Effect of Ultrasonic Treatment on Electromagnetic Properties of Composites Based on Multiwall Carbon Nanotubes at Microwave Frequency Range

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***Abstract* – Nanostructured composite materials have opened a new era for multifunctional materials (such as reflection, absorbing, conducting etc.). In particular, multiwalled carbon nanotubes (MWCNTs) can be applied in order to improve electromagnetic properties in composites. Polymer composite materials based on MWCNTs were obtained. In this paper, microwave properties of polymer composites based on MWCNTs have been analyzed. Frequency dependences of permittivity of MWCNTs/varnish composite films were investigated in the range 3 – 14 GGz. The multiwall carbon nanotubes used in the composite were about 9.4 nm and 18.4 nm in diameter. The results show that the ultrasonic treatment modifies the dielectric permittivity of the composite. The dependence of the real and imaginary parts of the permittivity of sonication time is non linear.**

***Index Terms* – MWCNT, composite, permittivity, ultrasonic treatment, microwave**

I. Introduction

POLYMER COMPOSITE materials are used in widely industries and science. They have more suitable mechanical properties than ceramic composite.

Multiwall carbon nanotubes (MWCNTs) are promising in different fields of material science. Carbon nanotubes have a wide range of non-studied potential applications in various technological areas due to their attractive structural, mechanical, end electrical properties [1] – [3]. Conductivity of carbon nanotubes is very high. Polymer composite, containing conductive fillers are very perspective for electromagnetic application in gigahertz [4] – [7] regions even at low concentration of nanotubes.

The binder material for production of polymer composite should have a good adhesive properties, high fluidity and high polymerization rate.

The microwave properties of a composite are described by the frequency dependence of complex permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts characterizing the dielectric polarization and losses in the composite, respectively. The permittivity depends on the nanotubes concentration in a composite [2], aspect ratio and the residues of catalytic metals [1], [7].

Methods of changes of electromagnetic properties of composite materials in external influence on their structure have been investigated [2], [3]. One way to change the internal structure of composite materials is ultrasonic treatment [8] – [11]. Ultrasonication can produce thermodynamically stable MWCNTs mixture and after sonication MWCNTs are separated.

The aim of this work is to study the electromagnetic properties that are present in varnish/MWCNTs polymer composites obtained by ultrasonic treatment. The impact of two types of MWCNTs on polymer composite's electromagnetic properties is also studied.

II. Experimental Results

A. MWCNT/varnish composite film preparation

The filler of composites was multi-walled carbon nanotubes (MWCNTs–2 and MWCNTs–3). Nanotubes were obtained by catalytic gas-phase deposition of ethylene in the presence of $FeCo/Al_2O_3$ catalyst in Institute of Catalysis SB RAS [12]. It is a lightweight, fluffy black powder containing individual nanotubes, tensions and aggregates of nanotubes, impurity of metal particles which were encapsulated in nanotubes, as well as the particles of the oxide supporter.

The average MWCNTs–2 diameter is 9.4 nm, length > 15 µm, purity > 97.5%. The average MWCNTs–3 diameter is 18.4 nm, length > 15 µm, purity > 90.0 %. MWCNTs–3 contain remainders of catalyst about 7.0 %.

Urethane alkyd varnish Tikkurila Unika Super (Tikkurila, Finland) was used for production of experimental samples. In the liquid state its viscosity is known to be small. This allows a filler to be moved easily.

The technology of obtaining experimental samples was described in Ref. [7]. For the production of mix for experimental samples 0.25, 0.5, 1.0, 2.0 wt. % of MWCNT was added to varnish. The mixture was placed in a glass beaker. The mixture was sonicated by the ultrasonic device "Alena" (Biysk Technological Institute, Russia). Probe was inserted into a glass beaker with mixture. The mixture was sonicated for 1, 2, 3, 4 and 5 minutes at 50 VA power. Mixtures were molded into a planar plate, which size is 70.0 × 25.0 × 0.5 mm^3.

Notice that when volume concentration was increased, viscosity of mixture was increased. It was restricted to a concentration of MWCNTs at composite mixture.

The process of polymerization was carried out for 48 h at the room temperature. The experimental samples used for microwave studies were thin strips 70.0 × 2.0 × 0.5 mm.

B. Measuring equipment

The cavity perturbation techniques were used for the evaluation of permittivity of experimental samples at SHF range. This technique is applicable for low loss samples and volume of the sample inserted should be very small in comparison to the volume of the empty cavity In this technique, a cavity was designed with a very small slot at the centre of the broad/short wall of rectangular waveguide in order to insert the sample material.

The device consists of vector network analyzer, Agilent Technologies E8363B, and different volume multimode rectangular cavities that cover the frequency range 3 – 14 GHz.

Measurements were made at temperature of 24 ± 1 °C.

C. SHF range measurement

The complex permittivities of experimental samples with different time of ultrasonic treatment at SHF range are shown in Fig. 1 – 4. The concentration of MWCNTs is equal to 0.5 wt. %. The complex permittivities of experimental samples 0.25, 1.0, 2.0 wt. % of MWCNTs have same character. The measurement error is about 5 percent for real part of permittivity and about 10 percent for imaginary part of permittivity.

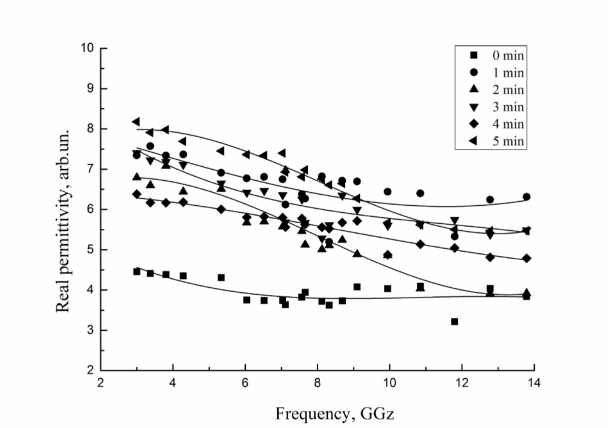

Fig. 1. Real permittivity of composites based on MWCNT – 2 for different time of ultrasonic treatment

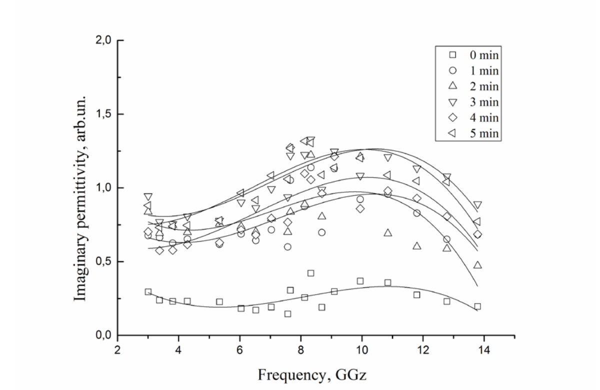

Fig. 2. Imaginary permittivity of composites based on MWCNT – 2 for different time of ultrasonic treatment

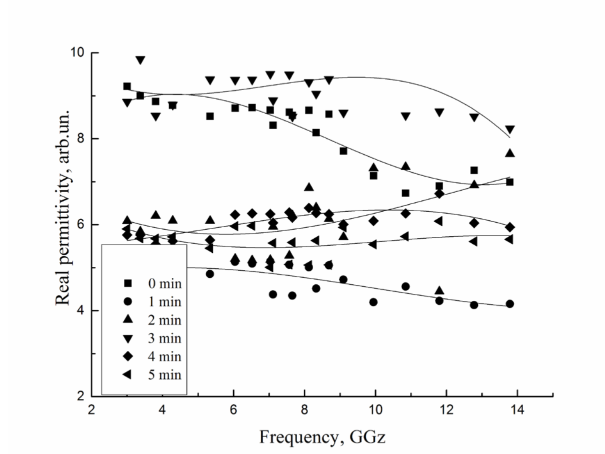

Fig. 3. Real permittivity of composites based on MWCNT – 3 for different time of ultrasonic treatment

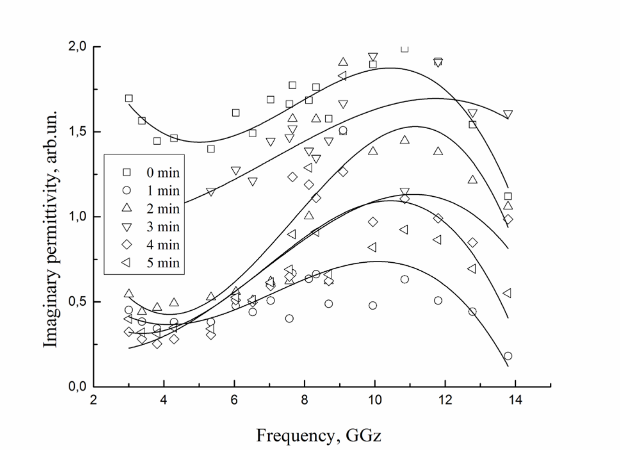

Fig. 4. Imaginary permittivity of composites based on MWCNT – 3 for different time of ultrasonic treatment

III. Discussion of Results

Urethane alkyd varnish has values of the permittivity 4 arb. un. at the frequency range 3 – 14 GHz [13]. Figs. 1 and 3 show that the composite based on 0.5 wt. % nanotubes has increased values of permittivity. The values of permittivity of composites based on MWCNTs–2 and MWCNTs–3 are different.

The ratio of imaginary permittivity of MWCNTs–3 to imaginary permittivity of MWCNTs–2 is equal to 8 (see Figs. 2 and 4). The large values of the real and imaginary permittivity of composite based on MWCNTs–3 are caused by a large percentage of impurities. Firstly, MWCNTs–3 contain remainders of catalyst about 7.0 %. Secondly, MWCNTs–3 diameter is twice as much as MWCNTs–2 diameter.

The ultrasonic treatment modifies the dielectric properties of the composite. For example, the sonication during 2 min MWCNTs–2 increased the value of real permittivity from 4.0 till 7.5 arb. un. (Fig. 1) The frequency dependence of both real and imaginary permittivity was not observed. Under such conditions polymer composite is nonpolar dielectric.

The increase of treatment time leads to emergence of the orientational polarization and there appears the frequency dependences of permittivity. This may be caused by the distraction of MWCNTs agglomerates is a reason of this fact.

The sonication during 2 min MWCNTs–3 decreased the value of real permittivity from 9.0 till 5.0 arb. un. (Fig. 3). MWCNTs–3 have many defects. They are destroyed by the ultrasonic treatment. The volume content of the amorphous part is increased in the composite. It leads to decreasing both real and imaginary permittivity (Figs. 3, 4).

IV. Conclusion

In this paper we investigated MWCNTs composite materials. Polymer composite materials, containing 0.5, 0.5, 1.0, 2.0 wt. % concentrations of multiwall carbon nanotubes and varnish as matrix were prepared. Multiwall carbon nanotubes/varnish mixtures were treated ultrasonically before polymerization [8]. The time of ultrasonic treatment was 1 – 5 minutes. The differences in electrical behaviors of varnish/MWCNTs polymer composites are traceable to the ultrasonic treatment.

It is shown that adding nanotubes increases permittivity of materials.

The main conclusion is that electromagnetic responses of multiwall carbon nanotubes/varnish composite are very sensitive to the time of ultrasonication.

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