

Microwave Curing of Epoxy Polymers Reinforced with Carbon Nanotubes

Ignatios Fotiou, Athanasios Baltopoulos, Antonios Vavouliotis, Vassilis Kostopoulos

Applied Mechanics Laboratory, Department of Mechanical Engineering and Aeronautics, University of Patras, Rio-Patras 26504, Greece

Correspondence to: V. Kostopoulos (E-mail: kostopoulos@mech.upatras.gr)

ABSTRACT: The driver for this study is the observation that heating of carbon nanotubes (CNTs) with electromagnetic field can offer a more efficient and cost-effective alternative in heat transfer for the production of composites. The idea of this study is twofold; CNT can work as microwave (MW) radiation susceptors and they can act as nanoreinforcements in the final system. To test these assumptions, a household oven was modified to control the curing schedule. Polymers with different CNT concentrations were prepared (0.5 and 1.0 wt %). The dispersion of the CNTs in the epoxy was achieved using shear-mixing dissolver technique. MW and conventionally cured specimens were also produced in a convection oven for reference. Thermal and mechanical tests were used as control point. A curing schedule investigation was further performed to quantify the energy and time-saving capabilities using CNT and MWs. The presence of CNTs into epoxy matrix has been proven beneficial for the shortening of the curing time. MW-cured composites showed the same degree of polymerization with the conventionally cured composites in a shorter time period and this time was reduced as the CNT concentration was increased. A good distribution of the CNT is required to avoid hot spot effects and local degradation. Mechanical performance was, in some cases, favored by the use of CNT. The benefit from the use of MWs and CNT could reach at least 40% in terms of energy needed and time without sacrificing mechanical performance. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2754–2764, 2013

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INTRODUCTION

Advanced polymer composite materials can cover the need for high performance and light weight in design. This is evident by the increasing adoption they receive in aeronautic, automotive, and marine industry applications. However, apart from the need for performance, energy efficiency during operation, energy needed during manufacturing, as well as time for production are also very important parameters in the general concern for environment and the selection of the manufacturing processing chain also becomes critical.¹ The high costs associated with manufacturing of carbon fiber-reinforced components in autoclaves have prompted interest in alternative processing methods, for example the route of out-of-autoclave production although these methodologies are not capable in achieving very high fiber volume fraction. In parallel, both for autoclave and for out-of-autoclave manufacturing techniques alternative heating techniques are currently explored (e.g., direct heating using carbon fibers as heating elements,^{2,3} induction heating for curing of composites⁴). Alternatively, microwaves (MWs) have

been proposed for heating and curing to produce polymeric composite parts. The driver for the application of MW technology to composites is the reduced energy needs for the manufacturing and the process time owing to increased energy efficiency, the lower investment costs,⁵ and the application scale.¹

The principles of MW heating for curing polymers⁶ and composites^{7,8} have been developed and described more than 20 years ago. More recently, MW has been evaluated in several studies as an alternative curing method for the production of composite components on an industrial scale.^{1,5} The advantage offered by MW heating technology is the generation of heat from within the composite with less power input. Electromagnetic waves are generated by a source (e.g., magnetron), penetrating the composite system and transferring energy into its volume through molecular interaction.⁹ This can deliver a direct and more rapid heating of the laminate, which can enable faster curing cycle times compared to convection heating ovens using substantially less energy.^{10,11} In an attempt to quantify the benefit from MWs in production, it has been indicated that cure cycles and

energy costs could be reduced by as much as possible, 50 and 90%, respectively.¹ To this end, customization of curing reaction rates has been proposed as the key parameter for this transfer.¹² Nevertheless, only the past decade developments in MW technology have made it technically and economically possible to apply MW curing to composites in an industrial scale⁵ although it has been used in other industries for much longer.^{6,13}

Some of the challenges related to MW processing have been among the reasons for delaying use of MWs in the composites industry. Among the most important are the nonuniform-generated heating and the performance of the composites produced.^{13,14} To tackle these issues, the use of fillers as susceptors in the polymer has been proposed.^{12,15} Research in the area of nanotechnology has delivered various nanofillers that represent promising additives toward the direction of MW curing.^{5,12,16} Some studies have reported on the combined use of MWs and carbon nanofillers (carbon nanofibers¹⁷ and carbon nanotubes [CNTs]¹⁸), thanks to the excellent MW-absorbing properties of carbon structures.¹⁹ In addition to the benefits offered in the processing of polymers, the incorporation of nanoscale fillers in the composites can enhance the performance of the composite system. In several occasions, the use of nanofillers (e.g., CNT) has been shown to benefit the mechanical,^{20,21} electrical²² performance, as well as enabling multifunctional performance.^{23,24}

In this study, the interaction of CNT with MW was investigated. This study deals with the MW curing of epoxy system reinforced with multiwall carbon nanotube (MWCNT) at various concentrations. Two complementary directions are researched:

1. The first direction deals with the comparison of convection and MW curing of various neat and MWCNT-reinforced systems. The comparison is done on the thermal and mechanical performance of the produced systems.
2. The second direction assesses experimentally the potential to customize the curing profile using MW curing to maximize the benefit of the alternative curing technique. This is done under the view of time and energy consumption having, as final aim, production parameters.

EXPERIMENTAL

Materials

An aeronautic epoxy (EP) system Araldite LY564/Aradur HY2954 was chosen as the host-matrix material for this study. The material was supplied by Huntsman Advanced Materials, Switzerland. MWCNTs were supplied by ARKEMA, France. The MWCNTs were produced by catalyzed CVD with purity of 98% according to the supplier's instructions. Their diameter ranged between 10 and 15 nm and their length was >500 nm, resulting in an aspect ratio of >30. As a common approach, prior to use the nanotubes were dried in an oven at 60°C overnight to eliminate humidity. MWCNTs were used as received without treatment or functionalization.

Mixture Preparation

To disperse the MWCNTs in the epoxy, a shear-mixing dissolver device (VMA Getzmann GmbH, Germany) was used.²⁵ The dissolver introduces high shear forces by creating a vor-

tex flow in the EP/MWCNT mixture. The vortex flow achieved by the geometry of the disk leads to continuous mixing of the compound. The shear forces disentangle the nanotubes and reduce the agglomerates that tend to form in such mixtures.

For preparing mixtures with the desired percentage of MWCNT, a masterbatch approach based on dissolver mixing was employed.²⁶ A masterbatch mixture containing 4 wt % MWCNTs was prepared by mixing Part-A of the EP system for 12 h at 1500 rpm rotor speed. The mixture was stirred in a vacuum container to avoid air inclusion. During processing, temperature, rotational frequency, energy input, and time are controlled and recorded for reproducible test conditions. Owing to the shear forces, the mixture tends to heat up. During processing, the temperature was controllable and was maintained around 40°C to control the viscosity of the mixture. Thus, a better CNT dispersion can be achieved, based on the previous experience with similar epoxy systems.^{22,23}

To produce the final mixture with the desired percentage of MWCNT, stoichiometric quantities of masterbatch and neat Part-A were mixed for 2 h to dilute the nanofiller concentration to the required amount. The same processing conditions mentioned before were applied here. As a final step, the mixture was placed in a sonication bath for 30 min to further enhance the dispersion quality by breaking any remaining agglomerations. Finally, Part-B of the system was added and mixed by dissolver for additional 5 min. The final mixture was degassed for another 5 min and then casted in dog bone-shaped molds for curing. For convection curing, aluminum molds were used. To avoid problems related to interaction between MWs and metal molds, plexiglas molds were produced and used for the MW curing campaign.

Three material groups were produced; the neat resin, specimens with 0.5 wt % MWCNT, and 1 wt % MWCNT contents.

Curing Methods

To cure the resin using MW, a commercially available household MW oven (750 W, 2.45 GHz) was modified. The MW oven was connected to a time circuit to control the time intervals between the activations of the MW source. A CALEX™ TL-TI IR pyrometer was used to measure the specimen's temperature inside the MW oven. The electromagnetic source of MW oven was activated for 4 s and then an IR pyrometer measured the surface temperature of the specimen. If the temperature exceeded a threshold value related to the curing profile, the oven remained deactivated until the temperature decreased below the threshold. Then, the oven was activated for another 4 s and so on. The oven control was set according to the nominal cure schedule of the EP system.

Conventional curing (CC) was done in a typical laboratory scale convection oven controlled by a Yumo PID controller with accuracy of 2°C. Specimens were cured at 80°C for 1 h followed by a postcure at 140°C for 8 h, according to the resin supplier.

The consumed energy for each curing method was measured with a typical wattmeter and power calculator with accuracy of 0.01 KWh.

Testing and Characterization Procedures

Differential Scanning Calorimetry (DSC) tests were performed on a DuPont Differential Scanning Calorimeter 910. Rectangular samples were cut and polished on one side and were then encapsulated in aluminum pans. In the tests, samples of 5–10 mg were heated from room temperature at a rate of 5°C/min up to 400°C for uncured mixtures and 250°C for cured samples. The test was performed under a nitrogen atmosphere. The temperature and heat flow scales were calibrated using the melting of high-purity indium samples before testing.

Performance assessment was carried out based on the mechanical response of the produced specimens under tension. Specimens were tested according to ASTM D638. Specimens of Type IV were prepared having a thickness of 4 mm. An Instron 8872 servo-hydraulic press fitted with a 25-kN capacity load cell was used to conduct the tensile test. Crosshead speed was set at 0.8 mm/min. Stain was measured with an Instron laser video extensometer. Elastic modulus, failure stress, strain to failure, and Poisson's ratio were automatically calculated by the measurement software suite. For each set of materials, a set of five specimens were tested.

For assessing the dispersion of CNT and the morphology of fracture surface, scanning electron microscopy (SEM) was used. A LEO SUPRA 35VP SEM at various levels of magnification was employed.

RESULTS AND DISCUSSION

Mixture Preparation and MW Curing

Preparation of the nanoreinforced epoxy mixtures using the shear mixing dissolver technique is a rather well-documented approach.^{20,22,23} However, the final dispersion in the cured polymer is affected by various parameters such as processing, curing kinetics, viscosity, and others. Thus, the effect of MW curing on these parameters is very important for developing nanoreinforced composite systems. These parameters for curing fibrous composites under MWs have been described by Lee and Springer,⁷ taking into consideration the MW interaction with the fibers.⁸

MW curing of nanocomposites is a less explored field compared to fibrous composites and to CC. The principle concept behind MW heating and, consequently, curing of polymer systems is the dielectric displacement or polarization of various charges in the material. When a material with dipoles is exposed to an electric field, the material is polarized.^{6,8,9} Materials dielectric properties and the frequency and power of the applied alternating electric field control whether the material will absorb MW energy and heat up or not. The difference between the materials developed in this study is dependent only on the dielectric loss of the materials.²⁷ Coupling of MW energy to the polymer specimens is achieved by interactions between the sustained electric field in the MW applicator and the dipoles contained in the polymer. It is believed that the nanoscale reinforcement (in this case CNT) can enhance this interaction. Although several theories have been proposed,^{28,29} the exact mechanism of CNT interaction with MW is still not well described or understood.

During curing of the neat epoxy resin, it was observed that as the reaction progressed the effect of MW heat transfer was decreasing.⁹ It was noted that some regions of the material remained soft and malleable. This is related to the number of available free functional groups to interact with MW.^{8,12} From the material point of view, this is expressed by the dielectric loss factor. Initially, the liquid resin couples well with MWs. The uncured resin exhibits much higher dielectric loss factor than the cured polymer.¹² As crosslinking proceeds, the dielectric loss decreases because changes in the resin viscosity affect the ability of dipoles to orient in the electric field.⁹ This is in accordance with the fact that cured plastics do not interact with MWs.⁶ This is the reason that at the final stages of the curing process, the mass of the resin was not heated by the MW. Therefore, curing is believed to have been achieved by residual-inertial heat within the material.

CNT-reinforced polymers did not exhibit such a behavior. CNTs interact with MW, then providing the necessary thermal energy for curing. In this case, the heat energy sources that are activated by MW are homogeneously distributed within the volume of the material and produce ideally an almost homogeneous temperature field. At the same time, the presence of CNTs within the mass of the epoxy resin increases substantially the heat transfer confidence of the resin, thus facilitating the realization of a homogeneous temperature field.

Interestingly, MW curing of nano-reinforced polymers exhibited hot spots as has been observed by Fotiou et al.³⁰ During the initial stages of the development of the MW curing setup, different areas of the specimens were overheated, leading to local degradation and char formation. Even after the final selection of the MW oven control parameters, there were occasions where the polymer had formed bubbles at certain spots of the surface, indicating a very high local increase of temperature. This can be attributed to two possible inter-related mechanisms; the first one is the nonoptimized MW source generating a nonuniform heating field and the second one is the nonoptimum dispersion of CNT within the polymer. The former one has already been identified as one of the challenging issues of MW technology for curing of composite. The MW source used in this study was a simple magnetron modified from a household MW oven. This is investigated further and analyzed using DSC measurements (next paragraph). The later one has been in the discussion of research scientists as the development of the first nanopolymers. As it happens with other physical properties of nano-reinforced polymers, a uniform dispersion of nanofillers is expected to have beneficial effects of MW curing. A good CNT dispersion supplies a homogeneous percolating network. This can provide increased energy transfer and homogeneous heating from within the polymer working like a mesh throughout the polymer. This can result in an organized network of polymer chains, resulting in stiffer mechanical response. However, achieving such an ideally homogeneous dispersion is not always easy or possible. At nanofiller loadings, larger than the percolation threshold, agglomerations cannot be avoided. For the material system used, it has been shown in the previous study that the percolation threshold is close to 0.1 wt %.²² At 0.5 and 1 wt % investigated in this study, the existence of agglomerations cannot be

avoided. A commonly observed dispersion result is a continuous network of individual CNTs that bridge the intermediate volume in between formed agglomerates. Large agglomerates are expected to cause high temperature around them. Owing to their high thermal conductivity, the whole agglomerate is believed to be heated reaching temperatures high enough for the system to polymerize around the agglomerates. Owing to the high concentration of CNT in agglomerates, higher amounts of energy are absorbed and thus temperature may rise higher, leading to a local increase of the reaction rates, leading to resin bubbles or burnt/degraded areas.

An important point to verify in MW heating processes is the effective heat transfer mechanism to reach cure. Ideally, the use of MWs for heating targets homogeneous volumetric heating of the composite from within. However, there are two phenomena that may suppress the effectiveness of this process. The first is the fact that the incident high-frequency radiation penetrates up to a finite depth in the composite and the second the fact that radiation may be reflected at the surface of the composite.

Regarding the penetration depth, the electric field penetrating a conductor drops exponentially with increasing depth into the conductor. For the materials studied, the skin depth depends on the conductivity of the materials. It is given by the following equation³¹:

$$\delta = \frac{1}{\sqrt{\pi\omega\mu\sigma}} \quad (1)$$

where μ is magnetic permeability = $\mu_0 \mu_r$, and μ_r = relative magnetic permeability [-], $\mu_0 = 4\pi \times 10^{-7}$ (H/m), and σ is electrical conductivity (S/m). The relative magnetic permeability is nearly 1 for composites. In essence, this means that the higher the conductivity of the material, the thinner the skin. The electrical conductivity of the nano-doped systems is in the range of 10^{-4} – 10^{-3} S/m according to the previous studies with the same MWCNT batch and dispersion routes.²² According to eq. (1), these materials are expected to have a penetration depth between 0.3 and 1.0 m. This means that effective volumetric heating is possible using MWs at the respective frequency. Literature works have reported a range of values for several related materials: between 30 and 73 cm for neat epoxies; 0.5–2.2 cm for prepreg carbon fiber layers.^{6,32,33}

The reflective capability of materials can be assessed using shielding effectiveness means. For reflection of the radiation by the shield, the shield must have mobile charge carriers which interact with the electromagnetic fields.³¹ As a result, the shield tends to be electrically conducting although a high conductivity is not required. However, electrical conductivity is not the scientific criterion for shielding. Therefore, even low levels of CNT loading may be sufficient to reflect incident EM waves. In EM shielding studies, though, it has been shown that to reach high reflectivity levels (above, e.g., 50%) concentrations above 4 wt % are needed.³⁴ At the concentration levels studied in this study (below 1%), a dramatic change in the reflectivity of the material is not expected. Therefore, it is believed that the reflectivity of all the studied materials is in the same performance range.

Both described mechanisms are effective in the MW curing process studied, to a different extent each. These mechanisms control the heating mechanism and change it from a volumetric to surface heating, based on the previously reported observations.³⁴

Differential Scanning Calorimetry

In this part of the study, the achieved curing of the developed material groups using thermal analysis DSC was evaluated. DSC measurements are used for investigating the cure kinetics associated with MC and determine the glass transition temperature (T_g) of the cured polymers. Figure 1(a) shows the recorded heat flow in temperature scan mode for uncured and MW-cured (MWC) nanopolymers having different CNT contents. T_g of each material group was derived from these curves. Values of characteristic thermal measures from DSC are listed in Table I.

The addition of CNT in the epoxy resin has an effect on the enthalpy of reaction. The increase of the amount of CNT concludes to an increase in the required energy for curing. Based on the DSC curves, it is seen that the exothermic peaks occur between 120 and 130°C, with an increasing trend with the addition of CNT.

The T_g of the MWC systems showed a rather large deviation. The neat system exhibited the highest T_g among the polymer groups. The trend observed was that the higher the CNT content the lower the achieved T_g . This is contradicting the initial assumption and the expected result. It is believed that the exhibited behavior could be to, some extent, attributed to the nonoptimal dispersion of the CNT into the epoxy matrix, and the presence of an important amount of agglomerates into the nanocomposite system. The presence of agglomerations leaves large free space within the polymer chain network. This allows the polymer chain sections to vibrate and move under the thermal input from the DSC.

Based on the reported results from other studies, it is still unclear how the T_g of the cured systems is affected by MW induced curing. It would be expected, as it has been claimed by Saccone et al.,¹⁵ that the high-energy input and the path the energy transfer follows could affect the polymerization processing, creating a more compact three-dimensional polymer chain network with lower free volume. This would result in a higher T_g . This was not observed in this study. Thus, it is believed that to achieve a more compact and dense network, a very well-distributed network of CNT is required.

Stanulovic and Feher¹¹ presented the idea that high-power MW heating not only reduces the curing time and increases the rate of reaction, but also reduces the percentage of curing and crosslinking density for plain polymers. To address this, the use of micro/nanosusceptors was proposed there. The dispersion, though is very important, and CNT agglomerations may create localized hot spots because of MW irradiation. This could well cross the decomposition temperature of the composites as it drastically reduces the thermal and mechanical properties. This is also described by Rangari et al.¹⁸ where T_g was negatively affected.

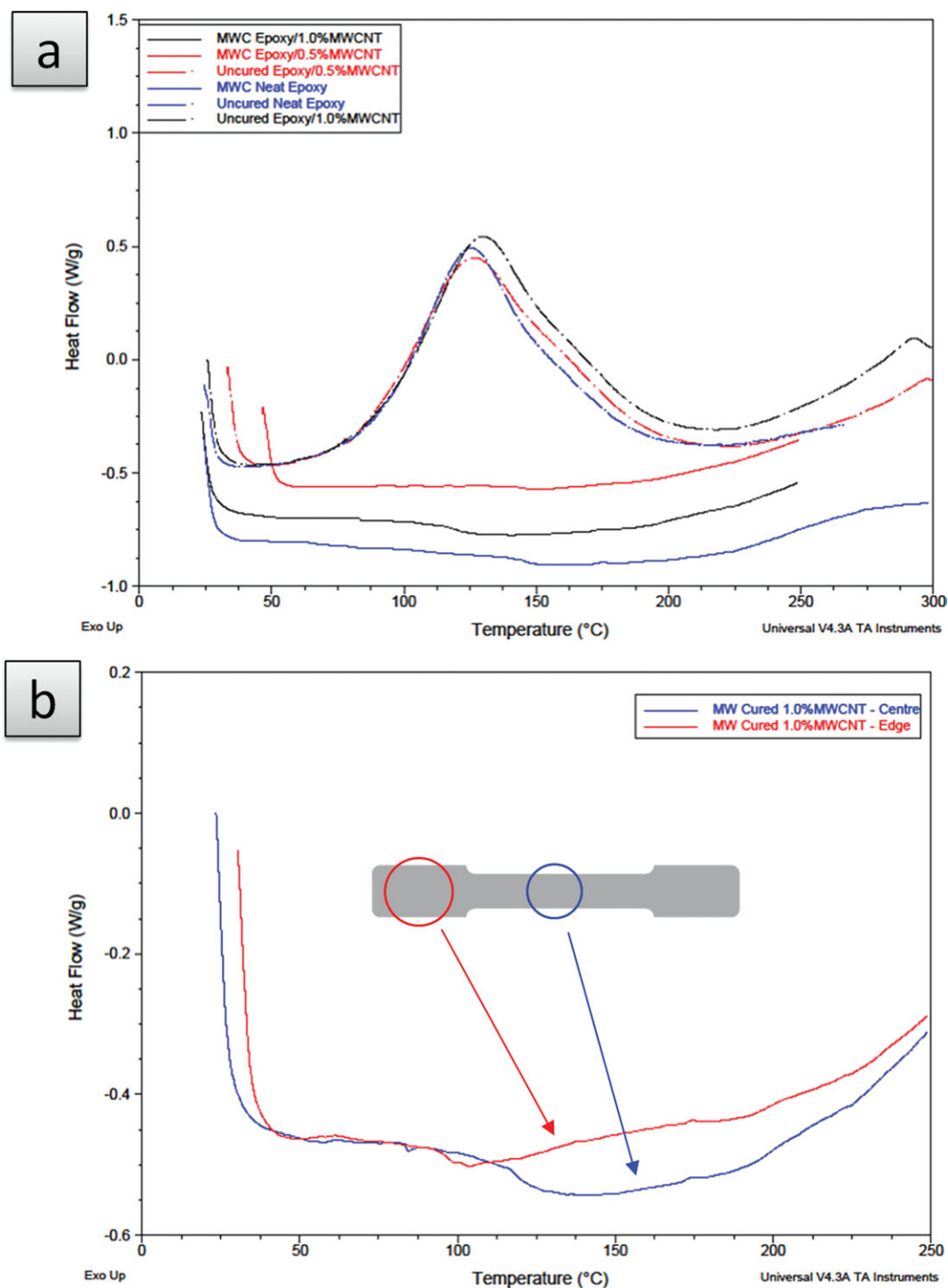


Figure 1. DSC heat flow in temperature scan: (a) uncured and MWC nanocomposite polymers (b) indication of nonuniform MW curing of epoxy/1.0% MWCNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 1(b) shows two DSC curves corresponding to different locations of the same tensile specimen of EP/MWCNT at 1 wt % cured using MWs. The difference in their thermal response is evident. Both curves show the same behavior up to ~ 100 °C. The difference between the two curves is expressed between 100 and 180 °C. Above 180 °C, the profile is nearly the same as degradation and decomposition of the material is initiated. At

100 °C, the central location expresses a more intense exothermic, whereas the sample from the edge of the specimen gives an endothermic, indicating the T_g . Similar thermal behavior was reported by Zhou and Hawley.¹² In our case, this difference is attributed to the relative position of the two spots to the MW source and the nonuniform field produced by the source. As the early attempts to develop MW heating and ultimately

Table I. Characteristic Thermal Values for MW-Cured Composites Based on DSC Curves^a

	Neat	0.5%	1.0%
Onset temperature (°C)	87.15	82.88	87.60
Peak temperature (°C)	124.97	126.30	129.62
Enthalpy of reaction (J/g)	304.0	327.7	332.7
T _g (°C)	148.64	132.14	118.30

polymer curing systems, a major problem was the nonuniform thermal field induced within the material.¹³ This was also noted in the development phase of this work's setup.³⁰ Contrary to other MW curing systems with more sophisticated arrangement of sources, here only one MW source was used.

Mechanical Performance of MWC Nanocomposite Polymers

The mechanical performance of the materials was evaluated through tensile tests. Typical tensile test curves for the conventionally cured and MWC nanocomposites are shown in Figure 2(a,b).

All material groups exhibit a nonlinear viscoelastic response as expressed through the slight curvature deviating from the linear response. Extensive yielding was not observed prior to fracture. From the recorded experimental data of each curve, three parameters were extracted; the Young's Modulus (taking into consideration the initial part of the stress-strain curve from 0 to 0.2% strain), the Strain to Failure and the Stress to Failure. All the values, both for CC and MWC, are listed in Table II. The mean values and standard deviation of the gathered data are presented. The results for the MWC nanocomposites are also compared against the results obtained from conventionally cured nanocomposites.

For the MWC specimens, the incorporation of CNT gives a consistent trend toward stiffer and more brittle behavior. This holds true also for the CC specimens. The findings are consistent between the two material groups for the CNT loadings studied. The Young's modulus increases with the addition of nanofillers, resulting in a stiffer system. The stress and strain to failure followed a decreasing trend with the increase of nanofil-

ler content. This stiffening behavior is characteristic of nano-reinforced polymer systems.

Specific interest exists in comparing MWC specimens with CC specimens in terms of achieved performance change, as this would provide experimental evidence for MW curing. Although MWC and CC show comparable or increased stiffness, increased stress and strain to failure, there are changes owing to the curing method. More specifically, based on the experimental results, there is evidence of increased performance in favor of MW curing as the Young's modulus, the Stress to Failure and Strain to Failure exhibit compared or increased performance around 4–5, 7–10, and 7–10% respectively. Comparable conclusions were reported in the case of modified polymers³⁵ and glass fiber composites.³⁶ Similarly, Yarlagadda and Hsu³⁷ have noticed an improvement of the flexural strength of the samples' MWC specimens, verifying the reported results of this study. This can be related to the different triggerings of the polymerization process. This could result in a different network of crosslinked polymer chains.¹⁵ Thermal results did not show such an enhancement; however, the underlying triggering mechanisms for each test are not the same.

SEM Examination

SEM was used to evaluate the microstructure of the polymer, to evaluate the dispersion of the CNT into the matrix, and to investigate the fracture surface of the polymers. Effective dispersion of nanoparticles is a major challenge for the advancement of polymer nanocomposite.³⁸ As the previous studies have shown, the dispersion of nanofillers in a host polymer can be seriously affected by the variation of parameters during curing (e.g., the viscosity change).^{39,40} The final dispersion can serve as an index of the curing thermal history of the polymer. The evaluation targeted the search for difference between the final nanofiller dispersion in the MWC and the conventionally cured specimens. Figure 3 shows SEM micrographs from the fracture surface of the nano-reinforced systems.

No voids were observed in the polymer, indicating that no voids were generated in the matrix during the curing process as a result of curing reaction. CNTs are present, as expected, both in agglomerated and in individually dispersed form. This is a

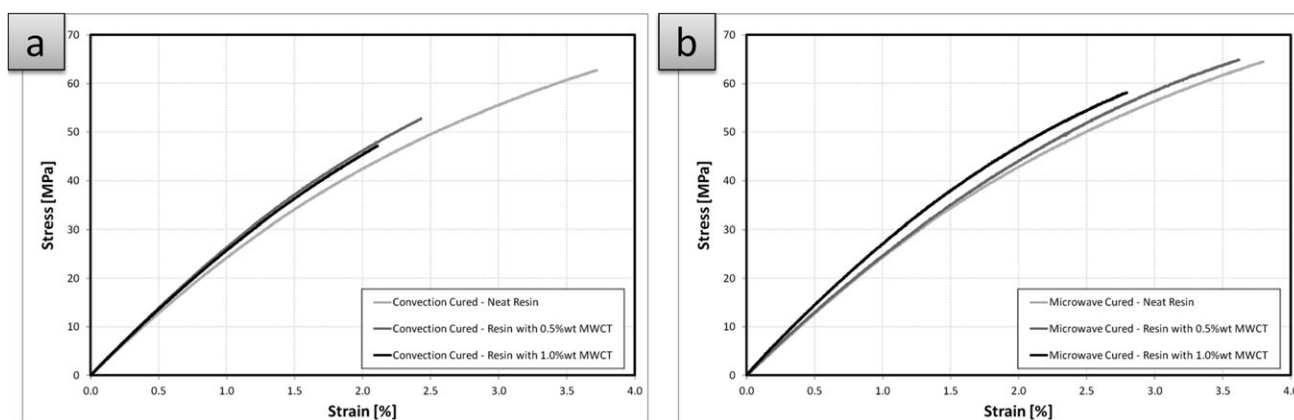


Figure 2. Mechanical performance: tensile test curves of (a) convection cured polymers (b) MW heating cured polymers.

Table II. Experimental Values for the Mechanical Properties of the Various Material Systems^a

	Neat resin		0.5 wt % MWCNT		1.0 wt % MWCNT	
	CC	MWC	CC	MWC	CC	MWC
Young's modulus (GPa)	2.50 ± 0.07	2.49 ± 0.11	2.78 ± 0.10	2.83 ± 0.13	2.77 ± 0.10	2.91 ± 0.08
Stress to failure (MPa)	70.4 ± 1.9	73.3 ± 2.1	63.3 ± 2.4	68.1 ± 2.2	54.5 ± 3.2	59.8 ± 3.0
Strain to failure (%)	4.54 ± 0.55	5.09 ± 0.63	3.72 ± 0.37	3.62 ± 0.42	2.00 ± 0.31	2.17 ± 0.38

^aCC, convection curing; MWC, microwave curing.

rather common phenomenon in nanopolymers at this level of nanofiller loading. Furthermore, good wetting of the CNT is evident. Even at agglomerated state, the resin infused the nanotubes creating a continuous material. This is also verified by the mechanical behavior analyzed earlier. Lack of continuum would result in stress concentration and premature failure.

As a general observation, CC specimens showed larger agglomerates compared to the MWC specimens. Linear cracks are evident in both specimens. MWC specimens showed clearer fracture lines. No major differences can be seen from the SEM micrographs. From the observations, there is no significant evidence to suggest that agglomerates acted as stress concentrations to decrease the load-bearing capability of the system. The increase in the CNT concentration pushed the system to a more brittle macroscopic failure.

In the study of Rangari et al.¹⁸ SEM observations showed that the MWC CNT-reinforced epoxy made the materials more ductile, a behavior attributed to the reduction of the percentage of cure and crosslinking density owing to the high-power MW curing. Welding phenomena were described to explain the change to a more ductile behavior although initially they were described to be applicable only to thermoplastics. No such effects were observed in this study.

Energy Consumption Assessment

The use of MW for curing is foreseen to provide great power-saving capabilities in manufacturing owing to better efficiency in heat transfer especially with the presence of CNT within the polymer.

To provide a quantitative measure of this capability, the energy consumption was measured during both the curing processes. Table III summarizes the gathered results for energy consumption for the two methods. It also includes data for all material groups developed to investigate the effect of the CNT presence in the material.

The energy consumption is nearly the same for all the CC. As a matter of fact, the addition of CNT is not expected to affect the CC system to such an extent. Convection heating has to transfer heat inside of the material by conduction, and hence first it must consume energy for the heating of the interior of the oven and then for the heating of the composite material. The total mass of the polymer is relatively small compared to the total mass of the metallic parts to be heated. As summarized in Table III, convection curing utilizes about four times more energy than the MW curing method. The beneficial characteristics of MC with respect to time and consequently energy have been investigated in the previously published studies.^{15,37} However, from this study, it cannot be conclusive as it should be noted that the size of the oven can accommodate more specimens for curing, which would result in a higher efficiency for the CC method, in terms of final cured mass.

Nevertheless, it is interesting to note the trend exhibited for MW curing. It is seen that energy consumption using MC for the neat epoxy system is higher than for the nanomodified system. This difference is reaching 40–50%. Reported results in the literature have shown that MW heating is significantly more energy efficient compared to the conventional convection heating.^{19,41} As explained earlier, this is attributed to lower dielectric

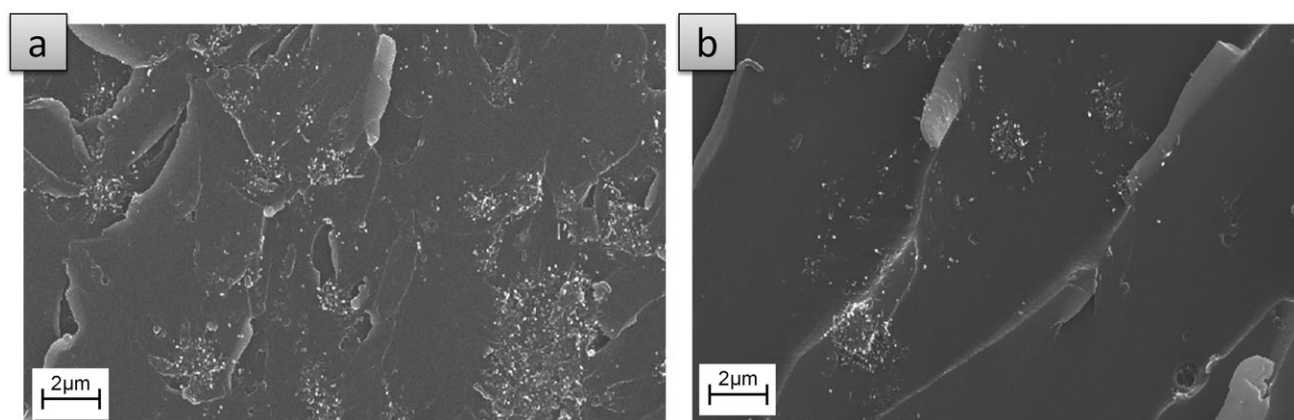


Figure 3. Fracture surface morphology of sample with 0.5 wt % CNTs content: (a) convection curing, (b) MW curing.

Table III. Energy Consumption of MW and CC Method for Specimens with 1 and 0.5% CNTs per Weight

	Energy consumption (KWh)	
	MW Curing	CC
Specimens without CNT	1.47	4.60
Specimens with 0.5% CNT	0.95	4.60
Specimens with 1.0% CNT	0.91	4.61

loss factor the cured polymer has. This meant that the efficiency of heat transfer through MWs decreased in the neat polymer as curing progressed and thus absorbing lower and lower amounts of energy for curing. This is the point where CNTs are believed to have contributed further. The addition of CNTs shows a reduction of energy consumption. The increase of CNT concentration from 0.5 to 1% resulted in a decrease of energy needed for the curing of nanopolymers from 0.95 to 0.91 kWh (nearly 4%). This shows a consistent direction toward the decrease of energy consumption.

The thermal properties (i.e., thermal conductivity and thermal capacity) of the mixtures play a very important role in the MW curing process. As the energy input to the mixture through the MW interaction with the CNT is very intense and higher than for the neat system, the temperature of the material increased rapidly. Thermal conductivity is not much changed by the addition of CNTs at these levels of concentration. Thus, the heat transfer is rather slow and the temperature remains high.

In the view of the above given information, analyzing the control of MW irradiation can provide some answers to these changes. As described by Wang et al.,¹⁹ intense heat can be released by MW radiation of CNTs. Temperature can reach up to 2000°C in continuous irradiation.⁴¹ To control the heat release, the MW source is activated in a pulsed manner according to the control parameters. The duration of the pulse in this study was 4 s. To proceed to the next activation period, the controller reads the surface temperature of the resin. If the polymer is above a certain level, it does not activate the source. If the temperature is below the control point, the source is activated for the next 4 s, and so on.

MW Curing Cycle Investigation

In the previous part of the study, the nominal curing cycle provided by the resin supplier was followed for both CC and MWC. However, having a very long curing schedule for MW

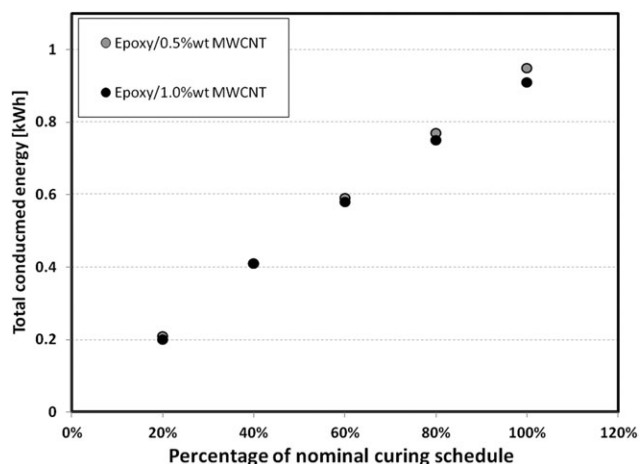


Figure 4. Measured energy consumption for the various MW curing schedules tested.

may mean a lot of wasted energy as explained previously. It may even create thermal cycling issues. Thus, it is obvious that the curing schedule is far away from optimum for use in MW and shorter curing durations could be implemented. The similar short curing cycles have been proposed by following a rather *ad hoc* approach.¹⁸ In this approach, MW curing was allowed for 10 min compared to a total of 8 h with convection curing.

It is an initial attempt to investigate the potential to customize the curing cycle for MC use. Different curing schedules involving both curing and postcuring steps as the nominal one are investigated for MW curing. For defining the curing schedule scenarios, the approach is to allow MW curing for a percentage of the nominal schedule. This percentage is applied to each step of the schedule. Five different curing cycles were investigated corresponding to 20% incremental decrease of the nominal durations. A summary of the tested cycles is presented in Table IV. The consumed energy along with mechanical and DSC test is used as a factor to evaluate the produced materials.

Figure 4 shows the values of energy consumption for MWC of nano-reinforced polymers for the different percentages of the nominal cure schedule. It can be seen that although starting at the same point and overlapping at 40%, the consumed energy for the 1 wt % CNT-loaded polymers is slightly lower than that of 0.5 wt % group. This may indicate increased efficiency of the process, which results in a nonlinear dependence of the energy to the duration (i.e., longer duration would need lower energy). As it is expected, the increased duration of MWC would result in an increase of the consumed energy.

Table IV. Durations Investigated for MW Curing Cycle Optimization

Nominal curing schedule	MW curing schedule investigation				
	% of Curing schedule duration				
	100% (Nominal)	80%	60%	40%	20%
Cure	1:00' at 80°C	0:48' at 80°C	0:36' at 80°C	0:24' at 80°C	0:12' at 80°C
Postcure	8:00' at 140°C	6:24' at 140°C	4:44' at 140°C	3:16' at 140°C	1:36' at 140°C

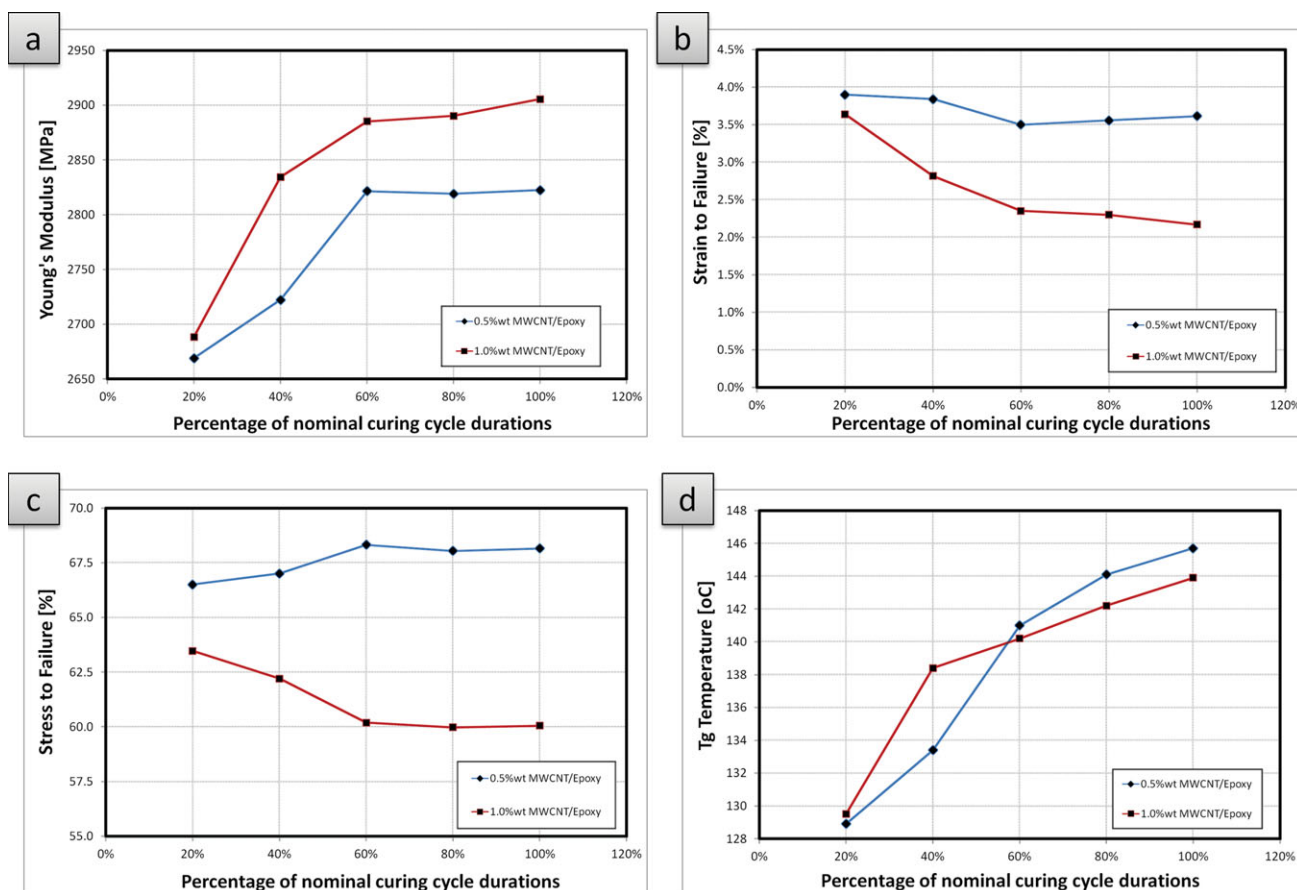


Figure 5. Properties of MWC systems as a function of the curing cycle duration: (a) Young's modulus, (b) strain to failure, (c) stress to failure, (d) T_g . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the experimental results for the various curing schedules: Young's modulus, strain to failure, stress to failure, and T_g . The starting point of each figure is the nominal duration (100%).

The behaviors exhibited are, in general, consistent for both CNT concentrations. A general trend can be noticed in the results; as the duration reaches the nominal one, the properties "converge" to their final value. The change of properties for durations more than 60% is relatively small ($\pm 3\%$). The properties reach a plateau. The Young's modulus decreases as the curing time is reduced. However, the values are already high enough for a polymer system. Only in the case of 20% of the nominal curing cycle, the difference is considerable. A similar behavior is seen for the strain to failure, following an increase at shorter durations. The T_g exhibits the largest changes. As the duration decreases, the T_g drops constantly, reaching a 20°C maximum difference compared to the nominal value at 100% curing. These observations can provide support to claim that using a curing schedule having 60% duration of the nominal one can deliver polymers with equally good performance as the nominal ones. This means that an energy saving of 40% can be achieved, in addition to CC methods. It is believed that as the duration shortens, the material is less crosslinked. This leads to the decrease of the materials' stiffness and the increase in strain it can reach until failure.

CONCLUSIONS

MWs have been proposed as a promising way for developing advanced composite structures with less energy and superior properties. This is based on the observation that heating with electromagnetic field offers a more cost-effective alternative in the production of composite materials than the conventionally used heating techniques (i.e., convection ovens).

To address the issues holding back the extensive use of MW in composites manufacturing, the use of CNT was proposed and investigated in this study. The target is twofold; CNT can work as energy susceptors and in addition they can act as nanoreinforcements for increased performance (e.g., enhanced properties).

The first part of this study, which investigated the use of CNT for enhancement of curing using MWs showed that:

- The addition of CNT in the polymer can result in a more efficient energy transfer using MWs while maintaining the mechanical performance of the material. This was indicated by the lower energy consumption for curing the same amount of material.
- The mechanical behavior of the CNT-reinforced polymers did not change dramatically with the use of MW. Nevertheless, a 5–10% change in performance was observed in the respective tensile measures (Young's modulus, stress to failure, and strain to failure) when compared with CC.

- The use of CNT for MW curing showed to be dependent on the effective dispersion of CNT. Agglomerations have created thermal spots and the resin degraded locally. Achieving a homogeneous distribution of nanofillers can support the application of MW heating systems for the production of advanced composite structures.

Based on the more efficient transfer of energy for heating and curing of the polymers, the possibility to customize the curing cycle for MWC was assessed. The duration of curing and postcuring steps was fractionally changed based on the nominal curing schedule. From the energy assessment part, it can be conclude that:

- The energy saving was quantified to be at least 40%. This is owing to the reduction of curing time that can be reached while attaining a qualifying level of mechanical performance. These findings could have great impact on the cost efficiency of composite manufacturing processes.
- Small changes in performance were observed even for very short curing durations (e.g., 20%). Mechanical properties showed deviations with curing durations; nevertheless, the values are already acceptable for use of the polymers as structural matrices.
- The T_g of the materials exhibited the greatest dependence on curing duration. The values showed a nearly asymptotic approach as the curing duration reached the nominal schedule.

It is believed that these findings are very important for processing and manufacturing of advanced composites. Considering the time and energy saving that can be achieved for production processes, higher production rates can be reached while attaining high performance. Furthermore, the addition of CNTs into the composite materials can make MW curing method applicable to more categories of composite materials, such as the ones with not interfering with electromagnetic fields, for example polymers reinforced with aramid or glass fibers. Further investigation, however, is required in understanding the polymerization process under MW energy input and the evolution of physical properties during this process.

REFERENCES

1. Witik, R. A.; Gaille, F.; Teuscher, R.; Ringwald, H.; Michaud, V.; Månson, J.-A. E. *J. Clean. Prod.* **2012**, 29–30, 91.
2. Zhu, L.; Pitchumani, R. *Compos. Sci. Technol.* **2000**, 60, 2699.
3. Athanasopoulos, N.; Kostopoulos, V. *Compos. Sci. Technol.* **2012**, 72, 1273.
4. Yarlagadda, S.; Kim, H. J.; Gillespie, J. W.; Shevchenko, N. B.; Fink, B. K. *J. Compos. Mater.* **2002**, 36, 401.
5. Feher, L.; Thumm, M.; Drechsler, K. *Adv. Eng. Mater.* **2006**, 8, 26.
6. Mijovic, J.; Wijaya, J. *Polym. Compos.* **1990**, 11, 184.
7. Lee, W. I.; Springer, G. S. *J. Compos. Mater.* **1984**, 18, 387.
8. Lee, W. I.; Springer, G. S. *J. Compos. Mater.* **1984**, 18, 357.
9. Thostenson, E. T.; Chou, T.-W. *Compos. A* **1999**, 30, 1055.
10. Benitez, R.; Fuentes, A.; Lozano, K. *J. Mater. Process Tech.* **2007**, 190, 324.
11. Stanculovic, S.; Feher, L. *J. Microwave Power EE* **2008**, 42, 55.
12. Zhou, S.; Hawley, M. C. *Compos. Struct.* **2003**, 61, 303.
13. Cordes, B. G. *MSc Thesis*, Worcester Polytechnic Institute, USA, **2007**.
14. Ku, H. S.; Lee, K. F.; Li, C. W.; Widjaya, B. *J. Reinf. Plast. Comp.* **2004**, 23, 1443.
15. Saccone, G.; Amendola, E.; Acierno, D. *Microw. Opt. Tech. Lett.* **2009**, 51, 2777.
16. Higginbotham, A. L.; Moloney, P. G.; Waid, M. C.; Duque, J. G.; Kittrell, C.; Schmidt, H. K. *Compos. Sci. Technol.* **2008**, 68, 3087.
17. Rangari, V. K.; Bhuyan, M. S.; Jeelani, S. *Compos. A Appl. Sci.* **2011**, 42, 849.
18. Rangari, V. K.; Bhuyan, M. S.; Jeelani, S. *Mater. Sci. Eng. B Adv.* **2010**, 168, 117.
19. Wang, C.; Chen, T.; Chang, S.; Cheng, S.; Chin, T. *Adv. Funct. Mater.* **2007**, 17, 1979.
20. Gojny, F. H.; Wichmann, M. H. G.; Kopke, U.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2004**, 64, 2363.
21. Karapappas, P.; Vavouliotis, A.; Tsotra, P.; Kostopoulos, V.; Paipetis, A. *J. Compos. Mater.* **2009**, 43, 977.
22. Vavouliotis, A.; Fiamegou, E.; Karapappas, P.; Psarras, G. C.; Kostopoulos, V. *Polym. Compos.* **2010**, 31, 1874.
23. Kostopoulos, V.; Vavouliotis, A.; Karapappas, P.; Tsotra, P.; Paipetis, A. *J. Intell. Mater. Syst. Struct.* **2009**, 20, 1025.
24. Baltopoulos, A.; Polydorides, N.; Vavouliotis, A.; Kostopoulos, V.; Pambaguian, L. Proceedings of 61st International Astronautical Congress 2010 (IAC 2010), 2010, Vol. 13, p 11004.
25. Hauptert, F.; Wetzel, B. In *Polymer Composites: From Nano- to Macro-Scale*; Friedrich, K., Fakirov, S., Zhang Z., Eds.; Springer: New York, USA, **2005**; Chapter 3.
26. Wichmann, M. H. G.; Sumfleth, J.; Fiedler, B.; Gojny, F. H.; Schulte, K. *Mech. Compos. Mater.* **2006**, 42, 395.
27. Tsangaris, G. M.; Psarras, G. C. *J. Mater. Sci.* **1999**, 34, 2151.
28. Ye, Z.; Deering, W. D.; Krokhin, A.; Roberts, J. A. *Phys. Rev. B* **2006**, 74, 075425.
29. Peng, Z.; Peng, J.; Ou, Y. *Phys. Lett. A* **2006**, 359, 56.
30. Fotiou, I.; Vavouliotis, A.; Kostopoulos, V. Proceedings of Annual Meeting of the Polymer Processing Society (PPS-24): Mixing & Compounding, Salerno, Italy, **2008**.
31. Chung, D. D. L. *Carbon* **2001**, 39, 279.
32. National Research Council (U.S.). Publication NMAB-473, National Academy Press, Washington, DC, ISBN 0-309-05027-8, **1994**.
33. Papargyris, D. A.; Day, R. J.; Nesbitt, A.; Bakavos, D. *Compos. Sci. Technol.* **2008**, 68, 1854.

34. Liu, Z.; Bai, G.; Huang, Y.; Ma, Y.; Du, F.; Li, F.; Guo, T.; Chen Y. *Carbon* **2007**, *45*, 821.
35. Ku, H. S.; Baddeley, D.; Snook, C.; Chew, C. S. *J. Reinf. Plast. Compos.* **2005**, *24*, 1181.
36. Mooteri, P. S.; Sridhara, B. K.; Rao, S.; Prakash M. R.; Rao, R. M. V. G. K. *J. Reinf. Plast. Compos.* **2006**, *25*, 503.
37. Yarlagadda, K. D. V. P.; Hsu, S.-H. *J. Mater. Process. Tech.* **2004**, *155–156*, 1532.
38. Khare, H. S.; Burris, D. L. *Polymer* **2010**, *51*, 719.
39. Baltopoulos, A.; Fiamegkou, E.; Vavouliotis, A.; Karapappas, P.; Athanasopoulos, N.; Fotiou, I.; Kostopoulos, V.; Maagt, P. D.; Rohr, T. Proceedings of SPIE—The International Society for Optical Engineering, 2009, 7493, 74932G.
40. Ma, P. C.; Mo, S. Y.; Tang, B. Z.; Kim, J. K. *Carbon* **2010**, *48*, 1824.
41. Imholt, T. J.; Dyke, C. A.; Hasslacher, B.; Perez, J. M.; Price, D. W.; Roberts, J. A.; Scott, J. B.; Wadhawan, A.; Ye, Z.; Tour, J. M. *Chem. Mater.* **2003**, *15*, 3969.