

A Comparison between β -Cyclodextrin and Chitosan as Soft Organic Materials for Surface Modification of MWCNTs

M. A. Aroon^{1*}, T. Matsuura², A. F. Ismail³

1- Membrane Research Laboratory, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, I. R. Iran

2- Industrial Membrane Research Laboratory, Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

3- Advanced Membrane Technology Center, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

(*) Corresponding author: maaroon@ut.ac.ir

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Abstract:

In this paper, synthesized (raw) multi-walled carbon nanotube (rMWCNTs) surfaces were modified with chitosan and β -cyclodextrin using Chen's soft cutting technique. Raw and surface modified multi-walled carbon nanotubes were observed by transmission electron microscope (TEM). The results showed that chitosan and β -cyclodextrin could attach to the outer surface of nanotubes, wrapping the nanotubes axially. In contrast to the chitosan, β -cyclodextrin not only would attach to the inner and outer surface of the MWCNT walls but also fill their hollow section. It was also found that the surface modified MWCNTs were shorter and their dispersion in organic solvent (NMP) was better than r-MWCNTs. Sedimentation test revealed that dispersion of β -cyclodextrin surface modified MWCNTs was better stabilized in NMP solvent than the chitosan surface modified MWCNTs.

Keywords: CNTs, Cyclodextrin, Chitosan, surface modification, functionalization, nanocomposite materials.

1. INTRODUCTION

In 1991, Iijima discovered for the first time the nano sized and tubular structure of the carbon nanotubes (CNTs) [1]. Later, in 1993 single-walled carbon nanotubes (SWCNTs) were synthesized by Iijima et al. [2] and Bethune et al. [3]. Carbon nanotubes are usually synthesized as single-walled or multi-walled form. Arc-discharge, laser-ablation and catalytic growth are the main techniques that are used for production of carbon nanotubes [4].

Nowadays, carbon nanotubes (CNTs) have found many applications due to their intrinsic thermal, electrical, mechanical and separation

properties. In particular, they have emerged as a new nano membrane material (NMM) for liquid and gas separation applications due to their large surface area and smooth internal surface. On the other hands, researchers usually prefer to fabricate nanocomposite materials using CNTs as inorganic dispersed phase embedded in the polymer continuous phase because they are difficult to process, expensive and fragile [5-7]. In nanocomposite materials (NCMs) containing CNTs the superior properties of carbon nanotubes are combined with flexibility of polymeric materials. As well, one can fabricate a low price high performance NCMs.

Despite CNTs superior separation, mechanical,

thermal and electrical properties, raw (untreated) CNTs contain different kinds of impurities and are usually long and closed ended [8-14]. Therefore, pretreatment of raw CNTs is needed either by chemical or physical method [15]. Moreover, raw CNTs are insoluble in water and organic solvents. Hence, their dispersion in the polymer matrix is difficult, which is the most serious problem in the NCMs preparation. The insufficient dispersion of carbon nanotubes in various organic solvents and polymers is caused by the weak interaction between the CNT walls (as inorganic phase) and the organic polymer chains [16-17].

The methods which have been applied by the investigators to disperse CNTs in the polymer matrix uniformly by enhancing CNTs-polymer interactions [18-25] are:

1. Non-covalent surface coating with surfactants
2. Non-covalent adsorption of hydrophilic non-charged polymer chains
3. Polymer coating which allows chemical attachment of molecular receptors to CNT sidewalls
4. Surface oxidation
5. Surface modification (functionalization) of CNTs by soft organic materials (SOMs)

Among these methods, surface modification of CNTs by their physical grinding in SOMs, called Chen's soft-cutting technique [26], has the following advantages [26-29]:

1. It is easy to apply.
2. Due to physical nature of this method, the pristine structure of CNTs remains nearly constant.
3. Dispersion of CNTs is almost stable.
4. CNTs can be cut and dispersed easily in water and solvents.

Among different SOMs, cyclodextrin and chitosan have been extensively used for modification of carbon nanotube surfaces [26-29].

Cyclodextrins are relatively water soluble, bottomless bowl shaped or truncated cone like macro-rings from cyclic oligosaccharides family which can bind to the nonpolar compound and CNT molecules and thus increase the solubility of these materials in water and other solvents [30]. Three major cyclodextrin types, their structure, and their properties have been reviewed by

Szejtli [31]. In particular, a review was made by Schneiderman and Stalcup on cyclodextrin applications in the separation science [32].

Similarly, chitosan is a biodegradable, biocompatible, non-toxic, low price and hydrophilic low molecular weight polymer (LMWP) from linear polysaccharide family, synthesized from partial deacetylation of chitin [33-34]. Due to its functional group (reactive hydroxyl and amino groups), chitosan is able to wrap the surfaces of carbon nanotubes [34-35].

The objective of this paper is to modify MWCNT's surfaces with chitosan and cyclodextrin, both known as SOMs, and to characterize MWCNTs before and after surface modification by transmission electron microscopy (TEM) and sedimentation (settling) test. Thus, the ultimate goal is to know the effect of SOMs on the surface modification of MWCNTs.

2. EXPERIMENTAL

2.1. Materials

Ethanol (EtOH) was purchased from Merck and used as diluent agent during the surface modification of CNTs. Chitosan (MW 100000-300000) was supplied by Acros Organic (CN). β -cyclodextrin was purchased from Sigma-Aldrich. Chitosan and β -cyclodextrin were used as received and employed as SOMs, in surface modification procedures. Multi-walled carbon nanotubes (MWCNTs) were synthesized by CCVD method in AMTEC (UTM) by the authors. 1-Methyl-2-pyrrolidone (NMP) was supplied by Merck Company and used in MWCNTs sedimentation test as organic solvent.

2.2. Surface modification of multi-walled carbon nanotubes

Surface of raw MWCNT walls was modified with chitosan and β -cyclodextrin as SOMs by applying Chen's soft cutting technique [26]. The surface modification procedure is as follows: raw MWCNTs and SOM (e.g. chitosan or cyclodextrin) were dried in an oven overnight to remove any adsorbed water. MWCNTs and the

SOM (1:30 wt. ratio) were mixed and ground in a mortar and pestle system for 10 min while ethanol was being added gradually to give a sticky and grayish mixture. This sticky mixture was further ground without addition of ethanol for 2 h to obtain a homogeneous black powder, hereafter called MWCNTs/SOM mixture (MSM), which was further dried in an oven at 80 °C overnight.

2.3. Characterization of raw MWCNTs and surfaced modified MWCNTs

2.3.1. Transmission electron microscope (TEM)

Structures of raw MWCNTs (rMWCNTs) and surface modified MWCNTs (smMWCNTs) were observed by a transmission electron microscope (TEM: JEOL JEM-2100). Preparation of rMWCNTs sample for TEM was made as follows. A small amount of the rMWCNTs was added to chloroform. Then the rMWCNTs/chloroform mixture was sonicated for 15 minutes. After sonication, rMWCNTs were picked up on the sample stub (a small blade shape plate) surface. In case of smMWCNTs, dried MSM was added to chloroform and the mixture was sonicated for 15 minutes. The residual SOMs are dissolved in chloroform during sonication and the particles left undissolved are thought to be smMWCNTs, which were picked up on the sample stub surface.

2.3.2. Dispersion stability (sedimentation test)

Usually, rMWCNTs are insoluble in water and organic solvents and they are immediately settled, while smMWCNTs are dispersed for a longer period. This is because of the presence of SOMs at the surface of MWCNTs, which enhances the affinity to the liquid media allowing smMWCNTs settle only slowly. Hence, the time required for the sedimentation of particles is considered a good measure of dispersion stability.

For the stability test (sedimentation test), 0.1 g of MWCNTs (rMWCNTs or smMWCNTs) were added into 20 cm³ NMP in glass tubes and the mixture was sonicated for 30 min. The MWCNTs/NMP suspension was kept stagnant and the sedimentation time of MWCNTs in glass tube was measured.

3. RESULTS AND DISCUSSIONS

3.1. TEM results

The used rMWCNTs were synthesized by catalytic chemical vapor deposition (CCVD) technique as presented in details elsewhere [36-37]. The synthesized rMWCNTs were characterized by TEM micrograph and the details of results reported in our recent publications [28, 38]. As Shown in Figure 1, TEM micrographs revealed that the average inner and outer diameters of the raw MWCNTs were nearly 3-3.5 nm and 10-13 nm, respectively.

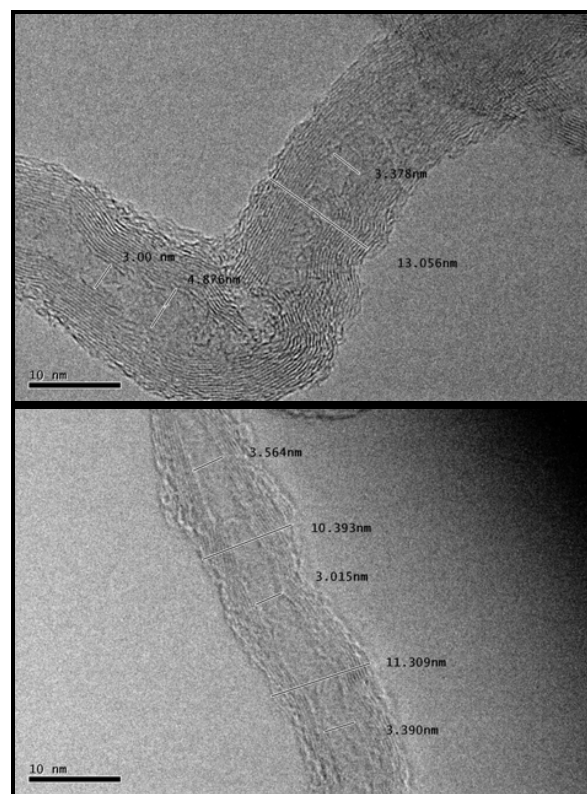


Figure 1: TEM micrographs of MWCNTs (inner and outer diameter have been shown by numbers)

As shown in Figure 2a [28], the impurities and surface defects were detected inside the carbon nanotubes. Figure 2b [28] shows that rMWCNTs are long and generally closed ended [28]. Moreover; as shown in Figure 2c [28]; the rMWCNT tips and also their outer surface are defective.

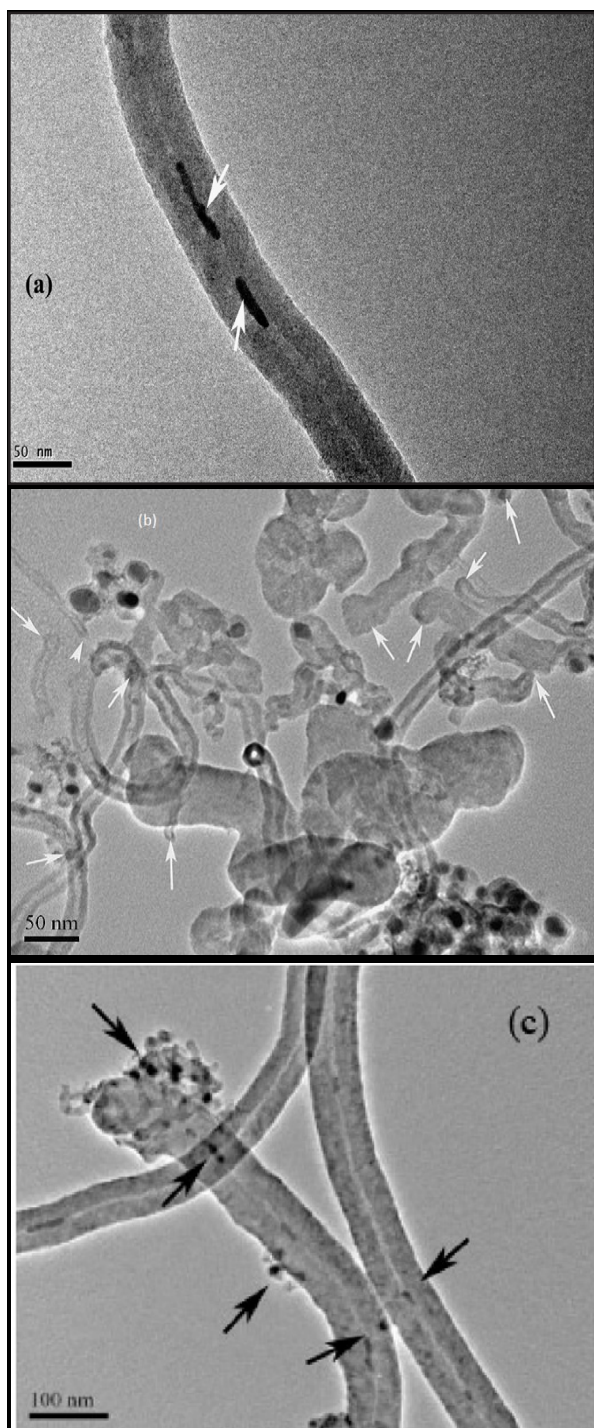


Figure 2: TEM micrographs of rMWCNTs [28, 38]; impurities and closed tips of the rMWCNTs have been shown by arrows

After surface modification of rMWCNTs with

chitosan and β -cyclodextrin, smMWCNTs were observed by TEM. As shown in Figure 3, chitosan polymer chains attach to the outer surface of the MWCNTs wall probably by van der Waals forces [26].

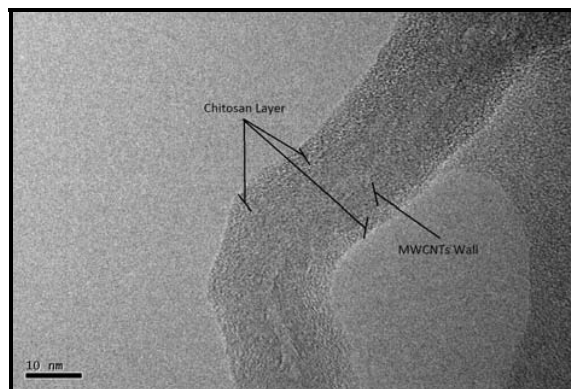


Figure 3: TEM micrograph of the chitosan smMWCNTs

Figure 4 shows that, similar to chitosan, β -cyclodextrin wraps also around the MWCNTs and attach onto the MWCNTs wall.

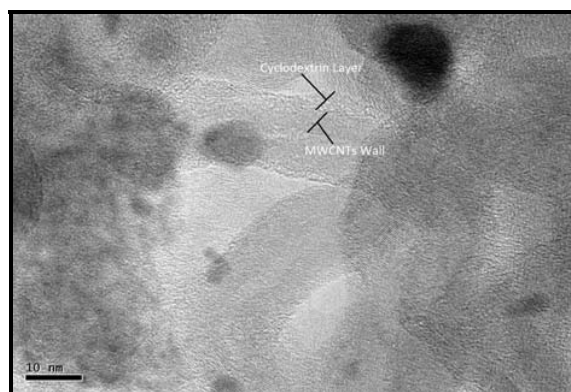


Figure 4: TEM micrographs of the β -cyclodextrin smMWCNTs

In contrast to the chitosan, β -cyclodextrin enters inside the hollow of the rMWCNTs and can not only attach to the inner and outer surface of the MWCNT walls but also fill their hollow section (see Figure 5). It can be probably attributed to the size of the β -cyclodextrin molecules, i.e. β -cyclodextrin's outer diameter, 1.66nm [30], is smaller than the inner diameter of the MWCNTs, 3-3.5 nm (see Figure 1).

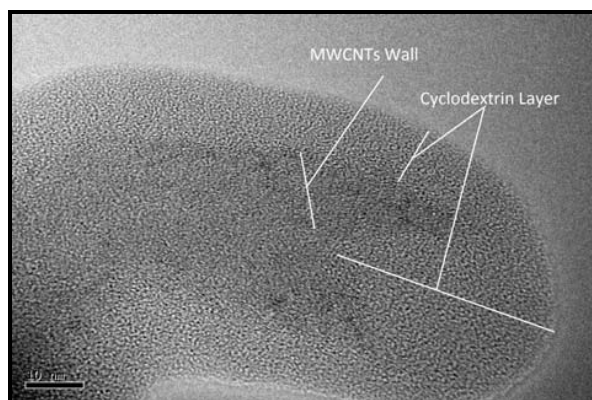
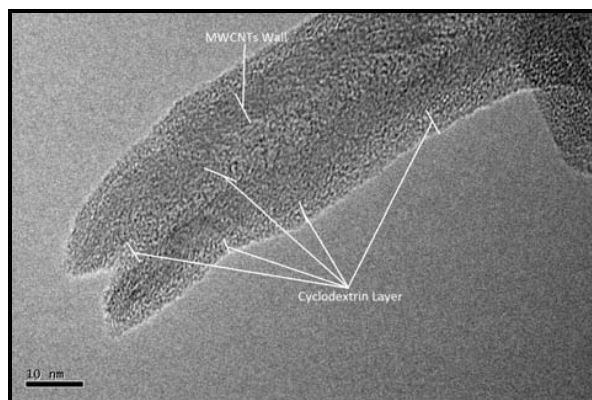


Figure 5: TEM images of the β -cyclodextrin smMWCNTs (arrows show the cyclodextrin layers on tips of MWCNTs and also inside and outside of the MWCNTs)

It is interesting that β -cyclodextrin not only attaches to the inner and outer surface of the MWCNTs but also can wrap around the impurities surface (Figure 6).

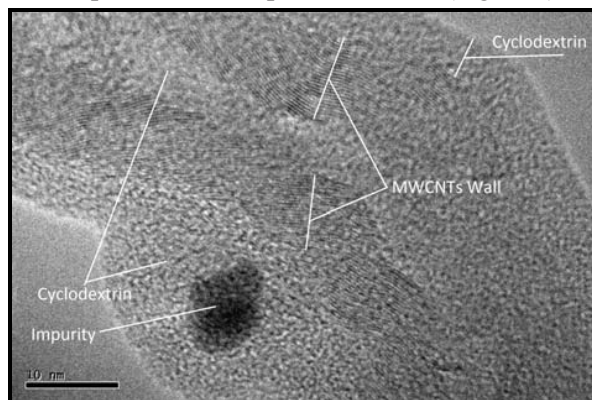


Figure 6: TEM image of the β -cyclodextrin around the impurities, inside the smMWCNTs and outside of the smMWCNTs (the slightly changed structure of MWCNT walls is distinguishable in this picture)

Figures 6 and 7 show that pristine structure of the both chitosan smMWCNTs and β -cyclodextrin smMWCNTs have been changed slightly after functionalization.

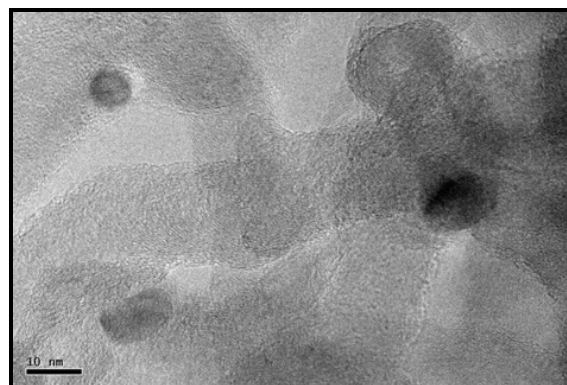


Figure 7: TEM image of the slightly changed structure of chitosan smMWCNTs

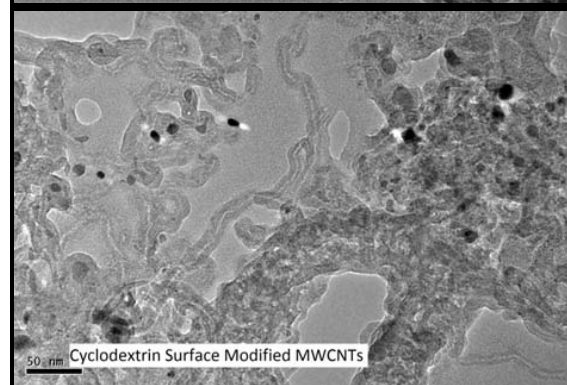
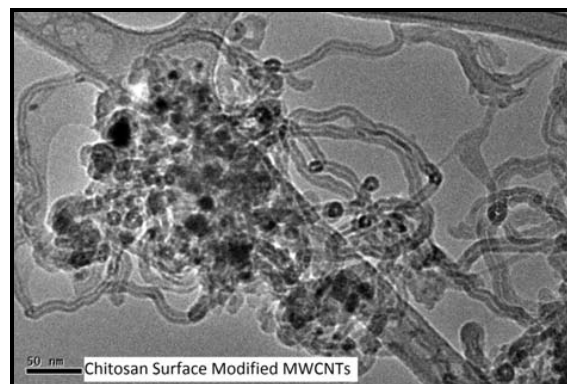


Figure 8: TEM micrographs of the short length smMWCNTs (black dots represent the impurities)

Figure 8 shows that the smMWCNTs have shorter length than the pristine rMWCNTs. It is likely that during the physical grinding of MWCNTs in the SOMs (chitosan and β -cyclodextrin) they were cut to the shorter length [28].

Although surface modification can reduce the length of MWCNTs, it cannot remove the impurities, as shown in Figures 6-8.

3.2. Dispersion stability of smMWCNTs and sedimentation test results

Raw MWCNTs were settled in nearly 30 min while it took more than 5 and 14 days respectively, for chitosan and β -cyclodextrin smMWCNTs to be settled. Dispersion stability of smMWCNTs in NMP (as an organic solvent) can be attributed to the attached SOMs on the surface of the MWCNTs walls (as proved by TEM micrographs). Because of the stronger affinity of SOMs to NMP, smMWCNTs are allowed to settle more slowly, enhancing the dispersion stability. The difference between chitosan and β -cyclodextrin as SOMs for surface modification of MWCNTs can be explained by:

1. Solubility of chitosan in NMP is less than β -cyclodextrin in NMP.
2. β -cyclodextrin modified MWCNT surfaces better than chitosan maybe due to its functional group.
3. β -cyclodextrin can diffuse into the MWCNTs and attach on the inner surface of the MWCNT walls.

Another explanation is that SOMs on the surface prevents the agglomeration of MWCNTs particles by the steric hindrance, increasing the dispersion stability. The higher stability of the β -cyclodextrin smMWCNTs than the chitosan counterpart is probably due to the thicker absorbed layer of β -cyclodextrin than chitosan (see Figures 3 and 4).

4. CONCLUSIONS

Chen's soft cutting technique was applied and rMWCNTs were surface modified by using chitosan (a low molecular weight polymer) and β -cyclodextrin (an oligosaccharide) successfully. TEM micrographs revealed that rMWCNTs have

been surface modified with both SOMs successfully. Dispersion of smMWCNTs and rMWCNTs was also characterized by measurement of sedimentation time of the MWCNTs in NMP. This experiment showed that smMWCNTs are more soluble in NMP (as an organic solvent). Although both chitosan and cyclodextrin could modify the MWCNT's surfaces, there were two important differences between cyclodextrin and chitosan as follows:

1. In contrast to chitosan, β -cyclodextrin can not only attach on the inner and outer surface of the MWCNT walls but also can fill their lumen side.
2. Dispersion of the cyclodextrin smMWCNTs in organic solvent (NMP) is better than that one for chitosan.

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REFERENCES

1. S. Iijima, Nature (London), Vol. 56, (1991), p. 354.
2. S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, Nature, Vol. 363, (1993), p. 603.
3. D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, Nature, Vol. 363, (1993), p. 605.
4. V. N. Popov, Carbon nanotubes: properties and application, Mater. Sci. Eng., R, Vol. 43, (2004), pp. 61-102.
5. D. Q. Vu, W.J. Koros, S. J. Miller, Mixed matrix membranes using carbon molecular sieves, I. Preparation and experimental results, J. Membr. Sci. Vol. 211, (2003), pp. 311-334.
6. D.Q. Vu, W.J. Koros, S.J. Miller, Mixed matrix membranes using carbon molecular sieves, II. Modeling permeation behavior, J. Membr. Sci., Vol. 211, (2003), pp. 335-348.

7. T. T. Moore, R. Mahajan, D. Q. Vu, W. J. Koros, Hybrid membrane materials comprising organic polymers with rigid dispersed phases, *AIChE J.*, Vol. 50, (2004), pp. 311–321.
8. P. X. Hou, S. Bai, Q. H. Yang, C. Liu, H. M. Cheng, Multi-step purification of carbon nanotubes, *Carbon*, Vol. 40, (2002), pp. 81–85.
9. Y. Liu, L. Gao, J. Sun, S. Zheng, L. Jiang, Y. Wang, H. Kajiura, Y. Li, K. Noda, A multi-step strategy for cutting and purification of single-walled carbon nanotubes, *Carbon*, Vol. 45, (2007), pp. 1972–1978.
10. J. Li, Y. Zhang, A simple purification for single-walled carbon nanotubes, *Physica E*, Vol. 28, (2005), pp.309-312.
11. J.-F. Colomer, P. Piedigrosso, A. Fonseca, J. B. Nagy, Different purification methods of carbon nanotubes produced by catalytic synthesis, *Synth. Met.*, Vol. 103, (1999), pp. 2482-2483.
12. Y. Wang, L. Gao, J. Sun, Y. Liu, S. Zheng, H. Kajiura, Y. Li, K. Noda, An integrated route for purification, cutting and dispersion of single-walled carbon nanotubes, *Chem. Phys. Lett.*, Vol. 432, (2006), pp. 205–208.
13. N. Zhao, C. He, J. Li, Z. Jiang, Y. Li, Study on purification and tip-opening of CNTs fabricated by CVD, *Mater. Res. Bull.*, Vol. 41 (2006), pp. 2204–2209.
14. E. Raymundo-Pinero, T. Cacciaguerra, P. Simon, F. Be'guin, A single step process for the simultaneous purification and opening of multi-walled carbon nanotubes, *Chem. Phys. Lett.*, Vol. 412, (2005), pp. 184–189.
15. A.F. Ismail, P. Goh, J.C. Tee, S.M. Sanip, A review of purification techniques for carbon nanotubes, *Nano*, Vol. 3, (2008), pp. 127-143.
16. R. Andrews, M.C. Weisenberger, Carbon nanotube polymer composites, *Curr. Opin. Solid State Mater. Sci.*, Vol. 8, (2004), pp. 31–37.
17. J.-H. Choi, J. Jegal, W.-N. Kim, Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes, *J. Membr. Sci.*, Vol. 284, (2006), pp. 406–415.
18. L. Qu, Y. Lin, D.E. Hill, B. Zhou, W. Wang, X. Sun, A. Kitaygorodskiy, M. Suarez, J.W. Connell, L.F. Allard, Y.-P. Sun, Polyimide-functionalized carbon nanotubes: synthesis and dispersion in nanocomposite films, *Macromolecules*, Vol. 37 (2004), pp. 6055–6060.
19. M.J. O'Connell, P. Boul, L.M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, R.E. Smalley, Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping, *Chem. Phys. Lett.*, Vol. 342, (2001), pp. 265–271.
20. E.E. Hill, Y. Lin, A.M. Rao, L.F. Allard, Y.-P. Sun, Functionalization of carbon nanotubes with polystyrene, *Macromolecules*, Vol. 35, (2002), pp. 9466–9471.
21. S.E. Baker, W. Cai, T.L. Lasseter, K.P. Weidkamp, R.J. Hamers, Covalently bonded adducts of deoxyribonucleic acid (DNA) oligonucleotides with single-wall carbon nanotubes: synthesis and hybridization, *Nano Lett.*, Vol. 2, (2002), pp. 1413–1417.
22. A. Eitan, K. Jiang, D. Dukes, R. Andrews, L.S. Schadler, Surface modification of multi-walled carbon nanotubes: toward the tailoring of the interface in polymer composites, *Chem. Mater.*, Vol. 15, (2003), pp. 3198–3201.
23. S. Banerjee, T. Hemraj-Benny, S.S. Wong, Covalent surface chemistry of single-walled carbon nanotubes, *Adv. Mater.*, Vol. 17, (2005), pp. 17–29.
24. K. Balasubramanian, M. Burghard, Chemically functionalized carbon nanotubes, *Small*, Vol. 1, (2005), pp. 180–192.
25. J. Deng, X. Zhang, K. Wang, H. Zou, Q. Zhang, Q. Fu, Synthesis and properties of poly (ether urethane) membranes filled with isophoronediiisocyanate-grafted carbon nanotubes, *J. Membr. Sci.*, Vol. 288, (2007), pp. 261–267.
26. J. Chen, M.J. Dyer, M.F. Yu, Cyclodextrin-mediated soft cutting of single-walled carbon nanotubes, *J. Am. Chem. Soc.*, Vol. 123, (2001), pp. 6201–6202.
27. F. Peng, F. Pan, H. Sun, L. Lu, Z. Jiang, Novel nanocomposite pervaporation membranes composed of poly(vinyl alcohol) and chitosan-wrapped carbon nanotube, *J. Membr. Sci.*, Vol. 300, (2007), pp. 13–19.

28. M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, T. Matsuura, Effect of chitosan as a functionalization agent on the performance and separation properties of polyimide/multi-walled carbon nanotubes mixed matrix flat sheet membranes, *J. Membr. Sci.*, Vol. 364, (2010), pp. 309–317.
29. G. Ke, W. Guan, C. Tang, W. Guan, D. Zeng, F. Deng, Covalent functionalization of multi-walled carbon nanotubes with a low molecular weight chitosan, *Biomacromolecules*, Vol. 8, (2007), pp. 322–326.
30. M. Chaplin, Water structure and science: Cyclodextrins, <http://www.lsbu.ac.uk/water/cyclodextrin.html>.
31. J. Szejtli, Introduction and general overview of cyclodextrin chemistry, *Chem. Rev.*, Vol. 98, (1998), pp. 1743–1754.
32. E. Schneiderman, A. M. Stalcup, Review, Cyclodextrins: a versatile tool in separation science, *J. Chromatogr. B*, Vol. 745, (2000), pp. 83–102.
33. Y. Liu, W. Chen, Y. Chang, Preparation and properties of chitosan/carbon nanotube nanocomposites using poly(styrene sulfonic acid)-modified CNTs, *Carbohydr. Polym.*, Vol. 76, (2009), pp. 232–238.
34. Q. Yang, L. Shuai, X. Pan, Synthesis of fluorescent chitosan and its application in noncovalent functionalization of carbon nanotubes, *Biomacromolecules*, Vol. 9, (2008), pp. 3422–3426.
35. P. Kumar, J. Dutta, V.S. Tripathi, Chitin and chitosan: Chemistry, properties and applications, *J. Sci. Ind. Res.*, Vol. 63, (2004), pp. 20–31.
36. J.C. Tee, M. Aziz, A.F. Ismail, Effect of reaction temperature and flow rate of precursor on formation of multi-walled carbon nanotubes, *AIP Conf. Proc.*, Vol. 1136, (2009), pp. 214–218.
37. J.C. Tee, A.F. Ismail, M. Aziz, T. Soga, Influence of catalyst preparation on synthesis of multi-walled carbon nanotubes, *IEICE Trans. Electron.*, Vol. E92-C, (2009), pp. 1421–1426.
38. M. A. Aroon, A. F. Ismail, M. M. Montazer-Rahmati, T. Matsuura, Effect of Raw Multi-Wall Carbon Nanotubes on Morphology and Separation Properties of Polyimide Membranes, *Sep. Sci. Technol.*, Vol. 45, (2010), pp. 2387–2397.