Journal of Membrane Science 546 (2018) 151–157

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Atmospheric pressure plasma - ARGET ATRP modification of poly (ether sulfone) membranes: A combination attack

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ARTICLE INFO

Keywords:
Surface modification
Activators regenerated by electron transfer
Atom transfer radical polymerization
Nanofiltration
Hydrophobic

ABSTRACT

A novel surface modification technique for grafting alkyl methacrylate monomers from commercial poly(ether sulfone) (PES) nanofiltration membranes is developed through a combination of helium and oxygen atmospheric pressure plasma treatment followed by Activators Regenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP). The resulting membrane surfaces show degree of grafting increases of 28%, 94%, and 270% for methyl methacrylate (C1), hexyl methacrylate (C6), and stearyl methacrylate (C18), respectively, when characterized with Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. Scanning Electron Microscopy and Atomic Force Microscopy (AFM) show a rippled, fibrous morphology for the PES membranes grafted with C18 and reinforced through molecular dynamics simulations. AFM of the PES membranes grafted with C18 show an increase of ~ 23% in root-mean square (RMS) roughness as well as 4x higher adhesion force when probed with a hydrophobic gold cantilever tip when compared with the unmodified PES membranes, confirming a successful surface grafting reaction and increase in surface hydrophobicity, respectively. This technique allows enhanced synthesis of polymer grafted membranes using relatively green reaction solvent and enables “structure-by-design” surface morphology control with future applications in membrane separation processes such as organic solvent nanofiltration, gas separations, and desalination.

1. Introduction

Developing new polymers for membrane filtration is an intense, long-term, open-ended problem in membrane sciences. Surface modification of commercial polymeric membranes with new interfacial properties offer alternate routes to tuning the performance of membranes during filtration. Examples include hydrophilizing relatively hydrophobic polymers such as poly(vinylidene fluoride) (PVDF) [1] or poly(ether sulfone) (PES) [2] or grafting polar non-selective brush layers to reduce protein adhesion [3,4] during bioprocessing. Chemical [5] and radiation [6,7] methods to activate and functionalize polymeric membranes have received much attention.

Treatment of polymeric surfaces with plasma originated in attempts to improve adhesive bond strength between polymeric parts [8]. Generally, desirable polymeric construction materials are chemically inert, thermally stable, and have excellent mechanical properties [9]. In addition to these characteristics, polymeric materials typically suffer from low surface energy, which results in reduced adhesive strength [9,10]. Plasma treatment of the mating polymer surfaces can cause an increase in polar functional groups, leading to a higher strength from the intermolecular forces between the surface and adhesive [9–12]. This results in the ability of the adhesive bond to withstand larger stresses before failure. Typically, plasma treatment causes scission of the polymeric chains, leading to formation of free radicals which can react with the gases supplied to the plasma chamber [12]. Plasma treatment can be performed either under vacuum [13–16] or at atmospheric pressure [9–12] to increase the surface oxygen content (i.e. activate), and therefore surface energy, of polymer surfaces. Several gases can be used to generate plasma to activate polymer surfaces, notably air [11], water [13], and a combination of helium and oxygen [9,10,12].

The free radicals created during atmospheric pressure plasma (APP) activation of surfaces [17] have been theorized to react with atmospheric oxygen to create thermally labile peroxides in some instances [18–21]. These peroxides can be thermally decomposed to recover the radicals and initiate a free radical polymerization reaction in the presence of vinyl monomers. Surfaces grafted with methacrylic acid

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http://dx.doi.org/10.1016/j.memsci.2017.10.014
Received 8 August 2017; Received in revised form 16 September 2017; Accepted 8 October 2017

[19,20], acrylamide [20], and N-methyl-2-pyrollidinone [18] have been reported using this method. In one case, the surface of a thin-film composite polyamide membrane with 30% NaCl rejection was grafted with methacrylic acid or acrylamide to obtain 94–95% salt rejection of a 1000 ppm NaCl feed solution [20]. Although these results seem promising, the amount of grafted material is generally very small and typically are not easily observed with techniques such as Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) spectroscopy. Therefore, measurements such as feature height distributions using Atomic Force Microscopy (AFM) are generally used to detect changes between the unmodified and modified surfaces to confirm grafting [20]. In addition, traditional free radical polymerization grafting techniques do not allow for tight control over polymer molecular weight distributions and cannot be used for more advanced surface functionalization techniques such as the grafting of block copolymers. This precludes "structure-by-design" engineering of membrane surface morphology and pore structure. In order to gain more precise control over the grafting of polymers to surfaces, living polymerization techniques such as Atom Transfer Radical Polymerization (ATRP) is attractive [22]. This can be accomplished by reacting a suitable ATRP initiator with reactive groups (e.g. naturally present or created through plasma treatment) available on the polymeric substrate.

A version of ATRP, known as Activators Regenerated by Electron Transfer (ARGET) ATRP, is particularly attractive due to its tolerance of low levels of oxygen [23]. Traditionally, the ATRP procedure requires rigorous deoxygenation of grafting solutions and handling of air-sensitive catalysts under an inert atmosphere [24]. These procedures are challenging to implement commercially, especially on large surfaces. The ARGET ATRP method circumvents the need for performing the reaction steps under a stringently inert atmosphere through the use of a reducing agent [23–25]. The monomers methyl methacrylate, styrene, and glycidyl methacrylate were polymerized from the surface of a cellulose filter paper after reaction with an organic initiator using the ARGET ATRP method [26]. The initiator was coupled to the surface through reaction with the native hydroxyl groups of cellulose to create ester bonds. After initiator coupling to the surface, the monomers could be polymerized to yield narrow molecular weight distributions [26]. A slightly different version of ATRP, known as Activators Generated by Electron Transfer (AGET), was used to graft 2-(dimethylamino)ethyl methacrylate polymers from a regenerated cellulose membrane surface [27,28]. The resulting modified regenerated cellulose membranes were able to bind more bovine serum albumin than commercial Sartobind® D membranes.

Poly(ether sulfone) (PES) is a commonly used polymer for membrane fabrication because of its excellent chemical, thermal, and mechanical properties [29]. Due to its chemical inertness, PES is difficult to modify with high grafting density. In order to circumvent this, several groups have tried modifying PES prior to membrane casting. Efforts such as blending amine-terminated PES into the casting solution prior to membrane formation have been used to introduce reactive amine groups for coupling ATRP initiators [30]. Other groups have attempted to functionalize a structurally related polymer, poly(sulfone), through chloromethylation reactions prior to membrane casting [31,32]. The benzyl chloride groups introduced into the poly(sulfone) were directly capable of initiating an ATRP reaction. These techniques require chemistry to be performed on the PES or related polymers prior to membrane casting, which is not ideal. Herein, to the best of our knowledge, we report the first use of ARGET ATRP to modify the surface of a commercial PES nanofiltration membrane (Fig. 1) [33]. This modification technique is not limited to membranes only, but can be used for any substrate made of PES and with both hydrophobic (Figs. 2 and 3**) and** hydrophilic monomers (Fig. S1). This is accomplished through the combined use of APP to activate the PES surface with reactive functionalities (i.e. hydroxyls) and ARGET ATRP to graft representative vinyl monomers from the surface. The chosen methacrylate monomers contain alkyl side chains with different numbers of carbons atoms. We hypothesize that optimal monomer alkyl chain length is needed to generate grafted polymer morphology for successful membrane performances.

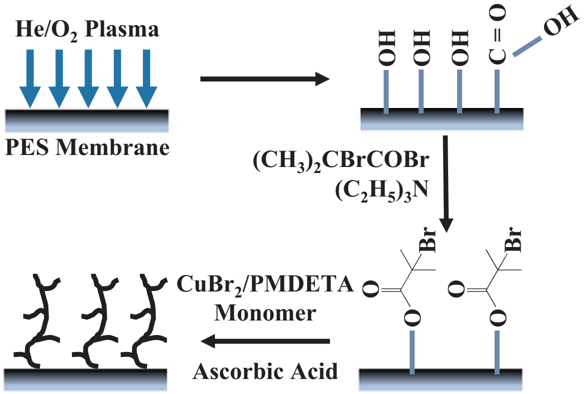

Fig. 1. Schematic of the combined APP-ARGET ATRP method for the grafting of various monomers from the surface of PES NF membranes.

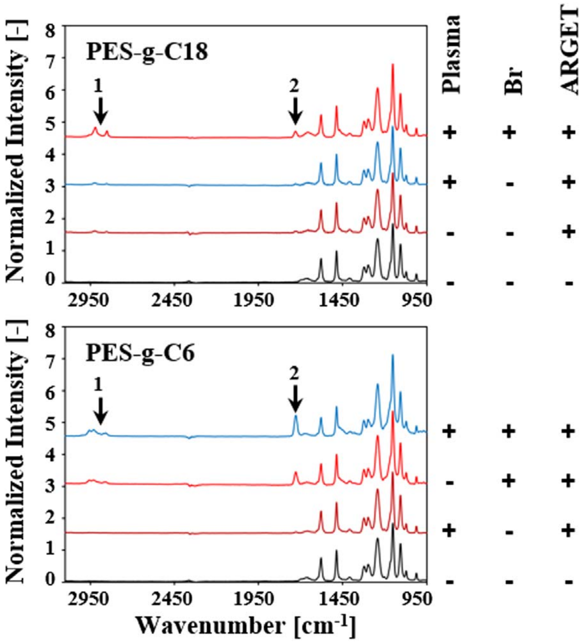

Fig. 2. ATR – FTIR spectra of PES NF membrane controls and grafted with C18 or C6 monomers for 15 h at 60 °C. The key to the right identifies which procedures the PES NF membranes were exposed to: plasma activation, bromination (i.e. initiator attachment), and ARGET-ATRP grafting. Procedures utilized on the membranes before spectra were recorded are identified with a '+ ' while those absent were identified with a '-'. Saturated hydrocarbon absorbance is labeled '1' (~ 2918 cm^{-1}) and ester functionality is labeled '2' (~ 1726 cm^{-1}).

2. Experimental

2.1. Materials

Methyl methacrylate (C1; 99%), hexyl methacrylate (C6; 98%), stearyl methacrylate (C18; mixture of stearyl and cetyl methacrylates), N,N,N′,N″,N″ Pentamethyldiethylenetriamine (99%, PMDETA), copper (II) bromide ($CuBr_2$, 99%), alpha-bromoisobutyryl bromide (BIBB, 98%), ascorbic acid (reagent grade), toluene (99.8%), and acetonitrile (99.8%) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate (Br-silane) was purchased from Gelest, Inc. (Morrisville, PA). Ethanol was purchased from the RPI stockroom. Milli-Q water with a resistivity