

3.1. Characterization of the porous PLA and rGPLA monoliths

The porous structures of rGPLA monoliths were observed using SEM. [Fig. 1](#) shows the SEM images of the cross sections of the

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