



Optimizing carbon nanotube-reinforced polysulfone ultrafiltration membranes through carboxylic acid functionalization



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ABSTRACT

Multiwalled carbon nanotubes (CNTs) carboxylated to varying weight percentages were added to polysulfone membranes. The degree to which the CNTs were retained within the membrane during membrane production, operation and cleaning was examined as a function of the extent of CNT carboxylation. The effects of CNTs on polymeric membranes – increases in tensile strength, changes in surface hydrophilicity, and changes in membrane permeability – were evaluated as a function of CNT carboxylation, which was found to be coupled to CNT retention within the membrane. It was found that CNTs functionalized to a higher degree form more homogeneous polymer solutions, which lead to greater improvements in the aforementioned membrane characteristics. However, CNTs functionalized to a higher degree were also found to more-readily leave the membrane during immersion precipitation and membrane cleaning. Therefore, a balance was discovered between the benefits associated with increased dispersibility and hydrophilicity, and the disadvantages associated with decreased retention, increased leaching, and decreased strength of CNTs with greater carboxylation.

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1. Introduction

Much attention in the past decade has been given to polymer nanocomposites, especially polymeric matrices suffused with carbon nanotubes (CNTs) [1–3]. The aim of CNT–polymer nanocomposites is to improve polymeric materials by capitalizing on the unique properties of CNTs, which include extremely efficient load transfer [4] and resistance to shear [5], as well as unparalleled electrical conductivity [6]. There are many proposed applications for such nanocomposites and membrane technology is among those that offer great promise [7–9].

Polysulfone (PSf) is one of the most widely used polymers to make ultrafiltration membranes; nevertheless it suffers from a few key negative characteristics [10,11]. PSf is a hydrophobic polymer with relatively low tensile strength. Hydrophobic membranes resist water permeability, which limits high water flux. Further, hydrophobic membranes are typically more susceptible to biofouling than hydrophilic membranes [12,13]. Secondly, polymers with low tensile strength are susceptible to breakage from operational stresses including applied high pressures and vibrational shear stresses commonly found within hollow fiber modules [14–16].

CNTs can potentially improve the properties of PSf membranes by incorporating them into PSf solutions as a composite. Even in quantities as low as 0.1% by weight of the final polymer membrane, functionalized or chemically tailored CNTs offer the opportunity to alter various membrane properties including surface chemistry [17], pore size [18], tensile strength [19], solute rejection [20], and polymer crystallinity [21]. Of particular interest, Choi et al. prepared MWCNTs/PSf blend membranes that appeared to be more hydrophilic than membranes made from PSf alone, due to the specific functionalization applied to the MWCNT surface [17]. CNTs have also been shown to have anti-bacterial properties, as demonstrated by Elimelech and others [22], which could have positive implications for membranes composed of CNT–polymer composites [18]. Finally, it is well established that electrically charged surfaces can cause significant detrimental effects to bacteria and viruses, hindering their biofouling capability [23–25]. CNT–polysulfone nanocomposite membranes may offer a realistic and practical platform for electrically conducting, and thereby fouling-resistant, water filtration membranes [9,26]. With this perspective, CNTs offer the potential for multiple improvements over the current state of technology.

The unique properties of CNTs are most readily exploited when they are homogeneously dispersed throughout polymer solutions [27]; a feat that provides significant challenges since CNTs bundle tightly and are highly insoluble due to the prevalent van der Waals interactions along their length. A significant amount of research

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has been devoted to CNT dispersion in solvents and polymers [28–30] including sonication of CNTs prior to mixing with polymers [31] and chemical sidewall-functionalization of CNTs to encourage debundling and enhance hydrophilicity [32]. The research group under Sun, for example, has developed a plethora of refined CNT functionalizations [33].

The most common and effective CNT functionalization is carboxylation [34]. Carboxylic functionalization of CNTs begins either by breaking sp^2 hybrid carbon bonds along the sidewalls or capped ends of CNTs, or by exploiting existing broken bonds found thereon. Exposing broken hybridized carbon bonds to strong acids oxidizes them and forms carboxylic acid functional groups on CNTs. This functionalization greatly increases CNT dispersibility in many common polar solvents [34]. The degree to which CNTs are functionalized is rarely determined, despite the prevalence with which many researchers subject CNTs to this functionalization. Subsequently, very little research investigates how varying the degree of functionalizations affects the properties of CNTs and their composites. Only recently, Fairbrother and others have thoroughly investigated the effect of different methods of carboxylation on CNTs [35]. To the best of our knowledge, published investigations into the effects that greater or lesser degrees of carboxylation have on the properties of polymers, in particular on polymeric membranes, are absent.

In this study, we have carboxylated CNTs at a range of weight percentages (0–10.55%), fabricated polysulfone ultrafiltration nanocomposite membranes with these CNTs, and investigated the changes in the tensile strength, hydrophilicity, and water flux of these membranes as a function of increasing carboxylation. In so doing we discovered that the change in membrane properties was not solely caused by the increasing dispersion due to greater functionalization, but that the stability of the CNTs within the polymer matrix played a crucial role. Higher degrees of functionalization caused greater loss of CNTs from the polymer membrane during formation and showed a greater tendency to leach CNTs from the membranes during membrane cleaning. This is of great import as there is concern that nanoparticles and CNTs, in particular, may have negative effects on humans and environmental ecosystems [36]. Although their possible toxicological effects remain a topic of active investigation, it is prudent to minimize their release into the environment from an environmental, practical, and economic perspective. No papers to date have investigated the potential for CNTs to leach from their polymeric membranes in which they are suspended. We have quantified the loss and/or leaching of CNTs during membrane production, use, and membrane cleaning as a function of %-carboxylation. In this way, we are able to identify the optimal %-carboxylation of CNTs for inclusion into PSf membranes. Finally, we propose ways in which CNTs can be maximally incorporated into polymeric matrices.

2. Experimental

2.1. Materials

Pristine multiwalled carbon nanotubes (pCNT) and 2.56% carboxylated CNTs were purchased from CheapTubes.com (www.cheaptubes.com) and used and functionalized without further purification (> 95 wt%). The diameter of these tubes was listed as 8–15 nm, and their length was listed as 100 μm . Polysulfone (PSf) and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich and had molecular weights of 35 kDa and 40 kDa respectively. Dimethyl formamide (DMF), purchased from Sigma-Aldrich as well, was used as a solvent for the polymers. De-ionized water (DIW) was used as the non-solvent in the immersion precipitation non-solvent bath. Trace metal grade nitric acid (67–70% HNO_3)

was purchased from Fischer Scientific, extra pure sulfuric acid (96% H_2SO_4) was purchased from Acros Organics, hydrochloric acid was purchased from Sigma Aldrich (36.5–38% HCl), sodium hydroxide was purchased from Fischer Scientific (N/100 0.0101–0.0099 N NaOH), and sodium hypochlorite (6.15% NaOCl) was purchased as standard household Clorox Bleach.

2.2. Carbon nanotubes

2.2.1. Carboxylation

CNTs were carboxylated to varying %-carboxylation following the traditional nitric and sulfuric acid oxidation process [34]. Briefly, CNTs were heat refluxed for varying amounts of time in nitric and sulfuric acid. A dilute slurry was separated by centrifugation, and then dialyzed until the solution reached pH 5.6–6. The suspension of CNTs was then frozen at 80 °C and sublimated in a freeze drier (LabConco FreeZone 2.5 Plus).

2.2.2. Analysis of CNTs

Transmission electron microscope (TEM, FEI Tecnai G² Twin) images of pristine- and carboxylated-CNTs were taken to demonstrate the CNT debundling effects of functionalization. Samples were imaged on lacey carbon copper grids.

X-Ray photoelectron spectrometer (XPS, Kratos Analytical Axis Ultra) spectra of pristine and functionalized CNTs were used to determine the number and type of oxygen bonds on the CNTs. From the percentage of oxygen on the CNT surface, the CNT %-carboxylation was determined.

2.3. Membranes

2.3.1. Formation of membranes

Polymer nanocomposite solutions for membrane formation were prepared in DMF with 17 wt% PSf and 6 wt% PVP with respect to the total volume of solution and 0.5 wt% CNTs with respect to the polymer constituents. Membranes containing either pCNTs or carboxylated carbon nanotubes (CNT-COOHs) with a range of carboxylation amounts were suspended in DMF before dissolution of the polymers. CNTs were added to DMF, cooled in an ice bath to 8 °C, then probe ultra-sonicated (Misonix Ultrasonic Liquid Processor) in intervals of 3 s interspersed by 3 s, to avoid localized heating, for a total of 1 h at a power delivery of 70 W. Once fully suspended, PVP was added to the CNT suspension and stirred for 30 min until fully dissolved. Mixing PVP with CNTs wraps CNTs in PVP. Following PVP wrapping, PSf was added to the CNT suspension. The mixture was heated to 60 °C and stirred continuously until the PSf was fully dissolved and the mixture was homogeneous. The final solution was then cast with a casting knife set to a distance of 250 μm away from a glass plate. The cast solution was allowed to equilibrate and de-gas on the glass plate before immersion in a known volume of DIW, in which the membrane precipitated and released from the glass plate. The membrane stayed in the bath for 20 min, was then transferred to fresh DI water, stored at 4 °C for 24 h, and then characterized and tested.

2.3.2. Characterization of membranes

Membrane samples were prepared for Scanning electron microscope (SEM, FEI XL30 SEM-FEG) imaging by sputter coating (Hummer 6.2 Vacuum Sputter) with Au atoms to a thickness of 5 nm. SEM images were taken using several different magnifications and beam strengths.

Stress-strain measurements (TA Instruments RSA III Micro-Strain Analyzer) of strips of the polymer membranes were performed. At least 15 strips were measured for each polymer membrane

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