Dielectric relaxation and alternating current conductivity of lanthanum, gadolinium, and erbium-polyvinyl alcohol doped films

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Fourier transform infrared (FTIR) spectrum dielectric constant, ϵ' , loss tangent, $\tan(\delta)$, electric modulus, M^* , and ac conductivity, σ_{ac} , of pure polyvinyl alcohol (PVA) as well as La-, Gd-, and Er-PVA doped samples have been carried out. The dielectric properties have been studied in the temperature and frequency ranges; 300–450 K and 1 kHz–4 MHz, respectively. FTIR measurements reveal that La^{3+} , Gd^{3+} , and Er^{3+} ions form complex configuration within PVA structure. Two relaxation processes, namely, ρ and α were observed in pure PVA sample. The first process is due to the interfacial or Maxwell-Wagner-Sillars polarization. The second one is related to the micro-Brownian motion of the main chains. For doped PVA samples, α -relaxation process splits into α_a and α_c . This splitting is due to the segmental motion in the amorphous (α_a) and crystalline (α_c) phases of PVA matrix. Electric modulus analysis was discussed to understand the mechanism of the electrical transport process. The behavior of ac conductivity for all PVA samples indicates that the conduction mechanism is correlated barrier hopping. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739752>]

I. INTRODUCTION

In recent years, lanthanide chemistry has attached great interest for the various molecular structures with different applications.^{1–3} A lot of work has been done to direct synthesize super-molecular compounds due to their interesting topologies and potential applications as a functional materials.^{4–7} The reasonable design of super-molecular structure depends on the concepts of non-covalent forces such as coordination and hydrogen bonds. Polyvinyl alcohol (PVA) anions are suitable bridging ligands for constructing network coordination polymers.^{5,6,8–10} PVA is a semi-crystalline polymer and its crystalline index depends on the synthetic process and physical aging.⁸ It has gained increasing attention in the biomedical field due to bioinertness.^{11,12} Polymers and polymeric composites have steadily gained growing importance in our daily life. Doping of transition metal salts into permanently polarized vinyl polymers in a multiphase system can induce pronounced changes in various properties of complexes. These complexes can be used as sensors electrochromic displays and solid state lasers.¹³

The dielectric constant and the dissipation factor are crucial quantities required in the design of devices. Furthermore, the temperature and frequency dependence of the dielectric constant and the dielectric dissipation reveal much information on the chemical and physical state of the polymer. The dielectric behavior of polymer is determined by the charge distribution and also the statistical thermal motion of its polar groups. The study of dielectric relaxation in polymeric films is a powerful approach for obtaining information about the characteristics of ionic and molecular interactions.

The dielectric parameters associated with relaxation processes are of particular significance in ion conducting polymers. The ac conductivity and the dielectric relaxation are both sensitive to the motion of charged species and dipoles of the polymer.

Rare earth complexes are suitable candidates for applications such as light emitting diode, optical fiber, laser materials, and optical signal amplifications. It was found that rare earth salts have a considerable effect on the structure, optical, and electrical properties of polymers.^{14,15} Therefore, the aim of this work is to study the effect of an additive LaCl_3 , GdCl_3 , and ErCl_3 on the dielectric properties of PVA films to shed light on their molecular relaxations and conduction mechanism as well as to improve the performance of these materials.

II. EXPERIMENTAL

PVA, obtained from Avondale Laboratories (Banbury Oxon, England), had an average molecular weight of 17 000. Lanthanum, gadolinium, and erbium chloride were obtained from Sigma–Aldrich (Steinheim, Germany). PVA powder was dissolved in triply distilled water at 80 °C with continuous stirring. The mixture was kept at 80 °C for 30 min until a clear solution was obtained. The solution was cooled slowly with continuous stirring at 50 °C. Lanthanides chloride (LaCl_3 , GdCl_3 , or ErCl_3) of 10 wt. % was dissolved in 0.5–1 ml of concentrated HCl, and the mixture was diluted by the addition of 10 ml of triply distilled water at 50 °C with continuous stirring. The mixture was added to the PVA solution at 50 °C with continuous stirring of the final mixture for 12 h. The aqueous solution of the mixture was cast into a Petri dish placed on a leveled plate at room temperature (35 °C) for 7 days until the solvent was completely evaporated. The obtained polymer film, 0.08 mm thick, was cut into square pieces and coated with silver paste to achieve ohmic contacts.

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Fourier transform infrared (FTIR) spectra of pure PVA and lanthanides chloride doped PVA samples were recorded using model Shimadzu 8201 PC. All the measurements were done in the range of $4000\text{--}400\text{ cm}^{-1}$. The spectra were obtained for the absorbance of the polymer as a function of wave number with resolution 1 cm^{-1} and accuracy better than $\pm 4\text{ cm}^{-1}$. The dielectric measurements were carried out with a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR, the accuracy of which for measuring the capacitance was of the order of 0.0001 pF . The temperature was measured with a T-type thermocouple with its junctions just in contact with the sample with accuracy better than $\pm 1^\circ\text{C}$. PVA films filled with mass fraction; W of 10 wt. % of lanthanides chloride (LaCl_3 , GdCl_3 , or ErCl_3) was prepared. W (wt. %) was calculated as follows:

$$W(\text{wt.}\%) = \frac{w_f}{(w_p + w_f)} \times 100, \quad (1)$$

where w_f and w_p represent the weights of the filler (lanthanides chloride) and polymer, respectively.

III. RESULTS AND DISCUSSION

A. FTIR analysis

Infrared spectroscopy has used to identify the interaction in polymer composites FTIR spectroscopy is very sensitive to the formation of hydrogen bonds.¹⁵ Figs. 1(a)–1(d) show FTIR absorption spectra for pure PVA and that doped with 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 . All IR bands^{16–18} in Fig. 1(a) are the characteristic bands of pure PVA. The observed strong bands at $3430\text{--}3244\text{ cm}^{-1}$ are assigned to O-H stretching vibration of hydroxyl groups¹⁵ of PVA. The band corresponding to C-H asymmetric stretching vibration occurs at 2941 cm^{-1} and C-H symmetric stretching vibration at 2855 cm^{-1} . The band at 1735 cm^{-1} corresponds to stretching vibration of an acetyl C=O groups of PVA ester. The band at 1568 cm^{-1} is assigned to O-H and C-H bending vibrations. The corresponding bending wagging of CH_2 vibrations is found at 1433 and 1375 cm^{-1} , respectively, and C-H wagging is observed at 1256 cm^{-1} . The band at about 1095 cm^{-1} corresponding to C-O stretching of acetyl groups present in PVA structure.¹⁶ The band at 945 cm^{-1} is due to the C-O symmetric stretching.

As seen from Figs. 1(a)–1(d), the IR bands for lanthanides chlorides doped PVA are not modified drastically. This indicates that PVA is not destroyed much due to the addition of LaCl_3 , GdCl_3 , and ErCl_3 . It is observed that the absorbance at $3430\text{--}3244\text{ cm}^{-1}$ shows a decrease in the intensity for PVA sample doped with LaCl_3 , GdCl_3 , and ErCl_3 ; see Figs. 1(b)–1(d), respectively. So, the decrease of the intensity of the bands at $3430\text{--}3244\text{ cm}^{-1}$ indicates a decrease of the intensity of the O-H groups for all doped PVA samples. This is due to the formation of the noncovalent bonds between La^{3+} , Gd^{3+} , and Er^{3+} ions and O-H groups of the PVA backbone. Also, the hydrogen bonds play an important role for the complex formation between the lanthanides ions, and cations of PVA structure.

In addition, the maximum broadening of the O-H stretching band was achieved for the sample of PVA doped

FIG. 1. FTIR spectra of (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples.

with 10 wt. % of ErCl_3 . This can be assigned to the electronegative value of Er, 1.24 eV (Ref. 19), which is higher than the electronegative value of La, and Gd, 1.1 eV .¹⁹ As a result, Er^{3+} ions can form metal-ligand complexes within the PVA structure. These complexes can be bounded via coordination and ionic bonds with O-H group of the next layer of poly-anion molecules. In this approach, multivalent Er^{3+} ions act intrinsically as structure-forming linking components for the formed material, and the multipole salt bridges and coordination bonds result in the formation of a condensed structure.

B. Dielectric properties

Figs. 2(a)–2(d) show the temperature dependence of the ϵ' for pure PVA and that doped with 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed frequencies. It is clear that ϵ' of pure PVA increases smoothly with increasing temperature due to the increase of the mobility of the dipoles within the polymeric sample. Then, the dipoles have sufficient energy to orient themselves easily in the direction of the applied field. Moreover, the dependence of ϵ' on temperature confirms the orientational distribution of polymer

FIG. 2. Temperature dependent of ϵ' (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed frequencies.

chains in the crystalline and amorphous phases inside the polymer.²⁰ The doped PVA samples exhibit higher ϵ' values than that of pure one. The values of ϵ' at 100 kHz and 320 K are 16, 19, and 37 for PVA doped with 10 wt. % of ErCl_3 , GdCl_3 , and LaCl_3 , respectively. This can be assigned to the polarizability of these metals and the increasing of the ionic radii, 0.96 Å, 1.02 Å, and 1.15 Å of Er, Gd, and La (Ref. 19) in the same order. The electronegative force of the rare earth ions will cause the displacement of O-H and the other anion groups of the PVA. Then, the hydroxyl groups may have an order phase within the amorphous phase of PVA matrix. Also, the formation of La-, Gd-, and Er-PVA complexes may increase the nature of the traps centers and lower the potential barrier to detrapping.²⁰ These traps may be a result of disorder, contributing to the observed hopping conduction mechanism. In other words, rare earth ions may reside at amorphous-crystalline boundaries and diffuse preferentially, via heating, through the amorphous regions of the sample and thus form a charge transfer within the

polymeric chains.^{9,21} All these factors play an important role for increasing of ϵ' of the doped PVA samples.¹⁵

Figs. 3(a)–3(d) depict the temperature dependence of $\tan(\delta)$ for pure PVA and that contains 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed frequencies. It is observed that $\tan(\delta)$ of PVA undergoes two relaxation processes called α and ρ at 360 K and above 420 K, respectively. The α -process corresponding to the segmental relaxation associated with the glass rubber transition temperature, T_g , at which the micro-Brownian motion of long chain segment in the amorphous phase of PVA takes place.⁵ The ρ -relaxation process for semi-crystalline polymer like PVA is related to chain trapping of interfaces or Maxwell-Wagner-Sillars (MWS) polarization phenomena within the sample.⁸ However, in the amorphous part of PVA, ρ -process can be assigned to conductive impurities, injected space charges, and electrode polarization. This process originates from the motion of space charges which accumulate in the polymer close the electrodes. Therefore, it depends on the

FIG. 3. Temperature dependent of $\tan(\delta)$ (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed frequencies.

nature of electrode and the presence of impurities such as water molecule.²² Moreover, ρ -relaxation process is always appearing above the dipolar α -peak; the latter arises from the displacement of charges, whereas the former arises from the gross motion of charges over macroscopic distance.

It is noticed from the Figs. 3(b)–3(d) that $\tan(\delta)$ of LaCl_3 -, GdCl_3 -, and ErCl_3 -doped PVA undergoes three relaxations called α_a , α_c , and ρ . α_a and α_c are observed at 330 K and 372 K for La-PVA, 326 K and 370 K for Gd-PVA, and 348 K and 380 K for Er-PVA, respectively. The α_c -process is probably due to the segmental motion within the crystalline phase of PVA doped samples. While α_a -process is probably due to the micro-Brownian motion along main chain motion in the amorphous regions of the investigated sample. ρ -relaxation process is observed for all doped PVA samples after 430 K. This process is related to the existence

of the multiple topologies phases which come from the configuration of the complexes between La^{3+} , Gd^{3+} , and Er^{3+} ions and O-H groups of PVA backbone.⁶

The frequency dependent of $\tan(\delta)$ for pure PVA and that doped with 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed temperatures is shown in Figs. 4(a)–4(d). The behavior of $\tan(\delta)$ for pure sample exhibits α_a -relaxation process at 320 kHz and ρ -process at temperature higher than 363 K at lower frequencies about 1 kHz. The behavior of $\tan(\delta)$ for the doped PVA samples undergoes α_c - and α_a -process. The α_a -peak was found at about 320 kHz for all doped PVA samples, while α_c -process was observed at 6 kHz, 6 kHz, and 2 kHz for La-, Gd-, and Er-PVA sample, respectively. The peak position of the α_c -peak was shifted to higher frequency with increasing temperature. This indicates that the dielectric behavior of this process is dipolar in nature.^{5,23}

FIG. 4. Frequency dependent of $\tan(\delta)$ (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed temperatures.

C. Electric modulus formalism

In polymers and composite polymeric materials, interfacial polarization is almost always present. This refers to the existence of the additives, filler or even impurities that make these materials heterogeneous. Usually, in materials that characterize by a conductive component, interfacial polarization is obscured by the conductivity and dielectric permittivity which can be very high at low frequencies and high temperature.²⁴ To overcome this difficulty, the modulus formalism²⁵ has been used to analyze the electrical conductivity data in ionic polymeric material like PVA. The electrical permittivity was transformed into dielectric modulus M^* formalism according to²⁵

$$M^* = M' + M'', \quad (2)$$

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2}, \quad (3)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}. \quad (4)$$

The real component M' and imaginary component M'' were calculated from the dielectric constant ϵ' and the dielectric loss factor ϵ'' .

Figs. 5(a)–5(d) illustrate the temperature dependence of M' for pure PVA and that contains 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed frequencies. It is clear that the value of M' for pure PVA sample increases with increasing of frequency. The almost zero values of M' at low frequency and high temperature indicate the removal of the electrode polarization for pure PVA sample.²⁶

FIG. 5. Temperature dependent of M' (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed frequencies.

However, the values of M' are not zero for all doped PVA samples at high temperatures and low frequencies (see Figs. 4(b)–4(d)). Therefore, we can suggest that there is a role of electrode polarization for all these samples. In other words, the concentration of the filler influences polarization as well as dc and ac conductivities. In rare earth-polymer composites, the existence of interfaces gives rise to interfacial polarization or MWS effect.⁶ This phenomenon appears in heterogeneous media due to the accumulation of charges at the interfaces and the formation of crosslinking configurations between La^{3+} , Gd^{3+} , and Er^{3+} ions and O-H and C=O groups of the PVA main chains. Interfacial polarization results, in the permittivity mode, in high values of ϵ' and $\tan(\delta)$ which decrease rapidly with increasing frequency.^{27,28} For our studied composites, the electric modulus presentation and the relaxation behavior can be attributed to MWS effect.

The frequency dependent of M'' for pure PVA and that doped with 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed temperatures is presented in Figs. 6(a)–6(d). A relaxation peak was observed for both pure and doped-PVA

samples. This pattern provides wider information about the charge transport process such as mechanism of electrical transport, conductivity relaxation, and ion dynamics as a function of frequency and temperature. The peak of this process shifts toward the higher frequency side on increasing the temperature. The low-frequency side of the peak signifies the range of frequencies in which ions can perform successful hopping from one site to neighboring site. The high frequency side of M'' peak represents the range of frequencies in which the ions are spatially confined to their potential wells and ions can make localized motion within the well. The region where the peak occurs is an evidence of the transition from long-range to short range mobility with increase in frequency. This type of behavior of the electric modulus spectrum indicates that the conduction mechanism for pure and doped-PVA samples is temperature-dependent hopping type conduction.²⁹

The angular frequency ω_m at which the maximum of M'' occurs, defines the relaxation time, τ , by $\omega_m\tau = 1$. The temperature dependent of τ can be described by the Arrhenius relation³⁰

FIG. 6. Frequency dependent of M'' (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed temperatures.

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right), \quad (5)$$

where E_a is the activation energy of the relaxation process, τ_0 is the relaxation time at infinite temperature, k is the Boltzmann constant, and T is the absolute temperature. Fig. 7 displays the plot of $\ln(\tau)$ vs. $1000/T$ for pure PVA and its composites. The calculated values of E_a for pure PVA, La-, Gd-, and Er-doped PVA samples are 0.67 eV, 0.34 eV, 0.48 eV, and 0.56 eV, respectively. The values of E_a indicate that the ionic conduction mechanism is predominant for the investigated samples.⁹ The M'' curves at various temperatures can be reduced to a master curve with the peak position ($f_{\max}$) and the peak height ($M''_{\max}$) for α -relaxation process. Figs. 8(a)–8(d) show the master curve for pure PVA and that doped with 10 wt. % of LaCl₃, GdCl₃, and ErCl₃ at some fixed temperatures. The shape

shows an asymmetric behavior and is broader than that of Debye relaxation.²⁹ This phenomenon is well described by a non-Debye type of relaxation time governed by the relation²⁵

$$\phi(t) = \exp(-t/\tau)^\beta, \quad 0 < \beta < 1, \quad (6)$$

where $\phi(t)$ is the time evolution of electric field within the sample and β is the Kohlrausch exponent. The smaller value of β , the larger the deviation of relaxation with respect to Debye type relaxation ($\beta = 1$) (see Ref. 25). A non-exponential type of relaxation governed by Eq. (6) suggested that the possibility that ion migration takes place via hopping accompanied by a consequential time-dependent mobility of other charge carriers of the same type in the vicinity. It causes additional relaxation of the applied field as is evident from Figs. 6(a)–6(d).

FIG. 7. The relation between $\ln(\tau)$ and $1000/T$ for pure and doped PVA samples.

Figs. 10(a)–10(d) depict the frequency dependent of ac conductivity, σ_{ac} , for pure PVA and that doped with 10 wt. % of LaCl_3 , GdCl_3 , and ErCl_3 at some fixed temperatures. The ac conductivity at low temperature can be described by⁶

$$\sigma(\omega) = \sigma_{dc} + A\omega^s, \quad (7)$$

where ω is the angular frequency, σ_{dc} is the direct current conductivity, A is the constant, and s is the exponent factor. When the frequency is increased, the mean displacement of the charge carriers is reduced and thus, the ac conductivity of PVA samples follows the power law ω^s . As seen, ac conductivity increases with increasing frequency and temperature. This indicates that the hopping conduction mechanism is predominant for all PVA samples. The s values were calculated from the slope of $\ln(\sigma_{ac})$ vs. $\ln(\omega)$ (see Fig. 9).

The temperature dependence of the exponent s for all investigated samples is shown in Fig. 10. It is evident that s values decreased with increasing of temperature for all

FIG. 8. Master curve of $M''/M''_{\max}$ versus $\log(f/f_{\max})$ for (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed temperatures.

FIG. 9. Frequency dependent of $\ln(\sigma_{ac})$ (a) pure PVA, (b) La-PVA, (c) Gd-PVA, and (d) Er-PVA doped samples at some fixed temperatures.

PVA samples. This suggests that the correlated barrier hopping (CBH) conductivity is dominant for the conduction mechanism. In CBH model, exponent s is expressed as⁵

$$s = 1 - 6kT/W_M, \quad (8)$$

where W_M is the binding energy of the carriers in its states. The binding energy, W_M , was calculated from the slope of $1-s$ against T curve. It was found that W_M value is 0.2 eV, 0.22 eV, 0.26 eV, and 0.2 eV for pure PVA, La-, Gd-, and Er-doped PVA, respectively. The calculated values of W_M are nearly equal to the half values that calculated for E_a of the PVA samples. This can be attributed to the existence of the micro-inhomogeneity of PVA structure.^{5,6}

IV. CONCLUSION

FTIR spectra show that the addition of LaCl_3 , GdCl_3 , and ErCl_3 to PVA causes a reduction of the density of O-H groups. This due to the complexes formation between La^{3+} , Gd^{3+} , and Er^{3+} ions and the O-H groups of PVA structure. Based on the temperature and frequency dependence of $\tan(\delta)$, three relaxation processes in pure and doped-PVA samples can be identified. The first one occurs at T_g (α_a) and

FIG. 10. Temperature dependent of the s exponent for Pure and doped PVA samples.

the second (α_c), which is attributed to the dipole relaxation inside the crystalline regions of PVA doped samples. The third one is space charge polarization (ρ) and is due to chain trapping of interfaces or MWS polarization within PVA samples. Electric modulus formalism indicates that there is a role of electrode polarization in the relaxation process for all PVA doped samples. Both electric modulus and ac conductivity reveal that the CBH is the most probable conduction mechanism for the investigated samples.

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- ¹K. P. Mrötl, J. P. Sutter, S. Golhen, L. Ouahab, and O. Kahn, *Inorg. Chem.* **39**, 1626 (2000).
- ²M. Tabatabaee, A. M. Sharif, F. Vakili, and S. Saheli, *J. Rare Earths* **27**, 356 (2009).
- ³M. Diallo, M. Diop, P. M. Haba, M. Gaye, A. S. Sall, A. H. Barry, C. Beghidja, and R. Welter, *J. Chem. Cryst.* **38**, 475 (2008).
- ⁴B. Moulton and M. J. Zaworotko, *Chem. Rev.* **101**, 1629 (2001).
- ⁵T. A. Hanafy, *J. Appl. Polym. Sci.* **108**, 2540 (2008).
- ⁶A. Hassen, T. A. Hanafy, S. El. Sayed, and A. Himanshu, *J. Appl. Phys.* **110**, 114119 (2011).
- ⁷S. Leininger, B. Olenyuk, and P. J. Stang, *Chem. Rev.* **100**, 853 (2000).
- ⁸F. H. Abd El-Kader, W. H. Osman, K. H. Mahmoud, and M. A. F. Basha, *Physica B* **403**, 3473 (2008).
- ⁹T. A. Hanafy, *Curr. Appl. Phys.* **8**, 527 (2008).
- ¹⁰M. A. Ahmed, A. M. Basha, H. K. Marey, and T. A. Hanafy, *J. Appl. Polym. Sci.* **79**, 1749 (2001).
- ¹¹C. H. Cholakis, W. Zingg, and M. V. Seffon, *J. Biomed. Mater. Res.* **23**, 417 (1989).
- ¹²Q. Jin, X. Wang, T. Jin, and G. Xu, *Polyhedron* **13**, 2957 (1994).
- ¹³D. K. Sardar, K. L. Nash, R. M. Yow, J. B. Gruber, U. V. Valiev, and E. P. Kokanyan, *J. Appl. Phys.* **100**, 083108 (2006).
- ¹⁴F. Xie and Z. Z. Heng, *Physica B* **349**, 415 (2004).
- ¹⁵S. Rajendran, M. Sivakumar, and R. Subadevi, *Mater. Lett.* **58**, 641 (2004).
- ¹⁶V. Ravindrachary, Ismayil, S. P. Nayak, D. Dutta, and P. K. Pujar, *Polym. Degrad. Stab.* **96**, 1676 (2011).
- ¹⁷E. M. Abdelrazek, I. S. Elashmawi, and S. Labeeb, *Physica B* **405**, 2021 (2010).
- ¹⁸Y. Bader and M. A. Mahmoud, *Spectrochim. Acta A* **65**, 584 (2003).
- ¹⁹*Table of Periodic Properties of the Elements* (Sagent Welch Scientific Company, Skokie, IL, 1979).
- ²⁰D. A. Seanor, *Electrical Properties of Polymers* (Academic, New York, 1982).
- ²¹G. M. Sessler, *Electrets* (Springer-Verlag, Berlin, 1980).
- ²²J. H. Daly and L. Bunton, *J. Mater. Sci.* **18**, 2817 (1983).
- ²³M. A. Ahmed and T. A. Hanafy, *J. Appl. Polym. Sci.* **109**, 182 (2008).
- ²⁴A. Kyritsis, P. Pissi, and I. Grammatikakis, *J. Polym. Sci., Part B: Polym. Phys.* **33**, 1737 (1995).
- ²⁵S. Mahrous, T. A. Hanafy, and M. S. Sobhy, *Curr. Appl. Phys.* **7**, 629 (2007).
- ²⁶C. V. Subba Reddy, X. Han, Q. Y. Zhu, L. Q. Mai, and W. Chen, *Microelectron. Eng.* **83**, 281 (2006).
- ²⁷G. M. Tsangaris, G. C. Psarras, and N. Kouloumbi, *J. Mater. Sci.* **33**, 2027 (1998).
- ²⁸G. C. Psarras, E. Manolakaki, and G. M. Tsangaris, *Composites, Part A* **33**, 375 (2002).
- ²⁹G. M. Tsangaris, N. Kouloumbi, and S. Kyvelidis, *Mater. Chem. Phys.* **44**, 245 (1996).
- ³⁰G. C. Psarras, E. Manolakaki, and G. M. Tsangaris, *Composites, Part A* **34**, 1187 (2003).