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2015 IOP Conf. Ser.: Mater. Sci. Eng. 93 012038

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Multifunctional composite material based on carbon-filled polyurethane

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Abstract. The research paper deals with the performance of composite resistive material heating coatings based on the polyurethane binder, filled with colloidal-graphite preparation C-1, which can be used in structures of electric heaters. Frequency dependences of transmission and reflection coefficients, dielectric permeability of composite materials with the various content of carbon fillers (technical carbon, graphite) in polyurethane varnish in ranges of frequencies 26–40 GHz and 110–260 GHz are experimentally investigated.

1. Introduction

Among composite materials developed nowadays of greatest interest are multifunctional composites used in various fields. Polymer-based composite materials with various fillers belong to these materials [1–3]. They are widely used in building, machine-building, oil refining, and light industries. These mostly include composite resistive materials (CRM), used as coatings for heating elements of technological equipment designs for industry and construction, such as heating press plates and ovens, wall plating and oil baths, tanks, pipelines, electric, and metal shields thermosetting formwork [4, 5].

The research analysis of CRM and their use as coatings for heating elements of technological equipment showed that some problems are still unresolved due to the lack of such heating coatings characteristics as stability and performance of electrical resistance in a long time and wide temperature ranges, high adhesive strength to metal surfaces, uniform temperature distribution on the surface and others. Different research organizations around the world try to find solution of this problem, including: Research Institute of chemical fiber and composite materials, Scientific and Production Center «Carbon fibers and composites», PERI, MITSUBISHI and others. Currently, when creating a CRM as binders such heat-resistant polymers as fluoroplastic, polyamide, polypropylene and others are widely used. However, these materials obtain a certain number of characteristics which complicate their use in CRM. They are low adhesion, a significant dimensional instability, the allocation of large amounts of volatile substances in polymerization. As a conductive component the dispersed metal or carbon fillers, where some nanoscale forms of carbon such as carbon black, carbon fibers, carbon nanotubes, graphite, graphene, being particularly attractive for the creation of CRM and rather advantageous with lightness and chemical inertness.

The use of a polyurethane CRM binder is promising as it has good adhesion to almost all existing materials, the ability to provide a solid contact with the conductive polymer molecules filler particles. This can lead to a unimodal distribution of particles in the mixture and, consequently, improve the



conductive properties of CRM with minimum heat deflection temperature. In recent years, there was a number of scientific publications describing advances in obtaining and using conductive composites based on polyurethane filled with carbon black, carbon fibers, carbon nanotubes, graphite, graphene [6, 7]. However, these studies lack the information on the use of polyurethane filled with carbon in CRM and study of composites performance on its basis, which can be used as a heating coating in the construction of electric heaters technological equipment.

In addition, it is well known that composites with carbon fillers are used as screens reflecting or absorbing electromagnetic radiation to protect biological objects against the harmful effect of microwave radiation and radio equipment against internal or external noise. Despite of many developments in this direction, search is continued of new materials having small weight, relatively small thickness, and well developed production technology.

The purpose of this work is to study of CRM performance based on carbon filled polyurethane and radioabsorbing and radioreflexion ability of composite materials containing polyurethane varnish and dispersed carbon fillers in the form of graphite and carbon black.

2. Experimental procedure

In this research paper flat samples of composite materials at the thickness of 0.3 mm were used, comprising of binder and carbon fillers. As the binder two-component polyurethane varnish VM 700 GLOSS is used. These materials have high indicators of chemical firmness, durability, and elasticity, shock firmness as well as high adhesion to metals and functionality in the conditions of high humidity in a wide temperature interval from minus 60 °C to 130 °C without essential deterioration of mechanical properties. On the basis of conductive fillers properties analysis for introducing into a polyurethane binder colloidal-graphite preparation C-1, graphite element GE-3 and channel black K-163 were chosen. These carbonaceous materials are chemically inactive with respect to oxygen and to most of the known binders in wide temperature range, which in its turn, according to minimizing the contact resistance between the particles, has a number of advantages compared with metals.

Coverings have been made under the following scheme: dispersive mixing of polyurethane varnish and carbon fillers during 2 hours; placing composition on a surface of a metallic substrate; drying of carbon-filled polyurethane coverings during one day at room temperature of 23 °C and its polymerisation at 120 °C during 2 hours [8].

For reliable assessment of specific volume resistance, hardness and adhesive strength CRM, experimental studies were performed using certified methods to certified equipment. Specific volume resistance was measured using two-probe method in accordance with GOST RF 20214-74 «Electrical conductive plastics. Test method for determination of specific volume electrical resistance at dc voltage». Hardness was determined in accordance with GOST RF 9450-76 «Measurements microhardness by diamond instruments indentation» hardness tester on Nano Hardness Tester company CSEM Instruments. The study was carried out on the adhesive strength measurement setup Micro Scratch Tester company CSEM Instruments in accordance with ASTM D 2197 «Standard Test Method for Adhesion of Organic Coatings by Scrape Adhesion». Frequency dependences of electromagnetic response properties (coefficients of reflection (R) and transmission (T)), and dielectric permeability ($\epsilon^* = \epsilon' - \epsilon''$) of polymer composite films were investigated at a radio spectroscopy constructed on the basis of the vector analyzer of chains E8363B of firm Agilent Technologies in frequency range 26–40 GHz or Mach–Zehnder interferometer based on backward wave oscillator for frequency range 110–260 GHz.

3. Results and discussion

The results obtained in experimental studies indicate that using VM 700 GLOSS as the binder polyurethane varnish and conductive filler C-1 (24 wt %) with a thickness CRM allows $(301 \pm 4) \mu\text{m}$ to obtain coatings with specific volume resistance $(1.59 \pm 0.06) \Omega\text{-cm}$, hardness $(407 \pm 9) \text{MPa}$, adhesive strength to the metal $(28.12 \pm 0.29) \text{N}$ and the stability of these parameters at the maximum

operating temperature (130 ± 0.7) °C during 8000 hours [8]. The resulting figures are optimal for use of CRM as heating surfaces in the construction of electric heaters technological equipment.

The technological process of CRM formation as a heating coating on the metal surfaces of the process equipment structural elements includes a series of sequential operations. The initial step is to prepare the metal surface of the structural element, which consists in making holes for electrical contacts (copper bars), cleaning and degreasing surfaces, insulation contact surfaces fasteners, electrical contact with the metal surface. Next, the application is carried out on the metal surface of the dielectric coating thickness of 100 µm of polyurethane varnish VM 700 GLOSS by spraying, followed by drying at 23 °C within 60 min. It is necessary for "joining" dielectric coating with CRM by formation of intermolecular hydrogen bonds, increasing the strength of the connection layers thick film electric heater. The dielectric layer thickness of 100 µm prevents electrical breakdown between the CRM and the metal surface due to excellent dielectric properties. Electrical contacts are secured to the CRM by bolting solid. The next stage is the optimal dosage component percentage. Further carbon filled polyurethane polymer composition as a low viscosity slurry was subjected to dispersive mixing within 120 min in a ball mill for 1 SHLM-fracture aggregates C-1 and its uniform distribution in the polyurethane binder. After that, the layering thickness of 300 µm CRM is carried out on the dielectric surface of the structural element with contacts by spraying. Heat treatment of the intermediate layers CRM 100 µm and 200 µm is carried out at a temperature of 50 °C during 30 min to remove the solvent and partial polymerization of the composition. Full cure and stabilizing heat treatment is carried out at CRM 120 °C during 120 min. If necessary, CRM is covered applied dielectric coating of polyurethane varnish thickness of 100 µm by spraying to prevent electrical shock.

The process CRM formation on metal surfaces of technological equipment allows to create heaters, which are characterized by simplicity of installation and operation, reliability, absence of external influences on CRM, providing a uniform distribution over the underlying surface of the structure.

To study the performance of the heating coatings for thermo shield casing (Figure 1a) and press plate (Figure 1b), by the method described above some electric heaters of CRM were made. Heater, disposed on the outer side of the shuttering panel and the press plate is formed as a thick CRM (301 ± 4) µm and electrodes, connected to the coating and attached to the formwork panel and the press plate. The insulating layers on both sides of electric heater are formed as coatings, one of which is a dielectric, and the second – thermal insulation, which reliably insulates heater, preventing heat loss during heating up and operation. The selected design scheme of the heating panel formwork and thermo heating press plate (shield plate – heater – insulating layer) ensures the absence of external influences on CRM and its durability and meets all the safety requirements of the work undertaken. The process of forming electric heater provides a choice of its configuration for specific tasks.

The uniformity of the press heating plates temperature field is an important prerequisite for producing high-quality material or product by pressing heated. Tolerance temperature heating plates for the manufacture or processing of most materials is ± 5 °C. Using CRM electric heater design to achieve uniform temperature field over the entire area of the heating shield thermosetting formwork (Figure 2) and the surface of the heating plate press. Temperature 80 °C, and its differential ± 0.5 °C at the inner side of the heating panel (Figure 2b), in contact with the concrete, corresponds to the allowable temperature deviation in the thermosetting heating concrete formwork (± 3 °C), as well as heat treatment materials under pressure in the heating press platens.

It was also found out that the maximum operating temperature (130 ± 0.7) °C and specific volume resistance (1.59 ± 0.06) Ω·cm electric heater thermo heating panels formwork and heating press platens during 2000 hours retain their values, indicating CRM performance. Repeated experiments have not led to a change in the values of these parameters and demonstrated good stability in electric heater with a lifetime of not less than 8000 hours.

Frost testing of the electric heater revealed that after 150 cycles of its heating to a temperature of (130 ± 0.7) °C and subsequent cooling to $-(40 \pm 0.2)$ °C, mechanical electrical properties and CRM performance do not change.

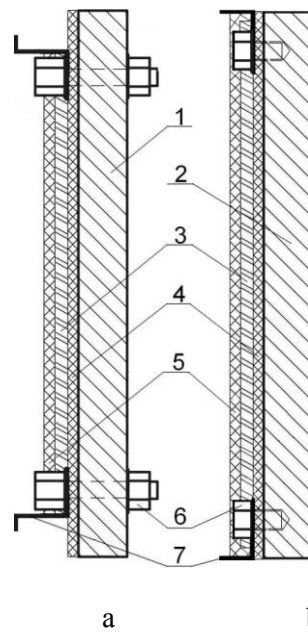
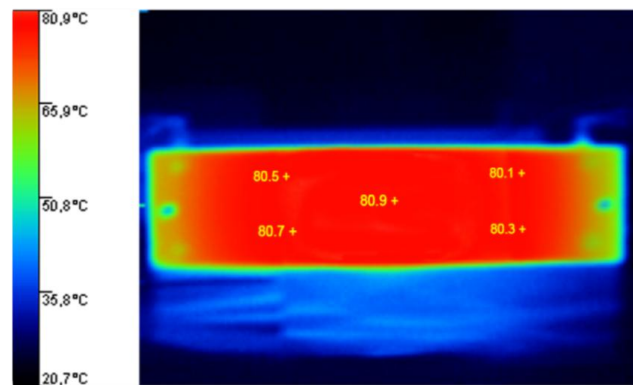
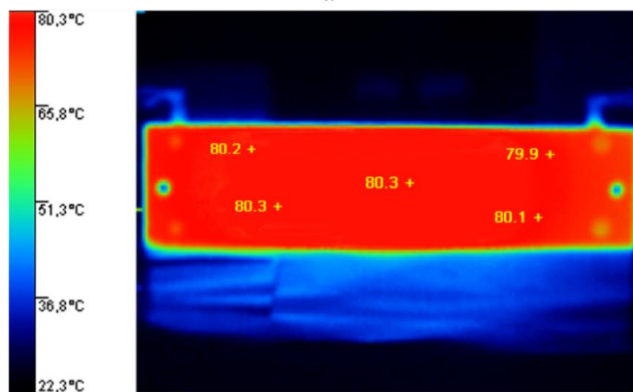


Figure 1. Design of heating thermo shield casing (*a*) and the heating plate press (*b*) in electric heaters of CRM: shield (1); plate (2); CRM (3); dielectric coating (4); thermal insulation coating (5); fasteners (6); electrodes (7).



a



b

Figure 2. Thermogram of heating thermo shield casing with CRM: *a*) electric heater; *b*) heating the inside of the shield.

3.1. Electromagnetic response and dielectric permittivity

Measurements of the parameters of electromagnetic response allowed us to retrieve the complex dielectric permittivity for the frequency band at which measurement was performed. Values of the parameter ϵ^* , being the numerical characteristic of polarizability of materials in an electric field, allow the electromagnetic characteristics of specimens at preset frequency, thickness, and geometric shape to be modeled. Our investigations demonstrated that with increasing mass content of the filler, the real (ϵ') and imaginary (ϵ'') components of the dielectric permittivity increased practically without frequency dispersion. Table 1 presents the results of investigations of electromagnetic radiation interaction with the developed composite material based on the polyurethane depending on the nature and content of the carbon fillers.

Table 1. Electrophysical characteristics of composites with C-1, GE-3, and K-163 fillers.

Frequency, GHz	Content of the filler in the binder, wt %	Reflection coefficient, dB	Transmission coefficient, dB	ϵ' , rel. units	ϵ'' , rel. units
Channel black K-163					
140	1	6.1	0.1	3.4	0.12
240	1	7.5	1.5	3.5	0.12
140	2	5.5	1.7	3.8	0.17
240	2	6.8	1.5	3.8	0.17
140	5	4.2	3.1	5.7	0.07
240	5	2.4	2.6	5.8	0.53
140	10	0.5	5.2	10.3	2.9
240	10	0.5	7.7		
Colloidal graphite preparation C-1					
140	1	6.1	2.0	3.6	0.34
240	1	13	1.0	3.4	0.11
140	2	7.2	2.0	5.2	0.11
240	2	7.1	3.0	5.0	0.16
140	5	5.2	4.8	9.5	0.95
240	5	5.1	5.3	9.4	0.92
140	10	0.5	10.5	20.1	3.1
240	10	0.5	11.3	21.3	2.7
Elemental graphite GE-3					
140	1	4.8	2.1	5.1	0.5
240	1	5.1	4.0	5.1	0.5
140	2	10.1	2.1	7.1	0.9
240	2	6.3	7.7	7.1	1.2
140	5	7.5	10.2	17.0	3.67
240	5	7.6	20.1	14.2	6.1
140	10	Near 0	23.0		
240	10	Near 0	Exceeding 40		

The least value of the real dielectric permittivity component for concentration exceeding 1 % was recorded for the composite based on channel black K-163. This can be explained by two ways. First, particles of this material are the least ones, and the surface unstructured layer starts to produce considerable effect on the effective dielectric permittivity of the composite as a whole. Second, particles of channel black, as demonstrated above, have spherical shapes, whereas particles of other carbon structures are flat. The spherical particles have the depolarization ratio equal to 1/3 in all directions, whereas the flat particles arrange in parallel in the process of composite preparation, that is, the structured material is obtained whose effective dielectric permittivity is higher.

It was demonstrated that composites in which channel black K-163, elemental graphite GE-3, or colloidal graphite preparation C-1 were used as fillers actively interacted with electromagnetic radiation in the range 26–260 GHz. With filler concentration exceeding 10 wt %, they can be used as reflecting coatings, and with filler concentrations up to 5 wt %, they can be used as coatings reducing the transmitted signal level. The most efficient were composite with GE-3 filler that reduced the level of the transmitted electromagnetic radiation signal by 7 dB in a wide frequency range and up to 20 dB in individual spectral regions when the composite thickness was 0.4 mm. The least values of the dielectric permittivity had composites with K-163 filler, which demonstrated the spherical shape of their particles (the highest depolarization ratio) and the least particle sizes (greater influence of the surface layer). Composite material with C-1 filler can also be used as a protective coating, because they transmit less than half of incident radiation. The efficiency of the examined composites can be increased by increasing the thickness of specimens up to 1–2 mm that is characteristic for modern wideband coatings.

4. Conclusions

Thus, the technological process of forming composite resistive material on the metal surfaces of structural elements technological equipment is developed, allowing to create electric heaters, which are characterized by simplicity of installation and operation, reliability, service life more than 8000 hours, the stability of the electrical resistance in a long time and a wide temperature range, high adhesive strength to metal surfaces, a uniform temperature distribution over the entire surface. Conducted CRM performance tests on the basis of carbon filled polyurethane in the construction of electric heaters heating panels thermosetting formwork, heating plate presses, oil baths for shrink fitting details are conducted, which confirm the effectiveness of its use in mechanical engineering.

Our investigations have demonstrated that the functionality of the developed CRM with carbon fillers can be expanded by their application as radio absorbing and radio reflecting coatings. It was demonstrated that the composites with the active phase from channel black, colloidal graphite preparation, and elemental graphite interacted effectively with electromagnetic radiation of terahertz range: with filler concentrations exceeding 10 % they could be used as reflecting screens, and with filler concentrations up to 5 %, they could be used as devices reducing the transmitted signal level.

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