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DIELECTRIC PROPERTIES OF POLYMER COMPOSITE MATERIAL BASED ON VANADIUM DIOXIDE

Results of investigation of the dielectric characteristics of "polyethylene-vanadium dioxide" composites with different volume fractions of filler within the radio frequencies range and the temperature range of 30-90 °C are presented. The two dispersion regions are found. The high-frequency region is due to the Maxwell charge separation on the boundaries of the polyethylene matrix - conductive filler of the crystallites VO_2. The low frequency region is associated with the presence of the transition layer at this boundary.

The semiconductor-metal phase transition is observed in the frequency dependence of the electrical conductivity of composite. This transition is realized in the filler particles of vanadium dioxide.

With increasing temperature, the relative permittivity of the composite has a tendency to the absolute value decrease. An increase of high-frequency electrical conductivity and a reduction of the dielectric relaxation time are observed.

Keywords: composite, polyethylene, filler, vanadium dioxide, permittivity.

Представлены результаты исследования диэлектрических характеристик композитов полиэтилен-диоксид ванадия с различными объемными долями наполнителя в диапазоне радиочастот и температурном диапазоне 30 – 90°С. Обнаруживаются две дисперсные области. Высокочастотная область обусловлена максвелловским разделением заряда на границе полиэтиленовая матрица – проводящий наполнитель (кристаллиты VO_2). Низкочастотная область связывается с наличием переходного слоя на этой границе.

В частотной зависимости электропроводности композитов проявляется фазовый переход металл-полупроводник (ФПМП) в наполнителе.

Относительная диэлектрическая проницаемость композита имеет тенденцию к снижению по абсолютной величине с ростом температуры. Высокочастотная электрическая проводимость увеличивается, а времени релаксации диэлектрика сокращается.

Ключевые слова: композит, полиэтилен, наполнитель, диоксид ванадия, диэлектрическая проницаемость.

Представлені результати дослідження діелектричних характеристик композитів поліетилен - двооксид ванадію з різними об'ємними частками наповнювача в діапазоні радіочастот та температурному діапазоні 30 – 90°С. Виявлено дві дисперсні області. Високочастотна область обумовлена максвеловським розділенням заряду на границі поліетиленова матриця – провідний наповнювач (кристаліти VO_2). Низькочастотна область пов'язується з наявністю перехідного шару на цій границі.

У частотній залежності електропровідності композитів проявляється фазовий перехід метал-напівпровідник (ФПМН) в наповнювачі.

Відносна діелектрична проникність композиту має тенденцію до зниження за абсолютною величиною з ростом температури. Високочастотна електрична провідність збільшується, а час релаксації діелектрика скорочується.

Ключові слова: композит, поліетилен, наповнювач, двооксид ванадію, діелектрична проникність.

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Introduction

Recently, polymer composites with conductive fillers, in particular carbon-based system in a polyethylene matrix, have found application as self restoring fuses and posistors [1, 2]. Use as a filler material with a phase transition of the semiconductor-metal could eventually allow the development of electronic elements, which apart protect against current overloads and high temperatures also implement other functions including shutdown at low temperatures.

In order to develop the optimum technology for producing such composites one need information about their electrical properties at alternating current and physical processes responsible for them.

This paper presents the results of investigations of the dielectric characteristics of polyethylene-vanadium dioxide composites with different volume fraction of filler in the radio frequency and ranges of temperatures 30-90 ^{0}C.

Samples and methods of investigation

The initial components of the composite were fine crystalline vanadium dioxide (VO_2), obtained by reduction of vanadium pentoxide (V_2O_5) with carbon [3], and high-density polyethylene LDPE (15803-020).

The process of synthesis of polyethylene -VO_2 composites was performed using the technological scheme, similar to the technology of making self recovering fuses of the PolySwitch type [1].

The volume fraction of filler p_V was varied from 25 to 60 volume per cents. The samples had a cylindrical shape with the base diameter of 10 mm and the height of about 1 mm.

The dielectric characteristics were performed with a Q meter BM-560 in the radio frequency range (50 kHz to 10 MHz). Studies have shown the near-electrode phenomena that the measured electrical values are determined by the bulk properties of the samples.

The sample was placed into thermostat for studying the temperature dependences. Data registration was carried out after the establishment of the thermodynamic equilibrium of the sample with the environment.

Experimental results and discussion

Fig. 1 shows a typical frequency dependence of permittivity $\varepsilon'(f)$ and electrical conductivity σ (f) of composites with different percentages of vanadium dioxide. As seen, dielectric dispersion takes place in the test frequency range.

A decrease of dielectric permittivity ε' and the increasing of electrical conductivity σ with increasing frequency f at a constant temperature at low volume fractions VO_2 (p_V <50%) were observed. Conductivity values depend weakly on the frequency f (see Fig. 1b, curves 4 and 5) with a higher filler content p_V. The resulting regularities are also observed at other temperatures of the investigated range.

Dependences of ε' and σ on the volume fraction of filler are shown in Fig. 2. As can be seen, relative permittivity and specific conductivity increase with increasing volume fraction of filler p_V.

The values of rapprochement σ, measured at different frequencies and the same temperature at high frequencies with increasing p_V is observed. It should be noted that the change in electrical conductivity of composite samples at the transition through temperature of VO_2 PTMS (68 °C) is not very high (less than one order) [4].

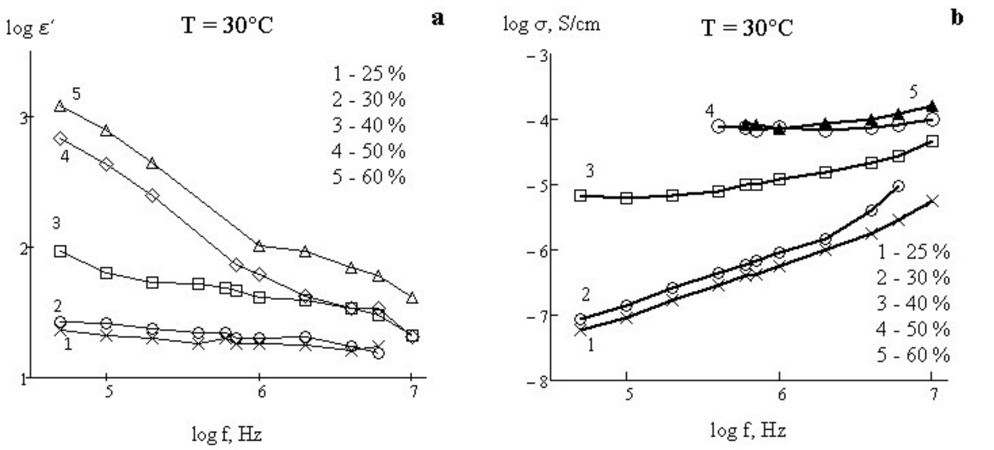

Fig. 1. The frequency dependence of the relative dielectric permittivity and conductivity of samples of composites based on polyethylene with different volume fractions of filler – vanadium dioxide (temperature 30°C)

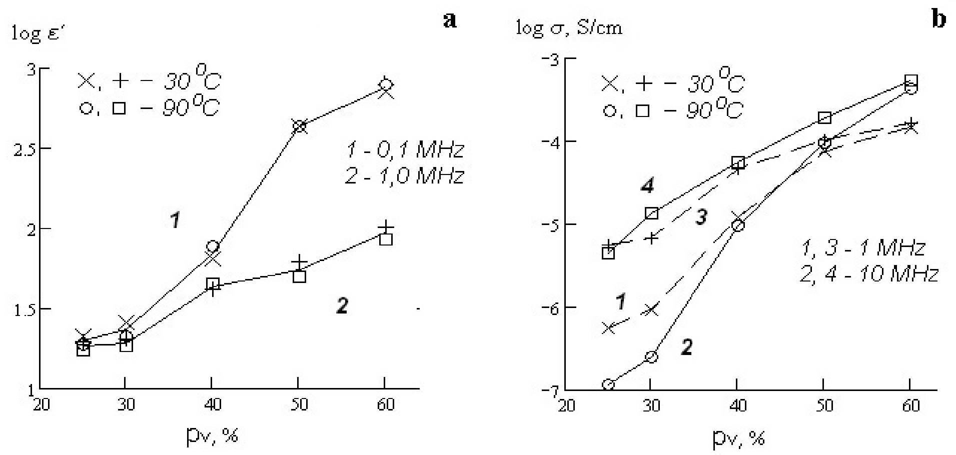

Fig. 2. The dependence of the relative dielectric permittivity (a) and conductivity (b) of composites based on polyethylene on the volume fraction of filler – vanadium dioxide at 30°C and 90°C

The effect of temperature on the dielectric spectra of the investigated composites is shown in Fig. 3.

It should be noted that the appearance of a minimum in the frequency dependence of the dielectric loss ε'' (Fig. 3b) was previously observed in other studies [5]. The presence of the minimum indicates the manifestation of two relaxation processes in the frequency range under consideration.

Decrease in values of ε' to those of the order of several units (Fig. 3a) indicates the Maxwell-Wagnerian nature [6] of high-frequency dispersion region.

The most likely reason of the low-frequency region dispersion is the presence of transition layers in the studied composite and polarization processes associated with them, as investigated and observed in other similar composites with conductive fillers [2, 7]. This assumption proves to be true because of anomalously high values of the low-frequency relative permittivity of the investigated structures.

The absolute value of the low frequency $\varepsilon'(f)$ is much higher than the values given by the two-component theory of dielectrics with conductive inclusions. So our calculations were performed with the use of the most correct well-known Bruggeman-Hanai formula $\varepsilon'_{th} = \varepsilon_{PE} / (1 - p'_V)^3$ [4] where ε_{PE} is a relative permittivity of polyethylene matrix $\varepsilon_{PE} \approx 2$ [2], and $\tilde{p}_V$ is the volume fraction of filler VO_2 ($\tilde{p}_V = p_V / 100 = 0.3$ for the data in Fig. 2, 3). They result in the value $\varepsilon'_{th} \approx 6$ that is significantly less than obtained in the experiment.

With temperature increasing to the temperatures in the range of the phase transition VO_2 (<68°C) the observed decrease in the absolute value of the relative permittivity of the samples corresponds to the thermal expansion of the polyethylene matrix [2].

Dispersion curves of $\varepsilon'(f)$ and $\varepsilon''(f)$ before PTMS (curves 1, 2, and 3 in Fig. 3) have fuzzy character that corresponds to a relaxation process with a wider scatter of relaxation times. Thus PTMS leads to increased homogeneity of the filler particles VO_2 at the electrical properties (conductivity).

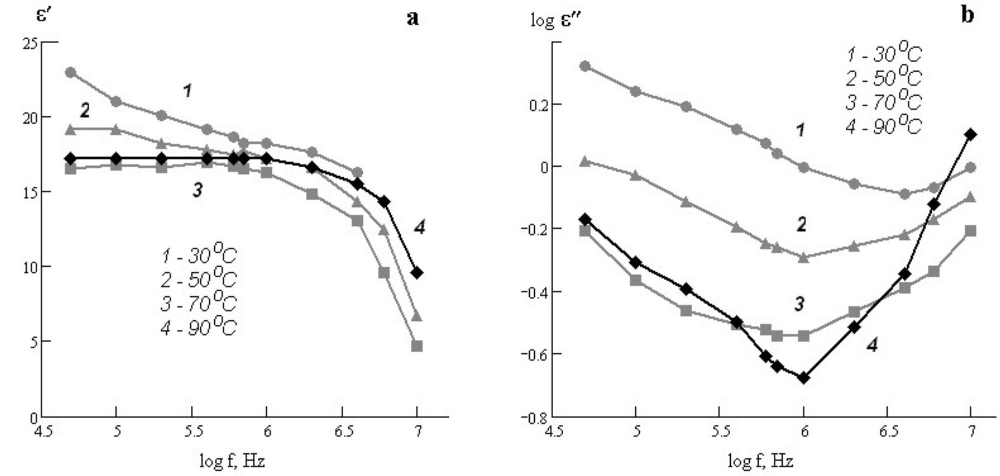

Fig. 3. The frequency dependence of the relative dielectric permittivity (a) and of the dielectric loss factor (b) of the composite sample based on polyethylene with a volume fraction of 30% of the vanadium dioxide at a temperature, °C: 1 – 30; 2 – 50; 3 – 70; 4 – 90.

Conclusions

Dielectric characteristics of “polyethylene - vanadium dioxide” composites with the volume fraction of filler from 25 to 60% show two dispersion area at radio frequency and temperature range from 30-90°C. The first one is the high-frequency region to be explained by the Maxwell charge separation at the boundaries of the polyethylene matrix-conductive filler of the crystallites VO_2. The second one is the low-frequency region associated with the presence of the transition layer at this interface.

In the frequency dependence of the electrical conductivity of the composites a phase transition semiconductor-metal occurring in the filler particles of vanadium dioxide is manifested. There is an increase of high-frequency electrical conductivity and reduced the set of the dielectric relaxation time.

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