Materials Science and Engineering C 42 (2014) 443–450

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Surface modification of polypropylene membrane by polyethylene glycol graft polymerization

Atiye Sadat Abednejad [a,*], Ghasem Amoabediny [b,c], Azadeh Ghaee [a]

[a] Department of Biomedical Engineering, Faculty of New Sciences and Technologies, University of Tehran, P.O. Box 14395-1561, Tehran, Iran
[b] Department of Life Science Engineering, Faculty of New Sciences and Technologies, University of Tehran, P.O. Box 14395-1561, Tehran, Iran
[c] Research Center for New Technologies in Life Science Engineering, University of Tehran, P.O. Box 63894-14179, Tehran, Iran

ARTICLE INFO

Article history:
Received 4 January 2014
Received in revised form 21 April 2014
Accepted 29 May 2014
Available online 4 June 2014

Keywords:
Polyethylene glycol
Polypropylene
Hydrophilicity
Plasma graft polymerization
Blood compatibility

ABSTRACT

Polypropylene hollow fiber microporous membranes have been used in a wide range of applications, including blood oxygenator. The hydrophobic feature of the polypropylene surface causes membrane fouling. To minimize fouling, a modification consisting of three steps: surface activation in H_2 and O_2 plasma, membrane immersion in polyethylene glycol (PEG) and plasma graft polymerization was performed. The membranes were characterized by contact angle measurement, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), tensile test, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Oxygen transfer of modified membranes was also tested. The stability of grafted PEG was measured in water and in phosphate buffer saline (PBS) at 37 °C. Blood compatibility of modified surfaces was evaluated by the platelet adhesion method. Water contact angel reduction from 110° to 72° demonstrates the enhanced hydrophilicity, and XPS results verify the presence of oxygenated functional groups due to the peak existence in 286 eV as a result of PEG grafting. The results clearly indicate that plasma graft-polymerization of PEG is an effective way for antifouling improvement of polypropylene membranes. Also, the results show that oxygen transfer changes in PEG grafted membranes are not significant.

1. Introduction

There has been an increasing demand for membrane processes in the field of gas separation (GS), medicine, waste water treatment, and so on during the last few decades. A blood oxygenator is a medical device that is used for patients with acute respiratory problems, immature babies and, in open heart surgeries [1]. It was first designed in 1950s as a bubble type oxygenator [2]. Subsequently, film oxygenators were produced. In bubble and film oxygenators, blood came in contact with oxygen directly, causing damage to blood cells. The remarkable blood compatibility of membrane oxygenators, however, rather than bubble and film types, made them the most common type in extracorporeal oxygenating systems. Blood contact with the polypropylene membrane (PP) surface is followed by several bodily immune system responses, as coagulation and complement activation, due to the PP membranes' hydrophobic surface, leads to adhesion.

Polypropylene membranes with high and well-controlled porosity, as well as non-toxic and chemical inertness properties, are used in various applications [3–5]. Polypropylene hollow fiber microporous membranes have been commonly used in blood oxygenators, as well as in ultra filtration devices for waste water treatment [6]. However, the hydrophobic surface of PP membranes causes membrane fouling. Surface properties of polymers have significant importance in many branches of industrial applications, which also affect the performance of polymeric membranes. Thus, many studies focus on the membranes surface modification [7,8]. In a number of attempts to improve the anti-fouling characteristics of the PP membranes, different methods such as UV irradiation, plasma treatment, gamma irradiation, and chemical reaction have been employed to modify the membrane surface [9]. Plasma surface modification of polymeric materials at a low temperature was developed several decades ago. Cold plasma processes are mainly used in both industrial applications and laboratory studies [10,11]. H_2O plasma treatment was used to enhance surface wettability of PP membranes by Yu et al. [9]. Choi et al. [10] used O_2 cold plasma to promote PP membrane surface hydrophilicity. Cheng et al. [12] tried to improve PP membrane hydrophilicity by argon plasma. Yu et al. [13–15] examined NH_3, air and N_2 plasma to improve PP membrane hydrophilicity, and Yu et al. [16] made an attempt to enhance PP membrane wettability by using CO_2 plasma. Even though surface wettability was improved in all the aforementioned modifications, this improvement was not stable. In other studies, hydrophilic polymers were grafted to the surfaces after cold plasma activation. Kwon et al. [17] grafted 2,3epoxypropylmethacylate (EPMA) to an activated membrane for biomedical purposes. This modification improved both surface hydrophilicity and blood compatibility. Glycidyl methacrylate was used

* Corresponding author. Tel.: +98 21 88618430.
E-mail address: atiyeabednejad@gmail.com (A.S. Abednejad).

http://dx.doi.org/10.1016/j.msec.2014.05.060
0928-4931/

to modify the PP membrane by Macmanus [18]; the membrane surface was also activated by UV radiation. PP membrane wettability enhancement and blood compatibility improvement were concluded in this modification.

In this research, polyethylene glycol (PEG) graft polymerization was carried out to improve PP membrane surface hydrophilicity and blood compatibility. PEG-modified surfaces prevent protein and platelet adhesion due to the PEG's hydrophilicity characteristic. PEG is a gel type polymer that hydrates and swells when in contact with water. This polymer is grafted to numerous membranes, such as polyacrylonitrile and polysulfone membranes, to prevent the adhesion of platelets [19]. Plasma-induced graft-polymerization is one of the most useful and effective methods of surface functionalization [20,22]. Both hydrogen and oxygen plasma were used for covalent grafting of PEG in different experiments through three steps: PP membrane surface chemical activation by oxygen and hydrogen plasma, membrane immersion in PEG solution, and plasma induced graft polymerization [23]. The formation of oxygenated functional groups on the PP substrate was confirmed by FTIR and XPS analysis. AFM and SEM images were used to present membrane morphology before and after modification.

2. Material and methods

2.1. Materials

Isotactic PP hollow fiber microporous membranes were commercially supplied by Membrana, Germany. The average inside and outside diameters of the fibers were 200 and 300 μm, respectively. The average pore diameter was 100 nm. Analytical grades of acetone, methanol, ethanol (98% vol/vol) NaOCl and glutaraldehyde (25%) were purchased from Merck. Phosphate buffer saline (PBS) was obtained from Medicago, Sweden and PEG (Mw: 1400) was supplied by Sigma Aldrich.

2.2. Surface modification of polypropylene membrane

H_2 plasma treatments (both surface activation and graft-polymerization) were carried out in Reactive Ion Etching (RIE) system composed of a cubic vacuum chamber and made in Anatech CO, USA. An electrode was externally connected to a 13.56 MHz—RF power supplier to provide radio frequency (RF) voltage. PP samples were inserted in the chamber and kept at a distance of 10 cm from the RF electrode. In this research, the device was evacuated to 10^{-3} Pa by means of a turbo-molecular pump combined with a rotary pump before operation. Plasma power was set on 15 W (higher power may damage the membrane) and gas flow was 5 SCCS (standard cubic centimeter per second).

2.2.1. Modification of PP membrane in H_2 plasma

Before modifying the surfaces, membranes were washed with acetone to remove chemicals and wetting agents adsorbed from surfaces. Then, samples were dried at room temperature for 24 h. Modification started with activation of PP samples which were shaped manually into squares with a total area of 150 cm^2. Surface activation of samples was performed in H_2 plasma for 1.5, 2, 2.5, 3 and 3.5 min [24]. If exposed for a longer duration, H_2 plasma would damage PP membrane surface [23]. Samples were then immersed in different concentration of PEG/ethanol solution (10, 15, 20, 25 and 30 g/l). The physically adsorbed PEG was grafted on membrane using H_2 Plasma for a longer period of time (3, 5, 7, 10 and 12 min) [24,25]. The samples finally were washed by methanol, NaOCl and deionized water, respectively, to remove any monomers or un-grafted PEG on the surface. The membrane surface modification was then followed by a stability test, which was conducted by immersion in phosphate buffer saline (PBS) for 24 h at 37 °C. The samples were perfectly dried at ambient temperature for 24 h.

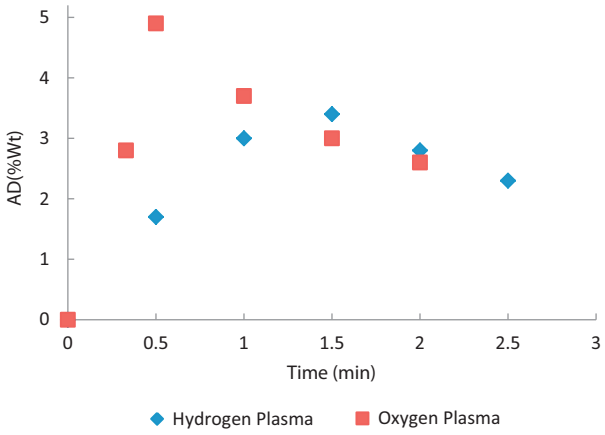

Fig. 1. Adsorption degree versus plasma duration in hydrogen and oxygen plasma.

2.2.2. Modification of PP membrane in O_2 plasma

The aforementioned procedure with H_2 plasma was repeated, this time, for O_2 plasma, with only the activation times and grafting step differing. Surface activation by O_2 cold plasma required less time than H_2 plasma due to higher feasibility of oxygenated functional groups formation [24]. Surfaces were activated for 10, 30, 90, 120 and 150 s. The grafting step was also performed for 1, 3, 5, 7 and 10vmin.

2.3. Characterization

2.3.1. Adsorption degree of PEG on PP membrane

The PEG adsorption degree (AD) was obtained by the following equation [14]:

$$AD = (W_a - W_0)/W_0 \quad (1)$$

where W_a is the weight of the membrane after immersion in PEG solution and W_0 is the weight of the unmodified membrane.

2.3.2. Grafting degree of PEG on PP membrane

The grafting degree (GD) was calculated by Eq. (2) [14]:

$$GD = (W_t - W_0)/W_0 \quad (2)$$

where W_t is the weight of the membrane after grafting, washing and drying and W_0 is the weight of the unmodified membrane. All of the results were based on the average of three parallel experiments.

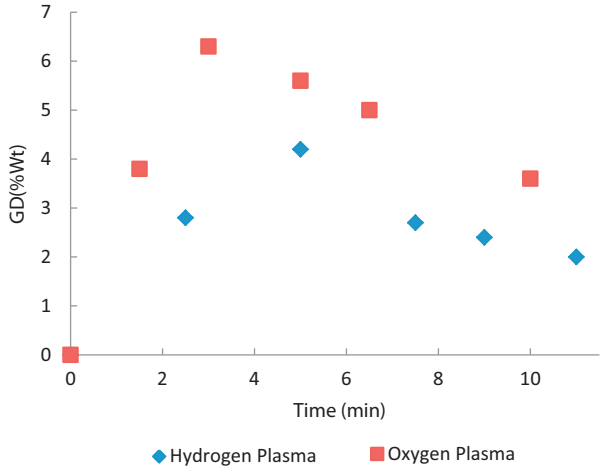

Fig. 2. Grafting degree versus plasma duration in hydrogen and oxygen plasma.