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Electrophysical properties of polychlorotrifluoroethylene — iron-containing carbon fiber nanocomposites

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The samples of polychlorotrifluoroethylene — iron-containing carbon nanofiber (PCTFE — Fe/C) with a thickness of 2 and 0.2 mm were obtained by thermal compression from the polymer melt. A set of electrophysical studies at low frequencies and in the ultrahigh frequency range was performed. It is shown that the percolation transition in the PCTFE — Fe/C 22/78 is achieved at a lower Fe/C 22/78 content and is 0.04 and 0.07 for the Fe/C 60/40, which is explained by the high content of carbon nanofiber in the source Fe/C filler. Impedance spectrometry has shown that at low concentrations of filler (before the percolation transition) in the system, with increasing frequency above 200 Hz, the conductivity increases due to the implementation of the hopping mechanism. Differential thermal analysis has established that the composites have thermal stability from room temperatures up to 280°C and can be used in this temperature range.

Keywords: carbon nanofiber, percolation transition, microwave range, electric conductivity, ferromagnetic.

Електрофізичні характеристики композитів поліхлортрифторетилен — залізовмісне вуглецеве волокно. *О.М.Лісова, О.М.Сєдов, Л.Я.Шварцман, С.М.Махно, Г.М.Гуня, П.П.Горбик*

Методом термічного пресування з розплаву полімеру одержано зразки систем поліхлортрифторетилен — залізовмісне карбонове нановолокно (ПХТФЕ — Fe/C) товщиною 2 та 0,2 мм. Проведено комплекс електрофізичних досліджень на низьких частотах та у надвисокочастотному діапазоні. Показано, що перколяційний перехід у композиті ПХТФЕ — Fe/C 22/78 досягається при меншому вмісті Fe/C 22/78 і становить 0,04 та 0,07 для композитів з Fe/C 60/40, що пояснюється більшим вмістом карбонового нановолокна у вихідних композитах Fe/C. Методом імпедансної спектрометрії показано, що при малих концентраціях наповнювача (до перколяційного переходу) у системі, яка перебуває у стані розгалуженого кластера, при збільшенні частоти вище 200 Гц провідність зростає внаслідок реалізації стрибкового механізму. Методом диференціального термічного аналізу встановлено, що композити виявляють термічну стабільність від кімнатних температур до 280°С і можуть використовуватися у даному температурному діапазоні.

Методом термического прессования из расплава полимера получены образцы систем полихлортрифторэтилен — железосодержащее углеродное нановолокно (ПХТФЕ — Fe/C) толщиной 2 и 0,2 мм. Проведен комплекс электрофизических исследований на низких частотах и в сверхвысокочастотном диапазоне. Показано, что перколяционный переход в системе ПХТФЕ — Fe/C 22/78 достигается при меньшем содержании Fe/C 22/78 и составляет 0,04 и 0,07 для композитов Fe/C 60/40, что объясняется большим содержанием карбонового нановолокна в исходных композитах Fe/C. Методом импедансной спектрометрии показано, что при малых концентрациях наполнителя (до перколяционного перехода) в системе, которая находится в состоянии разветвленного кластера, при увеличении частоты выше 200 Гц проводимость возрастает вследствие реализации прыжкового механизма. Методом дифференциального термического анализа установлено, что композиты проявляют термическую стабильность от комнатных температур до 280°С и могут быть использованы в данном температурном диапазоне.

1. Introduction

Carbon nanomaterials are now becoming relevant in various fields of science, engineering, technology, medicine, biology, biotechnology, ecology, since they are characterized by a wide variety of physical and chemical properties, operational characteristics, relatively low cost and manufacturability. Hybrid nanofibers with metallic inclusions occupy a special place among carbon materials [1, 2]. Such materials have a set of unique properties due to structural features, namely, the dimension of systems and the dispersion of metal particles, a combination of the properties of individual components, and a kind of synergy. The size and dispersion of metal particles are key factors affecting the activity of electrocatalysts [1]. They are widely used in electronics, as functional cells of fuel and solar cells [2], sensors for various purposes [3], construction materials, for shielding electromagnetic radiation in a wide frequency range [4].

The combination of magnetic and electrical components in metal-containing composites makes it possible to regulate their electromagnetic characteristics, which can be used for absorbing electromagnetic radiation. The components of such composites are ferromagnetic materials of various compositions that are promising for the development of screens. The studies of nanocomposites are relevant from the scientific and practical points of view [5], since they are characterized by a relatively low specific gravity, high corrosion resistance, satisfactory thermal, mechanical, magnetic and electrical properties, a wide absorption frequency band [6], and compatibility with matrices of various chemical nature.

The electrical and magnetic parameters of the composites are determined by the transfer phenomena in a heterogeneous polymer system, in which an electrically conducting continuous cluster of dispersed filler particles is formed [7]. When studying polymer composite materials (CMs) with carbon-containing nanofibers, it is necessary to take into account the nature of the interaction of polymer macromolecules with the filler surface, which in turn depends on the structure of the composite components and preparation conditions. If the formation of a composite occurs under the conditions of polymer melting, filler particles serve as nucleation centers for the crystalline phase, and the properties of composites are determined by the presence of supramolecular structures in the polymer matrix. It is known [8] that the quantitative ratio of crystalline and amorphous phases, especially in the case of flexible-chain polymer macromolecules interacting with rigid particles, significantly affects the strength and thermal properties of nanocomposites. In the region of low concentrations (up to 2 wt.%) of carbon-containing fillers in polymer composites, deviations from the additivity of performance characteristics (thermal conductivity, electrical conductivity) are observed.

These properties are most effectively manifested with a uniform distribution of the filler in the polymer matrix [9]. Since the original composites exist in the form of aggregates (linear dimensions up to 300 μm), two methods of dispersion are most often used to introduce them into the polymer. The first is the processing of a mixture of fibers with a polymer melt in a device that provides shear deformation (for example, rolling). The second is the dispersion of composites (for example, by ultrasound) in a large volume of solvent, followed by mixing the resulting solution with the polymer and subsequent removal of the solvent. Under such conditions, it is possible to partially reduce the aggregates [10]. The properties of nanocomposites depend on the volumetric content of the filler, the size and shape of inclusions (particles or their aggregates), contact phenomena between filler particles, the presence of polymer-filler interphase interactions, the structure of the polymer matrix, the spatial distribution of filler particles, technological and operating modes of formation, etc.

The aim of the work was to establish the relationship between the technology of obtaining iron-containing composites, the quantitative iron content and their electrophysical and magnetic properties, as well as the regularities of the processes of structure formation of composites.

2. Experimental

For the synthesis of Fe/C nanocomposites, the methods of pyrolytic gas-phase deposition and thermocatalytic decomposition of carbon-containing gases with the establishment of optimal modes of temperature, reactor pressure, and carbon-containing gas flow rate were used. The Fe/C composites were produced on two experimental flow installations. Acetylene and carbon monoxide were used as the working gas; the catalyst was a mixture of nickel and iron oxides. In the process of synthesis, catalysts convert the carbon-containing compound into tubular carbon [11], and they themselves are mainly partially encapsulated by graphitized carbon layers. Thus, together with the binder metals, they become part of the resulting fibrous product and give them new properties, for example, magnetic. However, metal impurities such as V, Cr could be problematic for many fiber applications, as they can cause, for example, toxicological problems in biomedical applications [12]. The particles had an elongated shape, outer diameter of 10–100 nm, length of 100–1000 nm.

The crystal amorphous polymer polychlorotrifluoroethylene (PCTFE) F-3M brand A was used for the production of PCTFE — Fe/C composites. Samples of the PCTFE — Fe/C system were prepared as follows. The polymer powder was moistened with ethyl alcohol, the required amount of Fe/C composite was added, stirred until a homogeneous consistency was formed, and distilled water was added. Then the material was dispersed with an ultrasonic dispersant (USDN-A) for 2 min. It was dried to constant weight, ground and pressed at a temperature of 513 K and a pressure of 2 MPa.

The X-ray phase analysis of Fe/C composites was performed by powder diffractometry on a DRON-4-07 diffractometer in CuKα radiation with a nickel filter in the Bragg-Brentano geometry.

Thermogravimetric measurements, namely mass loss (TG) and differential thermal analysis (DTA) were performed using a Derivatograf Q-1500 D (Hungary) in a static air atmosphere. The 100 mg sample was heated in a ceramic crucible from room temperature to 1273 K at a rate of 10 K/min.

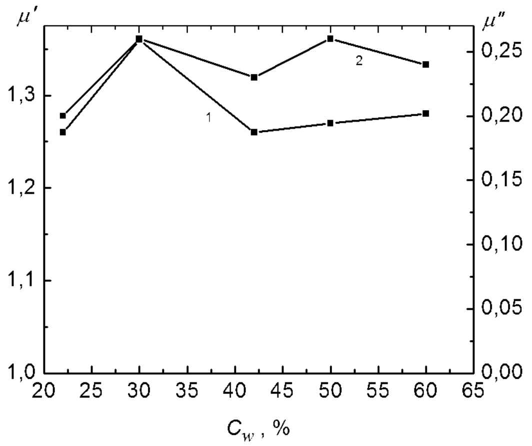

Fig. 1. The real μ′ (*1*) and imaginary μ″ (*2*) components of the complex magnetic permeability of Fe/C composites from the mass content of iron at a frequency of 9 GHz at a temperature of 20°C.

The study of the real (ε′) and imaginary (ε″epsilon prime prime) components of the complex dielectric constant and the real (μ′) and imaginary (μ″) components of the complex magnetic permeability of the composites was performed in the ultrahigh-frequency (UHF) range of 8–12 GHz using an interferometer (RFK 2-18, for measuring the phase difference) and a standing wave meter (R2-60) by the electrodeless method; electrical conductivity at low frequencies 0.1; 1 and 10 kHz was measured by a two-contact method using an E7-14 immittance meter [13]. The frequency dependences of the complex specific electrical conductivity of the composites were determined by calculating the impedance spectra obtained on the Solartron SI 1260 impedance spectrometer in the frequency range 10^{-2}–10^{6} Hz.

3. Results and discussion

The Fe/C fillers of various compositions are active with respect to electromagnetic radiation in the microwave range and have pronounced magnetic properties [4] (Fig. 1); experimental data indicate that the magnitude of the magnetic parameters does not directly correlate with the mass content of iron in the nanocomposites.

Figure 1 shows that the complex magnetic permeability Fe/C, within the error, does not depend on the iron content in the system; obviously, iron nanoparticles are in a chemically bound state and do not exhibit magnetic properties. Analysis of the chemical composition of the composites [4] indicates the presence of Fe, oxide, and iron

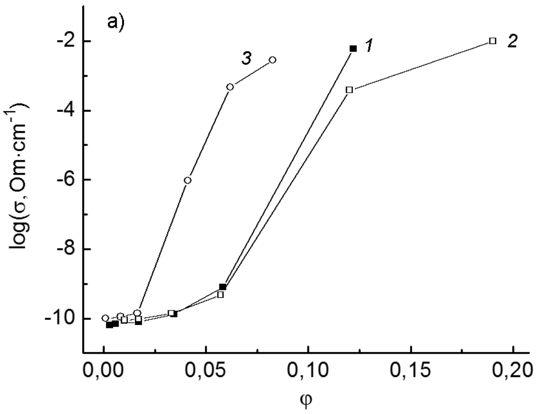

Fig. 2. The electrical conductivity of PCTFE — Fe/C composites at a frequency of 1 kHz for (*1*) thick (2 mm) and (*2*) thin (0.2 mm) samples containing Fe/C 60/40 nanocomposite; (*3*) thin samples containing Fe/C 22/78 nanocomposite: (a) in terms of the volume content of carbon; (b) in terms of the volume content of the filler at a temperature of 20°C.

carbide phases; it is assumed that the nonoxidized iron particles are covered with a carbon layer that protects the nanoparticles from further oxidation. It is these iron particles that are responsible for the presence of magnetic permeability at microwave frequencies; their relative amount is approximately the same in all composites.

Three series of PCTFE — Fe/C composites were obtained: thick specimens (2 mm thick) and thin (0.2 mm) specimens with a mass ratio of iron to carbon Fe/C 60/40; that is, the hybrid filler contained 60% iron, the average calculated density was 3.82 g/cm^3. The samples contained the hybrid filler in a concentration range of 0 to 20 wt.%. Thin samples contained Fe/C 22/78 (22 % iron) with an average calculated density of the filler of 2.62 g/cm^3. The content of the composite was from 0 to 10 % of the mass. Composites with the lowest (Fe/C 22/78) and the highest (Fe/C 60/40) iron content were chosen as fillers.

The values of the real μ' and imaginary μ'' components of the complex magnetic permeability of the PCTFE — Fe/C 60/40 and PCTFE — Fe/C 22/78 composites at a frequency of 9 GHz are presented in Table.

Table. The real μ' and imaginary μ'' components of complex magnetic permeability for composites at a frequency of 9 GHz at a temperature of 20°C

	μ'	μ''
Fe/C 60/40	1.28	0.24
80 % PCTFE — 20 % Fe/C 60/40	1.03	0.01

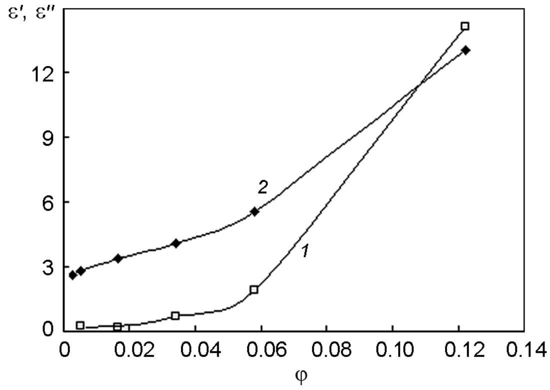

Fig. 3. The real (*1*) and imaginary (*2*) components of the complex dielectric constant of PCTFE — Fe/C 60/40 composites depending on the bulk content of the filler at a frequency of 9 GHz at a temperature of 20°C.

The electrophysical parameters of PCTFE — Fe/C composites (Fig. 2), namely the specific electrical conductivity at low frequencies (Fig. 2a) have a similar dependence on the volume content of the filler.

Low-frequency electrical conductivity has similar values at a low filler content of up to 0.02 volume fractions. In particular, the dependences for thick and thin samples initially containing Fe/C 60/40 are identical within the measurement error in the range of up to 0.1 volume fraction. The growth rate of electrical conductivity is higher for the system containing Fe/C 22/78; the percolation threshold calculated according to the equation of the percolation theory [10] is observed at a lower filler concentration and is 0.04 and 0.07 respectively, for Fe/C 60/40 composites. It is interesting to identify the true reason for this deviation. It is

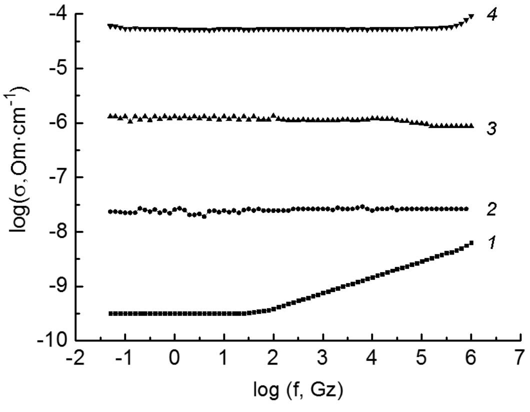

Fig. 4. The electrical conductivity vs the frequency for the system PCTFE — Fe/C with a thickness of 0.2 mm with a volume content of Fe/C 60/40: *1* — 0.016; *2* — 0.04; *3* — 0.06, *4* — 0.08 for temperatures of 20°C.

known from percolation theory that film composites have a lower percolation threshold, since they reach the state of a branched continuous cluster with a lower filler content; it is obvious that in this situation the main role belongs to another factor. It is appropriate to assume that the content of carbon nanofibers in the initial Fe/C composite can play such a role. For this purpose, the volume fraction of carbon in the studied composites was recalculated, and the dependence of the logarithm of the specific electrical conductivity on the volume fraction of carbon was shown (Fig. 2b).

The percolation threshold for carbon fiber (Fig. 2b) for the Fe/C 22/78 film composite is 0.04, for the Fe/C 60/40 composites — 0.07. The curves of the logarithmic dependences of the electrical conductivity are located closer to each other, which indicates the main role of the carbon component in the formation of continuous percolation clusters in these composites due to the resistivity and high aspect ratio.

The dependence of the real (*1*) and imaginary (2) components of the complex dielectric constant for the PCTFE — Fe/C 60/40 system at a microwave frequency increases with an increase in the content of the Fe/C component and has a nonlinear character (Fig. 3), which is associated with the presence of a percolation threshold in the systems. The imaginary component ε″ reaches a value of 14 already at a filler volume content of 0.12, and is comparable with the values for the composite "polyamide 1212 - graphene" [14], in which the imaginary component ε″ has a value of 4 at a graphene volume content of 0.12.

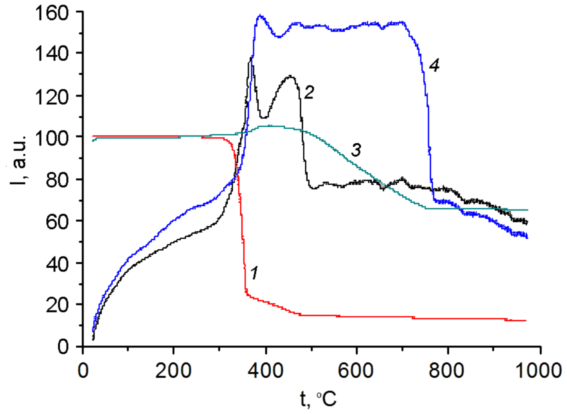

Fig. 5. The TG (*1*, *3*) and DTA (*2*, *4*) curves for Fe/C 60/40 composites (*3*, *4*) and PCTFE — Fe/C 22/78 system with 20 % Fe/C content (*1*, *2*).

The results of studies of PCTFE — Fe/C 60/40 film composites by impedance spectrometry are presented in Fig. 4.

Areas of a smooth increase in conductivity values with an increase in frequency above 200 Hz are observed for the sample with a content of 0.016 of the Fe/C 60/40 nanocomposite. This concentration corresponds to the structure of the system with separate clusters; the change in the slope of curve *1* (Fig. 4) is due to the jumping mechanism of conductivity and is satisfactorily described by the equation:

$$\sigma = \sigma_0\left(1 + \left(\frac{f}{f_0}\right)^n\right),$$

where σ_0 is the initial value of electrical conductivity, f_0 is the value of the frequency at which the slope of the electrical conductivity curve changes; n is the exponent. According to the experiment, $n \approx 0.8$.

The thermal stability of Fe/C 60/40 samples and 80 % PCTFE — 20 % Fe/C 60/40 composite is characterized by TG and DTA research data (Fig. 5). The DTA curve for the Fe/C 60/40 composite (Fig. 5, *4*) is characterized by a small peak at about 390°C, which probably corresponds to the oxidation process of carbon, which has a defective or partially amorphous structure. On the corresponding TG curve (Fig. 5, *3*), an increase in mass due to oxidation of metal particles was observed in the temperature range 390–440°C. The DTA dependence for the PCTFE — Fe/C system (Fig. 5, *1*) has two peaks at temperatures of about 380 and 430°C. Obviously, the first peak corresponds to the oxidation of the polymer; with an increase in temperature, the oxidation of the carbon component occurs, which corresponds to a change in the rate of weight loss on the TG curve (Fig. 5, *2*) in the form of a flat part of the curve in the temperature range 380–440°C. Thus, the composites exhibit thermal stability up to 280°C and can be used in the temperature range up to the specified temperature.

4. Conclusions

The iron/carbon nanofiber (Fe/C) composites were synthesized by the methods of thermocatalytic decomposition of acetylene and gas-phase deposition of carbon in the presence of a catalyst-forming iron-containing concentrate. Polymer composites of PCTFE — Fe/C were obtained. The functional filler Fe/C exhibits structure-forming properties; the percolation threshold for the PCTFE — Fe/C 22/78 system is 0.04, for the PCTFE — Fe/C 60/40 system — about 0.07, which is consistent with the of percolation theory. It is established that the carbon nanofiber plays the main role in the formation of continuous percolation clusters in the composites.

It is established that the magnetic properties of the composites at ultrahigh frequencies do not depend on the iron content; it can be concluded that magnetic properties are manifested the particles of carbide, encapsulated under the action of microwave. Obviously, these particles are the nuclei for fibers. It is shown that the complex magnetic permeability of Fe/C within the error does not depend on the iron content in the system, which indicates that the iron is in oxidized form and only some of it is in nonoxidized form and covered with a carbon layer. This layer protects nanoparticles of iron from further oxidation. Such iron particles are responsible for the presence of magnetic permeability in the microwave range.

Prior to the percolation transition in a system that is in a branched cluster state, when the frequency increases above 200 Hz, the conductivity is described by a hopping mechanism, as shown by impedance spectrometry.

The composites show thermal stability from room temperatures up to 280°C and can be used in this temperature range. Polymer composites are promising for technical, environmental and technological applications, use as sound, heat insulating and antifriction materials, protective screens and absorbers of microwave electromagnetic radiation.

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