ORDERED CARBON NANOTUBE MEMBRANES FOR LOW BURDEN PROTECTIVE CLOTHING APPLICATIONS: WATER TRANSPORT PROPERTIES

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Abstract

Current commercial moisture vapour permeable membranes cannot deal with the levels of sweat produced during high work loads. However, membranes containing ordered carbon nanotubes offer significant opportunities for the development of a moisture-vapour permeable membrane which replicates the water transport properties of skin by allowing both water vapour, and liquid water, transport according to demand. Membranes consisting of vertically aligned carbon nanotubes have been produced by the Center for Applied Energy Research (CAER) at the University of Kentucky (UK). These membranes have been evaluated for their water transport rates as a function of humidity, and have been compared with a conventional microporous membrane.

Introduction

Current commercial moisture vapour permeable membranes are based on two types of material. They either possess a microporous structure (e.g. expanded PTFE) or they are composed of a hydrophilic polymer. These materials act as a physical barrier towards liquid water but allow the diffusion of water vapour. Consequently, they cannot deal with the levels of sweat produced during periods of exertion, and the physiological burden of wearing systems comprising these materials will increase at higher work loads. Membranes that contain ordered carbon nanotubes offer the potential to provide membranes with significant water transport properties since it has been predicted that the interaction between water and the smooth graphite sheets of the CNT walls will result in nearly frictionless flow (Hummer *et al* 2001). There is also the possibility that unlike microporous or hydrophilic membranes, carbon nanotubes could accommodate the transport of liquid water. The preliminary results obtained on such a membrane system are discussed in this paper.

UK CAER has developed a chemical vapour deposition process for selectively producing high purity (>95%) multiwall carbon nanotubes (MWNTs); virtually no amorphous carbon is co-generated with the nanotubes. The synthesis proceeds by the reaction of a hydrocarbon vapour over a dispersed iron catalyst that is deposited *in situ* on quartz substrates (Andrews *et al* 1999). Commonly, a xylene-ferrocene liquid mixture is injected continuously into a pre-heater zone and is swept into the reactor by an argon or nitrogen carrier gas. Operating conditions are varied to control the type and morphology of the nanotubes that are formed. The reaction zone is typically controlled at a temperature in the range 700 - 850°C for optimum nanotube growth. The carbon nanotubes (CNTs) grow perpendicular to the quartz plates in parallel alignment, forming thick mats (Figure 1).

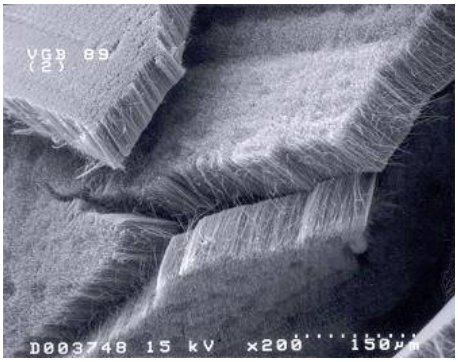


Figure 1. MWNT Produced at CAER

The diameter of the MWNTs is typically around 35nm with a core diameter of 4 to 7nm and lengths of 20 to 30µm. These dimensions can be controlled by adjusting the reactor operating conditions, relative proportions of the reactants and the atmosphere in the reactor.

It has been demonstrated that a highly engineered membrane could be produced if the space between the CNTs is filled with a continuous matrix (Hinds *et al* 2004). If the matrix is impermeable to liquid and vapour, then the cores of the nanotubes provide the only means by which any liquids or vapours can permeate through the membrane. Since it has been predicted that a state of nearly frictionless flow will occur for water passing through a carbon nanotube (Hummer *et al* 2001), and considering that the membrane would possess a stacked array of densely packed nanotubes at a population density of ~$5x10^{10}$tubes/cm^2, exceptionally high transport velocities can be envisaged for the flow of water through the nanotube membrane. The nanotubes produced are however generally capped with a fullerene carbon dome and a proportion of the nanotubes are blocked by the presence of discrete iron particles within the core- the residue from the ferrocene catalyst used in the continuous vapour deposition (CVD) process.

The fact that the nanotubes are sealed with a fullerene cap is however beneficial in terms of protecting the nanotube cores whilst a polymer resin is dispersed between the nanotubes (Hinds *et al* 2004). The fullerene caps must however be removed if ultimately fluid is to be able to flow through the nanotube channels. It has been found that the caps on the nanotubes can be removed by plasma etching to form a viable membrane containing nano-channels though its structure. Additionally, the same technique is also used to remove excess matrix covering the surface of the nanotubes. Minimizing the amount of overbearing material does, however, make the etching process less prone to failure and reduces the time and energy required for completion. The blockage of the nanotube cores by iron particles is more problematic and strategies to eliminate their formation or bring about their removal need to be explored.

Experimental

Preparation and Characterisation of Ordered Carbon Nanotube Membranes

The CNTs were grown on quartz substrates in the CVD process at 700°C using a ferrocene/xylene feed with a N_2 carrier gas. The aligned CNT film was then infused with a 50wt% solution of polystyrene (PS) in toluene and the excess polymer removed from the top surface using a spin coater. The film was dried in vacuum at 70°C and the quartz substrate removed using hydrofluoric acid. The thin layer of excess polymer on the top surface was removed by etching with a H_2O enhanced oxygen plasma leaving the CNT tips proud of the polymer surface, and simultaneously opening the CNT tips forming a membrane structure, as depicted in Figure 2.

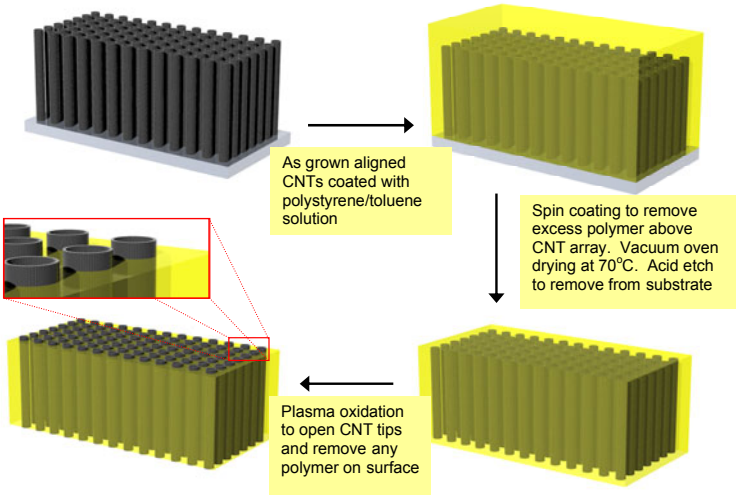


Figure 2. Schematic of Carbon Nanotube Membrane Fabrication Steps.

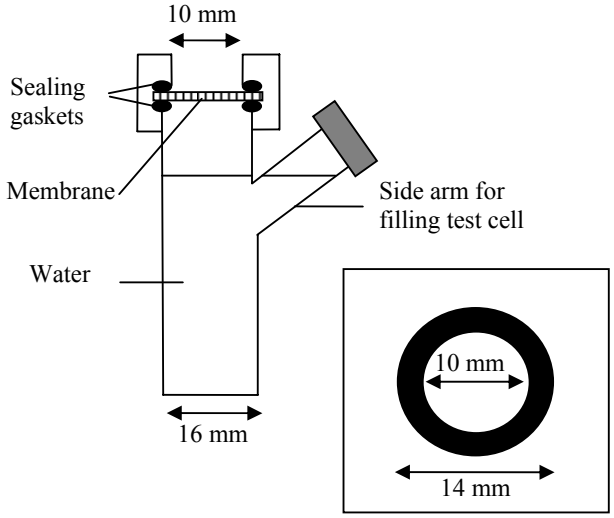
Confirmation that the plasma treatment had successfully exposed both ends of the nanotube was achieved by making conductivity measurements. If all of the excess polymer was removed, and the nanotubes are exposed on both sides of the membrane, then the membrane will be conductive. It was also assumed that at this point the caps on the nanotubes will have also been removed but, this was

confirmed separately, and is described below. The resultant membrane was then characterised in terms of its film thickness, and the average inner and outer nanotube dimensions. The film thickness was measured using profilometry, and the average nanotube dimensions were calculated from the TEM measurements of 100 individual tubes. The extent to which the iron particles had been removed from the nanotube cores, and therefore the percentage of unblocked nanotubes within the membrane, was determined by measuring the rate of diffusion of Ru-bpy molecules through the membrane. The ability of water to pass through these channels was demonstrated for both liquid and vapour flows (Majumder *et al* 2005,Andrews *et al* 2006).

Water Transport Properties of the Membranes

A commercial membrane system, expanded PTFE (ePTFE), was selected to provide the benchmark water transport properties for comparison with the carbon nanotube membrane systems that are the subject of this paper. The water vapour permeability of the test membranes was determined gravimetrically by measuring mass lost through the test membrane. This was achieved by mounting the test membrane in a specifically designed test cell (see Figure 3). The membrane to be tested was mounted in a water and gas tight test cell which was then placed on a balance within the oven. The membranes were tested in the upright test orientation where the membrane surface inside the cell was in contact with 100% RH water vapour but not in direct contact with liquid water (see Figure 3).

In order to accurately determine the permeability of the membranes towards water, careful control of the temperature and the relative humidity (RH) of the air surrounding the test cell were crucial. RH and temperature were controlled within a Swallow incubator (LTE Scientific Ltd.). Humidity control is achieved by blending wet air with dry air. Brooks mass-flow controllers (0-1L/min) were used to blend know quantities of these wet and dry air feeds. The dry air was obtained either from an air cylinder, supplied by BOC, or from the compressed air available in the laboratory. The wet air was achieved by bubbling dry air through two dreschel bottles, located outside the incubator, the first of which contained distilled water. This humid air was then passed through a third Dreschel bottle, containing water that was located inside the incubator- this enable higher RHs to be obtained. The wet and dry air feeds were then recombined and passed through a final empty dreschel bottle before being used to supply conditioned air to the test cell on the balance. The RH was monitored using an Oakton RH monitor. Both the conditioned air supply and the RH monitor were located within 2cm of the test cell. RH and temperature were controlled by a custom written Labview program, which remotely adjusted the oven and the flow settings on the mass flow controllers to allow the amounts of wet and dry air to be altered and thus control the environmental humidity within the test incubator. By using this automated set up it was possible to control the RH and temperature profiles over a given period of time. The water transport rate for the membranes was measured by recording the weight lost throughout the temperature and humidity controlled program. The weight loss, and therefore water transport rate, could then be directly compared between the membrane samples tested. All membrane water transport data reported is the calculated average from 3 runs of each set of test conditions. The validity of this procedure was demonstrated through comprehensive testing of the system with a well characterised water vapour permeable membrane, ePTFE.



Sealing gasket dimensions

Figure 3. Test cell arrangement for measuring water permeation across membrane samples

Results

Preparation and Characterisation of the Ordered Carbon Nanotube Membranes

Well-aligned MWNTs were successfully grown on quartz substrates (Figure 1). The thickness of the membrane was measured as approximately 70 μm. The MWNTs were found to have an average outer diameter of 23.4nm, and average inner diameter of 6 nm. Figure 4 shows the histogram of diameters of 100 individual tubes measured from TEM. Membranes were then constructed by spin coating the MWNTs with a toluene solution of polystyrene. Excess polymer and the caps on the nanotubes were then removed by plasma etching. The membrane was then finally recovered by immersion of the membrane in hydrofluoric acid to dissolve the quartz substrate.

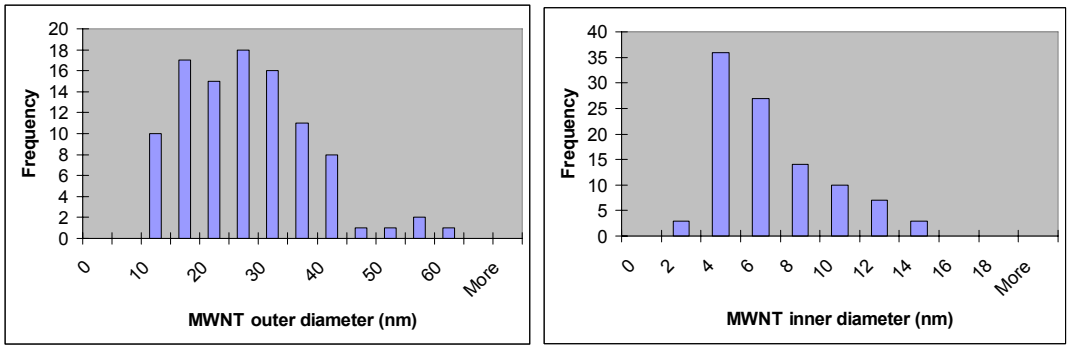


Figure 4: Histogram of MWNT outer diameter and inner diameter measure from 100 tubes.

Ideally at this stage, all of the carbon nanotubes will open and any internal iron catalyst particles that are blocking the internal cores will have been removed. The percentage of open pores, as determined by Ru-bpy diffusion measurements was however approximately 5%. It is believed that this was due to plugs of the iron catalyst forming in the nanotubes as they were grown. As an initial indication of the performance of this membrane it was investigated for its permeability towards water. In order to determine how this novel type of membrane performs when compared to a microporous PTFE membrane, a comparative assessment was required. Standard methods used to investigate moisture vapour permeable membranes exist but these require relatively large samples of membrane and are generally only conducted at a single relative humidity and temperature regime. A bespoke test protocol was therefore constructed so that the performance of the nanotube membrane could be compared with microporous PTFE over a variety of conditions.

Water Transport Properties of the Membranes

The test system and method were verified using a microporous ePTFE membrane to demonstrate the reproducibility of the procedure. The membrane samples were tested at a range of humidities between 15% RH and 75% RH at 25, 30, 35, and 40°C. The loss of water over a 30 minute period is displayed in Figure 5. It can be seen from this data that at a specific temperature and RH regime, the permeability of the PTFE was reproducible and that below an RH of 55% clear differences are observed for the mass loss through the membrane at the different temperatures. The reliability and reproducibility of the test system using ePFTE can be seen in Figures 5 and 6.

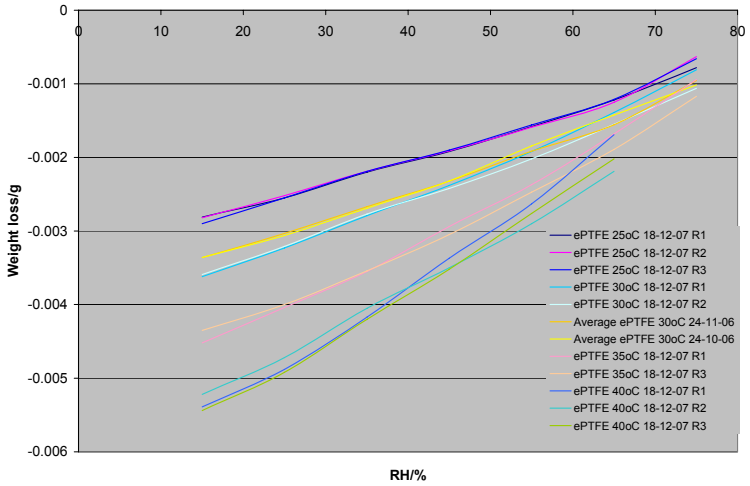


Figure 5. Water loss measured for ePTFE samples as a function of humidities over a range of temperatures.

The data also demonstrates the linear nature of the water permeation rate as a function of humidity, at each temperature. This feature of the permeation characteristics is demonstrated more clearly in Figure 6, by the calculation of regression lines for the data where the fit of the data exhibits an R^2 factor of 0.99.

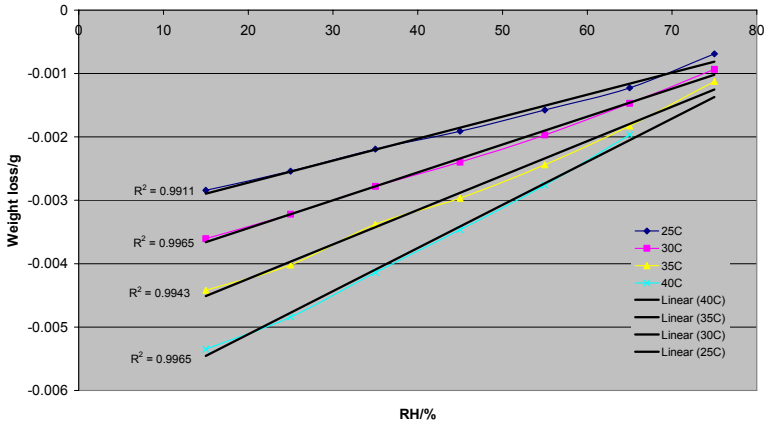


Figure 6. Linearity of water loss from an ePTFE membrane as a function of environmental humidity over a range of temperatures.

When the data for the MWNT membrane was obtained and compared with the data collected for the microporous ePTFE it can be seen that it exhibits a lower permeability (Figure 7). It should, however, be stressed that the MWNT membrane still contains nanotubes that are mostly blocked by the iron catalyst particles from which they are grown (~95%). Since the permeation through the nanotube membrane is likely to be directly proportional to the number of nanotubes, it is possible to theoretically predict what the mass loss of water could be for a MWNT membrane where 20%, 50% and 100% of the nanotubes are unblocked. When these calculations are used it is plausible that if 20-50% of the nanotubes are unblocked then permeation characteristics similar to, and indeed in excess of, microporous ePTFE would be expected (Figure 7).

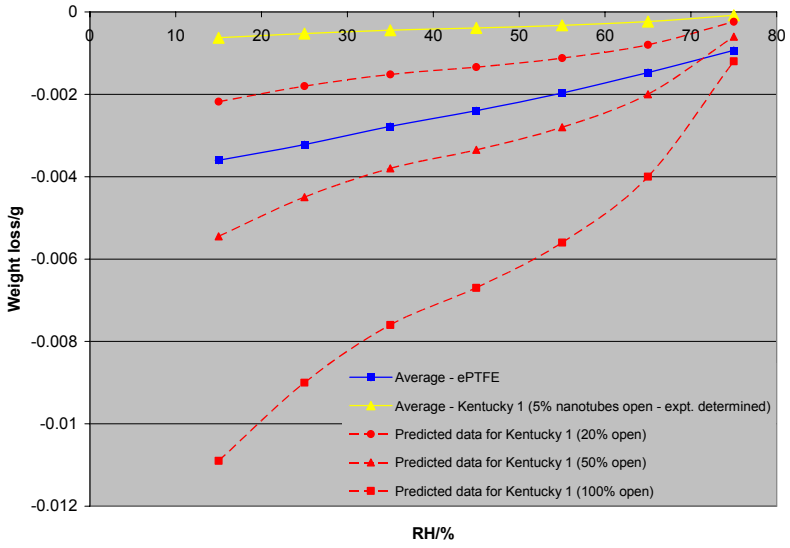


Figure 7. Performance of the ordered carbon nanotube membrane, compared to expanded PTFE, as a function of humidity at 30°C

Conclusions and Recommendations

The research to date has demonstrated that membranes composed of aligned carbon nanotubes do allow for the permeation of water vapour. Whilst the rate of water loss through this material is a factor of 10 less than that through a commercial microporous PTFE system, the data does need to be interpreted with the knowledge that most (95%) of the carbon nanotubes remain blocked. The blockage within the nanotubes is associated with the method from which they grown. Careful control of the carbon nanotube reactor conditions are necessary and although membranes have been previously synthesised that display favourable Ru-bpy diffusion rates, this has only been achieved with a very limited number membranes and replication of the process has proved to be difficult. In addition, the fabrication procedure is a time consuming process and the success rate for producing viable membranes has been very low. Hence, an alternative more practical route for producing membranes with the same exciting properties is being sought. The main goal of the future work will be to repeatedly produce MWNT membranes where the majority of the nanotube cores are open. It is anticipated that if this can be achieved then membranes with superior permeability characteristics for water diffusion compared to current microporous or hydrophilic systems will be achieved.

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