



Crystallinity, morphology and high dielectric permittivity of NiO nanosheets filling Poly(vinylidene fluoride)

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Abstract

Composite films based on Poly(vinylidene fluoride) (PVDF) polymer filled with Nickel oxide (NiO) nanosheets were prepared via the solution casting method. The effect of NiO filler introduction on the structure and morphology of the composite films were analyzed by X-ray diffraction, Fourier transformed infrared spectroscopy and Scanning Electron Microscopy. The results showed that the crystallinity, β -phase content and morphology are directly related to the NiO filler concentration into the polymer matrix owing to a heterogeneous nucleation. Electrical measurements revealed dielectric constants up to 45 at 1 kHz and an increasing in conductivity more than two orders of magnitude, with a percolation threshold of about 4.0% v/v of NiO filler content.

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1. Introduction

The development of new composite technologies has drawn significant attention largely as a result of its relatively easy integration into electronic devices. The combination of fillers with different characteristics and polymers with specific physical properties leads to composites with special characteristics enabling a wide range of applications in different fields, such as sensors, energy transducers, artificial muscles, among others [1–3]. The preparation of composites with specific properties depends largely on the interfaces between the different polymer phases as well as the fillers in the sense that the microstructure is directly linked to the physical properties of the final composite [4]. In this process, some characteristics of the composite are found to be determinant in the final application, among them

including phase transitions, geometric properties, critical dimensions, percolation threshold and crystallinity [5].

In recent years, electroactive polymers (EAPs) are under intense consideration for applications in new electronic devices due to its excellent characteristics of flexibility, chemical resistance, high stretching and low costs [6,7]. Among other EAPs, Polyvinylidene fluoride (PVDF) has emerged as a promising candidate in a broad range of applications on account of its good piezoelectric and pyroelectric response [7]. PVDF is a semi-crystalline and polymorphic material with four crystalline phases in which the α (alpha) and β (beta) phases are known to be the most common. Some studies have shown that the increasing observed in the β -phase is due to the enhancement of the stretching effect on polymer films with different fillers [8–10]. Furthermore, the electrical properties in PVDF-based composites are directly related to the filler particle size. Deepa et al. have shown that smaller the particle size of the filler, greater is the effect of polarization between

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them, resulting in a percolation threshold at lower filler concentrations [11].

As can be found in the literature, PVDF-based composites have been prepared with different filler materials in order to enhance a specific property, for instance, the capacitive properties using carbon nanotubes [12,13] or BaTiO₃ [14], or magnetic properties by filling the polymer with semiconductor materials, such as Fe₂O₃ [15]. However, most of the materials do not exhibit a good dispersion in a polymer matrix which leads to the reduction of percentage of beta-phase or crystallinity causing disadvantages of the composite properties. Among other semiconductors, few studies have indeed focused their concern on the factors that influence and control the insertion of p-type Nickel oxide (NiO) in a PVDF matrix. This material has attracted extensive investigation due to its excellent electrical and magnetic properties making it a promising candidate in a wide range of applications, such as gas and magnetic sensors, battery cathodes, catalysis and capacitors [16–18]. Bhatt et al. have shown the influence exerted by NiO nanostructures on the magnetic and electrochemical behavior of PVDF-based nanocomposites polymer, which contribute towards improving the conductivity and ferromagnetic behavior of NiO/PVDF composites [19].

In light of these predictions, the main goal of this study was to investigate the characteristics of NiO/PVDF (filler/matrix) composite films and their electrical and dielectric properties. Crystalline properties, α - and β -phases content, morphology and their relationship with the conductivity and dielectric constant of the composite films are presented and discussed as a function of the volume fraction of NiO filler. The microstructure and interfacial effect of the composite films were investigated in which theoretical models, including Maxwell model and the percolation theory, were discussed to explain the electrical behavior of the composite films.

2. Materials and methods

2.1. Filler synthesis

NiO filler was synthesized by a co-precipitation method [17]. Urea (Co(NH₂)₂, Aldrich) and Nickel (II) Sulfate Hexahydrate (NiSO₄·6H₂O, Merck) (1:4) were dissolved in deionized water under stirring at 80 °C for 3 h. The resulting precipitate was collected and annealed at 400 °C for 1 h (heating rate of 5 °C/min) under atmospheric air.

2.2. Composite films synthesis

Polyvinylidene fluoride (PVDF) polymer was used as the matrix of the composite films and the preparation of the NiO/PVDF composite films was by the solution casting method. In the first step, 1.00 g of PVDF (Solef 11010/1001) was dissolved in 14 mL NN-dimethylformamide (DMF) (PA Vetec ACS) at room temperature under stirring for 1 h. In the second step, 80 mg of NiO powder was dispersed in 10 mL of DMF resulting in a well-dispersed suspension. Then, the two solutions were mixed at room temperature and under stirring for 30 min

followed by casting in petri dishes of 5 cm diameter and a dry solvent treatment was performed at 60 °C for 12 h. The composite films were prepared in varying NiO/PVDF volumetric ratio of 0.0% (PN0), 0.25% (PN025); 0.85% (PN085); 2.0% (PN2); 4.0% (PN4); 6.0% (PN6) and 8.0% (PN8).

2.3. Characterization

X-ray diffraction (Rigaku diffractometer, model D/MAX-2500/PC) using CuK α radiation at room temperature was performed. Crystallinity percentage (%C) in the polymer and composite films were determined by the Hermans–Weidinger method [20] as follows:

$$\%C = \left(\frac{I_c}{I_c + \{KI_a\}} \right) \times 100 \quad (1)$$

where I_c is the absolute area of the peaks, I_a being the absolute area below baseline, and K the proportionality constant ($K_{PVDF}=1.26$) [9].

Infrared analyses were performed using Infrared Fourier-transformed (FT-IR) spectrophotometer (Jasco, Model 4100) operating at ATR mode in the range of 4000–400 cm⁻¹. The β -phase percentage relative to the α -phase can be estimated by taking a more intense peak related to the β -phase (840 cm⁻¹) and α -phase (763 cm⁻¹) – both by the deconvolution of IR spectrum, which relates the absorption of each phase as shown in Eq. 2 [21].

$$F\beta = \frac{\text{abs}_b}{1.26*\text{abs}_a + \text{abs}_b} \quad (2)$$

Morphology and thickness of the composite films were analyzed using a field emission gun scanning electron microscope (FE-SEM, JEOL, Model 7500F). Metal/composite/metal capacitor-like configuration was used in order to perform the dielectric measurements in which Ag electrodes (6 mm diameter) were made using silver paste through a shadow mask in both sides of the composite films. Dielectric constant (ϵ) and ac conductivity (σ) were obtained by impedance spectroscopy measurements by employing a frequency response analyzer (Metrohm Autolab B.V., model PGSTAT128N) in a range frequency from 100 Hz to 1 MHz using a voltage amplitude of 100 mV. [22].

3. Results and discussion

Fig. 1a shows a typical XRD pattern for NiO powders prepared by the co-precipitation method. The diffraction peaks can be indexed through a cubic structure with a space group Fm-3m according to the JCPDS 73-1519 card in which all planes were indexed. The sample obtained was free of secondary phases and the relative peak intensities indicate polycrystalline nanostructured samples without any preferential orientation. The PVDF film without NiO filler (see Fig. 1b) presents peaks mainly related to the α -phase demonstrating that the initial polymer used to prepare the composite films is predominantly composed of amorphous structures and α -phase crystallites [23]. On the other hand, the PVDF film with

8.0 vol% of NiO filler and all the other samples prepared with different NiO concentration exhibited peaks related to the β -phase, α -phase and NiO powder, though with more intense peaks related to the β -phase, as shown in Fig. 1c [2,23].

Analysis of infrared vibrational spectroscopy was carried out so as to investigate the structure of the powder, polymer and composite, as shown in Fig. 2. In the IR spectra of Nickel oxide powders (Fig. 2a), the following bands can be identified: stretch vibrations of hydroxyl groups between 3200 and 3500 cm^{-1} ; a bending vibration related to water between 1600 and 1700 cm^{-1} ; a stretching vibration of S=O bonds at 1100 cm^{-1} ; vibrations of chemical bonds of Nickel (Ni–O) at 460 cm^{-1} [24]. It is well known that high annealing temperature is required to eliminate sulfur from the surface of semiconductor oxides [25] and as such we expect that the hydroxyl groups and the sulfur ions are present only on the surface of the NiO powders due to an incomplete removal of these groups during the annealing process once that XRD patterns do not show any structural influence. Polymorphic characteristic bands can be observed in the PVDF polymer matrix (see Fig. 2b). The

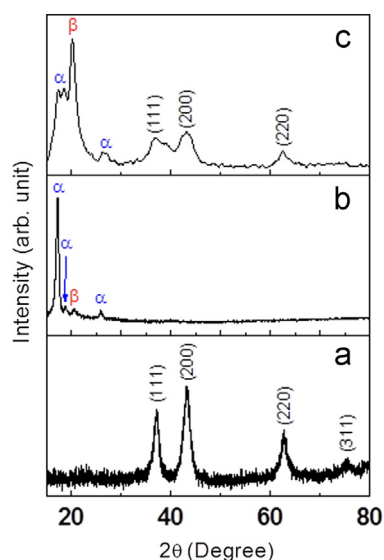


Fig. 1. XRD diffraction patterns of (a) NiO powders, (b) PVDF (PN0) and (c) NiO/PVDF (PN8) films.

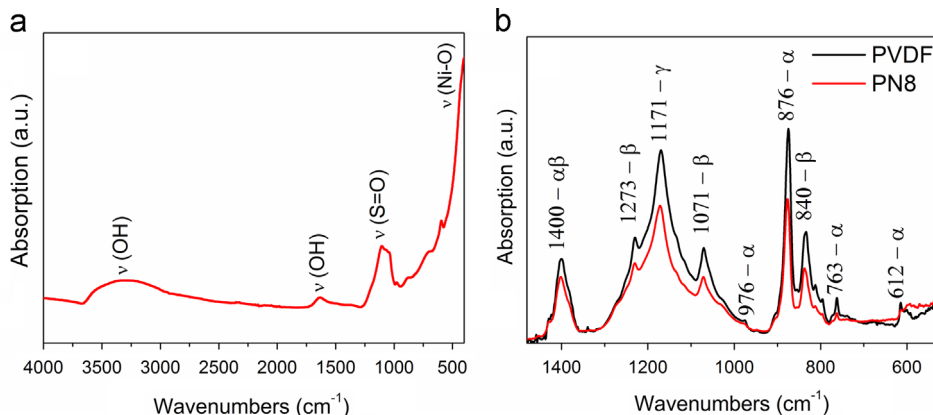


Fig. 2. FT-IR spectra of (a) Nickel oxide and (b) PVDF (PN0) and NiO/PVDF 8.0 vol% (PN8) composite films.

absorption bands at 1399 cm^{-1} , 976 cm^{-1} , 876 cm^{-1} , 763 cm^{-1} and 612 cm^{-1} are related to the α -phase while the β -phase absorptions are at 1398 cm^{-1} , 1273 cm^{-1} , 1071 cm^{-1} and 840 cm^{-1} [26]. The absorption at 1171 cm^{-1} is related to the γ -phase [26]. The same absorption bands were observed in the PN8 sample (and in all other samples) only with relative peak intensity changes which are clearly expected given that the composite formation does not induce changes in atomistic bonds in the polymer structure but rather changes in microstructure and degree of crystallinity, as observed in our results and corroborating literature results [5].

The degree of crystallinity and the relative β -phase percentage as function of filler concentration in the composite films are shown in Table 1. The degree of crystallinity was found to increase with the increasing of the NiO filler content into the PVDF matrix up to 60%, remaining constant for all composite films at higher concentrations (above 2.0 vol% NiO filler). The same behavior is observed for the β -phase percentage, i.e., the relative β -phase percentage increased up to 70% with the increasing of the NiO concentration, remaining constant for all composite films. These results confirm that the introduction of the NiO filler favors the arrangement of the crystalline chains into the polymer matrix which induces the growth of the polymer crystallites, mainly, by the presence of the polymorphic β -phase [21].

This effect is normally related to a heterogeneous nucleation which is a consequence of the introduction of materials with different interfacial energies into polymer matrices [27]. The

Table 1

Degree of crystallinity of NiO/PVDF composite films obtained from the Hermans–Weidinger method, percentage of β -phase and film thickness.

Samples	Film thickness (μm)	%C	β -phase (%)
PN0	30 (± 2)	33 (± 2)	43 (± 5)
PN025	40 (± 3)	36 (± 3)	72 (± 2)
PN085	40 (± 3)	51 (± 2)	72 (± 3)
PN2	45 (± 5)	63 (± 4)	70 (± 3)
PN4	60 (± 10)	60 (± 4)	72 (± 2)
PN6	60 (± 10)	62 (± 4)	69 (± 3)
PN8	60 (± 10)	62 (± 4)	71 (± 3)

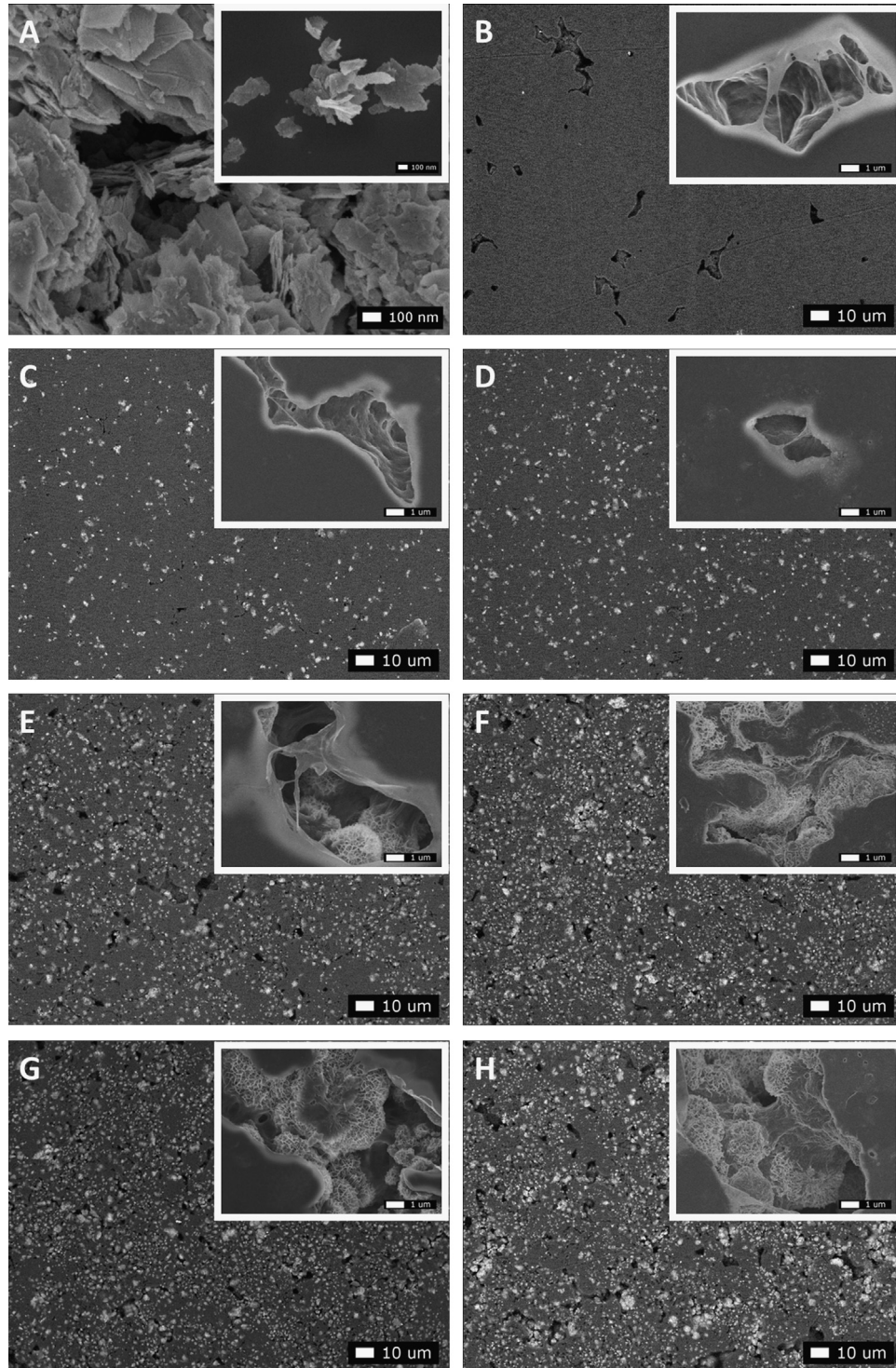


Fig. 3. SEM images of (a) NiO filler powder and surface of the composite films (b) PN0; (c) PN025; (d) PN085; (e) PN2 (f) PN4; (g) PN6; (h) PN8. Right inset: Magnified SEM images of the pores in the composite films obtained using a secondary electron detector.

filler is composed of NiO nanosheets (see Fig. 3a) presenting a bond energy of approximately 853.7 eV [28]. PVDF matrix is composed of monomers $[\text{CH}_2\text{CF}_2]_n$ showing a semi-crystalline structure and a bond energy between 285.8 eV (CH_2) and 290.4 eV (CF_2) [29]. This high difference of bond energy between the filler and matrix results in a weak interaction at the contact interface and thus giving rise to an oriented growth of the crystallites in the polymer chains. Sun et al. [13] using

carbon nanofibers in a PVDF matrix obtained results of crystallinity of up to 65% while Bhatt et al. prepared NiO/PVDF composites using NiO nanorods obtaining a degree of crystallinity of up to 56.2% [19]. Our results are in agreement with those ones reported in the literature corroborating that the interfacial energy exerts a direct influence on the growth as well as the ordering of crystallites on the polymer chains resulting in a heterogeneous material.

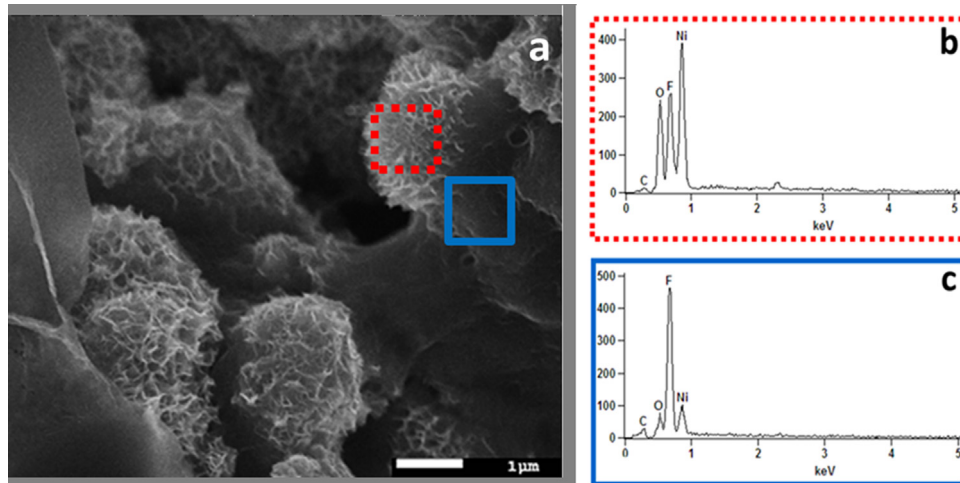


Fig. 4. (a) SEM image and (b, c) EDS spectra of the surface of composite film prepared with 8.0 vol% of NiO filler. SEM image obtained using a secondary electron detector in order to take a high resolution EDS spectra.

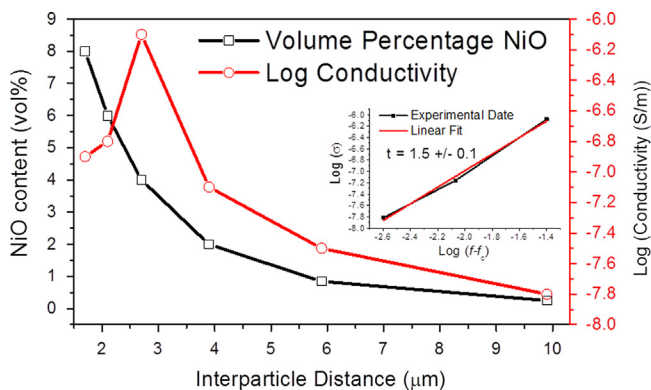


Fig. 5. NiO volume percentage and log conductivity versus the interparticle distance of filler in the NiO/PVDF composite films. Inset: Best fit linear of percolation threshold.

Fig. 3a presents the SEM image of the NiO filler showing to be predominantly composed of 2D nanosheets-like structures with flat and smooth surfaces and an average particle size of around 350 nm. Following their introduction into the PVDF matrix, the NiO nanosheets became agglomerated as though they were some sort of porous hierarchical structures with rounded shape encapsulated by the PVDF polymer (called as clusters in the discussion section) and with an average size of around 2 μm , quite in line with our expectations for a heterogeneous nucleation [27], as can be seen in Fig. 4 and insets in Fig. 3b–h.

SEM images of the composite films prepared as a function of NiO filler concentration are shown in Fig. 3b–h. Brighter clusters in the SEM images reveal the presence of heavier elements (NiO clusters) owing to the fact that the images were obtained using a backscattered electrons detector. Analyses by energy dispersive X-ray spectroscopy (EDS) were performed on the brighter clusters, as shown in Fig. 4, in which the presence of Ni and O was confirmed. The composite films showed well-dispersed NiO clusters with low porosity at lower NiO filler concentrations (see Fig. 3b–e). At concentrations above 2.0 vol% of filler, the density of NiO clusters and

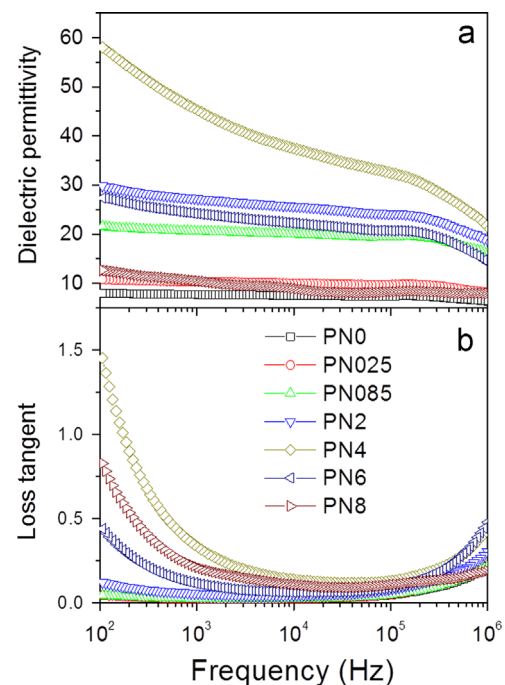


Fig. 6. (a) Dielectric permittivity and (b) dielectric loss tangent of NiO/PVDF composites.

porosity were found to increase as a function of the filler concentration, as shown in Fig. 3f–h. All these composite films presented a good dispersion of NiO clusters within the PVDF matrix and the thickness of the films was found to increase with the increasing of the NiO filler content, as shown in Table 1.

In order to identify the dispersion and agglomeration of the clusters in the polymer matrix, the variation of the distance between the centers of the filler clusters in the composite matrix was analyzed using Eq. 3 [11,30]:

$$d = r \left[\left(\frac{4\pi}{3V_f} \right)^{1/3} - 2 \right] \quad (3)$$

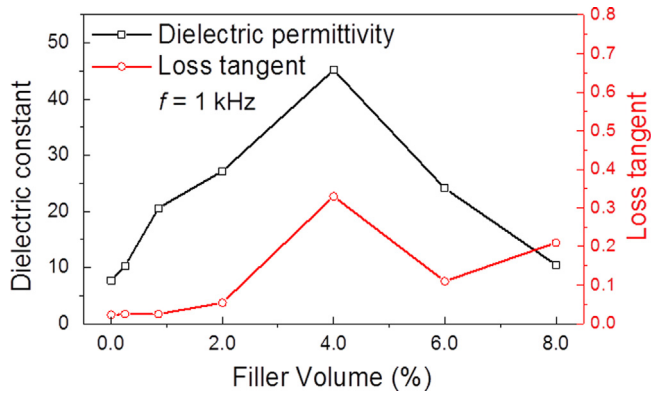


Fig. 7. Dielectric permittivity (ϵ) and dielectric loss tangent as a function of filler concentration in the NiO/PVDF composite films at 1 kHz and room temperature.

where r is the average radius of the cluster and V_f being the volume fraction of the NiO filler. The method used here is an approximation in the variation of the distance between the NiO cluster in the composite matrix, assuming spherical shape and uniform dispersion, once that Eq. 3 is commonly used for single particles. However, we could see a very good correlation between this approximation and the SEM images, as shown in Figs. 3 and 5. The interparticle spacing was seen to decrease exponentially when the concentration of the filler was increased, confirming the behavior observed in the SEM images that shows the approximation of the particles given an increasing in the NiO filler content.

Composites based on organic and inorganic phases present a direct relationship between the microstructure characteristics and the electrical properties, more specifically in the percolation threshold (f_c), of the composite films which is controlled by a critical filler concentration into the polymer matrix [12]. The percolation threshold (f_c) can be estimated using a power law relation (Eq. 4) which correlates the volume fraction of filler and the composite film conductivity. This law predicts an increasing of the composite conductivity when the filler content is increased:

$$\sigma_{eff} = \sigma_f (f_f - f_c)^t f_f > f_c \quad (4)$$

where σ_{eff} is the effective composite film conductivity, σ_f being the filler conductivity (obtained experimentally: 2.09×10^{-5} S/m), and t denoting the dimensionality of the percolation network, which can be extracted from the best linear fit of the log–log plot of the conductivity versus the volume fraction of filler. Our results showed $t = 1.5 \pm 0.1$ (R^2 : 0.989), as can be observed in the inset in Fig. 5, and a percolation threshold of 4.3 vol% of NiO filler content into the PVDF matrix, in agreement with the remarkable increasing in conductivity at 4.0 vol% NiO filler content, as shown in Fig. 5. In summary, the decreasing in the interparticle spacing as a result of the increasing in filler content is found to lead to an increasing in conductivity of the composite films up to the percolation threshold of about 4.0 vol% of NiO filler content. This behavior is a characteristic of semiconductor/insulator composites in which lower conductivity changes and larger increases (more than one magnitude) in the dielectric constant are observed [12,31].

Fig. 6 shows the dielectric constant as well as the loss tangent of the polymer and composites, with all the analyses performed at room temperature. The dielectric constant was found to decrease with an increasing in frequency and an increasing was observed in the loss tangent for lower frequency values. Fig. 7 shows the dielectric constant (ϵ) and loss tangent of NiO/PVDF composite as a function of filler concentration at 1 kHz and at room temperature.

These results show that the dielectric constant and loss tangent increased remarkably up to 4.0 vol%, and then decreased above this concentration, in which this behavior was observed in the whole range of frequency. The maximum dielectric constant at 1 kHz was 45 at 4.0 vol%, six-fold larger than the dielectric constant of the pure PVDF polymer; however, higher dielectric constant was followed by higher dielectric loss up to 30%. Furthermore, the higher dielectric loss can be related to the higher conductivity, as observed in Fig. 5 and predicted by the percolation law. Similar results were observed by Dang et al. for LiNiO/PVDF composites prepared at concentrations between 2 and 6 vol% showing that the highest dielectric constant values are obtained at concentrations near to the percolation threshold [31].

Assuming that the samples are heterogeneous materials, as discussed above, a Maxwell–Wagner interfacial polarization is expected with its effects increasing as the filler content increases [32]. Above the percolation threshold of 4.0 vol% of NiO filler content, there was a significant decrease in the interparticle distance in the composites, leading to a decreasing in the dielectric constant owing to the reduction of the ability to retain charges by the Maxwell–Wagner interfacial polarization. In addition, as also observed in the literature [33,34], there was a drop in both the loss tangent and conductivity indicating a lower connectivity of the network above the percolation threshold due to the agglomeration of the particles. These results may indicate that dielectric characteristic of the NiO/PVDF composite films above the percolation threshold are mainly controlled by the NiO dielectric characteristics with additional contributions coming from extrinsic factors such as porosity and agglomeration of the particles [31,32]. In summary, our results are in good agreement with those ones reported in the literature presenting higher dielectric constant when compared with composites prepared with traditional dielectric materials such as BaTiO₃ [14].

4. Conclusion

PVDF composite films were prepared using the solution casting method filled with NiO nanosheets synthesized by a co-precipitation method. X-ray diffraction and FT-IR results indicate that the introduction of the NiO filler favors the arrangement of the crystalline chains into the polymer matrix inducing the growth of polymorphic β -phase crystallites as a result of a heterogeneous nucleation. SEM results showed that the NiO nanosheets filler were agglomerated as hierarchical-like structures within the polymer matrix though with a homogeneous dispersion. As predicted by the percolation theory, the

conductivity of the composite films is controlled by the interparticle spacing and NiO filler content with a percolation threshold of about 4.0 vol%. The dielectric constant obtained in our samples is up to six-fold larger than the PVDF film without a filler. Explanation for this behavior was proposed in which the Maxwell–Wagner polarization was identified as the main mechanism responsible for this improvement in the dielectric properties. These results indicate that NiO/PVDF composite films could be used to manufacture electronic devices with enhanced dielectric and electrical characteristics, for example, high charge-storage capacitors or electronic flexible devices.

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