Hysteresis of sorption isotherm of multiwall carbon nanotube in paraxylene

V. K. Punyamurtula and Y. Qiao*

The sorption isotherm of a multiwall carbon nanotube in paraxylene is investigated through a pressure induced infiltration experiment. The inner space of the carbon nanotubes can be occupied by liquid molecules when an external pressure is applied so that the energy barrier caused by the lyophobic surface is overcome. The infiltration–defiltration curve is highly hysteretic, and therefore a significant amount of energy is dissipated in each loading–unloading cycle. The system performance is stable as the loading is applied repeatedly.

Introduction and relation to previous work

Nanofluidic behavior in carbon nanotubes (CNT) has been an active area of research for nearly a decade, and has drawn consideratable attention for nano/micro-transportation, drug delivery, nanomaterials synthesis, reaction control, etc.[1–4] Usually, in these studies the infiltration takes place spontaneously as the CNT is immersed in the liquid, forming molecular chains in the inner space.[5,6] The infiltration rate is dominated by the thermal diffusion process of the liquid molecules from the bulk phase to the vacuum area, and overcoming the associated energy barriers is often thermally aided.[7,8] If the inner surface of the CNT is lyophobic, the solid–liquid interaction would become more complicated. Under this condition – while eventually if the CNT is immersed in the liquid for a long enough time, it can still be filled – the density, configuration, and effective infiltration rate of the confined liquid become different compared with that of the lyophilic cases, primarily due to the variation in chemical potential.[9]

In the investigation of nanoporous materials, it has long been known that to promote the infiltration of a nonwetting liquid in nanopores, an external pressure can be helpful.[10–13] For instance, when the hydrostatic pressure in an aqueous suspension of hydrophobic nanoporous silica is higher than 18 MPa so that the capillary effect is overcome, pressure induced infiltration can occur, leading to fast 'inflow'.[14,15] The infiltration rate can be compatible with dynamic loading.[16] As liquid molecules are forced into the nanoporous silica, the solid atoms at the nanopore inner surface are exposed to them, resulting in a significant increase in system free energy. In many nanoporous materials, the infiltration processes are irreversible. That is, as the pressure is decreased, the repulsive forces between the solid atoms

and the liquid molecules can either trigger defiltration only when the pressure is much lower than the infiltration pressure or cannot cause defiltration at all.[17,18] Consequently, the excess solid–liquid interfacial energy cannot be fully released, and this system can be used for energy absorption, such as for protection layers, liquid armors, etc.

In a previous experimental study, it was noticed that by applying high pressure, paraxylene, a nonpolar liquid containing a benzene ring and two methyl substituents across it, could be forced into the inner space of a single wall carbon nanotube (SWCNT).[19] The energy absorption capacity per loading cycle was much higher than the systems based on other nanoporous materials. However, at a reduced pressure, about 70% of the confined liquid could not defiltrate, and, as the CNT inner space remained occupied, the energy absorption efficiency quickly decreased as the loading–unloading process continued. Therefore, this system did not work continuously under cyclic loading. In the current study, the authors investigate a multiwall carbon nanotube (MWCNT). The experimental results show that, although the peak energy absorption efficiency of the MWCNT is lower than that of the SWCNT, the repeatability of its performance is much better.
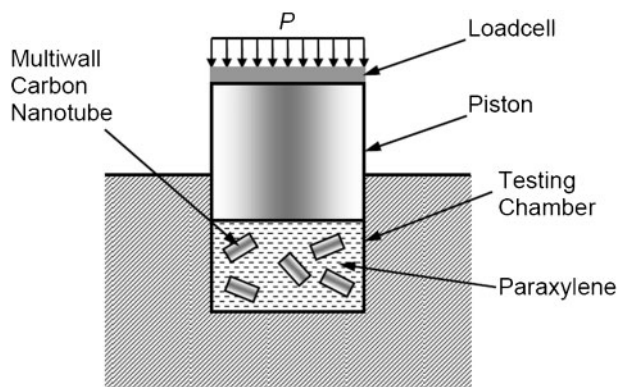
Experimental

The multiwall carbon nanotube investigated in the current study was obtained from VWR, Inc., with the CAS number of 1333-86-4. The purity was greater than 90%. The average diameter was ca. 35 nm and the average length was ca. 30 μm. Each CNT contained a few layers, and therefore the diameter of the inner space was much smaller than the outer diameter. They existed in bundle forms.

After thermal treatment at 120°C in air for 12 h, 0·5 g of MWCNT was mixed with about 8 mL of neat paraxylene, and sealed in a stainless steel testing chamber (Fig. 1). In order to obtain a relatively uniform liquid suspension, the mixture was stirred for 0·5 h. The testing chamber was sealed by an air-hardened piston

Department of Structural Engineering, University of California at San Diego, La Jolla, CA 92093-0085, USA

*Corresponding author, email yqiao@ucsd.edu

1 Schematic diagram of experimental set-up

2 Measured sorption isotherm curves, shifted along horizontal axis for self-comparison purposes

made of high-carbon steel equipped with a reinforced gasket. A compression load was applied using a type 5569 Instron machine. The load was measured by a 50 kN load cell. The piston displacement, d, was measured by a linear variable displacement transducer.

The infiltration–defiltration test was displacement controlled. Initially, the piston was compressed into the chamber at a constant rate of 0·5 mm min^{-1}, leading to an increase in pressure which was calculated as $P=F/A$, where F was the applied compression load and A was the cross-sectional area of the piston. Since the chamber wall was made of solid steel and its deformability was negligible compared with that of the liquid phase, the system volume variation could be estimated through the piston motion as $\Delta V=A \cdot d$. When P reached ca. 150 MPa, the piston was moved upward at the same speed of 0·5 mm min^{-1}, causing the decrease in pressure, until it returned to the original position and the pressure was reduced to zero. After resting for about 20 s, the same loading–unloading process was repeated. Figure 2 shows the measured sorption isotherm curves, where the specific volume change was defined as ΔV normalised by the mass of the CNT.

Results and discussion

At the initial low-pressure stage, since the diffusion rate of paraxylene molecules in the CNT inner space is much smaller than the piston rate, most of the external work is stored in the liquid phase as hydrostatic pressure. Consequently, the load increases quite linearly as the system volume decreases (Fig. 2). In addition to the compliance of the testing system, the slope of the sorption isotherm is determined by the compressibility of paraxylene and empty MWCNTs as well as the interaction between them.

The linear compression of the mixture of empty CNTs and the surrounding liquid phase continues as the pressure rises, until P reaches 28 MPa. At this pressure, the hydrostatic pressure in the liquid phase is sufficiently high to overcome the capillary effect of the inner walls of the largest CNTs. Consequently, the slope of the sorption isotherm abruptly decreases as the paraxylene molecules are compressed into the CNT inner space. As a liquid molecule first enters the energetically unfavourable CNT inner space, it would be partly separated from other paraxylene molecules by the CNT wall, which leads to an additional energy barrier. As it moves along the axial direction of the CNT into the interior, however, the energy state does not vary. That
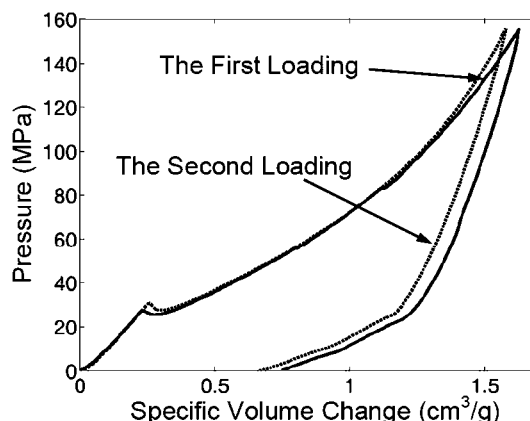
is, the pressure required to trigger the onset of paraxylene infiltration is higher than that required to maintain the infiltration. Therefore, after pressure induced infiltration begins, the pressure drops slightly as the system volume further decreases, until CNTs of smaller inner space size are involved in the infiltration process, which demands a higher infiltration pressure. As a first-order approximation, the equilibrium condition of the release of hydrostatic pressure and the increase in solid–liquid interfacial energy can be stated as

$$r = \frac{4K}{P^2}\Delta\gamma \qquad (1)$$

where K is the bulk modulus of paraxylene, r is the effective size of CNT inner space, and $\Delta\gamma$ is the excess solid–liquid interfacial tension.[19] It can be seen that for smaller r, the required infiltration pressure, P, is greater, which qualitatively agrees with the classic Laplace–Young equation.[20] Note that in the framework of conventional capillary theory, P is inversely proportional to r; while at the nanometer scale, as the hydrostatic pressure is taken into consideration, r is proportional to P^{-2}, indicating that the infiltration process is more pressure-sensitive. This should be related to the fact that in the nanoenvironment the continuum concepts such as the contact angle, pressure difference, and even the liquid surface cannot be well defined.[21]

As the piston is compressed into the testing chamber continuously, more and more paraxylene molecules are forced into smaller CNT inner spaces, leading to an increase in infiltration pressure. Since the infiltration is always associated with the release of hydrostatic pressure, the slope of the sorption isotherm should be smaller than that at the linear compression section. According Eq.(1), if K and $\Delta\gamma$ are taken as 2 GPa and 0·04 mJ m^{-2}, respectively, the effective size distribution of CNT inner space can be calculated as the curve shown in Fig. 3, which looks quite plausible. The value of $\Delta\gamma$ is assumed to be close to that of the paraxylene–SWCNT system.[19] It is relatively small compared with the excess solid–liquid interfacial energy of nanoporous materials, suggesting that the CNT inner wall in the current study is only slightly lyophobic.[22] It can be seen that the probability density decreases as r increases, except for the small area around 17–20 nm, where a local peak exists, probably due to the additional formation of layers of CNT walls during the synthesis process.[23]
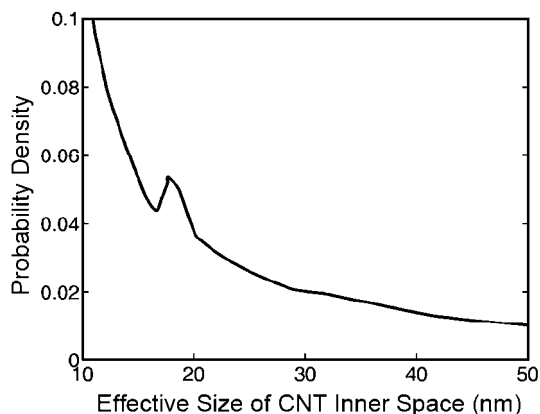
3 Calculated size distribution of CNT inner space using measured sorption isotherm curve at first loading

When the pressure reaches 150 MPa, the inner space of CNTs is nearly filled, and the slope of the sorption isotherm curve becomes close to that of the initial linear compression stage. As the pressure starts to decrease, the unloading path in Fig. 2 is quite different from the loading path. Even in the linear section, the slope of the sorption isotherm is much greater than that of the loading section. This phenomenon was also observed in the SWCNT system, where it was attributed to the increase in effective stiffness as a CNT was filled by liquid molecules.[19] The presence of the linear section during unloading indicates that removal of paraxylene molecules from the CNT inner space is difficult, for reasons still under investigation. This could be related to the irregular configuration in CNT walls, the hysteresis in liquid motion caused by pressure difference, or the nucleation and growth of nanobubbles.[21,24,25]

The defiltration starts when the pressure is much lower than the infiltration pressure, ca. 25 MPa. As a result, the sorption isotherm becomes much flatter, until the pressure is reduced to zero. From Fig. 2, it is clear that the defiltration plateau is narrower than the infiltration plateau, i.e. not all of the confined paraxylene molecules in the CNT inner space are released during the unloading process. Due to the pronounced hysteresis of the sorption isotherm – in the loading–unloading cycle – about 70 J g^{-1} of energy is dissipated, calculated as the area enclosed by the infiltration–defiltration loop. This value is much higher than that of nanoporous silica based energy absorption systems but lower than that of the SWCNT based system, which should be attributed to the relatively low infiltration volume.[14,15] This is in agreement with that fact that the inner space volume of a MWCNT is smaller than that of a SWCNT with a given outer diameter, since the effective wall thickness of the MWCNT is much larger.

When the loading–unloading process is repeated, according to the dashed line in Fig. 2, the system is relatively reusable. The second cycle is almost identical to the first, with the differences in volume and pressure within the resolutions of displacement and load transducers. This phenomenon is different to that of the SWCNT based system where the energy absorption capacity rapidly decreases as the loading cycle continues.[19] Clearly, during the resting period between the two cycles, the confined paraxylene molecules in the inner space of MWCNTs are released, probably via diffusion. Consequently, the system returns to its original configuration and the energy absorption capacity is nearly completely recovered. Such a system can work continuously as cyclic loading is applied, and is suitable for damping applications.

Conclusions

In summary, by immersing a MWCNT in paraxylene, an energy absorption system can be developed. When the external pressure is sufficiently high, the liquid molecules can be forced into the CNT inner space, leading to a considerable increase in system free energy. The excess solid–liquid interfacial energy cannot be fully released as the pressure is reduced to zero, and the dissipated energy per loading cycle is much larger than that of previously developed silica based systems. Compared with the absorbed energy in the first loading cycle of a SWCNT based system, the energy absorption efficiency of the MWCNT is relatively low, and the reusability is much better. That is, as the loading–unloading cycle is applied repeatedly, the energy absorption characteristics of the MWCNT are nearly the same, making it attractive for design of high-performance damping devices.

Acknowledgements

References Author: please confirm page ranges for all references.

1. M. J. O'Connell: 'Carbon nanotubes'; 2006, Boca Raton, FL, CRC Press.
2. K. Tanaka, T. Yamabe, K. Fukui: 'The science and technology of carbon nanotubes'; 1999, St. Louis, MO, Elsevier Science.
3. M. Meyyappan: 'Carbon nanotubes: science and applications'; 2004, Boca Raton, FL, CRC Press.
4. J. P. Salvetat, S. Bhattacharyya, R. B. Pipes: *J. Nanosci. Nanotech.*, 2006, **6**, 1857.
5. A. Kalra, S. Garde, G. HummerL: *Proc. National Acad. Sci. USA*, 2003, **100**, 10175.
6. D. J. Mann and M. D. Halls: *Phys. Rev. Lett.*, 2003, **90**, 195503.
7. F. Q. Zhu, E. Tajkhorshid and K. Schulten: *Phys. Rev. Lett.*, 2004, **93**, 224501.
8. R. Z. Wan, J. Y. Li, H. J. Lu and H. P. Fang: *J. Am. Chem. Soc.*, 2005, **127**, 7166.
9. J. C. T. Eijkel and A. van den Berg: (2005) *Lab on A Chip*, 2005, **5**, 1202.
10. F. B. Surani, X. Kong and Y. Qiao: *Appl. Phys. Lett.*, 2005, **86**, 151919.
11. F. B. Surani, X. Kong, Y. Qiao: *Appl. Phys. Lett.*, 2005, **87**, 251906.
12. X. Kong, Y. Qiao: *Phil. Mag. Lett.*, 2005, **85**, 331.
13. X. Kong, F. B. Surani and Y. Qiao: *J. Mater. Res.*, 2005, **20**, 1042.
14. F. B. Surani and Y. Qiao: *Phil. Mag. Lett.*, 2006, **86**, 250.
15. F. B. Surani and Y. Qiao: *Mater. Res. Innov.*, 2006, **10**,129.
16. F. B. Surani, X. Kong, D. B. Panchal and Y. Qiao: *Appl. Phys. Lett.*, 2005, **87**, 163111.
17. V. K. Punyamurtula, A. Han and Y. Qiao: *Adv. Eng. Mater.*, 2006, in press.
18. F. B. Surani, A. Han and Y. Qiao: *Appl. Phys. A.*, 2006, 093108.1.
19. V. K. Punyamurtula and Y. Qiao: *Mater. Lett.*, 2006 to be published.
20. D. Myers: 'Surfaces, interfaces, and colloids: principles and applications'; 1999, New York, Wiley-VCH.
21. A. Han, X. Kong and Y. Qiao: *J. Appl. Phys.*, 2006, **100**, 014308.
22. X. Kong and Y. Qiao: *J. Appl. Phys.*, 2006, **99**, 064313.
23. M. S. Dresselhaus, G. Dresselhaus and Ph. Avouris: 'Carbon nanotubes: synthesis, structure, properties, and applications'; 2000, New York, Springer.
24. P. J. F. Harris: 'Carbon nanotubes and related structures'; 2002, Cambridge, Cambridge University Press.
25. V. D. Borman, A. A. Belogorlov, A. M. Grekhov, V. N. Tronin and V. I. Trovan: *JETP Lett.*, 2001, **74**, 287.