FILTER MEMBRANE SELECTION STUDY FOR NANOTUBE BUCKY-PAPER FABRICATION

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Carbon nanotubes are a novel material with valuable properties including high electrical and thermal conductivity and high mechanical strength. To effectively facilitate large scale application of nanotubes, a sheet-like grouping of entangled carbon nanotubes known as buckypaper is produced. Buckypaper is made through a filtration process, where carbon nanotubes dispersed in solution are filtered on a microporous membrane material. The objective of this research is to identify the optimal membrane material based on filtration parameters and buckypaper quality. Nylon membranes are widely used, but have problems including lack of reusability and difficulty with buckypaper removal. A variety of membrane materials were tested and polycarbonate membranes showed the most promise, becoming the focal point of the study. The polycarbonate membranes have fewer entanglements with the buckypaper, leading to reduced peeling difficulty and potential reusability. Scanning electron microscopy imaging and analysis was very useful to understanding processing-structure-property relationships. Existing filtration models were extended to CNT filtration, revealing mechanisms for difficulties associated with buckypaper removal. As a result of using the polycarbonate membranes, a wet peeling technique was developed which could increase densification of nanotube networks, leading to increased buckypaper properties.

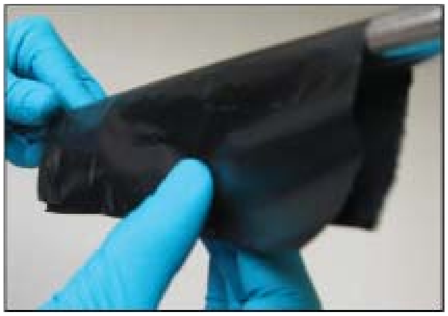
C**arbon nanotubes** (CNTs) are an allotrope, or different form of carbon, that have a long, cylindrical, hollow structure. CNTs have the "nano" designation due to their diameter, which is on the order of a billionth of a meter. CNTs possess an aspect ratio(length to diameter ratio), as high as 132,000,000, and can be up to nearly 18.5 cm in length. They possess novel properties that are extremely valuable in a number of fields. CNTs are very electrically conductive, thermally conductive, extremely strong, and lightweight. There are two types of CNTs, single-wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT).

Figure 1- Single-wall and Multi-wall Carbon Nanotubes[1]

Buckypaper (BP)

BP is a thin, sheet-like material composed of entangled networks of CNTs. BP has a large number of potential uses. In aviation, BP can be utilized as a layer on the skin of an aircraft for EMI (Electromagnetic Interference) shielding, Lightning strike protection, and radiation shielding.[2] Due to its high current-carrying capacity, BP could be added to the exteriors of airplanes. Lightning strike current would flow around the plane and dissipate safely.[3] BP's high thermal conductivity could allow it to be utilized as heat sinks for computers and electronic equipment. High electrical conductivity could allow BP to be utilized as electrodes for batteries, super-conductors, and fuel cells.[4] BP can also be used as a fire retardant film, as it is a dense layer of non-flammable carbon. Due to its high strength and light weight, BP can be used to reinforce body and vehicle armor.

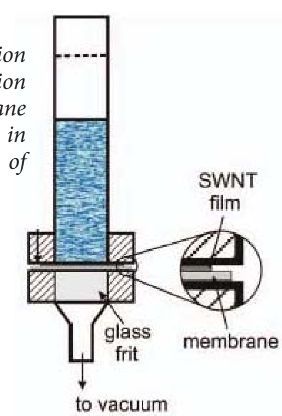
Figure 2- A BP sample demonstrating high flexibility



BP Fabrication Process

BP is fabricated through a filtration process.[5] BP fabrication begins with dry CNTs, which resemble powder-like loose dirt. The dry CNTs are weighed out and combined with surfactant and water. A surfactant is a soap-like liquid which reduces the surface tension of the water and helps prevent the CNTs from sticking to one another. CNTs tend to clump together, or agglomerate, whether dry or in aqueous suspension. The agglomeration of CNTs is undesirable, because when the CNTs are filtered, the agglomeration prevents evenly distributed entanglement of CNTs. This significantly limits the achievable properties of BP. The purpose of these dispersion techniques is to break apart agglomerated CNTs and separate them more evenly throughout the solvent. Mortar and pestle mixing is followed by sonication. Sonication works by emitting ultrasonic energy into the suspension. Sonication has been found to be effective in evenly dispersing CNTs in solution. After sonication, the suspension is filtered through a membrane material using positive or vacuum pressure.

Figure 3- Filtration of the suspension onto the membrane material results in the formation of buckypaper[6]



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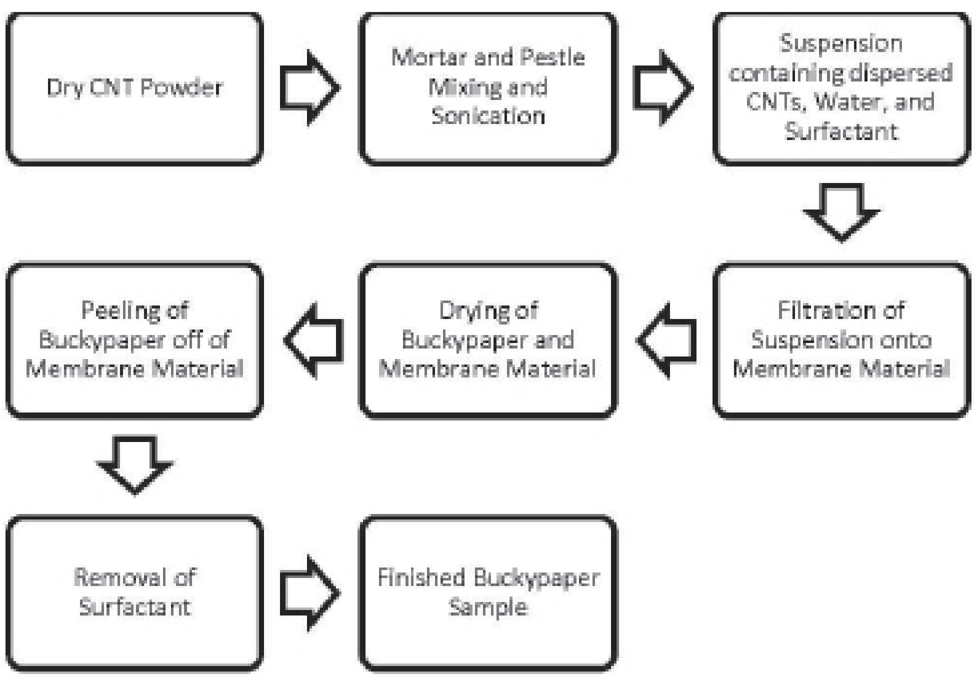
The liquid is filtered completely through, and BP is left on the top of the membrane. The membrane material and BP are allowed to dry before the BP is peeled off. As the surfactant has coated the surface of all the CNTs, it needs to be removed. The surfactant dried on the BP interferes with the interactions between CNTs. Removing the surfactant has been found to increase electrical conductivity, surface area and mechanical properties.[7] The surfactant remaining on the BP can be removed by two ways. This is accomplished by washing the BP in isopropyl alcohol (IPA), or by high temperature heat treatment in an inert gas, usually nitrogen or argon. To be thorough, both washing and heat treatment are performed to ensure the surfactant is removed.

Figure 4- Buckypaper Fabrication Flow Chart



Objective

This research focuses on selecting the optimal filter membrane material for CNT filtration. Scanning Electron Microscopy imaging is relied upon heavily to observe the microstructure of BP and to view the surface of the membrane materials, before and after filtration.

Experimental Methods

BP Filter Membrane Material Study

This study evaluates membrane materials for the purpose of making BP. The factors considered for each membrane material were cost, reusability, BP quality, filtration time, availability, and chemical compatibility. First, a number of different membrane materials were ordered, in a number of different pore size classifications from multiple suppliers. BP samples were produced on each membrane material, using both SWCNT and MWCNT. A variety of outcomes resulted from these samples. BP would form but not remove from some membranes. Other membranes would allow the suspension to filter but no BP would be formed. Some membranes prevented any suspension from passing through at all. However, a few of the membrane materials resulted in producing quality samples of BP. The best two of the functioning membrane materials were the nylon membranes, and the polycarbonate track-etched membranes.

Scanning Electron Microscopy (SEM) Imaging

In this research, scanning electron microscopy (SEM) imaging is an extremely useful tool. It is important to be able to see the microstructure, and correlate processing-structure-property relationships of BP and membrane materials. Specifically, it was essential to understanding how the membrane material interacts with the BP, and how the membrane properties affect BP properties and performance. The SEM was used heavily for the BP membrane selection study.

Figure 5- JEOL Scanning Electron Microscrope[8]

Nylon Membranes

The nylon membrane supplied by Sterlitech has been the primary membrane material for BP production for some time at our lab. It is a random porous nylon that does not have defined pores, but rather a pore size rating. The pore size rating of the nylon membrane in Figure 5 is 0.45 micron. Even though nylon membranes have been the membrane of choice for BP fabrication by many groups, there are numerous problems. The problem of BP removal is the main issue with nylon membranes. The BP and nylon membrane must be allowed to dry completely before peeling the BP off from the membrane. This waiting time slows down the entire production process, adding more to the costs of fabrication. Peeling the BP off the nylon membrane is extremely tedious, as the BP is very delicate. The SWCNTs, being of higher quality, will often peel off easier than the MWCNTs. However, with both SWCNTs and MWCNTs, peeling from a nylon membrane is frustrating, and often results in cracks and tears. As well as the difficulty with peeling, a significant amount of CNTs are left on the membrane, as shown in

Figure 7. The nylon branches in Figure 7 are darker and thicker due to being covered in CNTs. The CNTs left on the filter lead to discrepancies between the measured amount of CNTs used, and the actual amount of CNTs contained in the BP. This waste of CNTs adds up over time, as the price of CNTs, depending on the quality, can be between $50 and $2000 per gram. The leftover CNTs also prevent the membrane from being reused, meaning that a new membrane must be used for every sample made. This makes the fabrication process costly as a 47mm diameter nylon membrane costs $1.03.

Polybarbonate Membranes

After testing a number of different membrane materials, the polycarbonate track-etched (PCTE) membranes became the focal point of the membrane selection study. The PCTE membranes are noticeably smoother and thinner than the nylon membranes. The SEM analysis shows the differences in microstructure of the nylon and PCTE membranes.

Figure 6- Clean Nylon Material before suspension filtration

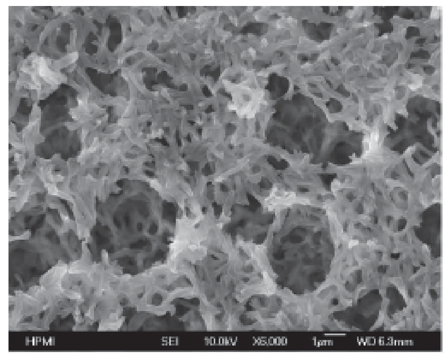
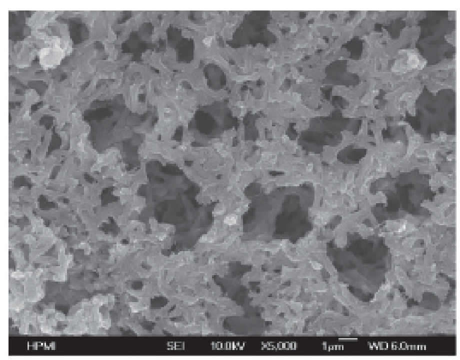


Figure 7- Covered with CNTs after filtration and removal of BP



Whereas the nylon membranes have random, undefined pores, the PCTE membranes have clearly defined pore geometry and sizes, randomly spaced throughout the membrane as well as smoother surface. This leads to a difference in the interactions that the CNTs have with the membrane during filtration and peeling. The CNTs have many interactions with the nylon membrane, a significant number being imbedded in the membrane, as shown in Figure 7. The PCTE membrane greatly reduces the number of interactions between the CNTs and the membrane. This leads to a number of changes in the resulting BP. First, the BP is much easier to remove from the membrane, and can even be removed while still wet. This reduces the fabrication time. Also, almost no CNTs remain on the membrane after the BP is removed. This allows for the possibility of reusing PCTE membranes. Being able to reuse membranes will greatly reduce the fabrication cost of each sample.

Results and Discussion

Nylon vs. PCTE Membranes

Figures 11 and 12 demonstrate two types of particle filtration. Figure 11 represents a dead-end filtration model, and Figure 12 represents a deep-bed filtration model.

Figure 8- A clean PC membrane before filtration

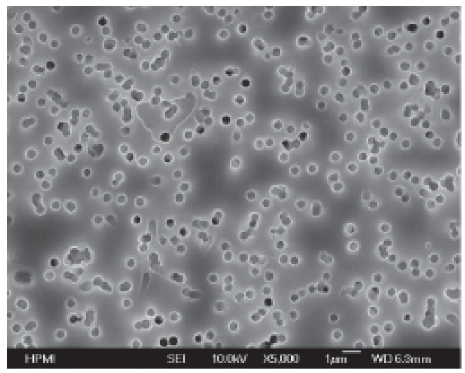
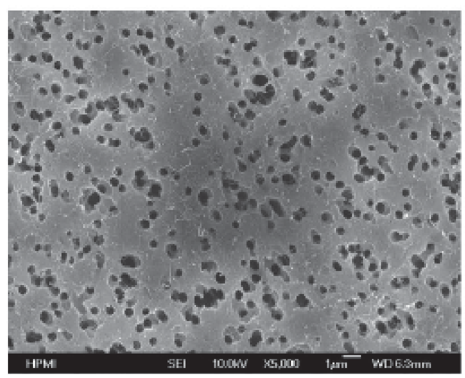
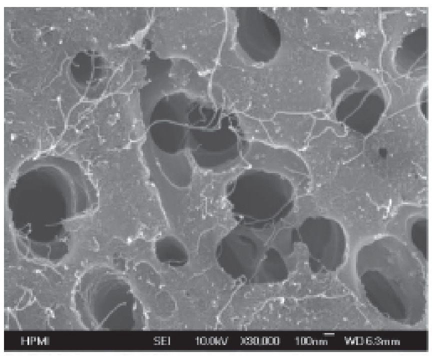


Figure 9- A PC membrane covered in CNTs after filtration and BP removalfiltration



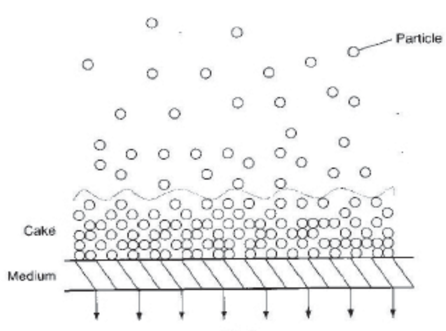
In the dead-end filtration model, particles immediately begin building on the surface of the membrane material, forming a filter cake. In the deep-bed filtration model, particles must first build up within the membrane material, before a filter cake develops on top of the membrane.

Figure 10- A higher magnification image of CNTs on the surface of a PC membrane



Even though Figure 11 and Figure 12 show general particles being filtered on a medium, it is representative of CNTs being filtered on a microporous membrane.

Figure 11- Figure 11: Dead-End filtration diagram.[9]



The PCTE membrane is represented by the dead-end filtration model. The filter cake (BP) immediately begins building the nanotube network upon the surface of the membrane due to their well-defined pore structure. The nylon membrane material goes through two stages of filtration. The deep-bed model represents the first stage of filtration using the nylon membrane. As soon as a sufficient amount of CNTs build up within the nylon membrane, it takes on the dead-end filtration model. CNTs cannot be removed from within the nylon membrane, resulting in wasted CNTs during the deep-bed stage of nylon membrane filtration. This model also demonstrates why it is difficult to remove BP from the nylon membrane. There are a large amount of interactions and entanglements between the CNTs and the nylon membrane, leading to the

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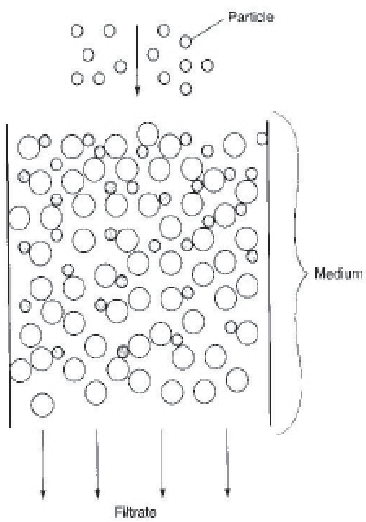
BP sticking to the membrane. These problems with BP removal prompted new investigations into peeling techniques.

Figure 12- Deep-Bed filtration diagram[10]



Development of 'Wet Peel' Technique

After the filtration process, it is necessary to let the sample dry. As the solvent evaporates from the BP, the CNTs contract, leading to densification. However, as the BP dries while still attached to the membrane material, which is unavoidable using nylon membranes, the membrane acts as a support matrix, preventing the contraction and densification of the BP as the CNTs contract.

It was observed that when the PCTE membranes are used, the BP can be peeled off while still wet from after filtration. Figure 13 shows the difference between the method used previously and the wet peel technique. This is possible due to the reduced CNT entanglement between the PCTE membrane material and the BP. This change in the fabrication process has some unique advantages. When the wet peel is preformed, the BP is allowed to dry freestanding. This lack of support allows the CNTs to contract and entangle uninhibited.

This increased contraction and entanglement leads to the densification of the BP. This BP densification could lead to increases

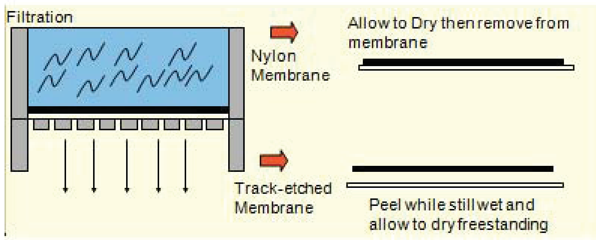
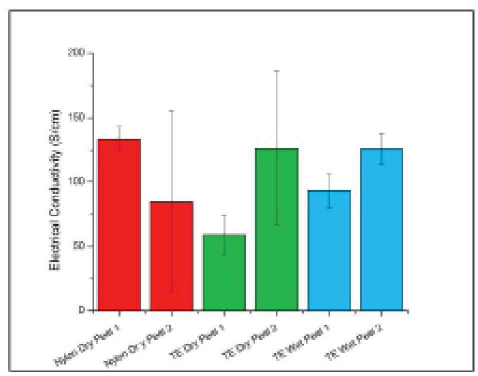


Figure 13: Demonstration of difference between nylon and wet peel of PCTE membrane technique.

in properties like electrical and thermal conductivity, tensile strength, and in turn increasing the quality and value of the BP. Initial electrical testing was done in order to determine if differences in electrical conductivity exist in samples fabricated using the different types of membranes and removal processes. Two samples of each fabrication type were measured to elucidate any variability between fabrication methods. Additionally six measurements were conducted for each sample to account for variability in the testing method and the average and standard deviation are shown in Figure 14. It can be seen that the wet peel technique did not necessarily yield the highest electrical conductivity. Due to the large amount of variability in this testing, no conclusions could be drawn without future testing.

Figure 14: Electrical Conductivity Data of BPs using different fabrication processes (TE is the PC membrane).



Conclusion

This research has demonstrated a number of improvements in the understanding of the BP fabrication process. The extended use of the SEM resulted in the creation of an improved procedure for obtaining high quality SEM images. The performance of various microporous membranes was investigated through SEM analysis and experimental studies of BP fabrication. The research led to the selection of the PCTE membranes as a new membrane material which may possess improved properties for CNT filtration and BP fabrication. This research was successful in extending existing filtration models to CNT filtration processes, which revealed the mechanisms of difficulties associated with BP removal from nylon membranes. Additionally, a new BP removal technique was developed and termed the 'wet peel' process. Although the wet peel process was found to circumvent issues with traditional BP peeling, high variability in the electrical conductivity test results prevented a clear conclusion from being drawn as to how the change in fabrication procedures affects the final properties of the BP. Further testing should shed light on whether the wet peel technique leads to significant increases in favorable BP properties.

Future research plans include additional electrical conductivity testing to minimize the variability found in the current results. Additionally, mechanical property characterization should be carried out comparing the wet peel technique to the BPs fabricated using the traditional nylon membranes.

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