

# Impedance Spectroscopy and Equivalent Circuit Modelling of Carbon Nanotube Dispersion in Thermosetting Blends

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**Abstract.** The dispersion of carbon nanotubes (CNTs) in a typical epoxy resin was monitored on line via the employment of impedance spectroscopy. The use of interdigital sensors has the advantage for in situ process monitoring during the dispersion process which is significant for the effective use of CNTs in modern technological products such as those used in marine applications. Monitoring the dispersion process ensures high quality of products and facilitates optimal material selection in the product formulation. The real and imaginary parts of the impedance were recorded during frequency scans at regular intervals in the course of the sonication of the mixture. The equivalent circuit analysis of the sensor signal assisted in the detection of the gradual progress of the process and also the indication of time of completion.

**Keywords:** carbon nanotubes, dispersion, impedance spectroscopy, interdigital sensors, equivalent circuit analysis

**PACS:** 82.35.Np Nanoparticles in polymers, 82.70.-y Disperse systems; complex fluid, 62.23.Pq Composites (nanosystems embedded in a larger structure), 61.46.Fg Nanotubes

## INTRODUCTION

Carbon Nanotubes (CNTs) were found to improve electrical, thermal and mechanical properties of polymer matrices when they used as fillers, similar to Carbon Black (CB) particles with the advantage that for building up the conductive percolation network, much lower weight content of CNTs is needed [1]. For the application of using CNTs in the matrix of smart tooling, the electrical as well as thermal properties enhancement is considered. In order to obtain conductive polymer/CNT composites, the CNTs are incorporated into the polymer matrix, where they form a three dimensional conductive network above a critical volume called the percolation threshold ( $p_c$ ) [2] inversely dependent on the aspect ratio (the ratio of the long dimension over the short dimension) of the inclusions. Therefore, the high aspect ratio of CNTs provides conductive carbon fibre reinforced polymers (CFRPs) with the inclusion of low filler concentration [3, 4].

The first major step of CNT reinforced CFRPs production depends on the homogeneous dispersion of the CNTs in the polymer matrix. Therefore depending on the desirable target properties, the processing parameters like the viscosity of the matrix, the size and geometry of the particles and the machine parameters like rotation speed, mixing time and temperature, the optimum filler content and manufacturing process can vary for each filler-matrix combination. One basic challenge consists in finding the best technology for the energy input to disperse the fibres without damaging them and the epoxy matrix. There are significant challenges and peculiarities when dispersing CNTs in thermoset resin systems.

On the other hand the CNT-reinforced resin systems are used as matrix material in CFRPs. This is usually achieved by prepregging, Resin Transfer Moulding (RTM), wet laminating or autoclave technologies. Critical parameters are amongst others the viscosity of the matrix, the dispersion quality and the particle size.

Dispersion and percolation behaviour depend on many factors. Shape and size of the dispersed particles, shear rate, viscosity and chemical functionalization; all of these parameters influence the dispersion result. However, once dispersed, the system is not in the state of equilibrium. The particles dispersed in a viscous material are subject to Brownian motion and hydrodynamic forces and the particles interact due to different attractive and repulsive forces.

While curing the epoxy/CNT composites, two processes counteract each other. Viscosity decreases with increasing temperature but once the curing reaction is initiated, cross-linking between the molecules will result progressively increment in viscosity with time. This leads to an accelerated re-agglomeration. It is well known that carbon nanotubes re-agglomerate during the curing process. There are methods to achieve a stable dispersion, either by modifying the potential curve or by stabilising the suspension via the existence of a potential barrier.

All the above demonstrate the significance for nanotube-reinforced polymers of the effective dispersion of the CNTs in the matrix system. Nano-scaled particles exhibit an enormous surface area (more than 1000 m<sup>2</sup>/g), which is several orders of magnitude larger than the surface of conventional fillers. This surface area acts as interface for a stress transfer, but is also responsible for the strong tendency of the CNTs to form agglomerates. An efficient exploitation of the CNT properties in polymers is therefore related to their homogeneous dispersion in the matrix or an exfoliation of the agglomerates and a good wetting with the polymer.

The precise characterisation of the dispersion quality is a complex issue. There are different, partly multistage procedures, interpreting the results of specific testing methods. The validation does not generate absolute values but has a relative, describing character. Low resolution analysis can be used to search for significant agglomerates inside a bigger area, while high resolution methods are able to evidence (or not) the existence of single dispersed CNTs.

## METHODOLOGY

Dielectric analysis, or dielectrometry, is a technique that can be used to investigate the processing characteristics and chemical structure of polymers and other organic materials by measuring their dielectric properties. Dielectric measurements are usually implemented as an electrical admittance measurement. This measurement can be accomplished by placing a sample of the material of interest between two electrically conducting plates (electrodes), applying a time-varying voltage,  $v(t)$ , between the two electrodes and measuring the resulting time-varying current,  $i(t)$  [5,6].

Impedance spectroscopy coupled with equivalent circuit modelling can be used in order to investigate the on-line monitoring of thermoset cure [7]. One limitation of using equivalent circuits is the non-uniqueness of the model because the material response can be represented by a variety of combinations of electrical components. Recent work has shown that when the

addition of CNTs induces a conductive response, impedance generally increases as crosslinking advances [8]. In the case of neat epoxy resin, this behaviour can be attributed to mobility limitations imposed on the charge carriers by the process of cure [9], while in the case where the epoxy matrix has been reinforced with SWNTs the frequency corresponding to the conductive mechanisms of the system increases with the process of cure [10].

Changes in a material's degree of electrical dipole alignment and/or its ion mobility can be used to infer information concerning its bulk material properties, such as its viscosity, rigidity, reaction rate, cure state, etc. Fundamental to the methodology of actually accomplishing dielectric (admittance) measurements is the critical assumption that the electrical response of the sample is linear and time-invariant [11].

A typical epoxy resin (Huntsman XU3508) was used for the dispersion of 0.1 %w/w multi-wall carbon nanotubes (MWCNTs) of more than 98% carbon basis, with outside diameter 6-13 nm and length 2.5-20  $\mu\text{m}$  from Sigma-Aldrich. Impedance measurements were performed using an Advanced Dielectric Thermal Analysis System (DETA-SCOPE by ADVISE) and commercially available GIA microsensors supplied at the site of the CNT mixing. The amplitude of the excitation voltage applied to the sensors was 10 V. A sweep of 12 frequencies between 10 Hz and 100 kHz was made. A control thermocouple was placed inside the resin tank in order to measure the temperature during the frequency cycles. The commercial dielectric sensor used (GIA sensors, Pearson Panke) comprise an assembly of interdigital copper electrodes, printed at a spacing of 300  $\mu\text{m}$  on a polymeric substrate film. The sensors were dipped into the resin/CNT dispersion and measurement were taken at regular intervals during the mixing process.

## DEVELOPMENT OF EQUIVALENT CIRCUIT MODEL

The application of the flat interdigital sensors allows for the in-process monitoring of the dispersion of carbon nanotubes in the epoxy matrix, as the transformation from the parallel plate capacitor to coplanar electrodes. These electrodes create fringing electric field lines which interact with the material. In this way, measurements may be one or two sided allowing for easy, non invasive measurements in most systems (Figure 1). The distance between the electrodes is proportional to the penetration depth in the material. In this way, the choice of sensor defines the representative volume that is interrogated with the method.

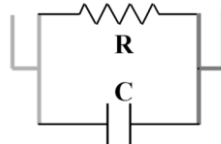


**FIGURE 1.** From the parallel to the coplanar capacitor configuration: the interdigital sensor and the resulting electric field.

The impedance response of the mixture is dominated by the behaviour of the conductive loose aggregates of nanotubes and the resin-rich areas acting as interfaces among them. The dielectric response of typical epoxy systems depends on the complex dielectric permittivity  $\epsilon^*$  which involves contribution from both dipoles and ion mobility:

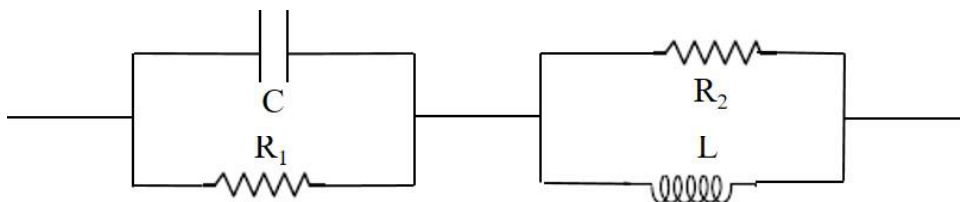
$$\epsilon^* = \epsilon_{dipolar}^* + \epsilon_{ionic}^* \quad (1)$$

When the electric field is interacting with the dielectric material, contributions from polarization of dipoles and ionic species take place at the vicinity of the capacitor plates or at randomly created interfaces in the material volume. Although the aforementioned contribution constitute an equivalent circuit where separate branches have to be accounted for in all distinct species, typically, in plain epoxy configurations the equivalent circuit is simplified, which directly relates to the resin viscosity and the degree of cure. In this case, the equivalent circuit is formed as a capacitor and a resistance in parallel (Figure 2), where the ionic contribution is characterized by the resistance  $R$ , and the mobility of the branches of the molecular network is represented by the capacitor  $C$ .



**FIGURE 2.** Simplified equivalent circuit for a typical epoxy cure reaction

In the case of the inclusion of the CNT phase, the equivalent circuit becomes more complicated. Previous works [12], [13] have revealed inductive contributions to electrical signal from the presence of CNT inclusions. In these studies a three branch circuit for the modelling of CNTs dispersion in the resin and of the curing process with the addition of hardener was used. The circuit representation was overall satisfactory for both mixing and curing of the resin, however an indication of the end of the dispersion process was not clearly observed. Therefore this circuit model needs to be improved. To this end, the three branch circuit of these studies [12], [13] is modified by shifting the branch corresponding to the contribution of the nanophase (a typical inertia element, i.e. a coil, and a resistance) to a new position in series to the other branches. In this way, it is believed that the equivalent circuit shown in Figure 3 has the inertia element (the inductance  $L$ ) in a more prominent role to represent accurately the dispersion of the nanophase (movement and structural changes of the CNTs). At the same time, the resistance  $R_2$  should be directly related to the conductivity of the mixture as dispersion stops percolation effects.



**FIGURE 3:** Equivalent circuit for the neat epoxy resin with CNT inclusions.

## ANALYSIS OF EXPERIMENTAL RESULTS

The temperature changes during the dispersion process were measured with a control thermocouple and the results are shown in Figure 4. It is observed that temperature is increasing at the initial stages of the dispersion and after 60 min it stabilises around 35°C.

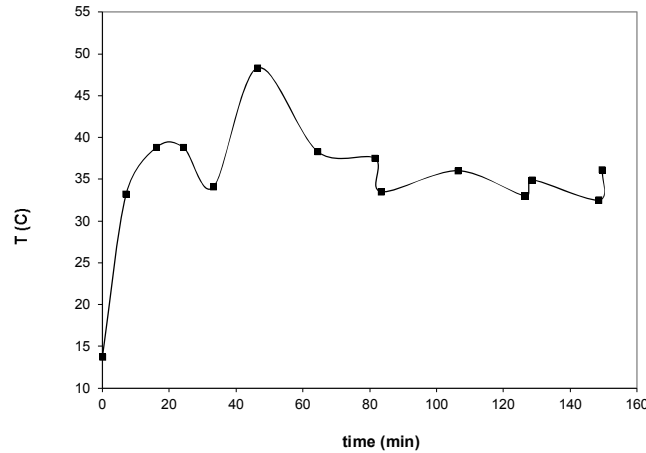


FIGURE 4. Values of  $T(t)$ , the temperature  $T$  vs. dispersion time.

The acquired impedance values during selected times at the course of CNT dispersion in the epoxy resin matrix were analysed and fitted to the circuit of Figure 3 by employing a complex non linear least square impedance fitting program developed by Ross Macdonald in 1999 and since then upgraded with additional features. The circuit of Figure 3 is adapted to standard circuit models embedded in the fitting software, where each circuit model consists of 40 elements. Out of the 40 parameters ( $P_1, P_2, \dots, P_{40}$ ) of the circuit model, only those related to the elements of the circuit of Figure 3 ( $P_1, P_6, P_7, P_8$  and  $P_9$ ) are variable, while all others are fixed to 0. Further details of the fitting method and the fitting software tool are provided in [13]. The main interface of the fitting software with the key settings used for the data treatment is shown in Figure 5.

**Fitting options** | Data lines

**Description of run**  
AZC A CKT. EXACT PAR. VALUES: ZC(2D6,1D0,0,3),1D+6,1D-12

**Data and fit types**

CNLS optimization operation (IOPT)	0	Input frequency format (FREEQ)	F, Ordinary, Hz	Model fitting function (FUN)	A	Help
Input data system (DINP)	Z, Impedance	Sign change of 2nd col (NEG)	No action taken	Residuals output type (IPAR)	0	
Fitting system (DFIT)	Z, Impedance	Type of data fit (DATYYP)	C, Complex	Function weighting (IFP)	0	
Complex input format (PINP)	R, rectangular	Capacitance of cell (CELCAP)	1.000000E+000	Residual weighting (IRE)	-11	
Complex fit format (PFIT)	R, rectangular	Robust regression (RQE) or -A/L	0.000000E+000			

**Data, weighting, and fitting specifications**

Evaluations (MAXFEV)	112	IGACC	2
Data weighting (IRCH)	2	NPRINT	0
Output level (IPRINT)	1	MODE	0
ATEMP	0.000000E+000	ICP	0
SD WC	3.639000E-001		
SD RC	3.639000E-001	# Data points	12

**Model parameters**

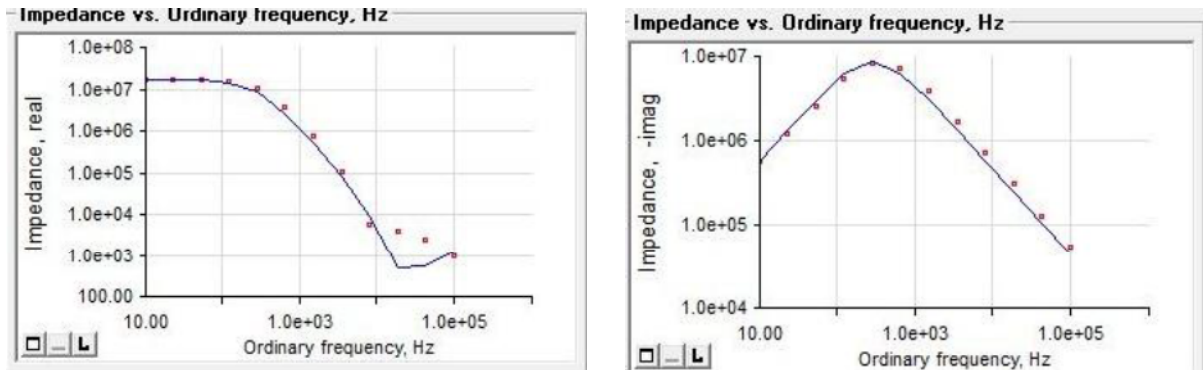
Number of model parameters (N) 40 Set

p[1]	2.1989265E+003	pos	p[2]	0.0000000E+000	fix
p[3]	0.0000000E+000	fix	p[4]	0.0000000E+000	fix
p[5]	0.0000000E+000	fix	p[6]	1.7472404E+007	pos
p[7]	5.5163504E-004	pos	p[8]	0.0000000E+000	fix
p[9]	1.0134804E+000	pos	p[10]	5.0000000E+000	DE1
p[11]	0.0000000E+000	fix	p[12]	0.0000000E+000	fix

FIGURE 5. User interface of the complex non-linear least square impedance fitting software for the analysis of the data obtained during CNT dispersion in epoxy resin matrix.

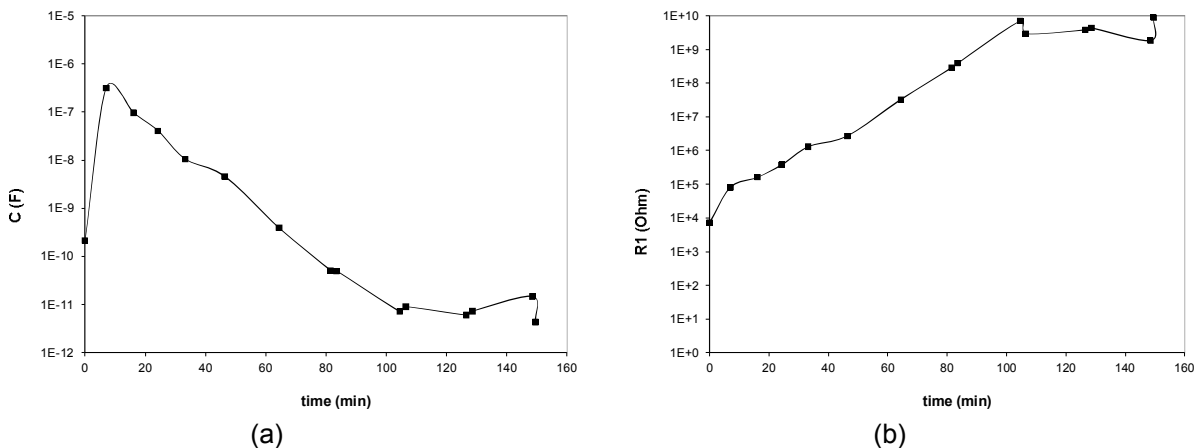
A typical fitting involved loading the measurement data from the specific impedance spectrum (real and imaginary impedance vs. test frequency) and running the fitting software with the above described model and settings of parameters. The predicted values of real and

imaginary impedance (model = continuous line) was compared with the measurement data (points = measurements) to assess the fitness of the model, as shown in Figure 6.



**FIGURE 6.** Comparison between data (points) and circuit model prediction (continuous line) for the real and imaginary impedance after the execution of the fitting routine.

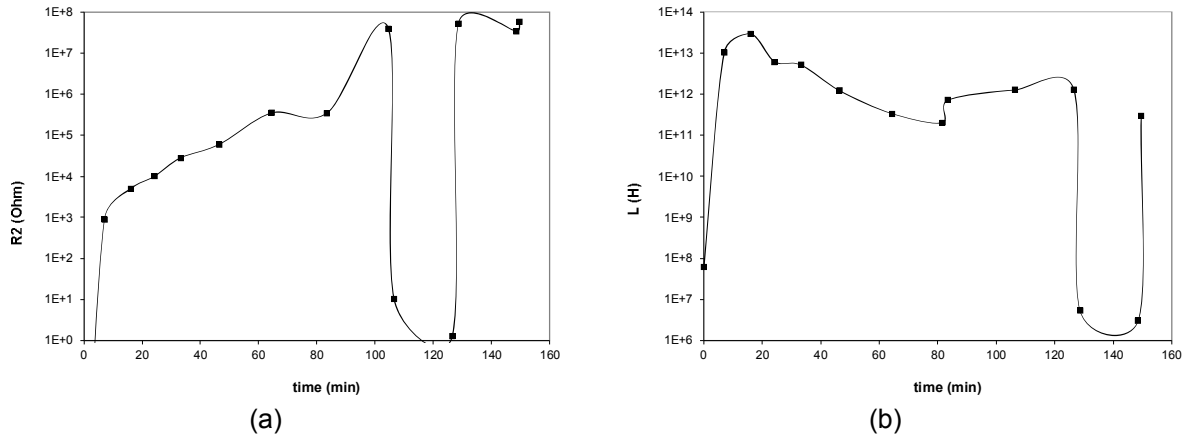
In the following description the values of the parameters of the equivalent circuit of Figure 3 are presented and the significance of the changes during the dispersion process is discussed.



**FIGURE 7.** Values of (a)  $C(t)$ , capacitance vs. dispersion time and (b)  $R_1(t)$ , resistance vs. dispersion time.

Figure 7 shows the values of the circuit elements in the branch representing the main relaxation and the charge separation in the material. There is a progressive change in the fitted values for both capacitance  $C$  and resistance  $R_1$ . As far as the capacitance is concerned (Figure 7a), there is an initial sharp increase at the start of the dispersion process, which is followed by a gradual drop in values up to 100 min in the process. At that time the capacitance value approaches the order of magnitude of capacitance in air showing that there are no significant relaxation processes in the signal any more. This levelling signifies the stability of the dispersion and an indication of the completion of the process. It is worth mentioning the high values of capacitance at the start of the process, which implies that the particular material structure at this stage is suitable for the development of energy storage devices. A potential freeze of the nanostructure at the specific formation would lead to an efficient capacity in charges separation.

As far as the resistance  $R_1$  is concerned (Figure 7b), the plot demonstrates similar gradual change, which is an increase for this element up to 100 min in the process. The starting value is around 10 k $\Omega$ , a low figure, as a result of low apparent viscosity of the resin under the initial conditions of the dispersion process (presence of few but large agglomerates of CNTs). As the dispersion proceeds, the agglomerates are breaking and the apparent viscosity increases causing the rise in resistance. The final level of the element  $R_1$  (corresponding to the resin component) in the order of G $\Omega$  indicates the reduced mobility of ions in the resin system. The time of levelling off is identical for both capacitance and resistance circuit elements.



**FIGURE 8.** Values of (a)  $R_2(t)$ , resistance vs. time and (b)  $L(t)$ , inductance vs. time.

Figure 8 shows the values of the circuit elements in the branch representing the conductive and inductive behaviour of the CNT structure within the liquid resin. There is a progressive change in the fitted values for both resistance  $R_2$  and inductance  $L$ . As far as the resistance is concerned (Figure 8a), there is an initial sharp increase at the start of the dispersion process, which is followed by a gradual increase in values. The final level is reached at 100 min in the process, but a disturbance in the behaviour is observed when the final level is reached. The disturbance has the form of very low values for a period of 20 min. The above changes are explained by the dispersion procedure, which breaks the nanoparticles agglomerates into smaller entities, thus increasing the length of conductive paths in the system. An effective dispersion process is expected to result in a significant increase of this resistive component. The increase in resistance is around four orders of magnitude. As far as the observed disturbance in resistance is concerned, this can be attributed to the occurrence of a 'conductive spike' in the system observed only at the CNT components of the circuit model.

As far as the inductance  $L$  is concerned (Figure 8b), the plot demonstrates also a sharp increase at the start of the process and then a gradual drop towards the final level at 100 min in the process. The starting value is around 100 MH and the final level is at 1 TH. As the dispersion proceeds, the agglomerates are breaking, the average distance between individual CNTs is increasing and the inductive effect is also increasing. A similar disturbance is observed in inductance.

The above description shows clearly how dielectric measurements in the dispersion process can be used to detect the main stages of the process and indicate its completion.

## CONCLUSIONS

The dispersion of carbon nanotubes (CNTs) in a typical epoxy resin was monitored on line via the employment of impedance spectroscopy. The system used interdigital sensors which allowed for in situ process monitoring during the dispersion process. The sensors were immersed in the epoxy/carbon nanotubes system which was subjected to dispersion. The real and imaginary parts of the impedance were recorded during frequency scans at regular intervals in the course of the sonication of the mixture. The equivalent circuit analysis of the sensor signal assisted in the detection of the gradual progress of the process and also the indication of time of completion.

The dispersion process is significant for the effective use of CNTs in modern technological products, such as those used in marine applications. Currently nanotechnology products are used for surface protection of principal structures, such as hulls, and also effective coating for the prevention of algae growth in submerged surfaces. The preparation of these products involves dispersion of CNT structures in the carrying liquid. Monitoring the dispersion process ensures high quality of products and facilitates optimal material selection in the product formulation.

## ACKNOWLEDGMENTS

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