

Composite materials for protection against electromagnetic microwave radiation

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Abstract

A fairly wide range of carbon-polymer composite materials was synthesized and studied in terms of their potential to protect people and electronic equipment from exposure to electromagnetic radiation (EMR). The materials studied included three main groups: (1) PVC polymer composites filled with various carbon-containing fillers (colloidal graphite, thermally expanded graphite, acetylene black, graphitized carbon black, carbon nanotubes, graphene) at concentrations ranging from 5 to 20%; (2) carbon cloth - commercial and modified with nano-metal additives (e.g., nanoparticles of Cu, TiN, etc.); (3) highly-filled polymer-carbon composites in the form of paint. The transmission rate α of electromagnetic radiation was investigated for such materials in the frequency range of 10 GHz as well as their electrical conductivity.

The results showed that the shielding ability of the materials of group (2) is significantly higher than that of the materials of group (1), which is probably due to the presence of strong internal skeleton of conductivity. Nevertheless, some highly-filled mixed polymer-carbon composites in the form of paint demonstrate even more shielding ability than carbon cloth and could be used for the defence against EMR.

1. Introduction

Electromagnetic radiation (EMR) influences population and electronic equipment because of increasingly widespread use of television and radiobroadcasting, microwave emitting devices and other modern technologies. However, it is not the entire spectrum of the signal and the higher harmonic components that is harmful to living things, but the waves whose lengths fall in the millimetre and centimetre range. Circulatory system, brain, eyes, immune and reproductive systems are known to be most susceptible to electromagnetic fields. It encourages the search for materials and technologies that can protect humans and equipment from ultra-high frequency (UHF) electromagnetic radiation, electromagnetic terrorism and weapon of directed energy [1, 2].

Some investigations of electromagnetic losses in carbon-epoxy composites have shown the sufficient influence of the type of carbon filler (multi-walled carbon nanotubes, carbon foams, etc.) and its content on the value of losses [3-5].

The main objective of this work was to create electroconductive polymer systems based on inexpensive and easy available carbon agents and polymer matrixes, which could block EMR and ensure quite good electromagnetic interference shielding effectiveness [6].

2. Experimental

A fairly wide range of composite materials have been synthesized and studied in terms of their potential to protect people from exposure to electromagnetic radiation.

The main materials studied included three main groups:

(1) polymer composites filled with various easy available carbon-containing fillers (colloidal graphite, thermally expanded graphite, acetylene black, graphitized carbon black) at concentrations ranging



from 5 to 20%;

(2) carbon cloth – commercial as well as modified with nano-metal additives (e.g., nanoparticles of Cu, TiN);

(3) highly-filled polymer-carbon composites in the form of paint.

2.1. The methodology for preparing conductive composites based on carbon fillers

In general, the methodology for preparing conductive composites involves mixing the components (polymer, softener, carbon fillers, etc.) and their subsequent plasticization at high temperature. We used the following specific methods:

In the first case the polymer was diluted in dioctyl phthalate (CAS #117-81-7) as a softener; after this the carbon filler (5-20 %) was added to the product and mixed for 1 hour. The finished composite was sputtered on the substrate and dried for 3 min at 200 °C.

The second method for preparing composites also included dilution of the polymer-powder in the softener, but the carbon filler was previously mixed with wetting agents (soybean oil, ethanol, etc.) and after that was mixed with the product. The conditions of drying were the same as in the first case.

The third method was similar to the second one, but the composites contained 60-80% of carbon additives. As a result, carbon highly-filled polymer paint was formed and then mapped on the surface of polymer sample.

2.2. The methodology for modifying carbon cloth with nanoparticles

The carbon cloth sample was placed in a container so that it would lie entirely in one plane. After this the sample was wetted with 2 ml «basic» CuSO₄ solution until complete wetting. Then, there was prepared the following mixture of substances: 2 ml of KI and 2 ml of Na₂S₂O₃ in a clear flask. The resulting mixture was poured onto a previously prepared re-wetting sample. As a result of the chemical reaction, CuI particles formed directly on the carbon fibres and between the fibre spaces. The sample was dried in air at temperatures of 50-100 °C to constant weight. Also the carbon cloth sample modified with TiN was produced by vacuum deposition techniques.

2.3. The measurement technique

Electrical conductivity and resistance are important parameters in determining the shielding effectiveness that the EMI screen or other shields would provide. They are much more critical at higher frequencies, where surface resistivity is predominant. Surface resistivity and volume resistivity are commonly tested for characterizing electrical conductivity of EMI screening materials as a quick and practical quality check.

2.3.1. The measurements of specific volume resistance

The measurements of specific volume resistance were carried out initially according to the common "three-electrode" method (technique 1) and then using the "four-electrode" method (technique 2).

Technique 1 involves measuring the current passing through the sample at a constant voltage. In this technique, constant voltage from the voltage source is applied to two high-voltage electrodes. A current is going through the thickness of the sample to the working electrodes or through the surface to the protective electrode (PE). From the PE the current is directed to the ground by passing the working electrodes.

Technique 2 uses the following four electrodes [2]:

- 1) two power current electrodes on the ends of the sample;
- 2) two measuring "potentiometric" electrodes in the middle part of the sample.

The voltage source was connected via the ammeter to the current electrodes and digital voltmeter was connected to the "potentiometric" electrodes.

The main condition of measurement accuracy is that the input impedance of digital voltmeter should be much higher than the possible contact resistance.

This technique enables one to exclude the contact resistance and to measure the true resistance of composite layer due to the negligible currents between measuring electrodes. As our experiments have shown, the contact resistance in our samples was quite high. So, technique 2 is more preferable in our case.

The volume electrical resistivity, ρ , is expressed as the electrical resistance of a material per unit length multiplied by the cross-section area:

$$\rho_v = U \cdot a \cdot b / l \cdot I(l) \quad ,$$

where U is the voltage, V; I is the current, A; a is the thickness, cm; b is the width, cm; l is the length between the measuring electrodes, cm.

2.3.2. The measurements of EMR blocking

Evaluation of the absorption of electromagnetic energy by the sample of composite, which was fixed between the horn antennas (figure 1), was carried out by comparing the measured values of the reflection coefficient module and transfer coefficient. Electromagnetic properties of radio absorption coatings were studied in the frequency range of 10 GHz.

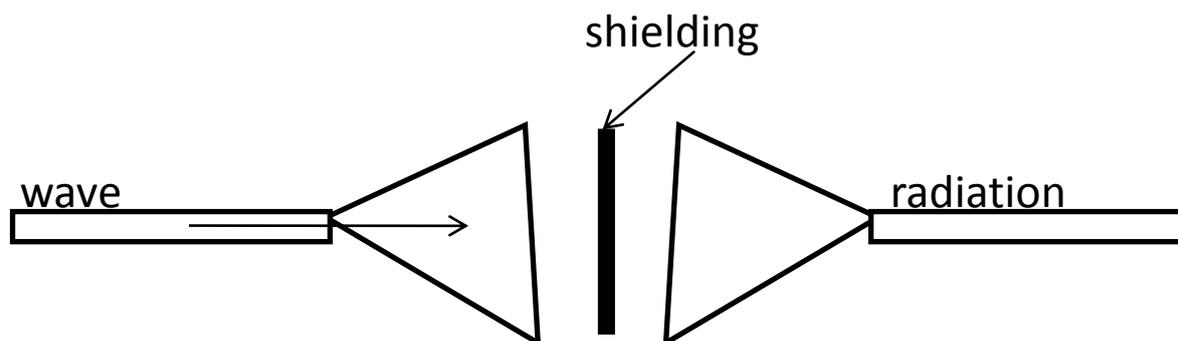


Figure 1. Simple scheme of the shielding measurement

3. Results and discussion

Fig. 2 shows the dependence of the resistance on the nature and concentration of carbon filler for the more typical carbon materials, which were investigated using technique 2.

Graphitized carbon black (commercial grade PUREBLACK[®] Carbons) and thermally exfoliated graphite (commercial grade ABG 1010) from Superior Graphite Co. Chicago, IL, USA have demonstrated the best conducting properties as conducting filler for the above-mentioned composites.

This effect can be explained not only by the well-developed surface area of these materials, which can reach and sometimes exceed the value of 50-65 m²/g, but also by specific nano-structure peculiarities of such carbon materials. A high conductivity requires so called “high structure” materials, whose macromolecules have multiple “branches” consisting of individual carbon nanoparticles [7]. These highly developed nano-sized branches are believed to create additional contact points, thus resulting in efficient conductivity enhancement at low concentrations of carbon additives. As a result, such materials are usually more conductive than traditional forms of acetylene-type conductive carbon black.

The percolation threshold for the graphitized carbon black and thermally exfoliated graphite is less than 5%. It is not possible to fix this threshold from Fig. 1 as we selected the range of carbon concentration from 5 to 20%.

At the same time, Ukrainian Zaval'e colloidal graphite preparation (grade S-1) from the Zavalyevsky graphite plant [8] has demonstrated a classical dependence of resistance on the

concentration of conductive additive. The corresponding graph shows the clear formation of percolation threshold, which occurs at concentrations of carbon material ca 10-12% in polymer-graphite composite (figure 2).

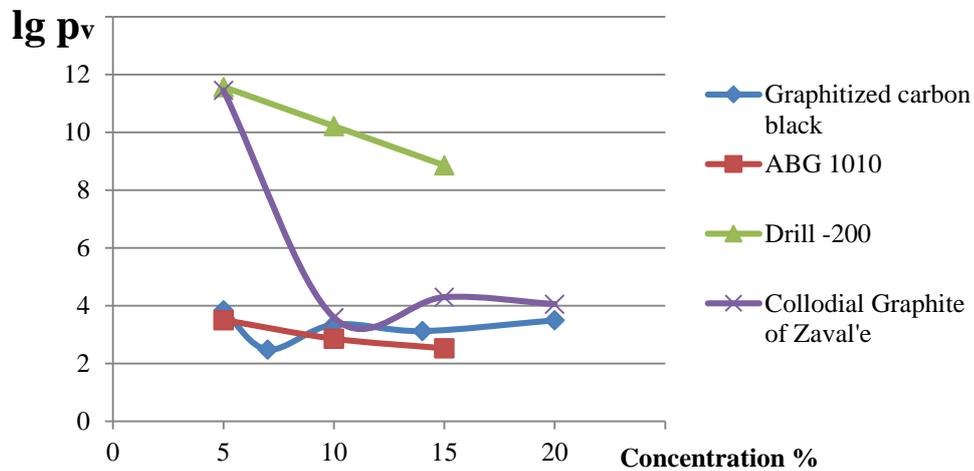


Figure 2. The experimental curves of dependence of the resistance vs the filler nature and concentration

The task of shielding electromagnetic waves is relevant both in the organization of EMC and in the protection of electronic equipment against powerful electromagnetic pulses. The dependence of shielding properties of materials on electrical conductivity is directly proportional (figure 3). We investigated the transmission rate, α , of electromagnetic radiation for such materials in the frequency range of 10 GHz (figure 3).

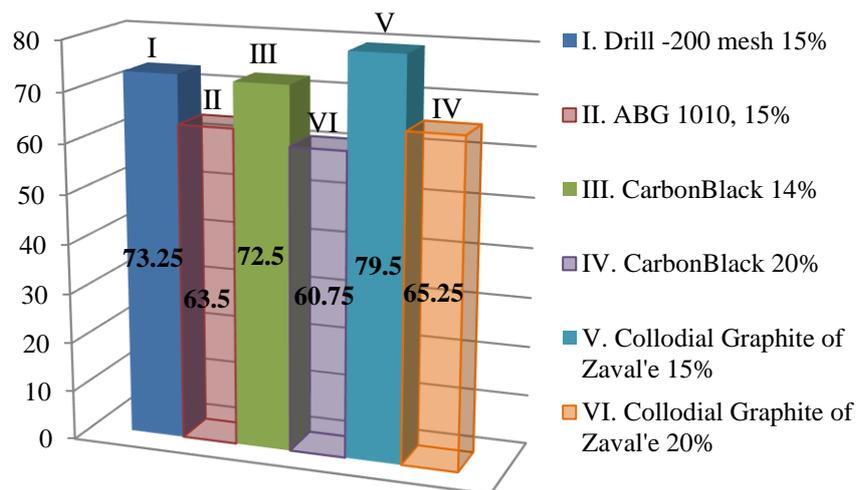


Figure 3. Value of transmission coefficient α of electromagnetic wave by composite sample, %

Fig. 3 shows that the highest effectiveness has been received for sample IV with 20% graphitized carbon black. The samples based on thermally exfoliated graphite and colloidal graphite have almost the same values, but these values of the transmission of electromagnetic energy are not enough for effective use. To create more efficient screening coverage, it is necessary to ensure

maximum electrical conductivity of the sample. To fulfil this task, a new type of samples was developed, in particular sheeting paint with a graphite filler content of more than 60%.

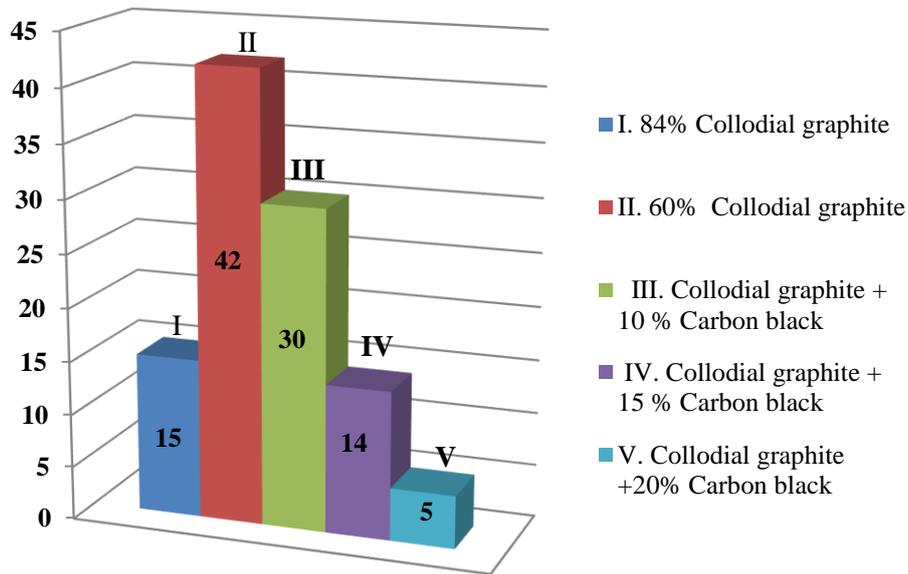


Figure 4. Value of transmission coefficient α of electromagnetic wave by composite sample, %

Figure 4 shows the coefficient of electromagnetic radiation transmission α of different composite materials. Colloidal graphite shows good characteristics, and it does not require additional operations (sifting, grinding, pre-wetting, etc.) in producing composite materials. Besides, it is based on home industry product, which makes it available [8].

The outside surface is an important attribute of the paint coating with a special function. It is important for the coating to have good adhesion and to be intact during its life. The high content of carbon fillers $\geq 80\%$, like that in colloidal graphite, provides decent protection from electromagnetic radiation, but leads to cracking of the system and, therefore, to delamination of the coating and poor performance. Adding even a small amount (10-20%) of graphitized carbon black can improve the composite system. Such a composite material is effective in terms of shielding properties and technological in terms of its ability to form a quality- surface uniform film.

Thus, a promising and competitive shielding composite material was created, which is capable of protecting important facilities and people from electromagnetic radiation and can ensure electromagnetic interference shielding effectiveness at least 10 dB in the range of about 10 GHz.

4. Conclusions

According to the obtained data it is clear that the shielding properties of the materials correlate in general with electrical conductivity (figures 3, 4).

It was shown that even a small addition of the material with a well-developed surface area (graphitized carbon black) improves effectiveness of electromagnetic wave absorption by graphite composite samples (figure 5).

The results showed that the shielding ability of the materials of group (2) is significantly higher than that of the materials of group (1), which is probably due to the presence of strong internal skeleton of conductivity. Nevertheless, some highly-filled mixed polymer-carbon composites in the form of paint demonstrate even more shielding ability than carbon cloth, could be used for effective defence of people and equipment from EMR and ensure electromagnetic interference shielding effectiveness at least 10 dB in the range ca 10 GHz.

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