Dielectric Performance of UHMWPE-MgFe$_2$O$_4$ Composites Depending on Polymer Crystallinity, and the Concentration and Size of Mechanochemically Synthesized Ferrite Particles

Tatiana Kiseleva 1,*; Tatiana Grigoreva 2; Svetlana Kovaliova 3; Maxim Il’in 1; Ekaterina Yakuta 1; Evgeniya Devyatkina 2; Inna Malyskina 1; Ilya Ivanenko 1; Sergey Vosmerikov 2 and Nikolay Lyakhov 2

1 Faculty of Physics, Moscow M.V. Lomonosov State University, 119991 Moscow, Russia; ilmax_v@mail.ru (M.I.); kipr@polly.phys.msu.ru (E.Y.); malysh@polly.phys.msu.ru (I.M.); ivanenko@physics.msu.ru (I.I.)
2 Institute of Solid State Chemistry and Mechanochemistry, SB RAS, 630090 Novosibirsk, Russia; grig@solid.nsc.ru (T.G.); zdekorator54@yandex.ru (E.D.); vosmerikov@solid.nsc.ru (S.V.); academ121@mail.ru (N.L.)
3 The Joint Institute of Mechanical Engineering, NASB, 220072 Minsk, Belarus; svetakov2021@gmail.com

Abstract: Mechanochemically synthesized particles of two types of magnesium ferrites, one of which with structural distortions and an average size of 170 nm, and another that is highly crystalline with an average size of 900 nm, were introduced into a matrix of ultra-high-molecular-weight polyethylene via the milling processing. The final material has been formed by hot pressing mechanocomposites based on ultra-high-molecular-weight polyethylene and magnesium ferrite particles of various fineness and concentration. Structural characteristics were studied using scanning electron microscopy, differential scanning calorimetry and X-ray diffraction analysis. The dielectric properties of the obtained composites were analyzed by testing the frequency dependence of the permeability, dielectric losses, and conductivity. The effect of filler concentration and particle size, as well as the crystallinity of the polymer, on the dielectric properties of the composite material were studied.

Keywords: magnesium ferrites; ultra-high-molecular-weight polyethylene; polymer crystallinity; mechanochemical synthesis; mechanocomposites; composite materials; dielectric properties

1. Introduction

Composite materials based on ultra-high-molecular-weight polyethylene (UHMWPE) modified with particles of magnetic oxides are very attractive for creating protective coatings on their characteristics, which are efficient in electromagnetic radiation personal protection of portable devices and humans, and for biomedical products such as stents changing their shape in external fields, etc. [1–3]. Materials based on UHMWPE are environmentally friendly because of their recyclability. UHMWPE is a semi-crystalline polymer that consists of crystalline and amorphous phases [4,5]. In the crystalline phase, the particular lamellar shape of crystallites is due to chain folding with the chain axis, which enlarges the chain fold area. In the amorphous phase, the chains are interconnected through occasional cross-links and random entanglements instead of proper chain folding. The crystallinity of UHMWPE depends on its volume percentage of crystallites. The UHMWPE properties are determined by links between the amorphous and crystalline phases. Enhancing the UHMWPE properties can be achieved by different methods through irradiation, surface modification, introducing effective textures, varying cross-linking, crystallinity percentage, reinforcements with particles or fibers [6]. Among the available publications, there are innovative developments related to the possibility of using composite materials based on UHMWPE to protect equipment from climate and environmental factors (exposure to aggressive media) [7–11], as well as their use as materials for microwave
applications [12] or substrates for dielectric resonators [13]. It is believed that for these purposes the polymer of choice should have a high permittivity, low dielectric losses, as well as high mechanical characteristics. At the same time, particles of both micro- and nano-sizes, of various shapes, may be used as fillers changing their electrical and thermal conductivity, with a deep effect on composite functionality [14–16]. Besides known modifiers, such as carbon fibers and graphene [17,18] and carbides [19], it was suggested to use iron oxides [20,21] as UHMWPE modification agents. Iron oxides (ferrites) have attracted the attention of researchers as components of composite modification due to their biocompatibility, low cost, chemical stability, and known unique magnetic and dielectric features. However, the properties of the obtained composite materials will depend on a number of factors such as the structural state of the polymer, composition, concentration, particle size and the crystallinity of oxide particles, interphase interaction at the particle–polymer boundaries. The uniformity of the distribution of particles in the polymer and the strength of the inter-particle interaction of fillers should be taken into account as well.

The dielectric properties of UHMWPE have been a subject of research for decades [14,21–24]. Polyethylene (PE) presents a very small dipole moment because of its non-polar chemical structure. The dielectric spectrum of UHMWPE is known to exhibit three main processes [25]. The $\alpha$-process is related to molecular fluctuations in the crystalline part. The $\beta$-process is assigned to the amorphous regions, and the $\gamma$-process is related to the mobile parts of the amorphous chains in the vicinity of the crystalline lamellae. Composites may demonstrate complex behavior with additional effects of the fillers and filler–to-polymer interactions.

In this work we have synthesized composites based on UHMWPE and ferrite MgFe$_2$O$_4$ particles using mechanosynthesized powder precursors followed by hot pressing. The choice of ferrite composition as model compound was due to its properties, low cost and known methods of synthesis. The aim was to study the effect of polymer crystallinity, ferrite particle size and concentration on the dielectric properties of composite materials.

2. Materials and Methods

The MgFe$_2$O$_4$ ferrite particles of different sizes as fillers were synthesized in two ways.

(1) The type 1 filler specimen was labeled as F-MS. Ferrite particles were synthesized by mechanochemical treatment from stoichiometric mixtures of MgO/Fe$_2$O$_3$ according to the reaction MgO + Fe$_2$O$_3$ $\rightarrow$ MgFe$_2$O$_4$. The mixture of magnesium and iron oxides was activated in a high-energy planetary ball mill AGO-2 (Russia) for 80 min. The drum volume was 250 cm$^3$, the ball diameter was 5 mm, the ball weight was 200 g, and the sample weight to be processed was 10 g. The drum rotation speed around the common axis was ~1000 rpm. Powders of MgO (analytical grade, sulfur-free: MgO = 98%, S = 0.002%, St_Petersburg, “Red Chemist”) and $\alpha$-Fe$_2$O$_3$ (analytical grade: 98.7%, St_Petersburg, “Vekton”) were applied.

(2) The type 2 filler specimen was labeled as F-MSA. The mechanosynthesis in mixtures of MgO/Fe$_2$O$_3$ was followed by annealing in a furnace at 1150 °C for 8 h.

To form a polymer/ferrite composite we used UHMWPE powder manufactured by Ticona GmbH (Germany), with a particle size of 100–160 µm and a molecular weight of $4 \times 10^6$ g mol$^{-1}$. Composite powder precursors were obtained by joint mechanical activation of xF-MS/(100 – x) UHMWPE and xF-MSA/(100 – x) UHMWPE mixtures in AGO-2 for 2 min. Two series of specimens with UHMWPE/ferrite mutual compositions: $x = 15, 30, \text{ and } 50$ wt.% were prepared. Then, these precursors were used for compacting in molds on an industrial press at 5 T in a temporary mode with heat treatment at a temperature of 120 °C. In this way, round tablets with dimensions of Ø5 × 5 mm were prepared.

X-ray structural analysis (XRD) of particles and composites was performed using an Empyrean diffractometer (PANalytical, Malvern, Worcestershire, UK, CuK$_{\alpha}$-radiation 1.5418 Å).

The microstructure of particles was studied by scanning electron microscopy (SEM) using a Quanta 3D FEG electron microscope (FEI, Toledo, Spain) with secondary electrons
signals. For the collection of SEM data, samples were dusted on a carbon dust tape. Particle size distributions were analyzed using ImageJ software [26].

The composites were studied by means of differential scanning calorimetry (DSC) using a DSC 8000 calorimeter (Perkin Elmer, Inc., Waltham, MA, USA), operating under an argon flow. Samples were sealed in corundum pans. A heating rate of 20° min⁻¹ was chosen to heat the samples from room temperature (25 °C) up to 200 °C.

The measurement of dielectric properties was carried out on a Novocontrol Concept 40 broadband dielectric spectrometer (Novocontrol Technologies, Hundsangen GmbH, Germany) in the frequency range from 10⁻¹ to 10⁷ Hz at room temperature. The sample material was mounted in a sample cell between two gold-plated electrodes forming a sample capacitor. The complex permittivity ε' of the sample was determined at room temperature by applying an alternating voltage \( U^\ast(\omega) = U_0\exp(i\omega t) \) with a fixed frequency \( f = \omega/2\pi \).

The voltage applied to the capacitor causes a complex current \( I^\ast(\omega) = I_0\exp(i\omega t + \varphi) \) flowing through the specimen, where \( \varphi \) is the phase angle between the voltage and the current. In this case, \( \varepsilon^\ast(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = -\frac{1}{\varepsilon_0 Z^\ast(\omega) C_0} \), where \( Z^\ast(\omega) = U^\ast(\omega)/I^\ast(\omega) \) is the complex impedance of the sample; \( C_0 \) is the capacity of a void capacitor of the same geometry.

3. Results and Discussion

F-MS ferrite particles were synthesized in irregular shapes with a size distribution from 100 nm to 2 μm. The mean particle size was 170 nm (Figure 1a,c).

![Figure 1](image)

**Figure 1.** SEM images and the corresponding particle size distributions from XRD phase analysis of MgFe₂O₄ ferrite powders, used as polymer fillers: F-MS (a,c), F-MSA (b,d).

F-MSA particles were obtained in a highly crystalline form with a size distribution from 200 nm to 7 μm, and the mean particle size was 900 nm (Figure 1b,d).

The main phase in the mechanochemically synthesized F-MS particles according to the XRD analysis was the cubic MgFe₂O₄ in a disordered state (Figure 2a). The main phase
of the annealed ferrite particles F-MSA was also the cubic MgFe$_2$O$_4$ phase but in a highly crystalline state.

![Figure 2](image1.png)

**Figure 2.** XRD patterns of MgFe$_2$O$_4$ ferrite particles F-MS, F-MSA (a) and UHWMPE (b).

Industrial UHMWPE powder has a mixed amorphous–crystalline state, in which the crystal structure is represented by orthorhombic (o) and monoclinic (m) phases distributed uniformly in the amorphous phase (Figure 2b).

X-ray phase analysis of the UHMWPE/F-MS and UHMWPE/F-MSA composites (Figure 3a,b) showed the absence of new phase formation: the diffraction pattern contains only structural maxima for UHMWPE and ferrite particles with only some changes in relative intensities, following to their mutual contents. An analysis of the line profile of composites via concentrations of the F-MS and F-MSA fillers indicates a decrease in grain sizes, both for ferrite particles and UHWMPE, relatively to the initial state.

![Figure 3](image2.png)

**Figure 3.** XRD phase analysis of xMgFe$_2$O$_4$/(100 − x) UHMWPE: F-MS (a), F-MSA (b).

The grain size of the ferrite phase is smaller compared to the initial state; the greater the concentration of particles in the composite is due to grinding as a result of the interaction between the plastic polymer and the enriched brittle ferrite components.

According to the XRD data, UHMWPE changed its degree of crystallinity. The corresponding part of the amorphous component disappeared with an increase in the F-MS and
F-MSA concentrations (Figure 3a,b). However, it was difficult to estimate the degree of UHMWPE crystallinity from the X-ray data with a high degree of reliability because of the significant difference in the scattering factors of UHMWPE and ferrite particles, and also due to the fact that the amorphous phase changes its composition resulting in ambiguous interpretation.

To estimate the degree of polymer crystallinity, we applied DSC curve analysis. DSC data (Figure 4a,b), obtained in the range of the UHMPE melting temperature, show some features related to polymer state. The melting temperature $T_m$ and enthalpy of melting $\Delta H_m$ were determined from the position and area of the heat effect peaks, respectively. Then, the degree of crystallinity was calculated by dividing the melting enthalpy of a sample by that of 100% crystalline UHMWPE (299 J g$^{-1}$) [27].

The degree of crystallinity ($X_{DSC}$) of UHMWPE/ferrite composites was determined according to [27]: $X_{DSC} = \left[\frac{\Delta H_c}{\Delta H_m^0(1 - x)}\right] \times 100\%$, where $\Delta H_c$ is obtained from the area of the melting peak, $\Delta H_m^0$ is the enthalpy of melting for 100% crystalline UHMWPE, and $x$ is the weight fraction of the particles.

Another parameter, the intra-chain cooperativity of melting, $\nu$, was determined according to the formula $\nu = 2R(T_{min})^2/\Delta T \cdot \Delta H^0$, where $R$ is the gas constant. $\nu$ determines the minimum number of repeating units in the chain sequence, transitioning as a whole from the crystallite to the minimized state of the polymer coil in a melt [28]. The dimensionless parameter expresses the number of CH$_2$ groups in the trans-region of the polymer chain that participate simultaneously in the act of melting. When $\nu$ is multiplied by the length of the C–C single bond, parameter $L = \nu h$ ($h = 0.124$ nm) can be compared to those of the supramolecular structure, including the dimensions of the lamellar formations [29].

The results of DSC analysis are presented in Table 1. It is evident that as a result of mechanical activation of UHMWPE with ferrite particles, the polymer structure is divided into regions with different melting temperatures, which are associated with changes in the sub-molecular structure of the polymer, that is, with the appearance of regions with different melting temperatures, and finally with change in the degree of crystallinity of UHMWPE. With an increase in the concentration of ferrite particles in UHMWPE, an increase in the size of lamellae and the parameter of intra-chain cooperativity was observed.
Table 1. The results of the DSC measurements (\(T_{\text{onset}}\), \(T_{\text{max}}\), \(T_{\text{end}}\)—temperatures of onset, max and end of the polymer melting, respectively, \(\Delta H\)—melting enthalpy, \(\nu\)—intra-chain cooperativity of melting, \(L\)—lamellar size, \(X_{\text{DSC}}\)—crystallinity degree).

<table>
<thead>
<tr>
<th>Samples</th>
<th>(T_{\text{onset}}) °C ±0.5</th>
<th>(T_{\text{max}}) °C ±0.5</th>
<th>(T_{\text{end}}) °C ±0.5</th>
<th>(\Delta H_m) J g(^{-1}) ±0.5</th>
<th>(\nu) ±13</th>
<th>(L), nm ±3</th>
<th>(X_{\text{DSC}}), % ±10</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE initial</td>
<td>117.5</td>
<td>154.4</td>
<td>180.3</td>
<td>175.5</td>
<td>160</td>
<td>20</td>
<td>69</td>
</tr>
<tr>
<td>15F-MS/85UHMWPE</td>
<td>129.7</td>
<td>148.7</td>
<td>178.1</td>
<td>136.2</td>
<td>204</td>
<td>25</td>
<td>53</td>
</tr>
<tr>
<td>30F-MS/70UHMWPE</td>
<td>128.5</td>
<td>146.7</td>
<td>167.2</td>
<td>98.8</td>
<td>253</td>
<td>31</td>
<td>47</td>
</tr>
<tr>
<td>50F-MS/50UHMWPE</td>
<td>129.7</td>
<td>143.4</td>
<td>165.1</td>
<td>90.4</td>
<td>272</td>
<td>34</td>
<td>35</td>
</tr>
<tr>
<td>15F-MSA/85UHMWPE</td>
<td>129.1</td>
<td>153.6</td>
<td>181.4</td>
<td>133.2</td>
<td>194</td>
<td>24</td>
<td>52</td>
</tr>
<tr>
<td>30F-MSA/70UHMWPE</td>
<td>130.1</td>
<td>146.2</td>
<td>175.5</td>
<td>101.2</td>
<td>225</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>50F-MSA/50UHMWPE</td>
<td>130.2</td>
<td>144.3</td>
<td>171.9</td>
<td>85.3</td>
<td>232</td>
<td>29</td>
<td>33</td>
</tr>
</tbody>
</table>

A decrease in the degree of polymer crystallinity is observed with an increase in the concentration of particles (Figure 5).

Figure 5. The degree of polymer crystallinity dependence via the concentration of particles.

UHMWPE consists of a carbon chain with hydrogen side groups with an exceptionally high molecular weight, and its dielectric permittivity is usually constant in the broad frequency range but the value depends on the production method, density, and degree of crystallinity [28]. MgFe\(_2\)O\(_4\) is magnetically dielectric, but its properties highly depend on size and structural perfection. The measured frequency dependence of the real part of the permittivity \((\varepsilon')\) (Figure 6a,b) and the loss tangent \((\tan\delta)\) plotted in Figure 6c,d for the composites, demonstrates different behavior both on the particle size and concentration.

The presence of ferrite particles in the synthesized composites reduces the UHMWPE dielectric constant and increases the value of losses. For specimens with 15, 30%, 50% F-MS, a constant value of the dielectric coefficient is observed in the entire frequency range up to \(10^7\) Hz. In samples with F-MSA, a constant value is observed for 15 and 30%, but the higher concentration leads to a relaxation behavior of pure micron-sized ferrites where \(\varepsilon'\) decreases with increasing frequency in the range from 1 kHz to 1 MHz. At a certain frequency \((\sim 10^2\) Hz) and characteristic of a particular composition \((x = 50\%)\), this decrease slows down and becomes constant.

A model description of the permeability behavior for ferrites is carried out on the basis of the migration model and spatial charge polarization. In the case of composites, it is necessary to take into account the polarization effects at the particle-to-polymer interface. In composites, the larger the value of \(\varepsilon'\) at low frequencies is most likely determined by the contribution from the polarization of the interface and space charge, which is formed due to the inhomogeneous structure.
Figure 6. Frequency dependences of the real part of permittivity $\varepsilon'(f)$ (a,b), dielectric losses $\tan\delta(f)$ (c,d) and conductivity $\sigma(f)$ (e,f) for F-MS/UHMWPE and F-MSA/UHMWPE composites with different concentrations.

All dielectric materials have two types of losses. One is a conduction loss, representing the flow of actual charges through the dielectric material. The other loss is due to the movement or rotation of atoms in an alternating field. $\tan\delta$ for samples with a particle concentration of 15 and 30% is practically independent of the particle size; however, at a higher concentration of particles, this value increases 10 times for samples with large and perfect particle sizes. From several known models determining the possible behavior of the composite, the final permittivity uses the assumption that particles have regular shape and single dispersion. In our case, the particle size distribution and its irregular shape may be accounted for in the model of effective medium where the inclusion of particle shape and size might not be the same throughout the polymer matrix.
The larger particles and interaction between them will determine the inter-particle interaction and increase in conductivity level (Figure 6e,f). The factors contributing to the carrier mobility are single chain or intramolecular transport, interchain transport, and inter-particle contact. These factors comprise a complicated resistive network which determines the effective mobility of the carriers. The level of conductivity just increases in composites with a high concentration of larger particles being in contact in the agglomerates and rising mobility of the carriers.

Using smaller particles let us achieve more homogeneity of the composite, and surprisingly the conductivity is practically independent of the concentration of composites, most likely determined by the conductivity of the UHMWPE only. The decrease in UHMWPE crystallinity at increasing particle concentrations and sizes acts as a factor in the fascination of inter-particle contact interactions, resulting in the observed dielectric properties.

4. Conclusions

Two types of magnesium ferrite particles were synthesized mechanochemically: one with a disordered structure and an average size of 170 nm, and one highly crystalline with an average size of 900 nm. It was shown that during mechanical treatment, when ferrite particles of both types are introduced into the UHMWPE matrix, a composite structure is formed without chemical interaction of ferrite with the polymer.

An increase in the concentration of ferrite particles leads to a decrease in the degree of crystallinity of UHMWPE, while the rate of decrease is significantly higher for larger ferrite particles.

The presence of ferrite particles in the synthesized composites reduces the dielectric permittivity of UHMWPE and increases the losses. For composites with finer ferrite particles, a constant value of the dielectric permittivity is observed over the entire frequency range of up to 107 Hz. In samples with large ferrite particles, a constant value of the dielectric coefficient is observed at a ferrite content of up to 30%. A higher concentration of MgFe$_2$O$_4$ leads to the dielectric relaxation behavior of pure micron-sized ferrites.

The conductivity of composite structures is determined by the size of the introduced ferrite particles and the interaction between them. The level of conductivity of the composite increases at higher concentrations of larger particles. The use of smaller particles makes it possible to achieve greater homogeneity in the composite, and the conductivity does not depend on the concentration of the introduced magnesium ferrite.

The dielectric properties of the obtained composite materials vary depending on the concentration of the filler and the size of its particles, as well as on the crystallinity of the composite polymer. Thus, this composite can be used to fabricate materials where the mechanical properties of the polymer are required along with variable electrical characteristics.

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