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Nanoporous Electrospun Cellulose Acetate Butyrate Nanofibres for Oil Sorption

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Abstract

Porous superhydrophobic nanofibrous networks based on cellulose acetate butyrate (CAB) were prepared using electrospinning. The morphology and wettability of the prepared fibrous networks was studied using scanning electron microscopy and static contact angle measurements. The porous nanofiber networks exhibited superhydrophobicity and superoleophilicity with a water contact angle of $\sim 165^\circ$ and an oil contact angle of $\sim 0^\circ$. The porous nature of the nanofibres themselves is thought to lead to an increased surface area making them suitable for sorption applications. Due to their hydrophobic and oleophilic nature, they were tested for their oil sorption capacity. They demonstrated an oil sorption capacity of ~ 60 g/g for motor oil, which is four times that of commercially used polypropylene. The nanofibrous mats also demonstrated excellent reusability, retaining $\sim 80\%$ of their sorption capacity for up to 5 cycles of use.

Keywords: Biomaterials, electrospinning, porous materials, superhydrophobic, oil sorbent

1. Introduction

Oily wastewater generated by industries inevitably finds its way into water bodies such as oceans, lakes and rivers, causing catastrophic damage to aquatic life and ecosystems in the long-term [1]. The existing treatment methods for oily waste water include adsorption, gravity separation, electro-coagulation, biological treatment and sedimentation in a centrifugal field [2], with adsorption being the most preferred method. Adsorption is preferred because adsorbents are cost-effective and do not cause secondary pollution. A range of materials have been investigated for oil adsorption, including sand, activated carbon, bentonite, peat, fibreglass, polypropylene, organoclay, and attapulgite [3]. The most commonly used commercial sorbent is organic synthetic polypropylene (PP). PP is commonly used due to its hydrophobic, oleophilic and buoyant nature, notable oil–water selectivity, and

ease of availability. However, PP suffers from low oil sorption capacity, ranging between 15–30 g/g for different kinds of oils [4].

Biopolymer based sorbents for oil water separation have not been widely investigated in the literature. Zhang et al. [5] recently reported a fluorine-free method to prepare a superhydrophobic and superoleophilic cellulose filter paper for oil/water separation. In this work, we report a facile one-step preparation of porous CAB nanofibres using electrospinning. To the best of the authors' knowledge this is the first time that the electrospinning of porous electrospun CAB nanofibres has been reported. CAB was chosen because is inherently hydrophobic due to the presence of butyryl chains [6]. Electrospinning was chosen as the fabrication method as it results in nanofibres with high surface area, high surface roughness (hydrophobicity), and inter-fibre porosity, all of which are beneficial for adsorption. A study on the nanofibres was done to explore their potential as oil sorbents.

2. Experimental

Materials: Cellulose Acetate Butyrate ($M_n \approx 65,000$) with a butyryl content of 16.5- 19.0 % and an acetyl content of 28.0- 31.0 %, acetone and dichloromethane were purchased from Sigma Aldrich, USA. Motor oil (Magnatec, 10W-40) from Castrol, UK was used for the oil sorption test.

Electrospinning: 10 wt.% CAB solution was prepared at room temperature by stirring CAB in a binary solvent system consisting of dichloromethane and acetone with a volume ratio of 1:1. Electrospinning was carried out using a flow rate of 1 mL/hr under an applied voltage of 15-18 kV and a tip-to-collector distance of 20 cm. The temperature was maintained at 25°C and relative humidity (RH) at 60%. Humidity is key in inducing surface porosity on the fibres.

Characterization: The morphology of the electrospun nanofibres was observed using scanning electron microscopy (FEI Quanta 200F). Wettability of the prepared sorbents was determined by static contact angle measurements (DSA100, Kruss, Germany) using a sessile drop technique at 25 °C.

Adsorption experiment: Motor oil was used to investigate the oil sorption capacity. For the sorption experiment, a 0.1g sample of the sorbent was immersed in a beaker containing 50 mL oil for 90 minutes. After 90 minutes, the sorbent was retrieved via tweezers and held vertically for 2 minutes to remove excess oil from the surface. It was then weighed to evaluate its maximum oil absorption capacity. The oil sorption capacity was calculated based on the following equation [7]:

$$Q_{max} = \frac{m_1 - m_0}{m_0}$$

where $Q_{\max}$ is the maximum oil sorption capacity of the sorbent (g/g), m_0 is the mass of the dry sorbent (g) before performing the test, and m_1 is the mass of the saturated sorbent (g) after being immersed in oil for 90 minutes, the test was repeated 3 times.

3. Results and Discussion

As seen in Fig. 1, the obtained nanofibres had pores on their surface; the average pore diameter was measured using ImageJ software, it was found to be in the range 65-80 nm.

Figure 1 Typical SEM images of the porous nanofibres at low and high magnifications, (A) 10,000x (B) 60,000x

The formation of nanopores can be explained using the ‘breath figures’ mechanism, which was first observed by Srinivasarao *et al.* [8]. In this mechanism, the rapid evaporation of the volatile solvent, in our case DCM, results in a large amount of heat being absorbed as it evaporates thereby cooling the surface of the fibres. This cooling effect causes water vapour from the humid environment to condense as droplets on the fibres surfaces. Upon drying, the water droplets evaporate leaving behind pores.

Figure 2 Wettability analysis of the porous mat: (A) Optical image of water droplets on the surface of the electrospun mat (water is dyed blue for clarity). (B) A water contact angle of 165°. (C) A water contact angle of 147° for nonporous fibres. (D) A side by side image of a water droplet and an oil droplet on the surface.

The contact angle of the prepared sorbent was measured at five different points along the sample, the average value is reported. As demonstrated in Fig. 2B, the porous nanofibres exhibited a superhydrophobic surface with an average water contact angle of 165° . High contact angles for electrospun nanofibres are attributed to the surface roughness of the nanofibres and air pockets [10]. The presence of pores on the fibres increased the surface roughness, further increasing their hydrophobicity. For comparison, we prepared non-porous CAB nanofibres using a different solvent system (Acetone: DMAc, 1:1 v/v); the nonporous fibres had an average water contact angle of 147° (Fig. 2C). This confirmed that surface porosity does indeed result in increased surface roughness and hydrophobicity, this phenomenon is well documented in literature [11]. And, is in line with the Cassie-Baxter model [12], which claims that on a rough surface the contact angle is due to the contact between the water droplet and the asperities at the top of the surface, and the solid material and air pockets located underneath the droplet. SEM images of the non-porous fibers are included in the supplementary information (S1).

Motor oil was used to investigate the wettability of the sample to oil (oleophilicity). CAB showed super oleophilic nature, absorbing the oil as soon as it came in contact with its surface. Fig. 2D illustrates the behavior of the water and oil droplet in contact with the CAB mat side-by-side. As can be seen, the water droplet maintains its spherical shape whereas the oil droplet spreads and wets the mat.

The sorption capacity of the fibrous mats for motor oil was 60 g/g, which is approximately four times higher than the sorption capacity of commercially used polypropylene [13]. The considerably higher oil sorption capacity of the porous fibres can be attributed to their high specific surface area due to surface porosity as is previously reported [14]. The oil sorption mechanism for these electro spun CAB sorbents is deemed to be a combination of absorption, adsorption, and capillary action [15]. Adsorption is thought to occur through physical trapping of the oil onto the fibres' surface, and in absorption the oil enters the inter-fibre voids. Capillary action causes the oil to diffuse into the fibres through the pores present on the fibre surface.

To further the sorption study, we investigated the prepared mats for oil sorption from a water surface. A 10 wt.% motor oil in water emulsion was prepared. 0.1 g of the mat was placed in a beaker containing the 10% oil water emulsion.

Figure 3 An illustration of the sorption behavior of the sorbent when placed in a 10wt% oil water emulsion.

As seen in Fig. 3, the sorbent removed all the oil. This occurred within 60 seconds. It is worth noting that even after taking up all the oil the sorbent remained afloat on the surface of the water (facilitating easy removal) and it does not disintegrate (reusable). The sorbent was also tested for its removal potential in an oil-water emulsion, the results can be seen in the supplementary information (S2)

To test its reusability potential, the sorbent was placed between two padding papers and was mechanically squeezed to remove the absorbed oil. It was then immersed in oil again, retrieved, weighed, followed by mechanical squeezing and then tested again. The reusability potential was tested up to five cycles. After the fifth cycle, a total drop in 20% of the initial sorption value was observed, indicating that the sorbent maintained a sorption capacity of 49 g/g of sorption even after five sorption cycles. A detailed account is included in the supplementary information (S3).

4. Conclusions

Porous CAB nanofibres were created by electrospinning in high humidity conditions. The porous, hydrophobic, oleophilic nature of the fibres makes them a viable candidate as a sustainable oil sorbent. The fibres exhibited an oil sorption capacity of 60g/g for motor oil, which is four times higher than that of commercially used polypropylene. The high surface porosity greatly increased the surface area of the fibres, which effectively means more contact area for the oil on the sorbent thus resulting in high oil sorption capacity. The porous sorbent maintained 80% of its sorption capacity up to five cycles showing impressive reusability potential.

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