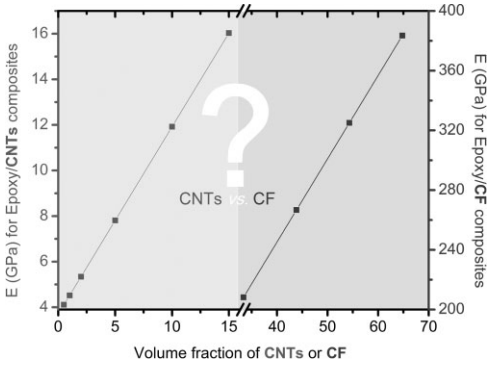
Is It Worth the Effort to Reinforce Polymers With Carbon Nanotubes?

Marcio R. Loos,* Karl Schulte

Carbon nanotubes (CNTs) show exceptional properties that render them attractive for incorporation in a new generation of high-performance engineering composites with tailored properties. While a great deal of work has been done toward using CNTs as a reinforcing agent in polymer composites, the full potential of CNTs has yet to be reached. In this work, two case studies were proposed in order to analyze the effectiveness of CNTs and carbon fibers (CFs) as reinforcing agents. Micromechanics models for the stiffness and strength of hybrid composites, comprising CNTs and CFs are derived by considering the concept of effective fiber. In addition, the 2009 prices of commercially available CNTs are reviewed. The strongest, the stiffest, and the cheapest CFs commercially available are compared with single walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs). The simulated results from the micromechanics models show that the use of CFs makes the acquisition of composites with maximum tensile strengths of 4.18 GPa possible. Analysis of the cost versus property relation showed that CNTs are the most viable strengthening option for achieving composites with strengths of up to 11.61 GPa. It is also shown that CFs are the most viable stiffening option, making composites with Young's moduli of up to 383 GPa possible at the expense of the material's toughness. Moreover, it is shown that, in order to achieve CNT's true potential, several challenges have to be faced. CNTs have to be produced with higher purity, longer lengths, better integrity, in larger amounts, and at lower cost. Moreover, issues such as orientation of the CNTs, their concentration, interfacial adhesion, distribution, and dispersion have to be overcome.



Introduction

Since Iijima's report in 1991, carbon nanotubes (CNTs) have been the focus of considerable research[1] (Figure 1). During the last decade, a great deal of effort has been given toward maximizing the potential of CNTs as reinforcing agents in polymer matrix composites. Despite this effort, the full potential of CNT-reinforced composites has not been realized because of processing difficulties and load transfer limitations between the matrix and the nanotubes. Results from simulations predict that composites containing CNTs

Dr. M. R. Loos
Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA
E-mail: marcio.loos@case.edu
Prof. K. Schulte
Institute of Polymer & Composites, Hamburg University of Technology, Denickestrasse 15, 21073 Hamburg, Germany

DOI: 10.1002/mats.201100007

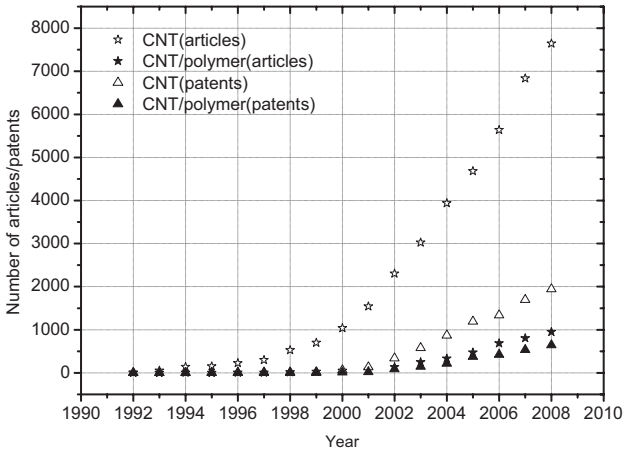


Figure 1. Number of published articles and patents on nanotubes or nanotube/polymer as a function of year.

should have exceptional mechanical properties.[2–4] Table 1 shows numerous results reporting the effect of CNTs on tensile properties of various polymer matrices. Although great improvements have been achieved, the results for the elastic modulus and strength of polymer composites have usually been disappointing, particularly when compared to advanced composites reinforced with high-performance continuous fibers.

Carbon fibers (CFs) refer to fibers that are at least 92 wt.-% carbon in composition.[57] The high moduli of CFs stem from the fact that the carbon layers tend to be parallel to the fiber axis. Moreover, the density of CFs is quite low, making the specific moduli (E/ρ) of high-modulus CFs exceptionally high. Carbon fiber-based composites, particularly those with polymeric matrices, have become the dominant advanced composite materials for aerospace, automobile, sporting goods, and other applications due to their high strength, high modulus, low density, and reasonable cost. As the price of CFs decreased with time, their applications have continued to broaden, and now even include the construction industry, which uses CFs to reinforce concrete.

Commercial CFs are fabricated by using pitch or poly(acrylonitrile) (PAN) as the precursor. Among the existing high-performance CFs, those based on pitch can attain higher moduli than those based on PAN because pitch is more graphitizable than PAN. However, the fibers based on PAN can attain a higher tensile strength and greater elongation than those based on pitch. While the tensile stress–strain curves of CFs are linear to fracture, the main drawback of CFs mechanical properties is their low ductility, which is lower than those of glass, quartz (SiO_2), and Kevlar fibers. The ductility of high-modulus CFs is even lower than that of high-strength CFs. Commercially available CFs can have a Young's modulus as high as 900 GPa, a tensile strength of up to 6.4 GPa, and for CFs with low moduli, an elongation at break of 2.2%.

On the other hand, for CNTs, experimental results have shown Young's moduli of up to 1 800 GPa, tensile strengths of up to 150 GPa, and elongations at break of up to 15%.[2] Figure 2 shows a comparison between the Young's modulus, tensile strength, and elongation at break of various CFs with SWCNTs and multiwalled CNTs (MWCNTs). The main advantages of CNTs over CFs are their extremely high-tensile strength and elongation at break. Another key point for CNTs is the possibility to process composites using standard industrial techniques like extrusion. Nevertheless, many issues have to be overcome in order to fully realize the potential of CNTs as reinforcing agents. The main challenges in this area are the purification and functionalization, the ability to disperse CNTs within the matrix, interactions between the CNTs and the host matrix, and alignment within the host matrix. In addition to these challenges, there is no known preparation method that gives CNTs with uniform proportions.

Surface modification of CNTs is the most common strategy used to increase nanotube–polymer interactions, decrease filler self-aggregation, and thus improve load transfer. Even by making use of such strategies or by aligning the CNTs, in many cases the improvements in tensile strength and modulus are coupled with a reduction in strain at break, indicating a decreased ductility.

After examining the full potential of CNTs as a mechanical reinforceming agent, the next issue is cost. Table 2 presents the 2009 prices of various commercially available CNTs. The prices are a function of diameter, length, purity, and method of manufacturing. For SWCNTs, double walled CNTs (DWCNTs), and MWCNTs, the prices per gram are in the range of \$32–2500, \$21–1600 and \$0.5–136, respectively. For CFs, the price per gram can vary between \$0.037 and \$1.8.

Considering both the mechanical properties and the cost of CFs and CNTs, the following questions arise: Is it worth the effort to reinforce polymers with CNTs? Will CNTs replace CFs as a reinforcing agent? These two questions cannot be fully answered simply by comparing the mechanical properties and price of CFs and CNTs. It is necessary to analyze the cost versus property relation of composites reinforced with these fillers.

In order to answer the above questions, this study involves deriving an equation based on the Halpin–Tsai model, and, using the concept of effective fiber, predicting the elastic modulus and tensile strength of epoxy matrix composites reinforced with CNTs, CFs, or a combination of the two materials. Based on the simulation results, the feasibility of the composite materials, that is to say of the CNTs and CFs as a reinforcement agent, is then ranked. In order to be as realistic as possible, we chose for our simulations the strongest, the stiffest, and the cheapest PAN-based CFs commercially available and compared them with MWCNTs.

Table 1. Mechanical properties enhancement of selected nanocomposite materials.

Matrix or polymer	Filler	Φ [wt.-%]	E_{matrix} [GPa]	E_{max} [GPa]	E %Increase	σ_{matrix} [MPa]	σ_{Max} [MPa]	σ %Increase	Year and reference
ABPBO	MWCNTs	5	1.8	2.6	+44	37	67	+81	2008[5]
Epoxy	MWCNTs	2	1.18	1.39	+18	52	62	+19	2002[6]
Epoxy	DWCNTs	0.1	3.29	3.50	+6	–	–	–	2004[7]
Epoxy	MWCNTs	8	1.05	0.750	−29	43	70	+63	2007[8]
Epoxy	SWCNTs	0.1	1.10	1.72	+56	–	–	–	2008[9]
Epoxy	MWCNTs	1	1.21	1.61	+33	26	58	+123	2008[10]
Epoxy	MWCNTs	0.7	0.52	0.95	+83	–	–	–	2008[11]
Epoxy	MWCNTs	0.1				47	65	+38	2008[11]
Epoxy	MWCNTs	5	1.9	2.9	+53	46	52	+13	2008[12]
Epoxy	MWCNTs	1	1.97	1.77	−10	47.3	47.9	+1	2008[13]
Epoxy	SWCNTs	1.0	2.76	3.49	+26	64.1	74.7	+17	2008[14]
Epoxy	MWCNTs	2	2.6	2.9	+12	–	–	–	2009[15]
Epoxy	SWCNTs	1	3.4	4.2	+24	–	–	–	2009[16]
Epoxy	MWCNTs	16.5	2.5	20.4	+716	89.1	231.5	+160	2009[17]
iPP	MWCNTs	2.5	0.60	1.42	+137	28.7	34.5	+20	2008[18]
LDPE	MWCNTs	10	0.24	0.44	+83	10.7	15.6	+46	2008[19]
Nylon 610	MWCNTs	1.5	0.9	2.4	+167	35.9	51.4	+43	2009[20]
PA6	MWCNTs	1	3.3	4.7	+42	60.4	71.5	+18	2008[21]
PA1010	MWCNTs	30	1.02	1.91	+87	–	–	–	2006[22]
PBO	MWCNTs	5	3.6	5.2	+44	68	119	+75	2008[23]
PBO	MWCNTs	0.54	66.6	99.8	+50	1.18	1.51	+28	2008[24]
PC	MWCNTs	0.5	1.48	2.16	+46	41.4	61.0	+47	2004[25]
PE	MWCNTs	8	≈1.3	≈1.7	+31	–	–	–	2009[26]
PE	SWCNTs	0.5	0.81	0.8	−1	34.1	33.3	−2	2004[27]
PEI	MWCNTs	1	1.47	2.05	+39	77.5	95.0	+23	2007[28]
PEN	MWCNTs	0.5	1.68	1.98	+18	66.3	87.8	+32	2008[29]
PEO	SWCNTs	1	0.06	0.15	+150	–	–	–	2002[30]
PI	SWCNTs	1	2.2	3.2	+45	105	105	0	2004[31]
PI	MWCNTs	5	–	–		92	133	+45	2006[32]
PI	MWCNTs	6.98	2.3	3.7	+31	102	134	+31	2007[33]
PI	MWCNTs	5	0.91	1.21	+33	–		–	2007[34]
PI	MWCNTs	14.3	2.84	3.90	+37	115.6	95.2	−18	2004[35]
PLLA	MWCNTs	3	0.21	0.32	+52	–	–	–	2008[36]
PolyENB	MWCNTs	1.6	1.89	2.02	+7	52.3	52.1	0	2009[37]
PMMA	SWCNTs	5	≈3.1	≈5	+61	–	–	–	2000[38]
PP	MWCNTs	1	4.4	5.7	+30	500	520	+4	2008[39]
PP	MWCNTs	5	1.28	2.15	+68	28.2	35.25	+25	2009[40]
PP	MWCNTs	1.5				25.16	60.74	+141	2008[41]
PP	MWCNTs	2.0	0.773	1.684	+118	–	–	–	2008[41]
PP	MWCNTs	0.3	1.570	2.107	+34	30.71	53.98	+76	2008[42]
PP	MWCNTs	5	4.6	7.1	+54	490	570	+16	2002[43]
PP	SWCNTs	0.8	4.2	4	−5	430	420	−2	2003[44]

Table 1. (*Continued*).

Matrix or polymer	Filler	Φ [wt.-%]	E_{matrix} [GPa]	E_{max} [GPa]	E %Increase	σ_{matrix} [MPa]	σ_{Max} [MPa]	σ %Increase	Year and reference
pPEK	MWCNTs	17	4.0	6.7	+68	–	–	–	2009[45]
PS	MWCNTs	1	≈1.19	≈1.69	+42	≈12.8	≈16	+25	2000[46]
PS	MWCNTs	2.5[a)]	2.02	2.72	+35	–	–	–	2008[47]
PU	MWCNTs	2.5	40	150	+275	–	–	–	2007[48]
PU	MWCNTs	10	0.235	0.444	+89	10.7	15.6	+46	2007[49]
PVA	SWCNTs	5	≈4	≈6.2	+55	–	–	–	2004[50]
PVA	MWCNTs	9.1	5.6	25.3	+352	15.7	42.3	+169	2005[51]
PVA	MWCNTs	5	1.95	4.68	+140	72.6	119.4	+64	2007[52]
PVOH	MWCNTs	1	1.8	10.4	+478	–	–	–	2007[53]
SAN	MWCNTs	1	1.48	2.23	+51	27.8	55.3	+99	2005[54]
TPU	SWCNTs	0.5	7.7	14.5	+88	12.4	13.3	+7	2006[55]
UHMWPE	MWCNTs	5	≈122.6	≈136.8	+12	≈3 510	≈4 170	+19	2006[56]

Φ, loading; E, Young's modulus; σ, ultimate tensile strength or tensile strength at yield.
Acronyms: ABPBO, poly(2,5-benzoxazole); iPP, isotatic polypropylene; LDPE, low density polyethylene; PA-6, polyamide-6; PA1010, polyamide-1010; PBO, poly(1,4-phenylene-*cis*-benzobisoxazole); PC, polycarbonate; PE, polyethylene; PEI, polyether imide; PEN, poly(ethylene naphtalene); PEO, poly(ethylene oxide); PI, polyimide; PLLA, poly(lactic acid); PolyENB, poly(5-ethylidene-2-norbornene); PMMA, polymethyl methacrylate; PP, polypropylene; pPEK, para-polyetherketone; PS, polystyrene; PU, polyurethane; PVA, poly(vinyl acetate); PVOH, poly(vinyl alcohol); SAN, styrene-acrylonitrile; TPU, thermoplastic polyurethane; UHMWPE, ultrahigh-molecular-weight polyethylene.
[a)]vol.-%.

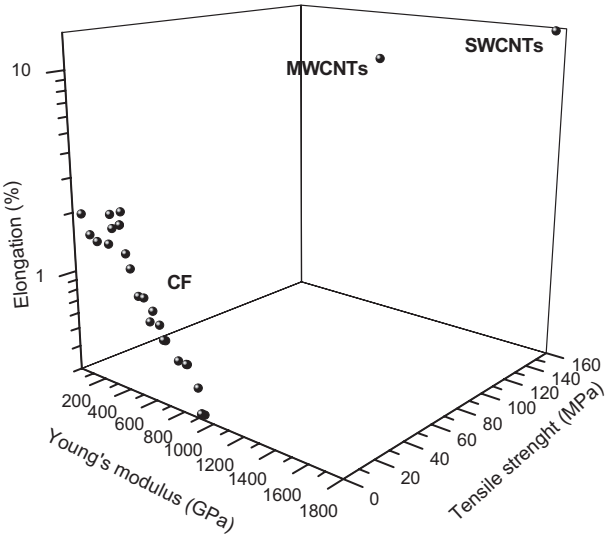


Figure 2. Modulus, tensile strength, and elongation at break for various CFs compared with SWCNTs and MWCNTs.

Theories

Micromechanics Modeling of Fiber Composites

A wide variety of micromechanics models are currently available to predict the tensile properties of fiber composites.[3,4,58,59] The Halpin–Tsai equations are a set of empirical relationships that enable the property of a composite material to be expressed in terms of the properties of the matrix and reinforcing phases considering their proportions and geometry. Despite of their empirical nature, these equations are quite popular in materials science. For the longitudinal Young's modulus of aligned fiber composites, the Halpin–Tsai equation states[3,60,61]

$$\frac{E_{11}}{E_m} = \frac{1 + \zeta\eta V_f}{1 - \eta V_f} \quad (1)$$

$$\eta = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + \zeta} \quad (2)$$

$$\zeta = 2\frac{l}{d} \quad (3)$$

where E_{11}, E_m, and E_f are the composite, matrix, and fiber elastic modulus, respectively, V_f is the fiber volume fraction, and ζ is a shape parameter dependent upon reinforcement geometry and orientation. The constant η takes into account the modulus of the matrix and fiber.

Table 2. Price and some properties of different types of CNTs commercially available.

Product	Supplier/Country	Purity [wt.-% or vol.-% ≥]	*d* [nm]	*l* [μm]	Cost [$ · g^{-1}]	Production method
SWCNTs	M K Impex/Canada	90% CNTs	1–2	5–30	32	CVD
SWCNTs	MER/USA	12% SWCNTs	1.2–1.4	10–50	35	CVD
SWCNTs	MicrotechNano/USA	90% CNTs/50% SWCNTs	<2	5–15	39	CVD
SWCNTs	NTP Shenzhen/China	90% CNTs/50% SWCNTs	<2	5–15	50	CVD
SWCNTs	CSI/USA	40–60% C	1.4	1.5	50	Arc discharge
SWCNTs	NanoCarbLab/Russia	40% CNTs	1.2–1.4	1–5	60	Arc discharge
SWCNTs	CheapTubes/USA	90% CNTs/5% MWCNTs	1–2	5–30	65	CVD
SWCNTs	Alpha Nano/China	90% C	1–2	5–20	65	CVD
SWCNTs	Heji/China	90% C	1–2	10–20	72	CVD
SWCNTs	BuckyUSA/USA	90% C	0.7–2.5	0.5–10	77	CVD
SWCNTs	Arry/Germany	90% C	1–2	5–20	90	CVD
SWCNTs	Nanoamor/USA	90% SWCNTs	1–2	5–30	100	CVD
SWCNTs	Nanothinx/Greece	85% CNTs	0.8–1.4	≥ 5	120	CVD
SWCNTs	Helix/USA	90% C	1.3	0.5–40	124	CVD
SWCNTs	YOUR-TOOL/Germany	90% CNT/60% SWCNTs	2	20	129	–
SWCNTs	Chengdu/China	90% C	1–2	–	180	CVD
SWCNTs	Nanoshel/USA	98% CNTs/70% SWCNTs	0.7–2	3–8	180	Arc discharge
SWCNTs	SES Research/USA	90% CNTs/50% SWCNTs	<2	1–5	199	CVD
SWCNTs	Nanomaterial store/USA	90% SWCNTs	1–2	5–30	280	CVD
SWCNTs	NanoCarbLab/Russia	70–80% CNTs	1.2–1.4	1–5	380	Arc discharge
SWCNTs	CSI/USA	90% C	1.4	0.5–15	400	Arc discharge
SWCNTs	Nanocyl/Belgium	70% C	2	–	447	CVD
SWCNTs	Carbolex/USA	70–90% SWCNTs	1.4	2–5	800	
SWCNTs	CNI technology/USA	95% CNTs	0.8–1.2	0.1–1	2000	HiPCo
SWCNTs	NanoLab/USA	90% SWCNTs	1–1.5	>10	2500	CVD
DWCNTs	Heji/China	60% C	1.3–5	–	21	CVD
DWCNTs	MicrotechNano/USA	90% CNTs/50% DWCNTs	<5	5–15	30	CVD
DWCNTs	Chengdu/China	60% C	2–4	–	30	CVD
DWCNTs	NTP Shenzhen/China	90% CNTs/50% DWCNTs	<5	5–15	50	CVD
DWCNTs	Nanoamor/USA	50% DWCNTs	<5	5–15	54	CVD
DWCNTs	Arry/Germany	80% C	1.3–3	5–15	83	CVD
DWCNTs	Helix/USA	90% C	4	0.5–40	124	CVD
DWCNTs	YOUR-TOOL/Germany	90% CNTs/60% DWCNTs	3	20	129	–
DWCNTs	Xintek/USA	85% CNTs	3	2–6	160	CVD
DWCNTs	Nanocyl/Belgium	90% C	3.5	1–10	179	CVD
DWCNTs	NanoCarbLab/Russia	20–30% DWCNTs	–	–	250	Arc discharge
DWCNTs	Nanomaterial store/USA	60% DWCNTs	<3	<20	310	CVD
DWCNTs	NanoLab/USA	95% CNTs	3–5	1–5	350	CVD
DWCNTs	SES Research/USA	90% CNTs/50% DWCNTs	<5	5–15	385	CVD
DWCNTs	NanoCarbLab/Russia	90% DWCNTs	–	–	1500	Arc discharge
DWCNTs	Xintek/USA	98% CNTs	2	2–6	1600	CVD
MWCNTs	Alpha Nano/China	95% C	20–30	5–20	0.5	CVD

Table 2. (*Continued*).

Product	Supplier/Country	Purity [wt.-% or vol.-% ≥]	*d* [nm]	*l* [μm]	Cost [$ · g^{-1}]	Production method
MWCNTs	Bayer/Germany	95% C	13	>1	0.60	CVD
MWCNTs	Bayer/Germany	99% C	13–16	>1	0.75	CVD
MWCNTs	Chengdu/China	95% C	<8	–	1.5	CVD
MWCNTs	CheapTubes/USA	95% MWCNTs	<8	10–30	2.5	CVD
MWCNTs	Nanoamor/USA	95% CNTs	8–15	10–50	4	CVD
MWCNTs	M K Impex/Canada	95% CNTs	<8	10–30	12	CVD
MWCNTs	Heji/China	95% C	<8	0.5–200	12	CVD
MWCNTs	Helix/USA	95% C	<10	0.5–40	13	CVD
MWCNTs	YOUR-TOOL/Germany	95% CNTs	<10	5–15	14	–
MWCNTs	Arry/Germany	95% C	5–10	5–20	14	CVD
MWCNTs	Nanothinx/Greece	98% CNTs	25–40	≥10	23	CVD
MWCNTs	NTP Shenzhen/China	85% CNTs	<10	5–15	25	CVD
MWCNTs	MicrotechNano/USA	95% CNTs	≈5	5–15	29	CVD
MWCNTs	MER/USA	90% CNTs/	25–45	30	35	CVD
MWCNTs	Nanomaterial store/USA	95% CNTs	<8	10–30	35	CVD
MWCNTs	Future Carbon/Germany	98% C	15	10–50	37	CVD
MWCNTs	Catalytic Materials/USA	99% CNTs	10	–	40	CVD
MWCNTs	Nanoshel/USA	90% CNTs/70% MWCNTs	4–12	3–10	45	Arc discharge
MWCNTs	Nanocyl/Belgium	95% C	9.5	1.5	45	CVD
MWCNTs	NanoLab/USA	95% CNTs	10–20	1–5	75	CVD
MWCNTs	BuckyUSA/USA	95% C	5–15	1–10	80	CVD
MWCNTs	Xintek/USA	90% CNTs	8	10–20	120	CVD
MWCNTs	SES Research/USA	95% CNTs	<10	1–2	136	CVD

d, average diameter; *l*, average length. The values showed above are just for reference. The cost may change accordingly to the amount of CNTs purchased. Here the cost was valued considering CNTs amounts from 1 to 1 000 g. The purity of CNTs is determined by using different methods such as TEM, Raman, TGA, or EA.

Thostenson and Chou[3] modified the Halpin–Tsai equation toward its applicability to nanotube reinforced composites. Considering that the outer wall of the nanotubes act as an effective solid fiber, with the same deformation behavior, diameter (*d*) and length (*l*) of the nanotube, the parameter η can be re-written as

$$\eta' = \frac{\left(\frac{E_{NT}}{E_m}\right) - \left(\frac{d}{4t}\right)}{\left(\frac{E_{NT}}{E_m}\right) + \left(\frac{l}{2t}\right)} \quad (4)$$

where E_{NT} is the nanotube elastic modulus, *l* and *d* are the length and average outer diameter of the nanotube, and *t* is the thickness of graphite layer (0.34 nm).

CNTs can be used as a single reinforcing phase (binary systems) or as an additional reinforcing phase in conjunction with CFs in hybrid composites (ternary systems). The former case has been widely considered in the literature experimentally as well as theoretically. Nevertheless, the later case has been studied experimentally at some extent, whereas, the modeling of such hybrid composites has been less considered.

We will now derive an equation based on the Halpin–Tsai model and in the concept of effective fiber[3] to predict the elastic properties of hybrids composites containing CNTs and CFs. As we will demonstrate, the equation predict the same values as the Equation (1–4) for the cases of composites containing only CFs or only CNTs.

For a hybrid composite containing CNTs and CFs the fiber volume fraction is expressed as

$$V_f = V_{NT} + V_{CF} \quad (5)$$

Substituting the equation above into (1) yield

$$\frac{E_{11}}{E_m} = \frac{1 + \zeta\eta V_{CF} + \zeta'\eta' V_{NT}}{1 - \eta V_{CF} - \eta' V_{NT}} \quad (6)$$

By substituting (2) and (4) into (6) and considering the limiting value of ζ when continuous aligned CFs are used $\zeta = \infty$.

$$\lim_{\zeta\to\infty} \frac{E_{11}}{E_m} \quad (7)$$

We get

$$E_{11} = \frac{E_{NT}[1 + \zeta' V_{NT} + (E_{CF}V_{CF}/E_m) - V_{CF}] + E_{CF}V_{CF}l/2t + E_m l/2t(1 - V_{CF}) - E_m\zeta' V_{NT}d/4t}{(E_{NT}/E_m)(1 - V_{NT}) + l/2t + V_{NT}d/4t} \quad (8)$$

$$\zeta' = 2\frac{l}{d} \quad (9)$$

The equation above gives the Young's modulus in the direction of the alignment of composites containing aligned CNTs, CFs, or hybrid composite containing both of them. A similar calculation can be used to derive an equation for the tensile strength of hybrids composites containing CNTs and CFs. The theoretical tensile strength parallel to the fiber in the composites can be approximated with reasonable accuracy by

$$\sigma_c = \sigma_f V_f + \sigma_m(1 - V_f) \quad (10)$$

where σ_c, σ_f, and σ_m are the composite, fiber, and matrix strengths, respectively. For composites containing CNTs where $l > l_c$ the composite strength can be described by[4]

$$\sigma_c = (\eta_s\sigma_{NT} - \sigma_m)V_{NT} + \sigma_m \quad (11)$$

$$\eta_s = 1 - \frac{l_c}{2l} \quad (12)$$

where η_s is the strength efficiency factor and l_c is the critical length. The equation above is not considering that the polymer–nanotube interaction result in the formation of an interfacial polymer region with properties different of the bulk polymer.[62] For a hollow cylinder, the critical length is given by[63]

$$l_c = \frac{\sigma_{NT}d}{2\tau}\left(1 - \frac{{d_i}^2}{d^2}\right) \quad (13)$$

where τ is the interfacial shear strength between the hollow tube and the surrounding polymer. For the case of MWCNTs (or DWCNTs) two cases can be considered: (i) only the outmost wall carries the load and (ii) all walls carry the load. In the former case the effective tensile strength of the CNT, according to the "effective fiber" definition[3] can be expressed as

$$\sigma_{eff} = \frac{4t}{d}\sigma_{NT} \quad (14)$$

while in the later case we have

$$\sigma_{eff} = \frac{(d^2 - {d_i}^2)}{d^2}\sigma_{NT} \quad (15)$$

The properties of the nanotubes are extremely dependent on the interaction between the outmost layers and the internal layers. Since, in the case of strength, the inter-wall sliding may occur before ultimate fracture of the nanotubes, and the internal layers of DWCNTS, and MWCNTs do not contribute fully to the nanotube strength, it is reasonable that the value obtained using Equation (14) or at least values between this and the one given by Equation (15) should be considered for modeling.

Substituting Equation (5) into (11) and assuming the strength efficiency factor to be equal to 1, for continuous aligned fibers in the direction of alignment we have

$$\sigma_c = \eta_s\sigma_{NT}V_{NT} + \sigma_{CF}V_{CF} + \sigma_m[1 - (V_{NT} + V_{CF})] \quad (16)$$

If $V_{NT} = 0$ then the equation above reduces to the Equation (10) while for $V_{CF} = 0$ Equation (16) becomes the Equation (11). The equation above gives the tensile strength in the direction of the alignment of composites containing CNTs, CFs, or hybrid composite containing both of them.

The density of hybrid composites can be calculated using a simple rule of mixture as

$$\rho_c = \rho_{NT}V_{NT} + \rho_{CF}V_{CF} + \rho_m[1 - (V_{NT} + V_{CF})] \quad (17)$$

where ρ_c, ρ_{NT}, ρ_m, and ρ_{CF} are the composite, CNT, matrix, and CFs densities, respectively. In addition, the final materials cost of the composites is defined as

$$C_c = W_m C_m + W_{NT}C_{NT} + W_{CF}C_{CF} \quad (18)$$

where C_c, C_{NT}, C_m, and C_{CF} are the composite, CNTs, matrix and CFs cost per kilogram, respectively. W_{NT}, W_m, and W_{CF} are the nanotube, matrix, and CFs weight fraction,

respectively. Due to several challenges in processing of CNT-reinforced composites, especially with aligned CNTs, the manufacturing costs involved in the preparation of composites are not accounted for.

Cost Versus Property Analysis

The following simple case studies are used in order to rank the feasibility of CNTs and CFs as reinforcing agents. Since cost is a crucial factor in material selection process, the following method compares the material cost for equivalent material property requirements.[64] The property could be any property critical to the application. Therefore, this method determines the weight required by different materials to meet the desired property. From the weight, it determines the cost of the material. For instance, for structural applications, the volume of the material required to carry the load is determined and then, by multiplying with the density, the weight is obtained. If tensile strength is the determining factor for the selection of a material, then the weight required by different materials of choice are determined to have the same tensile strength values.

Case Study I—Beam Designed to Carry an Axial Load

Let us suppose two materials, I and II are selected, for comparison purposes, for the fabrication of a beam. If the member is designed to carry an axial load P, then the cross-sectional area required by beam I and II will be

$$A_I = \frac{P}{\sigma_{\mathrm{I}}} \tag{19}$$

$$A_{\mathrm{II}} = \frac{P}{\sigma_{\mathrm{II}}} \tag{20}$$

where σ_{I} and σ_{II} are the tensile strengths of materials I and II, respectively.

If the member is a solid circular rod, then the ratio of the diameters will be

$$\frac{D_{\mathrm{I}}}{D_{\mathrm{II}}} = \left(\frac{\sigma_{\mathrm{II}}}{\sigma_{\mathrm{I}}}\right)^{1/2} \tag{21}$$

For rods of equal lengths, the weight ratio is

$$\frac{W_{\mathrm{I}}}{W_{\mathrm{II}}} = \frac{\rho_{\mathrm{I}}\sigma_{\mathrm{II}}}{\rho_{\mathrm{II}}\sigma_{\mathrm{I}}} \tag{22}$$

If the cost per unit weight of materials I and II is C_{I} and C_{II}, respectively, then the ratio of total material costs T_{I} and T_{II} will be

$$\frac{T_{\mathrm{I}}}{T_{\mathrm{II}}} = \frac{C_{\mathrm{I}}\rho_{\mathrm{I}}\sigma_{\mathrm{II}}}{C_{\mathrm{II}}\rho_{\mathrm{II}}\sigma_{\mathrm{I}}} \tag{23}$$

The ratio of total material costs for different materials enable us to rank or compare the feasibility of these materials. For example, Equation (23) gives values <1 when material I is more feasible for an application than material II. Of course when material II is more feasible than material I Equation (23) gives values >1.

Case Study II—Beam Designed for Bending Stiffness

Similarly to tensile strength, modulus can be a determining factor for the selection of a material. Let us suppose a beam is designed for bending stiffness.[64] For instance, deflection (δ) of a simply supported beam loaded at the center is given by

$$\delta = \frac{PL^3}{48EI} \tag{24}$$

where P is the load applied, L is the total length of the beam, E is the Young's modulus of the composite, and I is the moment of inertia of the cross-section. The stiffness of the beam may be given by

$$\frac{P}{\delta} = \frac{48EI}{L^3} \tag{25}$$

For the same length of beam, stiffness is proportional to EI. Therefore, for two materials, systems I and II

$$E_{\mathrm{I}}I_{\mathrm{I}} = E_{\mathrm{II}}I_{\mathrm{II}} \tag{26}$$

For a rectangular beam shape, with width b and thickness h, the moment of inertia is given by

$$I = \frac{bh^3}{12} \tag{27}$$

Considering two beams of the same width, from Equation (26) and (27) we have

$$\frac{h_{\mathrm{II}}}{h_{\mathrm{I}}} = \left(\frac{E_{\mathrm{I}}}{E_{\mathrm{II}}}\right)^{1/3} \tag{28}$$

The relative weight can be written as

$$\frac{W_{\mathrm{I}}}{W_{\mathrm{II}}} = \frac{\rho_{\mathrm{I}}}{\rho_{\mathrm{II}}}\left(\frac{E_{\mathrm{II}}}{E_{\mathrm{I}}}\right)^{1/3} \tag{29}$$

Thus, the ratio of total material cost of material I (T_I) and II (T_{II}) can be compared as

$$\frac{T_I}{T_{II}} = \frac{C_I \rho_I}{C_{II} \rho_{II}} \left(\frac{E_{II}}{E_I}\right)^{1/3} \quad (30)$$

Results and Discussion

In order to analyze the feasibility of CNTs as a reinforcement agent in relation to commercially available CFs, we propose different model composites comprising single phase reinforced epoxy composites as well as hybrid composites. Therefore, in order to be as realistic as possible we choose for our simulations:

(i) The stiffest commercial carbon fiber from Toray Industries, M60J, which have a Young's modulus of 588 GPa. This CF also happens to be the most expensive.
(ii) The strongest carbon fiber, T1000GB, which has an ultimate tensile strength of 6.4 GPa.
(iii) The cheapest carbon fiber, T700SC.
(iv) MWCNTs, which are assumed to have a Young's modulus of 950 GPa and tensile strength of 120 GPa.
(v) The epoxy resin/hardener-combination Aradur MY720/Aradur 9664-1, commercialized by Huntsman Advanced Materials. The MY720 system is a high-performance multifunctional resin frequently used in the preparation of prepregs for aircraft structures.

The properties of all the materials considered in our model composites can be seen in Table 3. We have chosen MWCNTs instead of SWCNTS or DWCNTs in our simulations because they can be produced in a higher amount and are the cheapest CNTs commercially available. We also considered only PAN-based CFs due to their higher ductility when compared to pitch based CFs. Considering the theoretical shear strenght $\tau = 50$ MPa[63] as a conservative value in Equation (13), the critical length of MWCNTs described in Table 3 was calculated to be 8.52 μm. It is worth noting that the interfacial shear strength of high-modulus CFs in epoxy usually ranges between 50 and 100 MPa. The effective modulus of the CNTs, i.e., the modulus considering that the outer wall of the nanotubes act as an effective solid fiber, was determined to be 882 GPa.

In addition, in this study we considered the tensile strength of the MWCNTs as the arithmetic mean of the two values obtained by using Equation (14), 11 GPa and Equation (15), 111 GPa. Thus a final value of 61 GPa was assumed during calculations. Even though MWCNTs can be purchased from \$0.60/g, we assumed here a price of \$10/g. We believe this price, or at least a value around this, better represents the CNTs described in Table 3, still with a purity of >99% MWCNTs rather than >99% C. Moreover, we did not take into account any waviness effect of the CNTs and assumed that they have a narrow distribution of diameter and length.

Table 4 gives the properties as calculated according to Equation (8) and (16)–(18), while Figure 3 and 4 are plots of the cost of different composite models as a function of their specific elastic modulus and tensile strength, respectively. The specific stiffness is a parameter which can be used to measure technical performance of one material relative to another. This parameter is of extreme importance in engineering applications, once both high stiffness and low density present major selection criteria.[67] The analyses of the results show that hybrid composites comprising both CNTs and CFs can be the most expensive ones, followed by the CNT-reinforced composites. Carbon fiber-reinforced composites are the cheapest ones. In addition, the highest specific stiffness is obtained by using CFs followed by hybrid composites (Figure 3). Moreover, CFs lead to the lowest specific strength between all composites (Figure 4). The highest specific strengths are offered both by CNT-reinforced composites or hybrid composites.

It is also worth noting that the real advantage of CNTs over CFs, considering the properties calculated here, is their

Table 3. Different properties of the materials composing the composites models considered in the simulations.[2,63–66]

Materials	ρ [g · cm^{-3}]	E [GPa]	σ_M [GPa]	d	l [μm]	Cost [\$ · g^{-1}]
MY720	1.25	3.7	0.060	–	–	0.044
T1000GB	1.80	294	6.4	5 μm	–	0.27
M60J	1.93	588	3.9	5 μm	–	1.8
T700SC	1.80	230	4.9	5 μm	–	0.037
MWCNTs	2.09	950	120	Ext: 15 nm/Int: 4 nm	50	10

ρ, density; E, Young modulus; σ_M, tensile strength; d, diameter; l, length.T1000GB, M60J, and T700SC: Catalog for TORAYCA, Toray Industries Inc. (Toray), High-performance carbon fiber Torayca, 2009.

Table 4. Mechanical properties, density, and price of different composite materials.

MWCNTs [vol.-%]	T1000GB [vol.-%]	M60J [vol.-%]	T700SC [vol.-%]	E_{11} [GPa]	σ_M [GPa]	ρ [g · cm^{-3}]	E_{11}/ρ [GPa/g · cm^{-3}]	σ_M/ρ [GPa/g · cm^{-3}]	Cost [$ · kg^{-1}]
0.5	–	–	–	4.11	0.34	1.25	3.28	0.27	127
1	–	–	–	4.52	0.62	1.26	3.59	0.49	209
2	–	–	–	5.34	1.18	1.27	4.22	0.93	373
5	–	–	–	7.81	2.85	1.29	6.04	2.21	849
10	–	–	–	11.92	5.65	1.33	8.93	4.24	1604
15	–	–	–	16.03	8.44	1.38	11.65	6.14	2312
–	35	–	–	105.30	2.28	1.44	73.00	1.58	143
–	45	–	–	134.34	2.91	1.50	89.71	1.95	166
–	55	–	–	163.36	3.55	1.55	105.23	2.28	188
–	65	–	–	192.40	4.18	1.61	119.69	2.60	208
–	–	35	–	208.20	1.40	1.49	139.92	0.94	841
–	–	45	–	266.64	1.79	1.56	171.36	1.15	1024
–	–	55	–	325.06	2.17	1.62	200.16	1.34	1192
–	–	65	–	383.50	2.56	1.69	226.65	1.51	1346
–	–	–	35	82.90	1.75	1.44	57.47	1.22	41
–	–	–	45	105.54	2.24	1.50	70.47	1.49	40
–	–	–	55	128.16	2.72	1.55	82.55	1.75	40
–	–	–	65	150.80	3.21	1.61	93.81	1.99	39
0.5	64.5	–	–	191.36	4.43	1.61	118.79	2.75	272
1	64	–	–	190.32	4.68	1.61	118.04	2.90	335
2	63	–	–	188.24	5.17	1.62	116.55	3.20	461
5	60	–	–	182.02	6.66	1.62	112.09	4.10	835
10	55	–	–	171.64	9.14	1.64	104.77	5.58	1451
15	50	–	–	161.25	11.61	1.65	97.58	7.03	2056
0.5	–	64.5	–	380.99	2.82	1.69	225.06	1.66	1397
1	–	64	–	378.49	3.08	1.69	223.48	1.82	1448
2	–	63	–	373.48	3.60	1.70	220.31	2.12	1549
5	–	60	–	358.44	5.16	1.70	210.85	3.03	1852
10	–	55	–	333.39	7.76	1.71	195.19	4.54	2354
15	–	50	–	308.33	10.36	1.72	179.68	6.04	2850
0.5	–	–	64.5	150.08	3.46	1.61	93.28	2.15	104
1	–	–	64	149.36	3.72	1.61	92.75	2.31	168
2	–	–	63	147.92	4.23	1.61	91.69	2.62	297
5	–	–	60	143.61	5.76	1.62	88.54	3.55	681
10	–	–	55	136.43	8.31	1.64	83.36	5.08	1311
15	–	–	50	129.24	10.86	1.65	78.28	6.58	1931

E_{11}, Young's modulus in the longitudinal direction; σ_M, ultimate tensile strength; ρ, density.

tensile strength. Also, as the elongation at break of the CFs is below that of most available polymers, an increase in elongation of composites shall not be expected. Nevertheless, CNTs have an elongation at break of up to 15%,[2] which could possibly lead to a higher improvement of the elongation and also ductility of composites.

In order to truly analyze the feasibility of the composite models simulated, we further analyze the cost versus

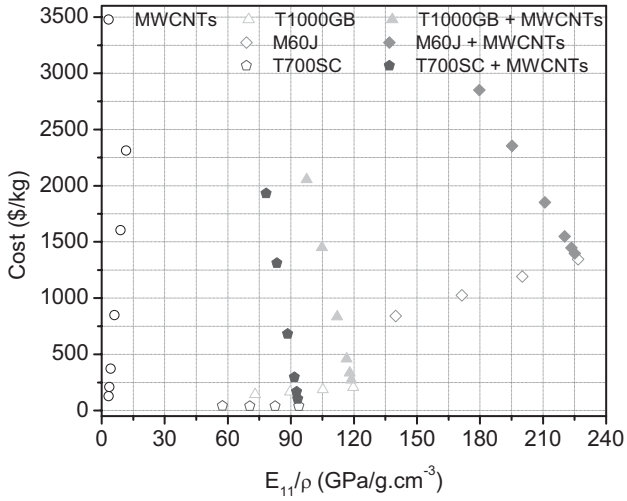


Figure 3. Cost of different composite materials as a function of their specific stiffness.

property relation of the two case studies proposed previously (Cost versus property analysis Section). Using Equation (23), considering tensile strength as the determining factor for the selection, we ranked the feasibility of the composite models showed in Table 4. The results are depicted in Figure 5. The lower the ratio T_I/T_{II} in Equation (23), the more feasible the composite is for the considered application. The CFs T700SC is the most viable option to tensile strengths of up to 3.21 GPa. However, for tensile strengths higher than this value, up to 11.61 GPa, hybrid composites containing CNTs and CFs are the most viable option. The highest tensile strength can only be achieved with hybrid composites (50 vol.-% T1000GB + 15 vol.-% MWCNTs). Note that the CFs considered here does not offer the possibility to obtain composites with tensile

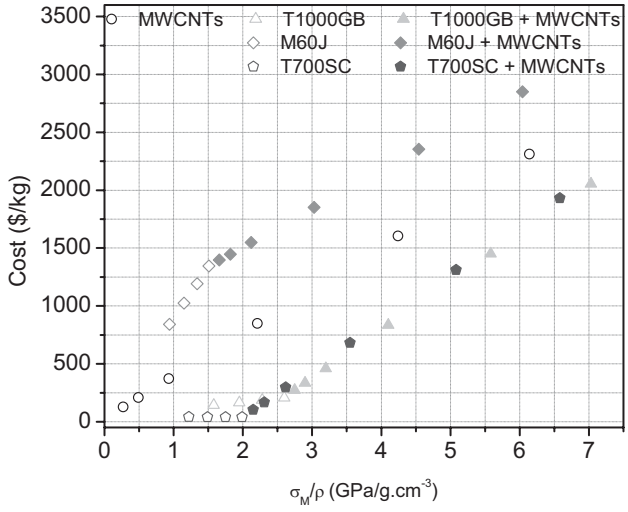


Figure 4. Cost of different composite materials as a function of their specific tensile strength.

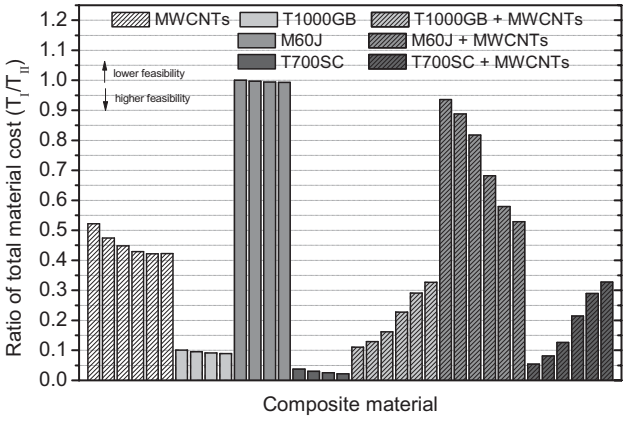


Figure 5. Cost versus property analysis, according to Table 4, considering tensile strength as a determining factor.

strength higher than 4.18 GPa. Figure 5 also shows that CNTs are more viable than the stiffest CFs, M60J. Thus, CNTs are the most viable strengthening option.

Using Equation (30), considering stiffness as the determining factor for the selection, we again ranked the feasibility of the composite materials showed in Table 4. The results are depicted in Figure 6. For Young's moduli of up to 150 GPa, the CFs T700SC are the most viable option. However, for intermediate and high moduli, the CFs T1000GB and M60J become the most viable option, respectively. Despite MWCNTs being the stiffest option of all the fillers considered during calculations, their cost makes them the least viable option.

Since their stength is around 20 times higher than that of the strongest carbon fiber and their elongation is seven times higher, CNTs should be considered as reinforcing filler for polymer nanocomposites. However, in order to achieve their true potential, several challenges have to be faced. CNTs have to be produced with higher purity, integrity, in larger amounts, and at lower price. They have to have longer lengths. Concerning the composites technology,

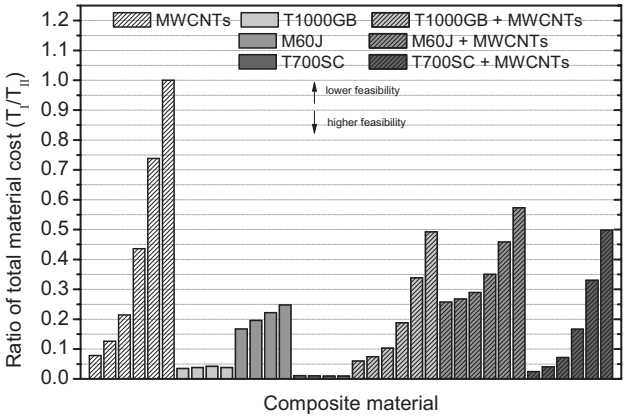


Figure 6. Cost versus property analysis, according to Table 4, considering stiffness as a determining factor.

issues such as orientation of the CNTs, their concentration, interfacial adhesion, distribution, and dispersion have to be overcome.[68]

The global market for chemical fibers and yarns is steadily increasing with growing world population.[69,70] With that, demand for new industrial fibers with special or improved properties emerges. Amongst other things, stronger and/or electrical conductive fibers are requested for applications as reinforcement fibers, smart clothing, electromagnetic shields, or armors.[71] An alternative route toward CNT-based materials with superior properties consists of using CNTs fibers. For production of fibers with diameters ranging between 10 and 100 μm, however, only nanoscaled fillers as CNTs can be used. The superior mechanical and physical properties of individual CNTs provide the input for researchers in developing high-performance continuous fibers based upon CNTs. Although the prices for high-purity nanotubes are still too high for commercial success, a breakthrough is expected within the next few years.

Conclusion

CNT-reinforced polymer composites are an emerging class of high-performance materials with unique and promising properties. The combined use of CNTs with more economic CFs is a way to reduce the cost of advanced composites. In this study, a micromechanical approach used for modeling fiber composites was modified considering the effective fiber concept toward its applicability to hybrid composites. Two case studies were proposed in order to rank the feasibility of CNTs and CFs as reinforcing agents. The results from calculations showed that the use of CFs makes the acquisition of composites with a maximum tensile strengths of 4.18 GPa possible. In addition, the analyses of the cost versus property relation showed that CNTs are the most viable strengthening option for achieve composites with strengths of up to 11.61 GPa. Considering the actual CNTs prices, CFs came out to be the most viable stiffening option, enabling composites with a Young's modulus of up to 383 GPa but with a loss of toughness. The discussion also showed that, in order to achieve the true potential of nanotubes, several challenges have to be faced. CNTs have to be produced with higher purity, integrity, in larger amounts, and at a lower price. They have to have longer lengths. Concerning the composites technology, issues such as orientation of the CNTs, their concentration, interfacial adhesion, distribution, and dispersion have to be overcome.

Acknowledgements: The author M. R. Loos wishes to thank Michelle K. Sing for her help in revising and editing this work.

Received: January 20, 2011; Revised: March 4, 2011; Published online: May 3, 2011; DOI: 10.1002/mats.201100007

Keywords: carbon fibers; carbon nanotubes; composite materials; composites; modeling; nanocomposites; nanotechnology; polymeric materials; reinforcement

[1] S. Iijima, *Nature* **1991**, *58*, 56.
[2] R. Andrews, M. C. Weisenberger, D. Qian, M. S. Meier, K. Cassity, "Carbon Nanotubes, Multi-Walled", in *Nanomaterials: Inorganic and Bioinorganic Perspectives*, Vol. 1, C. Lukehart, Ed., Wiley, UK **2009**, p. 7.
[3] E. T. Thostenson, T.-W. Chou, *J. Phys. D: Appl. Phys.* **2003**, *36*, 573.
[4] J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun'ko, *Carbon* **2006**, *44*, 1624.
[5] C. Zhou, S. Wang, Q. Zhuang, Z. Han, *Carbon* **2008v**, *46*, 1232.
[6] Z. Ying, J. H. Du, S. Bai, F. Li, C. Liu, H. M. Cheng, *Int. J. Nanosci.* **2002**, *1*, 425.
[7] F. H. Gojny, M. H. G. Wichmann, U. Köpke, B. Fiedler, K. Schulte, *Compos. Sci. Technol.* **2004**, *64*, 2363.
[8] P. Guo, X. Chen, X. Gao, H. Song, H. Shen, *Compos. Sci. Technol.* **2007**, *67*, 3331.
[9] L. Valentini, D. Puglia, F. Carniato, E. Boccaleri, L. Marchese, J. M. Kenny, *Compos. Sci. Technol.* **2008**, *68*, 1008.
[10] J. Y. Kim, S. I. Han, S. Hong, *Polymer* **2008**, *49*, 3335.
[11] W. Zou, Z.-J. Du, Y.-X. Liu, X. Yang, H.-Q. Li, C. Zhang, *Compos. Sci. Technol.* **2008**, *68*, 3259.
[12] M.-K. Yeh, T.-H. Hsieh, *Mater. Sci. Eng., A* **2008**, *483–484*, 289.
[13] A. Hernández-Pérez, F. Avilés, A. May-Pat, A. Valadez-González, P. J. Herrera-Franco, P. Bartolo-Pérez, *Compos. Sci. Technol.* **2008**, *68*, 1422.
[14] L. Sun, G. L. Warren, J. Y. O'Reilly, W. N. Everett, S. M. Lee, D. Davis, D. Lagoudas, H.-J. Sue, *Carbon* **2008**, *46*, 320.
[15] S.-Y. Fu, Z.-K. Chen, S. Hong, C. C. Han, *Carbon* **2009**, *47*, 3192.
[16] P. Hubert, B. Ashrafi, K. Adhikari, J. Meredith, S. Vengallatore, J. Guan, B. Simard, *Compos. Sci. Technol.* **2009**, *69*, 2274.
[17] Q. F. Cheng, J. P. Wang, J. J. Wen, C. H. Liu, K. L. Jiang, Q. Q. Li, S. S. Fan, *Carbon* **2010**, *48*, 260.
[18] D. Bikiaris, A. Vassiliou, K. Chrissafis, K. M. Paraskevopoulos, A. Jannakoudakis, A. Docoslis, *Polym. Degrad. Stab.* **2008**, *93*, 952.
[19] B. Fragneaud, K. Masenelli-Varlot, A. Gonzalez-Montiel, M. Terrones, J. Y. Cavaillé, *Compos. Sci. Technol.* **2008**, *68*, 3265.
[20] M. Kang, S. J. Myung, H.-J. Jin, *Polymer* **2006**, *47*, 3961.
[21] H. Meng, G. X. Sui, P. F. Fang, R. Yang, *Polymer* **2008**, *49*, 610.
[22] H. Zeng, C. Gao, Y. Wang, P. C. P. Watts, H. Kong, X. Cui, D. Yan, *Polymer* **2006**, *47*, 113.
[23] C. Zhou, S. Wang, Q. Zhuang, Z. Han, *Carbon* **2008**, *46*, 1232.
[24] C. Zhou, S. Wang, Y. Zhang, Q. Zhuang, Z. Han, *Polymer* **2008**, *49*, 2520.
[25] T. Ogasawara, Y. Ishida, T. Ishikawa, R. Yokota, *Compos. A* **2004**, *35*, 67.
[26] A. R. Adhikari, M. Chipara, K. Lozano, *Mater. Sci. Eng., A* **2009**, *526*, 123.
[27] X. Tong, C. Liu, H. M. Cheng, H. C. Zhao, F. Yang, X. Q. Zhang, *J. Appl. Polym. Sci.* **2004**, *92*, 3697.
[28] T. Liu, Y. Tong, W.-D. Zhang, *Compos. Sci. Technol.* **2007**, *67*, 406.
[29] J. Y. Kim, S. I. Han, S. Hong, *Polymer* **2008**, *49*, 3335.
[30] H. Z. Geng, R. Rosen, B. Zheng, H. Shimoda, L. Fleming, J. Liu, O. Zhou, *Adv. Mater.* **2002**, *14*, 1387.
[31] E. J. Siochi, D. C. Working, C. Park, P. T. Lillehei, J. H. Rouse, C. C. Topping, A. R. Bhattacharyya, S. Kumar, *Compos. B* **2004**, *35*, 439.

[32] B.-K. Zhu, S.-H. Xie, Z.-K. Xu, Y.-Y. Xu, *Compos. Sci. Technol.* **2006**, *66*, 548.
[33] S.-M. Yuen, C.-C. Ma, Y.-Y. Lin, H.-C. Kuan, *Compos. Sci. Technol.* **2007**, *67*, 2564.
[34] H. H. So, J. W. Cho, N. G. Sahoo, *Eur. Polym. J.* **2007**, *43*, 3750.
[35] T. Ogasawara, Y. Ishida, T. Ishikawa, R. Yokota, *Compos. A* **2004**, *35*, 67.
[36] J. Feng, J. Sui, W. Cai, J. Wan, A. N. Chakoli, Z. Gao, *Mater. Sci. Eng., B* **2008**, *150*, 208.
[37] W. Jeong, M. R. Kessler, *Carbon* **2009**, *47*, 2406.
[38] R. Haggenmueller, H. H. Gommans, A. G. Rinzler, J. E. Fischer, K. I. Winey, *Chem. Phys. Lett.* **2000**, *330*, 219.
[39] G.-W. Lee, S. Jagannathan, H. G. Chae, M. L. Minus, S. Kumar, *Polymer* **2008**, *49*, 1831.
[40] K. Prashantha, J. Soulestin, M. F. Lacrampe, P. Krawczak, G. Dupin, M. Claes, *Compos. Sci. Technol.* **2009**, *69*, 1756.
[41] B.-X. Yang, J.-H. Shi, K. P. Pramoda, S. H. Goh, *Compos. Sci. Technol.* **2008**, *68*, 2490.
[42] C. Zhou, S. Wang, Q. Zhuang, Z. Han, *Carbon* **2008**, *46*, 232.
[43] S. Kumar, H. Doshi, M. Srinivasarao, J. O. Park, D. A. Schiraldi, *Polymer* **2002**, *43*, 1701.
[44] A. R. Bhattacharyya, T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge, R. E. Smalley, *Polymer* **2003**, *44*, 2373.
[45] D. S. Bangarusampath, H. Ruckdäschel, V. Altstädt, J. K. W. Sandler, D. Garray, M. S. P. Shaffer, *Polymer* **2009**, *50*, 5803.
[46] D. Qian, E. C. Dickey, R. Andrews, T. Rantell, *Appl. Phys. Lett.* **2000**, *76*, 2868.
[47] B. Fragneaud, K. Masenelli-Varlot, A. Gonzalez-Montiel, M. Terrones, J. Y. Cavaillé, *Compos. Sci. Technol.* **2008**, *68*, 3265.
[48] N. G. Sahoo, Y. C. Jung, H. J. Yoo, J. W. Cho, *Compos. Sci. Technol.* **2007**, *67*, 1920.
[49] P. Guo, X. Chen, X. Gao, H. Song, H. Shen, *Compos. Sci. Technol.* **2007**, *67*, 3331.
[50] M. C. Paiva, B. Zhou, K. A. S. Fernando, Y. Lin, J. M. Kennedy, Y. P. Sun, *Carbon* **2004**, *42*, 2849.
[51] W. Chen, X. Tao, P. Xue, X. Cheng, *Appl. Surf. Sci.* **2005**, *252*, 1404.
[52] Y. Mi, X. Zhang, S. Zhou, J. Cheng, F. Liu, H. Zhu, X. Dong, Z. Jiao, *Compos. A* **2007**, *38*, 2041.
[53] K. P. Ryan, M. Cadek, V. Nicolosi, D. Blond, M. Ruether, G. Armstrong, H. Swan, A. Fonseca, J. B. Nagy, W. K. Maser, W. J. Blau, J. N. Coleman, *Compos. Sci. Technol.* **2007**, *67*, 1640.
[54] M. Wang, K. P. Pramoda, S. H. Goh, *Polymer* **2005**, *46*, 11510.
[55] W. Chen, X. Tao, *Appl. Surf. Sci.* **2006**, *252*, 3547.
[56] S. Ruan, P. Gao, T. X. Yu, *Polymer* **2006**, *47*, 1604.
[57] E. Fietzer, F. Künkele, *High Temp.—High Pressures* **1999**, *22*, 239.
[58] J. C. Halpin, J. L. Kardos, *Polym. Eng. Sci.* **1976**, *16*, 344.
[59] C. L. Tucker III, E. Liang, *Compos. Sci. Technol.* **1999**, *59*, 655.
[60] F. H. Gojny, M. H. C. Wichmann, U. Köpke, B. Fiedler, K. Schulte, *Compos. Sci. Technol.* **2004**, *64*, 2363.
[61] S. Peeterbroeck, L. Breugelmans, M. Alexandre, J. B. Nagy, P. Viville, R. Lazzaroni, *Compos. Sci. Technol.* **2007**, *67*, 1659.
[62] C. A. Cooper, S. R. Cohen, A. H. Barber, H. D. Wagner, *Appl. Phys. Lett.* **2002**, *81*, 3873.
[63] H. D. Wagner, *Chem. Phys. Lett.* **2002**, *361*, 57.
[64] S. Mazumdar, *Composites Manufacturing: Materials, Product, and Process Engineering*, CRC Publisher, USA **2001**.
[65] K. Stano, K. Koziol, M. Pick, M. Motta, A. Moisala, J. Vilatela, S. Frasier, A. Windle, *Int. J. Mater. Form* **2008**, *1*, 59.
[66] V. N. Popov, *Mater. Sci. Eng.* **2004**, *43*, 61.
[67] T. Xiao, Y. Ren, K. Liao, P. Wu, F. Li, H. M. Cheng, *Compos. Sci. Technol.* **2008**, *68*, 2937.
[68] M. R. Loos, K. Schulte, V. Abetz, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5172.
[69] P. Pötschke, H. Brünig, A. Janke, D. Fischer, D. Jehnichen, *Polymer* **2005**, *46*, 10355.
[70] A. Marcin, *Prog. Polym. Sci.* **2002**, *27*, 853.
[71] A. B. Dalton, S. Collins, J. Razal, E. Munoz, V. H. Ebron, B. G. Kim, J. N. Coleman, J. P. Ferraris, R. H. Baughman, *J. Mater. Chem.* **2004**, *14*, 1.