Electromagnetic properties of Carbon-Graphene Xerogel, Graphite and Ni-Zn Ferrite composites in polystyrene matrix in the X-Band (8.2 – 12.4 GHz)

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ABSTRACT

The electromagnetic properties of Carbon-Graphene Xerogel (CGX), Flaky graphite (GR) and Nickel-Zinc ferrite (FeNiZn) composites in polystyrene (PS) matrix were studied in the X-Band range (8.2 – 12.4 GHz). In this work the Expanded Polystyrene (EPS) waste material was processed into polystyrene through the recycling of EPS. The polystyrene obtained was utilized as dielectric matrix, mainly because PS is a well-known organic polymer that presents low dielectric loss and light weight, which contribute to applications in composites for the aerospace field. In order to produce the final composite specimens, the CGX additive was previously synthesized through a sustainable method that employed the use of waste from the paper and pulp industry (black liquor). Afterwards, the morphological and structural analysis were made through Scanning Electron Microscope (SEM) and Raman Spectrometer, respectively. On the other hand, the magnetic ferrite material, FeNiZn, was obtained for the composite production through calcination, whereas the GR utilized was commercially obtained. It was observed that the increase of CGX and GR influenced on the increase of the Complex Permittivity, and that 10 wt% CGX + 50wt% FeNiZn composite sample demonstrated an absorption peak at 10.5 GHz. The results are relevant concerning the recycling of EPS waste through its use as dielectric matrix, thus developing greener and low-weight composite materials to be used in microwave applications.

Keywords: Carbon-Graphene. Composite. Recycling. Polystyrene. Microwave.

1. INTRODUCTION

Electromagnetic Radiation Absorbing Composites (ERAC) have been studied in the recent years [1- 3] due to their applications in the aerospace, military and engineering fields, such as in electromagnetic shielding and sandwich structures. These areas often require materials with low density, heat insulation and chemical stability properties. Regarding composites, it is known that the impedance matching may be improved with the balanced combination of dielectric and magnetic materials, so that the electromagnetic wave (EMW) interacts better with the material [4, 5]. Carbonaceous materials like Carbon-Graphene Xerogel (CGX) and Natu-

ral Flaky Graphite (GR) have good mechanical properties, high conductivity and low density [6]. On the other hand, Ni-Zn Ferrite (FeNiZn) contributes to the magnetic behavior of a material with its chemical stability, and heat insulation property [7].

Carbon Xerogels (CX) are materials obtained through the carbonization of organic gels, which are often prepared by the sol-gel method utilizing organic monomers like resorcinol and formaldehyde [8]. It is known that textural characteristics of the CX such as surface area, pore volume and pore size distribution depend strongly on the experimental conditions of the synthesis method chosen [9]. Obtaining this CX is more simplified than other types of carbonaceous materials, such as carbon aerogels. Unlike carbon aerogels, in the CX method drying under natural conditions is employed to make this process not expensive, since the supercritical conditions used in carbon aerogels process induce high operating cost and hazardous handling [10]. Thus, in this work Carbon-Graphene Xerogels (CGX) were materials synthesized through a less costly method which employs the use of waste from the paper and pulp industry, the Kraft black liquor. This sustainable method allowed the incorporation of graphene in the CX structure, bringing the electrical properties of graphene to composites.

Polymers have been showing potential to be used as matrices in aerospace applications due to their low cost, ease of manufacture, light weight, etc [11]. Polystyrene (PS) is an organic polymer known for its extremely low density in dry state, low dielectric loss and excellent electrical resistance [11]. In the organic polymer PS, the phenyl (C_6H_5) groups play an important role, restricting the rotation of polymeric chains around C-C bonds, therefore it brings the rigidity property of the polymer [12]. The low electric properties of polystyrene might be explained due to the nonpolar characteristic of the polymer; it is known that PS has a small dipole moment because of the asymmetry at the phenyl side group [13].

This work is based on the study of the electromagnetic properties of CGX, FeNiZn and GR embedded in polystyrene (PS) matrix in the X-Band (8.2 – 12.4 GHz). The usage of polystyrene as the polymeric matrix is mainly attributed to its low weight and interesting low dielectric properties [14, 15] which are close to other materials commonly utilized as matrix, like silicon rubber and epoxy resin. The present work also aims the recycling of EPS waste material through its use as dielectric matrix for microwave applications. Large quantities of EPS waste are disposed of in landfills [16], and they cannot be decomposed in nature for many generations since EPS waste is fragmented into particles of microplastic, which can be highly environmentally negative to the aquatic life in the world [17]. It was estimated in 2014 that 125,000 tons of EPS were produced and only 1% was recycled [17].

2. MATERIALS AND METHODS

Composite samples with magnetic and carbonaceous additives were produced in order to analyze the electromagnetic properties and study the electromagnetic wave absorption performance of the composites in the X-Band.

2.1 Materials

The materials employed for processing the composites were: synthesized Carbon-Graphene Xerogel, Natural Flaky Graphite (250 μm > particulate > 106 μm) obtained from NACIONAL DE GRAFITE LTDA, Ni-Zn Ferrite ($Ni_{0,8}Zn_{0,2}Fe_2O_4$) powder obtained through calcination at 900ºC [18], and Expanded Polystyrene waste. The GR and FeNiZn powders were previously characterized in terms of morphology, structure and chemical composition [18].

2.2 Methodology

The materials required for the synthesis of CGX were resorcinol (7.5 g), formaldehyde (22 g), Poly (methyl methacrylate) (PMMA) (22.5 g), Kraft black liquor (50 g) and a commercial graphene dispersed in isopropyl alcohol (1 mL). The Kraft black liquor and the commercial graphene was kindly supplied by Suzano Papel e Celulose S.A. and Carbonium 3 Industria Quimica S.A, respectively. In order to synthesize the CGX, the precursor materials were agitated until a gel structure could be formed, subsequently the mixture was dried under natural conditions. Afterwards, the material was carbonized at 900°C under inert atmosphere, and, then, washed with distilled water. The morphological and structural analyses of the synthesized CGX powder were evaluated by Scanning Electron Microscope (SEM) JEOL JSM-5310 and Raman spectrometer HORIBA LabRam HR Evolution with excitation laser wavelength of 514 nm, respectively.

Currently there are various methods of recycling EPS waste [19], in this work the recycling method adopted was comprised of the dissolution of EPS [20] in acetone which is a non-solvent. Expanded Polystyrene waste

materials were weighed and reduced to Polystyrene (PS) by diluting the EPS waste in acetone at the ratio of 0.62 g/ml; subsequently composite samples 3-mm thick of CGX, FeNiZn and GR embedded in PS matrix were manufactured in different weight concentrations (Tab. 1). The mixtures of randomly dispersed particulates, for the composite specimens followed the dimensions of a ¼ Wavelength Shim, with width of 22.86 mm, height of 10.16 mm and maximum thickness of 9.78 mm.

Table 1: Composition of the composite samples produced.

SAMPLE	COMPOSITION
1	Pure PS
2	50 wt% FeNiZn
3	10 wt% CGX
4	10 wt% GR
5	50 wt% FeNiZn + 10 wt% CGX
6	50 wt% FeNiZn + 10 wt% GR

The complex permittivity, complex permeability and reflection loss of the composites were measured in the frequency range from 8.2-12.4 GHz by using a Vector Network Analyzer (VNA) with a rectangular waveguide, and the X11644A X-Band Waveguide calibration kit was used throughout the electromagnetic measurements. The reflection loss of the samples 5 and 6 was also calculated in order to estimate the effect of thickness change on absorption, varying from 2.5 mm to 3.5 mm. The calculus was made by the Reflection Loss (RL) and Intrinsic Impedance [4, 5], referring to Eq. (1) and Eq. (2), respectively.

$$RL = 20 \log_{10} \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \tag{1}$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left\{ j \left(\frac{2\pi f t}{c} \right) \sqrt{\mu_r \varepsilon_r} \right\} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 SEM Characterization

The micrograph in Fig. 1 (a) corresponds to graphene of commercial origin used in the synthesis. The predominant characteristics are the transparency and thin thickness of the graphene sheets [23]. Micrograph of CGX sample is shown in Fig. 1 (b). It is observed that this sample has lamellae in the bulk region, as indicated by the white arrow. Possibly, during the synthesis of CGX, an ordered layer formation occurred in the structure due to the incorporation of graphene material in the mixture.
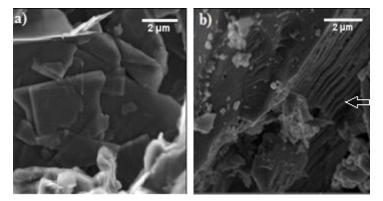

Figure 1: SEM picture of graphene (a), 30.0 kx and SEM picture of CGX (b).

3.2 Raman Spectroscopy

The Fig. 2 illustrates the Raman spectra obtained for the CGX and graphene samples. The peaks around 1340 cm^{-1} and 1580 cm^{-1} correspond to D and G band, respectively. These peaks are characteristic of carbonaceous

materials and, in general, defects and disorder are attributed to the D band. The G band contributes to the structural integrity of graphite and it is associated with the stretching movement of carbon atoms bonds with sp^2. The 2D band present in graphene spectrum can be attributed to the multilayer of graphene [21, 22]. After the insertion of graphene in the CX, an amorphous and defective structure is still prevalent, as already described elsewhere [23], probably because of its amorphous nature, characteristic of a short-range order, is evidenced in the spectrum by the widening of the D and G bands [21].
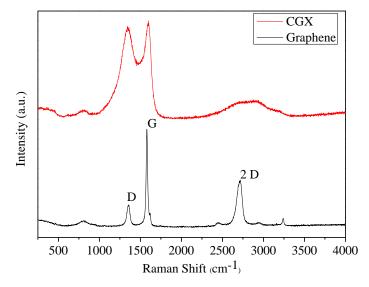

Figure 2: Raman spectra of CGX and graphene samples.

3.3 Electromagnetic Characterization

The Complex Permittivity, Eq. (3), and Permeability, Eq. (4), have real (ε',μ') and imaginary (ε'',μ'') components that represent the storage of electromagnetic energy and dissipation respectively [5].

$$\varepsilon = \varepsilon' - j\varepsilon'' \tag{3}$$

$$\mu = \mu' - j\mu'' \tag{4}$$

The real permittivity, Fig. 3 (a), demonstrates, firstly, that the Pure Polystyrene, sample 1, has reduced its capacitive reactance, indicating the EMW almost doesn't interact with it. The sample 1, which represents the specimen composed only by EPS waste material, also demonstrated ε' values close to the real permittivity values of the commercial polystyrene [15]. The samples with the mixture of Carbon-Graphene + Ferrite (Sample 5) and Graphite + Ferrite (Sample 6) showed the highest values of ε', thus, indicating that the impedance matching, is possibly being favored by the combination of dielectric and magnetic properties. The imaginary permittivity, Fig. 3 (b), demonstrate that all samples have ε'' values between 0.4 and 0.6 within the entire range of frequency, except the sample 1. The sample 1 have ε'' values around 0.3, thus demonstrating the lowest dissipative performance among all samples.
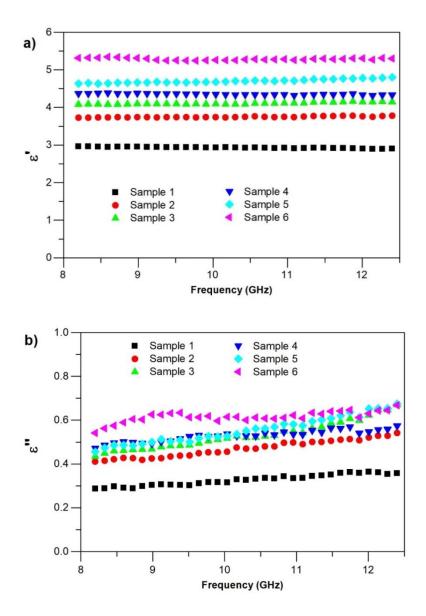
Figure 3: (a) Real Permittivity, (b) Imaginary Permittivity.

The complex permeability, Fig. 4 (a) and Fig. 4 (b), demonstrate that the samples with only the carbonaceous composition can be regarded as dielectric materials since they do not have enough magnetic response to the EMW. However, all the samples with magnetic additive, Ni-Zn ferrite, exhibited lower dielectric response, indicating that μ' and μ'' values are different from 1 and 0 respectively.
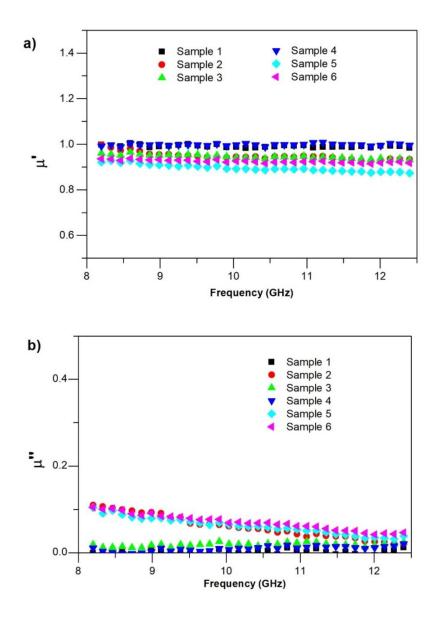
Figure 4: (a) Real Permeability, (b) Imaginary Permeability.

Regarding the RL, Fig. 5, it was verified that the samples with CGX and GR additives exhibited similar absorption, and tendency of resonance effect on higher frequencies in Ku-Band. Samples 5 and 6 showed RL values of -9 dB, however the sample 6 presented this value in the range 11 – 12.4 GHz, whereas the sample 5 exhibited this RL value at approximately 10.5 GHz. Therefore, it can be concluded that the combination of Ni-Zn ferrite and both CGX and GR may have contributed to the improvement of the impedance matching performance, thus increasing the absorption.
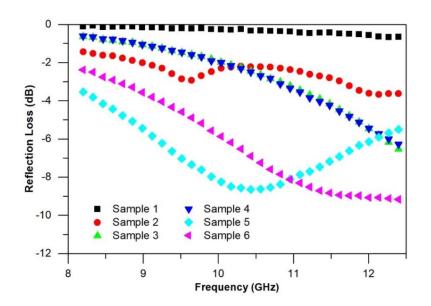
Figure 5: Reflection Loss.

According to the calculated RL values for the sample 5, Fig. 6, it was verified that the highest absorption may occur in thicker specimens, such as in samples 3.5 mm thick. The 3.5 thickness has RL value of -7 dB in the range 10 - 11.5 GHz. It could also be concluded that, the range of frequencies attenuated gets extended, since 3 mm thickness is increased to 3.5 mm.
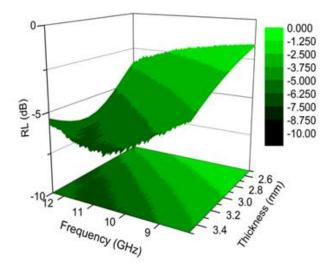

Figure 6: 3D Reflection Loss graph for sample 5 based on thickness variation.

It was observed, for the sample 6, Fig. 7 that the highest absorption peak occurs at approximately -6.5 dB in the range 9 - 10.5 GHz for specimens 3.5 mm thick, whereas when the thickness decreases to 3.2 mm for example, the -6.5 dB absorption peak appears for a smaller range of frequencies at 10 to 11 GHz, indicating that the increase of thickness possibly expanded the absorption band.
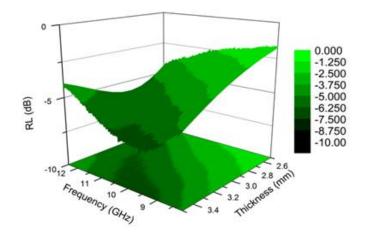
Figure 7: 3D Reflection Loss graph for sample 6 based on thickness variation.

4. CONCLUSION

It can be concluded that especially the samples with Carbonaceous materials combined with Ferrites demonstrated the highest absorption values, -9 dB (≈87% absorption), in the X-Band. This phenomenon can possibly be explained by the impedance matching favored by the balanced electromagnetic properties. The RL calculated values demonstrated that, the increase of thickness for both samples 5 and 6 increased the range of frequencies in which the highest absorption occurs. Therefore, in this work the samples with conductive and magnetic additives in a dielectric matrix of PS showed potential to be used as ERAC with highly low weight and thickness, thus transforming the EPS waste into a source of material to be used as dielectric matrix in composites for microwave applications in the aerospace field, and also showing the potential of the Kraft black liquor as an important precursor to the CGX synthesis, making the waste from the paper and pulp industry useful.

5. ACKNOWLEDGEMENTS

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