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NMR study of nanocarbon material/Nafion interface in a radio absorbing composite

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Inorganic-polymer composites are widely used as radio-absorbing materials, the study of their properties is important from the point of view of improving technical characteristics. The results of the study of Nafion/thermoexpanded graphite and Nafion/carbon black composites by nuclear magnetic resonance and thermogravimetry are presented. The formation of new compounds at the contact boundaries of the components, leading to thermal stabilization of the composites, is shown. Differences between thermally expanded graphite and carbon black upon interaction with Nafion are discussed.

Keywords: Nafion, graphene, carbon black, NMR.

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Inorganic-polymer composites are now being used more and more widely in various technical fields. The fabrication of antiradar coatings and coatings screening electromagnetic radiation is an important application niche for such materials. In addition to functional requirements, a number of requirements concerning the microstructure and certain physical and performance parameters are imposed on radio-absorbing materials. Specifically, it was mentioned in review [1] that an ideal radio-absorbing material should have a strong attenuation capacity within a wide frequency range, low density, fine thermal stability, low cost, and small thickness. Different molecular structures of carbon-based materials attract considerable attention owing to their low density, high (and adjustable) conductivity, large surface area, anticorrosion properties, reduced weight, and remarkable capacity to absorb electromagnetic waves. These properties have made such materials as carbon black [2], carbon nanotubes [3], and carbon fibers [4] widely used as microwave absorbers.

Composites based on the Nafion proton-conductive polymer and nanostructured carbon materials are relatively poorly examined [5], but appear to be promising in terms of providing a stable and uniform microstructure, since Nafion has well-pronounced surface-active properties and stabilizes nanoscale carbon structural elements, inhibiting their agglomeration; in addition, it has anticorrosion properties [6]. The introduction of carbon materials into a composite facilitates an enhancement of the thermal stability of Nafion [7].

The aim of the present study is to examine the causes and specifics of the stabilizing effect in a composite featuring dispersed carbon nanostructured materials of different morphology (pseudo-two-dimensional few-layer graphene and three-dimensional carbon black) in a Nafion polymer medium.

Thermoexpanded graphite (TEG), which was produced by NP Tomskii Atomnyi Tsentr in accordance with the fabrication procedure outlined in [8]; commercial carbon black Vulcan XC-72; and Nafion solution DE1021 (DuPont) were used. Mixtures of precisely weighed amounts of components in a water-isopropanol solution, which were then subjected to ultrasonic dispersion and dried in air, were prepared for examination.

Equipment provided by the Magnetic Resonance Research Centre at the St. Petersburg University was used to perform nuclear magnetic resonance (NMR) studies. Spectra were measured with a Bruker AVANCE III WB 400 spectrometer (the constant magnetic field strength was 9.4 T). A probe with a system for sample rotation at the magic angle was used. A sample was introduced into a zirconia rotor with an outer diameter of 4 mm and rotated at different frequencies (most often at 12.5 kHz). In certain cases, the level of 12.5 kHz could not be reached due to the high conductivity of material samples. Several frequencies were used for fluorine spectra (to determine isotopic spectrum components). The operating frequencies for ^{1}H, ^{19}F, and ^{13}C nuclei are 400, 376, and 104 MHz, respectively. Tetramethylsilane and an aqueous M-solution of lithium fluoride were used as external references for ^{1}H and ^{13}C nuclei and ^{19}F nuclei, respectively. A single-pulse sequence used for excitation had the following excitation pulse duration and relaxation delay values: 2.5 μs and 30 s (^{1}H nuclei), 1.2 μs and 30 s (^{13}C), and 2.9 μs and 2 s (^{19}F).

The thermal stability of composites was examined with a Mettler-ToledoTGA/DSC 1 derivatograph with STAReSystem software (Switzerland). Thermogravimetric (TG) curves were measured with air pumped through the

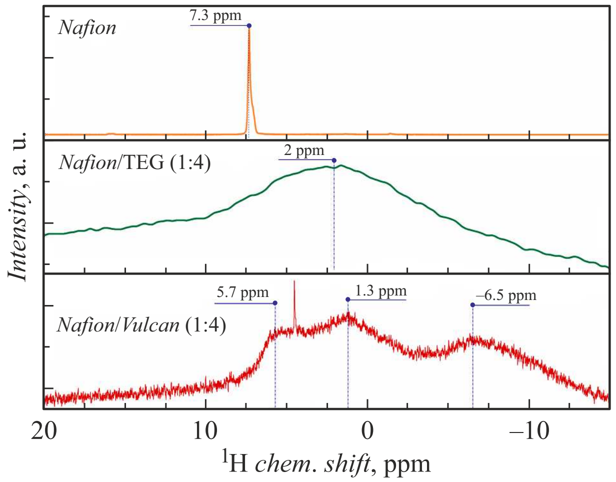

Figure 1. Solid-state ^{1}H NMR spectra for Nafion/carbon material composites (mass:mass).

derivatograph chamber at a rate of $30\,\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ under a steady temperature rise ($5\,\mathrm{K} \cdot \mathrm{min}^{-1}$) within the $35-1000^\circ$C temperature interval.

Figure 1 presents the ^{1}H NMR spectra of the examined samples. It should be noted that the signal-to-noise ratio for composites with carbon materials is significantly lower than the one for pure Nafion. This is attributable to the presence of a conductive phase of carbon materials and, consequently, to a reduction in the resonance circuit quality. It is evident that pure Nafion has a narrow intense nonuniformly broadened spectral line with a chemical shift of 7.3 ppm. This line is characteristic of water molecules in ionized Nafion pores and is not observed in Nafion/TEG and Nafion/Vulcan composites. A broad unresolved line with its maximum around 1.7 ppm is seen in the spectrum for Nafion/TEG. This may be attributed to an increased relaxation rate due to the presence of a highly conductive phase in the sample. The Nafion/Vulcan composite spectrum features three broadened components with approximate shifts of 5.7, 1.3, and -6.5 ppm and a low-intensity peak around 4.5 ppm. The narrow line is characteristic of free water that could get separated from the bulk of the sample in the course of rotor rotation. The line near 5.7 ppm may correspond to the signal of water atoms in Nafion pores with a low degree of intrapore ionization. Proton signals may shift to the negative part of spectra (as is the case with the signal near -6.5 ppm) if a hydrogen atom is screened additionally (e.g., resides in a metal matrix or a conducting matrix of a different type) due to the additional diamagnetic interaction [9–11].

A broad unresolved line around 111 ppm is seen in the ^{13}C NMR spectrum for pure Nafion, and a broadened line in the same chemical shift region is found in the spectrum for the Nafion/Vulcan composition. A ^{13}C NMR spectrum for the Nafion/TEG sample could not be measured.

Spectra containing a set of components typical of Nafion were recorded for ^{19}F nuclei in all samples. All components were resolved for Nafion and Nafion/Vulcan samples: -80 ppm (OCF_2 and CF_3), -117 ppm (SCF_2), -122 ppm ($(CF_2)_n$), -138 ppm ($CF(b)$), and -144 ppm ($CF(s)$) [12]. A single unresolved broadened line with its maximum around -122 ppm was observed for Nafion/TEG.

The significant broadening of ^{1}H and ^{19}F NMR lines and the infeasibility of measurement of the ^{13}C spectrum for Nafion/TEG are attributable to the high conductivity of TEG, which reduces the resonance circuit quality and/or speeds up the relaxation processes. At the same time, the presence of Vulcan particles in the Nafion/Vulcan sample does not result in a similar dramatic spectrum suppression, presumably because the conductivity of this composite is lower.

The lack of ^{1}H lines in the region of 7.3 ppm in composites with TEG and Vulcan is probably indicative of a low density of pores in the Nafion matrix, which is attributable either to filling of pores by modifying material particles or to monomolecular encapsulation of these particles by polymer Nafion fibers without the formation of such pores [13].

It can be seen from Fig. 2 that thermal destruction of Nafion in the Nafion/TEG composite proceeds in a single stage: the TG curve features one mass loss step, which corresponds to one pronounced peak in the differential thermogravimetric (DTG) curve (at $\sim 412^\circ$C). As for the Nafion/Vulcan composite, the TG curve has three mass loss steps, and the DTG curve features three resolved peaks (at ~ 348, ~ 374, and $\sim 402^\circ$C). Analyzed together with NMR data, this behavior is probably indicative of the formation of a fraction of Nafion in the composite without pores. These structural changes may cause an enhancement of thermal stability.

In complete agreement with the proximity of resonance frequencies in NMR spectra, Nafion/TEG ($\sim 412^\circ$C) and

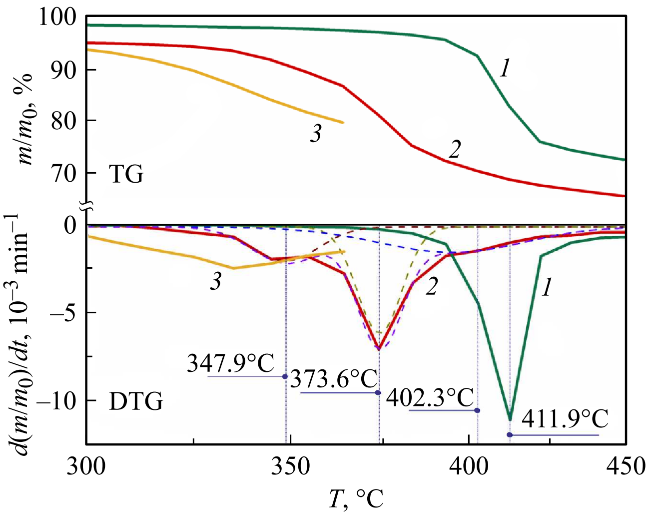

Figure 2. TG and DTG curves of destruction of Nafion and Nafion/carbon material (1:4) composites heated in air at a rate of $5\,\mathrm{K}^{-1}$. *1* — Nafion/TEG, *2* — Nafion/Vulcan, and *3* — pure Nafion.

Nafion/Vulcan ($\sim 402^\circ$C) composites have fairly close temperatures of destruction peaks.

The onset of destruction of pure Nafion corresponds to a lower temperature (see the peak at 336°C in the DTG curve in Fig. 2).

Thus, joint NMR and thermogravimetric studies of Nafion/carbon material composites revealed a strong influence of carbon materials on the polymer. TEG and Vulcan alter the structural, physical, and chemical characteristics of Nafion, enhancing its thermal stability.

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Conflict of interest

The authors declare that they have no conflict of interest.

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