Dielectric Properties and Electrical Percolation in MnFe₂O₄/Epoxy Resin Composites

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Broadband dielectric properties of epoxy composites containing the different additions of manganese ferrite (MnFe₂O₄) with two spherical particle sizes (28 and 60 nm) are studied in the wide temperature range from 150 to 500 K. The percolation thresholds in such systems are 30 and 29.3 vol% for small and large MnFe₂O₄ particles, respectively. The small difference in the percolation threshold value is related to a better distribution of larger nanoparticles. Composites above the percolation threshold are appropriate candidates for electromagnetic shielding applications. Above 380 K, the electrical conductivity is typical for all composites, both below and above the percolation thresholds due to the electrical transport in the polymer matrix. The activation energy strongly decreases with MnFe₂O₄ concentration indicating that the electrical transport occurs simultaneously in both MnFe₂O₄ and epoxy matrix subsystems.

1. Introduction

A composite material, as a heterogeneous system consisting of a polymer matrix and fillers embedded, acquires properties from all its components, which attracts the attention of many researchers. The possibility to control these properties (by a selection of polymer matrix, fillers, and fabrication process) makes composites interesting for many applications.[1,2]

An excellent candidate for the role of composite inclusions is manganese ferrite (MnFe₂O₄), which is considered as one of the most important inorganic materials due to their electrical, optical, magnetic, and catalytic properties.[3] MnFe₂O₄ is characterized by a variety of sizes[4,5] and forms,[6,7] and it can also be incorporated in carbon structures,[8,9] which also affects their properties. From the magnetic properties point of view, this type of particles is already quite well studied, and it is found that magnetic properties of these particles are strongly size-dependent.[7] On this basis, magnetic ferrite particles have found the applications in many directions, such as magnetic recording media devices,[10] ferrofluid,[11] biosensors,[12] and for biomedical applications (magnetic resonance imaging, magnetic hyperthermia for cancer therapy, cells and DNA separation, and so on).[9]

However, investigations of MnFe₂O₄ in terms of electrical properties can also be interesting, to make them applicable (along with very popular carbon materials) in fields such as electromagnetic shielding and radar absorbing coatings,[13] for electromagnetic compatibility.[14] Nevertheless, the electrical percolation phenomena was not studied in composites with MnFe₂O₄ inclusions. Some preliminary estimations of electrical percolation threshold in composites with MnFe₂O₄ inclusions were performed in the study by Meisak et al.[15] However, in this work,[15] composites with only several MnFe₂O₄ concentrations were investigated. The electrical percolation threshold is a very important parameter for various practical applications of composites, including electromagnetic shielding.[16] Moreover, the electrical percolation threshold can be substantially lower than it is expected by theoretical calculations and dependent from particle size, even for round particles.[17]

The purpose of this work is to study the dielectric properties of epoxy resin composites filled with MnFe₂O₄ nanopowder, which has two different spherical particle sizes (28 and 60 nm).

2. Results and Discussion

2.1. Room Temperature Region

Scanning electron microscopy (SEM) images of composites with different sizes of MnFe₂O₄ nanoparticles are shown in Figure 1. It can be concluded that nanoparticles are well distributed in both cases.

The frequency dependence at room temperature of the real part of dielectric permittivity (ε’) and the electrical conductivity (σ) of epoxy composites with different MnFe₂O₄ (60 nm particle size) loadings is shown in Figure 2. An increase in the MnFe₂O₄ concentration in epoxy resin leads to the monotonic increase in
the dielectric permittivity and electrical conductivity values. Moreover, for composites with a concentration of ≤20 vol%, the dielectric permittivity is a completely frequency-independent function, and the DC conductivity plateau is absent (similar to epoxy resin). However, for composites with concentration of >20 vol%, the dielectric permittivity is frequency dependent and at a maximum concentration of 30 vol% $\varepsilon'$ decreases strongly with the increasing frequency, and a weakly pronounced plateau of $\sigma$ appears, which indicates that the percolation threshold is close to 30 vol%.

Figure 1. SEM images of composites with different size MnFe$_2$O$_4$ nanoparticles (left particle size: 60 nm, right particle size: 28 nm).

Figure 2. Frequency dependence of the dielectric permittivity (left) and the electrical conductivity (right) for MnFe$_2$O$_4$/epoxy composites with 60 nm particle size at room temperature.

Figure 3. Concentration dependence of the real part of dielectric permittivity for MnFe$_2$O$_4$/epoxy composites with 28 nm particle size (left) and 60 nm particle size (right) at room temperature and 396 Hz (symbols), and fits with Equation (1) (solid curves).
To determine the percolation threshold of composites with 28 and 60 nm MnFe$_2$O$_4$ particle sizes, the dielectric permittivity at 396 Hz and room temperature was plotted as a function of concentration in Figure 3. Because all the studied concentrations (except the maximum one of 30%) did not have a frequency-independent plateau at low frequencies, the dielectric permittivity was fitted according to the classical power law for composites below the percolation threshold:\(^{[18]}\)

\[ \varepsilon' = \varepsilon_m(p_c - p)^{-t} \]  

where \(\varepsilon_m\) is the constant, \(p\) is the filler concentration, \(p_c\) is the critical volume fraction (percolation threshold), and \(t\) is the critical exponent. The obtained parameters and their standard errors for composites are shown in Table 1.

This calculation indicates that the electrical percolation for MnFe$_2$O$_4$/epoxy composites is reached when the filler concentration is close to 30 vol%. Moreover, it seems that the percolation threshold depends on the size of the MnFe$_2$O$_4$ spherical particles. However, according to the excluded volume theory,\(^{[19]}\) the percolation threshold depends only on the shape of the particles, and not on their size. Therefore, it should be assumed that the difference in the conductive capacity of composites based on different size MnFe$_2$O$_4$ is due to their different distributions in the polymer matrix.

### Table 1. Parameters of the percolation threshold law fit.

|   | \(\varepsilon_m\) | \(p_c\) [vol%] | \(t\) |
|---|------------------|----------------|------|
| Value | Standard error | Value | Standard error | Value | Standard error |
| 28 nm | 91.9 | 8.8 | 30 | 0.691 | 0.08 |
| 60 nm | 330.98 | 14.56 | 29.3 | 0.06 | 1.13 | 0.02 |

2.2. Temperature-Dependent Region

Let us consider the typical behavior of a composite below the percolation threshold using a sample with 20 vol% MnFe$_2$O$_4$ (60 nm particle size) as an example. For this composite temperature, dependences of the complex dielectric permittivity at different frequencies and frequency dependences of complex dielectric permittivity at different temperatures are shown in Figure 4 and 5, respectively. For comparison in Figure 4, the data for pure epoxy resin are plotted. In the temperature range of 150–250 K, the imaginary part of \(\varepsilon\) versus \(T\) and \(\nu\) is characterized by maxima, whose position is frequency- and temperature-dependent, respectively. With increasing frequency, the maximum of \(\varepsilon''(T)\) expands and shifts toward higher temperatures (Figure 4, right), whereas during cooling, the maximum of \(\varepsilon''(\nu)\) expands and shifts toward lower frequencies (Figure 5, right). The real part of \(\varepsilon\) versus \(T\) (Figure 4, left) and \(\nu\) (Figure 5, left) decreases with increasing frequency and decreasing temperature, respectively. Similar behavior was observed for each composite below the percolation threshold of both sizes, as well as for pure epoxy (see open symbols in Figure 4). This behavior is because of the dipole relaxation.\(^{[20]}\)

The relaxation time, defined as the reciprocal frequency value at the maximum of the imaginary part at a fixed temperature, increases according to the Vogel–Fulcher law with cooling (Figure 6):

\[ \tau = \frac{1}{\nu_{\text{max}}} = \tau_0 e^{\frac{E_b}{k_B(T_0 - T)}} \]  

where \(\tau_0\) is the relaxation time at very high temperatures, \(E_b\) is the activation energy, and \(T_0\) is the glass transition temperature.

![Figure 4](image-url)  
Figure 4. Temperature dependence of the complex dielectric permittivity for pure epoxy resin (open symbols) and epoxy composite (close symbols) with 20 vol% MnFe$_2$O$_4$ (60 nm particle size) at different frequencies.
The approximation parameters and their standard errors are shown in Table 2.

In composites, the glass transition temperature decreases with the MnFe$_2$O$_4$ concentration of any size compared with pure epoxy resin. Moreover, when concentration increases, the glass transition temperature slightly increases for smaller particles (28 nm) and decreases for larger particles (60 nm). For smaller particles, an increase with the concentration of the glass transition temperature is due to the decrease in the interfacial space between the polymer and nanoparticles, and the opposite situation is observed for larger particles.

2.3. Electrical Conductivity

For composites below the percolation threshold (e.g., Figure 4, right) at high temperatures (above 380 K), the imaginary part of the dielectric permittivity increases strongly and becomes higher than the real part, which means that the composite has become conductive. Indeed, (Figure 7) at high temperatures, the frequency dependence of the electrical conductivity demonstrates a frequency-independent plateau at low frequencies (corresponds to DC conductivity), and region increasing with frequency at high frequencies (corresponds to AC conductivity).

Therefore, the frequency dependence of the electrical conductivity can be fitted according to the universal power law

$$\sigma = \sigma_{DC} + A\omega^s$$

where $\sigma_{DC}$ is the DC conductivity and $A\omega^s$ is the AC conductivity. DC conductivity values for all investigated MnFe$_2$O$_4$/epoxy composites with 28 nm particle size are shown in Figure 8.

For composites below the percolation threshold (10–25 vol%) and for pure epoxy resin, DC conductivity values were obtained at higher temperatures only, above 380 K. This DC conductivity appearance is due to the epoxy resin becoming conductive at high temperature. $\sigma_{DC}$ can be fitted by Arrhenius law:

$$\sigma_{DC} = \sigma_0 \exp \left( - \frac{E_A}{k_B T} \right)$$

where $\sigma_0$ is the pre-exponential factor and $E_A$ is the conductivity activation energy. Obtained parameters are shown in Table 3. In composites, the conductivity activation energy decreases with filler concentration.

For composites above the percolation threshold (30 vol%), the DC conductivity is already observed at room temperature and also increases its absolute value during heating.

A similar conductivity behavior was observed for all other investigated MnFe$_2$O$_4$/epoxy composites with 60 nm particle size.
3. Conclusion

Dielectric properties of epoxy composites containing the different additions of MnFe₂O₄ with two spherical particle sizes (28 and 60 nm) have been studied in the wide frequency range from 20 Hz to 1 MHz. It was demonstrated that the percolation thresholds in such systems are 30 and 29.3 vol% for small and large MnFe₂O₄ particle, respectively. The small difference in the percolation threshold value is related with better distribution of larger nanoparticles. Above 380 K, the electrical conductivity is typical for all composites, both below and above percolation threshold due to the electrical transport in polymer matrix. The activation energy strongly decreases with MnFe₂O₄ concentration indicating that the electrical transport occurs together in MnFe₂O₄ and epoxy matrix subsystems.

4. Experimental Section

The commercially available MnFe₂O₄ nanopowder with two spherical particle sizes (28 and 60 nm) was used as a filler (https://www.us-nano.com/inc/sdetail/7019 and https://www.us-nano.com/inc/sdetail/595). Both nanopowder sizes were easily dispersed in the polymer matrix and enabled the production of composites with high volume concentrations.

In this work, a series of composite samples were produced using epoxy resin Epikote 828, a curing agent called triethylenetetramine (TETA) and 10, 20, 23, 25, 28, and 30 vol% of MnFe₂O₄ nanopowder filler. The procedure of composite manufacturing were described in detail in Bychanok et al. In summary, the MnFe₂O₄ nanopowders were mechanically crushed and stirred in ethanol during half an hour. Then, the particles were dispersed in ethanol with an ultrasonic bath for 1 h. Afterward, the alcoholic suspension of MnFe₂O₄ nanopowder was mixed with the epoxy resin and underwent ultrasonication by a probe for 2 h. After the ethanol evaporation, TETA hardener was added to the resulting mixture of epoxy resin and the mixture was degassed before pouring into the mold.
and MnFe$_2$O$_4$ particles, and mechanically mixed for 5–7 min. The blend was poured into molds and left in them for 20 h at a temperature of room temperature, and then for 2 h in an oven at a temperature of 200 °C. All composite preparation technology conditions were varied to obtain the lowest percolation threshold; it was determined that the aforementioned conditions were optimal.

The surface morphology was studied by SEM using a Helios NanoLab 650 microscope.

The complex dielectric permittivity was measured using an LCR HP4284A meter in the frequency range from 20 Hz to 1 MHz. Each measurement was followed by heating at 500 K and then cooling at 150 K with a rate of 1 K min$^{-1}$ in an air atmosphere. Silver paste was used for contacting. The measurement’s accuracy was better as 1%. The electrical conductivity $\sigma$ was calculated according to $\sigma = 2\pi\nu\varepsilon\varepsilon''$, where $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon''$ is the imaginary part of dielectric permittivity, and $\nu$ is the measurement frequency.

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Conflict of Interest

The authors declare no conflict of interest.

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