Dielectric study of syntactic foams based on polydimethylsiloxane and hollow glass microspheres at X-band microwave frequency

E E Mastalygina$^{1,2}$ and V Yu Chukhanov$^3$

$^1$ Scientific Laboratory “Advanced Composite Materials and Technologies”, Plekhanov Russian University of Economics, 115054, 36 Stremyanny lane, Moscow, Russia
$^2$ Department of Biological and Chemical Physics of Polymers, Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 119334, 4 Kosygina str., Moscow, Russia
$^3$ Department of Chemical Technologies, Vladimir State University named after Alexander and Nikolay Stoletovs, 600000, 87 Gorky str., Vladimir, Russia

Corresponding author: elena.mastalygina@gmail.com

Abstract. The dielectric characteristics of syntactic foams based on polydimethylsiloxane binder and hollow glass microspheres at the X-band microwave frequency were studied. Experimental studies were carried out to determine and calculate dielectric constant, dielectric loss tangent in the range from 8 to 12 GHz, as well as radio transparency of the obtained materials. According to the results, an increase in the binder content over 15-20 vol.% led to a significant loss of radio transparency. The treatment by hydrophobizing organosilicon liquid was shown as an effective method for decreasing the dielectric loss tangent and increasing the radio transparency at the microwave radio frequency range. The developed materials proved the temperature stability and fire resistance. The expected applications of syntactic foams based on the developed materials include the various fields of structural and industrial engineering, in particular, producing the protective constructions for stationary radar stations and radio telescopes.

1. Introduction

When constructing stationary radar stations, receiving antennas of satellite signals, and radio telescopes, there is a problem of protecting transmitting and receiving antenna systems from external adverse factors [1–5]. At the same time, the protective structures must maintain high dielectric characteristics in the microwave range. Due to the wide expansion of devices and instruments, the principle of operation of which is based on the use of microwave energy (>300 MHz), the demand for dielectric materials with minimal dielectric losses and, accordingly, the highest radio transparency in this range of radio frequencies goes up [6–8]. Owing to low density and high physical and mechanical characteristics, syntactic foams can be successfully applied to the protective constructions for microwave devices [9,10]. The structure of syntactic foams (hereinafter, SF) are hollow spherical fillers fastened with the polymeric matrix (binder) [11]. It is a given that both the filler and the binder must have sufficiently high dielectric characteristics. If additional functions of heat insulation and
thermal resistance are required, the both components must also be characterized by high thermal stability [12].

The authors assumed that the syntactic forms based on hollow glass microspheres (hereinafter, HGM) and organosilicon polymer binders meet the above-mentioned requirements. Since the published data on the dielectric characteristics of the SFs at the microwave range is extremely scarce and fragmented, the aim of the present work was to study the dielectric characteristics of new SFs, as well as to determine the effect of nature and the ratio of binder and filler on these properties.

2. Materials and methods

The materials under investigation were syntactic foams based on hollow glass microspheres with organosilicon binder (polymeric matrix). Serially produced HGM of grade “MS A9 gr. A2” supplied by PJSC “NZS” (Novgorod, Russia) were used as a filler. HGM are made of sodium borosilicate glass with Na₂O content of 25.5-28.2%, SiO₂ – 71.7-73.8%, B₂O₃ – 3.8-4.4%, Al₂O₃ and Fe₂O₃ – no more than 0.4%. The used grade of HGM has the following characteristics: true particle density of 0.26-0.32 g·cm⁻³, average particle size of 20 µm, 60% packing factor of no less than 60%.

A low molecular weight dimethylsiloxane rubber of grade “SKTN-1” (OJSC “Kazan Synthetic Rubber Plant”, Kazan, Russia) with terminal hydroxyl groups was used as an organosilicon binder for SFs. The used grade of PDMS (SKTN-1) was cured with a K-18 catalyst being a mixture of tetraethoxysilane and tin diethyldicaprylate. The curing process was accompanied by the interaction of terminal hydroxyl groups with the reactive ethoxy groups of tetraethoxysilane and the release of ethyl alcohol. Because of this reaction, polydimethylsiloxane rubber (hereinafter, PDMS) was formed, which has an increased thermal stability and satisfied dielectric characteristics. In a number of experiments, hydrophobizing liquid of grade “GKZh 136-41” (hereinafter, HPL) being a polymer of ethylhydroxyloxane (JSC “GNIIHTEOS Silan”, Lipetsk, Russia) was used.

The process of obtaining SFs consisted in mixing HGM with a given amount of dimethylsiloxane rubber with pre-added 3 wt.% of K-18 catalyst. The samples were moulded in the aluminium forms under a small excess pressure of 0.4 MPa. After 72 hours at 298 K, the samples were removed from the moulding forms and, if necessary, subjected to additional mechanical processing. The physico-mechanical and thermophysical characteristics of the obtained SFs were previously described in the works [13,14].

The dielectric characteristics of the samples were determined using an instrument including P1-20 precession measuring line, waveguide, tunable Gunn diode microwave generator, decoupling ferrite gate, and precession recording device. The sample was placed inside the waveguide, the end of which was short-circuited by a silver-plated copper plate. The dielectric loss tangent (tg δ) and dielectric constant (relative permittivity) (ε) were calculated based on the measurements of the position of voltage standing-wave ratio and its minimum, as well as the known propagation constant, wavelength in free space (λ₀) for a given operating frequency, and critical wavelength in the waveguide (λ₉). The dielectric characteristics were calculated from the obtained values by the MathCAD software. A detailed measurement and calculation procedure is given in the works [15,16].

3. Results and discussion

The curing process of the binder occurs as the result of an interaction of terminal hydroxyl groups of PDMS and reactive ethoxy groups of tetraethoxysilane in the presence of a tin diethyldicaprylate catalyst [17,18]. The obtained SF consists of three phases: glass, PDMS and air, wherein dielectric losses in air are extremely insignificant. Therefore, it can be concluded that the PDMS binder and the glass filler shells will have a decisive influence on the dielectric characteristics of the foam materials.

According to the conducted tests, it was shown that there is a significant increase in dielectric loss tangent with an increase in the binder volume fraction. Moreover, changes in dielectric characteristics
throughout the X-band range from 8.5 GHz to 11.5 GHz were little dependent on the frequency. Therefore, the dielectric constant at a content of PDMS of 50 vol.% at a frequency of 8.5 GHz is 2.44, at a frequency of 9.5 GHz – 2.41, and at a frequency of 11.5 GHz – 2.38.

As an example, Figure 1 shows the pattern of change in the dielectric loss tangent depending on the binder content at a frequency of 9.5 GHz.

![Figure 1. The dependence of the dielectric loss tangent (\(\tan \delta\)) on the PDMS content in the SF at a frequency of 9.5 GHz.](image)

For heterogeneous systems, an analytical relation (Lichtenecker's logarithmic mixture formula) connecting the dielectric constant of a composite with the dielectric constant of components [3] can be used for determining the effective permittivity of SF. The Lichtenecker's logarithmic mixture formula is given in Equation 1.

\[
\ln \varepsilon_r = \theta_1 \ln \varepsilon_{r1} + \theta_2 \ln \varepsilon_{r2} \quad (1)
\]

where \(\varepsilon_{r1}, \varepsilon_{r2}\) – dielectric constant (relative permittivity) of the 1st and 2nd components, respectively; \(\theta_1, \theta_2\) – volume fractions of the 1st and 2nd components, respectively.

Comparing the calculated and experimental values of the dielectric constant given in Table 1, it was stated that the calculated values were less than the experimental ones for the binder content of less than 50 vol.%. This can be explained by a presence of open pores in the SF at the low volume PDMS content due to incomplete filling of the interstitial space and, accordingly, the appearance of adsorbed moisture in the material.

The action of moisture on the surface glass shells led to a decrease in the surface electrical resistance of the material from \(1 \times 10^{13}\) Ohm to \(0.5 \times 10^7\). To reduce the moisture absorption of the SF, adding a hydrophobizing liquid (grade of “GKZh 136-41”) into the foam material was performed. This liquid by its nature is an organosiloxane containing side organic radicals and hydrogen substitutes. The use of water repellent agents should lead to the preservation of high surface electrical resistance of the HGM, avoiding the influence of ambient humidity. In turns, an increase in the surface electric resistance led to a decrease in the dielectric loss tangent. Thus, it can be assumed that the introduction
of a hydrophobizing liquid into the SF with a binder content of less than 50 vol.% will lead to an increase in the dielectric characteristics at the microwave range.

**Table 1.** The calculated and experimental values of the dielectric constant of SF

| Volume fraction of PDMS (vol.%) | Calculated values | Experimental values |
|---------------------------------|-------------------|---------------------|
| 10                              | 1.26              | 1.44                |
| 30                              | 1.82              | 2.06                |
| 50                              | 2.39              | 2.41                |
| 70                              | 2.72              | 2.75                |
| 90                              | 2.97              | 3.06                |
| 100                             | 3.15              | 3.15                |

Experimental data confirms that the introduction of a hydrophobizing liquid 136-41 into the SF with an open-porous structure leads to a noticeable improvement in dielectric characteristics. When adding 1.5 wt.% of HPL to the SF, the tangent of the dielectric loss angle decreased by 30%. Further introduction of HPL is impractical, since in this case the dielectric characteristics of the foam practically do not change. The dependence of the loss of radio transparency of the materials and moisture absorption on the content of hydrophobizing liquid also indicates the interdependence of these values (Figure 2).

![Figure 2. Dependence of the loss of radio transparency (\(\Delta P\)) on the content of hydrophobizing liquid (modifier) in the SF.](image)

The retention of the dielectric characteristics of SFs with an increase in temperature is subject to the temperature dependences of the dielectric characteristics of binder and filler. The dielectric properties of glass largely depend on its composition. For example, the dielectric characteristics of lithium-containing glass at high temperatures are much lower than that of potassium-containing glass. This fact can be explained by small size of the lithium atoms and, consequently, their high mobility...
resulting in reduction of electrical resistance [19]. Accordingly, the dielectric characteristics of the sodium-containing glass depending on temperature are characterised by an intermediate position between the above-mentioned glasses, since the size of sodium atoms is intermediate in the sizes of lithium and potassium atoms.

The change in the electrical properties of PDMS to a significant degree is affected only by the transition of the polymer from a glassy to a highly elastic state. In this area, the dielectric constant reaches its maximum value. At the highly elastic state, the changes in dielectric characteristics are not significant. Since the operating temperatures of the studied SFs are only in the region of a highly elastic state, it is important to retain electrical properties in this temperature range [11]. The temperature dependence of the dielectric constant of the SFs was insignificant, which ensured stable electrical properties of the materials up to 423 K.

An important property of the materials based on organosilicon binders is the retaining high dielectric characteristics after exposure to flame. It is allowed to use only such organosilicon binders that do not contain phenyl groups as side substituents on silicon atoms. The presence of phenyl groups leads to the formation of an electrical conductive coke layer, which sharply worsens the dielectric properties of materials [20].

The results of flame test resistance are shown in Table 2. It was proved that propane-air flame had not significant effect on the dielectric properties of the SFs with a PDMS binder content of 10 vol.%

Table 2. Change in the electrical properties of SF (10 vol.% of PDMS) after exposure to a propane-air flame (T = 1372 K).

| Flame exposure time (s) | Electrical properties of SF before exposure | Electrical properties of SF after exposure |
|------------------------|---------------------------------------------|-------------------------------------------|
|                        | dielectric constant | dielectric loss tangent (tg δ) | radio transparency (-∆P, dB) | dielectric constant | dielectric loss tangent (tg δ) | radio transparency (-∆P, dB) |
| 15                     | 1.44              | 2.60          | 0.80                  | 1.44              | 2.80          | 0.80                  |
| 30                     | 1.44              | 2.60          | 0.80                  | 1.50              | 3.30          | 0.90                  |
| 60                     | 1.44              | 2.60          | 0.80                  | 1.55              | 3.40          | 0.95                  |

4. Conclusions

The dielectric characteristics of syntactic foams based on polydimethylsiloxane binder and hollow glass microspheres at the X-band microwave frequency were studied. According to this study, with an increase in frequency at the X-band from 8.5 to 11.5 GHz, the dielectric characteristics of the syntactic foams changed insignificantly. An increase in the polydimethylsiloxane binder content in the syntactic foams over 15-20 vol.% led to a significant loss of radio transparency (> 1 dB per 10 mm of material thickness). A decrease in dielectric loss tangent and an increase in radio transparency by almost a factor of 4 at the microwave radio frequency range for syntactic foams with a binder content of less than 15 vol.% was achieved by introducing a hydrophobizing organosilicon liquid in an amount of 1.0-1.5 wt.%. The dependence of dielectric characteristics on temperature at the range of 273-423 K was insignificant, which makes it possible to operate the developed syntactic foams at elevated temperatures. The exposure to an open flame did not lead to a noticeable deterioration in the dielectric characteristics of highly filled syntactic foams. The expected applications of syntactic foams based on the developed materials include the various fields of structural and industrial engineering, in particular, producing the protective constructions for stationary radar stations and radio telescopes.

References

[1] Bardella L and Genna F 2001 Elastic design of syntactic foamed sandwiches obtained by filling of three-dimensional sandwich-fabric panels Int. J. Solids Struct. 38 307–33
[2] Peters S T 1998 *Handbook of composites* 2nd ed (Springer Sci. Bus. Media, California)

[3] Wolfe R 2000 Research challenges for structural use of small-diameter round timbers *For. Prod. J.* 50 21–9

[4] Allaoui A, Cheng H-M and Bai J 2002 Mechanical and electrical properties of a MWNT/epoxy composite *Compos. Sci. Technol.* 62 1993–8

[5] Chukhlanov V Y, Selivanov O G and Chukhlanova N V 2016 A sealing composition with high dielectric characteristics and increased optical transparency on the basis of epoxy diene resin modified with phenyl ethoxyxysilane *Polym. Sci. - Ser. D*

[6] Yoonessi M, Lebrón-Colón M, Scheiman D and Meador M A 2014 Carbon Nanotube Epoxy Nanocomposites: The Effects of Interfacial Modifications on the Dynamic Mechanical Properties of the Nanocomposites *ACS Appl. Mater. Interfaces* 6 16621–30

[7] Chen L, Chai S, Liu K, Ning N, Gao J, Liu Q, Chen F and Fu Q 2012 Enhanced Epoxy/Silica Composites Mechanical Properties by Introducing Graphene Oxide to the Interface *ACS Appl. Mater. Interfaces* 4 4398–404

[8] Alent'ev, A.Yu. Yablokova M Y 2010 *The binder for composite polymer materials* ed O N Avdeev, V.V. Alentiev, A.Yu. Lazoryak, B.I. Shornikova (Moscow: MSU publishing)

[9] Blythe T and Bloor D 2005 *Electrical Properties of Polymers, Second Edition* (Cambridge; New York: Cambridge University Press)

[10] Park S-J, Cho K-S and Kim S-H 2004 A study on dielectric characteristics of fluorinated polyimide thin film *J. Colloid Interface Sci.* 272 384—390

[11] Wouterson E M, Boey F Y C, Hu X and Wong S C 2005 Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures *Compos. Sci. Technol.* 65 1840–50

[12] Arora A, Sant G and Neithalath N 2017 Numerical simulations to quantify the influence of phase change materials (PCMs) on the early- and later-age thermal response of concrete pavements *Cem. Concr. Compos.* 81 11–24

[13] Chukhlanov V Y and Tereshina E N 2007 Polyorganosiloxane-based heat-resistant sealant with improved dielectric characteristics *Polym. Sci. Ser. C* 49 288–91

[14] Mastalygina E E, Ovchinnikov V A and Chukhlanov V Y 2019 Light heat-resistant polymer concretes based on oligooxyhydridesilmethylenesiloxysilane and hollow spherical fillers *Mag. Civ. Eng.* 90 37–46

[15] Cui H, Memon S A and Liu R 2015 Development, mechanical properties and numerical simulation of macro encapsulated thermal energy storage concrete *Energy Build.* 96 162–74

[16] Chukhlanov V Y and Selivanov O G 2016 Electrical Properties of Syntactic Foams Based on Hollow Carbon Microspheres and Polydimethylsiloxane *Russ. Phys. J.* 59 944–8

[17] Ramakrishnan S, Sanjayan J, Wang X, Alam M and Wilson J 2015 A novel paraffin/expanded perlite composite phase change material for prevention of PCM leakage in cementitious composites *Appl. Energy* 157 85–94