06

Effect of gamma-irradiation on the dielectric properties of Polypropylene Na+Na$^+$+montmorillonite composite

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Effect of gamma-irradiation on the dielectric properties of polymer composites based on polypropylene (PP) with Na$^+$–montmorillonite (MMT) nanoparticles has been investigated. It has been found that gamma-irradiation in the dose range of $100-200\,\text{kGy}$ leads to slight deterioration in the dependences of $\varepsilon = f(T)$ and $\text{tg}\,\delta = f(T)$ of the polypropylene-based composite with Na$^+$-MMT filler. It has been hypothesized that the deterioration of dielectric properties during irradiation in composites is due to changes in crosslinking and degradation processes within the polymer matrix and at the polymer−filler interface. It has been indicated that due to gamma-irradiation of polymer composites its dielectric and electrophysical properties can be expediently controlled.

Keywords: Polypropylene, Na$^+$--montmorillonite, gamma irradiation, dielectric constant, dielectric energy loss.

The production of new composite polymer materials with unique properties is one of the promising lines of development of materials science. The introduction of filler into a polypropylene (PP) matrix has a significant influence on the structure and properties of composite materials, which is attributable to interphase interactions and the formation of a boundary nanolayer near filler particles. The use of polymer materials enables the development of fundamentally new designs of various kinds of products, helps reduce their weight and maintenance and transportation costs, and is beneficial to their quality and appearance [1–4].

It is known that polymer composites are highly sensitive to various types of ionizing radiation [5–8]. A review of literature in this field reveals that low irradiation doses lead to a relative improvement in physical properties, while high doses induce material degradation, exerting a negative influence on physical properties. In this context, the study of electrophysical properties of polymer composites before and after exposure to gamma radiation is relevant. The processes of crosslinking, degradation, and oxidation induced by exposure to ionizing radiation alter the properties of the supramolecular structure of the matrix and the boundary layer. This translates into a change in the electroactive properties of composites, namely their electrophysical characteristics: temperature and frequency dependences of electrical conductivity (σ) and dielectric parameters (ε and $\text{tg}\,\delta$) [8–12].

It follows from literature data that the introduction of a certain amount of Dk$_1$ and Dk$_2$ nanoclays (2% by volume) into polypropylene exerts a slight positive influence on its physical and mechanical properties. However, the examined papers lacked data on the structure of these fillers and the degree of their compatibility with the matrix. Note, however,

that montmorillonites (MMTs) from different deposits have different modifications and particle size. The use of Na$^+$(MMT) as modifiers is due, first, to the amount of quaternary ammonium guanine cations present in them and, second, to the high adhesion of clay to polar polyolefin molecules [13,14].

In this connection, the present study is aimed at examining the dielectric properties and relaxation processes in as-prepared and irradiated polymer PP + Na$^+$(MMT) composites. Although the characteristics of Na$^+$(MMT) have been investigated extensively, the dielectric properties and features of interfacial phenomena in its composites with polymers remain understudied. We believe that research in this field should enable the production of electroactive composite materials with novel functional characteristics and the development of converters based on them.

Polypropylene and Na$^+$(MMT) nanoparticles were used to form the composites. Na$^+$(MMT) crystals have grains smaller than 100 nm and a complex structure with negative and positive charges, which provides the capacity to bind both cationic and anionic substances. A non-ionic substance often binds to montmorillonite through secondary valence. Montmorillonite has the capacity to bind large quantities of various harmful substances with its surface area and the space between the crystal layers.
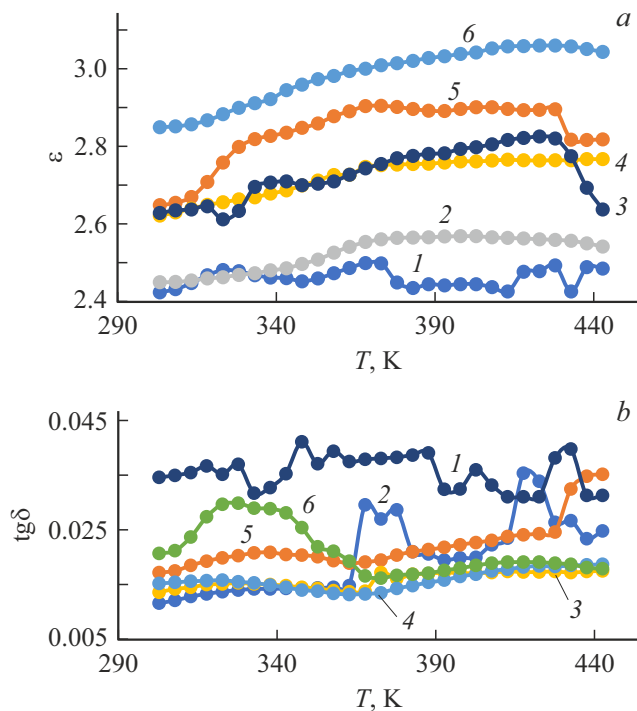
Disk-shaped composite samples were formed from a homogeneous mixture of PP + x vol.% Na$^+$(MMT) powders with particles up to 100 nm in size. The dielectric characteristics were measured using a E7-20 LCR meter within the $25-10^6$ Hz frequency range.

The data for the original polymer and the composite based on it are also shown in the presented dependences for comparison with irradiated samples. Being a polar poly-
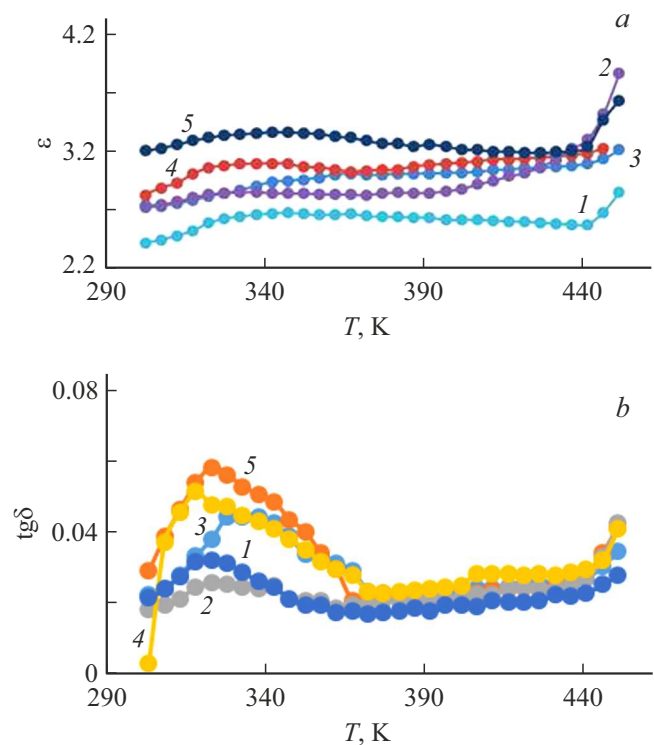
crystalline polymer, polypropylene has a significant dipole moment, which is manifested in temperature dependences of permittivity ε and dielectric loss tangent $\text{tg}\,\delta$.

Figure 1 shows temperature dependences $\varepsilon = f(T)$ (a) and $\text{tg}\,\delta = f(T)$ (b) for the non-irradiated polypropylene composite with 0, 0.5, 2, 3, 5, 7 vol.% Na$^+$(MMT) measured at frequency $\nu = 1\,\text{kHz}$. It can be seen from Fig. 1, a that permittivity ε of the original PP varies only slightly within the $320-450\,\text{K}$ temperature range. In addition, the $\varepsilon = f(T)$ dependence featured small maxima induced by the sample heterogeneity in the temperature regions of $330-333$, $370-380$, and $430-433\,\text{K}$. Curve 2 in Fig. 1, a demonstrates that when Na (0.5 %) is introduced into the polymer, the values of permittivity ε remain virtually unchanged within the temperature range of $300-350\,\text{K}$, but increase slightly with a further increase in temperature. Following irradiation with a dose of $200\,\text{kGy}$, the previously observed maxima in the regions of $370-380$ and $430-433\,\text{K}$ vanish (see Fig. 2, a), which may be associated with an increase in mobility of the polymer chain. Figure 1, a shows clearly that the value of ε increases within the $328-428\,\text{K}$ interval with an increase in Na content (2, 3, and 7 vol.%) in the polymer.

Figure 1, b presents temperature dependences $\text{tg}\,\delta = f(T)$ of the non-irradiated PP + 0, 0.5, 2, 3, 5, 7 vol.% Na$^+$(MMT) composite measured at frequency $\nu = 1\,\text{kHz}$. It follows from these dependences that the introduction of Na$^+$(MMT) into the polymer induces a fairly pronounced

Figure 2. Temperature dependences $\varepsilon = f(T)$ and $\text{tg}\,\delta = f(T)$ for the PP+Na$^+$(MMT) composite irradiated with a dose of $200\,\text{kGy}$ at frequency $\nu = 1\,\text{kHz}$. Na$^+$(MMT), vol.%: a) 1 — 0, 2 — 2, 3 — 3, 4 — 5, 5 — 0.5; b) 1 — 0.5, 2 — 5, 3 — 3, 4 — 2, 5 — 0.

Figure 1. Temperature dependences $\varepsilon = f(T)$ (a) and $\text{tg}\,\delta = f(T)$ (b) for the non-irradiated PP+Na$^+$(MMT) composite at frequency $\nu = 1\,\text{kHz}$. Na$^+$(MMT), vol.%: a) 1 — 0, 2 — 0.5, 3 — 7, 4 — 5, 5 — 3, 6 — 2; b) 1 — 2, 2 — 3, 3 — 5, 4 — 7, 5 — 0.5, 6 — 0.

maximum of $\text{tg}\,\delta$ in the as-prepared composite, which is associated with dielectric losses during dipole relaxation and relaxation of the accumulated charge in the interphase boundary of amorphous and crystalline phases in the polymer matrix and the matrix with Na$^+$(MMT) [15]. A comparison of the curves reveals that the observed maximum of the $\varepsilon = f(T)$ dependence and the corresponding shoulder in the $\text{tg}\,\delta = f(T)$ dependence of the composite may be seen as a result of relaxation of the charge accumulated at the interphase boundary between the polymer and the filler, which is released in the process of polymer matrix melting [16].

Dependences $\varepsilon = f(T)$ and $\text{tg}\,\delta = f(T)$ at $T = 300\,\text{K}$ and different irradiation doses were examined in order to study the effect of gamma irradiation on the dielectric properties of PP + Na$^+$(MMT) composites. Figure 2, a presents the temperature dependence of permittivity $\varepsilon = f(T)$ at frequency $\nu = 1\,\text{kHz}$ for the PP + 0, 0.5, 2, 3, 5 vol.% Na$^+$(MMT) composites irradiated with a dose of $200\,\text{kGy}$. It is evident that only $\varepsilon = f(T)$ curves 1, 2, and 5 recorded at an irradiation dose of $200\,\text{kGy}$ grow at a temperature of $440\,\text{K}$. Figure 2, b presents temperature dependence $\text{tg}\,\delta = f(T)$ at frequency $\nu = 1\,\text{kHz}$ for the PP + 0, 0.5, 2, 3, 5 vol.% Na$^+$(MMT) composites irradiated with a dose of $200\,\text{kGy}$. It is evident that the value of $\text{tg}\,\delta$ in the samples irradiated with a dose of $200\,\text{kGy}$ increases

within the $310-330$ K interval and remains constant within the $350-420$ K range. As the temperature increases further to $T > 440$ K, tg δ grows sharply, but then again assumes a constant value. This is indicative of deterioration of the properties of the composite material and the onset of degradation, suggesting that the process of polymer degradation is initiated at $T > 440$ K due to the interaction of the polymer matrix with radiation defects and filler nanoparticles.

A comparative analysis of frequency dependences $\varepsilon = f(\nu)$ and tg $\delta = f(\nu)$ at $T = 298$ K was carried out in order to investigate the effect of irradiation on relaxation processes in the PP + Na$^+$(MMT) composite. These dependences provide an opportunity to estimate the intensity of molecular mobility of various relaxation processes. Figures 3, a and b show frequency dependences $\varepsilon = f(\nu)$ and tg $\delta = f(\nu)$ recorded after irradiation with a dose of 100 kGy at temperature $T = 298$ K. It was noted in [17] that the transition of a polymer matrix in a polymer−filler system from a glassy state to a highly elastic one leads to a reduction in orientational stability of dipoles and an increase in mobility of the polymer chain, and the relaxation properties of a composite depend to a significant extent on these processes and the measurement temperature. At tem-

perature $T \sim 298$ K (Figs. 3, a and b), the tg $\delta = f(\nu)$ dependence for the irradiated PP + Na$^+$(MMT) composite samples has no relaxation maxima, and only its growth at high frequencies is observed within the measured frequency range.

The obtained results indicate that the active centers, radicals, and defects of the polymer structure formed after irradiation interact with filler nanoparticles and induce a reduction in mobility of the polymer chain and, accordingly, lower the values of ε and tg δ of the composite. It is also known from literature [18–20] that the introduction of fillers into a polymer matrix in composites leads mostly to a reduction in mobility of macromolecules of the polymer chain. Under exposure to gamma radiation, the interaction of polymer chains with the filler surface intensifies during crosslinking and gets weaker in the process of degradation. The tg $\delta = f(\nu)$ dependences reveal that the maxima at an irradiation dose of 100 kGy shift toward lower frequencies (relative to those typical of non-irradiated samples), which is associated with crosslinking and a reduction in mobility of the polymer chains.

The obtained results allow one to trace the influence of radiation on the relaxation of volume charges accumulated in the interphase polymer−filler boundary. The gentle maximum seen in the tg $\delta = f(\nu)$ dependence for the as-prepared PP + Na$^+$(MMT) composite measured at temperature $T \sim 298$ K has two components: the relatively low-frequency one corresponds to the relaxation of the volume charge at the interphase boundary, while the high-frequency one corresponds to the relaxation of dipoles in the matrix.
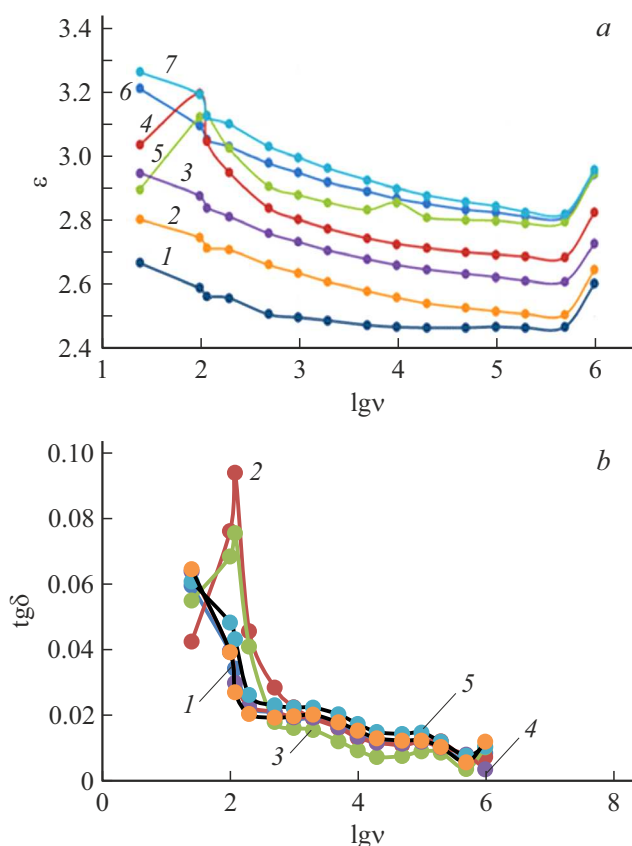
Thus, a comparison of the obtained results for the temperature and frequency dependences of the electrophysical properties of the as-prepared and gamma-irradiated PP + Na$^+$(MMT) composite suggests that the observed changes in these properties are governed by the balance between crosslinking and degradation processes occurring in the polymer matrix and in the interphase boundary between the polymer and the filler. It was demonstrated that gamma irradiation of polymer composites allows for effective control over their dielectric and electrophysical properties, which opens up opportunities for development of fundamentally new types of products.

Conflict of interest

The authors declare no conflict of interest.

Figure 3. Frequency dependences $\varepsilon = f(\nu)$ and tg $\delta = f(\nu)$ for the PP+Na$^+$(MMT) composite irradiated with a dose of 100 kGy at temperature $T = 298$ K. Na$^+$(MMT), vol.%: a) $1 - 2$, $2 - 3$, $3 - 5$, $4 - 6$, $5 - 7$, $6 - 0.5$, $7 - 0$; b) $1 - 0$, $2 - 0.5$, $3 - 7$, $4 - 5$, $5 - 2$.

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