ELECTRIC CURING OF NANOCARBON/EPOXY ADHESIVES FOR COMPOSITE REPAIR

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Abstract

This work shows results on the addition of conducting nanoparticles (e.g. CNTs, GO) to epoxy resins to obtain conductive adhesives which can be cured by Joule heating and used for composite repair. Importantly, the small amount of conductive nanofillers required for this process produces only a moderate increase in matrix viscosity, but still at a level compatible with adhesive applications. The electric curing process can be used to cure shapes of arbitrary size and shape. As examples, we demonstrate the bonding of metal to metal, CFRP – CFRP and CFRP to metal. The thermomechanical properties of the joint are also analyzed.

1. Introduction

Nanocarbons such as carbon nanotubes (CNT) and graphene possess a unique combination of mechanical [1,2] electrical [3] and thermal [4] properties in the plane of the graphitic layers, combined with very high specific surface and aspect ratio. One of the routes to exploit these properties on a macroscopic scale is in composites where the nanocarbons are dispersed in a polymer matrix. Typically, low volume fractions of nanocarbon result in more efficient improvements in matrix properties, whereas at higher volume fractions aggregation of the nanocarbon can reduce its effect on the polymer matrix [5,6]. Electrical percolation, for example, can be often achieved with less than 0.1vol% nanocarbon [7], with electrical conductivity reaching values in the range of 0.1 – 1S/m at small volume fractions of only 1vol% [8,9]. Previous results by the authors [10] showed that conductive CNT/thermosets can be cured resistively to bond metallic and CFRP parts. The process was shown to be potentially more efficient than oven-curing of adhesives.

The number of adhesive bonding applications in various industries is steadily growing. Typical examples of beneficial applications of the adhesive bonding technology are in the construction of aircraft, rail vehicles and in the automobile industry. Also adhesive bonding is one of most common repair techniques carried out in composite structures, either in the condition of temporary repair or permanent repair. As a temporary repair, it has the advantage of its easy application process especially when it is an external bonded repair.

2. Results and discussion

2.1. Adhesive preparation and curing

The curing process requires at least three components: thermoset, conductive filler and conductive parts/electrodes. The composition of the adhesive used for this work is Hunstman LY556 epoxy and XB 3473 amine hardener and 0.1-1% in mass of MWCNT produced by Thomas Swan LTD. The conductive parts/electrodes were aluminium or 8552/AS5 CFRP. A schematic of the components is shown in the Figure 1a.

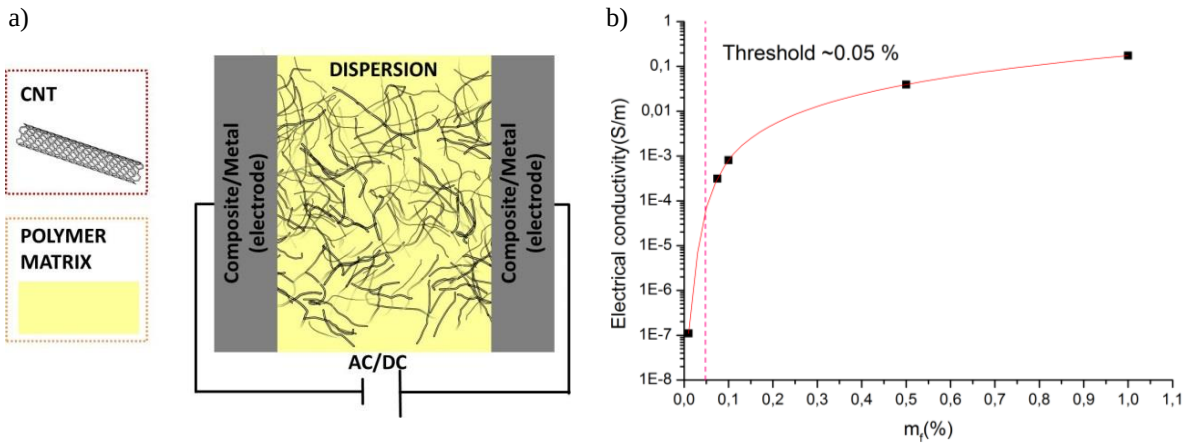

Figure 1. a) Schematic of the CNT-epoxy dispersion and the electrode set-up required to cure it. b) Typical percolation curve of the mixture epoxy-CNT.

The conductive adhesive is prepared following the next process. A known weight of CNTs is added to epoxy resin and dispersed using a EXAKT 80 E three roll mill at constant output roller speed of 250rpm (relative speed between rolls is 1:3.9) and gradually decreasing the gap between rolls from 125μm to 5μm. Next the hardener is added to the resin and manually stirred for a minute, after which the material is degassed in an equipment built in-house. At this point (even before hardener addition) the adhesive is already an electric conductor. Its electrical resistance is in the range kΩ-MΩ depending on characteristics of the dispersion of conductive nanoparticles such as aspect ratio, degree of particle separation and mass fraction. In this work, percolation was obtained at ~0.5% mass (Figure 1b).

For the application of the adhesive, the conductive resin is spread onto the surface of one of the conductive parts to be joined. The metallic parts used here were un-treated, cleaned only with acetone. In the case of the CFRP laminates used, their surface in contact with cables and resin had to be slightly sanded down by hand to obtain a good electrical contact.

After the two bonding parts are placed together in their final position with the adhesive between them, the electric connections between power supply, bonding parts, controller and temperature probe are made. Figure 2 shows a schematic of the set-up and a photograph of a typical configuration used to produce samples for subsequent mechanical testing in single-lap shear mode.

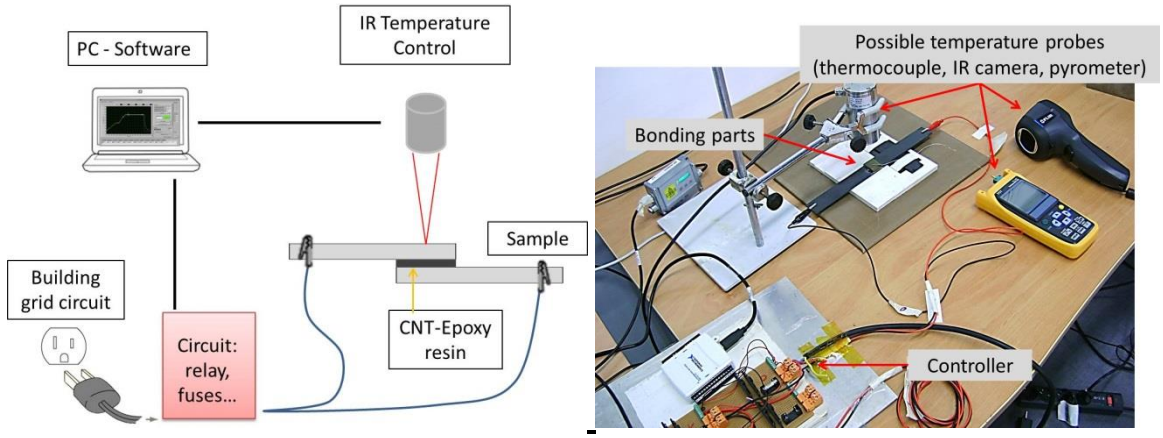

Figure 2. Schematic and photograph of the set-up and various components required for electric curing.

In this basic system the Lab-View controller regulates the power (voltage, current) delivered to the sample according to the temperature measured by one of the probes (thermocouple, camera or pyrometer) and following a pre-determined temperature ramp or set-point. An example of such a ramp and the sample surface temperature are shown in Figure 3 below. Note that the process permits in principle the use of any curing ramp within the limits of the specific thermoset curing kinetics.

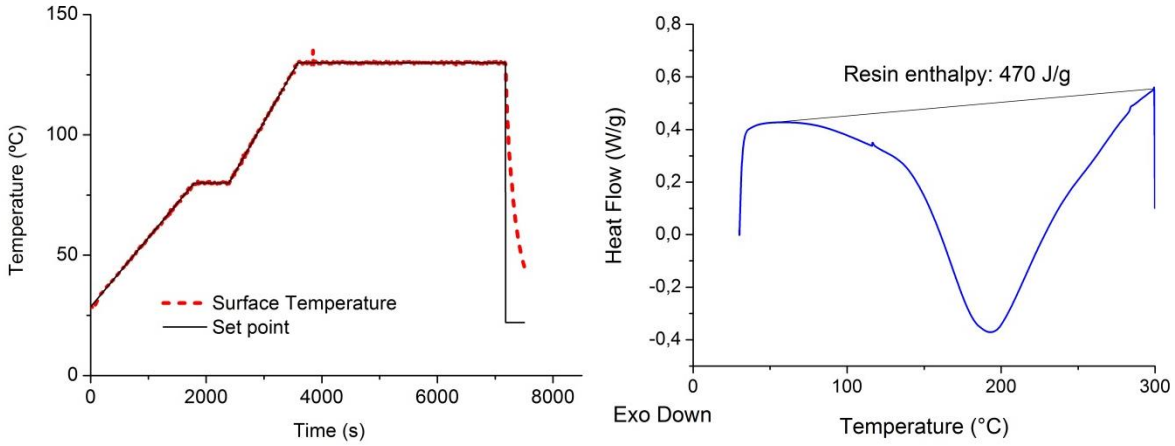

Figure 3. Set-point and sample surface temperature during electric curing of a CFRP plate sample subsequently tested in single-lap shear mode. Also presented the calorimetric curve of the resin what is fundamental for designing the curing ramp.

Also different joint geometries have been successfully cured, proving the capability of joining different material and with variable adhesive surface dimensions. In Figure 4 are shown several examples.

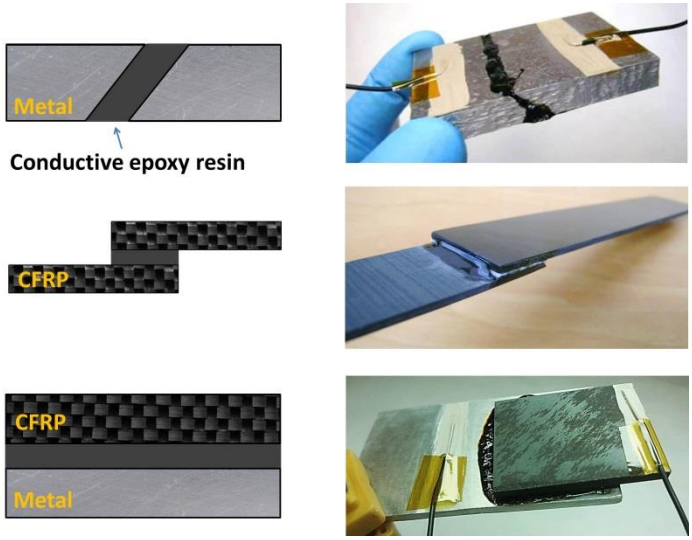

Figure 4. Different joint geometries successfully cured.

2.2. Electrical conductivity measurement.

It is worth first setting the basic general equations governing the curing process. To bond two flat parts of area A, separated by a distance l, then the resistance R of the epoxy contained in that volume will be $R = l/(\rho A)$, where ρ is the sample electrical resistivity. The power supplied for curing is $P = VI = V^2/R = I^2R$. Since Joule heating is a one-to-one conversion process, the heat supplied to the sample over time t is given by

$$Q = \frac{A}{l} \times V^2 t \times \rho \tag{1}$$

Where the first term corresponds to the bonding scenario and the third to the intrinsic properties of the adhesive. Naturally, there will be substantial heat losses in the system, which will depend on the specific arrangement of the parts to be bonded.

The starting point requires bearing in mind that the conductivity of the resin comes from the myriad of conductive nanoparticles that are dispersed in the matrix and forming a (percolating) network throughout the material. In its uncured state the resin is a viscous liquid, meaning that its small polymer constituents can move freely relative to each other by self-diffusion. In the process the conductive particles can move as well, which reshapes the network and therefore changes the bulk electrical resistivity of the matrix. This mobility of the conductors will be affected by matrix viscosity and external stimuli (mechanical or electric field).

From a macroscopic point of view the implication is that the electrical resistance of the resin can be a function of time, temperature, filler volume fraction and applied voltage. These variations can be taken into account during the curing process since the controller uses sample temperature directly and adjusts the power supplied accordingly, but controlling the process

becomes increasingly difficult for larger resistance variations. It is therefore of interest to understand these effects more closely.

A typical resistance change over time is presented in Figure 5. It shows a deep drop in the first day after dispersion of the CNTs in the resin but then reaches a stable value that remains constant in time. The drop can reduce electrical resistance by an order of magnitude and is due to re-aggregation of CNTs immediately after preparation of the CNT/thermoset mixture. Figure 4 also shows that temperature has a similar effect. As the sample temperature is increase from 20ºC to 180ºC its electrical resistance drops by about two orders of magnitude.

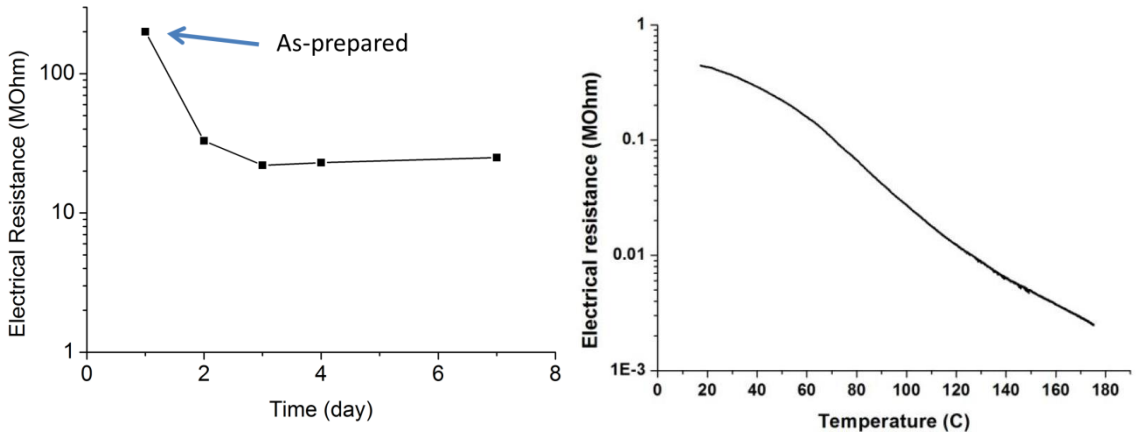

Figure 5. Changes in electrical resistance with time (left) and temperature (right) due to re-aggregation of CNTs and the consequent reshaping of the conductive network in the thermoset resin.

The combined dependence of electrical resistance on time and temperature is plotted in Figure 6 as the resistance at a given time divided by the original resistance at time = 0 and room temperature (RT), shown for samples at 80ºC and 120ºC. Clearly the effect is driven by the decrease in matrix viscosity and its effect on CNT mobility (CNT self diffusion is inversely proportional to viscosity) but the exact correspondence between resistance decrease rate with viscosity increase requires further experiments.

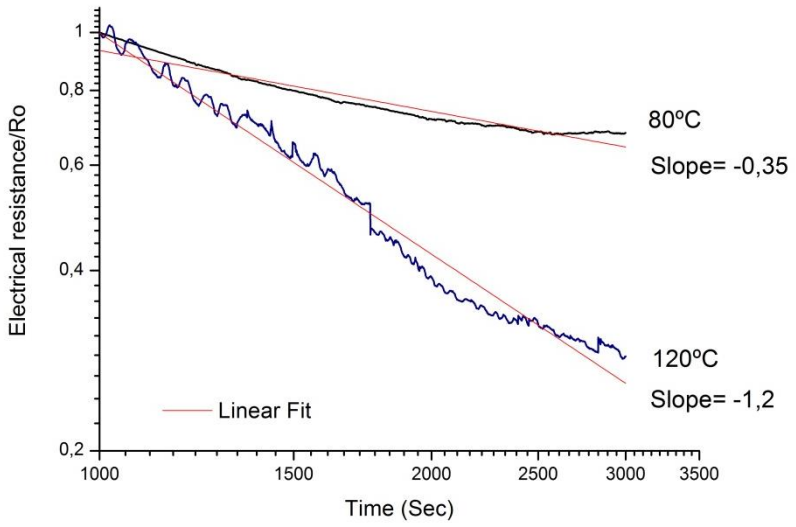

Figure 6. Electrical resistance drop over time for samples 0.1%CNT at 80C and 120C, showing the effect of viscosity.

2.3. Adhesive joint characterization

A simple and direct measure of the uniformity of the adhesive joint is the degree of curing of the thermoset, which can be easily obtained by Differential Scanning Calorimetry (DSC). Using heating rates and measurements determination of T_g was done according to industrial standards.

Also were prepared a set of samples for mechanical testing in order to obtain a preliminary assessment of the robustness of the joints obtained by electric curing compared to samples cured in an oven. EN 2243-1 normative for single lap shear test method was followed with little variations in the thickness of the adhesive. A typical sample consisted of two 8552/AS5 CFRP 100mm x 30mm rectangular parts overlapped by a length of 15mm and separated using two thin PTFE strips of 1 mm thickness.

We have found small variations in the degree of curing across the bonding surface. Figure 7 presents values of degree of curing for small extracts of thermoset taken from different positions in the joint, each from a different part. Also it shows the best results of stress-strain for oven and electric curing samples.

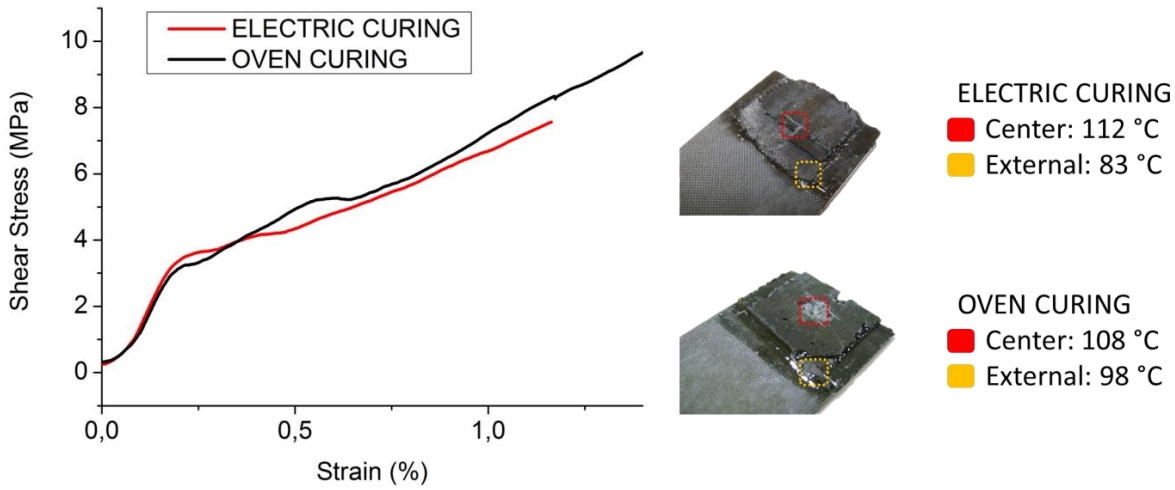

Figure 7. Stress-strain curves of samples subjected to single-lap shear test. The successfully e-cured sample is nearly identical to the oven-cured reference.

A comparison of fracture surfaces of the two samples shows that the electrically-cured has significantly more porosity, which we estimate by image analysis to reduce the adhesive/CF contact surface by 13-30%. Renormalizing the data to take into account this reduction in adhesive contact would give shear strengths in the range 9.4 – 10.8 MPa, the same as the oven part. This indicates that although the pores represent defects, the intrinsic mechanical properties of the adhesive are successfully obtained when curing electrically.

A preliminary comparison sing AC and DC was also established in this project. Overall, the use of AC is seen to result in better control of the curing process, with the sample temperature being more uniform throughout the joint and following more closely the set-point. This effect is particularly noticeable at small separation between bonding parts, and is likely to be due to charge migration, electrochemical reactions at the electrodes and the possible orientation of

conductive CNTs in the presence of the constant electric field, effects which are not expected when using alternate electric fields. Similar effects have been observed in electrically curable cements at least a decade ago [11].

3. Conclusions

A variety of geometries and conductive parts can be effectively bonded by electric curing of thermoset adhesives. The process can be controlled so as to follow a typical curing ramp of multiple steps and dwellings, with competitive ramps of a few degrees per minutes and stable up to temperatures of 200ºC.

The results of this work show that electrically-cured samples can reach more than 75% of the adhesive strength of comparable samples produced in an oven, with this shortfall being attributed to thermoset porosity due to ineffective resin degassing a curing process that is not yet entirely uniform. The use of AC is seen as simplifying control of process by removing possible charge build up at electrodes and arcing due to CNT field alignment.

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