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Processing and electrical characterization of a unidirectional CFRP composite filled with double walled carbon nanotubes

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Carbon nanotubes represent new emergent multifunctional materials that have potential applications for structural and electrically conductive composites. In the current paper we present a suitable technique for the integration of Double Walled Carbon Nanotubes (DWCNTs) in a unidirectional Carbon Fiber Reinforced Polymer (CFRP) with high volume content of carbon fiber. We showed that the electrical conductivity of the laminates versus temperature follows a non-linear variation which can be well described by the Fluctuation-Induced Tunneling Conduction (FITC) model. The parameters of this model for CFRP/DWCNTs and CFRP without DWCNTs were determined using best fit curves of the experimental data. This study has shown that DWCNTs have strong influence in the conductivity through laminate thickness. However, there are no significant effects on the electrical conductivity measured in the other two principle directions of the composite laminate. Furthermore, it was found that electron conduction mechanism of carbon fibers is dominated by the FITC.

1. Introduction

Significant progress has been made in the investigation of the multifunctionality of fiber reinforced polymers (FRPs). Beside their structural role, composite materials have the potential for deformation or temperature sensing when monitoring the electrical changes in the material. This self-sensing property is an attractive non-destructive evaluation method that undergoes intensive research. We believe that improving this sensing functionality or/and achieving new functionalities in conventional FRP can necessitate the addition of fillers in particular carbon nanotubes (CNTs). Carbon nanotubes are considered to be new emergent multifunctional materials that have potential applications for structural and electrically conductive composites [1–3]. The electrical conductivity of CFRP composites has interested many researchers for various applications such as damage and structural health monitoring of composite materials [4–7] and using carbon fibers as heating element [8]. The use of CNTs has made it possible to extend these applications to other dielectric composites such as glass fibers reinforced polymers (GFRPs). Intensive investigations are undertaken on the piezoresistivity of CNTs based-composites for

damages and structural health monitoring of composite materials [9–16]. Besides, other topic dealing with processing and characterization of conventional fibers reinforced polymer matrix filled with CNTs are up-to-date [3,17].

Regarding the CFRP composites and FRP containing CNTs composites, only few papers have investigated the effect of the temperature on the electrical conductivity of these composites. In practice, during their service, CFRP structures undergo thermal variation in different situations. For instance CRFP structures can be subjected to environmental changes where an increase in temperature can occur during different mechanical loads. When the variation of the temperature is not important, one can assume a linear relation between the temperature and the resistivity [16,19]. As in the work of Kupke et al. [18] in which the authors have monitored the mechanical damage during fatigue tests by measuring the electrical resistance in the specimens. To compensate the increase of temperature in composites during experiments, they proposed a linear relation between the electrical resistance and the temperature variation. However, in case of a strong variation of the temperature inside the composite structure this assumption can lead to significant errors if an accurate model is not used. To our knowledge, no work has been yet undertaken to investigate the effect of wide range temperature variation on the electrical conductivity of CFRP structures.

In order to process fiber reinforced polymers containing CNTs, there are mainly three techniques proposed in the literature,

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depending on the nature of the polymer matrix and the reinforcement fibers structure and volume content. The first technique is the impregnation of the reinforcement fibers with a polymer matrix filled with carbon nanotubes which is the most used technique because it is easy to implement. The dispersion of CNTs in the polymer matrix can be properly controlled [20]. CNTs/Liquid Polymer mix can be transferred to the fibers reinforcement (Preform) via resin transfer molding (RTM) or vacuum assisted RTM (VARTM) process. One major constraint of this method is the fiber volume content that must be relatively low because of the permeability of conventional fibers to CNTs [3]. Another constraint of this processing technique is the increase of the matrix viscosity caused by the CNTs [21,22]. The second technique is the deposition of CNTs on reinforcement surface [23,24]. This technique can be applied either by chemical functionalization of CNTs and carbon fibers to create chemical bonds or without chemical treatment. It was found that the chemical functionalization impairs the physical properties of CNTs and carbon fibers [25,26]. The third method of manufacturing FRP/CNTs composite consists of depositing dried CNTs on the surface of the prepregs plies. A prepreg is made of one layer of long fibers (woven or unidirectional) impregnated with a polymer matrix. This method has been used by Veedu et al. [1] and García et al. [27] to place layers of vertically aligned multi-walled CNTs named “forests of CNTs”. This technique increases considerably the out-of-plane mechanical properties of the composite but it has a limited influence on the electrical conductivity of the composite laminate.

In the present work we aim to manufacture CFRP composites with high carbon fiber content and filled with DWCNTs. We propose to study the frequency and temperature dependency of the electrical conductivity of the composites for a wide range of temperature; varying between -150°C and $+130^{\circ}\text{C}$. The polymer subjected to this study is an epoxy-based resin (RTM6) developed for processing high performance composite materials reinforced with unidirectional carbon fibers. Attention has been given to the analysis of the microstructure and the dispersion state of DWCNTs in the composite laminate.

2. Materials and methods

2.1. Materials and Epoxy/DWCNTs suspension preparation

2.1.1. Materials

The epoxy resin (RTM6) used in this investigation is provided by Hexcel composites (Hexcel Corporation, France). It is a mono-component resin in which the stoichiometric ratio of epoxy and amine hardener is already mixed and degassed. Carbon nanotubes used in this study are almost (80%) Double Walled Carbon Nanotubes (DWCNTs) [28] and were synthesized and purified at Paul Sabatier University (Institute Carnot-CIRIMAT) using Catalytic Chemical Vapor Deposition (CCVD) method [29]. Important characteristics of the present DWCNTs include their purity in Carbon atom (98% atomic), their average (BET) specific surface area (700 g/m^2) and the density 1.8 g/cm^3 [30]. The aspect ratio (length/diameter) of an individual DWCNT can be estimated to range between 1×10^3 and 1×10^4 . Carbon fibers are unidirectional (UD) reinforcing fabrics made of Toray T700S carbon fiber-type.

2.1.2. Preparation of the Epoxy/DWCNTs mixture

To process the CFRP containing DWCNTs we first prepared an Epoxy/DWCNTs suspension. DWCNTs suspended in water were sonicated in the presence of a suitable dispersion agent called Hexadecylamine using an ultrasonic bath for 1 h at room temperature. Then a strong sonication for 15 min was performed using a 13 mm probe tip. The power source for the probe sonication was

adjusted to 100 W. The weight ratio HDA:DWCNTs was taken as 1:1. This ratio was chosen based on a previous study conducted by Barrau et al. [31] on the dispersion of DWCNTs with amphiphilic molecules. The DWCNTs–HDA suspension was then mixed with the epoxy resin and stirred at 1000 rpm for 30 min at 80°C . The mixture was subsequently degassed for 2 h and 30 min at 80°C . Differential scanning calorimetric analysis and thermogravimetric analysis were performed on the degassed mixtures to ensure that they do not contain traceable water. Finally we used this suspension (Epoxy/DWCNTs) to impregnate UD carbon fabrics.

A preliminary study on Epoxy/DWCNTs nanocomposites showed that the electrical percolation threshold is achieved around 0.04 wt.% (0.025 vol.%) of DWCNTs. In order to achieve a high level of electrical conductivity in the material a concentration of DWCNTs in the epoxy resin equal to 0.4 wt.% (0.29 vol.%) has been used for processing the final CFRP composite.

2.2. Optical microscopy and scanning electron microscopy

The distribution and the quality of the carbon nanotubes dispersion in the composite laminates were examined using High Resolution Field Emission Scanning Electron Microscopy (HRFE-SEM). The samples were frozen in liquid nitrogen and subsequently fractured. The fractured surfaces were observed without any conductive coating using a field emission scanning electron microscope (JEOL JSM 6700-F) at a relatively low voltage of 0.7 kV.

For a qualitative and a quantitative analysis of the laminate, an optical microscope equipped with a camera was used. Five samples with dimensions of $30\text{ mm} \times 30\text{ mm} \times 2\text{ mm}$ were randomly cut out of each $[0^{\circ}]_8$ laminate plate. On each sample, two perpendicular edges (one $\perp$ to fibers and one $\parallel$ to fibers) were polished. The magnification is chosen as a function of the size of the largest void detected. Then, a large number of images (up to 100 images per kind of laminate) were analyzed using image analysis software (*imageJ*), which is a free image processing software developed by the National Institutes of Health–US. We calculated the void content in each laminate by counting the ratio of voids (dark contrast) to the remaining surface area for each image and finally we took the average. The quantitative analysis of micrographic images can provide us with an estimation of the void content in the material with a good accuracy [32,33].

2.3. Electrical conductivity—theory and experiment

Measurements were carried out by recording the impedance using a Solartron–Schlumberger frequency response analyzer together with a Novocontrol interface (broad-band dielectric converter). The alternative voltage is set to a maximum of 1 V so that self-heating of the samples can be neglected. The measurements were performed in the frequency ranged between 10^{-2} and 10^7 Hz at isothermal temperatures varying from -150°C to $+130^{\circ}\text{C}$ with a 10°C step. Two samples were cut randomly from each composite plate. The dimensions samples used were $20\text{ mm} \times 10\text{ mm} \times 2\text{ mm}$. The electrical conductivity measurements were performed on Epoxy/DWCNTs nanocomposites and Carbon fiber/Epoxy/DWCNTs composites. In order to ensure the electrical contact silver paint was applied to the surfaces. A preliminary study has been conducted in order to verify the repeatability and the accuracy of the two-point contact tests. Five samples were cut randomly from each composite plate and tested at room temperature with DC source using both two-point contact and four-point contact electrical measurements. To perform these measurements we used a DC current source (KEITHLEY Model 6221) coupled with a voltmeter (KEITHLEY 2182A). Four-point and two-point measurements gave similar values of conductivity.

Fig. 1. (a) Process for impregnation of a carbon fiber UD ply by epoxy resin. (b) Impregnated carbon fiber eight plies lay up in vacuum bagging.

Fig. 2. (a) Cure cycle in autoclave. (b) Vacuum bagging products after the curing cycle. (c) The laminate principal axis system.

The complex conductivity σ^* derived from the complex impedance is written as function of the frequency (ω):

$$\sigma^* = \sigma' + j\sigma''(\omega) \quad (1)$$

$$j^2 = -1$$

In this study we are interested in the real part $\sigma'(\omega)$ of the complex conductivity which characterizes the Ohmic conduction that occurs in the material. $\sigma'(\omega)$ can be expressed in the following form:

$$\sigma'(\omega) = \sigma(0) + \sigma_{AC}(\omega) = \sigma_{DC} + \sigma_{AC} \quad (2)$$

where σ_{DC} represents the Direct Current conductivity and appears at low frequency and σ_{AC} represents the Alternative Current conductivity which appears at very high frequency domain.

Jonscher [34] showed that the $\sigma'(\omega)$ can be written in the form of:

$$\sigma'(\omega) = \sigma_{DC} + A\omega^s \quad (3)$$

Fig. 3. Illustration of a CFRP composite cross-section; carbon fiber has a diameter of 7 μm and the inter-plies space is typically 20 μm .

where A is a constant dependent on temperature and s is an exponent function of temperature and frequency: $0 \leq s \leq 1$. This behavior of $\sigma'(\omega)$ is identified by Jonscher [34,35] as the "Universal Dielectric Response (UDR)" which describes the behavior of conductive systems in a disordered medium. It is therefore assumed that σ' reflects the mechanism of charge transport and the interactions

Fig. 4. HRFE-SEM micrographs of CFRP/DWCNTs composites laminate representing its section on the XY plane (a1) and (a2), on the XZ plane (b1) and (b2) and on the YZ plane (c1) and (c2).

Fig. 5. Optical micrograph of the composite laminates showing distinct phases. The dark gray contrast represents voids. (a) CFRP and (b) CFRP/DWCNTs.

between charge carriers when following its dependence with respect to frequency and temperature $\sigma(\omega, T)$.

The temperature dependence of the DC conductivity was modeled using the Fluctuation Induced Tunneling Conductivity (FITC) developed by Sheng [36,37]. This model predicts temperature dependence for the conductivity of the type:

$$\sigma_{DC} = \sigma_0 \exp\left(\frac{-T_1}{T + T_0}\right) \quad (4)$$

Sichel et al. [38,39] stated that T_1 may be regarded as the energy required for an electron to cross the insulating gap between the conductive medium (carbon fibers or CNTs clusters in our case)

Table 1

Void content the composites in determined by image analysis and acid digestion (EN 2564) and fiber volume content determined by acid digestion.

	Void (% vol) Image analysis	Void (% vol) Acid digestion	Carbon fiber (% vol) Acid digestion
CFRP	0.6 ± 0.3	0.9 ± 0.4	67 ± 2
CFRP/DWCNTs	1.4 ± 0.5	1.2 ± 0.4	66 ± 2

Fig. 6. Frequency dependence of conductivity $\sigma'(\omega)$ of Epoxy/0.4 wt.% DWCNTs nanocomposite at isothermal temperature ranging from -150°C to $+130^\circ\text{C}$.

and T_0 determines the temperature below which conventional elastic tunneling conduction dominates (i.e. temperature-independent conductivity below T_0). The pre-exponential factor σ_0 is treated as a constant.

The FITC can successfully explain the nonmetallic temperature dependence of the electrical conductivity in diverse materials such as carbon-black/polyvinylchloride films [35,28], CNTs thin films [40] and CNTs/Epoxy composites [41].

3. Results and discussion

3.1. Processing of carbon fiber/Epoxy/DWCNTs laminate and microscopic studies

Since we aim for processing a composite material containing DWCNTs with high volume content of carbon fibers ($V_{\text{fibers}} > 60\%$) a classic resin transfer molding process is not appropriate. This

process will lead to a high filtration of DWCNTs by the carbon fibers preform and non-uniform distribution of DWCNTs in the laminate.

The Epoxy/DWCNTs mixture we prepared can be used in a prepregger as shown in the work of Siddiqui et al. [42], to impregnate dry carbon fibers and prepare prepreps. An alternative way of using a prepregger is to impregnate the dry carbon fibers using resin film infusion which is suitable for lab-scale production of prepreps. Hence, to manufacture our Carbon Fiber/Epoxy/DWCNTs composites laminate we setup a liquid resin infusion process in order to impregnate individual UD plies of carbon fibers by the epoxy resin filled with DWCNTs see Fig. 1a. Series of eight individual UD plies with $300\text{ mm} \times 300\text{ mm}$ surface dimensions were impregnated by this process. Then the impregnated plies of carbon fiber were laid-up $[0^\circ]_8$ and cured in an autoclave using the temperature cure cycle recommended by Hexcel Composites (Figs. 1b and 2a). We must notice that the top plies were not impregnated with resin. For a comparative study the same process was performed to produce Carbon fibers/Epoxy composites unfilled with DWCNTs.

Despite the low permeability of carbon fibers to the DWCNTs, when examining the breather and bleeder plies after the curing process, we can see very few dark spots which evidence the migration of DWCNTs through thickness during the cure cycle; see Fig. 2b.

Microscopic structure and submicroscopic structure of our composite laminates were examined using an optical microscope and HREF-SEM. The scanning electron microscope enables us to study the distribution of DWCNTs in the composite laminate. The carbon fibers UD fabric structure contains gaps of different scales that can be filled with the polymer as illustrated in Fig. 3. DWCNTs are present in the resin rich regions. In the composite laminates we can distinguish two resin rich regions. The first one is between plies (inter-ply) of carbon fiber laminate and the second one is the resin rich area between tows (inter-tows) of carbon fiber in the same ply. Another resin space that can be identified is the resin inside carbon fibers tows (intra-tow).

All SEM images show homogeneous distribution of DWCNTs in the regions between plies; see Fig. 4a1 and a2. However, we observe that DWCNTs have not reached inside carbon fiber tows or intra-tow (Fig. 4b1, b2, c1 and c2) because DWCNTs aggregates are larger than the gaps inside the tows therefore they are filtrated. However, we noticed that DWCNTs do migrate through thickness, as seen in Fig. 2b, this is due to the structure of the UD fabric; one ply of UD fabric is made from assembling of carbon fiber tows, this assembling leads to some regular paths between tows (inter-tows) through which DWCNTs can migrate. Fig. 2b shows a regular pattern of DWCNTs dark spots on the vacuum bagging products.

The analysis of the optical microscope images reveals slightly more porosity in the material when the laminate is manufactured

Fig. 7. Frequency dependence of conductivity $\sigma'(\omega)$ at isothermal temperature ranging from -150°C to $+130^\circ\text{C}$. Measurement along the Z-direction (a) CFRP (b) CFRP/DWCNTs.

Fig. 8. Frequency dependence of conductivity $\sigma'(\omega)$ at isothermal temperature ranging from $-150\text{ }^{\circ}\text{C}$ to $+130\text{ }^{\circ}\text{C}$. Measurement along the Y-direction (a) CFRP. (b) CFRP/DWCNTs.

Fig. 9. Frequency dependence of conductivity $\sigma'(\omega)$ at isothermal temperature ranging from $-150\text{ }^{\circ}\text{C}$ to $+130\text{ }^{\circ}\text{C}$. Measurement along the X-direction; (a) CFRP. (b) CFRP/DWCNTs.

with DWCNTs but the overall microstructure of the composites is very similar; see Fig. 5a and b.

We determined the void content in the composite by analyzing the optical micrographs. Data from the quantitative analysis are presented in Table 1. These results are compared to the results obtained by using the acid digestion standard method (EN 2564) for determining fiber and void content, see Table 1. CFRP made with DWCNTs contain slightly more voids compared to the CFRP made without DWCNTs. We assigned the increase of voids to the increase of the viscosity induced by the addition of 0.4 wt.% of DWCNTs. The viscosity of the epoxy resin at $80\text{ }^{\circ}\text{C}$ increases from 0.4 Pa s to 6 Pa s when filled with 0.4 wt.% of DWCNTs.

3.2. Electrical conductivity of the CFRP

3.2.1. Frequency dependence of the electrical conductivity

The electrical conductivity measured as function of the frequency and at different temperatures is presented in Figs. 6–9. The real part of the complex conductivity as a function of frequency at various temperatures $\sigma'(\omega, T)$ of the Epoxy/DWCNTs nanocomposite in Fig. 6 shows typical behavior observed in for conduction in disordered materials [34]. The curves presented reveal similar features: a DC plateau up to certain critical frequency (ω_c) followed by a gradual increase of the conductivity at higher frequencies. According to Jonscher [34], in polymers filled with electrically conductive particles the charge transport occurs between localized states is produced by a disorder. This mechanism explains the frequency dependence of the conductivity. At a given temperature the critical frequency (ω_c) above which the conductivity behaves as a power law of the frequency depends strongly

Fig. 10. DC electrical conductivity versus inverse of temperature for (◊) Epoxy/0.4 wt.% DWCNTs, (◻) CFRP Z-direction, (◼) CFRP/DWCNTs Z-direction, (Δ) CFRP Y-direction, (◀) CFRP/DWCNTs Y-direction, (○) CFRP X-direction, (●) CFRP/DWCNTs X-direction (---) FITC mechanism, Eq. (4).

on the distribution, the size and the concentration of the conductive medium [43].

The results of electrical conductivity measurements through thickness (Z direction) for the CFRP laminate unfilled and filled with DWCNTs are presented in Fig. 7a and b respectively. The electrical conductivity measurements in the transverse (Y direction) are presented in Fig. 8a and b and along the fibers (X direction) Fig. 9a and b. At very high frequency, the AC electrical conductivity

Table 2

Parameters of the FITC model – Eq. (4) determined by fitting data from DC conductivity presented in Fig. 10.

Measured direction	Sample	σ_0 (S cm ⁻¹)	T_1 (K)	T_0 (K)	T_1/T_0
Through thickness (Z)	Epoxy/DWCNTs	1.2×10^{-3}	569 ± 33	121 ± 9	4.70
	CFRP	15×10^{-5}	382 ± 5	167 ± 4	2.29
	CFRP/DWCNTs	108×10^{-5}	200 ± 3	91 ± 2	2.19
Vertical to fibers (Y)	CFRP	7×10^{-3}	234 ± 3	226 ± 2	1.03
	CFRP/DWCNTs	18×10^{-3}	147 ± 3	153 ± 2	0.96
Along fiber axis (X)	CFRP	62	488 ± 30	73 ± 9	6.7
	CFRP/DWCNTs	63	420 ± 23	63 ± 7	6.7

determined perpendicular to the fibers axis (Z and Y directions) shows a frequency dependence in the form of a power law ($\sigma'(\omega) \propto A\omega^s$). This behavior disappears when the CFRP is filled with DWCNTs and the conductivity appears to be constant ($\sigma'_\omega = \sigma'_{DC}$). Carbon nanotubes contribute to increase the electrical conductivity level of the laminate in Z and Y direction and shift ω_C toward higher frequencies. The frequency dependence of the conductivity appears to be due to the existence of barriers (resin regions) between conductive media. This can be evidenced by the fact that the AC electrical conductivity measured along carbon fibers direction is independent of the frequency for both laminates (filled and unfilled with DWCNTs). The conductivity of the laminate along X direction is dominated by the electron transport through carbon fibers which can be considered as an infinite size conductive cluster.

Although the carbon fibers we used are transversally isotropic we found that the electrical conductivity values measured in the laminates perpendicular to the fibers-axis (Y and Z direction) are different due to the structure of the laminate as mentioned earlier in Figs. 3 and 5. The presence of resin rich regions between plies decreases the number of conductive paths through the thickness of the laminate. Consequently, this decreases the level of the electrical conductivity. For the CFRP unfilled with DWCNTs the DC electrical conductivity through the thickness at room temperature is 6.6×10^{-5} S cm⁻¹ and 5.3×10^{-3} S cm⁻¹, Figs. 7a and 8a. The difference between the electrical conductivity in Y and Z direction in CFRP laminate filled with DWCNTs is less pronounced, namely 6.3×10^{-4} S cm⁻¹ in Z direction and 1.2×10^{-2} S cm⁻¹ in Y direction, Figs. 7b and 8b.

3.2.2. Temperature dependence of the electrical conductivity

In order to study the temperature dependence of the DC conductivity (σ_{DC}) of the composite laminates we assumed that the values of $\sigma'(\omega)$, presented in Figs. 6–9, at $\omega = 10^{-1}$ s⁻¹ is equal to (σ_{DC}). The results presented in Fig. 10 showed about one decade variation of σ_{DC} over the considered range of temperature. The FITC mechanism modeled by Eq. (4) is in a good accordance with the experimental data. The values of the parameters T_0 and T_1 are listed in Table 2.

The values of T_0 and T_1 are strongly dependant on the nature and the distribution of the conductive phase. Hence it is not surprising to find different values for each measured direction.

As expected, DWCNTs increase the throughout thickness electrical conductivity of the laminate. This increase was about one order of magnitude and this in spite of the presence of conductive paths between carbon fibers through the thickness of CFRP, namely, contacts between carbon fibers due to the fibers misalignment. An increase of conductivity by the same order of magnitude has been reported by Yoo and Kim [44] after the addition of Single-Walled CNTs in CFRP. The value of T_0 decreases when carbon nanotubes are added in the laminate from 382 ± 5 K to 200 ± 3 K for the conductivity measured through thickness (Z-direction) and from

234 ± 3 K to 147 ± 3 K for the conductivity measured in the laminate plane, traverse to carbon fibers (Y-direction). This shows that carbon nanotubes reduce the energy required for an electron to overcome the energy barrier as predicted by the FITC model.

Furthermore the FITC model predicts that the ratio of T_1/T_0 is proportional to the gap width between adjacent conductive phases separated by an insulating phase. This ratio is reported in Table 2. We can see that the insulating gap between the conductive medium is reduced except for the conductivity value in carbon fiber axes for which this ratio remains almost constant. These results evidence that the CFRP and CFRP/DWCNTs laminates can be well described by the FITC model.

A non-expected result is that the electrical conductivity of the composite along the carbon fiber axis follows a FITC mechanism. This result supposes that the conduction along a single carbon fiber axis involves a thermally assisted tunneling mechanism. In fact carbon fibers structure can be described as fibrils of short and turbostratic graphite crystallites partially bonded to each other [45,46]. Thus the electrical conduction mechanism of our carbon fibers involves many transverse jumps beside direct current flow between fibrils in physical contact.

4. Conclusions

Lab-scale production of high performance CFRP laminate filled with CNTs can be implemented by impregnating individual carbon fibers plies with polymer matrix filled with CNTs then by lay-up. The characterization of these composites allows us to draw the following conclusions:

1. The relation between the electrical conductivity of CFRP laminates and the temperature is not linear.
2. The conductivity of CFRP and CFRP/DWCNTs is dominated by the fluctuation induced tunneling conduction mechanism for all measured direction and over a wide range of temperature.
3. The FITC is a pertinent model to predict the conductivity changes in FRP and in Epoxy/DWCNTs composites with respect to temperature.
4. Carbon nanotubes increase the electrical conductivity through thickness by one order of magnitude while in the other two directions the conductivity is not considerably affected. This could have an interesting application in detecting polymer matrix cracking and delamination detection.

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