Carbon Nanotube Bucky Papers with Tailored Porosity for Filtration Applications

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ABSTRACT

In this work, Carbon Nanotube Buckypapers (CNT-BPs) were prepared using vacuum filtration. Morphology and pore size distribution were investigated using scanning electron microscopy (SEM), and nitrogen gas adsorption. The prepared BPs were subsequently exposed to four different boiling solvents (acetone, IPA, THF and DMF) for 40 min and the morphology and pore size were re-evaluated. Results indicated that the type of solvent affects the pore size distribution with DMF giving more pores in the smaller pore size ranges. The findings confirm the potential of the solvent evaporation technique in tailoring the porosity of BP membranes for filtration applications.

Keywords: CNT buckypaper, filtration, porosity

1 INTRODUCTION

The steady development of membranes as filtration media has been helping in providing low cost membranes with enhanced properties to the water filtration industry. Conventional membranes made from polymeric materials have suffered problems in meeting good permeability and selectivity, poor chemical and heat resistance, and are also vulnerable to fouling [1]. Membranes based on nano-scale materials have been given mounting interest due to their unique properties that are superior to their bulk counterparts, and which could overcome some of these challenges [2].

At present, carbon nanotubes (CNTs) are considered to be one of the most promising nanomaterials, as they exhibit outstanding mechanical, electrical, thermal conductivity and adsorption properties [2-5]. The concept of using nanotubes in the separation and filtration industry has been put forward, but constructing macroscopic structures with controlled density, porosity, and morphology is still a challenge [2, 4].

Bucky paper (BP) is a material composed of randomly oriented CNTs in a woven or paper-like structure. The arrangement helps to provide a large specific area with a highly porous 3D network structure, which is useful for water filtration applications [2, 6]. The preparation of BPs basically entails the purification of CNTs, dispersion in suitable solvent, and their precipitation on a porous support [1]. The properties of BPs can be determined by several parameters during preparation such as the vacuum pressure, concentration and dispersion of CNTs, solvents used, surface functionalization of CNTs as well as their physio-chemical properties [7]. The use of CNT-BPs as filtration membranes is being investigated. For example, Yang et al. [8] investigated the use of buckypaper prepared from purified CNTs in removing humic acid (HA) from water and reported (>93%) removal rates. In order to widen their potential in filtration applications, control of the pore size is critical. Among the factors which affect the pore size are the CNT type, aspect ratio, purity as well as the substrate pore size.

Some researchers demonstrated that forests of CNTs can be densified by a process known as capillary forming which entails subjecting the CNT forests to the vapours of a boiling solvent [9-12]. Recently, Dumee et al. [10] investigated the effect of solvent evaporation on the densification of vertically aligned CNT forests using different solvents and confirmed that the type of solvent affects the CNT-CNT interactions. As far as the current authors are aware, solvent evaporation was never used to control the porosity of CNT-BPs.

In this work, CNT-BPs were prepared using vacuum filtration. Morphology and pore size distribution were investigated using scanning electron microscopy (SEM) and nitrogen gas adsorption. The prepared CNT-BPs were subsequently exposed to four different boiling solvents for 40 minutes and the morphology and pore size were re-evaluated.

2 MATERIALS AND METHODS

2.1 Reagents

All CNTs in this paper are Elicarb multi-wall CNTs produced by Thomas Swan (England) with a diameter of 10-12 nm, tens of microns in length and a density of 1.7-1.9 g/cm^3. Triton X-100 (Sigma Aldrich) was used as a dispersant. Deionized water was used from MilliPore-Q. Acetone (Sigma Aldrich), Isopropanol (IPA; Aldrich), Dimethylformamide (DMF; Sigma Adlrich) and Tetrahydrofuran (THF; Carlo Erba) were used for densifying the CNT-BPs.

2.2 Preparation of MWNT dispersions

25 mg of CNTs were added to 800 ml of Dionized (DI) water in different beakers with 28 ml of Triton X (TX). The solution was sonicated for 30 mins and then vacuum filtered using a vacuum filtration unit. The solution was filtered through a polytetrafluoroethylene (PTFE) membrane filter which has a pore size of 0.45 µm. Once, the solution was completely filtered, the BP was obtained on top of the membrane filter. The BP was then left overnight to dry before peeling it off the membrane filter. The BP was then washed in DI for 2 hours, then IPA for 5 hours, and then DI water again for 2 hours to ensure removal of the surfactant. The BP was finally left overight to dry at ambient temperature.

2.3 Exposure of BPs to boiling solvents

The prepared BPs were exposed to four different boiling solvents (Acetone, THF, IPA, and DMF). 150 ml of the solvent was poured into a beaker and boiled using a hot plate. The beaker with the solvent was covered with a wire mesh on which the BP was placed. A beaker with a similar size was placed on top of the bottom one, right above the wire mesh to ensure the passage of the vapor to the membrane (Figure 1).

2.4 Characterization Techniques

Scanning electron microscopy (SEM) investigations were carried out on the resulting BPs to investigate their surface morphologies.

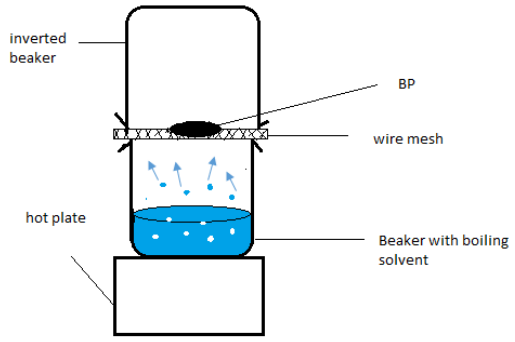

Figure 1 Schematic of the setup used to expose the BP to boiling solvent

A Micromeritics surface area analyser (ASAP 2020) was used to attain nitrogen adsorption/desorption isotherms for all BPs at 77 K. Samples were placed under vacuum at 200°C to remove any residual trapped gases. The produced isotherms were analysed using the multipoint Brunauer, Emmett, and Teller (BET) method to evaluate the pore size distribution.

3 RESULTS AND DISCUSSION

3.1 Surface morphology of buckypapers

The morphologies of the prepared BP membranes exposed to different boiling solvents are shown in Figure 2. The BP exposed to acetone shows aligned and compacted morphology, whereas that exposed to THF is not as smooth as the other ones. IPA and DMF exposed BPs have similar morphologies except that the DMF one appears to have a more compacted structure, showing smaller pores.

3.2 Pore size distribution

Figures 3 and 4 present the differential pore volume and surface area versus pore width, respectively, for the different BPs. Figure 3 shows that for all the membranes, the larger pores (>~ 20 nm) accounted for most of the differential pore volumes, with distinct values at pore widths of 25 nm, 29 nm, 37 nm, 50 nm, 54 nm, 68 nm, and 86 nm. It is noticeable that not all the samples exhibited maximum differential pore volume at the same pore size. It is also evident that the graph of the BP exposed to DMF lies lower than the other graphs confirming that it has relatively lower values of differential pore volume compared to the others. Also, by looking at the range of small pores in the inset (pore width 0-7 nm), it can be observed that small pores accounted for limited differential pore volumes with distinct values at pore widths of 3.4 nm, 4.0 nm, 4.6 nm and 5.4 nm. DMF exposure resulted in relatively higher differential pore volumes compared to other solvents. For example, DMF shows a peak at 3.4 nm equivalent to a differential pore volume of 0.15 m^3/g which is much higher than that of the THF (0.07 m^3/g).

The graph of differential surface area also showed a noticeable decrease in BP surface area upon exposure to DMF compared to other solvents. On the other hand, it showed the highest differential surface area at small pore widths (3.4 nm) confirming a considerable increase in the number of small pores due to exposure to DMF.

The differences between the BPs exposed to the different solvents which are evident in the BET graphs and in the SEM images could be attributed to the different surface tension and different boiling points of the solvents used (Table 1) which affected the capillary condensation effect which occurs in two steps: first the CNTs are drawn together through liquid capillary forces because each nanotube densifies individually, and secondly when the solvent evaporates upon drying of the BP, the van der waals between the CNTs adhere the tubes closer [10-12]. DMF has the highest boiling point of all solvents used and the highest surface tension, which could be the reason for the more effective densification observed.

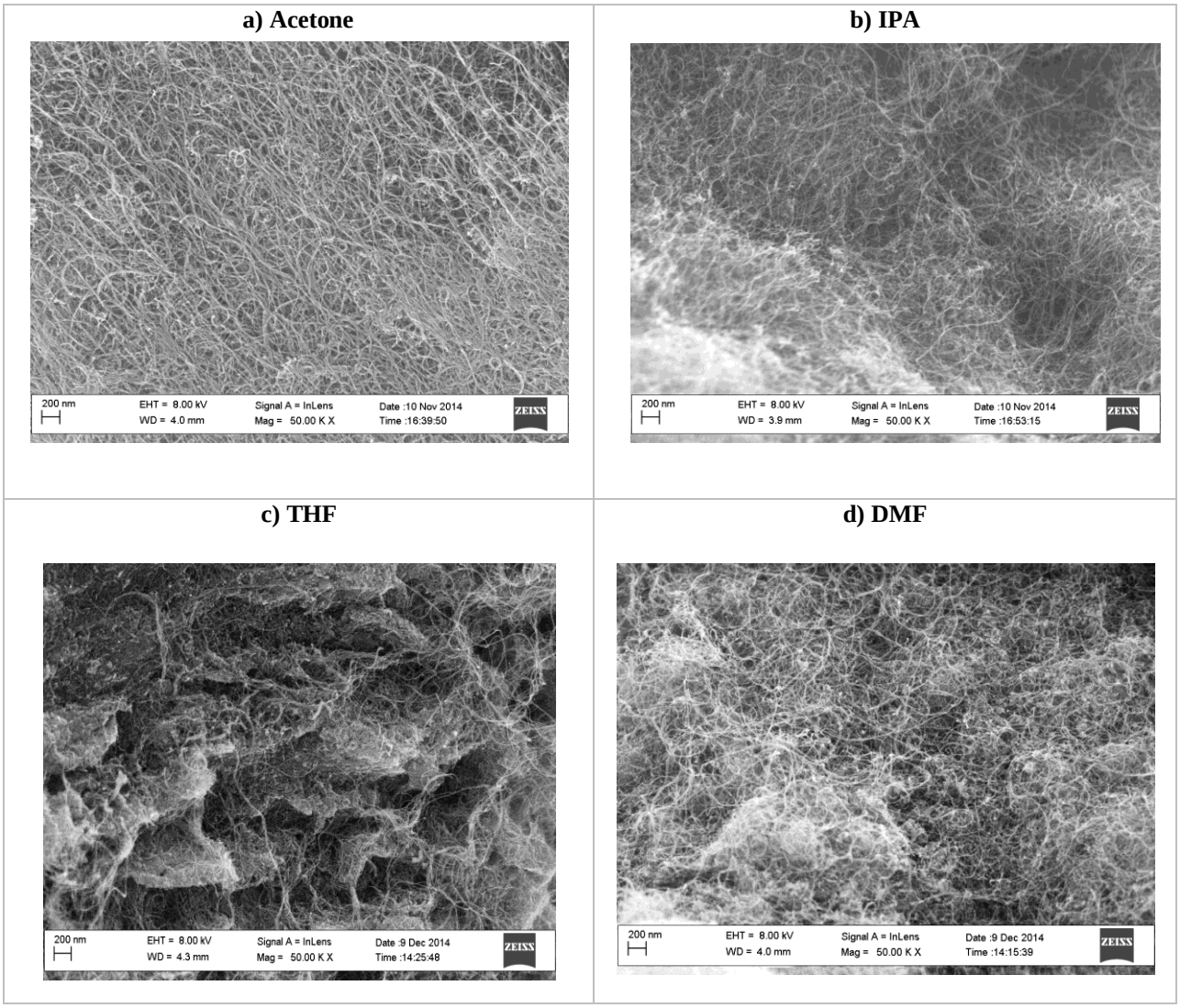

Figure 2 SEM images of different BPs imaged at 50,000 x magnification, (a) BP exposed to Acetone, (b) BP exposed to IPA, (c) BP exposed to THF, (d) BP exposed to DMF.

Table 1 Surface tension values and boiling points for the solvents used

Type of solvent	IPA	Acetone	DMF	THF
Surface tension (mN/m)	23	25.2	37.1	26.4
Boiling point (^{0}C)	82.6	56	153	66

4 CONCLUSIONS

This paper presented the results of a preliminary study in which the effect of exposing BPs to the vapours of different boiling solvents is evaluated. The results show that the porosity of BP can be modified and that DMF has the biggest effect in densifying the BPs and shifting the pores to smaller sizes. The findings confirm the potential of the solvent evaporation technique in tailoring the porosity of BPs for filtration applications.

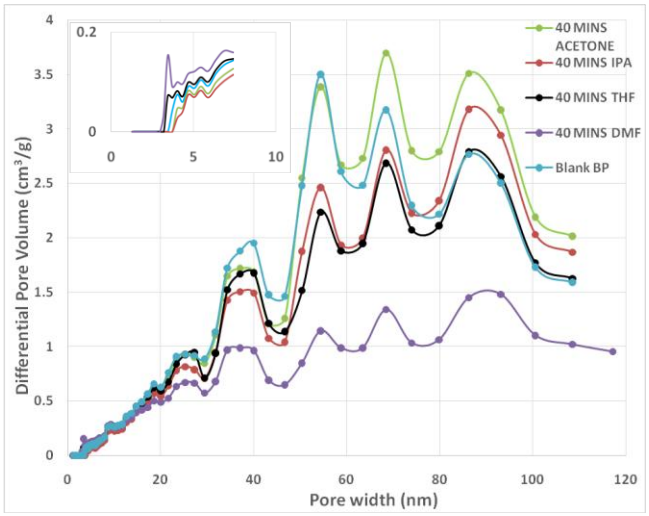

Figure 3 Differential pore volume vs pore width for the BPs exposed to different boiling solvents in the pore width range (0-120 nm). Inset shows pore width in the range (0-7 nm)

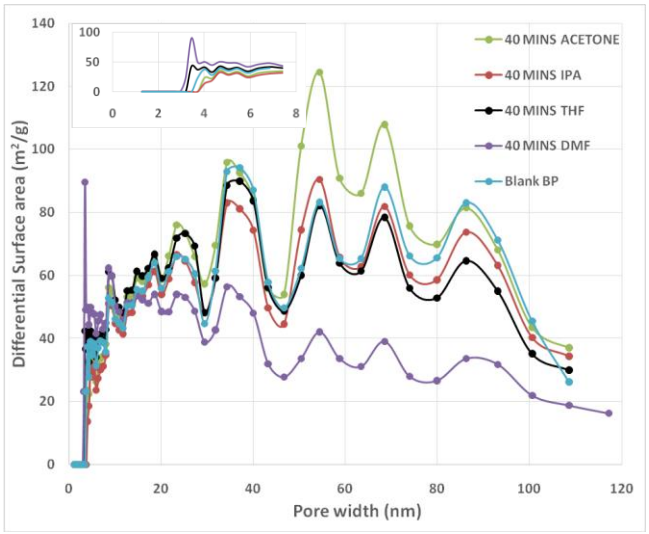

Figure 4 Differential surface area vs pore width for BPs exposed to different boiling solvents in the pore width range (0-120 nm). Inset shows pore width in the range (0-7 nm)

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