



Multiwalled carbon nanotube/polysulfone composites

Thomas Doohar and Dorian Dixon

A new theoretical technique could potentially take the guesswork out of which treatments, when applied to nanoparticles, will produce superior composites.

Since their discovery, researchers have been looking at ways to take advantage of the impressive properties of carbon nanotubes (CNTs) and to fabricate bulk materials using CNT/polymer composites.^{1,2} These composites are of great interest commercially. Another allotrope of carbon (carbon fiber) is increasingly being used in applications where strength and weight are important considerations. There are several practical issues in creating components with carbon fiber (because components have to be built up in layers, the process is slow and expensive) that limit their widespread adoption. Carbon nanotubes are stronger and stiffer than carbon fiber, and their physical dimensions mean it should be possible to create components cheaply using existing methods such as melt processing. This development could potentially allow CNT composites to be used in a much wider range of applications than is possible with fiber.

However, two main issues limit the effectiveness of these composites. The first is dispersion of the tubes: due to their chemical structure and surface area, individual CNTs form strong van der Waals forces with neighboring CNTs, which results in formation of large aggregates. The second is interfacial bonding between the CNTs and polymer molecules due to the inert nature of the nanotubes.³ In an attempt to overcome this, researchers have applied a number of surface modifications to CNTs, often by trial and error for want of an underlying theory. Here, we investigate the use of the solubility parameters to predict the effect of CNT surface modification on dispersion behavior.⁴

Solubility parameters are an extension of the 'like-dissolves-like' rule of thumb. If two different materials have a similar parameter, then, in theory, they should be fully miscible.⁵ The Hildebrand parameter, for example, is one such measure of cohesive energy.⁶ The idea is that if the solubility parameters of the CNT functionalization, polymer, and solvent (if used) are matched, perfect mixing should occur. It has

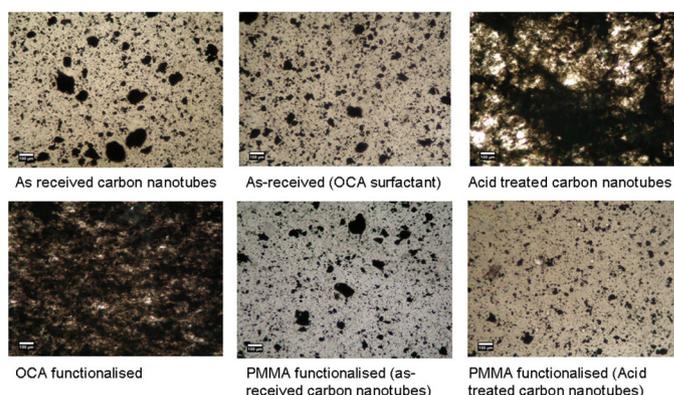


Figure 1. Optical microscopy of the 3wt% composites at 100% magnification. OCA: 1-Octylamine. PMMA: Poly(methyl methacrylate).

Table 1. Hildebrand solubility parameters for the materials used. CNTs: Carbon nanotubes.

Material	Hildebrand solubility parameter (MPa ^{1/2})
Polysulfone	23.7 ⁸
N-methyl-2-pyrrolidone	23.1 ⁹
As-received CNTs	13 ¹⁰
Acid-treated CNTs	17 ¹⁰
OCA	18.2 ⁷
PMMA	22.6 ¹¹

previously been shown that the solubility parameter of CNT surface functionalization can be used to predict the stability of CNT/solvent dispersions.⁷

To investigate the predictive capability of solubility parameters, we prepared composites using six types of CNTs in polysulfone through solvent casting. We used as-received CNTs as a control. We also

Continued on next page



Table 2. Solvent content of the composites (at 3wt% CNTs).

Composite type	Amount of solvent (wt%)
Solvent-cast polysulfone	15
As-received CNTs	9.1
Acid-treated CNTs	14.3
OCA surfactant	14.7
OCA-functionalized	14.7
PMMA-functionalized (made with as-received CNTs)	15.7 15.7
PMMA-functionalized (made with acid treated CNTs)	15.9 15.9

investigated simple acid treatment, which adds oxygen functionality to the CNT surface,¹² and the effect of adding 1-octylamine (OCA), both as a surfactant and chemically bound to the CNTs.¹³ Finally, we produced two batches of poly(methyl methacrylate) (PMMA)-functionalized CNTs (one made using as-received CNTs and another with acid-treated CNTs as the starting material).¹⁴ Table 1 provides the Hildebrand solubility parameters of the various CNT types, the polymer, and the solvent.

To prepare the CNT/polymer samples, we added the required amount of CNTs (to prepare 0, 1, 3, and 5wt% composites) to 1g of polysulfone and 10ml of *N*-methyl-2-pyrrolidone (NMP). When the polymer was dissolved, we sonicated the mixture by tip to break apart CNT bundles and disperse the CNTs throughout the mixture. We poured the mixture into a mold and heated it to evaporate the solvent. We then removed the composite from the mold and placed it in a vacuum oven to remove residual solvent.¹²

Prior to making composites, we conducted a drying study. In the literature, the influence of residual solvent content in solvent-cast composites is underreported. We had to strike a balance between not allowing the polymer to degrade while removing as much solvent as possible within a suitable timeframe. We obtained our results using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and carefully weighed samples. We found that the weight loss from solvent removal followed an exponential decay pattern. DSC confirmed there were two competing processes. As the polymer was heated, solvent evaporated (increasing the glass transition temperature), but any degradation reduced the glass transition point. We determined that the optimum drying time is the peak glass transition temperature, which occurred after 14 days of drying at 40°C and -800mbar pressure.

We analyzed the (3wt%) samples by means of optical microscopy (see Figure 1). Large agglomerates are visible in most of the composites. The composite with the best dispersion is that made with OCA-functionalized CNTs, which had uniform dispersion and distribution at the macro level. The sample prepared with OCA surfactant showed

good dispersion, but the distribution was not ideal because there were visible areas of high and low CNT content. Both sets of PMMA-functionalized CNTs show enhanced dispersion compared with untreated nanotubes, but here, too, it is clear that the dispersion is far from ideal. We observed that the use of solubility parameters cannot fully predict CNT dispersion. Subsequent tensile testing showed that only composites prepared with PMMA-functionalized CNTs displayed any significant improvement (~3–5% in stiffness) in mechanical performance over unreinforced polymer.

TGA confirmed that a large amount of residual solvent was trapped in the composites. Interestingly, the solvent content seemed to correlate with the Hildebrand solubility parameter. A close match in solubility parameters between the modified CNTs, polysulfone, and NMP resulted in greater levels of residual solvent (see Table 2).

In conclusion, while the Hildebrand solubility and similar parameters are useful for identifying promising types of CNT functionalization, they cannot fully predict final composite performance. The approach may be particularly useful in selecting appropriate CNT treatments for improved CNT/polymer composites prepared using melt processing, when residual solvent is not an issue. Further work is ongoing with colleagues working with CNT/epoxy composites to confirm the accuracy of the predictions made using the solubility parameters. Other members of the research team are in the process of testing whether the parameters can be applied to other nanocomposites (using graphene and gold nanoparticles in the place of CNTs).

Author Information

Thomas Doohar

University of Ulster
Newtownabbey, United Kingdom

Thomas Doohar has a PhD in the field of multiwalled CNT/high-temperature polymer composites from the University of Ulster.

Dorian Dixon

Nanotechnology and Integrated Bioengineering Centre
University of Ulster
Newtownabbey, United Kingdom

Dorian Dixon is currently a lecturer. His research interests include nanocomposites as well as nanoparticles for targeted drug delivery.

Continued on next page



References

1. N. Nan and L. Vincenzo, *Young's modulus of single-walled carbon nanotubes*, **J. Appl. Phys.** **84**, pp. 1939–1943, 1998.
2. J.-P. Salvetat *et al.*, *Elastic modulus of ordered and disordered multiwalled carbon nanotubes*, **Adv. Mater.** **11**, pp. 161–165, 1999.
3. J. N. Coleman *et al.*, *High performance nanotube-reinforced plastics: understanding the mechanism of strength increase*, **Adv. Funct. Mater.** **14**, pp. 791–798, 2004.
4. T. Doohar and D. Dixon, *Multiwalled carbon nanotube/polysulfone composites: Using the Hildebrand solubility parameter to predict dispersion*, **Polym. Compos.** **32**, pp. 1895–1903, 2011.
5. R. Mieczkowski, *Solubility parameter components of some polyols*, **Eur. Polym. J.** **27**, pp. 377–379, 1991.
6. J. Burke, *Solubility parameters: theory and application*, **AIC Book Paper Group Ann.** **3**, pp. 13–58, 1984.
7. J. Amiran *et al.*, *High quality dispersions of functionalized single walled nanotubes at high concentration*, **J. Phys. Chem. C** **112**, pp. 3519–3524, 2008.
8. G. Rajagopalan, K. M. Immordino, J. W. Gillespie, and S. H. McKnight, *Diffusion and reaction of epoxy and amine in polysulfone studied using Fourier transform infrared spectroscopy: experimental results*, **Polymer** **41**, pp. 2591–2602, 2000.
9. A. F. M. Barton, *Solubility parameters*, **Chem. Rev.** **75**, pp. 731–753, 1975.
10. M. L. Usrey, A. Chaffee, E. S. Jeng, and M. S. Strano, *Application of polymer solubility theory to solution phase dispersion of single-walled carbon nanotubes*, **J. Phys. Chem. C** **113**, pp. 9532–9540, 2009.
11. T. Lindvig, M. L. Michelsen, and G. M. Kontogeorgis, *A Flory-Huggins model based on the Hansen solubility parameters*, **Fluid Phase Equilib.** **203**, pp. 247–260, 2002.
12. T. Doohar, D. Dixon, and A. McIlhagger, *Multiwalled carbon nanotube/polysulfone composites*, **J. Thermoplast. Compos. Mater.**, 2010.
13. Y. Maeda *et al.*, *Dispersion of single-walled carbon nanotube bundles in nonaqueous solution*, **J. Phys. Chem. B** **108**, pp. 18395–18397, 2004.
14. G. L. Hwang, Y. T. Shieh, and K. C. Hwang, *Efficient load transfer to polymer-grafted multiwalled carbon nanotubes in polymer composites*, **Adv. Funct. Mater.** **14**, pp. 487–491, 2004.