Dielectric properties and thermal destruction of poly(dimethylsiloxane)/Fe$_2$O$_3$/SiO$_2$ nanocomposites

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1. Introduction

Polymer nanocomposites (usually at low filler content) have attracted attention due to their exceptional mechanical and other properties compared to those of conventional micro and macroscale composites. Incorporation of different inorganic components into siloxane-based structures has been carried out in order to improve the mechanical, thermal, electrical and optical properties and dimensional stability of the polymer matrix or to obtain new properties derived from the hybrid nature of the materials [1,2]. Aerogels and fumed silica composed of nanoparticles are the most preferred fillers for silicones. Other components such as ferric oxide, titanium dioxide or organometallic compounds can be added as heat stabilizers or pigments [3]. Addition of nanostructured materials such as TiO$_2$ or ZrO$_2$ to improve resistance to thermodegradation or Al$_2$O$_3$ to improve thermal conductivity, abrasive and flame resistance [4] can widen the applications of PDMS based nanocomposites. The effects of in-situ synthesized titania nanoparticles on thermal transitions, segmental dynamics and interfacial interactions in poly(dimethylsiloxane)/titania nanocomposites were studied in detail [5].

It is known that the properties of nanocomposites can be improved due to modification of a filler structure that results in changes in the polymer dynamics due to changes in interactions with filler particles. A great surface-to-volume ratio for nanoparticles leads to dominance of a polymer fraction located close to interfaces. Therefore, the composite properties strongly depend on the characteristics of this fraction. The polymer dynamics and the glass transition in nanocomposites are more complex than in neat polymers [5]. Therefore, the mechanisms of the interfacial phenomena in composites need additional and detailed investigation, in particular with respect to the effect of filler structure and modification. It was shown [6] that increase of the glass transition temperature $T_g$ in polymer nanocomposites is due to the nanoparticles, that restrict the mobility of the entire volume of the polymer. Reduction of $T_g$ was established in the case of weak interactions between a filler and a polymer [7]. In another work, addition of nanoparticles was found to cause insignificant changes in the glass transition of the polymer presumably because the effects causing an increase or decrease in the polymer mobility are present simultaneously and are effectively cancelled out [8]. The molecular dynamics...
of a series of poly(dimethylsiloxane) filled with silica nanoparticles synthesized in-situ were investigated [9] using differential scanning calorimetry (DSC), thermally stimulated depolarization current (TSDC) and broadband dielectric relaxation spectroscopy (DRS) and it was shown that polymer mobility is reduced in an interfacial layer 2–3 nm thick around the nanoparticles. 

Gee et al. [10] studied the effect of adsorbed water on the interfacial structure and dynamics in silica–polydimethylsiloxane composites using molecular dynamics (MD). They concluded that polymer chains mobility significantly decreased with decreasing hydration level. The reduced mobility of the PDMS chains in the interfacial domain reduced the overall, bulk, motional properties of the polymer, thus causing an effective “stiffening” of the polymer matrix.

Considering polymer/silica interactions using a variety of matrices studied by dynamical mechanical analysis (DMA) and DRS [11] results were interpreted using a three-layer model with strongly bound (which does not participate in the glass transition), loosely bound (responsible for a second glass transition) and quasi-bulk (unaffected by the particles) fractions of the polymer. On the other hand, DMA [12] and neutron scattering results [13] in polymer/silica nanocomposites were explained in terms of a two-layer model: a single interfacial layer with reduced dynamics and quasi-bulk polymer. The aim of this paper was to elucidate the influence of silica modification by Fe₂O₃ on the interfacial behavior of PDMS.

2. Materials and methods

2.1. Materials

Fumed silica (pilot plant of the Chukot Institute of Surface Chemistry, Kalush, Ukraine, 5 = 290 m²/g) was used as a matrix. Fe(III) acetylacetonate (Fe(acac)₃, Aldrich, >98% Fe(acac)₃) was used as a precursor of synthesized iron oxide nanoparticles on the silica surface.

Fe₂O₃/SiO₂ samples were synthesized by impregnation of the silica powder (pre-heated at 120 °C for 2 h) by Fe(acac)₃ dissolved in isopropanol at 3 wt% with respect to dry silica, with subsequent drying (82 °C) and oxidation (500–600 °C) in air. The concentration of iron oxide in the sample was 4 wt%.

Then PDMS (“Krempnypolimer”, Zaporozhye, Ukraine, molecular weight Wₘ = 7960, degree of polymerization 105) was adsorbed onto the initial silica and Fe₂O₃/SiO₂ samples in the amount of 10, 20, 30, 40, and 80 wt%. Before the adsorption, oxide samples were dried at 110 °C for 1 h, and then a solution of PDMS in hexane (oxide + PDMS ~ 11 wt%) was added and stirred. The suspension was dried at room temperature for 24 h and then at 80 °C for 3 h.

2.2. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)

The DRIFT spectra of dried powder samples (ground with KBr at the mass ratio 1:9) were recorded over the 4000–400 cm⁻¹ range in a diffuse reflectance mode using a ThermoNicolet Nexus FTIR spectrometer. The reflectance data were converted to absorbance using program “Omnic 6.1”.

2.3. Specific surface area

The specific surface area (Sₐ) was calculated using adsorption of argon (from an Ar/He mixture) at 77.4 K with a LKhM-72 (Russia) chromatograph and Silochrome-80 as a reference material.

2.4. Thermogravimetry (TG)

Thermal analysis of PDMS adsorbed on oxide samples (weight ~200 mg) was carried out in air at 288–1273 K using a Derivatograph Q-1500 D (Paulik, Paulik & Erdey, MOM, Budapest) with TG-DTA (differential thermal analysis) at a heating rate of 10 K/min.

2.5. Differential scanning calorimetry (DSC)

Thermal transitions of the materials were investigated in helium atmosphere in the –175–0 °C range using a TA Q2000 series DSC instrument, calibrated with Indium (for temperature and enthalpy) and sapphire (for heat capacity). Samples of ~8 mg in mass, taken from the produced powders, were closed in standard aluminum pans. Cooling and heating rates were 10 °C/min. It should be noted that PDMS crystals are melted at room temperature, so the first heating scan for erasing thermal history [14] was not necessary here.

Using the crystallization, cold crystallization and melting enthalpies, ΔHₓ, ΔHₓc, and ΔHₓm, respectively, as recorded through DSC and also normalized to the same polymer content XₚDMS for each sample, the degrees of crystallinity Xₜₐₜₐₜ and Xₚₐₐₐ were calculated according to Eqs. (1) and (2), in which ΔHₓ00% is the enthalpy of PDMS fusion, taken as 37.43 J/g [15]. We also normalized the heat capacity change at glass transition as recorded from DSC, ΔCₚ,DSC, to the amorphous polymer fraction according to Eq. (3).

\[
X_{c,\text{cryst}} = \frac{\Delta H_c}{(X_{\text{PDMS}} \times \Delta H_{\text{00%}})}
\]

\[
X_{c,\text{melt}} = \frac{(\Delta H_m - \Delta H_c)}{(X_{\text{PDMS}} \times \Delta H_{\text{00%}})}
\]

\[
\Delta C_p,\text{norm} = \frac{\Delta C_{p,DSC}}{(X_{\text{PDMS}} (1 - X_c))}
\]

2.6. Thermally stimulated depolarization current (TSDC)

Thermally stimulated depolarization current is a special dielectric technique working in the temperature domain and characterized by high sensitivity and high resolving power. The latter is due to the low equivalent frequency of the technique (10⁻⁴–10³ Hz) [16]. A sample (compressed to form a cylindrical pellet of 12 mm in diameter and 1–2 mm in thickness) was inserted between the brass plates of a capacitor, placed in a Novocontrol TSDC sample cell and polarized by an electrostatic field E_p (~100 V/mm) with a home-made voltage source at polarization temperature T_p = 20 °C for t_p = 5 min. With the field still applied, the sample was cooled to −150 °C (cooling rate 10 °C/min, under nitrogen flow), sufficiently low to prevent depolarization by thermal energy, then short-circuited and reheated up to 50 °C at a constant heating rate b = 3 °C/min. Temperature control was achieved by means of a Novocontrol Quatro cryosystem. A discharge current was generated during heating and measured as a function of temperature with a sensitive programmable Keithley 617 electronmeter.

2.7. Dielectric relaxation spectroscopy (DRS)

For dielectric relaxation spectroscopy [17] measurements, the sample (the same as used for TSDC measurements) was placed between the plates of a capacitor and an alternate voltage was applied in a Novocontrol sample cell. The complex dielectric permittivity, \( \varepsilon'' = \varepsilon' - i\varepsilon'' \), was recorded isothermally as a function of frequency in the range from 10⁻¹ to 10⁶ Hz at temperature from −150 °C to 60 °C (in nitrogen atmosphere) in steps of 2.5, 5 and 10 °C (depending on the process to be studied) using a Novocontrol
Alpha analyzer. The temperature was controlled better than ±0.5 °C with a Novocontrol Quatro cryosystem.

2.8. Hydrophobicity

The hydrophobicity of the samples was measured as a contact angle value for water drops placed onto a sample surface using a sessile drop method with a USB digital microscope (Sigeta, China, magnification ratio 20× to 200×). A drop of distilled water was applied to a pressed pellet with an oxide/PDMS sample previously heated at 80–700 °C for 0.5 h (this treatment results in temperature-dependent degradation of the PDMS layer differently affected by silica and Fe₂O₃/SiO₂ surfaces). Measurements were carried out in air at room temperature (18 ± 0.5 °C). The calculations were made using data described elsewhere [18].

3. Results and discussion

3.1. Characteristics of oxide and PDMS/oxide systems

The FTIR spectra (Fig. 1) show that PDMS molecules interact with the silica surface since the intensity of the band of free silanols at 3750 cm⁻¹ decreases with increasing polymer fraction due to the hydrogen bonding to PDMS. The content of adsorbed PDMS was controlled by changes in the C–H stretching vibrations of the CH₃ groups in the 2930–3110 cm⁻¹ range (using the Omnic 6.1 program) (Fig. 2). These values were normalized to the intensity of the band at 1865 cm⁻¹. The presence of Fe₂O₃ does not affect on the FTIR spectra of adsorbed PMPS. The spectral patterns depend on the amount of adsorbed polymer. The character of changes of the І_C–H value for these two series is the same and has a linear dependence on PDMS content (Fig. 2). That indicates equal content of the polymer on the surface of the samples.

It is known [19] that only a portion of the segments of adsorbed PDMS molecules can interact with a surface with formation of hydrogen bonds mMO–H–O[Si(CH₃)₂]ₙ (where M=Si or Fe). Notice that the surface of Fe₂O₃ has different number of hydroxyl groups on the surface (4–5 OH-groups per nm² [20]) and they can absorb water, which can promote the reactions of hydrolysis of the polymer, as well as participate in the adsorption of polymer.

3.2. Thermal decomposition of adsorbed PDMS

Thermal decomposition of PDMS on a silica surface was investigated in details [21–23]. Decomposition of PDMS alone can occur in air due to oxidation of methyl groups with the formation of silica (Scheme 1) [24] or due to depolymerization with the formation of hexamethyldisiloxane (HMETS) (Scheme 2).

\[
-\text{OSi(CH₃)₂} \rightarrow + 4\text{O}_2 \Rightarrow \text{SiO}_2 + 2\text{CO}_2 + 3\text{H}_2\text{O} \quad \text{(Scheme 1)}
\]

\[
-\text{OSi(CH₃)₂} \rightarrow \text{SiO}_2 + 2\text{CO}_2 + 3\text{H}_2\text{O} + \text{dimethylsilyl radicals} \quad \text{(Scheme 2)}
\]

The DTG curves for Fe₂O₃/SiO₂/PDMS samples exhibit three well-defined regions of the mass loss (Fig. 3b). There is correlation between the amount of PDMS (intensity of the peaks) and the temperature of onset of the mass loss (Table 1). The first region is attributed to the removal of physically sorbed water (T=50–120 °C), while the next two steps are due to oxidation of methyl groups and removal of volatile cyclic siloxanes according to Schemes 1 and 2. According to the content of PDMS in the samples, we calculated the final results of the mass changes in samples during the reactions proceeding according to Schemes 1 and 2. The experimental values of the mass losses of the samples were determined in the interval 120–1000 °C. The calculated and experimental data are presented for comparison in a diagram (Fig. 3).

The calculated lower curve (Fig. 3d) corresponds to Scheme 1 and the upper curve represents reaction (5). The experimental data (Fig. 3d) show that the destruction of dimethylsilyl groups in the Fe₂O₃/SiO₂/PDMS precedes mainly according to Scheme 2 with increasing contribution of depolymerization reaction at T>350 °C. Previously [23] it was shown that oxidation of PDMS/SiO₂ occurs mainly according to reaction (4).

It is evident from the obtained results (Fig. 3) that the thermal decomposition of PDMS on the surfaces of the modified silica begins at lower temperature than in case of initial PDMS/SiO₂. This makes it possible to assert that iron oxide leads to a partial depolymerization of adsorbed PDMS according to Scheme 2, followed by crosslinking of the polymer that leads to loss of flexibility of the chains and the density of PDMS layer increases so final destruction
occurs at higher temperature. That is illustrated in Fig. 3 by shifting of the DTG peaks toward higher temperatures with increasing of the intensity of the peaks according to the rising of PDMS content. In the case of SiO2/PDMS, on the contrary, the peaks are shifted toward lower temperature with increasing PDMS content.

The effect of Fe2O3 on the thermal destruction of PDMS is well observed in the FTIR spectra of treated samples. The integral intensity of the C–H (IC–H = 3100–2900 cm⁻¹) and O–H (IO–H = 3748 cm⁻¹) stretching vibrations depends on concentration of PDMS (Fig. 4). The SiO2/PDMS samples are characterized by a decrease in concentration of the methylsilyl groups (IC–H) at T > 350 °C due to the thermal oxidative destruction, whereas for Fe2O3/SiO2/PDMS, thermal destruction begins at lower temperature (~200 °C). The IC–H values regularly decrease at ~200 °C; however, restoring of OH groups is not observed at this temperature. This may be due to destruction of Si–CH3 groups leading to formation of silica deposits remaining on the surface, and restoring of Si–OH groups can be observed only after complete destruction of organic functionalities.

During the depolymerization, organopolysiloxane can undergo complete transformation into volatile products, which can be chemisorbed on the free silanols to form new arched structures. The oxidation of Si–CH3 groups is accompanied by the formation of Si–OH groups, which interact with each other to form siloxane bonds Si–O–Si [24]. This can be displayed as a significant increase in the specific surface area (Fig. 5).

The influence of mixed oxides on thermal transformation of the polymer can be estimated by measuring of the hydrophobicity of the samples since silica and iron oxide are hydrophilic but PDMS is hydrophobic. The adsorbed polymer forms a hydrophobic coating on the surface and oxidation of dimethylisyl groups leads to reconstruction of silanol groups and changing the hydrophobic properties toward hydrophilic ones. Dependence of the contact angle of water drops on calcination temperature of Fe2O3/SiO2/PDMS and SiO2/PDMS samples shows that the hydrophobic range of Fe2O3-contained samples is wider than in case of SiO2/PDMS (Fig. 6). The maximum contact angle of water drops of SiO2/PDMS is observed after heating at 300–400 °C and reached 112–116° (20% and 30% wt% of polymer). For samples Fe2O3/SiO2/PDMS, maximum angles of 114–116° are observed after heating at 200–350 °C (20–30 wt% of PDMS). Thus, iron oxide shifts the degradation of PDMS toward lower temperatures.

Increasing contact angle of water drops on the surface of the composites containing Fe2O3 is due to the formation of a denser PDMS layer under mild temperature conditions. Iron oxide affects the process of PDMS destruction. The chemisorption of the products

![Table 1](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss at different temperatures (%)</th>
<th>According to Eq. (4)</th>
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<tr>
<td></td>
<td>30–120 °C</td>
<td>120–350 °C</td>
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<tr>
<td>SiO2/PDMS40</td>
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<td>11.9</td>
</tr>
<tr>
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</tr>
<tr>
<td>Fe2O3/SiO2/PDMS20</td>
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<td>5</td>
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<tr>
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<td>Fe2O3/SiO2/PDMS40</td>
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<td>23.6</td>
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<td>Fe2O3/SiO2/PDMS80</td>
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<td>66.8</td>
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</table>
of PDMS decomposition on surface silanols enhances the hydrophobic properties. Further increasing of heating temperature up to 550 °C leads to complete oxidation of the methyl groups and restoring of the surface silanol groups; therefore, the surface becomes more hydrophilic. These results are in good agreement with the FTIR spectroscopy data (Fig. 4).

Thus, Fe2O3 nanoparticles in composites with silica and PDMS promote hydrophobic properties of the polymer coating. On the other hand, there is correlation between the reduction of the temperature of PDMS degradation and increasing hydrophobic properties in the presence of Fe2O3.

3.3. DSC measurements

Results obtained by the TSDC, RDS, and DSC techniques indicate the presence of an interfacial PDMS layer around the Fe2O3 and silica nanoparticles with the structure/morphology and chain dynamics modified in comparison with the bulk polymer.

DSC measurements of Fe2O3/SiO2/PDMS nanocomposites at different contents of PDMS (Fig. 7) give glass transition temperature Tg determined as a midpoint of the heat capacity step at glass transition [14]. The crystallization (Tc) and melting temperatures (Tm) were determined as the peak temperatures of the corresponding peak. In the cooling scans, the glass transition peak is observed around −130 °C (C_{PDMS} = 30 and 40 wt%), and the single exothermic peak of crystallization is at −97 °C (C_{PDMS} = 40 wt%). Heating scans show changes in the thermal transitions of the polymer in the temperature range from −175 °C to 0 °C with increasing PDMS content. The glass transition temperature tends to increase with increasing amount of polymer (Table 2). Here Tg refers to the fraction of amorphous polymer which is not immobilized. The rise of Tg of the amorphous mobile phase can be interpreted as packing of the polymer chains in voids between nanoparticles in aggregates [7]. At the same time, the glass transition range shows no systematic variation with composition (Fig. 7).

In the case of nanocomposites with a large content of PDMS, an exothermic event is observed close to the Tg region, representing cold crystallization [8]. This is a result of uncompleted crystallization during cooling. For lower PDMS contents and pure PDMS, this phenomenon is absent indicating that at the used cooling rate (10 °C/min) crystallization is completed. Thus, only with increasing polymer content and decreasing oxide nanoparticles content the
creation of crystallization nuclei is observed. It follows that crystallization in these materials takes place not close to the nanoparticles [15], which also provide constraints for the diffusion of the polymer chains and the growth of the crystals.

At higher temperatures, endothermic melting peaks are observed between −60 °C and −28 °C. Previously, double melting peaks have been observed in the PDMS systems [25]. The secondary weaker melting peak precedes the main one by 10–12 °C.

The crystallinity is observed only at C_{PDMS} = 80 wt%. The nonlinear concentration dependencies of the thermodynamic characteristics of the composites can be explained by changes in the relative amounts of polymers being in contact with filler nanoparticles and the corresponding changes in the mobility and density of PDMS in the interfacial layer in comparison with the bulk polymer.

Above 250 °C, the mass loss (Fig. 3d) results from the removal of strongly adsorbed water and from the dehydration of surface hydroxyls. It is known that Fe₂O₃ contains various forms of water and hydroxyl groups. According to [20], the number of hydroxyl groups per mm² of iron oxide surface is 4.4–10.0 (hematite), 5.1–9.8 (maghemite), and 5–5.2 (magnetite). Surface hydroxyl groups can be linked to one (FeOH), two (Fe₂OH) or three (Fe₃OH) surface iron atoms. There are geminal (twin) hydroxyls, i.e. two hydroxyls

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>T_c (°C)</th>
<th>ΔH_m (J/g)</th>
<th>X_{cryst} (±5%)</th>
<th>T_p (°C)</th>
<th>ΔG_{cr} (J/gK)</th>
<th>ΔH_{m} (J/g)</th>
<th>T_{m1} (°C)</th>
<th>T_{m2} (°C)</th>
<th>ΔH_m (J/g)</th>
<th>X_{cryst} (±0.05)</th>
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<tr>
<td>Fe₂O₃/SiO₂/PDMS10</td>
<td>−</td>
<td>0</td>
<td>0</td>
<td>−</td>
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<td>0</td>
<td>−</td>
<td>−</td>
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<td>0</td>
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</tr>
<tr>
<td>Fe₂O₃/SiO₂/PDMS30</td>
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<td>0</td>
<td>0.00</td>
<td>−129</td>
<td>0.22</td>
<td>0</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>0</td>
</tr>
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<td>Fe₂O₃/SiO₂/PDMS40</td>
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<td>0</td>
<td>0.00</td>
<td>−129</td>
<td>0.17</td>
<td>3</td>
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<td>−4</td>
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<tr>
<td>PDMs initial</td>
<td>−78</td>
<td>30</td>
<td>0.8</td>
<td>−124</td>
<td>0.81</td>
<td>30</td>
<td>−48</td>
<td>30</td>
<td>0.27</td>
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</tbody>
</table>

Note: Thermal (DSC) data determined from (i) cooling scan: crystallization temperature T_c, crystallization enthalpy ΔH_m and degree of crystallinity as calculated from the crystallization peak X_{cryst}. (ii) heating scan: temperature and normalized heat capacity change of glass transition T_p and ΔG_{cr} respectively, cold crystallization enthalpy ΔH_{cc}, melting peak temperatures T_{m1} and T_{m2}, melting enthalpy ΔH_m and degree of crystallinity calculated from the melting peak X_{cryst}.  

Fig. 6. Dependence of the contact angle of water drops on calcination temperature of (a) Fe₂O₃/SiO₂/PDMS and (b) SiO₂/PDMS.

Fig. 7. DSC thermograms of Fe₂O₃/SiO₂/PDMS heated at 80 °C at different polymer contents, during (a) cooling and (b) heating; inset in (b) shows the temperature region of glass transition.
bound to the same iron atom. Thus, appearance of the single exothermic peak of crystallization around \(-97^\circ C\) (Fig. 8), after calcination at 200 °C, can be attributed to the removal of physically adsorbed water that contained in the polymer. This water prevents the polymer chains mobility during freezing of the samples. After heating up to 150–200 °C, water evaporates and the chains remain more mobile during subsequent cooling.

3.4. Thermally stimulated depolarization currents (TSDC)

TSDC measurements of \(\alpha\) and \(\alpha'\) relaxations (Fig. 9) give information about the nature of interactions of the polymer with the oxide surface, since \(\alpha\) relaxation is the segmental relaxation of free (bulk) polymer chains, associated with the glass transition of the amorphous phase of PDMS, whereas \(\alpha'\) is defined as the segmental relaxation of PDMS chains in the interfacial layer close to the silica surface [8]. Chain mobility in the interfacial layer is constrained due to hydrogen bonding of the oxygens on the polymer backbone to the hydroxyls on the silica surface and dispersion interactions with silica particles [26]. The thermogram of pure PDMS shows a peak at \(-132^\circ C\), which corresponds to the segmental \(\alpha\) relaxation. The temperature \(T_m\) of the peak maximum is in good agreement with the DSC data (Fig. 2), of the \(\alpha'\) relaxation, located between \(-120^\circ C\) and \(-90^\circ C\) in the nanocomposites is absent in unfilled PDMS, in agreement with and in support of the assignment of the relaxation to polymer chains in the interfacial layer around the nanoparticles. The results in Fig. 9 show that the overall dielectric response and, in particular, the dielectric strength of both \(\alpha\) and \(\alpha'\) relaxations increases with increasing PDMS content.

For the Fe\(_2\)O\(_3\)/SiO\(_2\)/PDMS nanocomposites the peak temperature of \(\alpha\) relaxation (between \(-150^\circ C\) and \(-125^\circ C\)) shifts toward higher temperatures with decreasing PDMS content (arrows in Fig. 9b), indicating an overall reduction of molecular mobility of the polymer matrix with increasing filler content, due to constraints imposed by the filler particles [7]. Additionally, a shoulder appears on the high-temperature wing of the main \(\alpha\) peak extending up to approximately 30–40 °C higher, with its intensity increasing with increasing PDMS content. Following previous extensive work [5,26], the shoulder, present also in neat PDMS, is assigned to the \(\alpha_c\) relaxation of PDMS chains in a layer of amorphous polymer confined between crystal regions. Then, the main relaxation at about \(-132^\circ C\) in the composites is assigned to \(\alpha\) relaxation of the PDMS chains in larger amorphous regions that are sufficiently far from the oxides–nanoparticles. The \(\alpha_c\) relaxation (at about \(-123^\circ C\)) is faster and stronger than \(\alpha\) and its position is not affected directly by the nanoparticles. The strength of this relaxation decreases with reduction of crystallinity degree \(X_c\), which is in agreement with its assignment. Finally, the events recorded in

![Fig. 8. DSC thermograms of Fe\(_2\)O\(_3\)/SiO\(_2\)/PDMS (40 wt%) heated at various temperatures, during (a) cooling and (b) heating.](image_url)

![Fig. 9. Comparative TSDC thermograms of PDMS and Fe\(_2\)O\(_3\)/SiO\(_2\)/PDMS at various contents of PDMS. Thermograms are presented in full current range (a) and in more detailed scale for the nanocomposites (b). The arrows in (b) show changes with decreasing polymer content.](image_url)
the temperature range between −105 °C and −94 °C are related to cold crystallization.

3.5. Dielectric relaxation spectroscopy (DRS)

DRS was used to investigate molecular dynamics in the bulk and interfacial layers by following the temperature dependence of the corresponding dielectric relaxations. DRS results are presented here in the form of temperature (Fig. 10, isochronal plot) and frequency dependencies (Fig. 11, isothermal plot) of the imaginary part of dielectric permittivity (dielectric loss) $\varepsilon''$. We focus here on segmental dynamics, i.e., the dielectric relaxations $\alpha$, $\alpha_c$, and $\alpha'$ corresponding to the TSDC data in the temperature range between −70 °C and −150 °C (Fig. 9b). A higher frequency of 3 kHz was selected for (Fig. 10), as compared to TSDC (Fig. 9) to suppress conductivity effects [16].

Several relaxations can be observed in the isothermal plots of Fig. 10, the same as with TSDC (Fig. 9): $\alpha$, $\alpha_c$, and $\alpha'$, in the order of increasing temperature, with the assignment described above. Included in Fig. 11(a) are also results obtained with initial silica, where the response is dominated by a strong relaxation (S relaxation), arising from motion of hydroxyls on the silica surface, in agreement with previous results [5,8,10,11]. All these relaxations are thermally activated, shifting toward higher frequency with increasing temperature in the isothermal plots or to higher temperature with increasing frequency in the isochronal plots. Comparing the isochronal plots in Figs. 9 and 10 to each other, a shift of the relaxations to higher temperatures is observed in Fig. 10, obviously due to the higher frequency of presentation [26].

It can be seen that in the case of SiO$_2$/PDMS40, only $\alpha''$ and $\alpha_c$ relaxations are present. So all PDMS (40 wt%) interacts with the silica surface ($\alpha'$) or crystallizes ($\alpha_c$). In the case of Fe$_2$O$_3$/SiO$_2$/PDMS, $\alpha$ relaxation increases with increasing PDMS content, while $\alpha'$ relaxation decreases indicating, that the main part of PDMS is in amorphous phase and only a small part can interact with the oxide surface. The $\alpha_c$ relaxation can be observed only in samples with 40–80 wt% of PDMS. The results are in good agreement with the TSDC data.

The $\alpha$, $\alpha'$, $\alpha_c$ relaxations are observed for Fe$_2$O$_3$/SiO$_2$/PDMS also in the isothermal plots of Fig. 11, where their shift to higher frequency with increasing temperature can be also observed. It is interesting to note with respect to the S relaxation, arising from motion of hydroxyls on the silica surface, as mentioned above, that this relaxation practically disappears in the nanocomposites, even at high filler contents, indicating that the hydroxyls are now engaged in hydrogen bonding interactions with PDMS. Of particular interest is also that, based on the values of the crystallinity degree calculated from DSC data (Table 2) and the strength and frequency range of the $\alpha_c$ relaxation, we can confirm that this relaxation is similar to that observed in the TSDC thermograms.

The combined use of DSC, TSDC, and DRS provided clear evidence on the origins of the relaxations described above. Thus, we can use now the data for the dielectric strength from TSDC.
or DRS measurements, combined with the data for the degree of crystallinity, obtained from DSC measurements, to calculate the reduced mobility polymer fraction \( X_{\text{red}} \) (the fraction of polymer in the interfacial layer, Fig. 12) by the following equation

\[
X_{\text{red}} = \frac{\Delta F_d (1 - X_c)}{\Delta F_d + \Delta F_n}
\]

(4)

where \( \Delta F_d \) is the dielectric strength of each relaxation \([8, 26]\) and \( X_c \) is the crystallinity degree of each sample (Table 3). Calculations were carried out using both TSDC and DRS data and the results are presented in Fig. 12.

4. Conclusion

Nanoparticles of iron oxides in the Fe₂O₃/SiO₂/PDMS systems catalyze the thermal decomposition of PDMS and increase the contribution of depolymerization processes. Hydropathy of Fe₂O₃/SiO₂/PDMS heated at 100–650°C is higher than that of SiO₂/PDMS treated at the same temperatures. Molecular dynamics in the nanocomposites were studied using DSC and dielectric (TSDC, DRS) techniques. Three discrete relaxations in the region of the glass transition of PDMS were identified and studied, arising from the segmental mobility of the bulk (unaffected) polymer (\( \alpha \)-relaxation), the mobility of polymer chains restricted between condensed crystalline regions (\( \alpha_c \)-relaxation), and the segmental dynamics in the interfacial polymer layer around the oxide nanoparticles (\( \alpha' \)-relaxation).

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