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Functionalized Carbon Nanotubes for Mixed Matrix Membrane

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SUMMARY Carbon nanotubes (CNTs) have generated great interest within the many areas of nanotechnology due to their superior and outstanding physical properties. However effective dispersion in many solvents has imposed limitations upon the use of CNTs in a number of novel applications. Functionalization presents a solution for CNTs to be more soluble which make them integrate well into any organic, inorganic or biological systems. CNTs can be easily functionalized using cyclodextrin (CD) treatment. The CD modification of carbon nanotubes is both simple and effective. It requires no prolonged heating, filtration and washing which can severely damage the small diameter nanotubes. The formation of surface functional groups and changes of nanotubes structures of functionalized carbon nanotubes (f-CNTs) were monitored by Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM), respectively. From the TGA results, the amount of weight loss of the f-CNTs in varying ratios indicated the amount of CD that was functionalized. It was also noted that the FTIR spectra showed the presence of functional groups associated with CD in the f-CNTs. As a result, the cyclodextrin groups were found to be possibly adsorbed at the surface of the nanotubes walls. The f-CNTs showed substantial solubility in N-methyl-2-pyrrolidone (NMP) which helps in a better distribution of the CNTs in the mixed matrix membrane (MMM) prepared. Hence, the influence of the f-CNTs in the polymer matrix will give rise to enhanced physical properties of the MMM suitable for applications in gas separations.

key words: *functionalized carbon nanotubes, mixed matrix membrane*

1. Introduction

Carbon nanotubes (CNTs) are allotropes of carbon and members of fullerene structural family which also include buckyballs [1]. CNTs possess unique mechanical and electrical structures and found many potential applications across a wide field of areas such as nanocomposite, nanoelectric devices, sensors and biological applications such as drug delivery [2], [3]. Also recently, carbon nanotubes (CNTs) have been used as filters and membranes to separate various gases and liquids. Hybrid materials such as mixed matrix membrane (MMM) based upon organic-inorganic materials have been introduced to further improve the performance in membrane applications [4], [5].

Despite their excellent properties, CNTs have also found to be chemically stable [6] but unfortunately tend to agglomerate due to the strong inter-tube van der Waals forces and their high surface energy as a result of the curvature of the thin nanotubes. This has hindered many useful applications especially in the biological and chemical areas due to the inherent solubility and difficult modifications of CNTs in most organic and aqueous solvents [2], [7]. As a result, extensive research have now focussed upon modification, pretreatment or functionalization as a means to improve solubility of the CNTs and their ability to mix well in most organic substance [2], [3], [6]–[8]. Noncovalent functionalization by functional polymers and large organic molecules have shown to be a promising technique to improve solubility and compatibilty of CNTs in organic solvents [7]. The advantage of this method is that the structure and original properties of the CNTs remained unchanged after modification.

CNTs can be easily functionalized using cyclodextrin (CD) treatment. The CD modification of carbon nanotubes is both simple and effective. It requires no prolonged heating, filtration and washing which can severely damage the small diameter nanotubes [2], [9]–[11]. Chen et al. have shown that cyclodextrin (CD) have superior nanotube-dispersing capability and provide an excellent pathway to dispersion of CNTs in organic matrix through disentanglement of the nanotubes bundles. In this work, multi walled carbon nanotubes (MWNTs) synthesized via catalytic chemical vapour deposition (CCVD) were functionalized with β cyclodextrin (β-CD). The effect of MWNTs functionalization using CD were looked into and their physical properties characterized. It is anticipated that the functionalized MWNTs (f-MWNTs) will have improved solubility properties in the polymer matrix of the MMM. MMM were then prepared via casting technique and the resultant asymmetric MMM were characterized for their morphologies. Asymmetric membranes consist of an extremely thin surface layer supported by a thicker, porous substructure whereby the surface layer & the sub-layer maybe formed during a single operation technique.

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2. Method

2.1 MWNTs Synthesis

As-grown MWNTs samples for this study were synthesized by catalytic decomposition of acetylene (C_2H_2) over supported metal catalyst; iron and cobalt (Fe/Co). The support used was alumina hydrate (Al_2O_3) powder which was obtained from commercial sources. Before the addition of catalyst onto the support, the support was dried to eliminate water vapour and impurities. The catalysts were prepared by impregnation. The catalytic solution was prepared by dissolving metallic acetate (Fe/Co) in distilled water at a specific ratio. The supports were immersed in the solution until saturation, followed by overnight drying. The prepared supported catalysts were then used for the synthesis of CNTs. An economical and simple thermal catalytic chemical vapour deposition (CCVD) system has been designed and used for the synthesis of MWNTs. The MWNTs were produced on a fix-bed reactor at ambient pressure. A mixture of C_2H_2 and nitrogen (N_2) gas was passed through to react with the catalyst. The decomposition of C_2H_2 was performed at 700°C. The samples were collected as black powder covering the catalysts [12].

2.2 Functionalization of MWNT

The MWNTs were modified using β-CD according to the method described by Fubing et al. [11] and J. Chen et al. [9]. MWNTs were dispersed in β-CD with mixtures in weight ratios 30:1, 20:1 and 10:1 of β-CD to MWNTs. The mixtures were ground with a known amount of ethanol until a homogeneous powder is achieved. The mixtures were then further mixed through a ball-milling process. This procedure resulted in a fine homogeneous β-CD/MWNT grey powder for mixture ratio of 30:1 and fine homogenous β-CD/MWNT black powder for mixture of ratios 20:1 and 10:1.

2.3 Characterization of f-MWNTs

FTIR spectrometer was used to identify the presence of functional groups in the β-CD/MWNT. The FTIR spectrums were recorded on a Perkin-Elmer Spectrum™ 400 FTIR Spectrometer using KBr discs technique, with a nominal resolution of 4000 to 400 cm^{-1}.

Zeiss Supra 35 VP FESEM, equipped with wave (energy) dispersive x-ray (EDS) instrument was used to study the morphology of f-MWNT. SEM micrographs of the MMM were observed using JEOL JSM-5600 SEM.

TGA analysis was carried out using Mettler Toledo TGA/SDTA 851e with a heating rate of 20°C/min under compressed air. The temperature range was between 300–750°C.

2.4 Mixed Matrix Membrane Preparation

The f-MWNT were blended with the polyimide (PI) polymer in N-methyl-2-pyrrolidone (NMP) solvent with a polymer weight of 20–23%. The MMM were prepared by phase inversion process of the f-MWNT/PI solution using water as a coagulant. The prepared MMM were left in water for 24 h to encourage further solvent exchange. The MMM were then dried in atmosphere for 24 h.

3. Results and Discussions

3.1 Infrared Spectroscopy

Figure 1 depicts the spectra of β-CD and β-CD/MWNTs with ratios 30:1, 20:1 and 10:1. The different vibration peaks showed the characteristics β-CD peaks. The presence of these vibrational peaks confirms that β-CD has been attached to the surface of MWNTs. Peaks at approximately 3400 cm^{-1} are due to the stretching vibration of O-H that also confirmed the attachment of β-CD with MWNTs. The same phenomenon is also observed for C-H stretching vibration at peaks in the range of 2900 to 2800 cm^{-1}. The C=O stretching vibration at peaks range of 1730 to 1710 cm^{-1} was observed. C-H and C=O functional group peaks appear to decrease due to increased β-CD/MWNTs bonding [2]. The peaks at range 1180 to 1170 cm^{-1} are assigned to β-CD as the peaks resulted from C-O-C stretching of α-pyranose. While the C-O-H stretching vibration of α-pyranose can be observed in the range 1100 to 1000 cm. The spectra showed a slight shift from the pure β-CD due to the hindered and rigid bonding of β-CD formed with the f-MWNTs [2] and as a result of interaction of the MWNTs and β-CD which has changed the electron distribution of the groups in the β-CD chains [13].

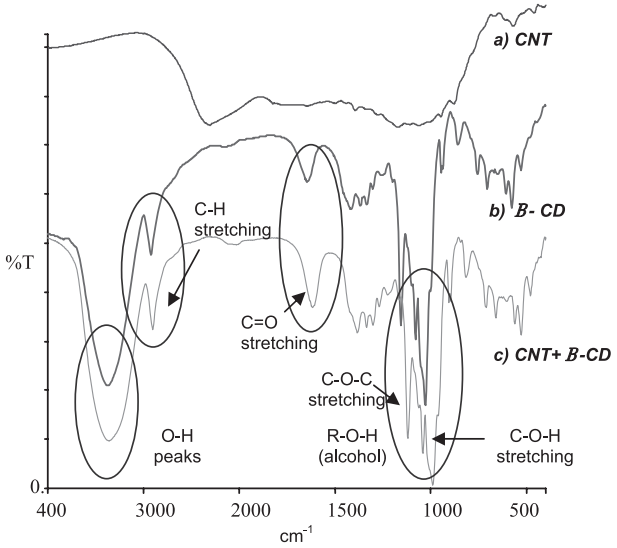
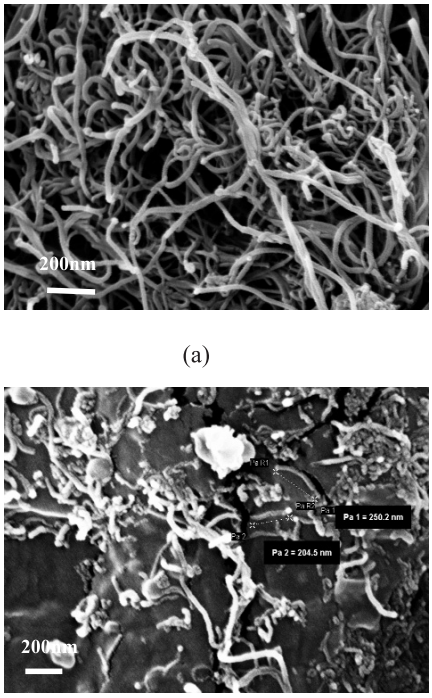


Fig. 1 FTIR spectra of a) as grown MWNTs, b) β-CD and c) β-CD/MWNTs with ratio 30:1.

Table 1 The amount of CD functionalization (%).

Content of β-CD	% of weight loss (mg)	amount of functionalized CD (%)
0	50.63	0
10	80.54	29.91
20	84.73	34.10
30	86.84	36.21



(a)

(b)

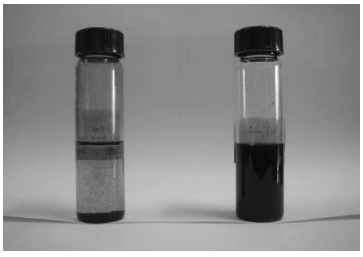
Fig. 2 FESEM micrographs (x 50,000 magnification) of (a) as-grown MWNTs (b) f-MWNTs with ratio 1:30.

3.2 Thermogravimetric Analysis

The degree of functionalization of MWNTs was also determined through TGA and the results obtained are as in Table 1. The analysis was carried out at temperature range of 300–750°C. The results indicated that the percentage of weight loss increases with increasing content of β-CD as shown in Table 1. The amount of CD onto the MWNTs corresponded to the percentage of weight loss of MWNTs to the functionalized MWNTs at different ratios. The degree of functionalization can therefore be controlled by varying the content of the β-CD. Therefore different morphology and structure of the MWNTs can be obtained by varying the functionalization content according to the application needs [13].

3.3 Field Emission Scanning Electron Microscopy

The FESEM micrograph in Fig. 2(a) showed the as grown



(a) (b)

Fig. 3 0.2g of (a) as-grown MWNTs and (b) f-MWNTs dispersed in 10 mL of NMP after several weeks.

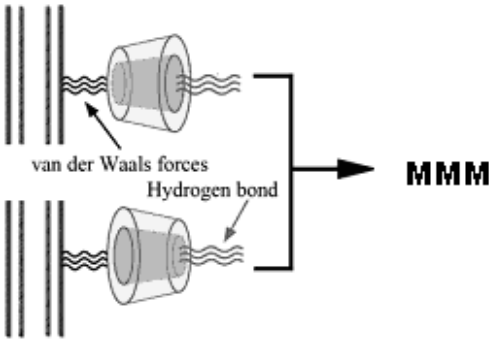
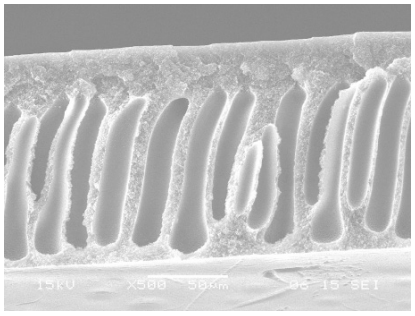


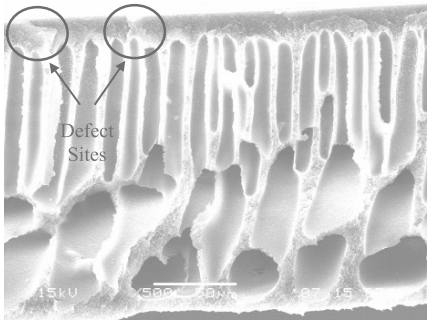
Fig. 4 Schematic representation of bonding sites between β-CD and MWNTs.

MWNTs. The MWNTs are entangled with the length of the tubes extending to more than 400 nm. Figure 2(b) showed MWNTs after functionalization with β-CD. The length of MWNTs has been found to be shortened to < 300 nm and became less entangled. The ball milling process has resulted in the cutting of the long and tangled tubes. While the nanotubes ability to be well dispersed in organic solvents however is a result of the presence of CD groups onto the MWNTs. This enhanced property was observed as in Fig. 3(a) where the as-grown MWNTs were dispersed in N-methyl-2-pyrrolidone (NMP) and sedimentation of the MWNTs was observed immediately as compared to the f-MWNTs in Fig. 3(b). The f-MWNTs showed substantial solubility in NMP even after several weeks. This is believed to be the result of the attachment of the β-CD onto the surface of the MWNTs via van der Waals interaction to the carbons in the MWNTs and to the hydrogen-bonding interaction to β-CD adjacent molecules. Both forces induced the ordered assembly and arrangement of β-CD onto the surface of MWNTs [14] as represented by the schematic diagram of the theoretical bonding sites in Fig. 4.

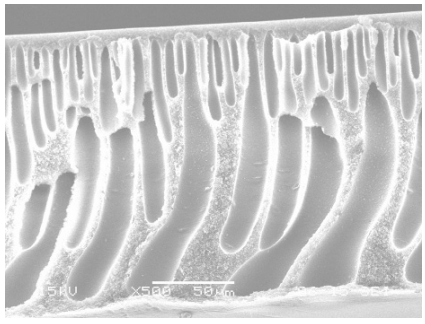
The SEM micrographs of the cross section of the MMM showed different morphologies for the 3 samples, i.e. f-MWNTs with PI, MWNTs with PI and neat PI (Figs. 5(a)–(c) respectively). The MMM with f-MWNTs showed uniform finger-like structures while both the MWNT-MMM and neat PI showed non-uniform structures. The formation of the different finger-like structures is the result of the difference in viscosity of the polymer-blend solutions and



(a) Mixed matrix membrane with f-MWNTs (x 500 magnification)



(b) Mixed matrix membrane with MWNTs (x 500 magnification)



(c) Polyimide membrane (x 500 magnification)

Fig. 5 SEM of the cross section of membranes.

also the rate of solvent exchange during the coagulation process [15]. The more viscous solution will result in a more uniform structure while a rapid solvent exchange process will result in thinner transition layer and longer finger-like structure as observed in the neat PI membrane (Fig. 5(c)). f-MWNTs MMM showed a uniform finger-like structure because of better distribution and dispersion of the MWNTs in the polymer matrix and this has resulted in a higher viscosity MMM polymer solution. Hence, the f-MWNTs MMM, Fig. 5(a), showed a better defect-free skin layer and thicker porous layer as compared to MMM with only MWNTs. This has resulted in a better enhancement of the gas transport properties in the MMM [16]. The gas performance test also indicated that the permeance of the f-MWNTs MMM for N_2 was more than 100 GPU as compared to the permeance of the neat PI membrane at only 20 GPU. The f-MWNTs with β-CD has resulted in a membrane structure possessing uniformity showing enhanced compatibility between the inorganic and the organic phases. However, a non-uniform finger-like structure is being seen for the MWNTs-MMM where 3 distinct layers of skin, finger-like and large pore holes were observed. Defects on the skin layer of the MWNT-MMM were also observed. This can be attributed to the incomplete dispersion of the MWNTs within the polymer matrix due to stronger interactions between the MWNTs bundles [17] and slower solvent exchange process during coagulation hence the formation of larger finger-like structures resembling pore holes.

4. Conclusion

The functionalization of multiwalled carbon nanotube using β-CD as the functionalizing agent was successfully carried out. β-CD treatment was effective in making the MWNTs less entangled and shortening the length of the tubes. This has resulted in the f-MWNTs with better dispersion and solubility properties in NMP. The FTIR results indicated that functionalization has taken place. The TGA analysis has also shown that the degree of functionalization increases with increasing ratio of β-CD and this can be correlated to the fabrication of MMM in which the structure and morphology of the f-MWNTs can be controlled accordingly.

The f-MWNTs have shown to have better compatibility with the polymer matrix. Thus, it is feasible to add MWNTs to polymeric membranes to enhance their gas separation performance.

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References

[1] J.-L. He, Y. Yang, X. Yang, Y.-L. Liu, Z.-H. Liu, G.-L. Shen, and R.-Q. Yu, "β-Cyclodextrin incorporated carbon nanotube-modified electrode as an electrochemical sensor for rutin," Sensors and Actuators B, vol.114, pp.94–100, 2004.

[2] J.-G. Yu, K.-L. Huang, S.-Q. Liu, and J.-C. Tang, "Preparation and characterization of soluble methyl-β-cyclodextrin functionalized single-walled carbon nanotubes," Physica E, vol.40, pp.689–692, 2008.

[3] C.H. Lau, R. Cervini, S.R. Clarke, M.G. Markovic, J.G. Matisons, S.C. Hawkins, C.P. Huynh, and G.P. Simon, "The effect of functionalization on structure and electrical conductivity of multi-walled carbon nanotubes," J. Nanopart. Res, DOI 10.1007/s1 1051-008-9376-1.

[4] S. Kim, J.R. Jinschek, H. Chen, D.S. Sholl, and E. Marand, "Scalable fabrication of carbon nanotube/polymer nanocomposite membranes for high flux gas transport," Nano Lett., vol.7, no.9, pp.2806–2811, 2007.

[5] T.-S. Chung, L.Y. Jiang, Y. Li, and S. Kulprathipanja, "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation," Prog. Polymer Sci., vol.32, pp.483–507, 2007.

[6] K. Balasubramaniam and M. Burghard, "Chemically functionalized carbon nanotubes," Small, vol.1, no.2, pp.180–192, 2005.

[7] C.-Y. Hong, Y.-Z. You, and C.-Y. Pan, "A new approach to functionalize multi-walled carbon nanotubes by the use of functional polymers," Polymer, vol.47, pp.4300–4309, 2006.
[8] H. Kuzmany, A. Kukovecz, F. Simon, M. Holzweber, C. Kramberger, and T. Pichler, "Functionalization of carbon nanotubes," Synthetic Metals, vol.141, pp.113–122, 2004.
[9] J. Chen, M.J. Dyer, and M.-F. Yu, "Cyclodextrin-mediated soft cutting of single-walled carbon nanotubes," J. Am. Chem. Soc, vol.123, no.25, pp.6201–6202, 2001.
[10] S. Samal and K.E. Geckeler, "Cyclodextrin-fullerenes: A new class of water-soluble fullerenes," Chem. Commun., no.13, pp.1101–1102, 2000.
[11] F. Peng, C. Hu, and Z. Jiang, "Novel ploy(vinyl alcohol)/carbon nanotube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures," Journal of Membrane Science, vol.297, pp.236–242, 2007.
[12] J.C. Tee, Synthesis and Characterization of Multiwalled Carbon Nanotubes on Supported Catalysts via Catalytic Chemical Vapour Deposition, MSc Thesis, Universiti Teknologi Malaysia, 2006.
[13] J. Qui, G. Wang, and C. Zhou, "Preparation and characterization of amphiphilic multi-walled carbon nanotubes," J. Nanopart. Res., vol.10, pp.659–663, 2008.
[14] K. Liu, H. Fu, Y. Xie, L. Zhang, K. Pan, and W. Zhou, "Assembly of β-cyclodextrins acting as molecular bricks onto multiwall carbon nanotubes," J. Phys. Chem. C, vol.112, no.4, pp.951–957, 2008.
[15] R.W. Baker, Membrane Technology and Applications, 2nd ed., John Wiley & Sons, 2004.
[16] H. Cong and M. Radosz, B.F. Fowler, and Y. Shen, "Polymer-inorganic nanocomposite membranes for gas separation," Separation and Purification Technology, vol.55, pp.281–291, 2007.
[17] E.V. Perez, K.J. Balkus, Jr., J.P. Ferraris, and I.H. Musselman, "Mixed matrix membranes containing MOF-5 for gas separations," J. Membrane Science, vol.328, pp.165–173, 2009.

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