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Complex dielectric permeability and optical characteristics of polypropylene + Na^+ montmorillonite composites

© E.M. Gojaev,[1] R.L. Mammadova,[2] A.M. Akhmedova,[3] S.N. Garibova[4,5]

[1] Azerbaijan Technical University, Baku, Azerbaijan
[2] Sumgait State University, AZ 5008, Sumgait, Azerbaijan
[3] Azerbaijan State University of Economics (UNEC), Baku, Azerbaijan
[4] Institute of Physics, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan
[5] Khazar University, Department of Physics and Electronics,
AZ-1096 Baku, Azerbaijan
e-mail: geldar-04@aztu.edu.az, rasmiyyamammadova70@gmail.com, arzu.70@bk.ru, sqaribova@.rambler.ru

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The paper presents the results of studying the frequency dependence of the real and imaginary parts of the dielectric constant of polypropylene modified with Na^+ montmorillonite. Using the experimental values of the complex dielectric constant, the optical functions such as the real and imaginary parts of the refractive index, optical conductivity, reflection and absorption coefficients, the characteristic function of the electron energy losses of PP+*x* vol.% $NaNa^+$ montmorillonite composites have been determined It is shown that on the basis of a high-pressure polymer with the use of Na + montmorillonite as a filler, it is possible to create composite materials with improved physical parameters. To obtain stable electrophysical properties, it is necessary to optimize the composition of the composite material and the volume of the filler. By the method of dielectric spectroscopy in the frequency course, information is obtained not only on the behavior of the complex dielectric constant, but also on the structure of the composite material, which is indispensable for the purposeful regulation of the volumetric content of the filler.

Keywords: Na^+-montmorillonite, polypropylene, dielectric constant, composite materials.

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Introduction

One of the promising fields of the material science is creation of new composite polymer materials with unique properties. These materials are successfully used as insulation of capacitive energy accumulators designed to operate at a pulse voltage. Depending on a purpose and an application field of the high-voltage pulse devices, the duration of the voltage impulse front can change from several dozens milliseconds to nanoseconds. That is why the composite materials for the capacitive energy accumulators must have stable electrophysical characteristics within the wide frequency range of the external electric field. The filler has been input into the polypropylene (PP) matrix to substantially modify the structure and the properties of the composite materials by interphase interactions and formation of a boundary nanolayer near the filler particles [1–8]. It determines the features of the time distribution of the local field within separate areas of the polymer system and the frequency dispersion of the effective complex permittivity of the composite materials [9–13]. Using cheap available nanosized clays of the Na^+-montmorillonite type results in improvement of physical and mechanical properties of the polymer composites, thereby reducing their cost. One of the important requirements to the polymer nanocomposites is stabilization of their structure and electrophysical properties by affecting them with radiation of a various nature as well as under thermal effects in the heating–cooling mode [14]. In this regard, development of the composite materials requires availability of the data about the spectrum of the complex permittivity of the polymer matrix of filler particles. In recent years, the studies have been intensely focused on the polymer nanocomposites modified by the Na^+-montmorillonite [15–23]. In the light of the above, the purpose of this study is to investigate the frequency dependence of the complex permittivity and calculate the optical functions of the composites PP+*x* vol.% Na^+-montmorillonite (MMT).

1. Experimental procedure

The silver paste has been used as a contact when measuring the dielectric parameters. The frequency dependence of the permittivity and the dielectric loss angle has been investigate using a digital instrument for measurement of the E7-20 impedance as described in [24]. The voltage applied to the sample was 1 V. The errors of measurement of the permittivity and the dielectric losses were 3 and 5%, respectively. The studies have been performed in the frequency range of $10-10^6$ Hz.

2. Experimental results and discussion thereof

The results of investigation of the frequency dependences of the permittivity and the dielectric losses of the propylene modified by the Na^+-montmorillonite are shown on Fig. 1.

The frequency dependence of the permittivity of the composites PP+x vol.% Na^+-MMT is shown on Fig. 1, *a*. As it is clear from the figure, the experimental dependences $\varepsilon(\omega)$ of the composites of the above-said type exhibit weak responses at the frequency of 100 Hz. The exclusion is pure polypropylene, whose dependence $\varepsilon(\omega)$ almost does not change within the frequency range of 10^2-10^5 Hz. However, with the increase in the volume content of montmorillonite in the composition and with increase in the frequency, there is evidently the relative decrease in the permittivity ε. At the frequencies above 10^5 Hz, all the studied composites have typically exhibited the increase in the permittivity ε. As follows from Fig. 1, *b*, within the frequency range of 10–100 Hz tg δ of the composites is decreasing relatively high, while in the frequency range of 10^3-10^5 Hz it is almost constant, but with further increase in the frequency from 10^5 to 10^6 Hz it is strongly decreasing.

The tg δ is also decreasing with the increase in the volume content of montmorillonite in the composition of the composite. The nature of the change of tg δ with the frequency change is almost the same for all the studied composites. If using the experimental values of the frequency range of the

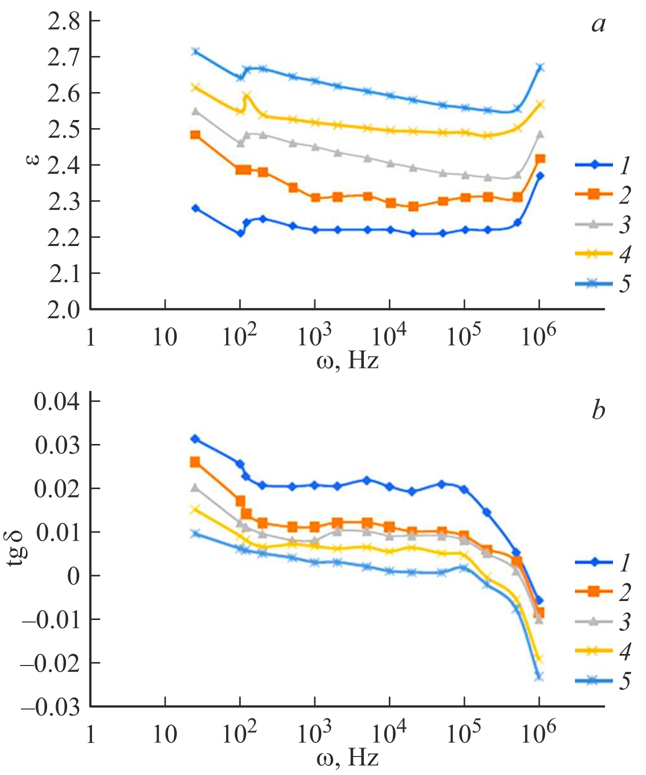

Figure 1. Frequency dependences of the permittivity (a) and the dielectric loss angle tangent (b) for the composites PP+x vol.% Na^+-MMT, x: *1* — 0, *2* — 10, *3* — 20, *4* — 30, *5* — 40.

dielectric loss tg δ and the permittivity (ε) of the solid body with the final conductivity within the range of $10-10^6$ Hz, then the frequency dependences of the complex permittivity $\varepsilon(\omega)$ are determined, and their imaginary part is correlated to the electric conductivity (σ) by the expression

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) = \varepsilon_r(\omega) + i\frac{4\pi\sigma}{\omega} = \left(\frac{c}{v}\right)^2$$

or by the frequency dependence of the complex refractive index

$$\bar{n}(\omega) = n(\omega) + ik(\omega) = \frac{c}{v},$$

where ε_r and ε_i — the real and imaginary parts of the permittivity, v — the phase speed of light in the substance.

It should be noted that the frequency spectrum of the dielectric loss is indicative of the availability of components causing a different contribution of dipole-orientation polarization to the total dispersion of the complex permittivity [25], which is caused by the fact that the studied polymer contains polar radicals as well as polar groups of plasticizer molecules. Besides, the input of the plasticizers results in the decrease in viscosity of the polymer due to the reduced energy of intermolecular interaction and the changed time of relaxation of the processes of the dipole-orientation polarization of the polar groups and radicals. The obtained results have shown that the change in the concentration of the Na^+-MMT filler resulted in shifting the relaxation frequency of all the spectrum components towards the lower frequencies, increasing the depth or full width of the dispersion of the complex permittivity in an approximate correspondence with the filler concentration and in the change of the contribution of the separate spectrum components to the dispersion of the complex permittivity [26]. It is known that the dielectric losses can be measured by the tangent of the angle δ, supplementing the angle φ to 90°

$$\mathrm{tg}\,\delta = \frac{I_{ac}}{I_{reac}} = \frac{\varepsilon_i}{\varepsilon_r},$$

where I_{ac} and I_{reac} — active and reactive current strength parts.

It is also known that the generalized permittivity is determined by the formula

$$\varepsilon^* = 1 + \frac{4\pi Ne^2}{m}\left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + f^2\omega^2} - \frac{if\omega}{(\omega_0^2 - \omega^2)^2 + f^2\omega^2}\right) = \varepsilon_r - i\varepsilon_i.$$

At the same time, the real ε_r and imaginary ε_i parts of the complex permittivity are equal to

$$\varepsilon_r = 1 + \frac{4\pi Ne^2(\omega_0^2 - \omega^2)}{m[(\omega_0^2 - \omega^2)^2 + f^2\omega^2]},$$

$$\varepsilon_i = \frac{4\pi Ne^2}{m}\frac{f\omega}{(\omega_0^2 - \omega^2)^2 + f^2\omega^2}.$$

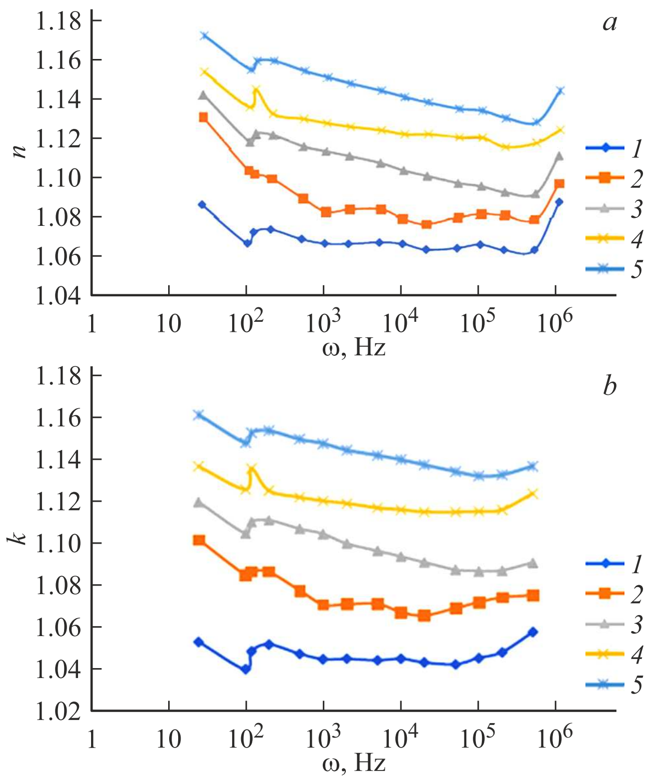

Figure 2. Frequency dependence of the real (a) and imaginary (b) parts of the refractive index of the composites PP+x vol.% Na^{+}-MMT, x: *1* — 0, *2* — 10, *3* — 20, *4* — 30, *5* — 40.

The real part of the refractive index was determined by the formula

$$n = \sqrt{\frac{1}{2}\left(\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2}\right)}.$$

The calculation results are shown on Fig. 2. As follows from Fig. 2, a, the real part of the refractive index is decreasing at the low frequencies (0–100 Hz) and within the frequency range from 10 to 10^5 Hz n is almost unchanging, while at the very high frequencies there is the strong growth of n. The nature of change of the real part of the refractive indices $n(\omega)$ of the composites is not different. With increase in the volume content of the filler, there is the decrease in the real part of the refractive index.

The imaginary part of the refractive index is determined by the formula

$$k = \sqrt{\frac{1}{2}\left(-\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2}\right)}.$$

As follows from Fig. 2, b, the frequency dependence of the imaginary part of the refractive index is of a similar nature, i.e. at the low frequencies there is weak decrease, while with the further increase in the frequency the imaginary part of the refractive index is almost unchanging with the change of the frequency.

The reflection coefficient is determined by the formula

$$R = \frac{(n-1)^2 - k^2}{(n+1)^2 + k^2}.$$

The results of calculation of the reflection coefficient are shown on Fig. 3. As follows from Fig. 3, the frequency of 100 Hz exhibits the maximums in the $R(\omega)$-dependence and with further increase in the frequency to 10^5 Hz R remains the same, while within the frequency range of 10^5–10^6 Hz R is growing.

The characteristic loss function of the electron energy is determined:

$$-I_m\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_i}{\varepsilon_i^2 + \varepsilon_r^2}.$$

The spectrum dependence of the imaginary part of the inverse magnitude of complex permittivity of the composites PP + Na^{+}-MMT is shown on Fig. 4. As it is clear, the $-I_m\left(\frac{1}{\varepsilon}\right)$-dependences evidently exhibit one maximum at the frequency of 100 Hz. It is found that with frequency

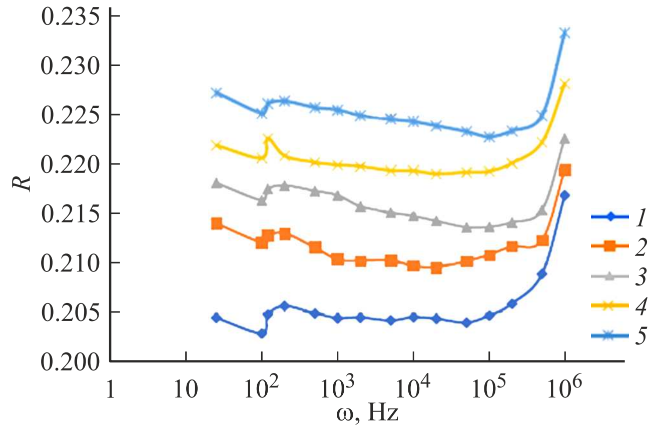

Figure 3. Frequency dependence of the reflection coefficient of the composites PP+x vol.% Na^{+}-MMT, x: *1* — 0, *2* — 10, *3* — 20, *4* — 30, *5* — 40.

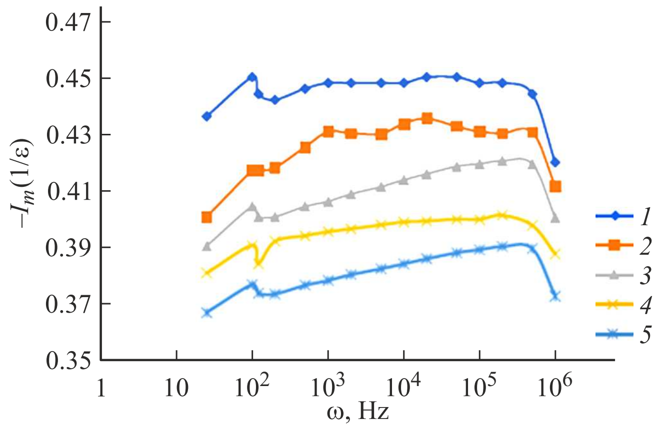

Figure 4. Frequency dependence of the energy losses of the composites PP+x vol.% Na^{+}-MMT, x: *1* — 0, *2* — 10, *3* — 20, *4* — 30, *5* — 40.

increase in the wide range of 10^2-10^5 Hz, $-I_m\left(\frac{1}{\varepsilon}\right)$ is somewhat increasing, so is strongly increasing within the range of 10^5-10^6 Hz. The real and imaginary parts of the optical conductivity are determined by means of the following formulas:

$$\sigma_r = \frac{\omega\varepsilon_i}{4\pi}, \qquad \sigma_i = \frac{\omega\varepsilon_r}{4\pi}.$$

The results of calculation of the real and imaginary parts of the optical conductivity of the composites PP + Na^+MMT are shown on Fig. 5. As follows from Fig. 5, in the frequency range of $10-10^5$ Hz the nature of the dependences for all the studied composites is almost unchanging. In the frequency range of 50–1000 Hz, the optical conductivities of the studied composites turn out to be the same independently of the filler content. It is apparently correlated to the fact that within the said frequency range a number of the current carriers both across and along the samples is the same and unchanging in dependence of the filler content. However, within the frequency range of 10^5-10^6 Hz the real part of the optical conductivity sharply increases. At the low frequency, the imaginary part of the optical conductivity is the same due to the above-said reason, while it sharply increases at the high frequencies. It is interesting to note that the real and imaginary parts of the optical conductivity of the studied composites turn out to be the same independently of the filler content.

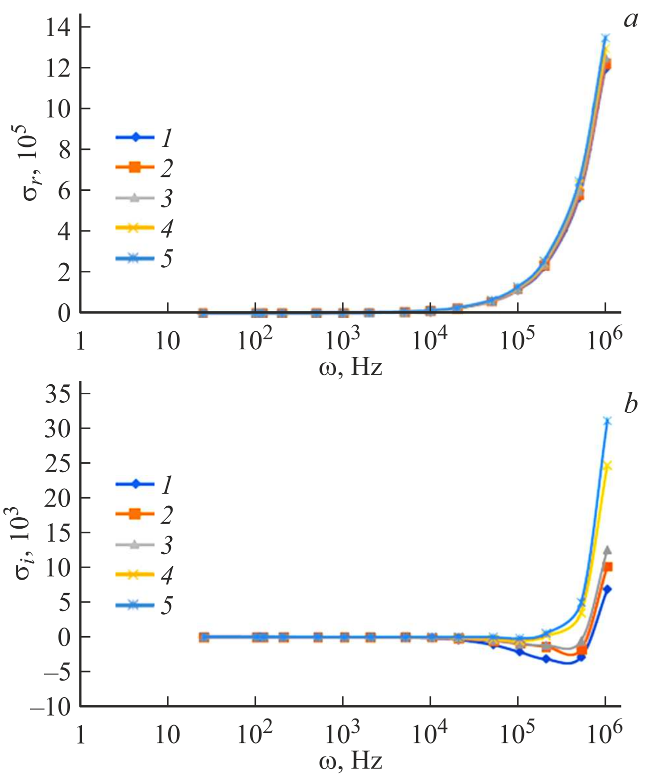

Figure 5. Frequency dependences of the real (*a*) and imaginary (*b*) parts of the optical conductivity of the composites PP+*x* vol.% Na^+-MMT, *x*: *1* — 0, *2* — 10, *3* — 20, *4* — 30, *5* — 40.

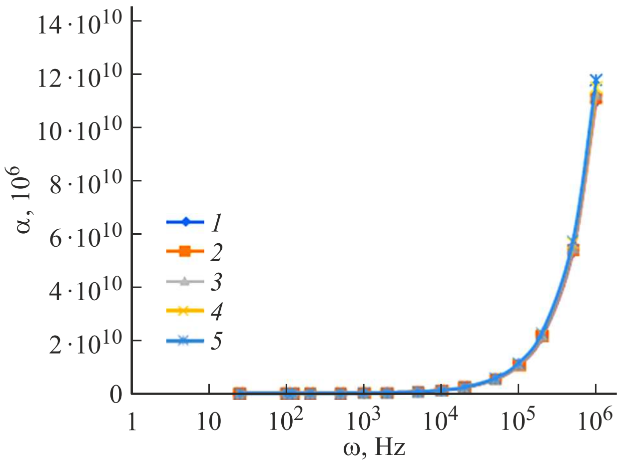

Figure 6. Frequency dependence of the optical absorption coefficient of the composites PP+*x* vol.% Na^+-MMT, *x*: *1* — 0, *2* — 10, *3* — 20; *4* — 30, *5* — 40.

The optical absorption coefficient is determined by the following expression

$$\alpha(\omega) = \frac{4\pi}{\lambda}k(\omega) = \frac{2}{c}\omega k,$$

where c is the speed of light. As follows from Fig. 6, the optical absorption coefficient of the composites PP+*x* vol.% Na^+-MMT within the wide frequency range of $10-10^5$ Hz is the same and does not depend on the volume content of the filler and the frequency, while within the frequency range of 10^5-10^6 Hz it is almost unchanging at the low frequencies.

Conclusion

New composite materials based on polypropylene have been obtained using the fillers Na^+-MMT. The frequency dependence of the permittivity and the frequency spectrum of the dielectric loss of the composites have been investigated to determine the optical characteristics of the said composites.

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Conflict of interest

The authors declare that they have no conflict of interest.

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