

Silicon core-iron siloxane shell nanoparticle polymer composites with multiferroic properties

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ABSTRACT: Multiferroic (MF) composites based on nanoparticles consisting of a silica core and a shell of spin-variable Fe(III) complexes in a polymer matrix (polystyrene) were synthesized and characterized by different methods. The nanoparticles had the formula $80\text{SiO}_2 \cdot 20\{\text{Fe}[\text{OSi}(\text{Me})(\text{OEt})_2]_3\}$, and their particle size was on the order of 5–7 nm. Dielectric and electron spin resonance studies showed the presence of two types of Fe ions in the nanocomposite. Iron ions in the low-spin state [Fe(III)-LS] and iron ions in the high-spin state [Fe(III)-HS], which were bound by indirect exchange interactions through oxygen and silicon atoms $\{[\text{Fe(III)-LS}] - \text{O} - \text{Si} - \text{O} - [\text{Fe(III)-HS}]\}$ were responsible for the MF properties of the composites with core-shell nanoparticles. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2019**, *136*, 47681.

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INTRODUCTION

The phenomenon of weak ferromagnetism was first discovered experimentally by Neel¹ for iron oxide Fe_2O_3 and by Borovik-Romanov and Orlova² for manganese and cobalt oxides. The phenomenon was explained in the works of Dzyaloshinsky and Moriah,^{3–5} and it was shown experimentally that substances with weak ferromagnetism can exhibit the magnetoelectric (ME) effect.^{6,7} The ME effect consists of the appearance of electric polarization upon application of a magnetic field or the appearance of magnetization under an applied electric field. When an alternating electric field, $E(\omega)$ or $H(\omega)$ (ω is angular frequency), is applied to such substances, alternating response fields, $H(\omega)$ or $E(\omega)$, can be detected. The simultaneous application of alternating and permanent magnetic fields (H_0) or permanent electric fields changes the magnitude of the response and allows one control over ME effect. This opens up interesting possibilities for applications of multiferroics (MFs) in electronics and sensor technology.

Although the discovery of the ME effect and the emergence of the term MF (a material possessing two or more ferroid properties)

occurred in the 20th century, the MF research boom occurred in the first decades of the 21st century. This was due to the fact that in 2003, two groups of researchers reported significant ME effects in the epitaxial layers of BiFeO_3 , TbMnO_3 , and TbMn_2O_5 .^{8–10} After these reports were published, research on new MFs began around the world. Studies were conducted with both single-phase and composite materials: inorganic, organic, and organoelemental. To date, a huge number of inorganic materials has been investigated. The single-phase MFs studied primarily include BiFeO_3 , where the bismuth ion is replaced by Pb and K ions and the iron ion is replaced by Co, Mn, Mo, Nb, Ni, Sr, Ti, V, and Zr ions.^{11–13} The manganites MMnO_3 (where M is Dy, Eu, Y, or Ho)^{14,15} and the so-called charge-ordered MFs (RFe_2O_4 , where R is Dy, Lu, Y, etc., and $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$)¹⁶ were also investigated.

Close attention has been paid to composite MFs with laminar structures created by the successive growth of the ferroelectric and/or magnetic phases from both gaseous media and the solution on single-crystal substrates. To date, nanostructured columnar MFs have also been created. The entire variety of

inorganic composite MFs have been described in numerous reviews, for example, in refs. 17–20.

However, to date, a very limited number of organic and organometallic MFs have been discovered and investigated; we have been responsible for all of the published results. These are MFs based on organometallic complexes, in which polarization occurs via proton transfer in $(\text{Me}_2\text{NH}_2)\text{—M—}(\text{HCO}_2)_3$ formate complexes (where M is Mn, Co, or Ni).^{21,22} Another example is a compound with the reversible shift of the oxygen atom between Mn or Co in binuclear Mn(II)—O—Mn(II) and Co(II)—O—Co(II) complexes; these exhibit the ME effect due to a change in the exchange and spin-orbit interactions after the shift in the charge and spin densities.^{23–25} There was also a brief report on the possibility of creating MFs based on spin-variable iron complexes.²⁶ In this article, the synthesis, structure, and electrophysical properties of composites {MFs based on nanoparticles consisting of a silica core and a shell of spin-variable Fe(III) complexes introduced into a polymer matrix [polystyrene (PS)]} are described in detail. The new data will open up the possibility of obtaining new MFs based on multilayer nanoparticles that can be used at room temperature as biocompatible nanocomposites for tissue engineering and ME procedures in the treatment of skin diseases.^{27,28}

EXPERIMENTAL

The following chemicals used in this study were all purchased from Aldrich: tetraethoxysilane, trimethylchlorosilane, methyl triethoxysilane, anhydrous ferric chloride, tetrahydrofuran, and toluene.

In core-shell nanoparticles, the silica core $[(\text{SiO}_2)_n]$, about 5 nm in size, was synthesized by the hydrolysis of hyperbranched polyethoxysiloxane by the method described in ref. 29. As a precursor for the shell synthesis, we used tris(methyl diethoxysiloxy) iron $\{\text{Fe}[\text{OSi}(\text{Me})(\text{OEt})_2]_3$ or TMDESI} synthesized from sodium salt of methyl triethoxysilane and iron(III) chloride.³⁰ We synthesized the nanoparticles by mixing a 5% solution of silica in tetrahydrofuran (80% by weight in terms of silica) and 10% iron siloxane solution in toluene (20% by weight in terms of iron siloxane). Most nanoparticles corresponded to the formula $80\text{SiO}_2 \cdot 20\{\text{Fe}[\text{OSi}(\text{Me})(\text{OEt})_2]_3\}$ (the preparation and possible structure are shown in Figure 1). Furthermore, these nanoparticles are denoted as silicon-iron siloxane nanoparticles (SIONs). The particles size was determined by gel permeation chromatography analysis of trimethyl silyl blocked $(\text{SiO}_2)_n$ particles with a universal calibration curve for the dependence of the molecular weight on the particle size published in refs. 31 and 32. The particle size in this approximation was on the order of 5–7 nm, and in the dried form, they are a powder similar to nanosized aerosil.

The nanoparticles were mixed in toluene with the PS matrix polymer (Polystyren PSE-1, molecular weight $\approx 89,250$) in the following amounts: 5, 20, and 40 wt %. The samples were then dried *in vacuo* and hot-pressed in two stages: 120 °C for 30 min and 180 °C for 15 min. This regime was chosen because the thermogravimetric analysis of SIONs showed that they contained up to 15% of the residual solvents tetrahydrofuran and toluene

(Figure 2). The solvents are removed upon heating in two stages; the first stage corresponded to the low-temperature bimodal peak in the differential thermogravimetry curve (curve 2 in Figure 2). This stage terminated at 180 °C. A further increase in the temperature led to the destruction of the silica core and the TMDESI shell and led to the formation of iron oxides and silicon dioxide. This stage of decomposition corresponded to the exothermic peak in differential thermogravimetry curve (curve 3 in Figure 2). The thermooxidative transformations of the SIONs terminated near 600 °C, with the total weight loss being about 30%.

The nanoparticles and composites were characterized by transmission electron microscopy (LEO 912 AB OMEGA electron microscope, Zeiss, Germany) and electron spin resonance (Bruker EMX ESR spectrometer). Investigations of dielectric properties were carried out with a Novocontrol Alpha-A impedance analyzer and a ZGS Alpha Active Sample Cell dielectric cell with gold-plated disc electrodes 20 and 30 mm in diameter; disk electrodes of 10 μm thick Al foil were adhered to the samples by electrically conductive Dotite silver adhesive (Japan). Investigations by Fourier transform infrared (FTIR) spectroscopy (frustrated total internal reflection) were performed with a Nicolet iS50 FTIR spectrometer and a built-in FTIR attachment (diamond crystal, measurement conditions: resolution = 4 cm^{-1} , number of scans = 32). Thermogravimetry studies were performed with DERIVATOGRAPH-C instrument (MOM, Hungary) in air at a heating rate of 10 °C/min. To investigate the ME properties of the composites, samples 10 $\times$ 10 mm^2 and 150 μm thick were prepared with aluminum foil electrodes applied to the opposite surfaces. Samples were placed at the antinode of the magnetic field of Helmholtz coils. The coils were located in the resonator of the ESR spectrometer (in the field of the ESR spectrometer magnet). The Helmholtz coils and electrodes were connected to a Tektronix MSO 2012 oscilloscope and/or sinusoidal signal generator AKIP 3402 (depending on the type of experiment). The Helmholtz coils, fed from the AKIP 3402 signal generator, generated an alternating magnetic field $[H(\omega)]$ with an amplitude of 12.5 mT. A signal generator connected to the electrodes generated an alternating electric field $[E(\omega)]$ of 650 V/cm. The constant magnetic field (H_0), generated by the ESR magnet, was varied from 0 to 600 mT and was parallel to the alternating magnetic and electric fields $[H(\omega)]$ and $E(\omega)]$. The experimental setup is shown in Figure 3.

RESULTS AND DISCUSSION

The infrared spectra of the PS films filled with SIONs are shown in Figure 4.

The increases in the absorption of the bands at about 810, about 590, and 450 cm^{-1} were due to the increase in the total TMDESI content in the composites because the absorption bands in these regions refer to the asymmetric vibrations of FeO bonds.³³ An increase of the intensity of absorption bands in the region 1150–1000 cm^{-1} was associated with the increasing content of nanoparticles from 5 to 40% in the PS matrix. The shift of the absorption band of the asymmetric valence vibrations of SiOSi bonds from 1080 to 1047 cm^{-1} was caused by the appearance of a band at about 1045 cm^{-1} ; this was related to the vibrations of

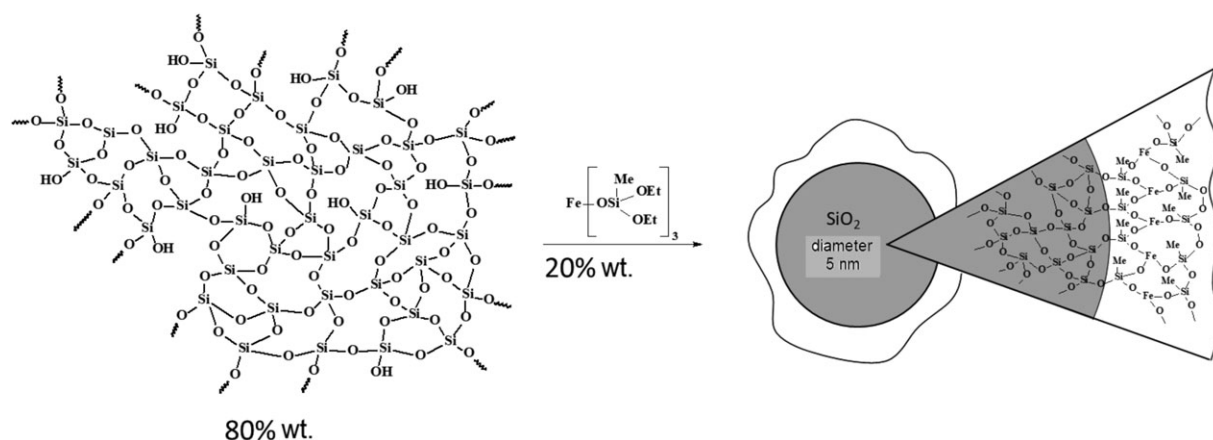


Figure 1. Synthesis and possible structure of the SIONs.

SiOFe bonds formed by the interactions of silica silanol groups with TMDESI or at a later stage during the hydrolysis of ethoxysilyl groups in the process of composite preparation.³⁴ Thus, we concluded that TMDESI was covalently bound to the silica core of the nanoparticles.

Scanning electron microscopy showed that the nanoparticles formed fairly uniformly distributed clusters in the polymer matrix in the form of ellipsoidal regions with dimensions of 20×60 to 40×100 nm² and about 10 nm thick [Figure 5(a–c)]. Electron diffraction showed that the composites were amorphous [Figure 5(d)].

Frequency dependences of the dielectric loss (ϵ'') at room temperature for composites with 5 wt % (curve 1) and 40 wt % SIONs (curve 2) are shown in Figure 6. Figure 7(a) shows the frequency dependence of ϵ'' at different temperatures for the composite with 40 wt % SIONs.

The contribution of the bulk conductivity [eq. (1) and curves 1c and 2c in Figure 6] and the relaxation process, described by the Havriliak–Negami function [eq. (2) and curves 1hn and 2 hn in Figure 6], were observed in the experimental frequency dependence of ϵ'' :

$$\epsilon^* = i \frac{\sigma}{\epsilon_0 \omega s} \quad (1)$$

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\alpha]^\beta} \quad (2)$$

where σ is the conductivity, ϵ^* is complex permittivity, ϵ_0 is electric constant, ϵ_∞ is high frequency permittivity, τ is relaxation time, α and β are parameters. For both composites, the frequency of the maximum (relaxation time) and the shape of the peak are practically the same, only the intensities differ by more than an order of magnitude. This relaxation process was due to the presence of SIONs, and its intensity increased with increasing concentration. In addition, the transition strength ($\Delta\epsilon$) differed significantly: for the composite with 5% of nanoparticles, it was 0.18, and for the composite with 40% of nanoparticles, it was 3.24. The value of $\Delta\epsilon$ was proportional to the concentration of dipoles (N_D) and the square of the dipole moment (μ_D) of the individual dipole.³⁶ Because $\Delta\epsilon$ increased superlinearly with respect to the concentration, we assumed that in addition to

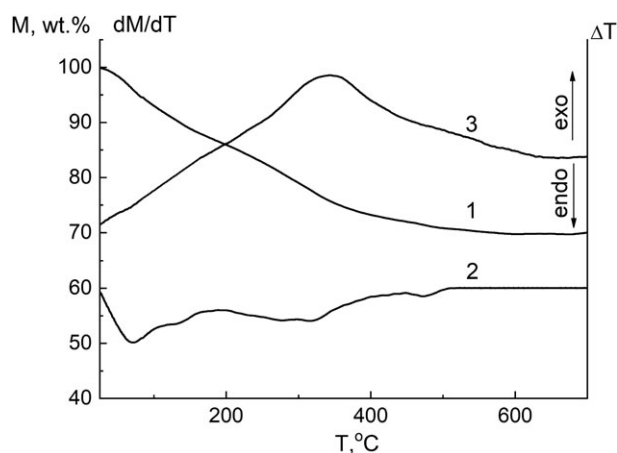


Figure 2. (1) Thermogravimetry, (2) differential thermogravimetry, and (3) differential thermal analysis curves for the SIONs at a heating rate of 10 °C/min in air. M, mass; T, temperature.

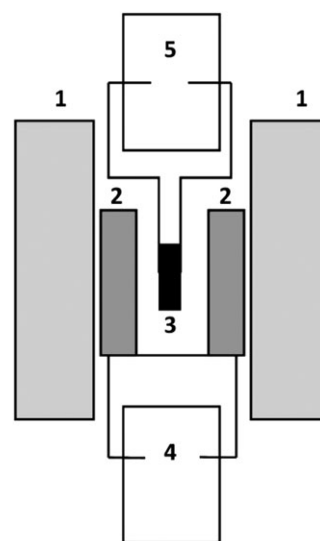


Figure 3. Block diagram of the measurement setup: (1) ESR spectrometer magnet, (2) Helmholtz coils, (3) sample, (4) signal generator, and (5) oscilloscope.

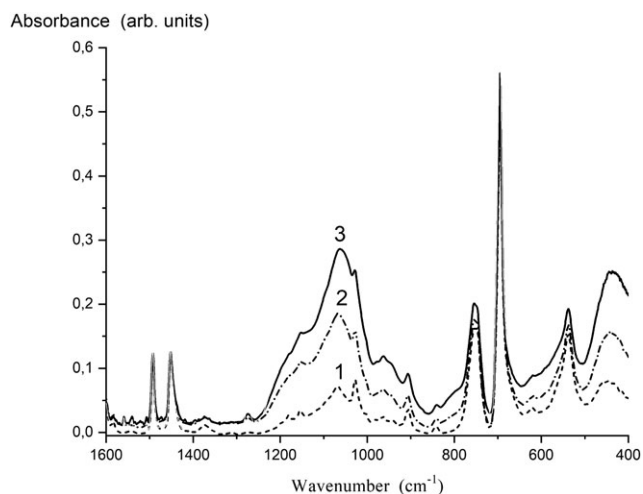


Figure 4. FTIR spectra of the PS films filled with SIONs at concentrations of (1) 5, (2) 20, and (3) 40 wt %.

the increase in the number of dipoles, the dipole moment also increased because of the interactions of nanoparticle shells, which led to increased polarizability.

The large value (0.1–0.01 s) of the relaxation time and the increase in the intensity of the process with increasing concentration of SIONs made it possible to identify it as a segmental relaxation process in the polymer matrix associated with the interface polarization process (the Maxwell–Wagner process) when the accumulation and relaxation of charge carriers occurred at the polymer–SION nanoparticle interface.³⁷ The value of direct-current conductivity of composites was about $10^{-13} (\Omega \text{ cm})^{-1}$. The alternating-current conductivity was weakly dependent on the frequency and was proportional to $\omega^{0.25}$; this indicated the hopping mechanism of conductivity between the SIONs in the volume of the polymer.

A comparison of dielectric properties of the composites, PS–40 wt % SIONs and PS–40 wt % $(\text{SiO}_2)_n$, allowed us to draw the following conclusions. The presence of the tris(methyl diethoxysiloxy) iron shell reduced the permittivity (ϵ') by almost two times (Figure 8). The shell shielded the silica core and reduced the concentration of hydroxyl groups on the surface; this, thereby, reduced the polarizability of the nanoparticle. An intensive relaxation process was observed for both nanocomposites (Figure 7). The amplitudes of the processes were practically identical; the activation energies (E_a s) in the temperature range where the relaxation time obeyed the Arrhenius equation were also practically equal ($E_a = 0.62 \text{ eV}$; Figure 9). For composites with nanoparticles without the shell, the

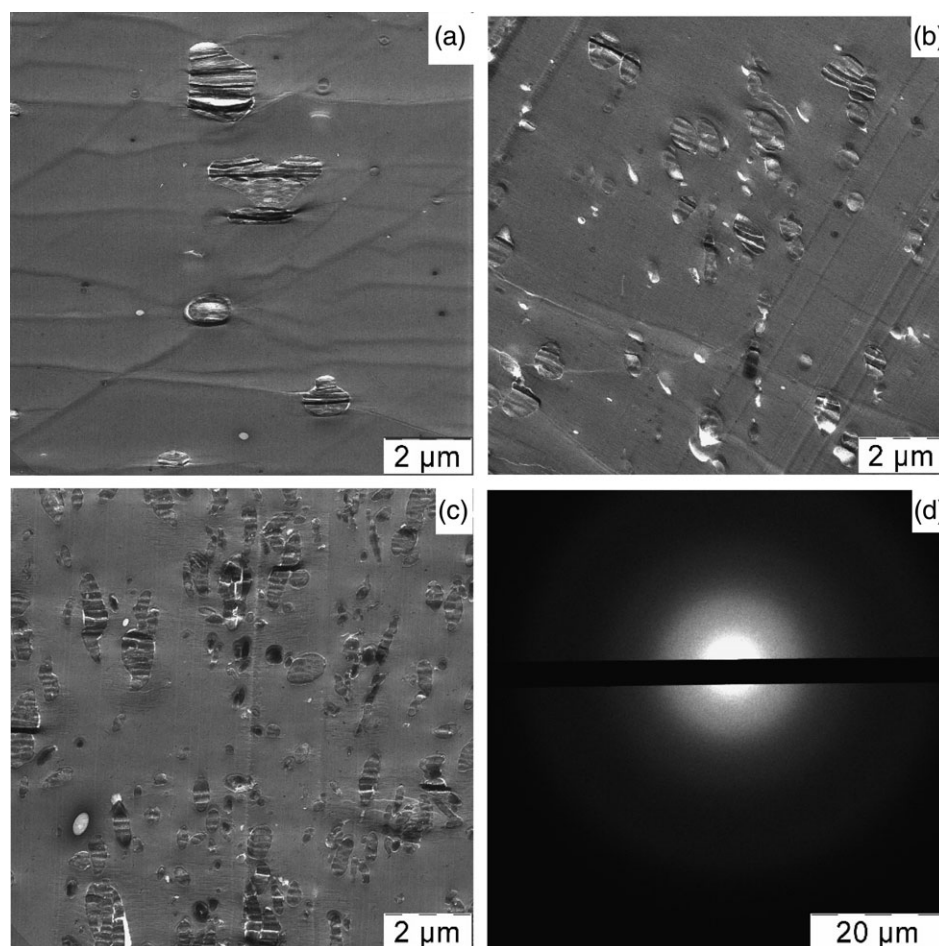


Figure 5. (a–c) Transmission electron microscopy microphotographs of the composites (5, 20, and 40 wt % SIONs) in the light field and (d) electron diffraction pattern for a composite (40 wt % SIONs).

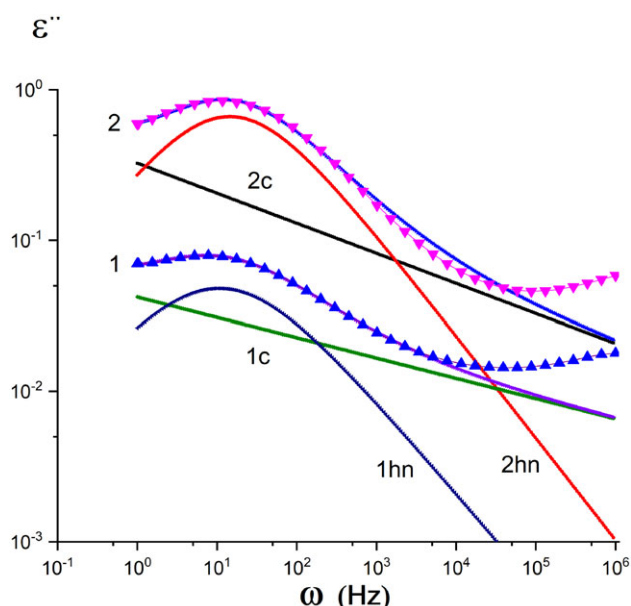


Figure 6. Experimental frequency dependence and approximation of ϵ'' at room temperature for the composites with (1) 5 and (2) 40 wt % SIONs: (1c,2c) conductivity contribution and (1hn,2hn) relaxation process as described by the Havriliak–Negami function.³⁵ The symbols represent experimental data, and the lines are approximations. [Color figure can be viewed at wileyonlinelibrary.com]

deviation from the linear Arrhenius dependence (Figure 9, curve 2) was observed; this was associated with the increasing intensity of segmental motion when the temperature dependence of the relaxation time followed the well-known Vogel–Fulcher–Tamman equation:

$$\tau(T) = \exp[E_a/(T - T_0)] \quad (3)$$

Here τ is relaxation time, T is temperature and T_0 is characteristic temperature. For the nanocomposite with a tris(methyl diethoxysiloxy) iron shell, the conductivity was somewhat higher

than the composite without the shell, and the values of E_a of conductivity were close (Figure 10). In the Cole–Cole diagrams, two relaxation processes were observed in both nanocomposites (Figure 11) with similar characteristics but displaced along the ϵ' axis for the silica particles because of their higher ϵ' . At the same time, a tail appeared in the silica particles nanocomposites with temperatures approaching the glass transition (Figure 11); this was caused by a sharp increase in the electrical conductivity. The high-frequency ($\sim 10^6$ c/s) weak relaxation process was due to the dipole group motions of polar groups in the polymer chain, and it had similar characteristics for both composites. The properties of the main process (1–10 c/s), on the contrary, differed; the transition strength values ($\Delta\epsilon'$) were 2.8 and 3.8 for composites without and with a shell, respectively. Because $\Delta\epsilon'$ was about $N_D(\mu_D)^2$, this difference was primarily due to the difference in the polarizabilities of the two types of nanoparticles, $(\text{SiO}_2)_n$ and SION, because of the presence of the TMDESI shell. The dielectric spectra of the nanocomposites are shown in the temperature range -30 to 30 °C. The nanoparticles themselves retained their structure up to higher temperatures; this is evident in Figure 2. Accordingly, such objects could operate for a long time at temperatures above 30 °C and were limited by the temperature stability of the polymer matrix.

Because the shell of the nanoparticles was composed of TMDESI, it was obvious that Fe(III) ions associated with the silica nucleus should have changed the spin–charge characteristics because of changes in the geometry of the bonds during the polarization of the nucleus. This point was not difficult to verify because the polarization of the composite was temperature-dependent. With the ESR method, room temperature, we observed an intense wide singlet (50 mT in width) was observed in the spectra in the region $g \approx 2.00$ where g is g -factor and a weak signal with a width of 15 mT in the region $g \approx 4.3$ (Figure 12). When the temperature was lowered to 77 K, the wide signal became broader, and the low-field signal increased in amplitude. Similar changes in the ESR spectra were due to the presence of iron ions in the low-spin state [Fe(III)-LS] with spin $S = 1/2$ in the investigated system (signal in the region $g \approx 2.00$) and iron ions in

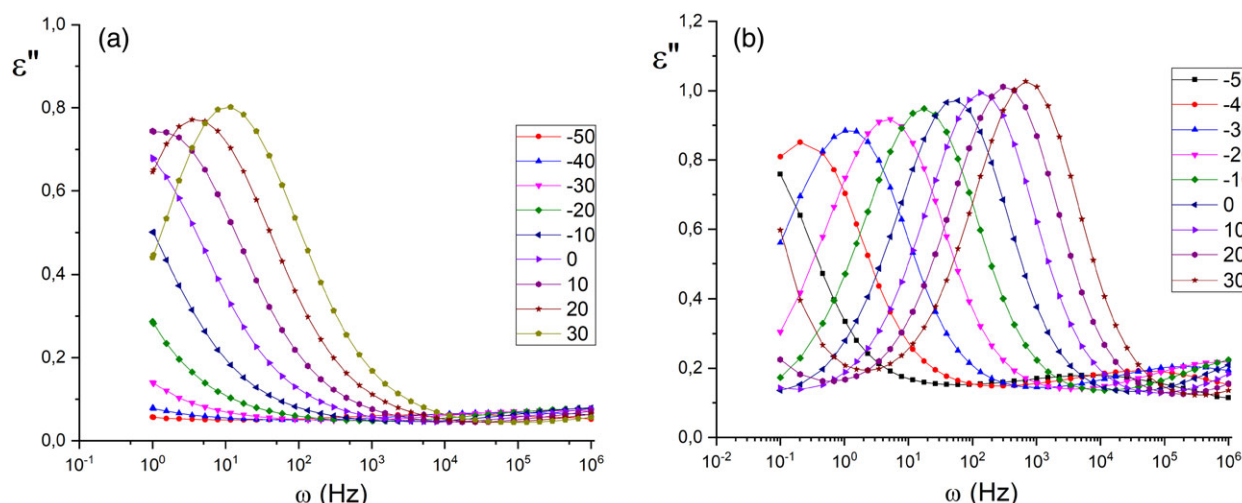


Figure 7. Frequency dependence of ϵ'' at different temperatures for the composites: (a) PS-40 wt % SIONs and (b) PS-40 wt % $(\text{SiO}_2)_n$. [Color figure can be viewed at wileyonlinelibrary.com]

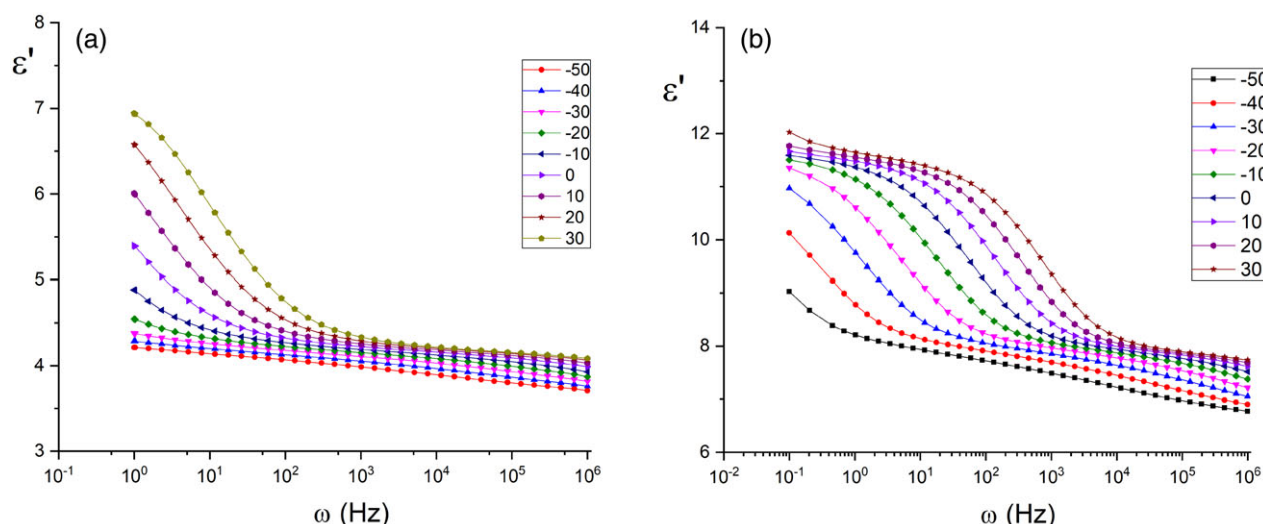


Figure 8. Frequency dependence of ϵ' at different temperatures for the composites: (a) PS-40 wt % SIONs and (b) PS-40 wt % $(\text{SiO}_2)_n$. [Color figure can be viewed at wileyonlinelibrary.com]

the high-spin state [Fe(III)-HS] with $S = 5/2$ (signal in the region $g \approx 4.3$).³⁸

It was shown in ref. 39 that both Fe(III)-LS and Fe(III)-HS covalently bound to oxygen atoms can exhibit MF properties. Taking into account this fact and supposing that the structure of the SIONs corresponded to that in Figure 1, we assumed that it was iron ions [Fe(III)-LS and Fe(III)-HS] that were bound by indirect exchange interactions through oxygen and silicon atoms [Fe(III)-LS—O—Si—O—Fe(III)-HS] that were responsible for the MF properties of the composites with SIONs. Thus, this composite was likely to exhibit dynamic magnetoelectric (DME) properties.

To establish the relation of the DME effect to the presence of Fe(III) complexes in the composites, comparative measurements were performed for the samples containing only silica nanoparticles.

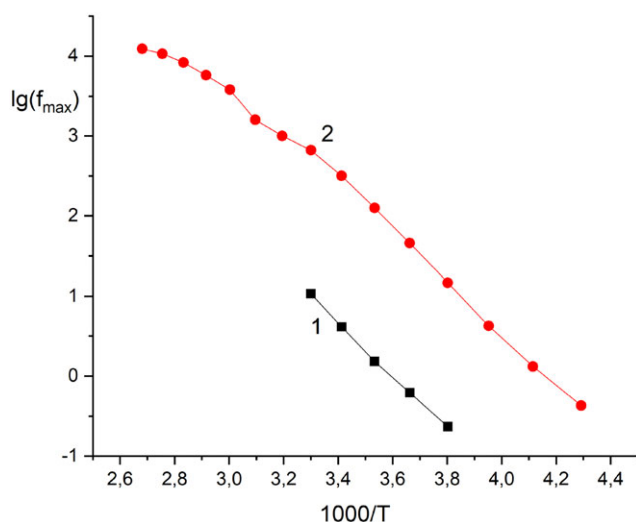


Figure 9. Arrhenius dependence of the frequency of the maximum of the relaxation transition for the composites: (a) PS-40 wt % SIONs and (b) PS-40 wt % $(\text{SiO}_2)_n$. [Color figure can be viewed at wileyonlinelibrary.com]

The DME effect was measured by the application of an alternating magnetic field $[H(\omega)]$ to the samples, with frequencies varying from 0 to 50 MHz, and the alternating electric field was measured for the samples:

$E(\omega) = V(\omega)/\delta$ where $V(\omega)$ is the alternating voltage at the aluminum electrodes and δ is the sample thickness. The value of the ME coefficient μ_E [$\mu_E = E(\omega)/H(\omega)$] was found to depend on ω_H and H_0 . Figure 13 shows the variation of μ_E with changing $H(\omega)$ for composites with SIONs (curve 1) and composites with silica nanoparticles (curve 2) when H_0 was 0. In spectrum 1 of the composite, when compared against the baseline (spectrum 2), there was an additional absorption band of A_E with a maximum at 32.3 MHz and, apparently, a broad band with a maximum at 48–50 MHz. The intensity [$\mu_E(A) = E(\omega)/H(\omega)$] for the A_E band in the absorption maximum varied with changing H_0 . Figure 14 shows the change in the intensity of the A_E band at the absorption maximum as a function of H_0 . All values in Figure 14 were normalized to the maximum value for the A_E band.

The DME effect was also investigated under a sinusoidal electric field $[E = E(\omega)]$ with an amplitude of 10 V ($\omega_E = 0$ –50 MHz) applied to the sample. The resulting alternating magnetic field was registered with Helmholtz coils, and the value of the ME coefficient [$\mu_H = H(\omega)/E(\omega)$] varied with ω_E as shown in Figure 13 (spectrum 3 belongs to the sample of the composite with SIONs, and spectrum 4 belongs to the sample of polymer with silica particles). We observed that for this type of action, an additional absorption band (A_H) with a maximum at 34.8 MHz appeared in the spectra of the composite. The position of the maximum of A_H was independent on the external H_0 in the range 0–600 mT, whereas the intensity of this band at the absorption maximum varied. Figure 14 shows the change in the intensity [$\mu_H(A_H)$] of the A_H band at the absorption maximum as a function of the value of H_0 . All values of $\mu_H(A_H)$ were normalized to the maximum values of the band A_H . We also found that silica particles weakly absorbed the alternating electric field; this process was indicated by the appearance of a low-intensity band with a maximum at 32 MHz (curve 4 in Figure 13).

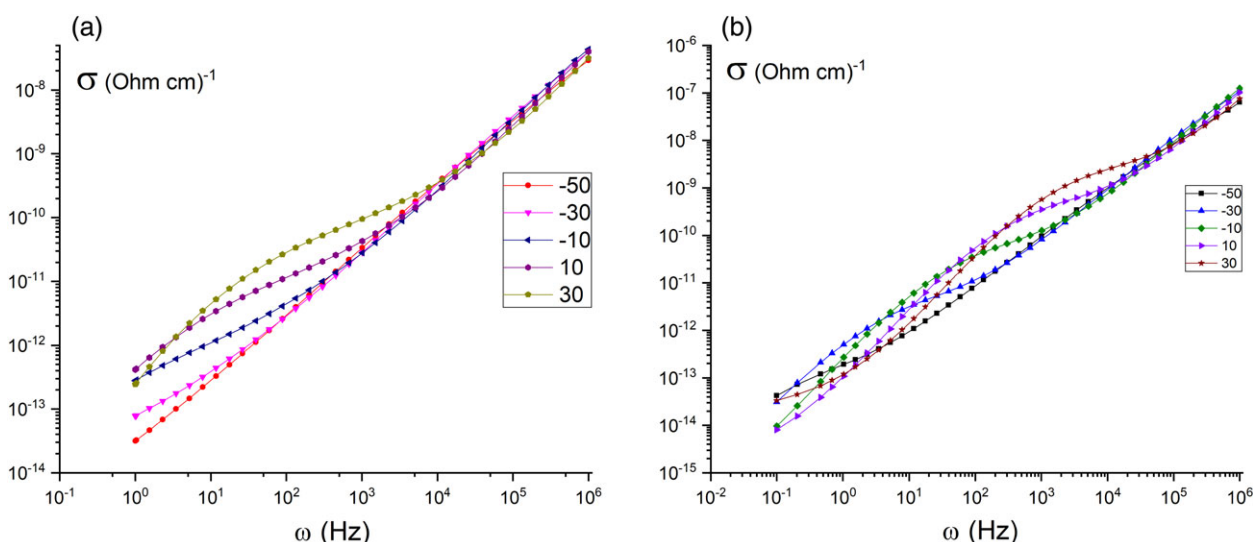


Figure 10. Frequency dependence of σ at different temperatures for the composites: (a) PS-40 wt % SIONs and (b) PS-40 wt % $(\text{SiO}_2)_n$. [Color figure can be viewed at wileyonlinelibrary.com]

This was consistent with the ϵ' data of the composites described previously. It has been previously theoretically justified that the DME effect should be observed in the form of banded spectra;⁴⁰ this also agreed with our data.

Figure 14 shows that the response to the alternating electric field appeared at a low field, the amplitude being almost five times higher [hysteresis loop $\mu_H(A_H)$ from H_0], and because the hysteresis loop was narrow, it corresponded to a narrow absorption line in the ESR spectrum (Figure 12), which was due to complexes $[\text{Fe(III)-HS}]$. At the same time, under the action of the alternating magnetic field, the hysteresis loop had a low intensity and was stretched over a constant magnetic field [the dependence of $\mu_E(A_E)$ on H_0 in Figure 14]; this was apparently correlated with the wide high-field absorption band in the ESR spectrum (Figure 12), which referred to the iron complex Fe(III)-LS . However, this assumption needs further study.

We did not find anisotropy of the multiferroic properties of the composites with different orientations of the sample with respect to the external magnetic field (H_0). For samples parallel or perpendicular to H_0 , the dependencies shown in Figure 14 were similar. This was probably because the nanoparticles with MF properties represented an almost spherical polycrystalline nucleus on the surface of which a monolayer of TMDESI was formed and whose molecules were also uniformly distributed in different directions. Indeed, one silica core 5 nm in diameter (radius $R = 25 \text{ \AA}$) was formed of about 2000 SiO_2 . The surface area of this particle was $7850 \text{ \AA}^2$. At the same time, the area covered by one TMDESI molecule was about $114 \text{ \AA}^2$. Thus, the surface of a single silica core could fit about 70 TMDESI molecules. Because the ratio of the components was such that silica nanoparticles were 80% by weight and TMDESI particles were 20%, it was easy to determine that one core of 2000 SiO_2 (120,000 AU) accommodated

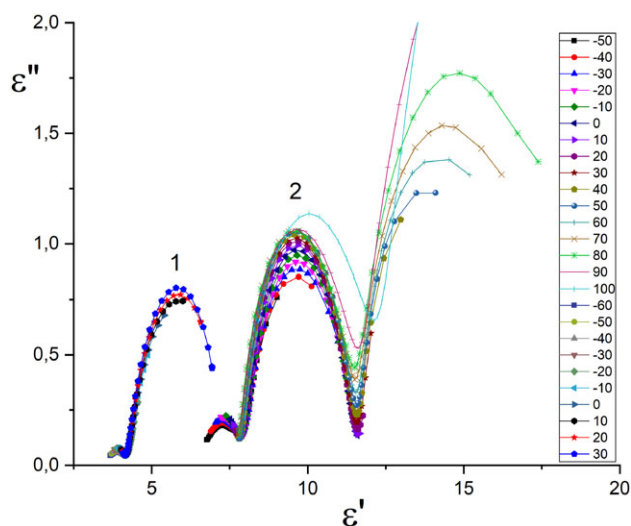


Figure 11. Cole-Cole diagrams for the composites at different temperatures: (a) PS-40 wt % SIONs and (b) PS-40 wt % $(\text{SiO}_2)_n$. [Color figure can be viewed at wileyonlinelibrary.com]

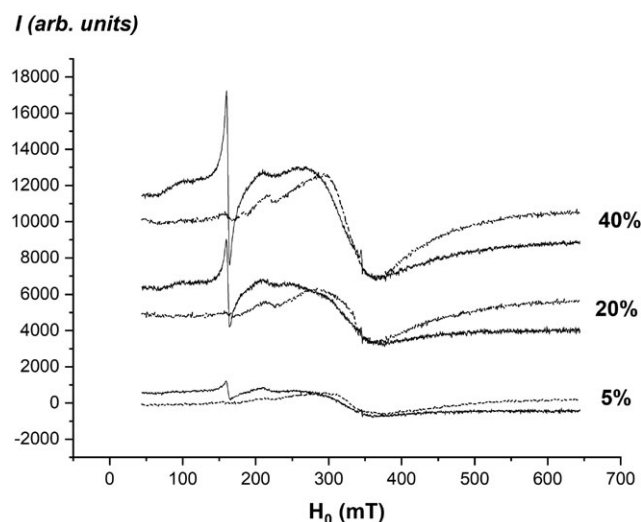


Figure 12. ESR spectra of the composites with 5, 20, and 40 wt % SIONs at room temperature (dashed lines) and 77 K (solid lines).

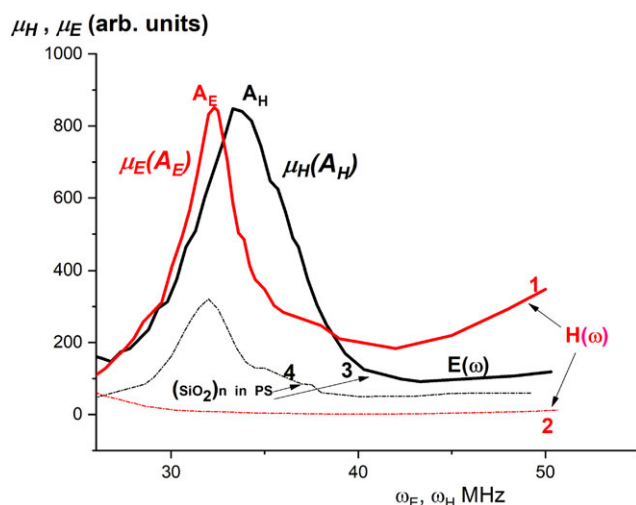


Figure 13. Variation of μ_H and μ_E as functions of $H(\omega)$ and $E(\omega)$, the frequencies of the alternating electric and magnetic fields, respectively, applied to samples at a constant value of $H_0 = 0$ mT for samples containing silica particles $[(\text{SiO}_2)_n]$ or SION particles in the PS matrix. [Color figure can be viewed at wileyonlinelibrary.com]

40,000 AU of TMDESI (atomic weight 503 AU); that is, about 80 molecules. Thus, we considered that the silica nanoparticles were coated with a monolayer of TMDESI. In the polymer matrix, the particles formed elliptical polycrystalline objects with dimensions of $200 \times 500 \text{ nm}^2$ and a thickness of about 50 nm. This is clearly shown in Figure 5(a–c). For these objects, electron diffraction did not reveal the presence of ordered structures [Figure 5(d)]. From this, it followed that the nanocomposites had an isotropic structure and did not exhibit anisotropy of ME properties.

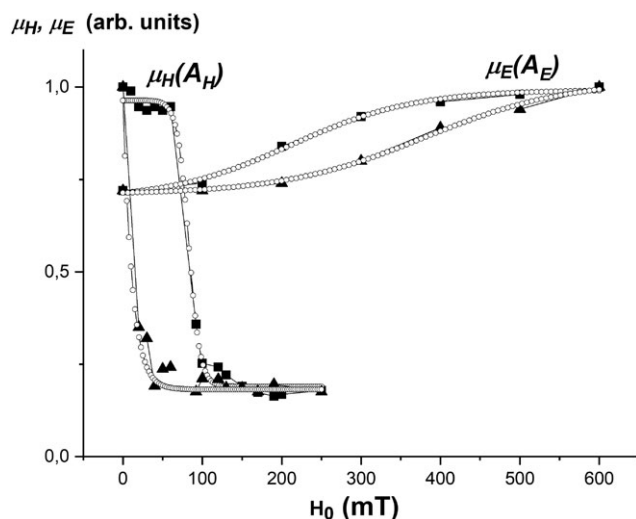


Figure 14. Variation in the values of μ_E for the A_E band at the absorption maximum (frequency of the alternating magnetic field = 32.3 MHz) with the value of the constant H_0 and variation in the values of μ_H for the A_H band at the absorption maximum (frequency of the alternating electric field = 34.8 MHz) with the value of constant H_0 . Solid symbols represent the experimental data, and hollow symbols represent approximations.

CONCLUSIONS

The previous investigation demonstrated the possibility of creating a new class of MFs: polymer composites operating at room temperature and above and based on nanoscale core-shell particles, where the silica nanoparticles act as nuclei and the Fe(III) complexes in the low-spin and high-spin states act as the shell. Fe(III)-LS and Fe(III)-HS, which were bound by indirect exchange interactions through oxygen and silicon atoms $[\text{Fe(III)-LS-O-Si-O-Fe(III)-HS}]$ ensured the MF properties of the composites with SIONs.

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Author Contributions

A. I. Aleksandrov supervised the research and wrote the manuscript. V. G. Shevchenko measured the dielectric properties and edited the manuscript. I. A. Aleksandrov measured the ME properties. N. A. Tebeneva, I. B. Meshkov, and A. A. Kalina synthesized the nanoparticles. E. N. Degtyarev, A. A. Dubinskii, and A. L. Kovarsky measured the ESR spectra. S. B. Zevin performed electron diffraction measurements. V. G. Krasovskii performed FTIR experiments. S. S. Abramchuk performed transmission electron microscopy investigations. M. I. Buzin performed the thermogravimetric analysis and differential thermal analysis experiments. A. M. Muzafarov supervised the synthetic strategies of the study.

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