Rapid curing and additive manufacturing of thermoset systems using scanning microwave heating of carbon nanotube/epoxy composites

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ABSTRACT

Here we show that the heating response of multi-walled carbon nanotube (MWCNT) fillers to applied microwave fields can provide a means to rapidly cure epoxy composites; this is useful for eliminating thermal gradients and decreasing cure times, even in the unconstrained environments common to additive manufacturing. We demonstrate this by comparing 5.0 wt% (2.2 vol.%) MWCNT-loaded epoxy samples cured in different environments: (i) in a conventional oven, (ii) under a forced thermal gradient in order to simulate industrial-scale non-uniformities, and (iii) scanned beneath a microwave waveguide. We assess both cure speed and cure uniformity in conductivity and composition. Microwave-cured samples show ~1 order of magnitude higher conductivity than oven-cured samples, whereas the forced thermal gradient results in extreme variations in conductivity. This rapid cure allows for thermosets to be used in processing techniques that had previously been very difficult to achieve due to the long cure times necessary for a thermally curable epoxy. The concept of additive manufacturing of thermosets is demonstrated by completing a novel deposition-and-scan technique that results in a patterned structure of cured epoxy. This indicates that the microwave scanning technique is a feasible way to quickly cure multiple layers of unconstrained epoxy in an additive manufacturing context.

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1. Introduction

Epoxy resins are commonly used in industry as coatings, laminates, and as aircraft/automobile components due to their exceptional mechanical and adhesive properties as well as their corrosion resistance [1,2]. Despite the utility of these materials show extremely promising properties, the processing of heat-curable epoxies is difficult due to long cure times and the thermal gradients that develop during the conventional curing process. These materials have successfully been used in manufacturing techniques such as 3D printing, but the process was limited due to a slow extrusion rate and the long curing times necessary for epoxy or specialty ultraviolet (UV)-curing chemistries [3–6]. In many cases, nanofillers such as carbon nanotubes (CNT) are added to the epoxy matrix to reinforce the mechanical and electrical properties [7–9].

Long cure times may lead to nanofiller aggregation (specifically that of CNT) within the epoxy. This is because the CNTs are not dispersed as a stable colloid; once stirring stops, sedimentation and aggregation will begin to occur if the epoxy is still in liquid form, as reported by Chang et al. [10] Aggregation of the CNTs may lead to inhomogeneities in properties such as electrical conductivity. Thus, it is important to develop new strategies for fast curing of epoxy that avoid aggregation during the cure [10–12].

The most common way to cure an epoxy system is through the use of conventional external heating, often under vacuum. This method of curing often requires long cure times, especially for large or thick samples [13]. A major concern is that large, conventionally cured samples suffer from varying temperature fields (or gradients), leading to non-uniform cure throughout the sample [14]. This non-uniform curing of large, thick composites can introduce high stresses and trap voids within the material [15,16] which in turn cause significant non-uniformities in both mechanical and electrical properties. It is particularly difficult to eliminate such thermal gradients in large structures (such as those in the aerospace

industry or in wind turbine blades [17]) given the use of external heating.

One intriguing solution to this problem is the use of carbon nanotubes as heating elements for volumetric heat generation rather than external heat transfer [18,19]. CNT are known to rapidly heat under microwave fields [18,20—23]. This heating effect has been observed for both single- and multi-walled carbon nanotubes (SWCNT and MWCNT) [24,25], so the use of CNT (or other microwave susceptors) could allow a nanotube-filled epoxy to rapidly cure from the heat generated by the dispersed susceptors. The use of microwave-nanotube heating interactions for curing epoxy systems has been previously demonstrated [10—12]; many of these studies focused mainly on decreasing cure time relative to CNT aggregation times and avoiding large aggregates.

Our group had previously developed a technique for using MWCNT as microwave susceptors to heat 3D-printed polymer structures in order to improve weld strength of the final printed product [26—28]. This may be accomplished by scanning the 3D-printed structures under a microwave horn applicator. This scanning method may be adapted and utilized as a means to rapidly and uniformly cure CNT-loaded epoxy, even allowing for rapid deposition and curing as a means to 3D printing of thermosets.

In this study, we examine property variation as a function of location within the sample. We demonstrate that a scanning microwave approach allows for increased uniformity and cure rate relative to uniform oven or stationary microwave curing of large industrial samples. Samples cured using an oven, under a forced thermal gradient used to mimic industrial samples, and using a microwave-scanning technique are considered. A novel deposition-and-scan technique is also developed that could be used for additive manufacturing.

2. Experimental

2.1. Materials and sample preparation

The epoxy (Mix Ratio 3:1, Pot Life 120—140 Minutes, Specific Gravity 1.12—1.13 g/cm³, Mixed Viscosity 925—975 cps, Systems 2000 resin and 2120 hardener, produced by Fiberglass) composites were prepared by adding 5.0 wt% (2.2 vol.%) MWCNT (Outer Diameter 30—50 nm, Length 10—20 μm, purity >95%, Cheaptubes) to the premeasured epoxy resin. This was stirred thoroughly by hand and the appropriate amount of hardener was measured into the MWCNT/resin mixture and again stirred thoroughly by hand. The epoxy was poured into a Teflon mold ((12 mm × 12 mm × 8 mm) for microwave responsiveness testing and 50 mm × 10 mm × 10 mm for all other samples). No release agent was used. Note: We benchmark our cure times against the manufacturer's curing recommendations, which involves a pot life of 2 h at 23 °C plus extended cure times at higher temperatures.

For the oven cured sample, the filled mold was placed in a preheated oven at 80 °C for 2 h. For the thermal gradient sample, one end of the mold was placed in an ice bath and the other end was placed against a hot plate set at approximately 220 °C. A Forward-Looking Infrared (FLIR) camera was set up to watch this sample reach steady state and cure. This process took approximately 7 h. In the case of the scanned microwaved sample, the mold was scanned at a constant rate of 0.16 cm/s underneath the waveguide inside the Faraday cage. The microwave/Faraday cage setup can be seen in Fig. S1. The microwave power was set to 750 W. The FLIR camera was used to watch this sample pass under the waveguide and examine how the sample heated.

In each case, the sample was allowed to remain in the mold for 24 h prior to removal. Once removed, the top, bottom, and sides of each sample were sanded completely in order to minimize skin effects in the measurements and the sample was sliced into pieces using a micro table saw.

2.2. Additive manufacturing

Approximately 1 mm MWCNT-loaded epoxy (5.0 wt%, 2.2 vol.%) was extruded and doctor-bladed onto a piece of Teflon and scanned at a linear rate of 0.08 cm/s under the waveguide in the Faraday cage with the microwave setting at full power (1250 W). As additional layers were added, the power was decreased to 750 W for layers 2 and 3 and then 625 W for layer 4 and finally 500 W for the final layer 5. The decrease in power was necessary to avoid burning the sample. The deposition-and-scan process was repeated 5 times until a total thickness of approximately 4.6 mm was reached. The FLIR camera was used to monitor the temperature profile of each of the layers.

2.3. Characterization

2.3.1. Microwave heating response

The microwave absorbance measurements as a proxy for AC conductivity measurements were completed using an Opthos Microwave source and standing waveguide. In the case of the initial (before cure) microwave susceptibility measurements, the power was set at 75 W and the microwave was on for 7.5 min. In the case of the AC measurements (post-cure susceptibility), each slice was placed in the center of the standing waveguide. The wattage was increased 25 W every 2 min beginning at 25 W and ending at 150 W. A FLIR thermal imaging camera was used to visualize and record the increase in temperature that occurred during both of these processes.

2.3.2. Thermogravimetric analysis

The MWCNT content was measured using a Q50 thermogravimetric analyzer (TGA; TA Instruments, New Castle, DE). The measurements were completed in an oxidizing atmosphere ramping from room temperature to 850 °C at 15 °C/min. The reported MWCNT content was determined from the remaining weight at 500 °C.

2.3.3. DC conductivity

The electrical conductivities of the epoxy/MWCNT composites were characterized using four-point-probe (Signatone HR4-620850FN) resistivity measurements to determine the DC conductivity. The four-point-probe head has four osmium tips with a 5 mil (0.127 mm) radius, 85 g pressure, and 62.5 mil (1.5875 mm) tip spacing. The tips have cone-shaped ends as shown in Fig. S2. Samples were sliced along the cross sectional area into pieces approximately 10.2 × 5.0 × 5.6 mm in size (for the samples in the mold), centered on a four-point-probe stand (Lucas Labs) and measured using a differential voltage system (two Keithley 6514 electrometers, Keithley 2000 digital multimeter) with current sourced by a Keithley 6221. Starting at the lowest possible current for each sample, voltage drops were measured at three increasing decades to ensure the linear Ohmic behavior of the samples. Three measurements were taken on each face of the sample and the voltage drop was taken from the average of these measurements. Volume resistivity (inversely conductivity) was calculated according to the following formula:

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot t \cdot k$$

where ρ is the resistivity in Ohm-m, V is the voltage drop in Volts, I is the current in Amps, t is the thickness in meters, and k is a