

INFLUENCE OF THICKNESS ON ELECTRICAL PROPERTIES OF POLYSILOXANE-CARBON NANOTUBE COMPOSITES

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In orbit, satellites are exposed to significant thermal variations. In order to ensure reliable operation of their on-board systems and equipment, a thermal control of the spacecraft is necessary using cold, neutral or warm coatings. The Materials and Coatings Laboratory of the Thermal Control Service at CNES has elaborated a cold coating version by using a polysiloxane deposit on a metal substrate (such as polished aluminum or vacuum deposited silver). In geostationary orbit, polysiloxane, which has a high electrical resistivity ($>10^{17}\Omega.m$), can accumulate implanted charges which can give rise to electrostatic discharges and damage the neighbouring electronic systems. To prevent any electrostatic discharge problems in geostationary orbit, the resistivity of coatings should be reduced without altering their thermo-optical properties. Several methods have been studied to this effect. At present, the incorporation of carbon nanotubes (CNTs) in the polysiloxane matrix is in the process of being tested. Nanotubes are particularly interesting for their electrical properties and their geometry. In this paper, the influence of thickness on electrical and thermo-optical properties of CNT-Polysiloxane composites is reported. This study was performed within a temperature range of -100 to $+200^{\circ}C$, carbon nanotube content remaining constant throughout.

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1. Introduction

In order to be protected against strong thermal variations, satellites use thermal control coatings. Materials used for these coatings are subjected to numerous significant thermal constraints, both electrical and mechanical in origin. They must carry out their task for many years in a hostile environment subjecting them to temperature ranging from $-170^{\circ}C$ to $+140^{\circ}C$, energetic protons, ultraviolet rays and special vacuum. All these lead to an accelerated mechanical and chemical ageing. Satellites can equally be subjected to electrons (of high energy level: $E = 20$ keV) capable of charging the dielectric part of the satellite to a high level and inducing electrostatic discharges damaging to the on board electronic equipments.

Thermal control coatings are defined by their thermo-optical properties, i.e., α_s and ϵ_T . α_s quantifies the amount of solar rays absorbed by the coating and ϵ_T translates its capacity to convert its thermal energy into rays (mainly infrared rays) in order to evacuate them into space. The Material and Coatings Laboratory of the Thermal Control Service of CNES Toulouse, has developed a 'cold' coating, with low solar absorbance and high thermal emissivity, which can be flexible or rigid, known under the trade name of FSR (Flexible Solar Reflector) or RSR (Rigid Solar Reflector).

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Our study centres upon the increase in electrical conductivity of the polymer matrix of the reflectors. In order to do this, we are studying the incorporation of CNTs in the polymer resin; their effect on the electrical and thermo-optical properties of the solar reflectors. The effect of the variation in concentration rate of CNTs in the resin has been the subject of a previous article [1]. Here, we are going to present the evolution of thermo-optical and electrical properties in relation to the sample thickness.

2. Coatings

Coatings are composed of a flexible or a rigid substrate, an aluminium or silver reflecting layer and a polymer resin. The FSRs are made up of a substrate of aluminised Kapton upon which the resin is deposited. In the RSRs, the substrate is a polished aluminium plate, serving both as substrate and reflector. An electrochemical silver deposit can be made to minimise α_s .

The resin used is a polysiloxane. When the resin is a solution, CNTs are added. The blend is subjected to ultrasounds for 10 min. This stage enables the separation of the CNTs and the homogenizing of the blend. In spite of this some CNT agglomerates remain present. In order to eliminate the larger ones amongst them we strain the composite resin using 55 μm sieve before applying the resin to the substrate. The deposit is made with an airgun by applying successive coats, each of 5 to 10 μm thickness. Once the resin has been deposited, the reflectors are polymerised at a temperature of 200 °C for 1h. The first set of samples permitted the determination of the percolation threshold of our composites. Their thickness ranged between 50 and 60 μm , and their CNT concentration between 0.01 wt.% and 0.8 wt.%. Next, in order to determine the influence of the thickness on the properties of coatings, we produced a set of samples loaded at 0.4 wt.% and of thickness ranging between 4 and 117 μm .

3. Electrical properties

3.1. Percolation

Direct current conductivity (σ_{dc}) as a function of the CNT mass fraction (p) is presented in Fig. 1. This curve shows the transition of the composite from the insulating state to the conducting state. This transition is described by the percolation theory via the equation:

$$\sigma = \sigma_0 (p - p_c)^t \quad \text{pour } p > p_c \text{ et } p - p_c \rightarrow 0 \quad (1)$$

with $\sigma_0 = 1.7 \times 10^{-4}$ a constant, $p_c = 0.27$ the percolation threshold, and $t = 1.2$ a critical exponent. Percolation threshold is the limit at which the first interconnections nanotubes-nanotubes are carried out. The very important aspect of (length/diameter) ratio of CNTs allows very low mass fraction percolation threshold compared to composites loaded with black carbon. The extrapolation to $p = 100\%$ of equation 1 gives a theoretical conductivity of 4.3×10^{-4} S/m. In practice this is 5 orders of magnitude lower (i.e., 50 S/m [2]). Kilbride and al. attribute this discrepancy in conductivity to a coating of CNTs by the insulating host material. Particles are not connected directly, a thin insulating layer separates them which results in a poor electrical contact, thereby reducing the conductivity of the composite. The critical exponent t is associated with the dimension of the path of electrons crossing the network. So it is related to the dimensional aspect of the network. For a 3D percolating network, the percolation theory predicts an exponent $t \sim 1.94$, and for a 2D system $t \sim 1.33$. With $t = 1.2$, our network is nearer 2D percolating systems. This must come from the thickness of our sample comparable to the size of the bigger agglomerates.

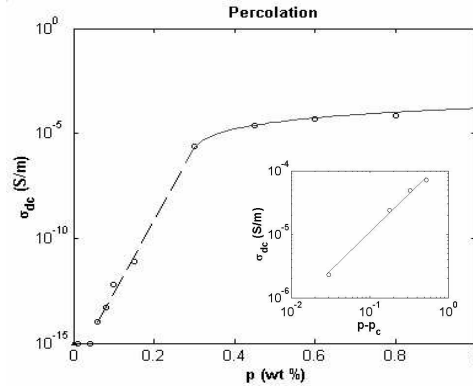


Fig. 1. CNT loaded solar reflector percolation plot. The inset plot is that of conductivity as a function of reduced concentration. The critical exponent ‘t’ is determined from the slope of this curve.

3.2. AC conductivity

In a study on the AC conductivity of composite materials, Connor & al. [3] show that the shapes of the conductivity curves as a function of frequency is independent of the concentration in inclusions. An interpretation based on the percolation theory links the parameters of conduction to the correlation length ξ , itself related to the size of the clusters.

We consider the travel of an electron inside a CNT cluster under an alternating field. ω_0 is the pulsation of transition defined as $\sigma(\omega_0) = 1.1 \times \sigma_{dc}$. If we admit that charge carriers travel over a half period through a length L inversely proportional to the frequency ($\omega \propto L^{-1/a}$ with $0.5 < a < 1$, ‘a’ indicating the level of bias imposed to the material), we can distinguish two separate cases. Below the critical frequency ω_{ξ} , the travel of the charge carriers is limited by the cluster length of the conducting network, which leads to a limitation of the material conductivity. At high frequencies, the electron path decreases and becomes equal to the size of bigger clusters at a critical frequency f_{ξ} . At still higher frequencies, the travel span of carrier is even smaller; consequently the contribution of electrons from clusters smaller still which results in an increase in the conductivity of the composite material. In [4], S. Barrau shows that the hypothesis $\omega_0 \equiv \omega_{\xi}$ is exact.

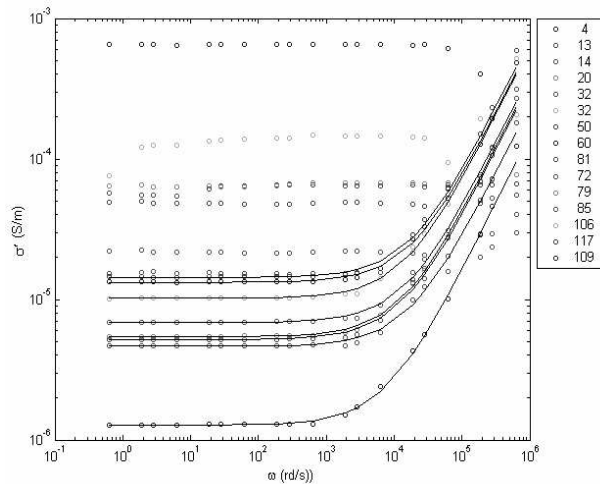


Fig. 2. Dependence of the reflector electrical conductivity on frequency, as a function of resin thickness.

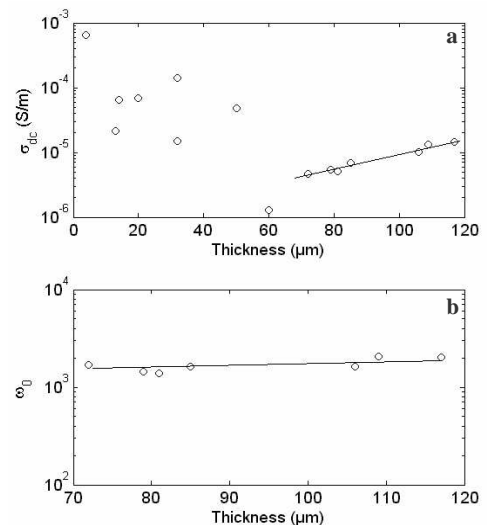


Fig. 3. study of the DC conductivity (3a) and transition angular frequency as a function of thickness.

In Fig. 2, the variation of the conductivity is presented as a function of the sample thickness, for a 0.4 wt.% CNT concentration. These curves come from a spectrometric dielectric characterization.

At thicknesses $d \leq 60 \mu\text{m}$, we do not remark the frequency response as above. An explanation can be that the thickness of the bigger agglomerates ($\sim 55 \mu\text{m}$) is higher than the thickness of the resin. The aluminium electrode deposited is in contact with a thin coat of polymer, followed with CNT agglomerates themselves in contact with the second electrode through another thin polymer coating. So, the frequential behaviour of these samples can not be compared with that of a classical composite material because of too high bulk inhomogeneities.

At a higher thickness ($d \geq 60 \mu\text{m}$), the frequential behaviour is that described above. Conductivity $\sigma'(\omega)$ can be decomposed into a constant component, and an alternative component σ_{ac} which follows a power law. The curves from Fig. 2 have been fitted into the equation:

$$\sigma'(\omega) = \sigma(0) + \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^S \quad (2)$$

Parameters of the fit are presented in Table 1. On the representation of σ_{dc} as a function of the thickness (Fig. 3a), two distinct regions can be distinguished. At thicknesses below $60 \mu\text{m}$, measurements are very much disturbed by the bulk inhomogeneity of the materials, whereas we observe a small increase in the conductivity at sample thicknesses in excess of $70 \mu\text{m}$. It may come from the higher number of carriers in a thicker material. Despite the constant weight fraction there are more CNTs in a thicker material, so the number of carriers capable of contributing to the electrical conduction is higher. We do not observe any sensitive variation of the frequency transition with thickness (Fig. 3b), indicating that the correlation length is not a function of the composite material thickness ($\omega\xi \propto \xi^{-1/a}$).

Table 1. synthesis of the fitting parameters of electrical properties.

Sample	Thickness	σ_{dc}	A	ω_0	s
FSR1	72	4.6×10^{-6}	2.4×10^{-10}	1.7×10^3	1
FSR2	79	5.4×10^{-6}	3.7×10^{-10}	1.4×10^3	1
FSR3	81	5.2×10^{-6}	3.5×10^{-10}	1.4×10^3	1
FSR4	85	6.8×10^{-6}	4×10^{-10}	1.6×10^3	1
FSR5	106	1×10^{-5}	6.2×10^{-10}	1.6×10^3	1
FSR6	109	1.3×10^{-5}	6.5×10^{-10}	2×10^3	1
FSR7	117	1.4×10^{-5}	7.2×10^{-10}	2.1×10^3	1

4. Thermo-optical properties

Thermo-optical properties constitute the main element of a thermal control coating. These properties are mathematically interpreted as the integral of the absorption and emission spectra and are averaged by the solar illumination spectrum. The integrated total solar absorption factor was measured with an integrating sphere (Cary 2300) equipped Perkin Helmer Lambda 9 spectrometer. The total normal infrared emissivity factor was measured with a portable emissometer Gier Dunkel DB100. In Fig. 4, the results of the thermo-optical coefficient measurement from Table 2 are presented along with the respective smoothing curves. The solar absorbance α_s follows a Lambert's law. This is a classical absorption law equation as a function of thickness; χ representing the coefficient of extinction of the material, λ the associated wavelength and d the thickness. These two laws are similar but not identical. The differences originate first from the integrated form of the absorbance and next, from our measurements which are reflection related and not transmission related. So, the absorption takes place in polymer and in the reflecting layer.

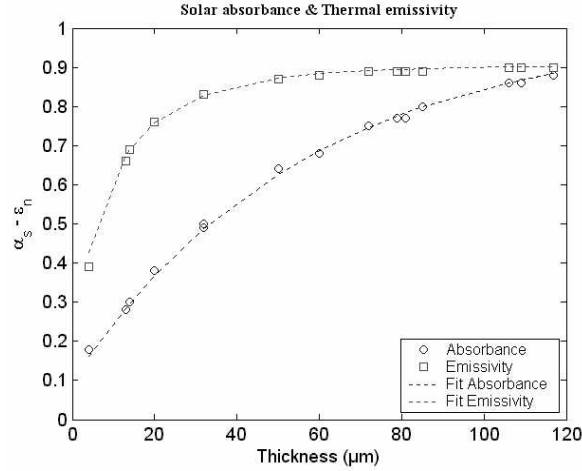


Fig. 4. Thermo-optical characteristics of the samples as a function of their thickness. The dotted lines indicate fitting curves associated with the equations (4) and (5).

Table 2. Set of samples used with their respective thicknesses and thermo-optical properties.

Samples	p (wt.%)	d (μm)	α _s	ε _T
FSR1	0.4	4	0.18	0.39
FSR2	0.4	13	0.28	0.66
FSR3	0.4	14	0.30	0.69
FSR4	0.4	20	0.38	0.76
FSR5	0.4	32	0.50	0.83
FSR6	0.4	32	0.49	0.83
FSR7	0.4	50	0.64	0.87
FSR8	0.4	60	0.38	0.88
FSR9	0.4	72	0.75	0.89
FSR10	0.4	79	0.77	0.89
FSR11	0.4	81	0.77	0.89
FSR12	0.4	85	0.80	0.89
FSR13	0.4	106	0.86	0.90
FSR14	0.4	109	0.86	0.90
FSR15	0.4	117	0.88	0.90

$$\alpha(d) = 1 - \frac{I(d)}{I_0} = 1 - e^{-\frac{4\pi\chi d}{\lambda}} \quad (3)$$

$$\alpha_s = 1 - a \times e^{-nd} \quad (4)$$

$a = 0.9$
 $n = 17.6 \times 10^3$

Thermal emissivity is fitted with a law bordering on the absorption law. ε_∞ is the emissivity of the material at an infinite thickness. In both cases, suitable multiplier of the exponential is used to correct the equations. We have good correlation between the experimental data and the theoretical equation. Unfortunately, it is difficult to interpret the origin of the coefficient ℓ . However, it also figures in the dependence of the emissivity on CNT mass concentration [1].

$$\begin{aligned} \varepsilon = \varepsilon_{\infty} - a \times e^{-nd^{\ell}} & \quad a = 0.88 \quad n = 2.53 \times 10^3 \\ \varepsilon_{\infty} = 0.904 & \quad \ell = 0.67 \end{aligned} \quad (5)$$

5. Conclusions

This study presents both electrical and thermo-optical properties of CNT-Polysiloxane composites as a function of polymer thickness. At thicknesses below 60 μm , which corresponds to the size of bigger agglomerates, electrical measurements do not show a classical behaviour as a function of frequency on the part of a composite sample. At thicknesses above 60 μm , an increase in conductivity with increasing thickness is observed and this can be attributed to an increase in CNT content, i.e., electrical carriers. Correlation length is independent of the thickness. Furthermore, thermo-optical properties are strongly dependent on the polymer thickness. Thermal emissivity and solar absorbance parameters have been fitted using laws related to the Lambert's law. The differences arising from the utilization of these laws and the Lambert's law have been attributed to our experimental conditions.

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