Separation and Purification Technology 122 (2014) 262–269

Contents lists available at ScienceDirect

Separation and Purification Technology

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

High purity multi-walled carbon nanotubes: Preparation, characterization and performance as filler materials in co-polyimide hollow fiber membranes

Evangelos P. Favvas [a,c,*], Stephanos F. Nitodas [b], Andreas A. Stefopoulos [b], Sergios K. Papageorgiou [a], Konstantinos L. Stefanopoulos [a], Athanasios Ch. Mitropoulos [c]

[a] Division of Physical Chemistry, NCSR "Demokritos", Terma Patriarchou Grigoriou Str, 153 41 Ag. Paraskevi, Attica, Athens, Greece
[b] Glonatech S.A. TE.S.P.A "Lefkippos", Terma Patriarchou Grigoriou Str, 153 41 Ag. Paraskevi, Attica, Greece
[c] Department of Petroleum & Natural Gas Technology, Eastern Macedonia and Trace Institute of Technology, Ag. Loukas 654 04, Cavala, Greece

ARTICLE INFO

Article history:
Received 4 September 2013
Received in revised form 8 November 2013
Accepted 11 November 2013
Available online 20 November 2013

Keywords:
Carbon nanotubes
Functionalized MWCNTs
Composite membranes
Gas separation
Hollow fiber membranes
Free volume

ABSTRACT

Functionalized MWCNTS were used as filler materials for the preparation of composite polymeric hollow fiber membranes based on the BTDA-TDI/MDI (P84) co-polyimide. As a first step high purity multi-walled carbon nanotubes (MWCNTs) were synthesized using a novel catalytic CVD (chemical vapor deposition) technique, which enables large-scale production at low cost, while maintaining high purity and exceptional material properties at the same time. Covalent modification of pristine MWCNTs was applied in order to optimize both their nanoscale morphology and their dispersion in organic solvents. The functionalization process introduced certain functional groups, namely phenol groups, on the external surface of the nanotubes. Both pristine and functionalized MWCNTs with phenol groups were characterized using a variety of techniques such as XRD, SEM, TGA and Raman spectroscopy. The functionalized nanotubes were found to result in a uniform dispersion in NMP solvent. The best dispersion was observed in the case of phenol-functionalized MWCNTs. The effect of the concentration of carbon nanotubes on the composite membranes was investigated by carrying out DSC, SEM and gas permeability experiments. The prepared composite membranes were crack free and they presented high permeability values and ideal helium–nitrogen selectivities. In addition, the gas permeance coefficients increased linearly with the MWCNT concentration suggesting an increase of the free volume of the polymer matrix.

1. Introduction

In plurality of the chemical, pharmaceutical, petrochemical and oil industries the separation processes is the heart of the majority of the units. The most popular natural separation techniques are: the distillation, the extraction, the crystallization, the sorption and the separations using membranes. These units, as the industries report, will be remained the primary processes of separation for the short future. The main reasons why these techniques are difficult to change soon, are the long-time creditability joint with the existed high infrastructure investments as well as the difficulty of the entirely designing of the new candidate industrial units. Nevertheless, the low operating cost of the membrane technology operations instate this type of materials in the first line of the research priorities in the area of both the materials and the chemical engineering science. By this time is remarkable to note that the hybrid technologies, such as PSA (***P**ressure **S**wing **A**dsorption*) or cryogenic units with membranes, are used in pilot plants units and they will also be applied in the future modern industrial units, especially for O_2 separation from the air [1]. Nowadays gas separation membranes find many applications such as hydrogen separation [2], oxygen–nitrogen separation [3], natural gas separation [4], vapor–vapor separation [5], and dehydration of air [6]. The development of gas separation membranes started when Loeb and Sourirajan developed high-flux asymmetric cellulose acetate membranes [7].

In the last decades many research groups around the world work in the area of the preparation and performance of polymeric membranes, in flat, spiral wound and hollow fibers conformations [8]. Polymeric membranes can be used in many applications-processes such as desalination [9,10], water purification [11,12], heavy metal removal [13,14], and hemodialysis [15,16]. A very interesting field, both scientifically and industrially, is the gas separation

* Corresponding author at: Division of Physical Chemistry, NCSR "Demokritos", Terma Patriarchou Grigoriou Str, 153 41 Ag. Paraskevi, Attica, Athens, Greece. Tel.: +30 2106503663; fax: +30 2106511766.
E-mail address: favvas@chem.demokritos.gr (E.P. Favvas).

1383-5866/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seppur.2013.11.015

research using polymeric membranes. In current industrial membrane gas separation technologies, glassy and rubbery polymers are extensively used. The most popular glassy polymers are: cellulose acetate [17], polyimides [18–20], polysulfone [21,22], polycarbonates [23] and poly(phenylene oxide) [24]. As well, ethylene oxide [25], poly(dimethylosiloxane) [26] and amide copolymers [27] are the most referred rubbery polymers in membrane gas separation technologies. One of the mostly referred polymers used in the membrane community are the polyimides. Polyimides are polymers with good thermal properties (*Tg around 300 °C*), they can easily be modified in different configurations (*flat, hollow fiber*), they are cheap and they also provide good mechanical properties. It should be noted that the polyimide membranes are one of the best precursors for preparing carbon molecular sieve membranes [19,28–31].

On the other hand the preparation of blends and composite membranes is a new promising field mainly because they enhance the thermal, mechanical and separation properties of the membranes. To this end many types of materials such as zeolites [32], clays [33] and carbon nanotubes [34] are used as fillers in polymeric membrane matrices [6].

Polymer nanocomposites continue to receive tremendous attention for application in areas such as microelectronics, organic batteries, optics, catalysis and gas separation membranes. Polymer–inorganic nanocomposite membranes present an interesting approach to improve the separation properties of polymer-based membranes because they possess the advanced properties of both organic and inorganic membranes such as good permeability, selectivity, mechanical strength, thermal and chemical stability [35]. To this end functionalized carbon nanotubes are very promising candidate materials for use as inorganic fillers in membrane preparation [34,36].

In this study multi-walled carbon nanotubes (MWCNTs) prepared by CVD method and functionalized with phenol groups. The functionalized MWCNTs were used as filler material into BTDA-TDI/MDI (*P84*) co-polyimide hollow fibers which were developed by the dry/wet phase inversion process. A series of MWCNTs/PI nanocomposite membranes with a nominal MWCNTs content between 1 and 4 wt% were prepared by spinning method, in which the very fine MWCNTs were embedded into the glassy polymer membrane. Detailed characterization of morphology (SEM), thermal stability (TGA) and crystalline structure (XRD) has been conducted to understand the properties of both types of materials, MWCNTs and nanocomposite polymeric membranes. The different MWCNT loadings were analyzed to decide the optimum loading at which the maximum permeability of the membranes will be achieved and high membrane selectivity values in gas separation processes will be attained.

2. Experimental

2.1. MWCNTs preparation and modification

Multi-walled carbon nanotubes were produced in a fluidized bed chemical vapor deposition vertical reactor (FBCVD) which has been tailored for the synthesis of high-purity MWCNTs using proprietary catalysts [37]. Temperature was controlled by a controller with three Pt/Pt–Rh thermocouples. The experimental device was completed by mass flow controllers and flow read-out units. After stabilization of the system at the operating temperature, which varied between 650 °C and 800 °C, the gaseous feed stream was supplied to the reactor. Diluted, in helium, ethylene or acetylene was employed as carbon precursor. The CNTs synthesis techniques involved novel reactor design and specifically sized catalysts that can achieve narrower CNTs diameter distribution and purities of up to 99%. A variety of MWCNT diameters could be produced in the FBCVD system that lie in the range from under 10 nm up to 50 nm. The MWCNTs used in this study ranged from 15 to 40 nm.

Covalent modification of pristine MWCNTs was applied in order to optimize both the nanoscale morphology and their dispersion in organic solvents [38,39]. The functionalization process introduced certain functional groups, namely phenol groups, on the external surface of the nanotubes [40,41]. The functionalization procedure towards the – phenol moieties attachment, was converted through "wet chemistry" by the addition of p-aminophenol reactants to form sigma bonds with the p_z orbitals of the carbon atoms on the outer surface of the nanotube.

2.2. Hollow fiber membrane preparation

The produced functionalized multi-wall carbon nanotubes (MWCNTs) were used as filler materials in order to produce composite MWCNTs/polyimide hollow fiber membranes. In particular 1, 2 and 4 wt% concentrations of functionalized MWCNTs were dispersed in NMP solvent using a sonicator instrument at 50 °C. Afterwards 28.5 wt% of commercial BTDA-TDI/MDI (P84) co-polyimide were added in the solution and mixed mechanically for eight hours isothermally (50 °C). The solutions were filtered using a metal filter of 450 mesh and leave in overnight for outgassing. The extrusion was done using a special spinneret with the follow dimensions: needle ID = 0.5 mm, needle OD = 0.7 mm and orifice ID = 1.2 mm. The spinning conditions were constant for all the prepared membranes and described follow: (i) dope solution composition: 28.5% (P84/NMP), (ii) bore fluid composition: 70/30 (NMP:H_2O), (iii) dope flow rate: 5 ml/min, (iv) bore fluid flow rate: 3.7 ml/min, (v) air gap: 0 cm, (vi) room temperature: 20 °C, (vii) relative humidity: 36%, (viii) take up velocity: 7.6 m/min, (ix) dope solution temperature 50 °C and (x) the temperature of the coagulations baths was at 25 °C. The MWCNTs concentration was 0% for the S1 membrane, 1% for the C1, 2% for the C2 and 4% for the C4.

The involved spinning set up is already described in our previous works [29,42].

2.3. Characterization of MWCNTs and MWCNTs/PI hollow fiber membranes

Both pristine and phenol-functionalized multi-walled carbon nanotubes were characterized using various advanced techniques, such as Scanning Electron Microscopy (SEM) which was used in order to evaluate the shape and the dimensions of MWCNTs. The dimensions and asymmetric structure of the four studied hollow fiber membranes were also investigated by scanning electron microscopy (SEM). Furthermore TGA was applied as a tool for the performance of the MWCNT purity and the grade of the surface fictionalization. XRD and Raman techniques were also used for the evaluation of the crystallinity and the kind of the graphite structure of the prepared materials.

The instruments used were a JEOL-JSM-6390LV Scanning Electron Microscope and a Jeol JSM 7401F Field Emission both connected with energy dispersive X-ray analysis. The effect of carbon nanotubes, in the membranes matrices, on the thermal properties was investigated by DSC, using a temperature-modulated differential scanning calorimetry (TA Instruments, Model MDSC 2920) as well as a TGA/DTA–DSC Thermogravimetric/Differential Thermal Analyzer (Setaram, Setsys Evolution 18) and a micro-Raman RENISHAW-Invia type. Final the gases permeation measurements were performed using the variable pressure method in a high-pressure (70 bar) stainless steel permeation rig [29].