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Electromagnetic properties of polyurethane template-based carbon foams in Ka-band

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Abstract

The electromagnetic (EM) properties of polyurethane template-based reticulated carbon foams were investigated in the 26–37 GHz microwave frequency range (Ka-band). It was experimentally proved that carbon foams of a thickness of 2 mm and a density of 22–55 mg cm^{-3} are almost not transparent to microwave radiation, and this is especially true for the densest ones. Depending on bulk density, the EM response of carbon foams in the microwave region can be mainly accounted for by either reflection or absorption. EM shielding efficiency of more dilute samples is due to absorption mechanisms, whereas denser foams provide up to 80% reflection of EM signals. EM properties of carbon foams in the Ka-band can be accurately predicted by a very simple model based on Fresnel formulae developed in this communication.

Keywords: carbon foams, electromagnetic response, Ka-band

1. Introduction

Carbon-based materials have been widely investigated, especially during the previous two decades, due to their challenging and promising electromagnetic (EM) properties in a wide range (from static to infrared) of frequencies [1–4]. Many modern practical applications are closely related to the development of heterostructures with a controllable EM response in microwaves. The interaction of microwave radiation with various carbon-based materials is intensively investigated by many scientific groups worldwide [5–8]. Understanding, predicting, and controlling the EM properties of such materials are primary tasks for modern studies in materials and solid-state sciences.

Carbon foams are relatively new, easily prepared and, for a few of them, 'green' materials [9, 10]. Recent works have reported their significant shielding efficiency [11–13].

The present paper presents new results of the EM response of polyurethane template-based reticulated carbon foams filled with epoxy resin in the microwave 26−37 GHz frequency range (Ka-band), with special focus on their absorption and reflection properties.

2. Methods

2.1. Foam synthesis

Reticulated carbon foams were synthesized using template polyurethane matrices according to a procedure described below. Four types of commercially available polyurethane foams (R30Fr/CFS R Fr30, R45Fr/CFS R Fr45, R60Fr/CFS R Fr60, and R80Fr/CFS R Fr80, kindly supplied by Custom Foams (http://customfoams.co.uk)) were used as templates to produce carbon foams with various bulk densities. The data in the labels of these materials are related to the cell size; e.g., R80Fr/CFS is a reticulated polyurethane foam having a linear cell density of 80 pores per inch (ppi); i.e., an average cell diameter of 320 μm. Polyurethane foam samples (0.12 g) were soaked in an aqueous solution composed of 30 g of water in which 0.7 g of formaldehyde solution (37 wt.%),

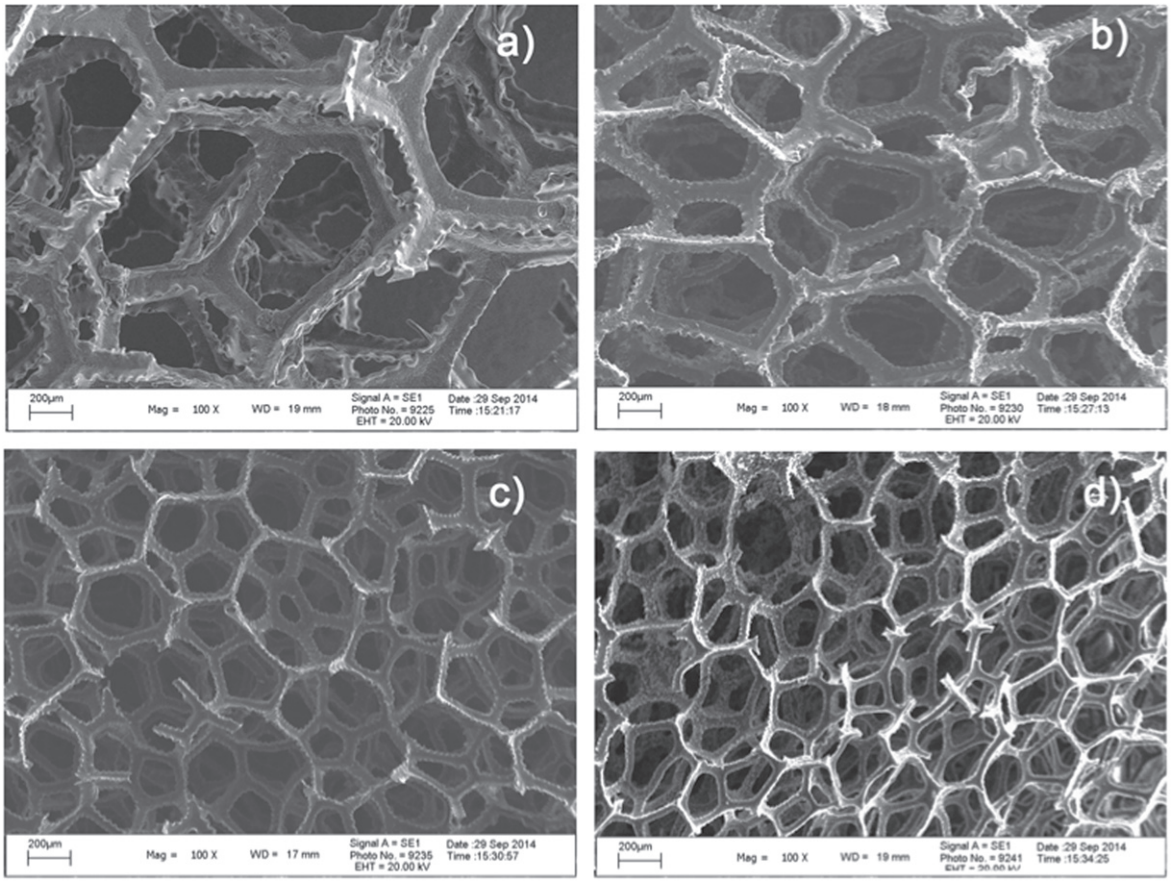

Figure 1. SEM images of polyurethane template-based reticulated carbon foams having different bulk densities and cell sizes: (a) Fr30, (b) Fr45, (c) Fr60, and (d) Fr80 template-based foam.

Table 1. Parameters of impregnated carbon foams and glassy carbon.

	Fr30	Fr45	Fr60	Fr80	glassy carbon
Bulk density, mg cm^{-3}	22	29	31	55	1310
Static conductivity, S/m	22.5	28.2	31.0	44.0	2877.2

0.475 g of resorcinol, and 22 g of $Ni(NO_3)_2{\cdot}6\,H_2O$ were dissolved. The whole was installed in an autoclave at a temperature of 150 °C for 24 h. After this time, the samples were recovered and washed in water, dried at 80 °C, and then carbonized in a tubular furnace at 1000 °C for 2 h, using a heating rate of 1 °C/min in a stream of pure nitrogen flowing at 100 mL/min. In a final step, the nickel nanoparticles which formed at the surface of the carbon foams and which were used as graphitization catalysts during pyrolysis were removed by washing the samples with concentrated hydrochloric acid during 24 h.

The SEM images of the resultant reticulated carbon foam samples are presented in figure 1. The structure of carbon foams is the same as that of the precursor polyurethane matrices, although the shrinkage occurring during pyrolysis produced much smaller cell sizes. The bulk densities of the obtained carbon foams are presented in table 1.

As the resultant carbon foams were very fragile, their practical use and investigation for microwave applications were not easy. To overcome this problem and to obtain more reliable and repeatable results, the foams were impregnated with epoxy resin. For that purpose, we used Buehler EpoThin Epoxy Resin 20-8140-32 with Hardener 20-8142-16 and Buehler Vacuum Impregnation Equipment I No. 20-1382-160. This device and the related resin and hardener are those typically used for impregnating samples with resin for metallography studies.

Such a vacuum technique allowed us to obtain carbon foam samples completely filled with epoxy resin without air bubbles inside. As expected, impregnation with epoxy resin significantly improved the mechanical strength of the investigated samples with practically no impact on EM properties (see details below). Additionally, the impregnation of carbon foams allowed us to improve the electrical contact between foam and waveguide. The problem of contact was recently reported in [12, 13] and leads to reduction of shielding effectiveness of carbon foam. The dc electrical conductivities of impregnated carbon foams and bulk glassy carbon

(measured using a standard two-point technique [14]) are presented in table 1.

2.2. Microwave measurements

The microwave measurements were carried out with a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania), including a sweep generator, waveguide reflectometer, and indicator unit (personal computer). The EM responses of samples were measured within the 26–37 GHz frequency range (Ka-band) as ratios of transmitted/input (S_{21}) and reflected/input (S_{11}) signals. The measurements and calibration procedure were performed as described in[5]. The carbon foams filled with epoxy resin were precisely cut in a parallelepiped shape for fitting the waveguide cross section of 7.2 × 3.4 mm. All investigated samples had thicknesses within the range 1.5 mm $<\tau <$ 2 mm.

The conductivity of bulk glassy carbon was measured in the Ka-band using a technique described in [15]. The obtained value $\sigma_{mw} = 900$ S/m is around three times lower than the measured static conductivity σ_{gc} of glassy carbon presented in table 1. This is in agreement with recent published results [13, 16].

2.3. Simulation details

We based our simulations on the following concepts of EM radiation interaction with carbon foam structures. First of all, it should be noticed that the wavelength at frequency 30 GHz is 1 cm. The investigated foams are porous carbon materials. The average diameter of Fr30, Fr45 and Fr60, Fr80 samples cells is less than 1 mm and 0.5 mm, respectively. Therefore, the wavelength is considerably greater than the typical size of the samples' inhomogeneities. Secondly, it should be pointed out that the EM properties of foams are mainly controlled by the highly conductive skeleton consisting of glassy carbon.

As a first approximation, the impregnated carbon foams can thus be considered as semi-homogeneous solids characterized by macroscopic 'average conductivity' σ, corresponding to the electrical conductivity of bulk parallelepipeds of the investigated material, irrespective of their inner structure. σ may be easily related to the complex dielectric permittivity ε using the well-known equation for conductive materials:

$$\varepsilon(\omega) = 1 + \frac{\mathrm{i}\sigma}{\varepsilon_0 \omega}, \tag{1}$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum, ω is the angular frequency, and i is the imaginary unit. The dependence of dc conductivity presented in table 1 on the bulk density ρ of foam, the bulk density ρ_{gc} of glassy carbon, and the conductivity σ_{gc} of glassy carbon can be expressed by the phenomenological formula [12]:

$$\sigma = B\left(\rho/\rho_{gc}\right)\sigma_{gc} \tag{2}$$

with parameter $B = 0.40$ estimated by the least-squares procedure. When the complex dielectric permittivity of the investigated sample is known, it is possible to calculate its EM response using the following relationships based on Fresnel formulae:

$$S_{11} = \frac{-\sin(\gamma\tau)\left(\gamma_0^2 - \gamma^2\right)}{\sin(\gamma\tau)\left(\gamma^2 + \gamma_0^2\right) + 2\mathrm{i}\gamma\gamma_0\cos(\gamma\tau)}, \tag{3}$$

$$S_{21} = \frac{2\gamma/\gamma_0}{-2\gamma/\gamma_0\cos(\gamma\tau) + \mathrm{i}\left((\gamma/\gamma_0)^2 + 1\right)\sin(\gamma\tau)}; \tag{4}$$

where $\gamma = \sqrt{\left(\frac{2\pi}{\lambda}\right)^2\varepsilon - \left(\frac{\pi}{a}\right)^2}$, $\gamma_0 = \sqrt{\left(\frac{2\pi}{\lambda}\right)^2 - \left(\frac{\pi}{a}\right)^2}$, τ is the sample's thickness, $a = 7.2$ mm is the width of the waveguide, and ε is the complex dielectric permittivity of the investigated sample. A similar model was used in a recent work [12] in the 1–4 GHz range. Reflection, transmission, and absorption coefficients may then be easily obtained from S-parameters: $R = S_{11}^2$, $T = S_{21}^2$, $A = 1 - R - T$. It should be noticed that this approximation is valid as long as the wavelength is larger than the characteristic materials' inhomogeneity size. For verifying the model proposed above, let us consider the experimental results.

3. Results

3.1. Experimental measurements

First of all, it was estimated that impregnation with epoxy resin practically does not affect the reflection coefficient of carbon foams (see figure 2(a)). The small transmission coefficient of carbon foams is further decreased after impregnation because of better contact between sample and waveguide (see the more representative shielding effectiveness SE(dB)= $-|S_{21}|$ (dB) in figure 2(b)). The EM properties of foams are indeed mainly controlled by the highly conductive glassy carbon skeleton. Substituting air from the foams' porosity with a non-conductive epoxy (the typical value of dielectric permittivity of epoxy in microwaves is $\varepsilon \approx 3$) does not significantly change the boundary conditions influencing EM radiation scattering.

All investigated foams presented similar EM responses in the Ka-band (see figure 3).

From figure 3 it can be seen that the investigated samples are practically not transparent to microwave radiation (i.e., less than 5% of the power of the initial radiation was transmitted throughout all investigated samples). The carbon foams mostly differ from each other in terms of reflection coefficient R. It was estimated that this coefficient is practically independent of the thickness of the samples. Analysis of figure 3 shows that reflection coefficients are correlated to bulk density and average conductivity of the investigated samples (see table 1). The lowest reflection coefficients

[5] Standard test method for measuring relative complex permittivity and relative magnetic permeability of solid materials at microwave frequencies 2009 astm d5568-08.

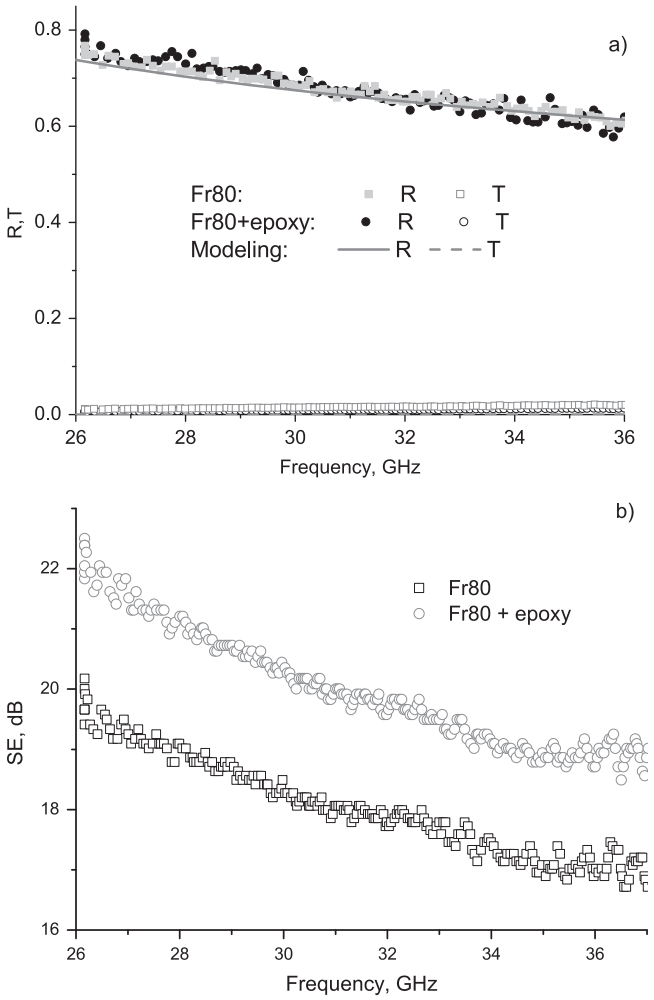

Figure 2. (a) Reflection and transmission coefficients of impregnated and empty foams (symbols); results of theoretical modelling of electromagnetic response (lines); (b) comparison of shielding effectiveness of impregnated and empty foams.

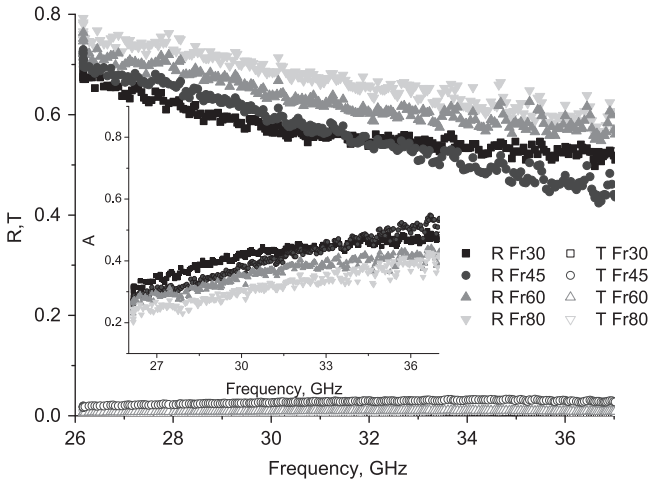

Figure 3. Reflection and transmission coefficients of impregnated reticulated carbon foams with different bulk densities (inset: absorption spectra of the same materials).

correspond to the samples having the lowest bulk density and average conductivity. The reflection coefficients of all investigated foams increased with the bulk density, except for the Fr30 sample for frequencies higher than 31 GHz. This sample indeed has the highest cell size and skeleton thickness, and their structure starts to affect EM response at higher frequencies. This is the most plausible reason why the reflection coefficient R decreased more slowly with frequency in comparison to other samples.

Unlike R, the absorption coefficient A significantly decreased when the bulk density of foams increased. Absorption also increased with frequency for all investigated samples. The decreasing wavelength indeed led to a deeper penetration of radiation into the bulk of the materials and, hence, to multiple reflections and scattering inside the samples. Hence, it can be concluded that, with regard to absorption applications, carbon foams with low bulk densities are preferable.

Contrariwise, the increase of cell size and the corresponding decrease of the bulk density of the investigated carbon foams lead to higher transmission coefficients T. This means that, at constant samples thickness, an optimal cell size exists, producing the highest shielding effectiveness (in other words, the best balance between absorption and transmission coefficients). The experimental results presented here are in good agreement with our recent report [11] and with investigations made in a lower frequency range (1–6 GHz) [12, 13].

3.2. Theoretical modelling

Based on the model presented in section 2.3, the EM response of raw and impregnated foams could be fitted (see lines in figure 2). For these calculations, a sample thickness $\tau = 2$ mm and an electrical conductivity $\sigma = 45$ S/m were used. The latter value of σ is very close to the measured dc conductivity of the Fr80 sample. The results of theoretical modelling of R, T and A coefficients of 2 mmthick foams with other average conductivities from table 1 are presented in figure 4.

Though the conductivity of bulk glassy carbon measured in dc and in Ka-band differs by a factor of three, we can see by comparing figures 3 and 4 that the experimental results related to absorption and reflection coefficients may be satisfactorily fitted by their dc conductivity. This will be discussed more in details in the next section.

The good fits of the impregnated foams' behavior and the universality of the electromagnetic response of all investigated foams (see figure 3) both support the validity of the simple model proposed here to describe the absorption and reflection coefficients of carbon foams in the 26–37 GHz microwave frequency range.

4. Discussion

The results obtained in the present work agree with previous investigations related to carbon foams and pyrolytic carbon films [11–13, 17, 18]. The present experimental

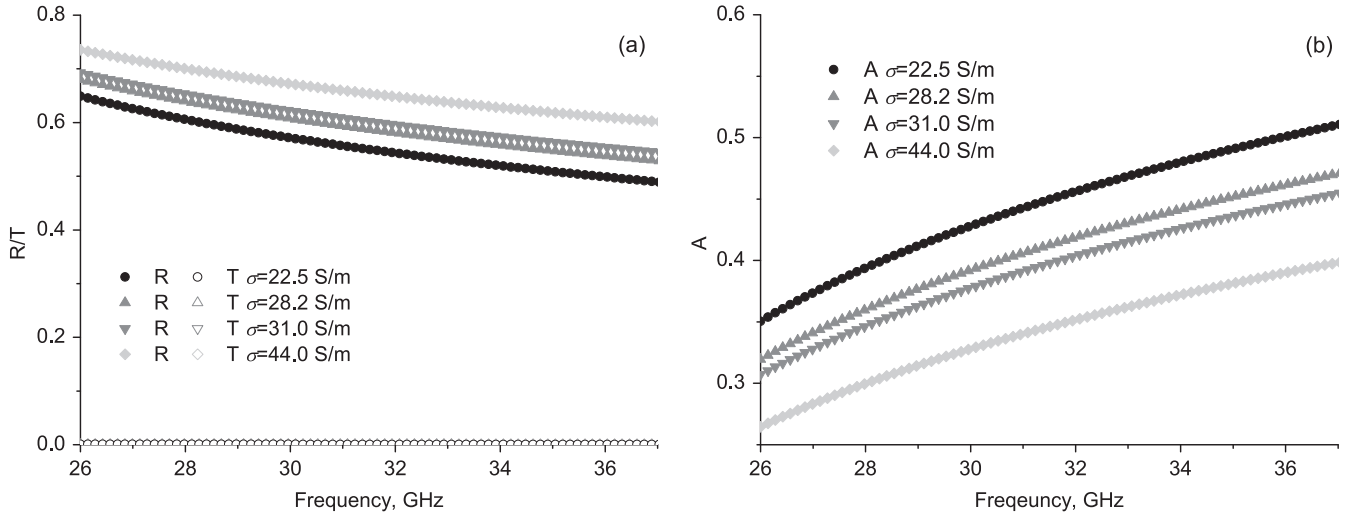

Figure 4. Modelled dependence of (a) reflection/transmission and (b) absorption coefficients of carbon foams with various average conductivities and thickness $\tau = 2$ mm.

measurements showed that the EM response of polyurethane-based carbon foams is related to average bulk density and electrical conductivity. Using the very simple model proposed here, it is possible to predict the most important experimentally observed features of reflection and absorption coefficients of carbon foams in the Ka-band. However, the question about a broadband (for example, applied in both microwave and terahertz ranges) theoretical model relating the macroscopic 'average conductivity' of the foams to their geometrical structure (for example, to their bulk density), is still open.

Figures 3 and 4 show that the proposed model is in good agreement with the experimental data for reflection and absorption coefficients. At the same time the predicted values of transmission coefficients are significantly lower than experimentally observed ones. This is most probably related to contact problems between the carbon foam and the sample holder, as reported in [13]. The impregnation of foam with epoxy resin improved the contact (see figure 2(b)) but did not fully solve this problem. Secondly, the proposed model totally neglects the inner structure of carbon foams. Equation (2) is the simplest linear fit, which is valid only in long-wave approximation. The model allows fitting satisfactorily the least dense sample FR30 in low frequencies. For terahertz measurements, the direct broadband relationship between bulk density, cell size, and average conductivity should be theoretically determined.

Finally, for fitting, we used the experimental data of dc conductivity of foams, though the conductivity of bulk glassy carbon measured in dc and in the Ka-band differs by a factor of three. This fact can be explained by the following arguments. The skin depth of bulk glassy carbon at 30 GHz is about 60 μm. It means that at high frequencies, just the surface of the macroscopic sample of glassy carbon interacts with EM radiation. This directly leads to a decrease of effective conductivity of bulk glassy carbon with frequency. Contrariwise, the carbon foams have an extra-large surface area, and their skeleton has a thickness comparable to skin depth. So the effective conductivity of such structures decreases much more slowly, and dc measurements may be applicable at high frequencies until the skin depth is greater than the skeleton thickness.

5. Conclusion

It was experimentally assessed that the highest EM absorption of carbon foams is achieved when the latter present the lowest bulk density. The most important features of reflection and absorption coefficients of polyurethane-based reticulated carbon foams in the Ka-band may be described using a very simple model, based on classical Fresnel formulae and the dielectric permittivity equation for conductive materials. The obtained results of theoretical modelling are in good agreement with experimental data and with our previous investigations and may be useful for predicting reflection properties and design of effective absorption of EM radiation in carbon foam based materials.

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