

Electrical characterization of polymer matrix – TiO₂ filler composites through isothermal polarization / depolarization currents and I-V tests.

Research Article

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Abstract: Specimens of polymer matrix - ceramic TiO₂ filler composites were prepared. The contribution of the filler content on the electrical conductivity and energy storage properties of the samples was examined. I-V and Isothermal Polarization/Depolarization Current (IPC/IDC) measurements were conducted. Dc conductivity values directly calculated from the I-V curves exhibited excellent agreement with corresponding values derived from the IPC/IDC recordings. Standard models were employed for fitting the IPC/IDC data. In specific, the short and the very long depolarization times were fitted by use of power laws of different slopes, while the intermediate depolarization times were fitted as a sum of three exponential decays. The present study reveals a strong dependence of the depolarization and polarization processes, as well as of the dc conductivity, on the filler concentration.

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1. Introduction

In recent years, composite materials have attracted great attention, mainly due to the fact that integrating two complementary media in a new composite structure enables wide control of the physical and chemical properties of the final product [1–3]. A significant family of composite materials consist of polymer matrices filled with ceramic particles. Such polymer-ceramic structures are currently

employed in a wide range of applications that include batteries, capacitors and elastic-wave sensors [4, 5].

Electrical methods are emerging as an exciting tool for the characterization of composite structures. In this direction, time domain analysis of depolarization or decay current processes may provide valuable information regarding their dielectric response. The time dependent relaxation process that follows a sudden removal of a polarization field, may be considered as a succession of stages dominated by different time constants [6–13]. The occurrence of polarization/depolarization procedures with different time constants or relaxation times is attributed to the presence of different relaxation processes (multi-

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stages). These processes arise from both the polymeric matrix and the filler (interfacial polarization). Each of these stages is dominated by a particular type of transition: The initial stage corresponds to a rather short time duration ($t < 10^{-12}$ s) immediately after removing the applied field and may be considered as the delay required to establish the “flip” processes [6].

The second stage ($t < 5$ s) is dominated by small “flip” transitions which are stimulated by large number of dipoles attempting to relax and simultaneously interacting with each other [6, 8, 9]. The depolarization current during this stage follows a power law of the form t^{-n} [6, 8]. During the third stage, corresponding to intermediate depolarization times ($5 \text{ s} < t < 1000$ s), long range interactions (that may be attributed to the trap behavior) prevail [8, 9]. During this period of time the traps excited by the applied polarization are released and thus, the electric current I decreases monotonically [6–14]. This behaviour depends upon various mechanisms, each one corresponding to different time components [10–13]. These time components are related to discrete trap levels [10] and may be revealed by fitting experimental data with a sum of exponential decays of the form $I_0 + a \cdot e^{-\frac{t}{\tau_i}}$, where a and τ_i are constants strongly related to the material properties [10, 11].

During the final stage, that is the long depolarization times (i.e. $t > 1000$ s), the directional processes of the previous stages are replaced by fluctuations of the flip-flop transitions during which there is no further change of the dipole moment. Instead, a local redistribution of the energy establishes, providing slow relaxation processes according to the t^{-m-1} power law [6].

Furthermore, it should be stated that Isothermal Polarization/Depolarization Current (IPC/IDC) measurements may be used for estimation of the dc conductivity of dielectric materials [15–17]. Such measurements may easily provide information regarding polarization and conduction mechanisms in the bulk of a dielectric material.

In this work, we present an investigation on the charge storage ability and electrical conductivity of polymer matrix-TiO₂ composites by means of I-V and Isothermal Polarization/Depolarization Current techniques. Epoxy resin was employed as the polymer matrix, due to its stable thermomechanical properties, resistance to corrosive environments, ease of processing and attractive adhesive nature that allows the hosting of various fillers [18–20]. Furthermore, titanium dioxide (TiO₂) particles were chosen as the ceramic filler, mainly due to the fact that TiO₂-based composites have been proven excellent candidates for use in a wide range of applications, including integrated decoupling capacitors, angular acceleration accelerometers, acoustic emission sensors, and electronic

packaging [21–24].

To the best of our knowledge, only one previous study exists on the dielectric properties of polymer-TiO₂ composites [23]. In this work, the authors reported relaxation phenomena in the frequency range 0.1 Hz–1 MHz and for temperatures ranging between 370 K and 420 K, exhibiting contributions from both the polymer matrix and the reinforcing phase. Since the IPC/IDC experimental technique is the time domain equivalent of dielectric spectroscopy, complex dielectric permittivity may be also determined by measuring the time dependent dc current of a charged specimen [25]. Consequently the IPC/IDC method is suitable for materials which can be polarized such as ceramics, glasses, polymers and composites.

2. Experimental details

2.1. Materials

Polymer matrix – ceramic TiO₂ specimens were prepared in different concentrations, namely pure polymeric matrix, 10 phr (parts per hundred weight of ceramic TiO₂), 15 phr, 20 phr, 25 phr 30 phr and 50 phr. The thickness of the specimens varied between 1.5 mm and 2.5 mm while the diameter of all specimens exceeded 30 mm. The polymer matrix was prepared using the low viscosity epoxy resin Epoxol 2004 A (Neotex S.A., Athens, Greece) and the curing agent Epoxol 2004B. The ceramic titanium dioxide powder with a mean particle diameter of less than 5 μm was provided by Sigma-Aldrich. The preparation methodology of the specimens has been previously described in detail [23].

2.2. Experimental set-up

The specimen under investigation was mounted on a custom made cell. The cell was installed inside a metallic chamber in order ensure that external electrical noise was not affecting the measurements. Additionally, a vacuum pump (providing a vacuum in the order of $10^{-1} - 10^{-2}$ mBar) was used to remove any moisture from the chamber. Two gold plated electrodes were attached to the specimen surface with the use of springs in order to avoid mechanical load effects. A silica isolation of the current electrode was also used in order to reject additional electrical currents that were not related to the specimen. The empty cell geometric capacitance was measured to be approximately 30 pF.

Isothermal measurements were performed under an actively controlled constant temperature of 300 K ± 0.5 K. The built in voltage source module of a Keithley 617 sensitive electrometer was used to apply the required electric

field, while the electrical current was measured using a Keithley 6514 programmable electrometer. Instrumentation control and data acquisition was conducted through IEEE488 and Serial interfaces.

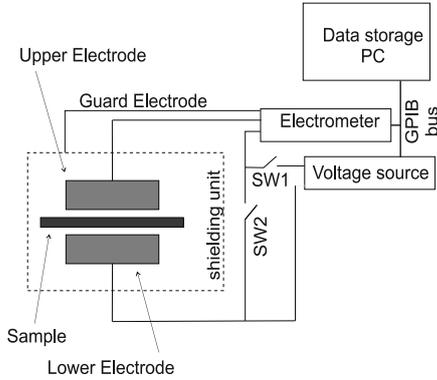


Figure 1. Schematic diagram of the electrical connections used to conduct electrical conductivity and isothermal polarization and depolarization current measurements.

A schematic diagram of the experimental setup is shown in Figure 1. During the polarization time (t_p) the switch 1 (SW1) was closed and switch 2 (SW2) was open. During the depolarization time (IDC) SW1 was open and SW2 was closed. To conduct the IPC/IDC measurements an electric field $E_p = 1$ kV/cm was applied to the specimens ($E_p = \frac{V_p}{d}$ where V_p is the polarization voltage and d is the thickness of the specimen). The IPC was measured for a polarization time $t_p = 30$ min at a temperature of $300 \text{ K} \pm 0.5 \text{ K}$. The duration of the polarization was proven to be sufficient for the polarization current (I_p) to be stabilised. Subsequently, IDC measurements were conducted for time t_d until the depolarization current (I_d) reached a background level. The time t_d was experimentally observed to be longer than 10^3 s.

The above instrumentation was also employed for the I-V measurements. It should be noted that in this case an alternating dc electric field was applied to the specimen prior to each measurement, in order to avoid electrode polarization effects.

2.3. Results – discussion

Following the previously described experimental procedure, the IPC and IDC were recorded and are shown in figures 2a and 2b respectively for all specimens (pure polymeric matrix and composite specimens from 10 phr to 50 phr TiO₂ composites).

The times t_p and t_d control the energetic level of the activated traps and the consequent behaviour of the IPC and IDC. During experiments it was realized that throughout the short polarization and depolarization times ($t < 1000$

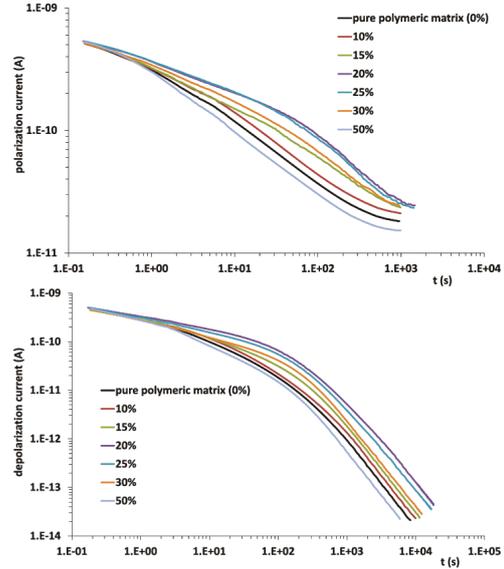


Figure 2. (a) Isothermal Polarization Current recordings for epoxy resin - TiO₂ particles composite specimens at various filler concentrations, (b) Isothermal Depolarization Current recordings for epoxy resin - TiO₂ particles composite specimens at various filler concentrations.

s) the IPC and IDC obtained the same values. This observation may be attributed to dipole reorientation and low-energy trap activation. During longer t_p times the charge is located in higher energy traps having low impact on the IPC.

The experimental IDC curves were fitted using the following relations:

$$I_d(t) = I_0 \cdot t^{-n} \text{ for short depolarization times} \quad (1)$$

$$I_d(t) = I_0 + \sum_{i=1}^3 A_i \cdot e^{-\frac{t}{\tau_i}} \text{ for intermediate depolarization times} \quad (2)$$

$$I_d(t) = I_0 \cdot t^{-1-m} \text{ for long depolarization times.} \quad (3)$$

For the short and long depolarization times - the Jonscher depolarization model [6] was used to describe the behaviour of the IDC curve (Eqs. (1) and (3)) while the intermediate times were fitted as the sum of three exponential decays (Eq. (2)) [10–14]. In all cases, when using - the Jonscher depolarization model, the short depolarization times were limited in the first 2 s to 5 s approximately while the long depolarization times were assumed to exceed 10^3 s.

Figure 3 shows a representative IDC curve fitted according to Eqs. (1), (2) and (3). The curve corresponds to the

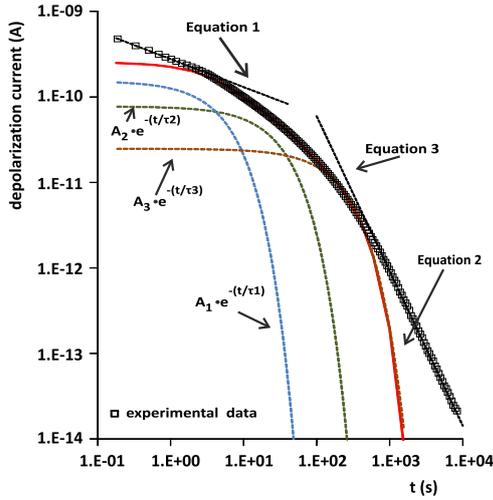


Figure 3. The IDC curves for the 10 phr specimen and the corresponding fitting curves. The colored lines describe the temporal behavior of each of the components of the summation of Eq. (2) during the intermediate depolarization times.

Table 1. The fitting parameters (i.e. the exponential factors n and m as well as the times τ_1 , τ_2 and τ_3 for all the filler’s concentrations, according to the Eqs. (1)-(3)).

%	n	m	τ_1 (s)	τ_2 (s)	τ_3 (s)
0	0.33	0.81	5.0	29	206
10	0.29	0.80	6.0	33	247
15	0.27	0.79	6.0	40	261
20	0.24	0.76	8.4	70	417
25	0.27	0.70	7.1	62	354
30	0.31	0.76	5.9	49	274
50	0.35	0.78	4.0	24	162

10 phr TiO_2 filler content. The colored lines of the figure show the behaviour of the three discrete exponential decays as described in Equation (2). Table 1 summarizes the computed fitting parameters for all the filler’s concentrations as well as for the pure polymeric matrix specimens, namely the exponential factors n and m as well as the times τ_1 , τ_2 and τ_3 .

Figures 4a and 4b show the behavior of the factors n and m as well as the behavior of the characteristic times τ_1 , τ_2 and τ_3 for all the filler concentrations as well as for the pure polymeric matrix. The characteristic times (τ_1 , τ_2 , τ_3) achieve their maximum values at the 20 phr and 25 phr concentrations. During the initial times of the depolarization process the low activation modes take place while gradually, for longer times, deeper traps are excited. This fact suggests that when the values of τ_1 , τ_2 and τ_3 become higher, implying that a longer time is required

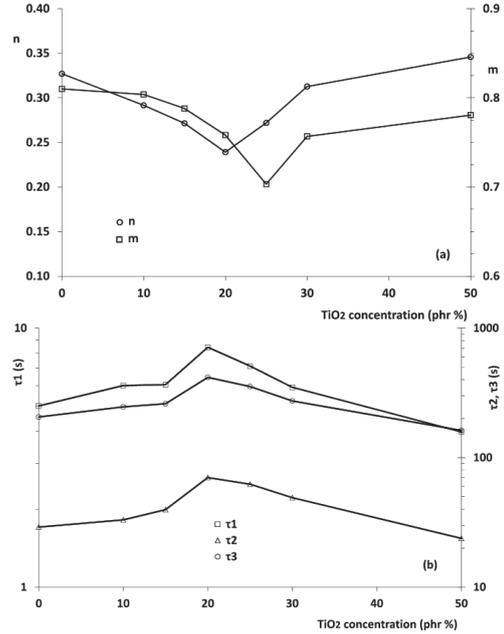


Figure 4. (a) The values of factors n and m with respect to the filler concentration (phr) and (b) the corresponding behavior of the times τ_1 , τ_2 and τ_3

to activate the deep traps, higher charge quantities are stored.

The examined composite systems may be considered as a distributed network of capacitors within the polymer matrix. Charging of specimens is directly related to the energy storing capability on the TiO_2 particles. Polarization currents reflect the amount of the cumulative stored charge according to $Q = \int_0^{t_p} IPC(t) dt$. Figure 5 shows the calculated charge storage with respect to the TiO_2 filler content. It is clear that the specimens with 20 and 25 phr TiO_2 filler content achieve maximum charge storing capability.

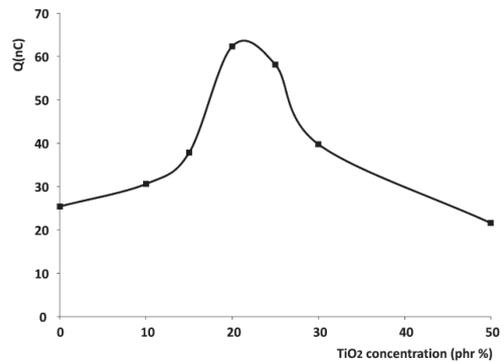


Figure 5. The behaviour of the stored cumulative charge during each polarization process with respect to the TiO_2 filler content.

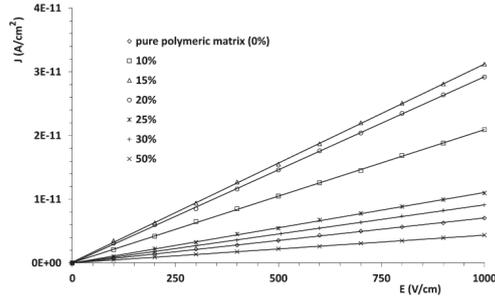


Figure 6. The J-E plots for all the studied composites versus filler concentration (phr).

Sequentially, I-V measurements were conducted. From the experimental results – the electric field (E , V/cm) as well as the electrical current density (J , A/cm²) were calculated. The corresponding J-E curves are shown in Figure 6.

It can be clearly seen that the J-E curves are linear and provide a direct way to calculate the electrical conductivity through:

$$\sigma = \frac{J}{E}. \quad (4)$$

In parallel, the electrical conductivity may be also calculated from the IPC/IDC curves via [16, 17]:

$$\sigma \approx \frac{\epsilon_0}{C_0 \cdot U_0} \cdot [i_p(t) - i_d(t)], \quad (5)$$

where ϵ_0 is the vacuum permittivity, C_0 denotes the measured geometric capacitance, U_0 is the polarizing step voltage value and $i_p(t)$ and $i_d(t)$ are the polarization and depolarization electrical current time functions.

The electrical conductivity values calculated based on both alternative approaches, as a function of the filler content are plotted in Figure 7.

It is worth noting that the electrical conductivity is expected to be time-independent due to its linear relation to the polarization and depolarization current time functions. This effect was clearly observed for this complex system. However, this approach may not provide detailed information regarding the independent conductivity contributions of the filler and the epoxy resin.

Figure 7 shows that the dc conductivity preserves a peak for the TiO₂ filler content around 20 phr. This behavior may be attributed to the location and the density of the filler particles, as well as the conductive paths that are formed, and implies the existence of an optimum filler concentration. Optimum electrical performance achieved at an intermediate filler concentration has been previously reported in the literature in polymer matrix/polar oxides

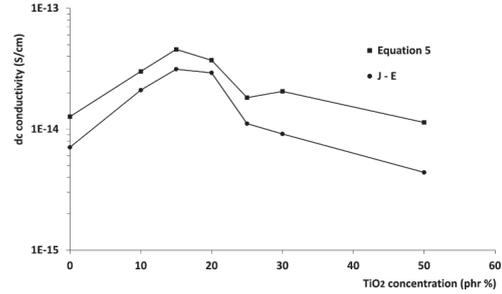


Figure 7. The electrical conductivity with respect to the specimen filler content using the slope of the J-E curves and the difference between the polarization and depolarization currents.

composites [26–28]. In these previous studies, this effect was interpreted via the presence of orientation obstructions, voids, and extensive agglomerates.

3. Concluding remarks

Isothermal Polarization/Depolarization Current (IPC/IDC) and I-V measurements were conducted on epoxy resin matrix – TiO₂ particles composites of various filler concentrations. The IPC/IDC curves were analyzed using well known models and the storage capability of the specimens was estimated. It was revealed that concentrations around 20 phr achieve maximum energy storage capability. Additionally, the dc conductivity was calculated indirectly from the IPC/IDC curves, as well as directly from the I-V measurements; both calculations indicated that electric conductivity also acquires maximum values for TiO₂ particle concentration in the range of 20 phr.

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