RADAR ABSORBING MATERIALS: THE STUDY OF FUNCTIONALIZED CARBON NANOTUBES BEHAVIOR ON THE ATTENUATION OF ELECTROMAGNETIC WAVES IN X-BAND

MATERIAIS ABSORVEDORES DE RADIAÇÃO ELETROMAGNÉTICA: ESTUDO DO COMPORTAMENTO DE NANOTUBOS DE CARBONO FUNCIONALIZADOS NA ATENUAÇÃO DE ONDAS ELETROMAGNÉTICAS NA BANDA X

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Abstract: Carbon nanotubes (CNT) were functionalized with ethanol, nitric and sulfuric acid. From the obtained nanocomposites, electrical permittivity, magnetic permeability and reflectivity complex parameters were studied in the frequency range of 8.2 to 12.4 GHz (X-band). The results of reflectivity for nanocomposites, functionalized with CNT, showed an attenuation of - 21 dB and -18 dB, at the frequency of 10.4 GHz and 12.4 GHz, respectively, with approximately 99% of attenuation, demonstrating, then, that they are promising for application as Radar Absorbing Materials (RAM).

Key words: Radar Absorbing Materials; Carbon nanotubes; Functionalization; Reflectivity; Permittivity; Permeability.

Resumo: Nanotubos de carbono (NTC) foram funcionalizados com etanol, ácido nítrico e sulfúrico. A partir dos nanocompósitos obtidos, os parâmetros complexos de permissividade elétrica, permeabilidade magnética e refletividade foram estudados na faixa de frequência da banda X, 8,2 a 12,4 GHz. Os resultados de refletividade dos nanocompósitos obtidos com os NTC funcionalizados apresentaram uma atenuação de, -21 dB e -18 dB, na frequência de 10,4 GHz e 12,4 GHz, respectivamente, com aproximadamente 99% de atenuação, demostrando serem promissores para aplicação como material absorvedor de radiação eletromagnética (MARE).

Palavras-chave: Materiais Absorvedores de Radiação Eletromagnética; Nanotubos de carbono; Funcionalização; Refletividade; Permissividade; Permeabilidade.

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1 INTRODUCTION

The excessive use of electronic devices has created major problems of electromagnetic interference, which can affect civilian and military areas. In order to solve problems caused by the increase of electromagnetic interference in both areas of application, Radar Absorbing Materials (RAM) have become highly necessary. The World War II marked the emergence of RAM with promising results, such as, the technology into practice on aircraft of the Lockheed series, the German GO 229 and the American Nortrop YB-49. Stealth technology was developed in two ways: absorbent materials and the design with right angles (Silva & Rezende, 2018, 2020).

In the military area, the scattered energy from a target (echo-radar) can be used for its detection by radar. However, that detection can be more difficult when the target is coated with RAM. In the civil area there are many important applications of RAM, with benefits of their use in electromagnetic interference (EMI) shielding effectiveness (SE) applications, for example, in the telecommunication sector, for protecting cellular devices and radio-transmission antennas, in medical area, for protecting pacemakers, in research and industrial applications coating anechoic chambers, among others (Bahret, 1993; Kumar & Singh, 2018).

Radar Absorbing Materials convert the energy of the electromagnetic wave and dissipate it as heat. This mechanism can be classified as dielectric, magnetic losses or both (Silva & Rezende, 2020). Adjusted in terms of operating frequency, these materials attenuate the electromagnetic radiation of the incident wave that is dissipated in form of heat through the Joule effect (Silva & Rezende, 2018; Kashi et al., 2016). RAM can be classified as magnetic or dielectric, according to the additive load in the RAM matrix, which favors the energy losses by physical and chemical processes (Silva & Rezende, 2018; Trintinalia, 2008).

The electric and magnetic properties of RAM can be manipulated to reach a specific property, making them absorbers in a determined frequency (resonant absorbers) or in a broad spectrum of frequencies (broadband absorbers). Magnetic RAM are usually processed by using magnetic and dielectric materials in a polymeric matrix (Silva & Rezende, 2018; Bahret, 1993).

Efficient RAM have as main characteristics: high attenuation capacity in a wide band of frequencies, low density, low cost, and good thermal stability. The RAM microwave absorption properties are defined by their microstructure and mainly by their complex parameters of magnetic permeability (μ) and electrical permittivity (ε) (Bahret, 1993).

Carbonaceous materials, more specifically carbon nanotubes (CNT), are promising candidates for RAM processing. CNT have been intensively studied as microwave absorbing centers, mainly due to their excellent electrical and thermal characteristics, reduced density, high surface area, and reduced mass percentages needed in RAM processing (Kumar & Singh, 2018; Puthucheri et al., 2016; Trintinalia, 2008).

CNT are widely studied for various microwave applications, such as active devices for oscillators, mixers and nanoelectromechanical systems. Among these potential applications, the use of CNT in RAM are favorable due to their superior electronic properties. The RAM filled with CNT demonstrated conductive properties and high absorption with low concentration of load in the matrix. In addition, this material exhibits high permittivity in the frequency ranging from 8 to18 GH (Kim & Lee, 2009). Due to the van der Waals forces, CNT tend to agglomerate, making dispersion in the polymer matrix difficult, which can influence attenuation results. Different RAM preparation methods are used to assist in the dispersion of CNT such as processing with solvents, ultrasound, treatment with surfactants and chemical modification (Che et al., 2015).

In this context, the present study aims to contribute to the RAM processing area showing the reflectivity behavior and the complex parameters of magnetic permeability and electrical permittivity, in the frequency range of 8.2 – 12.4 GHz. Samples prepared were obtained from the commercial CNT and the results were compared with the CNT functionalized by ethanol, sulfuric and nitric acid.

1.1 ELECTROMAGNETIC CHARACTERIZATION

When an electromagnetic wave hits a target, the radiation can be totally or partially reflected on the first surface of the material or transmitted through it. When the electromagnetic wave is transmitted, the energy of the wave can be attenuated in the material by intrinsic absorption and/or multiple reflections. Thus, the attenuation depends on the reflection mechanisms of the material surface, on the absorption of the wave that travels through the material and on multiple wave reflections at the interfaces present in absorber. The attenuation of the electromagnetic wave in a material is often indicated by reflection loss (RL) (Equation 1) (Munir, 2017; Silva & Rezende, 2018).

$$\boldsymbol{RL = -20\, log\, log \left|\frac{Zin-1}{Zin+1}\right|}\ , \qquad (1)$$

where:

$$\boldsymbol{Zin = \sqrt{\frac{\mu' - j\mu''}{\varepsilon' - j\varepsilon'' - j\sigma(\omega\varepsilon_0)}}\ tanh\left(jd\ \frac{\omega\sqrt{(\mu' - j\mu'')\,(\varepsilon' - j\varepsilon'' - j\sigma/(\omega\varepsilon_0)}}{c}\right)} \qquad (2)$$

$$\boldsymbol{\omega = 2\pi f}\ , \qquad (3)$$

where: *Zin*, *μ'*, *ε'*, *μ"*, *ε"*, ε_0, □, *f*, *d*, and *c* are the impedance of the incident electromagnetic wave, the real part of the magnetic permeability and electrical permittivity; the imaginary part of the magnetic permeability and electrical permittivity; the electrical permittivity in vacuum, equal to 8.854 x 10^{12} Fm^{-1}, the electrical conductivity, the frequency of the electromagnetic wave, the RAM specimen thickness, and the light velocity, equal to 3,0x10^8 ms^{-1}, respectively.

The permittivity and permeability parameters have a direct correlation with the RAM absorption characteristics. Its real and imaginary components allow evaluating the energy dissipation in the form of heat in a microwave absorber (Silva & Rezende, 2018, 2020).

The relationship between the attenuation in dB and the percentage of electromagnetic radiation absorbed (energy absorbed by the material) is shown in Table 1 (Lee, 1991).

Table 1 - Relationship between reflectivity and the energy absorbed.

Radiation attenuation (dB)	Absorption of incident radiation (%)
0	0
-3	50
-10	90
-15	96,9
-20	99
-30	99,9
-40	99,99

Source: **(**Lee, 1991**)**.

2 METHODOLOGY

2.1 CARBON NANOTUBES FUNCTIONALIZATION

CNT multiple walls 90% Nanocyl-NC7000 (1–9 nm diameter,1.0–1.5 μm long) underwent three different types of functionalization, with ethanol, sulfuric and nitric acids. The functionalization was based on Nurjahirah Janudin and collaborators **(**Janudin et al**.**, 2017**)**. CNT was added in a beaker with sulfuric acid solution (3 $mol.L^{-1}$). The mixture was placed in an ultrasonic bath (50W) heated up at 40 ^{o}C, during 2h. After the sonication process, the mixture was filtered under vacuum. The functionalized CNT obtained was washed several times with deionized water. The CNT filtered sample was dried at 80 ^{o}C for 24 h. The same procedure was carried on for CNT samples in ethanol (96º) and nitric acid solution (8 $mol.L^{-1}$).

2.2 ELECTROMAGNETIC CHARACTERIZATION

Nanocomposites were prepared with functionalized CNT samples and paraffin base (2% w/w). Measures of reflectivity loss and permittivity and permeability complex parameters were performed applying a waveguide technique in the 8.2 to 12.4 GHz frequency band (X-band), using a two-port vector network analyzer Agilent Technologies Vector Network Analyzer, model PNA-L-5230C. The measures were evaluated at *Laboratório de Guerra Eletrônica*, *ITA (Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brasil).*

3 RESULTS AND DISCUSSION

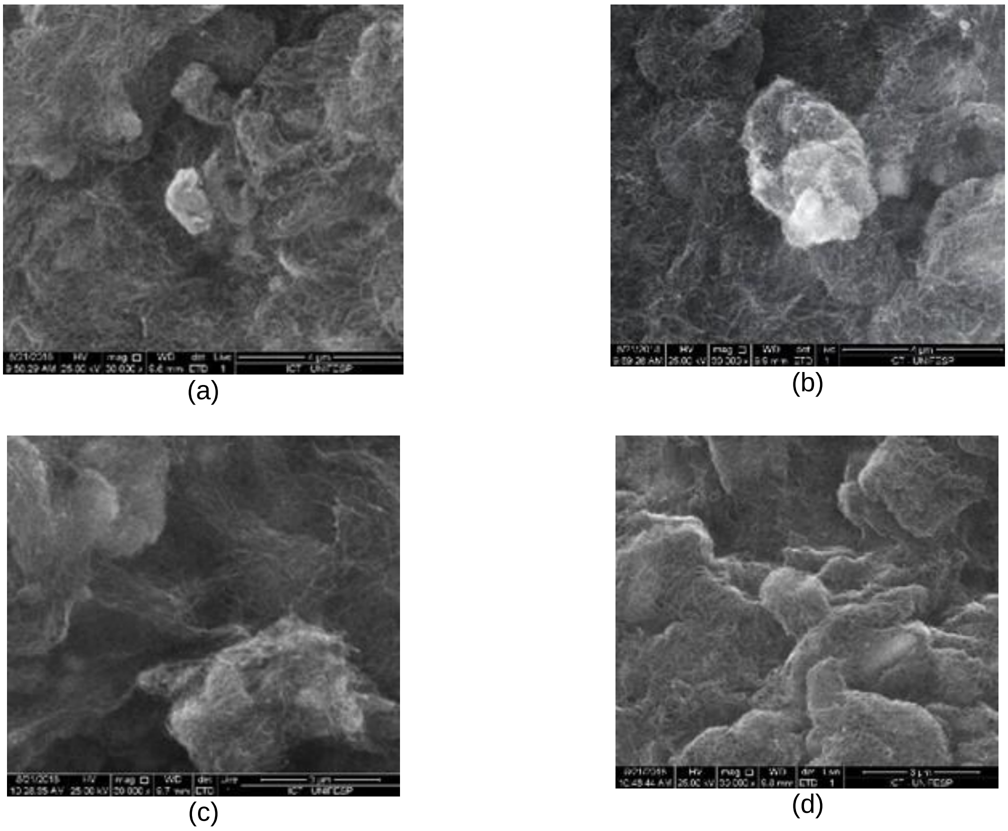
3.1 CARBON NANOTUBES FUNCTIONALIZATION

The processes of covalent and noncovalent functionalization have been suggested as one of the options for better dispersion of nanotubes. The chemical modification of the nanotube surface through covalent functionalization results in reduction of the aspect ratio with the formation of sp3 carbons on nanotube surface, which decreases the electrical conductivity of nanotubes **(**Silva & Rezende, 2020**)**.

CNT form aggregate structures due to the attractions of van der Waals. CNT functionalized with ethanol show fewer aggregated structures **(**Che et al., 2015**)**. Figure 1 shows the SEM of the non-functionalized and functionalized CNT: the Scanning Electron Microscopy (SEM) analysis for the samples CNT non-functionalized (a);

functionalized with ethanol (b), with sulfuric acid (c) and with nitric acid (d). It demonstrated that it wasn`t possible to notice any type of degradation of CNT caused by functionalization. CNT functionalized present the same aspects as non-functionalized. In this case, for a better understanding, further studies shall be carried out, with field emission scanning electron microscopy, SEM-FEG (Field Emission Gun), and Raman spectroscopy.

Figura 1 - CNT non functionalized (a); CNT functionalized with ethanol (b); CNT functionalized with sulfuric acid (c) and CNT functionalized with nitric acid (d).



3.2 ELECTROMAGNETIC MEASUREMENTS

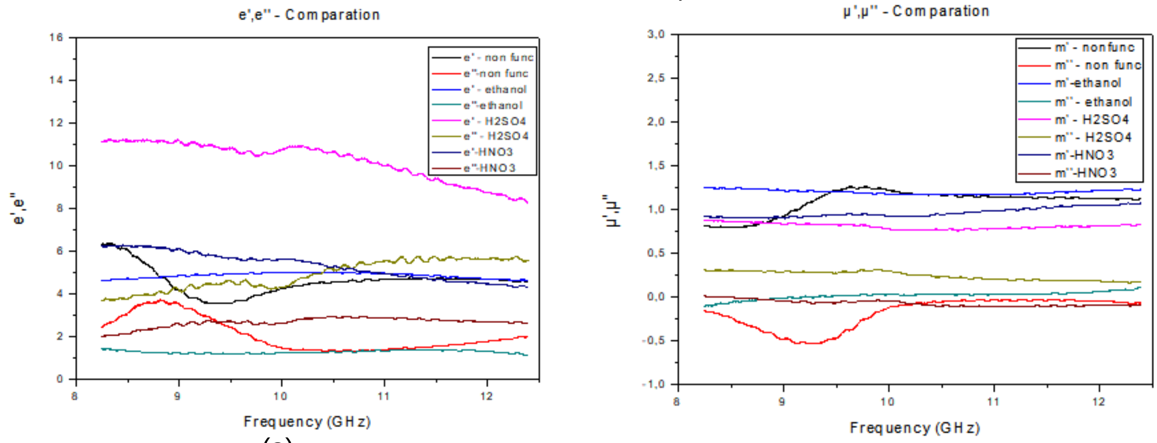
Measures of magnetic permeability, electric permittivity complex parameters and reflectivity depending on the frequency (8,2-12,4 GHz) are presented in the Figures 2 (a), Figure 2 (b) and Figure 3, respectively.

The results of real and imaginary permittivity and permeability are shown in the Figures. 2, (a) and (b).

It is possible to see that the functionalization of CNT influences the real permissiveness, (ε’), of nanocomposites, which is a component in the dielectric energy. Non-functionalized CNT have values that vary from 4 to 6 across the frequency range. Functionalization with HNO3 and ethanol, present similar values of e ', i.e., around 4 for the studied frequency range. The RAM functionalized with H2SO4, presents a minimum value of 9 and a maximum of 11.

The μ' measurements have mean values close to 1.0 across the frequency range and μ has mean values of 0.01. This behavior is expected, knowing that the CNT are dielectric materials, where the complex parameters of magnetic permeability are practically constant with increasing frequency, with μ' ~ 1.0 and μ“ close to zero (Silva & Rezende, 2020).

Figura 2 - Real and imaginary permittivity (a) and permeability (b) measurements of CNT functionalized nanocomposites.



(a) (b)

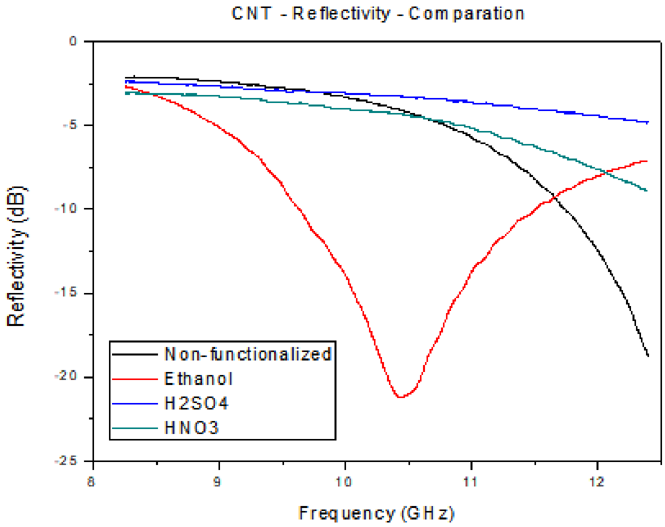
The reflectivity of an absorber material is the relation between the reflect electromagnetic energy and the material incident energy expressed in dB, represented by Equation 1, given incident energy (Ei) and reflected energy (Er):

$$\text{Reflectivity (dB)} = \log 10\, E_r/E_i \qquad \text{(Equation 1)}$$

CNT are dielectrics applied in higher frequency bands, up to 30 GHz. Functionalization promoting greater compatibility between CNT with the polymeric RAM matrix and contributing to dispersion, allowing the attenuation in the studied frequency range (8.2 to 12.4 GHz) **(**Kotsilkova et al., 2015**)**.

The reflectivity curves are showed in Figure 3. It is possible to see that the nanocomposites prepared with the non-functionalized CNT and functionalized with H_2SO_4 and HNO_3 show the same attenuation behavior. The values obtained present, at the beginning of the frequency range, a minimum of reflectivity around -2 dB at 8.2 GHz and a maximum of -3 dB for the CNT functionalized with H_2SO_4. The CNT functionalized HNO_3 showed -8dB at 12.4 GHz. The maximum values for nanocomposites with non-functionalized NTC was -18 dB at 12.4 GHz. The nanocomposites functionalized with ethanol demonstrated the better attenuation behavior, which showed a reflectivity of -21.5 dB, that is 99% electromagnetic wave attenuation, with a resonance peak around 10.5 GHz and band coverage ranging from 9.5 to 11.6 GHz.

Figure 3 - Reflectivity measures of CNT functionalized nanocomposites.



The correlation between the complex parameters (Figure 2) and the reflectivity (Figure 3) showed that RAM processing is a complex task. It is related with the complex parameters (electrical permittivity and magnetic permeability) and reflectivity. Other parameters are also considered, such as the concentration and thickness of the samples and the wavelength of the incident radiation, as shown in Equation 1.

Studies show the functionalization of CNT with inorganic acids for the formation of functional groups and metallic particles for application in RAM. It contributes to increasing the dielectric and magnetic losses in the nanocomposites, for achieving greater absorption of the electromagnetic wave in a wide frequency range **(**Hussein et al**.**, 2020**)**. So far, there has not been reference in the literature to functionalization with ethanol for RAM application.

4 CONCLUSIONS

Based on the results presented, we may suggest that the functionalization of CNT presented in this work contributed to increasing the eletromagnetic attenuation behavior of the RAM filled with this molecules in the studied frequency range (X band). Functionalization with H^2SO^4 presented the greatest increase in electrical permittivity values. Ethanol functionalization, a polar organic solvent, did not change the ε parameters, but showed attenuation of the electromagnetic wave.

The best attenuation behavior demonstrated the reflectivity of -21 dB, approximate 99% attenuation of the incident electromagnetic wave and the possibility to tune the study region with maximum absorption. So far, no studies with ethanol have been found for this application.

The current results belong to the studies of CNT application in microwave absorbers. Preliminary results showed that CNT functionalized with ethanol are promising for application as RAM filler.

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