DEVELOPING COMPOSITE POLYMER SHIELDING MATERIALS FOR THE UHF RANGE

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This work deals with solving the engineering problem of preventing escape of electromagnetic energy from the inside of electronic equipment. Paint-like polymer composites based on a polymer binder, carbon materials and some metal oxides are proposed as promising electromagnetic shielding materials. Our studies show that carbon-graphite coatings enable an electromagnetic shielding efficiency of -24 dB at frequencies from 17 to 27 GHz. Modifying the composites with metals or their oxides allows an increase in the shielding efficiency up to -30…-33 dB in the above frequency range.

Keywords — composite materials; electromagnetic energy; shielding efficiency.

The ongoing technological development results in increasing electromagnetic smog. This is due to the increased use of plastic housings for electronic equipment which are “transparent” to electromagnetic waves. Another reason is the necessity to make the construction materials lighter and cheaper.

To prevent the escape of electromagnetic energy from the inside of an object, different methods of protection are used, the most popular one being metal shielding. However, this method has a number of disadvantages such as high cost, complexity of use. In addition, metals are not universal in terms of the frequency range. Materials used for electromagnetic shielding of electronic equipment should allow a combination of different mechanisms (absorption and reflection).

By its nature, a polymer is not a conductive material and therefore it does not interact with electromagnetic energy, especially when thin films are mentioned. Electromagnetic waves easily penetrate the bulk of a polymer. Nevertheless, polymers are essential components of composite materials as the composite performance depends on them.

A wide range of scientific papers deal with development of new materials for electromagnetic shielding, including composite polymers [1-5].The right combination of polymer matrix and fillers can provide expectable high efficiency. According to the ultimate aim, common polymer binders are polyvinyl chloride, acrylates, epoxy resins, etc. For instance, some reported results [6-8] show that the use of carbon-graphite fillers in composites can provide electromagnetic shielding efficiencies in very wide range of -10 to -85 dB.

A great number of efficient shielding composite materials available on the market today contain metals (sheet, mesh, fibers) or a thick layer (more than 1mm) of absorbent. In terms of shielding the inner space of electronic equipment, the thickness of absorbent is a fairly critical factor. Therefore, the most important task is developing a composite material which would be no more than 200 μm thick and at the same time would provide a shielding efficiency of - 30 dB, i.e. 1000-fold.

A range of paint-like composite materials has been developed at the Department of Electrochemical Energy Engineering and Chemistry of KNUTD. Such materials are easily applied to any surface, reliably prevent the escape of electromagnetic energy, provide high adhesion to the construction material of the housing and most importantly high shielding efficiency at a thickness of no more than 200 μm.

Research methodology

Basic starting materials

Carbon materials of different morphology were studied in this work: colloidal graphite (Zavalivskii Graphite, Ukraine), graphitized carbon black (Superior Graphite Co. Chicago, Illinois, the USA), oxides of manganese, nickel, zinc and iron.

Methods of samples preparation

Composite materials were prepared as follows. At first, a polymer solution was prepared by dissolving (w/w) 10 % of the polymer powder in (w/w) 90 % of ethanol while stirring constantly until the polymer is fully dissolved. A mixture of dry materials including 3 parts of graphite and 1 part of graphitized black was prepared in a separate dish and then modified with oxide additives. After that, the polymer solution was added to the dry mixture in a mixer and stirred thoroughly for 30 min. The composite produced was applied to a radio-transparent substrate by the contact method and dried at room temperature.

Methods of samples investigations

The shielding efficiency of the composite samples produced was studied in the 17 – 27 GHz frequency range. The measurements were carried out using a (MX) P-2-66 automatic measuring complex of microwave characteristics by the standard scheme of measuring fading at the four-poles. Evaluation of electromagnetic losses under electromagnetic wave passing through the composite sample placed in the waveguide was carried out by comparing the coefficients of reflection and transmission.

Results and discussion

The first type of the paint produced was based on an alcohol-soluble polymer and pure carbon materials of different morphology (graphite and carbon black).

Adhesion of composites

A polymer, which contains hydroxyl and other active groups, provides strong chemical bonding with a wide range of materials (metals, ceramic, glass, etc.). This allows one to predict high adhesion even to such materials as plastics.

The strength of adhesion of the composite layer to a plastic, for example polyacetal, was assessed by the conventional scratch grid test method [9]. The pull off of sticky tape showed that the composite is peeled partially (up to 35%). This occurs mainly along the cut lines, where there is an increase in internal tensions under mechanical stress, which causes destruction of the composite. The value of composite adhesion by the cross-cut method was 3. It is noteworthy that the destruction had a cohesive nature, i.e. the adhesive force was higher than the cohesive one.

To improve the performance of composites, it was necessary to strengthen the surface layer of coating. For this purpose, various finishes or top coats, in particular varnishes are used. Our decision was to use pure solution of the polymer used for the polymer matrix of the composite as a finish.

Applying a thin layer of the polymer solution to the surface of the fabricated conductive paint enables considerably improved characteristics. The adhesion of the composite to the substrate increases up to 5. Besides, the coating adheres strongly to the surface, does not split off, peel, flake or chalk. This can be accounted for by the fact that the polymer solution “flows” in the porous surface layer of the paint and therefore strengthens it without changing the total thickness of coating to any noticeable extent.

Synergistic effect

Combining carbon materials of different nature yielded a sharp increase in electromagnetic shielding, which was due to the synergistic effect of individual components. In particular, the composite fabricated by blending graphite and carbon black shows an average increase in the shielding properties by -14 dB compared to the individual contribution of each component (Fig. 1).

One of the mechanisms for such a synergistic effect may involve an increased number of interfaces in the system between the particles of graphite, carbon black and polymer.

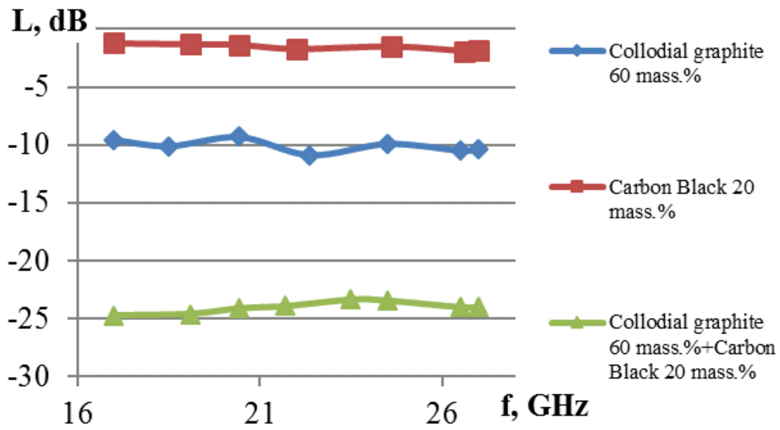

Fig. 1. Electromagnetic losses for carbon materials and their blends

In such a multi-phase system electromagnetic energy losses occur due to multiple reflections from the surface of conducting particles. Besides, electromagnetic energy decreases due to vortex currents generated under the action of electromagnetic field.

Peculiarities of graphitized carbon black, which is a porous material [10], and the composite itself, which becomes porous after complete drying, contribute to the increased electromagnetic losses. Firstly, the porosity of the composite material creates irregularities on the surface, which enhances reflections of the electromagnetic flux in different directions. Secondly, the presence of pores causes better permeability of the electromagnetic energy into the bulk of material, where it is partly absorbed and partly reflected.

The absorption (scattering) of electromagnetic energy was determined from the equation:

$$A = 100 - R - T,$$

where A is the absorption coefficient, %

R is the reflection coefficient, %

T is the transmission coefficient, %.

Our calculations show that total losses and the above - mentioned coefficients depend on the coating thickness. This dependence is more pronounced for thicknesses of 145-160 μm, but then it stabilizes considerably (Table 1).

Table 1. Dependence of composite characteristics on the coating thickness

Characteristics	Thickness, μm			
	40	114	145	160
Total losses, dB	-10.1	-17.6	-23.1	-24.0
Transmission coefficient T,%	9.70	1.80	0.50	0.40
Absorption coefficient A,%	70.8	45.2	33.1	29.7
Reflection coefficient R,%	19.5	52.9	66.4	69.9

The composite is employed successfully in manufacturing thermal vision devices at the enterprise «Thermal Vision Technologies» (Kyiv, Ukraine) to provide «electronic compatibility» and decrease in «electronic visibility» in the radio wave and lower UHV range.

Modifying the paint with transition metal oxides

The presence of transition metal oxides, in particular nickel oxide, manganese oxide and mixed iron oxide, which possess high magnetic permeability and a large number of unpaired electrons, can provide efficient shielding of the magnetic component of electromagnetic wave. Electromagnetic losses can be considerably increased due to the energy losses required for making excited and ionized states of atoms and molecules. The excited states appear when bonded electrons in the atoms and molecules of absorbent gain extra energy and move to a higher energy level.

However, to employ the modifying oxides in paints, it is necessary not only to select the right oxide of a certain metal but also to determine its amount in the composite. Our results reveal that unjustified increase in the concentration of the oxide component can yield deterioration of the composites shielding capability (Fig. 2).

For instance, the carbon composite containing 40 % of the mixture of Ni_2O_3 and MnO_2 at a ratio of 1:1 showed the result (-15 dB) half as good as the same composite containing 16% of the oxide mixture, whose electromagnetic losses are -30 dB.

Such an effect was also observed for other composites modified with oxides. This effect may be accounted for by a decrease in the composite conductivity due to an increased number of non-conducting oxide particles, whereas in the ultrahigh frequency range the conductivity is one of the major parameters for providing electromagnetic shielding.

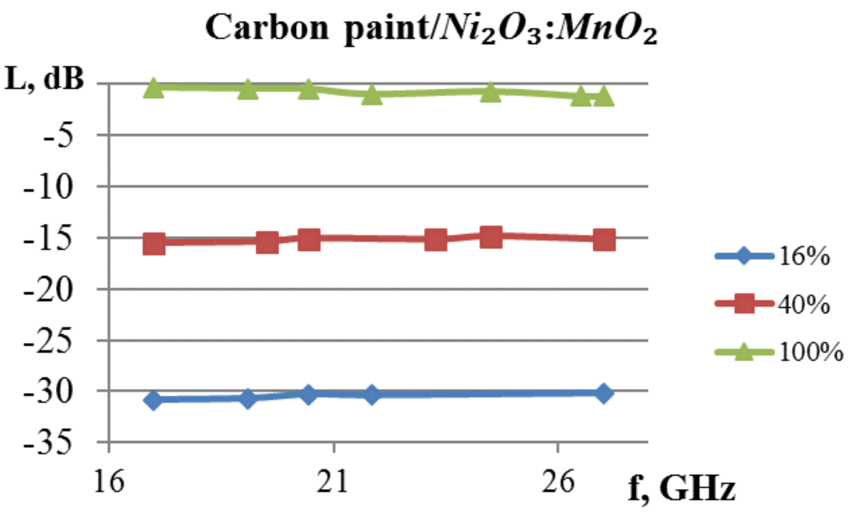

Fig. 2. Effects of the amount of oxide mixture on electromagnetic characteristics of composite

Our studies yielded good results for the composites containing 19-28.6% of *MnO_2* and *ZnO,* which showed attenuation of electromagnetic energy of -30...-33 dB. The composite modified with *Ni_2O_3* at the oxide maximum content of 28.6% with increasing frequency showed an increase in electromagnetic losses in the -25…-27 dB range. The unarguable leader in the series of synthesized oxide-containing composites is the composite containing 19% of *$Fe_2O_3 \cdot FeO$,* which provides a shielding of -35 dB in the frequency range 17-27GHz .

Such coatings can be successfully used as shielding materials for electronic equipment in the radio wave and ultrahigh frequency range as well as components of materials protecting people exposed to UHF radiation, in information security systems, building industry, etc.

Conclusions

1. As a result of our studies, a composite material in the form of carbon-paint was proposed. The material can be easily applied to any surface of different construction materials.

2. It was established that combining carbon materials of different nature (graphite and carbon black) results in synergistic effect, which manifests itself in an increase in shielding efficiency by 14 dB.

3. To strengthen the surface of carbon paint, it was proposed to apply a reinforcing layer of polymer solution. It was established that in using the polymer solution adhesion of the composite to the substrate is 5 (by the grid cut method).

4. The effects of oxide additives on the shielding properties of the composites were analyzed. It was found out that the optimum content of oxides in the carbon paint ranges between 16 and 29 (w/w) **%.**

5. Possible applications for these materials were proposed as components of shielding materials for electronic equipment, people exposed to UHF radiation, in information security systems, building industry, etc.

6. The developed composites are employed successfully in manufacturing thermal vision devices at the enterprise «Thermal Vision Technologies» (Kyiv, Ukraine) to provide «electronic compatibility» and decrease in «electronic visibility» in the radio wave and UHV range.

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