

ELECTRICAL AND THERMAL PROPERTIES OF POLYMER COMPOSITES BASED ON POLYVINYLIDENE FLUORIDE

S. M. Lebedev and O. S. Gefle

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Results of investigation into electrically conductive polyvinylidene fluoride/carbon nanotube composites and thermally conductive polyvinylidene fluoride/graphite composites are presented. Methods of dielectric spectroscopy and scanning electron microscopy are used to study these polymer composites. The thermal conductivity of the polyvinylidene fluoride polymer composites is estimated at room temperature using a thermal conductivity analyzer.

Keywords: electrically conductive polymer composites, thermal conductivity, single-wall carbon nanotubes, dielectric spectroscopy.

INTRODUCTION

At present very much attention is given to investigations of a partially-crystalline ferroelectric polyvinylidene fluoride (PVDF) polymer due to its high dielectric permittivity, chemical resistance, good technological properties, and high melting temperature. These properties allow PVDF to be used in various fields, such as capacitor devices [1, 2], converters, sensors [3, 4], and electromagnetic interference shielding [5–9]. Electrically and thermally conductive PVDF composites filled with technical carbon (TC) and/or graphite (G) are widely used in industry [10–14]. For example, changes in the resistance of binary (PVDF/TC) and ternary (PVDF/TC/ultra-high-molecular-weight polyethylene and PVDF/TC/high-density polyethylene) composites were investigated in detail at various temperatures in [11–13].

The thermally conductive carbonaceous composites based on PVDF are widely used in the manufacture of heat exchangers, built-in capacitors, polymer electrolyte power supplies, printed circuit boards, and microelectronic devices [15, 16]. As a rule, to achieve the necessary level of electric and thermal conductivity and to form a distributed conductive network, the content of fillers in such composites is made very high. However, a high content of carbonaceous fillers in the PVDF matrix leads to deterioration of the technological properties and rheological and mechanical characteristics of these composites. Thus, electrical, mechanical, and rheological properties of highly filled PVDF/G composites for polymer electrolyte power supplies were investigated in [16], where it was shown that the content of graphite in these composites should be at least 75 wt.%, which significantly complicates processing of these composites by the conventional methods of processing of polymer composite materials due to deterioration of their rheological properties.

Among the most promising fillers for new electrically conductive polymer composites are carbon nanotubes (CNTs) due to their very high conductivity, low weight, and excellent corrosion resistance. Numerous investigations showed that adding a small amount of CNTs makes polymer materials electrically conductive, but this does not lead to a noticeable increase in the thermal conductivity of the polymer/CNT composites [17–19]. In the

Institute of High-Technology Physics at National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: lsm70@mail.ru; gefleos@mail.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 1, pp. 98–103, January, 2017. Original article submitted July 26, 2016; revision submitted November 16, 2016.

present work, electrical and thermal properties of PVDF/CNT, PVDF/G, and PVDF/G/CNT composites are described depending on the content of the filler.

1. EXPERIMENTAL

1.1. Materials and samples

Polyvinylidene fluoride powder (LLC “Ftorpolimer,” Saint Petersburg, Russia) was used as a polymer matrix. Single-wall carbon nanotubes (TUBALL™, OCSiAl LLC, Novosibirsk, Russia) and natural graphite powder (GE-3, GOST 17022-81) with an average particle size of 65 μm were used as fillers. PVDF and the fillers were used without additional treatment. The PVDF composites were prepared using a laboratory mixer of 50 EHT type (Brabender, Germany). After loading of the PVDF powder into the mixer chamber preheated to a temperature of 180°C, the fillers were gradually incorporated into the polymer melt in preset proportions and mixed for 15 minutes until the filler was uniformly distributed in the melt. After that, the composites were granulated using a granulator (Brabender, Germany).

Samples for investigation were prepared from the pellets by the method of hot pressing. Molds filled with granulate were placed into a vacuum oven heated to a temperature of 180°C, where they were held for 3 hours. To eliminate air from the material melt, a vacuum of 10^{-3} mm Hg was created in the oven. After that, the molds were placed into a hydraulic press and were held at a pressure of 12.5 MPa for 20 minutes with simultaneous cooling at a rate of 4°C/min. Then the molds with samples were cooled at the above-indicated pressure to room temperature in air with uncontrolled cooling rate. The samples were prepared as plates 85 × 65 mm with thicknesses from 1 to 6 mm. The CNT content (C_{CNT}) in PVDF/CNT composites was 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 wt.%. The graphite content (C_{G}) in the composites varied from 5 to 40 wt.%.

1.2. Measurement of the properties of polymer composites

The real part of the ac conductivity $\gamma_a = \omega \epsilon_0 \epsilon' \tan \delta$ (where $\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m is the electric constant, ϵ' is the real part of the complex dielectric permittivity, $\omega = 2\pi f$ is the circular frequency, and $\tan \delta$ is the tangent of the dielectric loss angle) and the phase angle φ between the current and voltage were measured in alternating current at a voltage of 3 V in the frequency range from 10^{-1} Hz to 1 MHz using a measuring system (Solartron Analytical, UK). For each sample, from five to ten measurements per frequency decade were performed.

The thermal conductivity of the prepared polymer composites was investigated by the *transient hot bridge method* (modified hot wire method) using a Linseis (Germany) THB-100 thermal conductivity analyzer. A measuring sensor, including a heater and four thermoresistors, was placed between two plates with a thickness of 6 mm made of the same composites. The submolecular structure of the polymer composites was investigated using a Leo Evo 50 scanning electron microscope (SEM) (Zeiss, Germany) at an accelerating voltage of 20 kV. Fractures of the composite samples prepared in liquid nitrogen were investigated. Silver was deposited on the fractured surface.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. Dielectric spectroscopy

Figure 1 shows the frequency dependences of γ_a and φ for PVDF and PVDF/CNT composites. It can be seen that γ_a increases sharply by 5–7 orders of magnitude compared with PVDF when the CNT content exceeds 0.2 wt.%. It was established that the angle φ for the PVDF matrix and PVDF/CNT composites with the CNT content smaller than 0.2 wt.% decreased from about 89° to 70°, and the angle δ ($\delta = 90^\circ - \varphi$) increased from 1° to 20° in the entire examined frequency range. For the PVDF/CNT composites with the CNT content exceeding 0.2 wt.%, the angle φ decreased from 78° to about 0° (the angle δ increased from 12° to about 90°, respectively). That is, the PVDF/CNT composites with the CNT content exceeding 0.2 wt.% become electrically conductive materials.

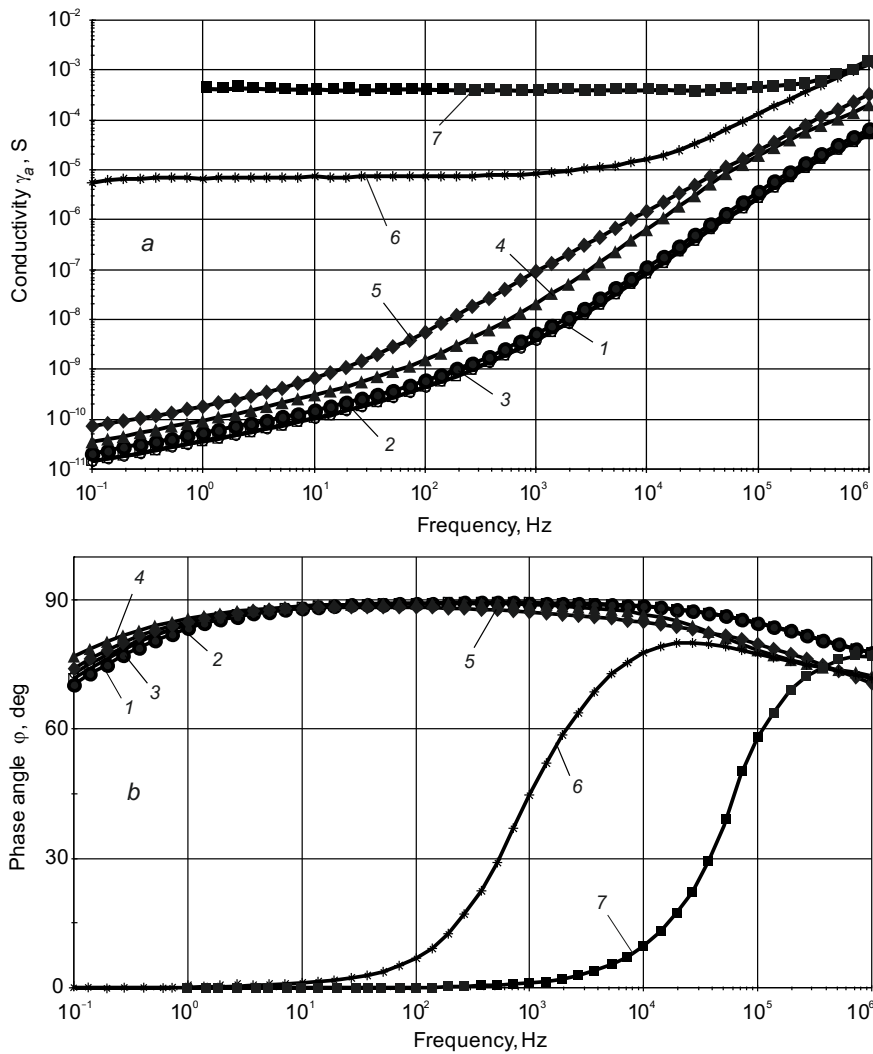


Fig. 1. Frequency dependences of γ_a (a) and φ (b) for the PVDF and PVDF/CNT composites with the CNT content of 0 (curve 1), 0.01 (curve 2), 0.05 (curve 3), 0.1 (curve 4), 0.2 (curve 5), 0.4 (curve 6), and 0.6 wt.% (curve 7).

Figure 2 shows the γ_a values measured for the PVDF/CNT composites depending on the CNT content at a fixed frequency of 1 Hz in the logarithmic scale. It is clearly seen that this dependence has a typical percolation character with the inflection point (the so-called percolation threshold) at the CNT content of about 0.2 wt.%. This fact indicates that even for this small CNT content, the volume conductivity network providing the sharp increase of the conductivity of the material is formed in the polymer composites.

2.2. Thermal conductivity

The relative change in the thermal conductivity λ for PVDF/CNT composites is illustrated by Fig. 3, where λ_K and λ_M are the thermal conductivities of the composites and the PVDF matrix, respectively. It is obvious that the thermal conductivity increases linearly with the CNT content in the composites. The coefficient λ for the PVDF/CNT composite with CNT content of 1.0 wt.% increases by about 35% compared to PVDF. It should be noted that the conductivity γ_a for the PVDF/CNT composites increases with CNT content almost by 7 orders of magnitude (Fig. 2),

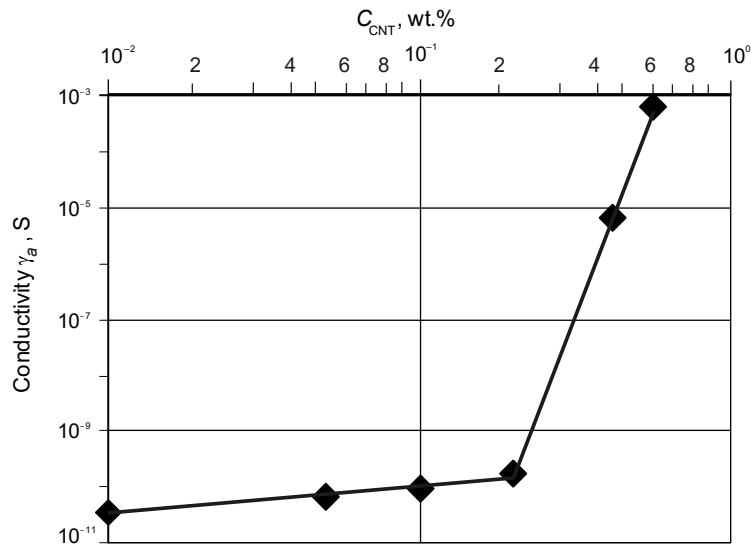


Fig. 2. Dependence of γ_a on the CNT content for the PVDF/CNT composites at a frequency of 1 Hz.

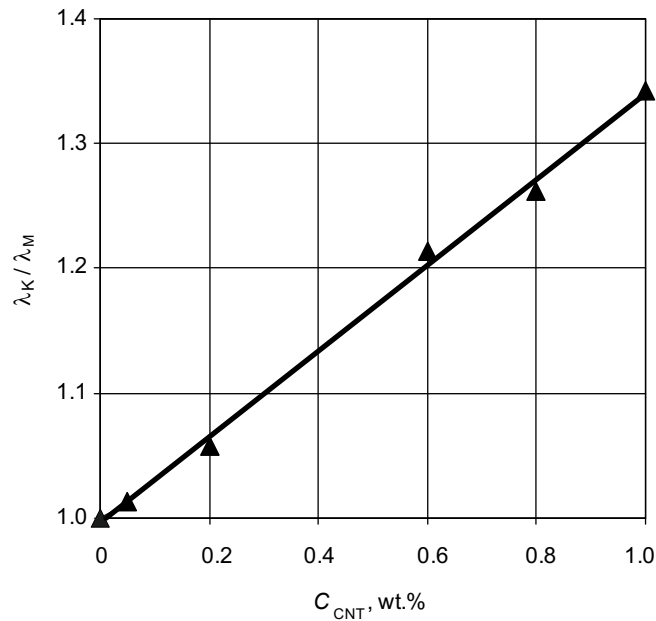


Fig. 3. Dependence of λ on the CNT content for the PVDF/CNT composites.

while λ increases only by 35% (Fig. 3). This is due to the fact that the electric current in these binary PVDF/CNT composites is caused by charge carrier transfer along the conductive CNT network, whereas the heat diffusion is caused by the transport of phonons, and the thermal conductivity significantly decreases due to phonon scattering on the PVDF/CND boundaries [17–19].

Figure 4 shows the dependence of the thermal conductivity on the graphite content in the binary PVDF/G and ternary PVDF/G/CNT composites. It can be noted that the thermal conductivity of the PVDF/G composite increases by more than 17 times compared to the polymer matrix. In this case, the percolation threshold is observed when the graphite content is about 25 wt.%.

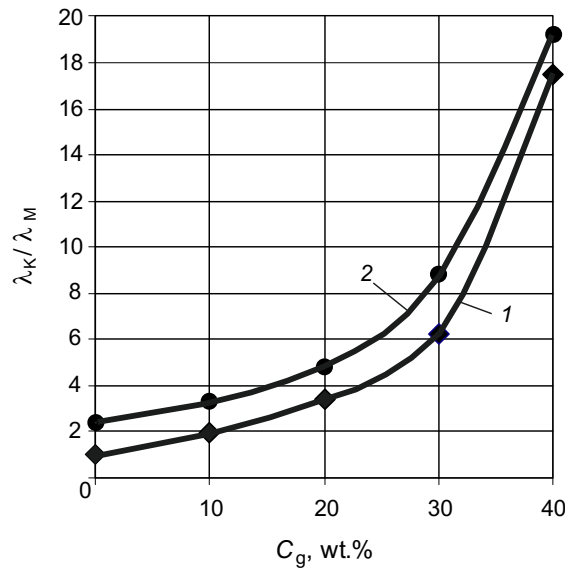


Fig. 4. Dependences of λ on the graphite content for the PVDF/G (curve 1) and PVDF/G/CNT composites (curve 2).

The thermal conductivity can be increased by no less than 10% by adding 0.6 wt.% of CNT to the binary PVDF/G composites. For example, it is seen that λ of the ternary PVDF/G/CNT composite with graphite content of 15 wt.% is practically equal to that of the binary PVDF/G composite with graphite content of 23 wt.%. A similar regularity is retained for other C_G values. In this case, the graphite content can be reduced by 3–15 wt.% compared with the binary PVDF/G composites by adding a small amount of CNTs.

This experimental fact is in good agreement with the results of SEM analysis (Fig. 5). It is clearly seen that the graphite particles are stochastically distributed in the polymer matrix and form a branched three-dimensional conductive network. The network becomes even more branched with increasing graphite content due to the formation of numerous particle-particle contacts, which leads to the formation of additional pathways of the conductive network and the increase of its density. Addition of a small amount of CNTs to the PVDF/G composite leads to the formation of an additional conductive network, which tightly adjoins the graphite particles (Fig. 5b). The increase in the area of contact between the PVDF matrix and the three-dimensional hybrid conductive network reduces sharply the interface thermal resistance [20] leading to an increase in the thermal conductivity.

Thus, the established effect of a small amount of CNTs on the thermal conductivity of the binary composites makes possible a significant reduction in the content of graphite in the ternary PVDF/G/CNT composites. This leads to the improvement of the technological properties of the ternary composites (facilitating processing of the ternary composites by the conventional processing methods, such as injection molding or extrusion) by improving the rheological properties, in particular, by increasing the melt flow index of the composites.

CONCLUSIONS

The PVDF polymer compositions with high electrical and thermal conductivities have been prepared and investigated. The electrical conductivity of the binary PVDF/CNT composites can be increased by 5–7 orders of magnitude compared to the PVDF matrix for the CNT content exceeding 0.2 wt.%. It was shown that the thermal conductivity of the binary PVDF/G composites can be increased by 17 times compared to the PVDF matrix. Addition of a small amount of CNTs to the binary PVDF/G composites led to the increase of the thermal conductivity at least by 10% that allows the content of graphite to be decreased and the technological properties of the composites to be improved.

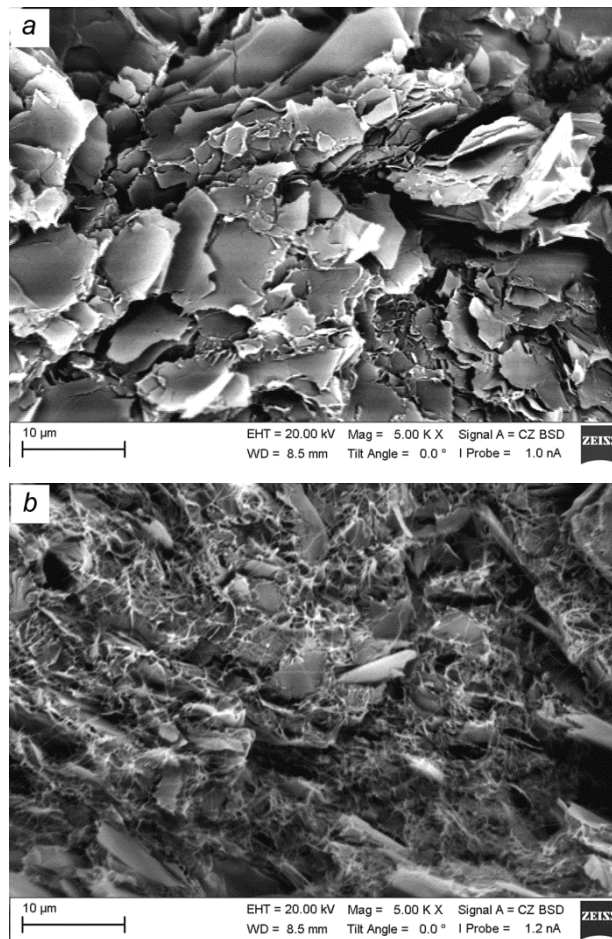


Fig. 5. SEM photomicrographs of the binary PVDF/G (a) and ternary PVDF/G/CNT composites (b).

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