Surfactant grafted PDA-PAN nanofiber: Optimization of synthesis, characterization and oil absorption property

A. Almasian [a,*], M.L. Jalali [b], Gh. Chizari Fard [a], L. Maleknia [a]

[a] Nanotechnology Research Center, Islamic Azad University, South Tehran Branch, Tehran, Iran
[b] Department of Environmental Protection, Niroo Research Institute, Tehran, Iran

HIGHLIGHTS

- Synthesizing of a superhydrophobic and oleophilic nanofiber.
- Preparation of a high absorption capacity absorbent for the removal of oil sillage.
- Functionalization of PAN polymer with dopamine through a covalent linkage.
- Optimization the condition of functionalization and grafting processes.

GRAPHICAL ABSTRACT
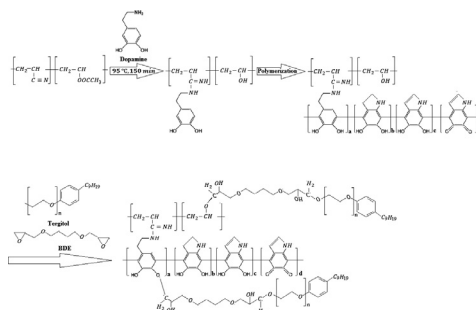
ABSTRACT

In this paper, surfactant grafted polydopamine (PDA)-polyacrylonitrile (PAN) nanofiber with the aim of separation the oil spillage was synthesized. Firstly, the electrospun PAN nanofiber was functionalized by dopamine in an alkali condition. Secondly, the Tergitol as a nonionic surfactant was grafted onto the surface of functionalized PAN nanofiber. The conversion amount (C_n%) of nitrile group to amidine group and the grafting yield of surfactant on the surface of PAN nanofiber were evaluated. Also, the optimum conditions in functionalization and grafting processes were reported. In order to characterize the synthesized nanofibers, FTIR, SEM, AFM, XPS and BET analyses were used. The pore size distribution of synthesized nanofibers was investigated by BJH method. The results showed that the dopamine and surfactant were attached to the nanofiber surface through the covalent linkages. SEM images exhibited the deposition of a dense layer on the surface of grafted nanofibers. Moreover, AFM analysis revealed that the surface of nanofiber became rough after the functionalization and grafting processes. In order to evaluate the superhydrophobic properties of nanofibers, contact angle and surface energy analyses were investigated. The synthesized absorbent showed a high absorption capacity of 148.58 and 62.53 g/g for heavy motor oil and diesel fuel, respectively. The absorbed oil was easily removed by a vacuum filtration and the nanofiber could be reused for several cycles while keeping high absorption capacity.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Water pollution is a major issue of developing the various industries around the world. Generally, the water pollutant can be divided to insoluble and soluble compounds. Oily compounds as an insoluble pollutant threat the people's health and aquatic life due to their toxic nature [1]. Many methods including mechanical

* Corresponding author.
E-mail addresses: almasian-ar@icrc.ac.ir (A. Almasian), mjalali@nri.ac.ir (M.L. Jalali), chizarigh@gmail.com (G.C. Fard), melika02@azad.ac.ir (L. Maleknia).

extraction, chemical degradation, dispersants, air flotation, skimming and combustion has been used for purifying the polluted water [2–4]. However, these methods are limited because of low separation efficiency, energy-cost and complex separation instruments.

In the last decade, absorbent materials with superhydrophobic and superoleophilic nature have been attracted many researchers because of the economy and efficiency for the removal and collection of oily compounds [5,6]. It is known that three factors including surface energy, surface roughness, and homogeneity control the wetting of a solid [7]. Many absorbent such as zeolite, perlite, graphite, carbon nanotube, cellulose-based materials and polyurethane are widely used in oil spill cleanup [8,9]. Among them, synthetic organic products include polymeric materials are considered as the most effective oil sorbent because of their high absorption capacity and reusability [10,11]. Despite the various absorbents with high absorption capacities have been made in different shape and scale, some drawbacks such as low specific surface area and difficulty in the removal of absorbed oil still exist and need to be overcome [12]. In this regard, producing the sorbents with high reusability and high surface area is highly desired.

Electrospun nanofibers as a 1D material have a great potential in water treatment because of highly porous and interconnected pore structure, submicron pore sizes, and a large surface area to volume ratio. Nanofiber mats can be easily removed from the solution, which reduces the operation cost [13]. Furthermore, electrospinning is known as a powerful technique to provide sufficient surface roughness for superhydrophobicity [14]. Polyacrylonitrile (PAN) nanofiber as an inexpensive and environmental stable polymer has been widely used in water treatment processes. Cellulose acetate grafted PAN membrane, ethanol grafted PAN fiber and polyamide/PAN membrane were prepared for the separation of oil from oily wastewater [15–17]. As it was previously stated, the nitrile group of PAN reacts with the primary amines containing compounds and it converts to the amidine group [18]. In this regard, many attempts are performed on modification of PAN with various amine containing compounds such as ethylenediamine, diethylenetriamine and polyamidoamine (PAMAM) dendrimer [19,20].

Dopamine as a non-toxic biopolymer belongs to a class of catecholamines which is able to self-polymerize under basic reaction conditions and form a polydopamine (PDA) [21]. PDA has often been employed as a modifier to improve the hydrophilicity and reactivity of substrates [22,23]. PDA has been used for numerous membrane modifications because of the capability to increase the hydrophilicity of a surface [24,25]. Also, it is used as antifouling coatings for thin film composite selective layers used in oil/water separations [26] and as modification for feed spacers for biofoulant adhesion resistance [27]. Furthermore, PDA Nano sphere was used as an adsorbent for the removal of Hg^{2+} [28]. Dopamine modification of PAN nanofiber via physical absorption with the aim of improving the filtration flux was performed [29]. However, a literature review indicted no study on the functionalization of PAN nanofiber with dopamine through a covalent linkage. In this study, PDA was covalently bonded to the surface of PAN nanofiber then, the Tergitol as a nonionic surfactant was grafted to the PDA-functionalized PAN nanofiber (hereafter; PDA-PAN NF) by 1,4-Butanediol diglycidyl ether (BDE) and its potential to remove oily compounds was investigated.

2. Experimental

2.1. Materials

Polyacrylonitrile copolymer (93.7% acrylonitrile and 6.3% vinylacetate with M_w = 100,000 g/mol) was purchased from Isfahan Polyacryl Inc. (Iran). *N,N*-Dimethylformamide (DMF), sodium hydroxide, and potassium carbonate were purchased from Merk, Germany. Dopamine hydrochloride (99%), 1,4-Butanediol diglycidyl ether (BDE) and Tergitol NP40 (nonylphenol ethoxylate surfactant) were obtained from Sigma-Aldrich Co., St. Louis, MO, USA.

2.2. Preparation of PDA-PAN NF

PAN nanofiber mats were obtained by electrospinning as previously reported [19]. The obtained nanofiber was immersed into an aqueous solution containing dopamine (2 g), potassium carbonate (catalyst; 0.3 g), and distilled water (50 mL) in a 150-mL beaker connected to a reflux column at different temperature (55, 75, 95 and 110 °C) and different reaction times (30, 60, 120, 150 and 180 min). The solution pH was 8.5. After the reaction, the nanofiber was washed with deionized water and ethanol (with the ratio of 2:1) for several times to remove the unattached PDA, and dried in an oven at 80 °C for 24 h.

2.3. Surface grafting of Tergitol onto PDA-PAN NF

The PDA-functionalized PAN nanofiber was immersed in a batch containing distilled water (50 mL), NaOH (0.01 g) and different amount (2, 4, 6, and 8 mL) of surfactant and then, the solution was placed on a shaker for 30 min. The solution pH was 8.5. After that, 1,4-Butanediol diglycidyl ether in desired amount was added drop by drop to the prepared solution and the shaking was continued for 1 h. Then, the nanofiber was washed with distilled water to remove excess crosslinking agent and self-crosslinked surfactant molecules and dried. The resulted nanofiber was named PDA-PAN-X NF, X = 2, 4, 6 and 8.

2.4. Characterization

The surface morphology and topography of nanofibers characterized by Scanning Electron Microscope (SEM, LEO1455VP, ENGLAND) and an Atomic Force Microscope (AFM, Dual Scope C-26, DENMARK), respectively. Change in the chemical composition of the samples which occurred in different processes was examined by Fourier transform infrared (FTIR) spectroscopy, (ThermoNicolet NEXUS 870 FTIR from Nicolet Instrument Corp., USA). The average diameter of different nanofibers was determined by an image analyzer (image SXM 196). In this study, 5 images were captured from each sample, and the diameter of all nanofiber was evaluated.

The contact angle between nanofiber mats and the liquid phase was measured using static digital method described in the standard D5725-97 (ASTM, 2003). The nanofiber mats were placed on a lifting table mounted of an optical microscope (Olympus SZ e STU2) equipped with a digital camera (Olympus Camedia C-3040). The droplets of liquid (heavy motor oil, diesel fuel, diiodomethane and water) were placed onto the surface of the mats by a microliter syringe. Digital images of droplets on the surface of the mats were captured and the contact angle calculated.

The total surface energy, the dispersive surface energy and the polar surface energy were estimated from the contact angle (θ) of a liquid over a solid surface. To do this, a linear equation (Eq. (1)) was used which was developed by Owens, Wendt, Rabel, and Kaelble (Eq. (1)) [30].

$$\frac{(1 + \cos\theta) * \gamma_1}{\sqrt{\gamma_{1d}}} = \sqrt{\gamma_{sp}}\sqrt{\frac{\gamma_{1p}}{\gamma_{1d}}} + \sqrt{\gamma_{sd}} \tag{1}$$

where γ_{sp}, and γ_{sd} are the polar surface energy and the dispersive surface energy of the solid surface, respectively. The total free surface energy was estimated as the sum of the polar surface energy of the solid surface and the dispersive surface energy of the solid sur-