Magnetic Properties of Poly(trimethylene terephthalate-block-Poly(tetramethylene oxide) Copolymer Nanocomposites Reinforced by Graphene Oxide–Fe₃O₄ Hybrid Nanoparticles

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Thermoplastic elastomeric nanocomposites based on poly(trimethylene terephthalate-block-poly(tetramethylene oxide) copolymer (PTT-PTMO) and graphene oxide (GO)–Fe₃O₄ nanoparticles hybrid are prepared by in situ polymerization. Superparamagnetic GO–Fe₃O₄ hybrid nanoparticles before introducing to elastomeric matrix are characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The effect of loading (0.3 and 0.5 wt%) of GO–Fe₃O₄ nanoparticle hybrid on the phase structure, tensile, and magnetic properties of synthesized nanocomposites is investigated. The phase structure of nanocomposites is evaluated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Dispersion of GO–Fe₃O₄ nanoparticles in elastomeric matrix is evaluated by transmission electron microscopy (TEM). Magnetic properties of GO–Fe₃O₄ nanoparticle hybrid and nanocomposites with their content are characterized using two different techniques: direct current superconducting quantum interference device (dc SQUID) magnetization measurements as a function of temperature (from 2 to 300 K) and external magnetic field and ferromagnetic resonance (FMR) at microwave frequency.

1. Introduction

The interest in magnetic nanoparticles based on iron oxides is enormous due to their wide range of potential applications, especially in biomedicine, catalysis, waste water treatment, energy storage, and spintronics.[1–9] Magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are the most important ferromagnetic compounds among all iron oxides.[10] Saturation magnetization of magnetite reaches 92 emu g⁻¹ at room temperature (RT) in bulk material. In contrast, maghemite is more stable than magnetite, more biocompatible, although presenting a slightly smaller bulk saturation magnetization.

Recent intense research on graphene and its derivatives follows the trend of exploration of novel low-dimensional systems and is driven by possible promising applications of...
graphene-based magnets in spintronics. However, due to delocalized π bonding network, graphene lacks localized magnetic moments and is intrinsically nonmagnetic. Magnetic resonance spectroscopy measurements have confirmed theoretical predictions that in a single-layer graphene the carrier-mediated exchange interaction leads to antiferromagnetic coupling.[30] The same experimental technique was used to study the magnetic correlations at zig-zag edges of a single-layer graphene.[31] It was found that the zig-zag spins are ferromagnetically correlated. Point defects such as the zig-zag edge states, vacancies with the trapped electron, or chemical doping of foreign atoms, can introduce magnetic moments, but make the structural stability of graphene lower. Despite the efforts of increasing the magnetism of graphene materials, they usually display a weak Curie-type paramagnetism and magnetization below 0.2 emu g⁻¹. Recently, it has been demonstrated that N-doping of graphene oxide (GO) can dramatically increase its magnetization up to 1.66 emu g⁻¹ and makes the magnetism of GO change from purely spin-half paramagnetism to ferromagnetism with Curie temperature of ≈100 K.[8] In another work, it has been shown that it is also possible to inject spins to a single-layer graphene from an adjacent ferromagnetic material (dynamical spin injection).[32] A pure spin current was pumped into graphene from the processing magnetization of the ferromagnet with very high efficiency.

Many researchers have shown that integrating GO or reduced graphene oxide (RGO) with inorganic nanoparticles allows for the properties of the nanocomposite to be engineered for specific applications. For example, a new type of hybrid material—graphene/Fe₃O₄—has been recently synthesized and found a broad range of applications, e.g., in targeted drug delivery, magnetic resonance imaging, lithium-ion batteries, ion removal, sensor, catalysts, etc.[32,33] These multifunctional nanomaterials combine the beneficial effects of graphene—high conductivity and large surface-to-volume ratio—with strong magnetism, low price, and low environmental toxicity of magnetite. Magnetic properties of GO–Fe₃O₄ nanocomposites have been investigated by measuring magnetization of produced samples in an external magnetic field.[34–37] At RT no magnetic hysteresis loop was observed, as expected, because the blocking temperature of the nanocomposite was below RT. Saturation magnetization smaller than in magnetite nanoparticles was explained by low loading of Fe₃O₄ in nanocomposite. In each studied nanocomposite, monodispersed magnetite nanoparticles were successfully attached to graphene sheets.[37]

Graphene magnetic nanocomposites also include more complex systems such as Cu/GO/Fe₃O₄,[38–40] Ag/GO/Fe₃O₄,[41] Pd/GO/Fe₃O₄,[42,43] hybrids which were recently synthesized using plant extracts as biological materials under mild conditions. These hybrid nanocomposites can be used as magnetically separable and reusable catalyst for cyanoation of aldehydes to nitriles[38] or for the reduction of 4-nitrophenol and organic dyes.[39–41]

The dispersion of the highly exfoliated GO nanoplatelets decorated by Fe₃O₄ nanocrystals in polymer matrix is the crucial factor that determine the quality and reliability of nanocomposites and their expected magnetic properties. Shen et al.[44] have shown lightweight, multifunctional polyetherimide/graphene–Fe₃O₄ composites foams for shielding of electromagnetic pollution. Our recent studies have shown that introduction of small amount (up to 0.5 wt.%) of highly exfoliated GO,[45] graphene nanoplatelets (GNP), or hybrid system being a mixture of GNP and single-walled carbon nanotubes (SWCNT)[46–48] into polyester elastomeric nanocomposites, improved their mechanical properties and can provide them new functional properties as electrical and thermal conductivity.

In this work, superparamagnetic GO–Fe₃O₄ hybrid nanoparticles were prepared and used as nanofiller for polyester thermoplastic elastomeric matrix. The magnetic properties of the polyester thermoplastic polymer nanocomposite reinforced by GO–Fe₃O₄ nanoparticles hybrid were characterized using two different techniques: dc SQUID magnetization measurements as a function of temperature and external magnetic field, and FMR at microwave frequency. The results of measurements are correlated with morphological features of the studied samples.

2. Results and Discussion

2.1. Structural Characterization of GO–Fe₃O₄ Nanoparticle Hybrid

X-ray photoelectron spectroscopy (XPS) has been used to analyze the nature and the relative amount of iron and oxygen-containing functional groups present on the graphene surface. C1s XPS spectrum of GO synthesized via Hummers method is as follows: sp²-C: 6.09%; sp³-C: 42.26%; C—O: 18.49%; C=O: 24.32%; O=C—O: 4.40%; π—π: 1.16%. For GO–Fe₃O₄, C1s XPS spectrum shows: sp²-C: 56.59%; sp³-C: 23.91%; C—O: 9.65%; C=O: 4.57%; O=C—O: 4.15%; π—π: 1.13%; whereas, the O1s XPS spectrum (Figure S1, Supporting Information) shows: FeO₄: 66.88%, C=O/Fe–OH: 16.27%; C—O: 13.27%. After successful functionalization of Fe₃O₄, clearly visible changes in C1s XPS spectrum were observed. An increase of sp³ hybridized carbons from 6.09% to 56.59%, and at the very same time a decrease in sp² hybridized carbons from 42.26% to 23.91%, can be noted. The XPS spectrum of GO–Fe₃O₄ consists of functional groups such as sp² (C=C), epoxy/hydroxyl (C=O), carbonyl (C=O), and carboxylates (O—C=O).[49] Moreover, in the case of GO–Fe₃O₄, XPS spectra indicate the presence of FeO₄ in the amount of 66.88%, which certainly points to the chemical incorporation of iron oxide. To confirm the attachment of Fe₃O₄ nanocrystals on the surface of GO, the thermogravimetric analysis (TGA) in air was performed on as-received GO, GO–Fe₃O₄ hybrid, and Fe₃O₄ nanoparticles. The Fe₃O₄ nanocrystals content in the GO–Fe₃O₄ hybrid can be estimated from the residual weight percentages. The total weight loss of the Fe₃O₄ nanoparticles is 3.3% (Figure 1a) for the whole temperature range because of the removal of adsorbed physical and chemical water. As shown in Figure 1a, the TGA curves of GO show a three-step weight loss between 273 to 1073 K with a total weight loss of ≈98%, whereas GO–Fe₃O₄ hybrid in this temperature range undergoes a weight loss of 29.6%, which is closely related to the oxidation of GO and confirms high concentration of Fe₃O₄ nanocrystals (≈70 wt%) on GO nanosheets.

Figure 1b shows X-ray diffractions of GO–Fe₃O₄ and Fe₃O₄ nanoparticles synthesized in the same conditions.
The diffraction peaks at 30.26°, 35.60°, 43.35°, 53.76°, 57.25°, and 62.95° correspond to the (220) (311) (400) (422) (511) (440) and are in good accordance with the inverse cubic spinel phase of Fe₃O₄ (magnetite, JCPDS card No. 85-1436). Using the most intense reflection (311), the average size of Fe₃O₄ nanocrystals at GO surface was calculated to be 8.9 nm. In our earlier work, it was shown that the GO powder had characteristic diffraction peak at 2θ≈10° attributed to the (001) reflection. The disappearance of this peak in X-ray diffraction (XRD) pattern of GO–Fe₃O₄ hybrid suggests that the layer stacking of the GO sheets has been destroyed by the loading of Fe₃O₄ nanocrystals.

The morphology of synthesized GO–Fe₃O₄ nanoparticle hybrid and GO used for their preparation was characterized by scanning electron microscopy (SEM). As shown in Figure 2a, the surface morphology of GO resembles strongly folded curtain, which indicates that GO flakes were rather overlapped than aggregated. In contrast, when the synthesis of GO–Fe₃O₄ was carried out by an inverse chemical co-precipitation method, the formation of Fe₃O₄ took place on the GO sheets. SEM image (Figure 2b) shows that these Fe₃O₄ nanoparticles are densely distributed on GO sheets and they are not separated but decorated in bunches on the curled and thin wrinkled sheets, having a rather uniform distribution on the surface of GO. It can be observed from the SEM images that the average diameter of Fe₃O₄ nanocrystals at GO surface was around 10 nm, which is close to the value determined from the XRD pattern.

2.2. Dispersion of GO–Fe₃O₄ in the PTT-PTMO Matrix

The distribution of GO–Fe₃O₄ in poly(trimethylene terephthalate-block-poly(tetramethylene oxide) (PTT-PTMO) copolymer matrix was studied by transmission electron microscopy (TEM). Representative images of nanocomposites containing 0.5wt % of GO–Fe₃O₄ are shown in Figure 3. Nanocomposites exhibit rather uniform distribution of GO–Fe₃O₄ in the matrix (Figure 3a–e) and there were no large areas of GO that were not decorated with Fe₃O₄ nanoparticles. The high transparency of the GO sheets indicate that GO was well exfoliated into few layered sheets decorated by Fe₃O₄ nanocrystals. The observed morphology of GO–Fe₃O₄ at higher magnification have shown the sphere-like nanoparticles with sizes from 4 to 16 nm (Figure 3b–c,e) distributed on the surface of the GO sheets. Based on a total number of...
(N = 124) particle sizes determined from several TEM images (Figure 3f), an average Fe3O4 particle size of 9 nm (2.1 nm) was estimated, which is in good agreement with the particles size determined from XRD data. The areas with a more densely distributed nanoparticles (Figure 3d) were also observed locally. Likewise, the edges of GO flakes of several sheets can be clearly observed in Figure 3c. It can also be noted that Fe3O4 (Figure 3) were firmly attached to the GO sheets, that even preparation of specimen for TEM analysis did not affect the samples, which indicates that an excellent adhesion between GO and Fe3O4 particles has been achieved. Moreover, the presence of much smaller GO sheets densely decorated by Fe3O4 nanocrystals (Figure 3d) compared with the size of GO sheets used for preparation of these hybrid, was observed. Probably, due to high concentration of Fe3O4 nanocrystals (confirmed by TGA analysis) on GO sheets after inverse co-precipitation, some of them were cut into smaller pieces.

2.3. Effect of the Presence of GO–Fe3O4 on Phase Structure and Tensile Properties of Nanocomposites

In polyester block copolymers, the heterophase structure, which can be reproducible in heating–cooling cycles, is responsible for their elastic and thermoplastic properties. The presence of GO–Fe3O4 can affect their micro- and nanophase separation. When a synergy between the crystalline lamellae of polymer
and the hybrid nanofiller is created, the improvement in the macroscopic properties of these composites can be expected. Values of intrinsic viscosity \( [\eta] \), \( M_n \), and polydispersity (Table 1) of obtained composites are comparable to the values for the neat block copolymer. These results can indicate that at low loading of nanofillers, in situ polymerization allows obtaining materials with comparable values of molecular weight, which have no effect on phase separation structure.

The effect of the presence of GO–Fe₃O₄ in PTT-PTMO matrix on the phase transitions (glass transitions, physical crosslink melting) in the obtained nanocomposites was studied by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) analysis. The storage modulus (\( E' \)), loss modulus (\( E'' \)), and loss factor (\( \tan \delta \)) as a function of temperature are shown in Figure 4 for the neat block copolymer and its nanocomposites with GO–Fe₃O₄. Nanocomposites with GO–Fe₃O₄ show similar \( E' \) and \( E'' \) profiles as the neat block copolymer matrices. Considering the experiment precision, it can be inferred that the rubber moduli for nanocomposites are practically the same as for the neat block copolymer. The \( \tan \delta \) curves for all samples show two \( \beta \)-relaxation peaks, \( \beta_1 \) and \( \beta_2 \). These two relaxations are attributed to the glass transition of polyether-rich (\( \beta_1 \)) phase and amorphous polyester (\( \beta_2 \)) phase, respectively. It can be seen (Figure 4, Table 2), that the \( \beta_1 \)-relaxation in nanocomposites is shifted to lower temperatures in comparison with the neat block copolymer. This confirms that addition of GO–Fe₃O₄ to the copolymer matrix improves the phase separation in the system. The final sample softening to a polymer melt, during which physical crosslinks (crystalline PTT domains) disrupt, takes place in the range of 450–475 K in all samples.

In Figure 5 and Table 2, the DSC results obtained during cooling and heating of the nanocomposites are shown. DSC data confirm conclusions obtained by DMTA. Herein, the addition of GO–Fe₃O₄ slightly shifted the value of \( T_{g1} \) (\( T_{g1} \) on DMTA plots) toward lower temperatures. Moreover, no notable effect on the melting temperature (\( T_m \)) can be observed. In contrast, analysis of the cooling scans of nanocomposites and the neat block copolymer indicate that GO–Fe₃O₄ in PTT-PTMO copolymer could improve the crystallization of polymer matrix, as the crystallization temperature increased by 3–19 K. The degree of super cooling (\( \Delta T = T_m - T_{g1} \)) of nanocomposites is smaller than that of neat PTT-PTMO copolymer, which indicates that the presence of GO–Fe₃O₄ in PTT-PTMO block copolymer increases the rate of crystallization of PTT segments in these copolymers. This might be relevant to the processing properties of these materials. In contrast, however, while the presence of nanoparticles accelerates the formation of crystalline phase, it does not correspond to the melting enthalpy, \( \Delta H_m \), and designated on its basis the degree of crystallinity (values of \( x_c \) are comparable to one another). It proves that GO–Fe₃O₄, randomly distributed in the copolymer matrix, promotes nucleation of PTT crystallites.

As a result of the presence of GO–Fe₃O₄ and enhancement of phase separation in PTT-PTMO matrix at their low loading, the improvement of tensile and cyclic tensile properties of nanocomposites was observed. The representative stress–strain curves for nanocomposites obtained in the cyclic and noncyclic uniaxial tensile tests are shown in Figure 6 and the results are summarized in Table 3. The yield stress and tensile strength as well as yield strain and stress at break of nanocomposites slightly increases with GO–Fe₃O₄ loading in the copolymer matrix. The values of permanent set (PS) in tension direction resultant from the attained strain of 100% and 200% (Table 3, Figure 6b) for nanocomposites are close (within errors range) to the values obtained of the neat block copolymer.

### 2.4. Magnetic Properties of GO–Fe₃O₄ Nanocomposites

The magnetic properties of PTT-PTMO/GO–Fe₃O₄ nanocomposites and GO–Fe₃O₄ nanoparticles used for their preparation were studied using a SQUID magnetometer to investigate the temperature dependence of dc magnetic susceptibility and isothermal magnetization as a function of magnetic field as well as a magnetic resonance spectrometer to examine the ferromagnetic/paramagnetic spectra at microwave frequency.

When sample is cooled to the lowest temperature without external magnetic field (ZFC [zero-field-cooled] mode), the magnetic moments of each nanoparticle align along the easy axis in the lattice, and since the crystallites are oriented randomly, the overall magnetic moment of the sample will be zero. As the temperature is increased, thermal energy releases some magnetic moments from the easy axis and they will be aligned along the external field. The magnetocrystalline energy \( K_V \)

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**Table 1.** Characteristics of the synthesized PTT-PTMO based nanocomposites.

| Sample         | GO–Fe₃O₄ [wt%] | [\( \eta \)](a) | \( M_n \)(b) [g mol\(^{-1}\)] | \( M_w \)(c) [g mol\(^{-1}\)] | \( M_w/M_n \)(d) |
|----------------|----------------|-----------------|------------------------------|------------------------------|-----------------|
| PTT-PTMO       | 0              | 1.422           | 41720                        | 83850                        | 2.01            |
| PTT-PTMO/0.3GO–Fe₃O₄ | 0.3           | 1.423           | 42440                        | 87850                        | 2.07            |
| PTT-PTMO/0.5GO–Fe₃O₄ | 0.3           | 1.420           | 41980                        | 88570                        | 2.11            |

(a)\( [\eta] \)—intrinsic viscosity; (b)\( M_n \)—number average molecular weight of the samples after filtration of nanofiller determined by size exclusion chromatography (SEC) according procedure; (c)\( M_w \)—weight average molecular weight; (d)\( M_w/M_n \)—polydispersity.

**Figure 4.** Storage and loss modulus and \( \tan \delta \) for neat PTT-PTMO copolymer and PTT-PTMO/GO–Fe₃O₄ nanocomposites containing of 0.3 and 0.5 wt% of GO–Fe₃O₄.

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K is magnetocrystalline anisotropy energy density constant and V the volume of a nanoparticle) plays a dominate role in that temperature range. At a specific temperature (T_B—blocking temperature), the largest number of moments is aligned along the external field and gives maximum magnetization. Often a simple relation between magnetocrystalline and thermal energy is used to estimate T_B:

\[ K \cdot V = 25kT_B \]  

where k is Boltzmann’s constant. Above T_B the Zeeman energy \( \mu H \) (where \( \mu \) is the magnetic moment and \( H \) external magnetic field) is smaller than the thermal energy, which causes randomization of the moments and the net magnetization will decrease with the increase in temperature (superparamagnetic phase). In contrast, when the sample is cooled from high temperature in the presence of a small external field (FC [field-cooled] mode), the decrease in thermal energy causes orientation of moments along the direction of the field and subsequent increase in magnetization. The ZFC and FC curves coincide or show the same tendency as the temperature is decreased. The situation changes on further cooling below T_B; the Zeeman energy overcomes the thermal energy and causes the moments to orient partially along the applied field, which results in separation of ZFC and FC magnetization curves. At the lowest temperature, the Zeeman energy causes the maximum orientation of moments in the field direction and the biggest magnetization.

In Figure 7–9, the temperature dependence of magnetization in ZFC and FC modes is shown for GO-Fe_3O_4 nanoparticles and PTT-PTMO/GO-Fe_3O_4 nanocomposites. Four panels in each figure present M(T) curves taken in four different magnetic fields: \( H = 10, 100, 1000, \) and \( 10\,000 \) Oe. These figures show the characteristic thermal irreversibility anticipated for an assembly

| Sample                  | \( T_{\beta 1} \) [K] | \( T_{\beta 2} \) [K] | \( T_{g1} \) [K] | \( T_m \) [K] | \( \Delta H_m \) [J g\(^{-1}\)] | \( T_c \) [K] | \( \Delta H_c \) [J g\(^{-1}\)] | \( \Delta T \) [K] | \( x_c \) [%] |
|-------------------------|------------------------|------------------------|------------------|---------------|-------------------------------|--------------|-------------------------------|-----------------|-----------|
| PTT-PTMO                | 244                    | 308                    | 207              | 477           | 31.9                          | 399          | 32.1                          | 78              | 21.8      |
| PTT-PTMO/0.3GO-Fe_3O_4  | 235                    | 321                    | 205              | 477           | 31.1                          | 402          | 31.4                          | 75              | 21.3      |
| PTT-PTMO/0.5GO-Fe_3O_4  | 234                    | 309                    | 205              | 347           | 31.6                          | 418          | 31.6                          | 60              | 21.6      |

\( T_{\beta 1}, T_{\beta 2} \)—temperatures of \( \beta_1 \) and \( \beta_2 \)-relaxation corresponding to the glass transition temperatures determined from maximum of tan \( \delta \); \( T_{g1} \)—glass transition temperature of amorphous soft phase; \( T_m, \Delta H_m \)—temperature and enthalpy of melting of polyester phase; \( T_c, \Delta H_c \)—temperature and enthalpy of crystallization of polyester phase; \( \Delta T \)—degree of supercooling; \( x_c \)—degree of crystallinity.
of single-domain magnetic particles due to the blocking–unblocking process of magnetic moments during variation of the thermal energy. In general, all samples show a rather broad-size distribution of magnetic nanoparticles, which is evidenced by the broadness of $\chi_{\text{ZFC}}$ curves and a large separation of the blocking temperature $T_B$ (maximum in ZFC mode) and the irreversibility temperature $T_{\text{irr}}$ (temperature of splitting of $\chi_{\text{ZFC}}$ and $\chi_{\text{FC}}$ curves). The latter is associated with the blocking of the biggest particles. Another evidence of a broad-size distribution is no saturation of FC magnetization at low temperature.

Comparison of Figure 9 with Figure 8 shows a very similar thermal behavior of magnetizations in both nanocomposites PTT-PTMO/0.3GO–Fe$_3$O$_4$ and PTT-PTMO/0.5GO–Fe$_3$O$_4$. In contrast, comparison of magnetic susceptibilities of both nanocomposite samples with GO–Fe$_3$O$_4$ sample reveals a significant difference—nanocomposites seem to display two blocking temperatures, because two shallow maxima can be discerned in $\chi_{\text{ZFC}}$ curves, whereas only one maximum is visible in $\chi_{\text{ZFC}}$ curve of GO–Fe$_3$O$_4$ sample. Thus, the procedure of synthesis of polymer samples affects to some degree their magnetic properties, producing bimodal-like distribution of the blocking temperatures. A simple explanation of this phenomenon involves the presence of a magnetite–polymer interface that produces the core-shell structure of magnetite nanoparticles in these samples. It is also apparent that there is no evidence of Verwey transition in magnetization curves in the neighborhood of 120 K. There is another interesting feature noted in the temperature dependence of magnetic susceptibility in both block copolymer samples, which is absent in GO–Fe$_3$O$_4$. At low temperatures ($T < 20$ K) and in high magnetic fields ($H > 1$ kOe), it is manifested in the upturn in dc susceptibility of PTT-PTMO/0.3GO–Fe$_3$O$_4$ and PTT-PTMO/0.5GO–Fe$_3$O$_4$. Similar behavior was observed for composites of Fe$_3$O$_4$ nanoparticles with alginic acids.\textsuperscript{16} It was interpreted in terms of the excitation of the spin waves with discrete spectrum. At higher temperatures, the magnetic energy levels are broadened and form a continuous excitation spectrum. In that case, the temperature dependence of magnetization can be the same as in bulk materials. The proposed interpretation of

| Sample                  | $\sigma_y$ [MPa]\textsuperscript{a} | $\varepsilon_y$ [%]\textsuperscript{a} | $\sigma_b$ [MPa]\textsuperscript{b} | $\varepsilon_b$ [%]\textsuperscript{b} | PS(100) [%]\textsuperscript{c} | PS(200) [%]\textsuperscript{c} |
|------------------------|--------------------------------------|----------------------------------------|-------------------------------------|-----------------------------------|-----------------------------|-----------------------------|
| PTT-PTMO               | 12.1 ± 0.1                           | 41.7 ± 0.1                              | 23.5 ± 0.2                          | 622 ± 12                          | 38 ± 2                      | 95 ± 3                      |
| PTT-PTMO/0.3GO–Fe$_3$O$_4$ | 12.4 ± 0.1                           | 42.7 ± 0.1                              | 24.8 ± 0.6                          | 668 ± 24                          | 38 ± 1                      | 93 ± 2                      |
| PTT-PTMO/0.5GO–Fe$_3$O$_4$ | 12.6 ± 0.2                           | 43.2 ± 0.3                              | 26.8 ± 0.9                          | 680 ± 31                          | 38 ± 2                      | 95 ± 3                      |

\textsuperscript{a}$\sigma_y$, $\varepsilon_y$—yield stress and strain respectively; \textsuperscript{b}$\sigma_b$—stress at break; \textsuperscript{c}$\varepsilon_b$—strain at break; \textsuperscript{d}PS(100)—was taken as the strain at which zero load was measured on the first unloading cycle to 100% strain; \textsuperscript{e}PS(200)—was taken as the strain at which zero load was measured on the first unloading cycle to 200% strain.

Figure 7. Temperature dependence of magnetic susceptibility in ZFC and FC modes in four magnetic fields (10, 100, 1000, and 10000 Oe) of GO–Fe$_3$O$_4$ sample.
Figure 8. Temperature dependence of magnetic susceptibility in ZFC and FC modes in four magnetic fields (10, 100, 1000, and 10000 Oe) of PTT-PTMO/0.5GO–Fe₃O₄ sample.

Figure 9. Temperature dependence of magnetic susceptibility in ZFC and FC modes in four magnetic fields (10, 100, 1000, and 10000 Oe) of PTT-PTMO/0.5GO–Fe₃O₄ sample.
magnetization upturn at low temperature assumes the presence of small nanoparticles because the involved quantum effects are magnified in restricted dimensions. Bimodal-like distribution of blocking temperatures in our polymer nanocomposite samples and the presence of magnetite–polymer interface suggest other possible explanation of magnetization upturn at low temperature-ordering of spins in the nanoparticle shells in the magnetic field of already ordered spins in the magnetite cores.[53]

The blocking temperature depends on the applied magnetic field and is expected to shift to lower temperatures on increasing the field strength, because magnetic field lowers the barrier between two easy axis orientations. In Figure 10, this dependence is shown for GO–Fe₃O₄ nanoparticles and nanocomposites with their content. For both nanocomposites, as there are two blocking temperatures, there will be two branches of \( T_B(H) \) curves. It is easy to see that the high-temperature branch for GO–Fe₃O₄ and PTT-PTMO nanocomposites coincides and only the low-temperature branch is specific for both nanocomposites samples. Double-peak \( M_{ZFC} \) could be explained as a result of existence of two different subsystems of nanoparticles with different effective average sizes. The high-temperature \( T_B(H) \) branch represents one collection of larger nanoparticles in GO–Fe₃O₄ and PTT-PTMO nanocomposites and the low-temperature branch is specific to PTT-PTMO nanocomposites. In the latter, the core of a nanoparticle is effectively smaller because of the existence of a shell layer having different magnetic properties. Applying Equation (1) to the common-to-all samples blocking temperature approximated to zero magnetic field \( (T_B(0) = 250 \text{ K}) \) and using an average nanoparticle size obtained from TEM images \( (D = 9 \text{ nm}) \), it can be calculated that \( K = 2.2 \times 10^5 \text{ erg cm}^{-1} \), which is much larger than that for bulk Fe₃O₄ \( (1.35 \times 10^5 \text{ erg cm}^{-1} \) at RT). This enhancement of the particle's anisotropy is likely associated with a surface having larger anisotropy (aggregation of nanoparticles).

In Figure 11, the isothermal \((T = 2 \text{ K})\) magnetizations of GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites in magnetic fields up to 70 kOe are shown. As anticipated, magnetization in the form of hysteresis loop is observed as the samples are in the blocked, ferromagnetic state. The diamagnetic contribution of polymer matrix has been subtracted in case of PTT-PTMO/0.3GO–Fe₃O₄ and PTT-PTMO/0.5GO–Fe₃O₄ samples. In contrast, at RT, no hysteresis loop is registered, because this temperature is higher than the blocking temperature and the samples are in superparamagnetic state. The parameters of the observed loops (saturation magnetization, remanent magnetization, coercive field) at \( T = 2 \text{ K} \) are listed in Table 4.

![Figure 10](image1.png)

**Figure 10.** Dependence of the blocking temperature on external magnetic field in investigated GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites. The solid lines are merely guides to the eyes.

![Figure 11](image2.png)

**Figure 11.** Isothermal magnetization at \( T = 2 \text{ K} \) for GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites. The solid line in the upper panel is the fit to the sum of ferromagnetic and paramagnetic components. The insets show expanded views of the low magnetic field behavior (the solid lines are guides for the eyes).
Table 4. Hysteresis loop parameters at T = 2 K of GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites. Saturation and remanent magnetizations are expressed on a unit mass (1 g) of the whole sample, including GO and polymer masses.

| Sample       | H_c [Oe] | M_s [emu g⁻¹] | M_r [emu g⁻¹] | M_s/M_r |
|--------------|----------|---------------|---------------|---------|
| GO–Fe₃O₄    | 114      | 13.2          | 69.3          | 0.19    |
| PTT-PTMO/0.3GO–Fe₃O₄ | 400      | 0.08          | 0.24          | 0.33    |
| PTT-PTMO/0.5GO–Fe₃O₄ | 415      | 0.14          | 0.40          | 0.35    |

The values of the saturation magnetization and the remanent magnetization in Table 4 are calculated for a unit mass (1 g) of the whole sample, including GO and copolymer masses. Considering that in 1 g of GO–Fe₃O₄ sample, the mass of magnetite is 0.686 g (this can be calculated from XPS data), it follows that the saturation magnetization would be 101 emu g⁻¹(Fe₃O₄). This is slightly more than for bulk magnetite at that low temperature. But this value has to be reduced because the registered magnetization of GO–Fe₃O₄ sample does not reach saturation even in 70 kOe magnetic field. Thus, the observed signal were treated as composed from two components: ferromagnetic, saturated below 20 kOe and paramagnetic that will not be saturated.

The magnetization curves in Figure 12 cannot be adequately fitted using a single Langevin function with a single magnetic moment or an exchange coupled superparamagnetic array of magnetic moments (when the direction of the easy axis does not play a role).

\[ M = M_s (\coth(x) - \frac{1}{x}) \]

where \( M_s \) is saturation magnetization, \( x = \frac{\mu H}{kT} \) is the ratio of magnetic to thermal energy, \( \mu \) is the magnetic moment, and \( k \) is Boltzmann’s constant. Fitting of \( M(H) \) curve for GO–Fe₃O₄ sample in 20–70 kOe range by the sum of Equation (2) and a constant (representing already saturated ferromagnetic component) was very accurate and gave the saturation magnetization of the ferromagnetic component to be 99 emu g⁻¹(Fe₃O₄) and the paramagnetic moment of 2.7 \( \mu_B \) (Bohr magnetons). The fit is shown in Figure 11 (upper panel) by a solid line.

Comparison of the values of the other loop parameters (\( H_c, M_s/M_R \)) for GO–Fe₃O₄ with both nanocomposite samples brings up a striking difference between them (Table 4). The coercive field is roughly three times and the \( M_s/M_R \) ratio (the squareness ratio coefficient \( Q \)) is two times bigger in the PTT-PTMO/GO–Fe₃O₄ nanocomposites in comparison with GO–Fe₃O₄. For non-interacting, randomly oriented particles with uniaxial magnetocrystalline anisotropy \( Q = 0.5 \), whereas for particles with cubic magnetocrystalline anisotropy \( Q = 0.831 \). As the squareness ratio represents the fraction of blocked particles at a specific temperature, its value increases with decrease in temperature. Small values of this parameters indicate that the individual particles are single domains and show a strong random anisotropy.

Reduction in \( Q \) could be due to different reasons such as interparticle interaction, distribution of particle sizes, the presence of various defects, and so on. Petrychuk et al. investigated samples containing interacting magnetic nanoparticles forming clusters of different sizes. For small-sized magnetic clusters, the magnetic energy may be small enough to enable thermal energy the enhancement of the superparamagnetic contribution into magnetization. This results in small values of coefficient \( Q \). In contrast, for larger cluster, the magnetic energy is high, which leads to the corresponding enhancement of its superferromagnetic properties. The hysteresis loop becomes more rectangular and the squareness ratio coefficient increases. These considerations suggest that \( Q \) value might be considered as a measure of cluster sizes in a strongly interacting system of ferromagnetic nanoparticles.

Figure 12. Normalized magnetization of GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites in an external magnetic field at \( T = 300 \) K. The solid lines are the least-squares fits to the sum of two Langevin functions with different magnetic moments and a small term linear in magnetic field.
The obtained magnetic moments probably do not have much physical meaning—there are only indication of a spread of magnetic moment values (and corresponding nanoparticle sizes) in our samples.\(^{[60]}\) Reduction of magnetization in intermediate fields in case of sample GO–Fe\(_3\)O\(_4\) might be explained by an interparticle interaction causing formation of flux closer loops.\(^{[61]}\)

### 2.4.1. Ferromagnetic Resonance

Selection of FMR spectra in the form of magnetic field dependence of the field derivative of the microwave absorption registered at different temperatures in 90–300 K range is shown in Figure 13 for GO–Fe\(_3\)O\(_4\) (upper panel) and PTT-PTMO/0.5GO–Fe\(_3\)O\(_4\) nanocomposite (lower panel).

All FMR spectra are dominated by an intense, broad, and asymmetrical line. The registered FMR spectra reflect very complex spatial arrangements of magnetic particles and a broad range of different interactions they are involved. To obtain information, albeit approximate and limited, about particles and their interactions, the spectra were decomposed on components described by Gaussian line shape functions.\(^{[62–64]}\) Two Gaussian components were needed to obtain a very good agreement between the experimental and calculated spectra. As a result of fitting, the values of the resonance field, linewidth, and amplitude of each component were obtained at specific temperatures. Another important parameter—the integrated intensity—was calculated as the product of the amplitude and the square of linewidth. The results of fittings are presented in Figure 14, 15, and 16 which show the temperature dependence of the resonance fields, linewidths, and integrated intensities, respectively.

A remarkable difference between the two studied polymer nanocomposite samples on the one hand, and the GO–Fe\(_3\)O\(_4\) on the other hand, is noted in Figure 14 that shows the temperature dependence of the resonance fields in each component (designated as comp. 1 and comp. 2) for three studied samples. Two characteristic features of these dependencies are easy to notice: there is a different splitting of the two components in polymer as compared with GO–Fe\(_3\)O\(_4\) samples (large for the former and small for the latter) and there is a different shift of the split

![Figure 13](image1.png)

**Figure 13.** FMR spectra registered at different temperatures of GO–Fe\(_3\)O\(_4\) (top panel) and PTT-PTMO/0.5GO–Fe\(_3\)O\(_4\) nanocomposite (lower panel).

![Figure 14](image2.png)

**Figure 14.** Temperature dependence of the resonance fields of the component lines (designated as comp. 1 and comp. 2) for GO–Fe\(_3\)O\(_4\) and nanocomposites. The solid lines are guides for the eyes.

![Figure 15](image3.png)

**Figure 15.** Temperature dependence of the line splitting between two components (top panel) and line shift (bottom panel) from magnetic field corresponding to \(g = 2\) for GO–Fe\(_3\)O\(_4\) and PTT-PTMO/GO–Fe\(_3\)O\(_4\) nanocomposites.

![Figure 16](image4.png)

**Figure 16.** Temperature dependence of the linewidths of the component lines for GO–Fe\(_3\)O\(_4\) and PTT-PTMO/GO–Fe\(_3\)O\(_4\) nanocomposites. The solid lines are guides for the eyes.
components from the magnetic field \( H_{\text{r0}} \) corresponding to \( g = 2 \) (no internal field, superparamagnetic case) in both types of samples. These differences are shown in Figure 17. Top panel in Figure 17 shows the temperature variation of the line split into two components in our three samples. Both polymer nanocomposites show a similar, large splitting of approximately 700 Oe, whereas that splitting in GO–Fe₃O₄ sample is significantly reduced and below 200 Oe. It is interesting to notice that similar differences were observed for the coercive fields in these samples, which suggests a common mechanism behind those two different phenomena. Bottom panel in Figure 17 shows the temperature dependence of the line shift in the middle between comp. 1 and comp. 2 lines. Contrary to the case of line splitting, this shift is large for GO–Fe₃O₄ (above 500 Oe and increasing with temperature decrease) and small (below 100 Oe) for both polymer nanocomposites. The reasons for these differences should be searched in morphological differences between GO–Fe₃O₄ and both PTT-PTMO/GO–Fe₃O₄ nanocomposites. In the following, the large shift of the resonance line from \( H_{\text{r0}} \) in GO–Fe₃O₄ will be explained by agglomeration of magnetite nanoparticles in that sample and the large split of two components in both polymer nanocomposites by a significant contribution of the surface energy due to a strong polymer and magnetite interface.

Study of temperature dependence of the resonance field in FMR experiments could provide valuable information on spin dynamics of ferromagnetic nanoparticle samples. In FMR studies, the following resonance condition must be satisfied:

\[
\frac{\omega}{\gamma} = \frac{6K_{s}}{RM} + H_{\text{ex}}
\]

where \( M \) is magnetization. The surface anisotropy term contains \( K_{s} \) (surface anisotropy constant) and acts as an additional uniform field. Its strength depends on particle size: the smaller the particle, the stronger that field. The equations for both resonance fields of the two split components are the following:

\[H_{r}(1) = \frac{\omega_{0}}{\gamma} \frac{6K_{s}}{RM} - H_{a}
\]

when the external field is parallel to the anisotropy axis, and

\[H_{r}(2) = \frac{\omega_{0}}{\gamma} \frac{3K_{s}}{RM} + \frac{H_{a}}{2}
\]

when the field is perpendicular to the axis. In Equation (4) and (5), \( R \) stands for the radius of a nanoparticle. Subtracting Equation (4) and (5) and multiplying the result by 2/3, one gets

\[
\frac{2}{3} [H_{r}(2) - H_{r}(1)] = \frac{6K_{s}}{RM} + H_{a}
\]

In our samples, the spread of anisotropy axes is random, so in fact only a single broad line is registered, but its decomposition on two components allows to find resonance fields in

![Figure 17. Dependence of component linewidth on the line shift from the reference field \( H_{\text{r0}} \) in GO–Fe₃O₄ (left panel) and on the line splitting in PTT-PTMO/GO–Fe₃O₄ nanocomposites (right panel). Solid lines in the left panel are linear fits; solid lines in the right panel are guides for the eyes.](image)
Equation (4) and (5). For GO–Fe₃O₄ sample, the surface term (the first in the right-hand side in Equation (6)) could be omitted as the bulk magnetocrystalline energy is supposed to be bigger than the surface energy. In that case, the anisotropy field \( H_a \) calculated from the line splitting \((\approx 180 \text{ Oe})\) in GO–Fe₃O₄ is equal to 120 Oe. This value is very close to the coercive field of the sample measured in isothermal magnetization. In fact, this is to be expected because for the coercive field \( H_c \) the same expression is valid as for \( H_a \) (see Equation (3)). If the anisotropy field is the same in both polymer nanocomposites as in GO–Fe₃O₄ then Equation (6) allows to calculate the surface anisotropy constant \( K_s \). Substituting \( \approx 700 \text{ Oe} \) for the line splitting, \( R = 4.5 \text{ nm} \), and \( M = 90 \text{ emu g}^{-1} \), the value of 0.15 erg cm\(^{-2}\) for \( K_s \) is obtained. The surface of magnetite nanoparticles can be strongly influenced by bonding to the polymer matrix.

A large shift of FMR lines from the reference field \( H_{0} \) in GO–Fe₃O₄ sample could be explained by agglomeration of magnetite nanoparticles in the form of elongated assemblies along the lines of an external magnetic field. In contrast, in PTT-PTMO nanocomposites, the polymer matrix prevents such rearrangements, so the FMR shift is expected to be small or vanishing. Shape anisotropy field \( H_s \) depends on the relative value of the three orthogonal demagnetization factors, \( N_a \), \( N_b \), and \( N_c \), where \( N_a + N_b + N_c = 4\pi \). For elongated particles or assemblies \((N_b = N_c)\), \( H_s = (N_a - N_b) \); \( M_s = \Delta N - M_s \), where \( M_s \) is the saturation magnetization. For elongated needles \((N_b = 2\pi, N_c = 0)\), \( H_s = 2\pi M_s \). The shape anisotropy field is adding as a vector to the external magnetic field. If elongated aggregate of nanoparticles is situated parallel to the external field directions, the following well-known equations could be used

\[
\frac{\alpha_{0}}{\gamma} = H_t + \Delta N \cdot M_s \tag{7}
\]

According to this equation, the observed resonance field \( H_t \) decreases by a factor proportional to the saturation magnetization and the difference of the demagnetization factors. The observed increase in the shift for GO–Fe₃O₄ sample with decreasing temperature can be explained by increase in magnetization. The value of \( \Delta N \) calculated from Equation (7) is approximately 0.10 for GO–Fe₃O₄. Although this particular approach to orientation dependence of the resonance field in FMR experiment seems adequate for our sample, more general one was previously reported. \(^{69-71}\)

In Figure 15, the temperature dependence of the linewidths of the component lines for the three investigated samples is shown. In general, all linewidths increase with decreasing temperature. This is usually attributed to a gradual suppression of the averaging effect of thermal fluctuations with decreasing temperature.\(^{72,73}\) The linewidths of two components in GO–Fe₃O₄ show almost linear increase during cooling down this sample from RT and the largest linewidth is found for the perpendicular component (comp. 2 in Figure 15). Line components linewidths in both nanocomposites show more complex thermal behavior, but a general tendency of increasing with temperature decrease is easily recognized, especially below 150 K. The observed temperature dependence of components linewidths shows a remarkable similarity to the temperature dependence of internal fields producing shift and splitting of FMR lines (see Figure 17). In Figure 16, the dependence of the component linewidths as a function of the line shift from the reference field \( H_{0} \) in GO–Fe₃O₄ and on the line splitting in the PTT-PTMO/GO–Fe₃O₄ nanocomposites is shown.

The observed trend in linewidth broadening clearly indicate inhomogeneous broadening created by the spread of easy-axis directions in regard to appropriate internal field (demagnetization field in case of GO–Fe₃O₄ and surface anisotropy field in case of polymer nanocomposite samples) as a major contributor to the linewidth.\(^{28}\) In contrast, it could not be the only factor that determines the component linewidth because the observed linewidths are bigger than the appropriate internal fields. Other factors, such as distribution of nanoparticle or cluster sizes should also have an effect on the observed component linewidth because size distribution directly influences the magnitude of the internal fields.\(^{72,73}\)

In Figure 18, the temperature dependence of the normalized (at RT) integrated FMR intensities \( I_{FMR} \) (calculated as the sum of two components) for the PTT-PTMO/GO–Fe₃O₄ nanocomposites and GO–Fe₃O₄ is shown. \( I_{FMR}(T) \) curves show a very interesting behavior. Initial cooling from RT causes a slight increase in \( I_{FMR} \), but near 260 K, a very rapid drop in FMR intensity is observed for GO–Fe₃O₄ and PTT-PTMO-based nanocomposites. The magnitude of this decrease is slightly smaller for GO–Fe₃O₄ (40% drop) than for both polymer nanocomposites (60% drop). This might be explained by relatively more intense FMR spectrum of the latter samples at high temperatures in comparison with GO–Fe₃O₄ sample. As the behavior of \( I_{FMR}(T) \) is similar to \( \chi_{ZFC}(T) \), it is possible to introduce the notion of FMR blocking temperature. It is surprisingly close to the blocking temperature determined from dc magnetization. FMR measurements should give a much higher value of the blocking temperature than determined from SQUID magnetization, as the time windows \( \tau \) for the two methods are very different: \( \tau_{FMR} \approx 10^{-9} \text{ s} \), \( \tau_{SQUID} \approx 10^{2} \text{ s} \). But as noticed by Ramos et al.,\(^{74}\) the notion of blocking in FMR has a different meaning than in SQUID magnetization. That difference is the consequence of the fact, that in FMR the measurements are done in much stronger magnetic fields (approximately a few kOe) than in magnetization studies.

**Figure 18.** Temperature dependence of the normalized (at RT) integrated intensities for the GO–Fe₃O₄ and PTT-PTMO/GO–Fe₃O₄ nanocomposites. The solid lines are guides for the eyes.
(only a few Oe). In consequence, if the effective anisotropy field becomes greater than $H_{eo}$, the nanoparticles whose easy axes are close to the direction of the applied field will no longer reach the resonance condition and a drop in FMR intensity will be registered. This idea might be supported by the observation that the components with the largest linewidth have the biggest contribution to the FMR intensity decrease below 260 K. Thus, the intensity decrease cannot be used as a feature that indicates the change in components with the largest linewidth having the biggest contribution.

As the magnitude of the internal anisotropy fields is similar in GO–Fe₃O₄ and PT–PTMO/GO–Fe₃O₄ nanocomposites, FMR intensity drop is registered at a similar temperature $\approx$260 K. On further cooling, the $I_{MR}$ curve levels down and below 120 K starts to slowly increase on temperature decrease. This increase is probably correlated with magnetization increase on temperature decrease observed in SQUID magnetization studies.

3. Conclusions

The polyester thermoplastic elastomeric nanocomposites with improved phase-separated structure were obtained by in situ polymerization. Homogenous dispersion of GO–Fe₃O₄ nanoparticles hybrid in the PT–PTMO matrix was confirmed by the TEM analysis. The average size of Fe₃O₄ nanocrystals distributed on GO sheets was $\approx$9 nm. Due to presence of GO–Fe₃O₄ in copolymer matrix and better phase separation, the improvement of tensile properties of PT–PTMO/GO–Fe₃O₄ nanocomposites was observed. Suppermagnetic behavior for GO–Fe₃O₄ hybrid nanoparticles and nanocomposites with their content was observed at RT as well as hysteresis due to blocking of magnetic fields is similar in GO–Fe₃O₄ particles.

Due to low toxicity and of GO–Fe₃O₄ hybrid nanoparticles, the prepared elastomeric nanocomposites with their low loading could be developed for its potential application as a contrast agent in magnetic resonance imaging (MRI), but this application requires further laboratory and in vivo investigations, especially with regard to the use of more biocompatible elastomer matrix. The used here PT–PTMO thermoplastic elastomer as nanocomposite polymer matrix is more of an engineering material, but it is possible to replace it by a more biocompatible elastomer, e.g., PT–PEO copolymer or PLA copolymer. In surgical implants loaded with superparamagnetic GO–Fe₃O₄ hybrids acting as image contrast, the sensitivity of MRI will be enhanced.

4. Experimental Section

Materials: Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), ammonium hydroxide, dimethyl terephthalate (DMT), poly(tetramethylene oxide) glycol (PTMG) with molecular weight of 1000 g mol⁻¹, tributyl ortho-titanate (TBT) were delivered by Sigma-Aldrich and used as received. Bio-1,3-propanediol (bio-PDO, Susterra 190042), bio-1,4-propanediol (bio-PDO, Susterra 1900402) was purchased from DuPont Tate & Lyle (USA). Antioxidant Irganox 1010 was purchased from Ciba-Geigy (Switzerland). The GO nanoplatelets used for preparation of nanoparticle hybrid were prepared by a modified Hummers method. For GO synthesis, the expanded graphite with an average size of 5 µm from (SGL Carbon, Germany) was used.

Preparation of GO–Fe₃O₄ Hybrid Structures and Their Characterization:

The GO–Fe₃O₄ hybrid nanoparticles were synthesized by inverse chemical co-precipitation method according to the following procedure. GO powder (50 mg) was exfoliated in 150 mL of deionized water by ultrasonic treatment for 30 min and followed by the addition of 1.6 g FeCl₃·6H₂O and 0.6 g FeCl₂·4H₂O. The mixture solution was added dropwise into a 250 mL three-necked flask containing 25 mL of 30% ammonium hydroxide under vigorous mechanical stirring. To prevent oxidative reaction, the system was kept under nitrogen atmosphere. The resulting black solution was maintained at 80 °C for 1 h and then cooled to RT. The black precipitate was isolated by a permanent magnet and washed three times with deionized water and three times with ethanol. The collected magnetic material was dried at 50 °C in vacuum.

Synthesis of PT–PTMO/GO–Fe₃O₄ Nanocomposites: PT–PTMO/GO–Fe₃O₄ nanocomposites were synthesized by a two-step polycondensation reaction of DMT (Sigma-Aldrich), bio-PDO, and PTMG in the presence of TBT as catalyst and Irganox 1010 as an antioxidant. Details of the preparation method of PT–PTMO-based nanocomposites could be found in our previous publications concerning GO and a hybrid system of GNP and SWCNT. Before carrying out the polymerization, a dispersion of GO–Fe₃O₄ was prepared by dispersing the appropriate amount of functionalized GNP in bio-PDO through ultrasonication for 15 min using a laboratory homogenizer (Sonopuls HD 2200, with frequency of 20 kHz and 75% of power 200W) and subsequent intensive mixing for 15 min using high-speed stirrer (Ultra-Turrax T25). The content of rigid PT and soft PTMO segments was approximately the same (i.e., 50 wt% of each).

Characterization: The synthesized GO–Fe₃O₄ was characterized by XPS performed on Kratos Axis ULTRA X-Ray photoelectron spectrometer equipped with monochromatic Al Kα (hv = 1486.6 eV) radiation to quantitatively analyze the chemical composition of the nanofiller. XRD data were obtained using the X’Pert PANalytical diffractometer using Cu Kα radiation (i = 0.154056 nm) at an operating voltage and current of 40 kV and 40 mA, respectively. The nanocrystal size (d) was estimated according to Scherrer’s equation:

$$d = \frac{K \lambda}{B \cos \theta}$$

where K is the Scherrer constant (0.89), B is the full width at half maximum (FWHM) of the strongest reflection peak, and \(\theta\) is the diffraction angle. TGA was performed using a SETARAM TGA 92-16 instrument in air flow (20 mL min⁻¹) using a heating rate of 10 K min⁻¹ in a temperature range from 298 K up to 1073 K. Indium and aluminium were used for temperature calibration. The amount of applied samples was $\approx$10 mg. Two parallel runs were performed for each sample. The surface morphology of the GO and GO–Fe₃O₄ was observed by using FEI Quanta 3D 200i dual beam microscope combining focused ion beam (FIB) instrument and scanning electron microscope (SEM).

The microstructure of nanocomposites was observed by TEM on Topcom 002B—UHR microscope working with an accelerated voltage of 200 kV and a point-to-point resolution of 0.17 nm. Prior to the analysis, thin slices of polymers were prepared by cryo-cutting technique and deposited on the copper grid.

The thermal transitions of neat copolymer and prepared nanocomposites were investigated with DSC on a Q100 thermal analyzer (TA Instruments). A standard heat–cool–heat program with heating/cooling rate of 10 K min⁻¹ was performed between 173 and 523 K. The cooling and second heating scans were used to determine the glass transition temperature, crystallization, and melting peaks. The degree of crystallinity (\(x_c\)) was calculated using the following equation:

$$x_c = 100 \times \left( \frac{\Delta H_m}{\Delta H_m^0} \right)$$

where \(\Delta H_m\) is the melting peak area of an examined sample on DSC thermograms, and \(\Delta H_m^0\) is the enthalpy of fusion (146 J g⁻¹) of fully 100% crystalline PTT.
The DMTA was performed using a Polymer Laboratories MK II apparatus working in a bending mode. The samples were heated in the temperature range from 153 K to the polymer melting temperature and the heating rate of 3 K min\(^{-1}\) at a frequency of 1 Hz was used.

The tensile and cyclic tensile properties of nanocomposites were performed on an Autograph AG-X plus (Shimadzu) tensile-testing machine equipped with a 1 kN Shimadzu load cell, an contact optical long travel extensometer, and the TRAPEZIUM X computer software, operated at a constant crosshead speed of 100 mm min\(^{-1}\). Measurements on dumbbell samples were performed at RT with the grip distance of 20 mm according to DIN 53455 standard. The values of yield strength, stress, and elongation at break, PS (with error bars representing the 95% confidence interval) were calculated from the stress–strain curves.

Magnetic properties measurement system (MPMS)-7 SQUID magnetometer was used for dc magnetization measurements in the 2–300 K temperature range in the ZFC and FC modes and for isothermal (\(T = 2300\) K) magnetization in magnetic fields up to 70 kOe. Magnetic resonance study was conducted on a conventional X–band (\(v = 9.4\) GHz) Bruker E 500 spectrometer with the 100 kHz magnetic-field modulation. The FMR spectra were taken in the 90–290 K range and were in the form of the first derivatives of microwave absorption with respect to the sweeping external magnetic field.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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