

Nanomechanical characterization of dispersion and its effects in nano-enhanced polymers and polymer composites

Alan L. Gershon · Daniel P. Cole · Arun K. Kota ·
Hugh A. Bruck

Received: 30 January 2010 / Accepted: 4 May 2010 / Published online: 22 June 2010
© Springer Science+Business Media, LLC 2010

Abstract In this paper, a new approach for characterizing dispersion in nano-enhanced polymers and polymer composites using nanomechanical characterization is developed. Dispersion of Carbon nanofibers (CNFs) as a model nanoscale ingredient is characterized in two model polymer systems: (a) a thermoplastic polymer processed using a Twin Screw Extruder, and (b) a thermoset epoxy processed using sonication during solvent processing. For the first time, the modulus of agglomerated nanofibers was isolated from the polymer matrix enhanced with dispersed nanofibers by using nanomechanical characterization. Thus, it was possible to use these nanomechanical properties in a microstructural model using a Rule-of-Mixtures (ROM) formulation to determine the *fraction of dispersed nanofibers*, which yielded a *dispersion limit* of 3 vol% CNFs in the nano-enhanced thermoplastic polymer and 3.5 vol% CNFs in the nano-enhanced thermoset epoxy. It was also possible to predict the modulus measured using microtensile testing, and to determine an effective modulus of 30 GPa for the CNFs, which was attributed to a spring-like effect from kinking along the nanofibers. Applying this characterization to control of dispersion through sonication in the nano-enhanced thermoset epoxy, it was possible to determine the *degree of dispersion* with sonication time which was described using an Avrami equation. Finally, a carbon-fiber mat was used to create a model nano-enhanced polymer composite whose properties were found to be insensitive to sonication time due to filtering effects from the carbon-fiber mat and varied with CNF concentration in a

manner where the CNF modulus could be extrapolated to 30 GPa, consistent with the nano-enhanced polymers.

Introduction

With the current focus on nanotechnology, it has become possible to engineer composite materials at the smallest length scales using nanostructured ingredients to control the distribution of properties and interaction of different material phases at the nanoscale [1–3]. As a result, the development of advanced composite materials can now focus on the addition of limited quantities of nanoscale ingredients in order to *nano-enhance* mechanical performance. In this manner, certain properties of these composite materials, such as thermal conductivity, stiffness, and strength, may be tailored beyond the limitations of current microscale technology [4]. Thus, it has now become possible to create nano-enhanced polymer and polymer composites that have complex microstructures due to the nanoscale ingredients.

The microstructures that form by adding nanoscale ingredients to polymers and polymer composites are typically considered to organize at the nanoscale and then proceed to form microscale structures in what is termed a bottom-up approach. When there is no interaction between the nanoscale ingredients, they are considered *dispersed*. At very low wt% of a nanoscale ingredient, a three-dimensional interconnected network forms in a sample with sufficient dispersion that is considered *percolated*. At this point, the nano-enhanced material displays a significant change in certain properties, such as electrical conductivity. If this percolation is not continuous throughout the material but is highly localized, then it is considered *agglomerated*. The formation of a complex microstructure

A. L. Gershon · D. P. Cole · A. K. Kota · H. A. Bruck (✉)
Department of Mechanical Engineering, University of Maryland,
College Park, MD 20742, USA
e-mail: bruck@umd.edu

consisting of the dispersed/percolated and agglomerated nanoscale ingredients can be viewed as hierarchically structured. Both the degree of dispersion and concentration of nanoscale ingredients play a key role in the formation of the hierarchical structure, and the ability to control these parameters can be important for structure–property relationships. Alternatively, microscale ingredients like carbon-fibers can be added to the nanoscale ingredients in order to create hierarchical structures using what would be considered more of a top–down approach where the microscale features are predetermined rather than being assembled from the nanoscale.

The greatest stumbling block to the large-scale production and commercialization of nano-enhanced polymers and polymer composites is the dearth of cost effective methods for controlling the dispersion of nanoscale ingredients in polymer matrices. There is a critical need for establishing processing techniques that will be effective at the nanoscale yet are applicable to macroscopic processing [5]. The absence of structure–property relationships presents a significant impediment to a more extensive use of nano-enhanced polymers and polymer composites. Some work in this field has been accomplished using carbon nanotube (CNT) reinforced epoxies [6–11] and functionalizing carbon-fibers with CNTs for composites [12], but in general the structure and properties of these nano-enhanced polymers (a.k.a., polymer nanocomposites) are still being established [13–17]. Thus, there is a need for new techniques to characterizing and modeling the structure–property relationships in nano-enhanced polymers and polymer composites. For example, quantitative techniques for characterizing dispersion have been developed using scanning transmission electron microscopy and image processing to relate to properties such as electrical conductivity [18].

In this paper, a new approach is developed for characterizing dispersion by using nanomechanical characterization in a microstructural model based on a Rule-of-Mixtures (ROM) formulation. Nano-enhanced polymers are created from two model polymer systems: (a) high impact polystyrene (HIPS) as a thermoplastic polymer, and (b) West System 105 as a thermoset epoxy. Carbon nanofibers (CNFs) were used as the nanoscale ingredient to study dispersion. The nano-enhanced thermoplastic polymer is processed using a Twin Screw Extruder (TSE) in a short-residence time, high-shear rate continuous mixing process, while the nano-enhanced thermoset epoxy is processed using sonication during solvent processing in a long-residence time, low-shear rate batch mixing process. The nano-enhanced thermoplastic polymer is first used to develop a microstructural model of the effects of dispersion on the tensile modulus that is based on a ROM formulation using nanomechanical characterization. The nano-enhanced

thermoset epoxy was then studied at various sonication times to apply the dispersion characterization model and understand the effects of processing on the control of dispersion. Finally, the nano-enhanced thermoset epoxy is used to infiltrate a carbon-fiber mat to create a model nano-enhanced polymer composite to compare the effects on dispersion with the nano-enhanced polymers processing.

Materials

Nano-enhanced thermoplastic polymer

In order to produce the nano-enhanced polymers used in this research, a model nanoscale filler and a compatible polymer matrix were chosen that are appropriate for use in a TSE. PR-19 grade Carbon Nanofibers (CNFs) were obtained from Applied Sciences and used as nanoscale filler. They have a diameter of 100–200 nm, length 10–30 μm , and density 1.87 g/cm^3 . A high-strength thermoplastic, high impact polystyrene (HIPS) was obtained from Nova Chemicals and previously used as a thermoplastic matrix for establishing processing–structure–property relationships in polymer nanocomposites that were processed in a TSE [19–23].

A 28-mm-screw diameter Werner and Pfleiderer co-rotating, intermeshing TSE was used with a slit die (25 mm wide \times 1 mm high) to produce the nano-enhanced thermoplastic polymers. Feeders fed both CNFs and HIPS by weight into the TSE. The extruder was operated at a screw speed of 200 rpm and operating temperatures were 210 $^\circ\text{C}$ for all five barrel zones and 165 $^\circ\text{C}$ at the die. The extrudate was passed through a slit die in order to prepare 1 mm thick specimens for mechanical characterization. To create the polymer nanocomposite, 0.2 lb/h of CNFs were step fed into a 1.8 lb/h steady flow of the HIPS melt, yielding specimens ranging from 0 to 10 wt% CNF via a combinatorial approach previously developed for polymer nanocomposites [21].

Nano-enhanced thermoset epoxy

West System 105 epoxy resin with 206 hardener was chosen as the polymer matrix for the nano-enhanced thermoset epoxy because of its pervasive application in marine structures. In order to create the nano-enhanced composite materials for mechanical characterization, CNFs were added to the epoxy resin. Once thoroughly mixed, the resin–CNF mixture was placed in a VWR Aquasonic model 75D ultrasonic bath for 1.5, 3, or 6 h to help break up agglomerations of CNFs. The ultrasonic bath produced an average sonic power of 90 Watts, and a peak power of 180 Watts. A fourth set of composites was made with no

sonication. After sonication, the resin–CNF mixture was placed in an ice bath to cool the mixture down to room temperature, which prolongs the useful working time after the hardener is added.

Once the resin–CNF mixture is at room temperature, West System 206 hardener was added in the ratio of 5:1 epoxy to hardener. Immediately after adding the hardener, the mixture was homogenized using a dual propeller mixing impeller. The mixing impeller was mounted on a drill press, and the epoxy, hardener and CNF mixture was mixed for 3 min. Mixtures containing CNFs were made with 1, 3, 5, 7, and 10 wt%. After mixing, the nano-enhanced epoxy was degassed in a vacuum chamber at 560 mmHg for 15 min. The composite was sandwiched between two 0.5-mm-thick sheets of Nylon 6/6, and sealed in a polyethylene bag fitted with a valve attached to a Gast ROC-R model ROA-P131-AA vacuum pump. A cotton mat was placed beneath the valve to prevent blockages in air flow, as well as to prevent excess polymer from entering the vacuum lines. The polyethylene bag containing the curing composites was placed between the platens of a Carver hydraulic unit model #3912 press using minimal force to ensure an even thickness throughout the material. These composites were cured at 450 mmHg vacuum at room temperature for 48 h, and then cured for an additional 48 h at 80 °C at atmospheric pressure.

Experimental methods

Nanomechanical characterization

A Hysitron TriboIndenter[®] was used to measure material properties at the nanoscale. The TriboIndenter is capable of nanoindentation in both a quasi-static mode and in a nanoscale dynamic mechanical analysis (nanoDMA) mode. The spatial resolution in both modes is limited by the nanoindenter tip radius. In this research, a Berkovich tip was used, with a radius of approximately 150 nm. The Berkovich tip is pyramidal, with a total angle of 142.3°. In quasi-static mode, the TriboIndenter was used to determine the hardness and reduced modulus of materials at the nanoscale at a desired indentation depth for individual features of the microstructure, such as the microscale agglomerates and the polymer matrix with dispersed CNFs.

Microtensile testing

A custom-built microtensile tester was used to accurately test small-scale specimens using loads of less than 25 N, which accommodated sub-scale ASTM tensile specimens

of the nano-enhanced polymer and polymer composites with a total length of 25.4 mm, a gauge length of 5 mm, a gauge width of 1.25 mm, an overall width of 3.75 mm, and approximate thickness ranges between 100 µm and 1 mm [23]. Specimens were machined from CAD drawings that were created in ProEngineer Wildfire 3.0 and CNC machined on a Boxford A3HSRmi² with a 0.40 mm end mill. The microtensile tester employed custom linear air bearings from Nelson Air Corporation to minimize friction, and New Focus model 8302 picomotors for actuation. A Point Grey Flea2 (FL2-14S3C) digital camera mated to a stereo microscope from Edmund Industrial Optics was used as a video extensometer for data acquisition of the strain in the gage section of the specimen. The sample was illuminated with an Edmund Industrial Optics model MI-150 high intensity fiber optic illuminator. The video extensometer uses Correlated Solutions (Columbia, SC) Vic-Gauge 2006 software to acquire strain data through real-time Digital Image Correlation (DIC) analysis. Vic-Gauge 2006 also allows the acquisition of load data, which is acquired after processing via a National Instruments PXI-1042. Customized picomotor control software was written in National Instruments LabView to apply quasi-static loading at strain rates of 10⁻⁴/s.

Microstructural characterization

To characterize the microstructure of our nano-enhanced polymers and polymer composites, three different microstructural characterization techniques were used. In order to determine the effects of sonication on the structure of the nano-enhanced thermoset epoxy, optical micrographs were obtained with an OptixCam Summit 5.0 digital camera mated to a Versamet-2 Unitron 7103 inverted microscope with a ×5 objective lens using transmitted light. To directly visualize the CNF agglomerates and dispersion, a FEI Quanta Environmental Scanning Electron Microscope (SEM) with advanced Energy Dispersive Spectroscopy (EDS) was used. To provide more detailed information of the microstructure at the nanoscale through property distributions, the Hysitron TriboIndenter was used in nanoDMA mode to raster across the specimen surface while oscillating the tip in a controlled manner. Thus, in nanoDMA mode it is possible to measure the viscoelastic properties at each of the 256 × 256 points in a region of interest of up to 60 µm², which is referred to as *modulus mapping*. Modulus mapping can therefore provide an image of dynamic nanomechanical properties, however, the contact depth is much shallower than what is used for an individual indent because forces are typically limited to 10 µN or less in order to raster the surface.

Experimental results and discussion

Characterizing dispersion in nano-enhanced thermoplastic polymer using nanomechanical characterization

The nano-enhanced thermoplastic polymer was processed in a TSE to first study dispersion in a short residence time, high-shear rate continuous mixing process. Secondary Electron SEM images from a 5 wt% CNF in HIPS specimen in Fig. 1a clearly indicate the presence of agglomerates of CNFs in the nano-enhanced polymers, which were determined to be 10 vol% through image analysis. Additional details of the structure of the agglomerates and the dispersion of the CNFs can be seen in Fig. 2a from a backscattered SEM image of the 5 wt% CNF in HIPS specimen. This gives rise to the microstructural model of the hierarchical structure seen in Fig. 1b that is formed by the interaction between the agglomerates and the polymer matrix reinforced by a percolated network of dispersed CNFs.

Using nanomechanical characterization, it was possible to isolate the modulus of the microscale structures represented by the agglomeration of CNFs from that of the matrix material reinforced by dispersed CNFs. By isolating the moduli of the microscale structures from the nano-reinforced polymer matrix, it is possible to develop a dispersion characterization model for the effects of nanofiber dispersion in a manner that is similar to a model we

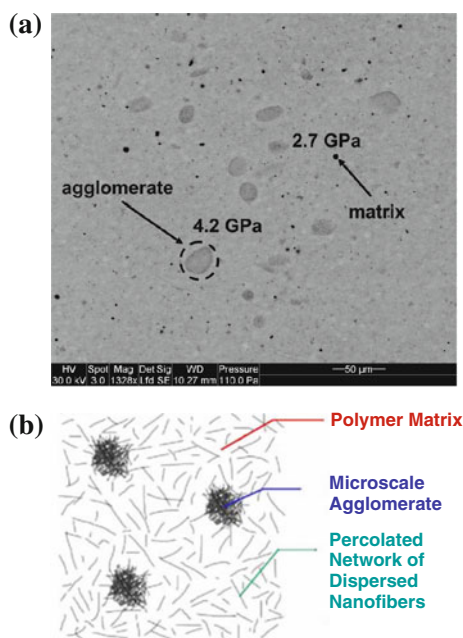


Fig. 1 **a** Averaged nanomechanical characterization results agglomerates and matrix in HIPS nano-enhanced with 5 wt% CNF that was used as a model thermoplastic polymer processed in a TSE, and **b** the microstructural model of the nano-enhanced polymer

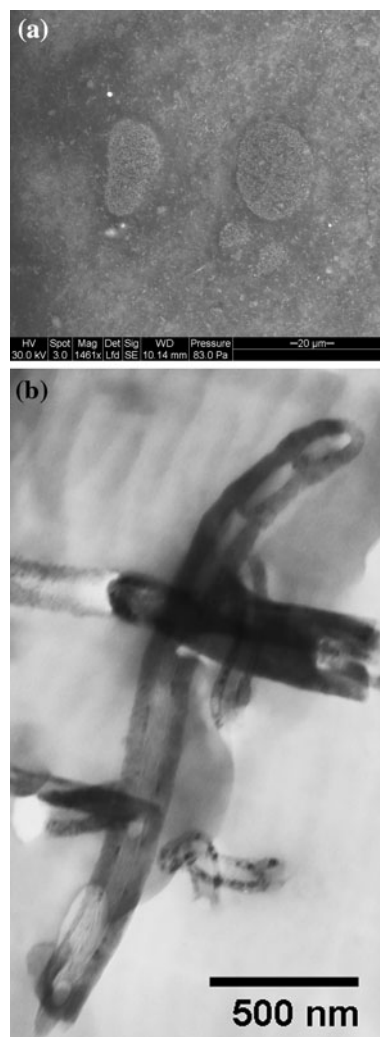


Fig. 2 **a** Secondary electron SEM image of agglomerates and surrounding dispersed/percolated CNFs from a 10 wt% CNF in HIPS specimen, and **b** TEM image of kinking in nanofibers

previously developed for describing the effects of MWCNT percolation on rheological properties of the composite in the melt state [20]. For the 5 wt% CNF specimens, the average modulus of the agglomerates was determined to be 4.2 GPa, while the matrix surrounding it was 2.7 GPa.

In the dispersion characterization model, the percolated network of CNFs forms an interpenetrating-phase microstructure with the remaining polymer matrix, similar to the previously developed model for rheological properties. The matrix is reinforced by the microscale agglomerates of nanofibers, which were found not to be fully infiltrated by the polymer and were thus considered to be highly filled CNF regions coated by the polymer. To determine the relative concentration of agglomerated CNFs, $v_{\text{CNF agglomerate}}$, in the composite, the volume fraction of the agglomerates, $v_{\text{agglomerate}}$, was directly determined from the optical

micrograph, and then used with the modulus of the CNFs, E_{CNF} , and the modulus of the agglomerate determined from nanoindentation, $E_{agglomerate}$, in a linear ROM formulation (i.e., isostrain) as follows:

$$v_{CNF_{agglomerate}} = \frac{E_{agglomerate} v_{agglomerate}}{E_{CNF}} \tag{1}$$

In addition, the elastic modulus of the matrix determined from nanoindentation, E_{matrix} , was also used to determine the volume fraction of fibers in the matrix, $v_{CNF_{matrix}}$, in a linear ROM formulation as follows since the resulting microstructure formed by the polymer and percolated CNFs was modeled as an interpenetrating phase composite:

$$v_{CNF_{matrix}} = \frac{E_{matrix} - E_{polymer}}{E_{CNF} - E_{polymer}} \tag{2}$$

It was then possible to calculate the macroscale elastic modulus of the composite, $E_{composite}$, from the modulus of the matrix and the modulus of the reinforcing agglomerated CNF particles using an inverse ROM formulation (i.e., isostress) as follows:

$$E_{composite} = 1 / \left(\frac{1 - v_{agglomerate}}{E_{matrix}} + \frac{v_{agglomerate}}{E_{agglomerate}} \right) \tag{3}$$

Experimental data for the nano-enhanced thermoplastic polymer processed using TSE can be seen in Table 1. Since the nanoscale contribution to the modulus from the CNFs was not known, it was determined indirectly by fitting Eqs. 1 and 2 in the model to the data in Table 1 using a modulus of 1.95 GPa for the thermoplastic polymer matrix. The results can be seen in Fig. 3a and indicate that E_{CNF} is 30 GPa, which is at least an order of magnitude lower than typically assumed. One explanation for this is kinking along the nanofibers cause them to behave with a spring-like effect that reduces the effective stiffness (see TEM images of nanofibers from the nano-enhanced thermoplastic polymer in Fig. 2b). The substantial reduction in modulus due to waviness of carbon nanofibers has been recently reported through direct measurements [24]. The nanomechanical moduli were then used with Eq. 3 to compare with the microtensile testing data previous

Table 1 Constants obtained for the ROM formulation for quantifying the effects of the dispersion of CNFs on the mechanical properties of a nano-enhanced thermoplastic polymer

wt% CNF	v_{CNF}	$v_{agglomerate}$	E_{matrix} (Gpa)	$E_{agglomerate}$ (GPa)
1	0.007	0.02	2.1	4.1
3	0.020	0.06	2.4	4.0
5	0.034	0.10	2.7	4.2
7	0.048	0.20	2.8	4.1
10	0.069	0.30	3.0	4.6

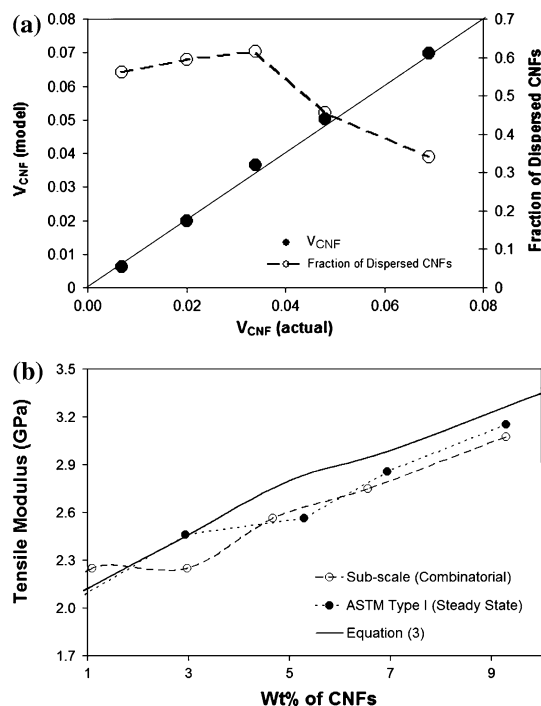


Fig. 3 a Fit of actual volume fraction of CNFs to the model using a modulus for CNFs of 24 GPa, and b fit of Eq. 3 to data for the nano-enhanced thermoplastic polymer processed in a TSE using E_{CNF} of 30 GPa

determined for the nano-enhanced thermoplastic polymer in Fig. 3b [23]. This data indicated reasonable correlation that supported the assumed isostress reinforcement by the agglomerated CNF particles of the polymer matrix with the percolated CNF network.

From the data in Table 1, it was also possible to use Eqs. 1 and 2 to determine the *fraction of dispersed nanofibers* in the polymer matrix. The results can also be seen in Fig. 3a. These results indicate that approximately 70–75% of the CNFs are dispersed by the TSE process at lower wt% loadings. However, as the loading is increased, the volume fraction of dispersed CNFs decreases. In fact, the decrease is consistent with a maximum volume fraction of dispersed CNFs of approximately 3 vol%. Thus, it would appear that there is a *dispersion limit* to the amount of CNFs that can be dispersed in the polymer matrix using the TSE process. This dispersion limit corresponded to the percolation threshold previously determined for these polymer nanocomposites, and could explain why only limited quantities of nanoscale ingredients are typically used to nano-enhance polymers [22].

In addition to using this model to extract the modulus of the CNF, Eq. 3 can be used to determine the maximum value that would be expected for no agglomerates. For example, a 5 wt% CNF-HIPS polymer nanocomposite would have a maximum modulus of 2.9 GPa, which is

only about 11% greater than the 2.6 GPa that was obtained from a sample with 10 vol% agglomerates. Thus, it may be concluded that the modulus of the polymer nanocomposite will change only modestly with further dispersion.

Control of dispersion in nano-enhanced thermoset epoxy using sonication

In addition to studying dispersion in the nano-enhanced thermoplastic polymer processed using the TSE, the nano-enhanced thermoset epoxy was prepared using sonication during solvent processing to control dispersion in a long-residence time, low-shear rate batch mixing process. Optical micrographs of the nano-enhanced thermoset epoxy can be seen at different sonication times in Fig. 4 for 7 wt% CNF, which was the highest loading whose microstructure could be easily distinguished using the transmitted light mode. It can clearly be seen that the length of sonication time has a direct effect upon the agglomeration size and the subsequent dispersion of the CNFs into the polymer matrix. As the CNFs become more dispersed and percolated, the overall transmissivity of the composite decreases and the images become darker. It does appear, however, that the amount of energy delivered to the agglomerations during sonication is not sufficient to completely disperse the CNFs. Thus, the optical micrographs provide direct qualitative evidence of the break-up of agglomerates and increase in dispersion with sonication time.

More quantitative characterization of the control of dispersion with sonication time was obtained using the new

characterization approach. Microtensile testing results can be seen for 1, 3, 5, 7, and 10 wt% CNF in Fig. 5 for tensile modulus, tensile strength, and strain to failure as a function of the wt% CNF loading. In Fig. 6, the data is presented as a function of the sonication time. In both figures, it can easily be seen that the material properties are affected by sonication time. However, it appears that increasing the wt% of CNFs does not necessarily result in a continuous increase in the mechanical properties with sonication time. Thus, it would appear that the evidence of the limit of dispersion seen in the optical micrographs is also evident in the tensile properties.

Optical measurements of the volume fraction of agglomerates and average nanomechanical measurements of the moduli for the agglomerates and matrix can be seen in Table 2. A plot of the resulting moduli obtained from Eq. 3 for the composites as a function of the sonication time can be seen with the experimental data in Fig. 6a using the previously determined modulus of 30 GPa for the CNFs. The moduli obtained from the model are very similar to the experimental results, thus indicating that the characterization approach can be used to determine the effects of dispersion on the tensile modulus of the nano-enhanced thermoset epoxy reasonably well. The subsequent volume fraction of CNFs determined from using Eqs. 2 and 3 of the model can be seen in Fig. 7, and are also in good agreement with the actual CNF volume fraction.

The values for the model indicate that there is a volume fraction of agglomerates that is significantly greater than

Fig. 4 Effects of sonication on hierarchical structure in 7 wt% CNF in thermoset epoxy. **a** No sonication, **b** 90 min sonication, **c** 3 h sonication, **d** 6 h sonication. Images obtained using transmission light microscopy

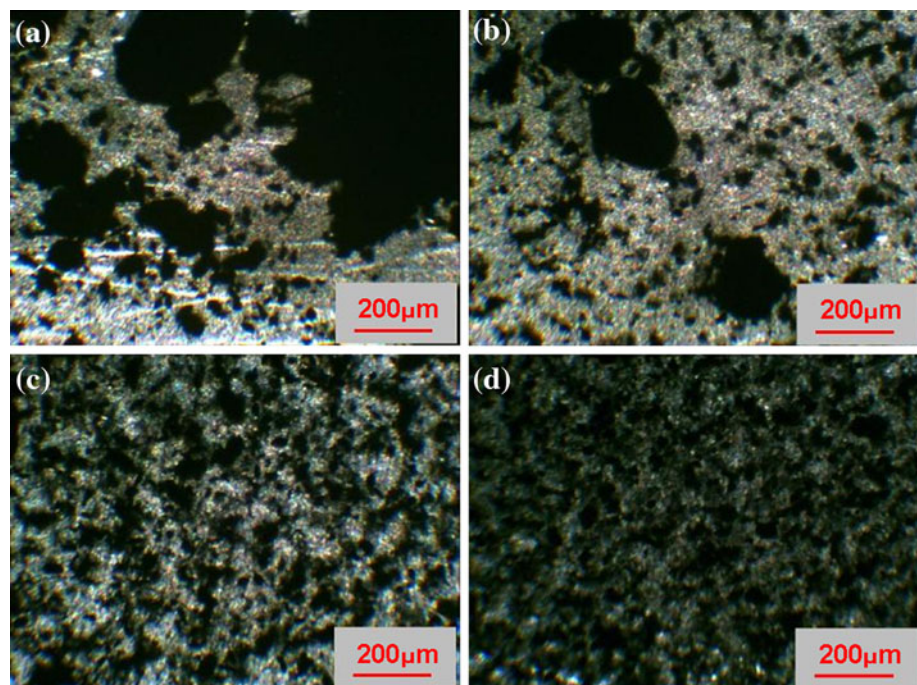


Fig. 5 Mechanical properties as a function of CNF loading nano-enhanced thermoset epoxy: **a** tensile modulus, **b** tensile strength, and **c** strain to failure

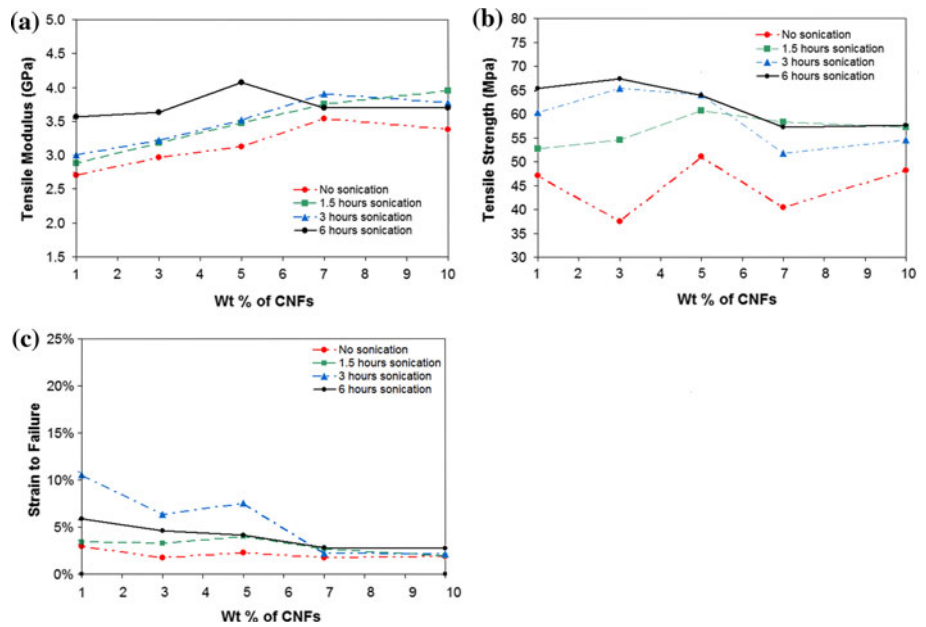
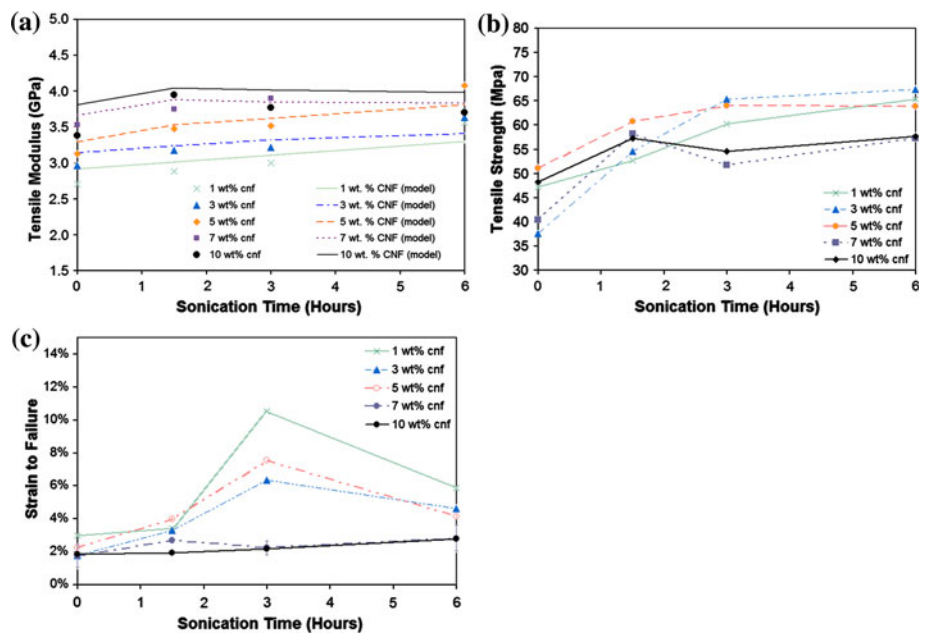


Fig. 6 Mechanical properties as a function of sonication time of the nano-enhanced thermoset epoxy: **a** tensile modulus, **b** strength and **c** strain to failure. Model predictions from Eq. 3 for the tensile modulus of the nano-enhanced thermoset epoxy can be seen in (a) using E_{CNF} of 30 GPa



that expected for the wt% CNFs since the agglomerates are dispersed over larger volumes. Furthermore, they are much harder than the matrix material, consistent with the effects seen in the melt-processed thermoplastic polymers. As sonication time increases, these agglomerates are broken up, but there appears to be a dispersion limit to the amount of dispersed CNFs that can be absorbed into the matrix. This value was approximately 3.5 vol% from the measurements of agglomerate volume fraction and the properties of the agglomerates, and indicates a dispersion limit for the CNFs in the sonicated nano-enhanced thermoset

epoxy that is similar to that observed in the nano-enhanced thermoplastic polymer processed using the TSE. This dispersion limit is most probably a function of the temperature and the ultrasonic energy. Increases in both will most likely increase the dispersion limit to higher values due to lower viscosity.

From the data in Table 2, it is now possible to determine the *degree of dispersion*, D , as a function of sonication time, t , where the degree of dispersion is defined as the instantaneous concentration of agglomerated CNFs, $v_{CNF\text{agglomerate}}(t)$, relative to the dispersion limit, $v_{CNF\text{agglomerate}}(\infty)$, as follows:

Table 2 Constants obtained for the ROM formulation that quantifies effects of sonication time on tensile modulus of the composite due to enhanced dispersion of CNFs

wt% CNF	Sonication time (h)	$v_{\text{agglomerate}}$	E_{matrix} (GPa)	$E_{\text{agglomerate}}$ (GPa)
1	0	0.02	2.9	4.2
1	1.5	0.01	3	4.4
1	3	0.01	3.1	4.3
1	6	0.00	3.3	n/a
3	0	0.06	3.1	4.0
3	1.5	0.04	3.2	4.5
3	3	0.02	3.3	4.6
3	6	0.01	3.4	4.3
5	0	0.10	3.2	4.4
5	1.5	0.06	3.5	4.1
5	3	0.02	3.6	4.8
5	6	0.01	3.8	4.7
7	0	0.14	3.5	5.1
7	1.5	0.10	3.8	4.8
7	3	0.06	3.8	4.7
7	6	0.04	3.8	4.9
10	0	0.18	3.6	5.2
10	1.5	0.16	3.9	5.0
10	3	0.14	3.9	4.9
10	6	0.12	3.9	4.7

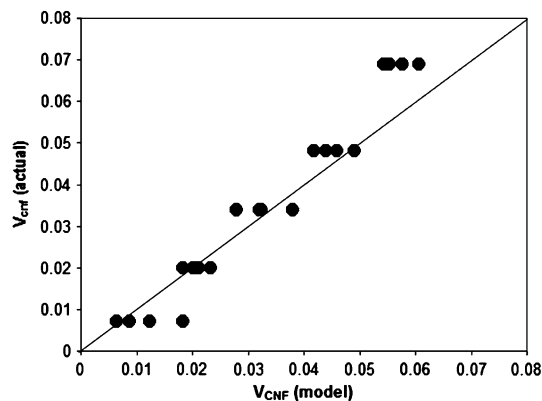


Fig. 7 Fit of actual volume fraction of CNFs to the model using a modulus for CNFs of 30 GPa

$$D = 1 - \frac{v_{\text{CNFagglomerate}}(t) - v_{\text{CNFagglomerate}}(0)}{v_{\text{CNFagglomerate}}(\infty) - v_{\text{CNFagglomerate}}(0)} \quad (4)$$

The dispersion process itself can be modeled using the following conventional Avrami equation for nucleation and growth:

$$D = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^p\right) \quad (5)$$

where τ is the time constant for the dispersion process and p is the Avrami exponent. Thus, the Avrami equation can be used to extract the time constant for the dispersion process associated with sonication. The degree of dispersion

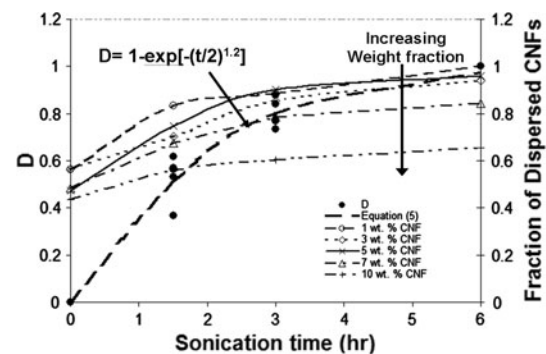


Fig. 8 (left axis) The degree of dispersion versus sonication time with the Avrami fit to determine the time constant for processing the nano-enhanced thermoset epoxy, and (right axis) the fraction of dispersed CNFs at each weight fraction indicating saturation at higher weight fractions

determined from the data in Table 1 and the resulting fit of the Avrami equation can be seen in Fig. 8, along with the fraction of CNFs that are dispersed. The resulting time constant for the diffusion process was determined to be 2 h, while the exponent was determined to be 1.2. Thus, the physics of the dispersion process for sonication is such that 2 h would be the time required to achieve reasonable enhancements of dispersion. Also, as the weight fraction increases, the fraction of dispersed CNFs becomes insensitive to the sonication time. This is because there are enough CNFs at higher weight fraction to disperse without sonication close to the dispersion limit.

Characterization of dispersion for nano-enhanced polymer composite

After characterizing the effects of sonication on dispersion in nano-enhanced polymers using the thermoset epoxy nanocomposite, the effects in nano-enhanced polymer composites were studied by using the nano-enhanced thermoset epoxy to infiltrate a 0.05 mm thick carbon-fiber mat. The carbon-fiber mat that was chosen is engineered to not significantly enhance structural properties due to its intended use for EMF shielding, therefore the microfibers are not expected to provide substantial enhancement of the epoxy properties upon infiltration unless they interact with the CNFs. Only 3 wt% of carbon-fiber mat was used, which resulted in a tensile modulus of 3.4 GPa that was approximately 25% higher than the tensile modulus of 2.8 GPa for the next epoxy with a substantial decrease in strain to failure from approximately 0.05 to approximately 0.01 and no significant impact on tensile strength. Tests were conducted using the CNF nano-enhanced epoxy at different sonication times and the 1, 3, 5, 7, and 10 wt% loadings that were previously investigated.

The nano-enhanced polymer composite did not appear to be as sensitive to sonication time as the nanocomposite without the carbon-fiber mat. As the uncured nano-enhanced thermoset epoxy flows around the carbon-fibers, CNFs agglomerates tended to be attracted to the intersection of microfibers and along them. Transmitted light micrographs can be seen in Fig. 9, where once again the

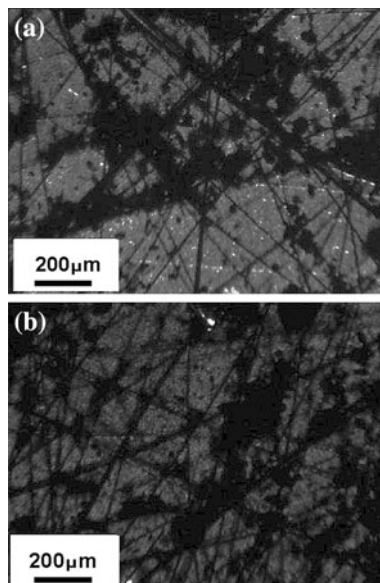


Fig. 9 Agglomeration of CNFs at carbon-fiber junctions in the model nano-enhanced thermoset epoxy with 5 wt% CNF and 3 wt% CMF reinforcement: **a** 90 min sonication and greater dispersion between the carbon-fibers at **b** 6 h sonication. Images were obtained using transmission light microscopy

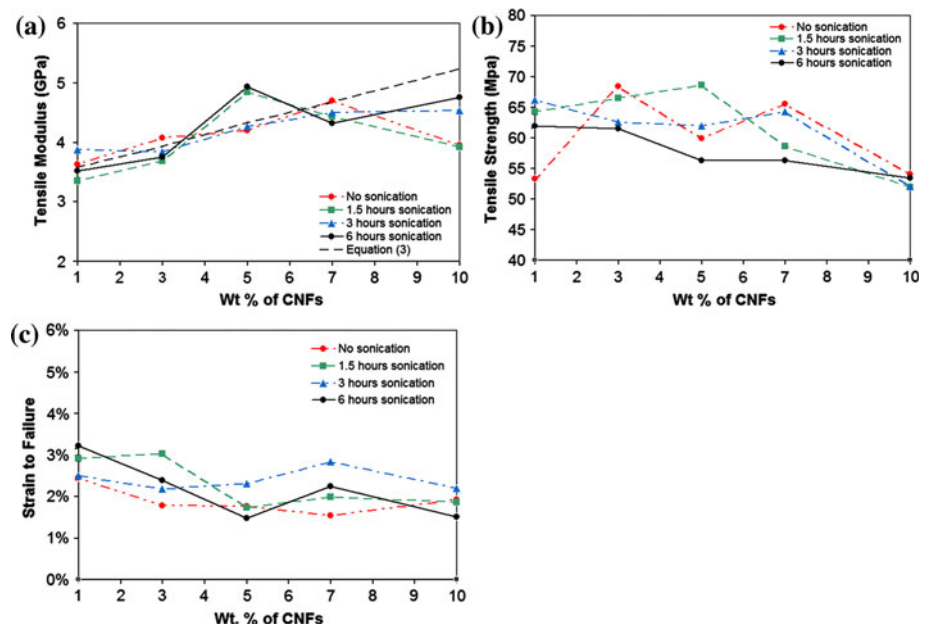
enhanced dispersion of the CNFs due to sonication time is directly evident by the darker matrix.

Microtensile results for the nano-enhanced polymer composites can be seen in Fig. 10 as a function of wt% CNF for the tensile modulus, tensile strength, and the strain to failure. Addition of the CNFs to the epoxy with the carbon-fiber mat does change the mechanical properties substantially. Upon addition of over 5 wt% CNF, the modulus of the epoxy can increase by more than 50% to between 4.5 and 5 GPa. However, the strength does not change appreciably until 10 wt% CNF loading. Furthermore, it is even greater than observed for the nano-enhanced thermoset epoxy, although the strain to failure is much lower. Thus, it would appear that the CNFs are interacting with the carbon-fibers in such a way that they are enhancing load transfer and therefore enabling the carbon-fibers to constrain the epoxy when they would not be able to otherwise. In fact, the modulus data follows a trend that is well-predicted by the model using the CNF modulus of 30 GPa with no agglomerates. Thus, it would appear that the potential benefits obtained from nano-enhancement in polymer composites will be similar to polymers.

What is most surprising about these results is the apparent insensitivity of the mechanical properties to sonication time. In the presence of the carbon-fiber mat, the CNFs do not appear to be creating the same kind of hierarchical microstructure that affected the evolution of the mechanical properties with sonication time in the nano-enhanced polymers. Instead, it appears that the carbon-fiber mat is acting more like a filter that appears to be limiting the introduction of dispersed fibers into the epoxy matrix. This effect is also clearly evident in the optical micrographs. As a result, it appears to homogenize the properties of the CNF-filled epoxy microstructure independent of sonication time. Thus, there is much greater consistency in the properties of the nano-enhanced polymer composites processed than the nano-enhanced polymers. However, if there is too low of a degree of dispersion or the agglomerates were too large, it is possible that the carbon-fiber mat could become clogged and the filtering benefits on mechanical properties substantially reduced. There is some evidence to this effect in Fig. 10 when the concentration of CNFs exceeds 5 wt%.

In order to better understand the effects at the nanoscale, nanoDMA modulus mapping was completed for a representative sample at two different sonication times. The complex modulus maps can be seen in Fig. 11. In view of the fact that the carbon-fibers are generally beneath the surface of these hierarchically-structured materials, a relatively high dynamic force of 10 μ N was used to see effects due to the carbon-fibers in the nanoDMA modulus mapping. This greater force allows the indenter tip to probe

Fig. 10 Comparison of sonication times as a function of wt% CNF in nano-enhanced thermoset epoxy with carbon-fiber mat. **a** Tensile modulus, **b** tensile strength, and **c** strain to failure



further into the material, garnering information from more of the surrounding volume.

The presence of the carbon-fibers can clearly be seen in Fig. 11a. Of greater interest are the regions of higher complex modulus indicating that CNFs are accumulating around the fibers at lower sonication times. This is much less prevalent in Fig. 11b, where 6 h of sonication provides a more homogeneous dispersion throughout the matrix. Thus, it would appear these results are consistent with the carbon-fiber mat acting like a filter to attract CNF agglomerates, which are far more prevalent at lower sonication times as indicated from the characterization and modeling of the epoxy without the carbon-fiber mat. Furthermore, they appear to enhance the interface with moduli values that are very close to the 30 GPa previously obtained for the CNF reinforcement. Thus, it would appear that these interfaces become highly filled with CNFs and enhance the mechanical properties in such a way as to balance the effects of dispersing them into the polymer matrix with longer sonication times. It is interesting to note that the modulus of the stiff carbon fibers is very low, which we have attributed to debonding of the polymer from the carbon fibers during polishing that reduces the effective stiffness on top of the fiber.

Conclusions

A new approach for mechanical characterization of dispersion in nano-enhanced polymers and polymer composites was developed. This approach was first used to study the effects of dispersion in nano-enhanced thermoplastic

polymers using HIPS as a model thermoplastic system and processed using a TSE in a short-residence time, high-shear rate continuous mixing process. It was then extended to a model nano-enhanced thermoset epoxy using West System 105 as a model thermoset system processed using sonication during solvent processing in a long-residence time, low-shear rate batch mixing process. The new dispersion characterization approach enabled the *fraction of dispersed nanofibers*, *degree of dispersion* and *dispersion limit* for CNFs in nano-enhanced polymers to be determined. Dispersion in a model polymer composite was also studied using carbon-fiber mats infiltrated by the nano-enhanced thermoset epoxy.

The development of the new dispersion characterization approach involved the use of nanomechanical characterization to isolate the individual moduli of agglomerates from the polymer matrix reinforced by dispersed nanofibers. From these measurements, it was possible to develop a dispersion characterization model for quantifying dispersion. To develop the dispersion characterization model, the microstructure of the nano-enhanced polymer was modeled as a polymer matrix with a percolated network of dispersed CNFs forming an interpenetrating phase composite reinforced by microscale agglomerates that were considered to be highly filled regions of CNFs coated by the polymer. Based on the microstructural model, a ROM formulation could then be developed to relate the nanomechanical properties to the distribution of CNFs in the agglomerates and polymer matrix, as well as to the modulus determined using microtensile testing.

Using the dispersion characterization model, the effective modulus of the CNF reinforcement was determined to

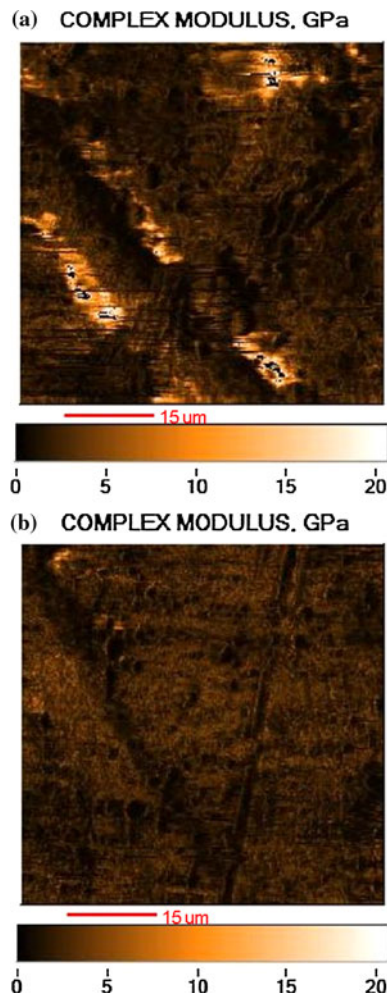


Fig. 11 Complex moduli obtained using nanoDMA modulus mapping of the thermoset epoxy with 5 wt% CNF and carbon-fiber mat after **a** 90 min sonication and **b** 6 h sonication. These results indicate that the carbon-fiber mat acts as a filter to concentrate CNFs near the carbon-fibers at lower sonication times

be 30 GPa by correlating the volume fraction of CNFs predicted by the model to the actual volume fraction. The variation of modulus for the nano-enhanced thermoplastic polymer with CNF loading could also be determined from the model, and correlated reasonably well with previously reported microtensile measurements. The model enabled the modulus for a perfectly dispersed nano-enhanced polymer to be predicted, which was determined to be only 11% greater than measured. Furthermore, it was possible to determine that 70% of the CNFs were dispersed at lower wt% loadings, and as the loading increased the percentage decreased due to a dispersion limit of approximately 3 vol%. The dispersion limit is consistent with the percolation threshold, and could explain why only limited quantities of nanoscale ingredients are typically used to nano-enhance polymers.

The characterization approach was then applied to the nano-enhanced thermoset epoxy to model the variation in tensile modulus with sonication time and CNF loading. Using the CNF modulus of 30 GPa previously determined in the model, it was possible to quantify the degree of dispersion as a function of sonication time. By fitting an Avrami equation to the degree of dispersion results, a time constant of 2 h for the dispersion process was identified. Furthermore, it was determined that there was a dispersion limit of approximately 3.5 vol% CNFs which was similar to that determined for the thermoplastics even though lower shear forces and longer processing times are associated with it. Furthermore, the complex microstructure that develops in the thermoset epoxy is similar to the thermoplastics, even though a batch mixing process is used for the thermosets that has lower shear force and longer processing time associated with it than the TSE process for the thermoplastic polymer.

Finally, the effects of sonication on dispersion in a nano-enhanced polymer composite were studied. Depending on the dispersion of CNFs in the thermoset epoxy, different hierarchical structures were formed through the combination. At lower levels of dispersion, the carbon-fiber mat acted as a filter to trap CNF agglomerates that enhanced the properties at the interface of the carbon-fibers with the epoxy. The result was a mechanical behavior that was independent of sonication time varying with CNF concentration in a manner consistent with using a CNF modulus of 30 GPa with no agglomerates in the model. However, there was some evidence that at CNF loadings above 5 wt%, there could be a reduction of this benefit due to clogging of the mat. Evidence of the attraction of CNF agglomerates to the carbon-fibers was obtained through nanoDMA, and quantitatively yields complex modulus results that were similar to the 30 GPa obtained from the extrapolation of the microtensile testing data. Thus, it would appear that these interfaces become highly filled with CNFs and enhance the mechanical properties in such a way as to balance the effects of dispersing them into the polymer matrix with longer sonication times, which leads to the more process-independent mechanical behavior.

Acknowledgements This work was supported by ONR award number N000140910640.

References

1. Bervas M (2005) PhD Dissertation, Rutgers University
2. Kubacki RM (2006) In: Proceedings of the 56th electronic components and technology conference, p 161
3. Zhong D, Kim KH, Park IW, Dennin T, Mishra B, Levashov E, Moore JJ (2004) In: Nanostructured thin films and nanodispersion strengthened coatings, vol 155. Kluwer Academic Publishers, Netherlands, p 91

4. Veedu VP, Cao C, Li X, Ma K, Soldano C, Swastik K, Ajayan PM, Ghasemi-Nejhad MN (2006) *Nat Mater* 5:452
5. Balazs AC, Emrick T, Russell TP (2006) *Science* 314:1107
6. Allaoui A, Bai S, Cheng HM, Bai JB (2002) *Compos Sci Technol* 62:1993
7. Gojny FH, Wichmann MHG, Kopke U, Fiedler B, Schulte K (2004) *Compos Sci Technol* 64:2363
8. Gojny FH, Wichmann MHG, Kopke U, Fiedler B, Schulte K (2005) *Compos Sci Technol* 65:2300
9. Seyhan AT, Gojny FH, Tanoglu M, Schulte K (2007) *Eur Polym J* 43:374
10. Zhou Y, Pervin F, Lewis L, Jeelani S (2007) *Mater Sci Eng A* 452–453:657
11. Zhou Y, Pervin F, Lewis L, Jeelani S (2008) *Mater Sci Eng A* 475:157
12. Kepple KL, Sanborn GP, Lacasse PA, Gruenberg KM, Ready WJ (2008) *Carbon* 46:2026
13. Ajayan PM, Schadler LS, Braun PV (2003) *Nanocomposite science and technology*. Wiley-VCH, Weinheim
14. Esawi AMK, Farag MM (2007) *Mater Des* 28:2394
15. Zhou RJ, Burkhart T (2010) *J Mater Sci* 45:3016. doi: [10.1007/s10853-010-4304-z](https://doi.org/10.1007/s10853-010-4304-z)
16. Ciecierska E, Boczkowska A, Kurzydowski KJ (2010) *J Mater Sci* 45:2305. doi: [10.1007/s10853-009-4192-2](https://doi.org/10.1007/s10853-009-4192-2)
17. Armentano I, Del Gaudio C, Bianco A, Dottori M, Nanni F, Fortunati E, Kenny JM (2009) *J Mater Sci* 44:4789. doi: [10.1007/s10853-009-3721-3](https://doi.org/10.1007/s10853-009-3721-3)
18. Sumfleth J, Adroher XC, Schulte K (2009) *J Mater Sci* 44:3241. doi: [10.1007/s10853-009-3434-7](https://doi.org/10.1007/s10853-009-3434-7)
19. Kota AK, Cipriano BH, Gershon AL, Duesterberg M, Powell D, Raghavan SR, Bruck HA (2007) *Macromolecules* 40:7400
20. Kota AK, Cipriano BH, Duesterberg M, Powell D, Raghavan SR, Bruck HA (2007) *Nanotechnology*. doi: [10.1088/0957-4484/18/50/50575](https://doi.org/10.1088/0957-4484/18/50/50575)
21. Kota AK, Murphy L, Strohmer T, Bigio DI, Bruck HA, Powell D (2008) *AICHE J* 54:1895
22. Cipriano BH, Kota AK, Gershon AL, Laskowski CJ, Kashiwagi T, Bruck HA, Raghavan SR (2008) *Polymer* 49:4846
23. Gershon AL, Kota AK, Bruck HA (2009) *J Compos Mater* 43:2587
24. Ozkan T, Naraghi M, Chasiotis I (2010) *Carbon* 48:239