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Influence of nanomodification on physical

properties of polymer nanocomposites

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ABSTRACT

Prior to the discovery of nanotubes, no other material known to mankind possessed such a unique combination of extraordinary properties. It is this fact that most of the research work in the field of nanotechnology has been concentrated in the past decade around CNTs and their applications. CNTs are proven to be the stiffest, strongest and the toughest fiber ever known. The values of tensile strength that have been reported are by far the highest for any material. Their outstanding electrical conductivity values make the polymer to exhibit metallic-type conductivity by incorporating them as filler. Continuing along this

line of research, novel CNT-based composites have been fabricated using different methods, expecting that the resulting composites would possess enhanced or completely new set of physical properties due to the addition of CNTs.

INTRODUCTION

Carbon nanotube, a novel crystalline carbon form is basically a cylindrical tubule containing sp^2 hybridized carbon-carbon bond along its lengths with out any defect as far as structure is concerned because of its nano size [1]. Again a single walled Carbon nanotube or the outer wall of a multi layered carbon nanotube could be viewed as a single molecule so it could be defined as one graphene layer or many graphene layer wrapped onto themselves [2]. Several theoretical and experimental works reveals their interesting mechanical and physical properties besides electrical, which in turn expands its application arena. One of the most remarkable application of CNT is its role as a filler in polymer /CNT nanocomposites, which in fact has been found to enhance the mechanical property of polymers [3]. Generally it helps in preparing high strength and lightweight polymer composites. However the developments in polymer/CNT nanocomposites has been limited by the problems with the dispersion of the fillers as well as the load transfer across the CNT polymer interface due to atomically smooth CNT surface. In this case a polymer /CNT nanocomposite has been prepared by taking epoxy as the polymer matrix and by adding about (1-2)% percentage of CNT to it by ultrasonication route for better dispersion. It has been found that the mechanical strength of a polymer becomes hundred times better even by addition of 1% of CNT.

NEED FOR CARBON NANOTUBE-BASED COMPOSITES

Although CNTs have been observed to possess a broad range of extraordinary properties, they are essentially existent at the nanoscale level. Therefore, in order to be able to utilize CNTs and their properties in real-world applications, there must exist certain means or ways that would help us realize the properties of these fascinating nanostructures at macroscopic levels. Significant research work is being done in this area, in an effort to establish standard methods that can accomplish this task of utilizing the properties of CNTs at macroscopic levels. Some of the past work done in this area involved the inclusion of CNTs in a variety of polymers by numerous methods, which resulted in the imparting of some of the properties of nanotubes to the nanocomposites thus formed.

WORK DONE STILL FAR

The first work on a CNT-polymer composite was reported by Ajayan et al. in 1994 [4]. Purified arc-discharge MWNTs were dispersed in a liquid-epoxy base resin by mechanical stirring. After evacuation to remove trapped air bubbles, pastes of the material were hardened by heating above 60°C for 2 hours. Thin slices were cut and observed by TEM. It was demonstrated that, during cutting, the majority of MWNTs were straightened in the strain direction rather than broken. This result suggested, first, that MWNTs have excellent mechanical properties and second that anisotropy can be induced by a flow in such a material. Only several years later, in 1998, were other works published on CNT-polymer composites.

Schadler et al.[5] reported the dispersion of 5 wt% MWNTs in an epoxy resin by an ultrasonic treatment. Although the MWNTs were well separated, they remain poorly distributed. Mechanical tests and associated Raman spectroscopy revealed that the load transfer to the MWNTs were much higher in compression than in tension. It was inferred that, under loading, only the outer layers of the MWNTs are stressed in tension because all the inner tubes are sliding within the outer, where as all the layers are stressed in compression.

Further investigation on the load transfer in such materials were reported. Both laser-ablation SWNTs and arc-discharge MWNTs were used. It was found [6] that the compressive strength of thin- and thick walled CNTs is more than two orders of magnitude higher than the compressive strength of any known material, which is close to 0.05 Gpa. Compressive stresses were induced in composites films, 200 μm thick, from the shrinkage of the matrix due to polymerization and by further quenching from room temperature to low temperatures (223-81K) [7,8]. The frequency of some Raman bands being stress-sensitive, it has been demonstrated that this spectroscopy can be used to study the strain distribution in fiber composites and to calculate the Young's modulus [9]. The obtained values were close to those previously reported for SWNTs and MWNTs, about 5 and 1.8 Tpa, respectively [10,11]. The fracture of a SWNT-epoxy composite, observed in real time by TEM, revealed a good polymer-CNT wetting and significant CNT-polymer adhesion [12]. Raman spectroscopy investigations of SWNT-epoxy and MWNT-epoxy composites [13] allowed one to determine the effective modulus of the CNTs (about 1Tpa and 0.3 Mpa for the SWNTs and MWNTs, respectively). Stress transfer between the different phases was demonstrated.

On the basis of Raman spectroscopy results and SEM observations, the authors inferred that the load transfer is limited because the SWNTs are slipping, under tension strain, within the bundles. It was also reported [14] that the combination of standard mechanical tests and Raman scattering tests allows the determination of residual strains due to matrix shrinkage, the elastic properties of embedded SWNTs/bundles, their dispersion, and load transfer effectiveness.

The influence of the interfacial interaction between CNTs and the epoxy matrix was evidenced by Gong et al.[15]. Dynamic mechanical measurements and SEM observations were performed on 1 wt% CNT-epoxy composites, prepared either with or without a nonionic surfactant addition (polyoxyethylene 8 lauryl). For the former composite, the glass transition temperature was increased from 63 to 88⁰C and the elastic modulus was also increased by more than 30% in comparison with the matrix. In contrast, the latter composite, prepared without

surfactant addition, presents only moderated improvements of these properties. SEM observations confirmed that the surfactant addition improved the dispersion of the CNTs, thus allowing the dramatic effects of CNTs on the properties of the material.

CCVD MWNTs (inner diameter 5 nm, outer diameter 10 nm, length a few micrometers) were dispersed in an epoxy matrix (0.0225-0.15 wt% MWNTs)[16]. The exposure to ultrasound early in the process and the subsequent intense stirring of the resin dramatically improved the dispersion of the MWNTs in the matrix. The percolation threshold was found to be between 0.0225 and 0.04 wt% MWNTs. An electrical conductivity of about 10^{-2} S/m, sufficient for antistatic applications, was achieved with 0.04 wt% MWNTs, that is, using a loading about one-tenth of that needed using carbon black. It is noted that at these low filler fractions, neither the processing behavior of the matrix nor the surface finish of the samples is adversely affected and that the mechanical properties of the epoxy matrix should not be compromised.

CHARACTERISATION

Raman spectroscopy analysis could be conducted on polymer/CNT fiber with and with out nanotube. The spectra could be recorded using a micro spectrometer by using a diode laser, which corresponds to equivalent photon energy of 1.58ev. Typical peaks of CNT could be detected from the polymer/CNT composite that serves as a direct confirmation of the successful filling of the polymers with the nanotubes.

The CNT contents in the polymer nanofiber can be detected by the *thermogravimetry* method. In which both pure polymer and polymer/CNT nanofiber were heated in the air atmosphere at the rate of 20°C/min. The difference in decomposition temperature of both the sample indicates that CNT in polymer nano fiber increases polymers thermal stability. The difference of remaining weight between two samples can help in determining the CNT content in polymer/CNT nanofiber.

The *atomic force microscopy (AFM)* not only helps in characterizing the surface topography of the fibers but also to investigate their mechanical, electrical and thermal properties. The highly spatial resolution of AFM makes it an ideal tool to measure the structural, mechanical, electrical and thermal properties of the composites individually.

ENHANCEMENT IN PHYSICAL PROPERTIES

Turning to mechanical properties, SWNTs have the highest young's modulus of about 1 TPa if normalised to their diameter and, therefore, all types of CNTs have attracted much interest for low weight structural composites. It could be hoped that their performance might eventually exceed that of carbon fiber reinforced composites. However, to date, their performance has been rather disappointing. A simple analysis assuming the rule of mixtures would expect the modulus of a composite to be at least $1000x/3$ Gpa, where x is the nanotube content, 1000 Gpa is the basic nanotube modulus, and the factor of $1/3$ allows for isotropically oriented CNTs, assuming the host has minimal modulus. In practice, much lower values are found. This is because, firstly, SWNTs are usually not dispersed in the matrix but distributed as bundles. Secondly, only small amounts of CNTs are dispersed in the host and, thirdly, their insufficient bonding across the nanotube/host interface to transfer forces. So far, these composites tend to fail either by fracture at the nanotube/host interface or, for MWNTs, by pull out of different shells of the MWNTs. Stronger bonds between CNTs and host are needed, For example by creating covalent bonds by functionalization along long tubes [17]. A second way would be to use secondary bonds such as hydrogen bonds, although only 5% as strong as covalent bonds could bond to more sites.

Many groups are turning to fibers, by aligning CNTs. Vigolo et al. [18] drew nanotube/polyvinyl alcohol fibers, a process which has been taken further by Dalton et al.[19]. An alternative is to learn lessons from other strong fibers such as Kevlar. Davis et al.[20] dispersed SWNTs in 102% sulfuric acid, which possibly protonates the sidewalls, separating individual tubes, and allows fibers to be drawn. Allaoui et al.[21] claimed to have quadrupled the elastic modulus

and the yield strength (measured through tensile test) of an epoxy matrix by the incorporation of 4 wt% of both very large CCVD MWNTs and VGCFs (15-400nm in diameter). Conductivity measurements revealed that the insulator-conductor transition occurred for MWNT contents in the range 0.5-1 wt%. Their outstanding electrical conductivity values make them the first polymer to exhibit metallic-type conductivity. The thermal conductivity of CNTs is observed to be twice that of diamond, which was the best thermal conductor before the discovery of CNTs. The thermal conductivity value obtained for a pure and defect-free CNT was roughly 28.9W/cm.K, which is much higher than that of conventional materials. Thostenson et al. [22] reported the direct growth of MWNTS on carbon fibers by CCVD. Embedding the coated fibers in an epoxy matrix produces a multistage composite. Single-fiber composites were prepared. It is reported that the MWNT coating improves the interfacial load transfer, possibly by local stiffening of the polymer matrix near the fiber/matrix interface.

APPLICATION OF EPOXY-CNT NANOCOMPOSITE

The high aspect ratio (length to radius) and high conductivity of CNTs makes them excellent for conducting composites. A mixture of conducting and insulating phases becomes conducting when the volume fraction of conducting phase exceeds a 'percolation threshold' of 16 %, the minimum amount to give a continuous path across the whole sample. This threshold is independent of the size and shape of the conducting phase, as long as its particles are equiaxed. When the conducting phase consists of long thin particles, the chance of contact increases, which reduces the percolation threshold so that conduction occurs at much lower loading.

Existing conducting composites are made of carbon black in polymers. This should require about 16% of carbon, but it has been reduced by clever processing. Composites of MWNTs in epoxy resin achieve percolation at loadings of 0.01% and even 0.004% with careful processing [23]. These are extremely low loadings. The first use of such composites was by Hyperion for electrostatically applying paint onto car components [24]. Nanotube composites have a much better surface finish than the previous carbon black or carbon fiber composites. Another use of nanotube

composites is as antistatic shielding, on airplane wings and fuselages for example. This is a realistic application. A future use is for shielding of electromagnetic interference, a critical application for many industrial sectors. This would require a composite with conductivity of 1 S.cm. This requires that the carbon phase should be highly conducting and is probably only achievable if SWNTs are used as the loading. It is achievable, however, and is a credible application. A fourth application of conducting composites is as a transparent conductor. There is a huge market for transparent electronic conductor such as indium tin oxide (ITO) in displays. In this field, there is a drive towards flexible displays on plastic substrate. ITO is less good for this situation as it is brittle and has poor adhesion to plastic. Conducting composites of SWNTs can be transparent if thin enough [25]. They have the huge advantage of being truly flexible and compatible with polymer substrates. This is a large potential market with few competitors.

REFERENCES:

- [1] Asa H. Barbar, Sidney R. Cohen, Shmuel kenig, H.Daniel Wagner, Interfacial fracture energy measurements for multi walled carbon nanotubes pulled from a polymer matrix, *Composites Science and Technology*, 2004, 64, 2283-9.
- [2] A. Allaoui, S. Bai, H. M. Cheng, J. B. Bai. Mechanical and electrical properties of a MWNT/epoxy composite, *Composites Science and Technology*, 2002, 62, 1993-8.
- [3] Frank. K. Ko, Sakina Khan, Ashraf Ali, Yury Gogotsi, Nevin Naguib, Guoliang Yang and Christopher Li, Hideo Shimoda and Otto Zhou, Michael J. BroniKowski, Richard E. Smalley, Peter A. Willis, *Structure and property of carbon nano tube reinforced nano composites*, *AIAA*, 2002, 1426.
- [4] P.M. Ajayan, O. Stephan, C. Colliex, and D. Trauth, *Science*, 265,1212 (1994).
- [5] L. S. Schadler, S. C. Giannaris and P.M. Ajayan, *Appl.Phys.Lett.*, 73, 3842 (1998).

- [6] O. Lourie, D. M. Cox and H. D. Wagner, Phys. Rev. Lett., 81,1638(1998).
- [7] O. Lourie and H. D. Wagner, J. Mater. Res.13, 2418(1998).
- [8] O. Lourie, H. D. Wagner, Y. Zhang and S. Iijima, Adv.Mater.,11, 931 (1999).
- [9] C. Galiotis and D. N. Batchelder, J.Mater.Sci.Lett., 7, 545 (1988).
- [10] M. M. J. Treacy, T. W. Ebbesen and J. M. Gibson, Nature (London) 381, 678 (1996).
- [11] G. Overney, W. Zhong and D. Z. Tomanek, Z. Phys., D 27, 93 (1993).
- [12] O. Lourie and H. D. Wagner, Appl. Phys. Lett., 73, 3527(1998).
- [13] C. A. Cooper, R.J. Young and M. Halsall, Composites, A 32, 401 (2001).
- [14] V.G. Hadjiev, M. N. Ilieva, S. Arepalli, P. Nikolaev and B.S. Files, Appl. Phys. Lett., 78, 3193, (2001).
- [15] X. Gong, J. Liu, S. Baskaran, R. D. Voise, and J.S. Young, Chem. Mater., 12, 1049 (2000).
- [16] J. Sandler, M. S. P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte and A. H. Windle, Polymer, 40, 5967 (1999).
- [17] Cadek, M., et al., Nano Lett. (2004) 4,353
- [18] Vigolo, B., et al., Science (2000) 290,1331
- [19] Dalton, A.B., et al., Nature (2003) 423,703
- [20] Davis, V.A., et al., Macromolecules (2004) 37, 154; Zhou, W., et.al., J.Appl.Phys. (2004) 95, 649.
- [21] A. Allaoui, S. Bai, H. M. Cheng and J. B. Bai, Comp. Sci. Technol., 62, 1993 (2002).
- [22] E. T. Thostenson, W. Z. Li, D. Z. Wang, Z. F. Ren and T. W.Chou, J.Appl. Phys., 91, 6034 (2002).
- [23] Sandler, J.K.W., et al., Polymer (2003) 44,5893
- [24] Baughman, R.H., et al., Science (2002) 297,787
- [25] Park, C., et al., Chem. Phys. Lett. (2002) 364, 303. www.eikos.com
