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Removal of oil from water using magnetic bicomponent composite nanofibers fabricated by electrospinning

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ABSTRACT

In the present study, a magnetic nanofibrous composite mat composed of polystyrene (PS)/polyvinylidene fluoride (PVDF) nanofibers with selective incorporation of iron oxide (Fe_3O_4) nanoparticles (NPs) on/in PS was successfully prepared via a facile two-nozzle electrospinning process for oil-in-water separation. Field emission scanning electron microscopy and infrared spectroscopy showed the mats to be highly-porous in structure and confirmed the presence of the Fe_3O_4 NPs on/in the nanofibers. Both PS and PVDF nanofibers exhibited oleophilic and hydrophobic properties. The results showed improved mechanical properties when PVDF was added to the composite mat compared to the pristine PS mat. In addition, the incorporation of magnetic Fe_3O_4 NPs in the composite mat helps in the easy recovery of the mats after the oil-in-water sorption process. The composite mats showed good oil sorption capacity (35–46 g/g) and improved mechanical property. The present electrospun magnetic PVDF/Fe_3O_4@PS nanofibers could be potentially useful for the efficient removal of oil in water and recovery of sorbent material.

1. Introduction

The issue on oil pollution has drawn continuous attention of the society in recent years. Oil spills are mainly caused by shipping accidents, offshore or marine vessel leakage and illegal discharges of oily wastes [1], which consequently endanger the ecosystem and marine lives, and contaminate beaches and shorelines [2]. Additionally, domestic and industrial wastes which contain excess oil or fuel and drained in sewers or carried in waterways are also sources of pollution [3]. These oil pollution problems have prompted a necessity to develop a cost-effective and environment-friendly way of oil spill cleanup. Among the commonly used methods include in *situ* burning of oil on water [4], mechanical extraction [5], chemical degradation [6], and centrifugation and gravity separation. Each of these methods has its own limitation. In most cases, the cleanup requires the use of several techniques together. The common potential risk is the secondary pollution from the cleanup such as the generation of smoke and dust from the in *situ* burning of oil on water and contamination by toxic compounds from the use of commercial chemical dispersants [7]. Furthermore, these oil cleanup methods have low separation efficiency, complex equipment, and high operation cost.

Among the cleanup methods, the use of sorbent materials as a mechanical extraction method is considered to be a promising technique. Sorbents are very commonly used during oil spills for their cost-effectiveness and affordability [8]. These sorbents include natural materials, inorganic mineral products and organic synthetic fibers. An ideal sorbent material should have high hydrophobicity, high oleophilicity, high uptake capacity and rate, adequate buoyancy, and good recoverability of the adsorbed oil [9]. Recently, considerable research on natural organic sorbents was

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carried out such as the use of Kapok fiber [10], cotton, and rice husks [11]. A recent study reported on the coating of graphene on cotton for oil/water separation [12]. Even though natural organic sorbents are mostly biodegradable, some of them absorb both water and oil thus lessening the separation efficiency, and some of them may also sink during absorption with harsh sea condition [13]. Mineral products suffer from low buoyancy and low oil sorption capacity.

On the other hand, synthetic sorbents are man-made materials designed to combat oil spillages. Due to their excellent (super/) hydrophobic and (super/) oleophilic properties, they normally achieve higher sorption capacity [14]. The most widely used synthetic sorbents consisted of high molecular weight polymers, such as polyurethane (PU), polyethylene (PE), or polypropylene (PP) [15]. Nonwoven PP fibrous mats are widely used for oil spill cleanups due to their good oleophilic-hydrophobic properties, adequate buoyancy, and their scalable production. However, nonwoven PP fibers have low oil-sorption capacity. As synthetic fibers are mostly non-biodegradable, the full recovery of the sorbent after adsorption is very important to avoid secondary pollution. Sorbents could sink and are sometimes hard to recover after adsorption due to many factors including environment conditions such as wind, current, tides, etc. Providing a magnetic property on the sorbents can be useful in the recovery process from the water surface. Chen et al. [16] and Adriana et al. [17] fabricated different oil sorbents both providing magnetic properties to achieve the idea of easy re-pick after the sorbents are saturated. Wei et al. used a biosurfactant to clean used oil PP sorbents and more than 95% removal of oil from the sorbents was achieved with certain washing conditions [18]. Other reports have also indicated the potential for recycling the used sorbent on other synthetic sorbents. The β-cyclodextrin oil-absorbents made by Ding et al. [19] were reusable. The oil can be desorbed by a chemical extraction method [19].

With the advances in science and technology, it is now possible to fabricate materials at the nanoscale level. Electrospinning is one of the well-known techniques in the fabrication of polymeric fibers with ultrafine diameters from a polymeric solution or melt [20,21]. The resulting micro/nanofibers are formed in a nonwoven structure, which possess high porosity, interconnected pores, high surface area-to-volume ratio, and high strength-to-weight ratio [22,23]. Depending on the desired morphology and properties, the materials and process parameters for electrospinning can be manipulated. Solid or internally-porous fibers, or smooth or rough fiber surface can be obtained by just a simple manipulation of several parameters. Composite mats can also be fabricated by incorporating nanoparticles through simple blending with the polymer solution to provide additional functionalities [24], or the combination of different polymeric nanofibers into one hybrid mat through multi-nozzle electrospinning [25]. Multi-nozzle electrospinning combines the properties of different polymers to provide a synergistic property effect on the hybrid mat [26]. Several studies have reported promising results on the use of electrospun nanofibers for oil-sorption [27] and other applications [28–31].

Polystyrene (PS) nanofibers have shown good oleophilicity and hydrophobicity, and good oil sorption capacity [32]. But it is extremely light weight and has a cotton-like appearance, which makes it tend to flow and drift in air. In addition, the poor mechanical properties of PS fiber mats might cause problems during transportation and pick-up after oil absorption in the open water. Hence, one way to improve the mechanical properties of PS nanofibers is to combine it with other material forming a composite while utilizing its oil-sorption potential. In this study, we utilize the good properties of polyvinylidene fluoride (PVDF) to add mechanical stability to the PVDF/PS membrane. PVDF is widely applied in filtration systems as membranes [33,34]. Electrospun PVDF fibers are hydrophobic, have high chemical resistance and good mechanical strength, excellent thermal stability, and steady performance for long-term application [33]. The addition of PVDF nanofibers could provide increased mechanical properties of the composite mat. Additionally, to aid in the better recovery of the sorbent material, the provision of magnetic properties in the composite mat would be a good strategy. Among the available nanoparticles, magnetic iron oxide (Fe_3O_4/γFe_3O_4) are proven to have low degree of cytotoxicity even at high concentrations [35], thus its possible use in oil-sorption sorbents would be viable. Magnetite (Fe_3O_4) nanoparticles have been studied for use in water treatment where they show promising ability in removing heavy metal ions with high efficiency [36]. The magnetic properties of Fe_3O_4 nanoparticles and their proper dispersion in the composite polymeric materials would provide magnetic properties for easy recovery of the sorbent material.

In this study, we prepared and fabricated a nanocomposite sorption membrane consisting of two different polymeric components: PS and PVDF, which were simultaneously fabricated into one mat by one-step two-nozzle electrospinning. The PS component nanofibers were selectively incorporated with Fe_3O_4 NPs to provide magnetic properties. PVDF nanofibers serve as a support for the mechanical integrity of the composite membrane. The objective of this study was to study the effect of both PVDF nanofibers and Fe_3O_4 NPs on the mechanical properties and sorption efficiency of the PS-based composite membranes. We investigated the oil sorption capacities of the fabricated composite membranes as well as evaluated their different physical and chemical properties through various characterization methods and measurements.

2. Experimental

2.1. Materials

Polystyrene (PS, Mw = 250,000 g/mol) and polyvinylidene fluoride (PVDF, Mw = 180,000 g/mol) were purchased from Arcos and Sigma–Aldrich, respectively. N,N-dimethylformamide (DMF, 99.5%), tetrahydrofuran (THE, 99.5%), and acetone (99.5%) were bought from Samchun Chemical, Korea. The present magnetic Fe_3O_4 nanoparticles (NPs) (Alfa Aesar) showed an average diameter of 200 nm from scanning electron microscopy (SEM) observation (result not shown). Four types of oil were used during the experiments: sunflower oil from Rio Santo, soybean oil from Beksul, motor oil (5W-30) and diesel oil (5W-40) from Mobil 1. Table 1 shows the viscosity and density of the oils measured at room temperature. All of the materials were used as received without further treatment.

2.2. Electrospinning

PVDF solution (20 wt%) in DMF/acetone (7/3 ratio) mixed solvent and PS solution (20 wt%) in DMF/THF mixed solvent (3/1 ratio) were prepared by overnight stirring at 55 °C and at room temperature, respectively. Fe_3O_4 nanoparticles (5 wt% w.r.t. the weight of PS) were added in PS solution and the solution was subjected to bath sonication for 2 h to disperse the nanoparticles.

Table 1
Properties of the oils used in the present study.

Type of oil	Viscosity (cP)	Density (g/cm^3)
Sunflower oil	64.55	0.874
Soybean oil	61.4	0.855
Motor oil	142.2	0.806
Diesel oil	214.73	0.821