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Superhydrophobic and superoleophillic surface of porous beaded electrospun polystrene and polysytrene-zeolite fiber for crude oil-water separation

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ABSTRACT

This research presents a cheap route procedure for the preparation of a potential adsorbent with superhydrophobic/superoleophillic properties for selective removal of crude oil from water. In this study, expanded polystyrene (EPS) was electrospun to produce beaded fibers in which zeolite was introduced to the polymer matrix in order to impart rough surface to non-beaded fiber. Films of the EPS and EPS/Zeolite solutions were also made for comparative study. The electrospun fibers EPS, EPS/Zeolite and resultant films were characterized using SEM, BET, FTIR and optical contact angle. The fibers exhibited superhydrophobic and superoleophillic wetting properties with water ($>150^0$) and crude oil (0^0). The selective removal of crude oil presents new opportunity for the re-use of EPS as adsorbent in petroleum/petrochemical industry.

1. Introduction

The need to develop materials with high selectivity for oil and low affinity for water have increased over the years due to environmental pollution problems associated with crude oil spills (Sarkar and Mahapatra, 2014). In the petroleum industry, there have been several cases of accidental leaks or crude oil spills (Sarkar and Mahapatra, 2014) which have polluted the environment particularly the water bodies. Several techniques for the removal of crude oil from water bodies have been reported and these include: mechanical separation (Sarkar and Mahapatra, 2014), chemical dispersant (Kujawinski et al., 2011), absorbent (Adebajo et al., 2003; Bayat et al., 2005; Aziz et al., 2010), UV/Visible degradation (Genuino et al., 2012), micro-organism (Aziz et al., 2010) and *in situ* burning. The use of adsorbents have increased tremendously over the years due to numerous advantages associated with the process (Yan et al., 2011). One of these important properties associated with adsorbents is selectivity of the adsorbents, (the ability to remove oil without dissolving in the water). Another advantage can be explained from the fact that, there is a high possibility of surface modification of adsorbent materials and this is very crucial for the control of crude oil spill.

Surface modifications consequently improve parameters such as contact angle (CA) which expresses the degree of wetting on the surface of a solid material. When the surface has a CA > 150^0 with water, such surface is known to posses superhydrophobic property (Wang et al., 2011, 2014), CA of 0^0 with oil is known as superoleophillic (Cengiz et al., 2012; Wang et al., 2014). Increasing surface roughness and chemical heterogeneity affect the surface wetting property (Cengiz et al., 2012). Cassie–Baxter equation explains the heterogeneous wetting state of superhydrophobic and superoleophillic properties (Wenzel, 1936; Quere, 2005). The liquid comes into contact with the solid surface at the top of the protrusions on a fraction, which is the ratio of the total area of the solid–liquid and liquid–air interfaces in a plane geometrical area of unity parallel to the rough surface (Yan et al., 2011). Hence the smaller solid fraction and larger air contact fraction favours superhydrophobic property of the surface (Zhang et al., 2013) while

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larger solid fraction and smaller air contact favours superoleophillic property. Currently, various techniques have been used to modify material surfaces, namely: etching and lithography (Ma and Hill, 2006), sol gel (Lin et al., 2013), template (Wang et al., 2013a,b), solution immersion (Li et al., 2012; Cheng et al., 2013), phase separation (Levkin et al., 2009; Liu et al., 2014), electrospinning (Chen et al., 2010; Wang et al., 2011, 2013) and laser method (Yong et al., 2013).

The technique known as electrospinning has become one of most popular methods for micro and nanofiber fabrication with controllable compositions, morphology, size, surface-to-volume, nano-pore formation, unique chemical and physical functions of composite fiber (Koombhongse et al., 2001; Sun et al., 2003; Kessick and Tepper, 2004; Zhao et al., 2007; Ding et al., 2008; Jin et al., 2010; Chang, 2011; Yang et al., 2011). Electrospun fiber can be manipulated to create protrusions on the fiber surface in order to enhance surface roughness. The protrusions can be pores, (Zhao et al., 2007; Wang et al., 2011) beads (Wang et al., 2011; Cengiz et al., 2012) and composite fibers. Beads on fiber are as a result of lower polymer concentration than critical value and solution viscosity required to maintain a stable polymer jet (Cengiz et al., 2012). Pores formation is due to rapid evaporation of volatile solvent causing fast phase separation in the spinning jet which results in solventless and polymer rich phases on the fiber surface (Alayande et al., 2012).

In this study, we prepare porous-beaded, non-beaded-porous polystyrene and porous polystyrene/zeolite electrospun fiber from expanded polystyrene (EPS) with modified surfaces for the motive of separating crude oil from water. EPS solution for electrospinning was prepared by dissolving in tetrahydrofuran (THF). EPS and EPS/Zeolite solution were also made into films. Zeolite was added to modify the surface of the non-beaded electrospun fiber. The surface wetting properties with water and crude oil of the films and electrospun fibers were compared. EPS is commonly used as insulator and packaging material. It is used industrially because of its versatility, dimensional stability, cleanliness and low cost. EPS ends up in landfills or incinerators (Alayande et al., 2012). Surface modification of EPS for crude oil removal (Shin et al., 2005; Lin et al., 2012) from water will favour the recycling/re-use of this polymer waste and address the environmental pollution of water bodies. Zeolite is a cheap oleophillic adsorbent (Sakthivel et al., 2013), modifying the surface of EPS with zeolite will enhance oil adsorption capacity of the composite adsorbent, resulting to superoleophillic membrane. This will greatly favour the re-use of EPS in the petroleum industry.

2. Experimental section

2.1. Materials

EPS as packing material for electronic devices (computers) was used in this work. Tetrahydrofuran (THF) (99%) was purchased from Sigma Aldrich (St Louis, MO,USA). Clinoptrololite Zeolite was obtained from Zeochem Ltd., Slovania. Crude oil was obtained from Nigeria National Petroleum Company, Nigeria.

2.2. Electrospinning of EPS submicron sized fibers

Parameters that affect formation of porous and beaded fibers are solvent dielectric constant, solution viscosity and solution flow rate (Wang et al., 2011; Cengiz et al., 2012; Haridas et al., 2014). THF has dielectric constant of 7.5. 10 and 20 wt % EPS solution was prepared by dissolving EPS in THF at room temperature using magnetic stirrer for 4 h. The solutions were electrospun horizontally to yield fiber as shown in Fig. 2. The size of the needle syringe was 20 gauge and 20 cm was fixed as the distance between the tip of the syringe and collector (Al foil). The flow rate was 30 μL/min, voltage between 10 and 20 kV. 0.5 g of zeolite was added to EPS solution and electrospun. EPS and EPS/Zeolite solution were made into film on petri dishes through evaporation of solvent in the fume cupboard.

2.3. Characterisation of film and fiber

The size and surface morphology of electrospun EPS and films were analysed using Scanning Electron Microscopy (SEM) TESCAN model at an accelerating voltage of 20 kV. Prior to imaging, the samples were sputter coated with gold using a sputtering unit, then dried in the oven at 60 °C for 30 min to remove moisture. While the fiber, bead and pore size were calculated using ImageJ software. The molecular bonds were analysed with Fourier Transform Infrared Spectroscopy (FTIR). The surface properties of the fibers and films with water and crude oil were analysed using DataPhysics Optical Contact Angle with 15 EC GOP, SCA 20 software. Braum 1 ml disposable syringe with dosing rate of 5 μL/s and dosing volume of 2 μL. The surface area, porosity and pore volume were analysed using Brunauer–Emmett–Teller (BET) method using surface analyser of Micrometrics ASAP 2020. The EPS fiber and film samples of 200 mg weight analysed by nitrogen adsorption and desorption isotherms at a degassing temperature of 120 °C for 360 min.

3. Results and discussion

3.1. Surface morphology analysis of electrospun EPS submicron fiber and EPS films

The effect of varying voltage, increasing the polymer concentration and addition of zeolite is shown in Fig. 1. When EPS solution was electrospun at 10–18.5 kV, fibers with micron sized beads morphology were formed as observed in Fig. 1 (A–F). The bead formation in 10% EPS solution can be attributed to polymer concentration and high feed rate (Haridas et al., 2014). The federate determines the amount of EPS solution available at the needle tip. At a federate of 30 μL/min, greater volume of 10% EPS solution will be drawn from the tip at a given voltage. This was obvious during the experiment (Fig. 2), solution drops from the needle tip to form ball shape with elastic skin which decreases with increase in voltage (solvent evaporation from outer layer). When voltage was supplied, there was distortion in stability of the Taylor cone formed as a result of non-equilibrium between the voltage and feed-rate. The increase in voltage increased the distortion of Taylor cone with resultant increase in area of bead. A plot of area of bead against voltage shows slight variance in the direct proportionality, this may be as a result of variation in the fiber width during electrospinning (Fig. 3). The formation of beaded fiber of PS in THF had been reported by Jarusuwannapoom et al., 2005 and Haridas et al., 2014, due to low dipole moment and conductivity of the solvent.

Increase in the polymer concentration results in fibers shown in Fig. 4(A1 & A2). The fibers were beadless and porous. The mechanism for the formation of pores on fiber surface had been discussed widely by many authors (Alayande et al., 2012; Haridas et al., 2014). The formation of pores on fiber/beads is due to rapid evaporation of the highly volatile solvent used. This results in solventless and polymer rich phases creating voids on fiber/bead surface or breath figure. Formation on non-beaded fiber in 20% EPS and 20% EPS/Zeolite was as a result of equilibrium between feed-rate and polymer concentration. The fiber sizes were 5751.8 nm, 165 nm and 8443.5 nm for 20% EPS electrospun at 11.25 kV, 15 kV and EPS/Zeolite respectively. Addition of zeolite to 20% EPS resulted in a rough fiber obtained in Fig. 4(B1 & B2). The Surface morphology of the polymer and composite film is shown in Fig. 5. The micrographs