Mechanical properties and connectivity evaluation of a conductive coated piezoceramic/polymer composite

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In the present work, piezoelectric composite films made of Polyaniline (PANI) coated Lead Zirconate Titanate (PZT) particles immersed into polyvinylidene fluoride (PVDF) matrix were characterized by mechanical tests, and the connectivity of the composite sample was determined using dielectric measurements and applying the Poon–Shin model. The composite was considered a binary system with coated PZT particles as one phase and the polymer matrix the other one. To support the result obtained from theoretical analysis, scanning electron microscopy of the composites were done. It was observed a decrease up to 85% on the mechanical resistance when the ceramic volume fraction increases from 0% to 40%. Furthermore, the composite film no longer can be considered with 0–3 connectivity when the ceramic content is 30 vol.% or over.

Keywords: Piezoelectric composite; mechanical resistance; Poon–Shin model; 0–3 connectivity.

1. Introduction

Ferroelectric composites appear to be an efficient alternative to solve problems related to materials used in the transduction of electromechanical signal because they combine the excellent mechanical properties of the polymers with the excellent piezo and pyroelectric properties of the ferroelectric ceramics while pure ceramics have low mechanical resistance and pure polymer has poor electroactivity.^{1,2}

Although the polymer matrix-based ferroelectric composites are a promising alternative, its use has limitations which arise by the individual characteristics of the phases of the composite sample: One limitation is the low permittivity of the polymer phase that hinders the poling process of the ceramic phase.^{3–5} Another is the composite's low ceramic content, which results in low piezo- and pyroelectric coefficients. However, if the ceramic content is high, this increases the electroactive properties of the composite, with adverse effects on its mechanical properties.

To overcome these problems, and to make the polarization process more efficient using low ceramic volume fraction, Fuzari *et al.*⁶ proposed the incorporation of lead zirconate titanate (PZT) particles coated with polyaniline (PANI), a conducting polymer in which the electrical conductivity can be changed by protonation process^{7,8} (i.e., changing the pH) into a polyvinylidene fluoride (PVDF) matrix. They observed

effective polarization of the composite and the piezo- and pyroelectric coefficients optimized for composite films with 30 vol.% of ceramic phase coated with PANI partially protonated and stabilized at a pH of 3.7.

Theoretical models to explain poling process in polymer-based ferroelectric composites have been widely disseminated and the important role played by the third phase (conducting phase) in increasing the dielectric constant of the polymer matrix and thus optimizing the polarization process have been reported.^{1,5,9–12} In most cases, the composites have 0–3 connectivity, which means that the ceramic particles are not self-connected in any direction.¹³ However, it can be difficult to state that the composite has 0–3 connectivity even when electronic microscopy is applied. Moreover, electronic microscopy is a very difficult technique to use in polymeric materials because multiple images are needed to analyze the sample. In this context, electrical measurements can be a good alternative. The theoretical permittivity of a homogeneous composite with 0–3 connectivity can be determined using Bruggeman's equation^{14,15} as shown below:

$$\frac{\epsilon_c - \epsilon}{\epsilon_c - \epsilon_p} = (1 - \phi) \left[\frac{\epsilon}{\epsilon_p} \right]^{1/3}, \quad (1)$$

where the subscripts *c* and *p* are related with the ceramic particles and polymer matrix, respectively, ϕ is the volumetric

fraction of the inclusions. Lau *et al.*¹⁴ obtained an excellent relation between theory and experimental results for PZT polyurethane (PZT/PU) composites. The good fitting of the experimental data using Eq. (1) indicates that the composite has 0–3 connectivity and good homogeneity. However, a nonlinear equation is needed to find the dielectric constant ε when a simple expression is desired. Recent works show very good results for 0–3 composite using Poon–Shin⁸ model, even when the sample had a high ceramic volume fraction.^{9,11,16} In the Poon–Shin model, the electric displacement in a typical inclusion is approximated to be the sum of displacements due to the inclusions and the medium, which is considered as a matrix of randomly, distributed electric dipoles.¹⁰ A simple formula of effective dielectric constant for two phase composites systems with 0–3 connectivity is derived as:

$$\frac{\varepsilon(\nu_i)}{\varepsilon_p(\nu_i)} = 1 + \frac{\phi[\varepsilon_c(\nu_i)/\varepsilon_p(\nu_i) - 1]}{\phi + (1 - \phi)\{[\varepsilon_c(\nu_i)/\varepsilon_p(\nu_i)][1 - \phi] + \phi + 2\}/3} \quad (2)$$

In the present work, composite films were prepared with PZT particles coated with PANi partially protonated at a pH of 3.7, and the limit of ceramic volume fraction was examined to determine the concentration threshold of 0–3 connectivity in the Poon–Shin model, considering the PANi coated PZT particles as one phase and PVDF matrix the second phase of the composite. To support the results of the model, scanning electron microscopy (SEM) was carried out for each ceramic volume fraction in the composite film. Furthermore, the variation of mechanical properties was analyzed by changing the amount of the ceramic particles.

2. Experimental Procedure

Samples: The composite films were prepared as follows: PZT and PVDF (α form) powders were mixed together and pressed in the melting temperature range of the polymer. The PZT particles had been partially coated with PANi previously. Details of the procedure have been described in previous work.^{6,12}

2.1. Measurement

Stress–Strain tests: The samples were prepared according to the D882 standard using an Instron model 4204, 13 mm/min velocity and load cell of 5 ton.

Dielectric Constant: Dielectric measurements were carried out using the Impedance Analyzer HP 4192A LF. The samples used were: PZT coated with PANi in tablet form; and PVDF and composites in film form.

Field emission gun scanning electron microscopy (FEG-SEM): The composite films with different ceramic volume fraction were analyzed using SEM-FEG Zeiss, model Supra

35 from Laboratório Interdisciplinar de Eletroquímica e Cerâmica, LIEC, UFSCar, São Carlos.

3. Results and Discussion

The evaluation of mechanical properties of the composite is related to its flexibility and resistance to shock. These parameters depend on the volume fraction of the ceramic in the composite. Figure 1 shows the behavior of the composite sample in a stress–strain test. Samples with 20 vol.%, 30 vol.% and 40 vol.% of ceramic were used, and their mechanical properties were compared with those of a pure polymer sample. Elastic deformation is related with the atomic bond stretching while the plastic deformation is due to the viscous flow. Increasing the ceramic particle amount in the composite sample, both atomic bond stretching and viscous flow become more difficult, reducing the deformation of the sample.

The maximum values of stress and strain were analyzed in both regimes: elastic and plastic. Figure 2 shows the results indicating the influence of the ceramic content on the fragility of the composite sample.

The results displayed in Fig. 1 show a large reduction in stress and deformation of the composite in comparison with the pure polymer. In general, the Young's modulus and mechanical resistance can be improved by adding small volume fraction of the ceramic fillers. However for the piezoelectric property of the composite, small amount of ceramic is not useful because the piezoelectric response is quite negligible.

The Young's modulus was also studied as a function of the ceramic volume fraction. We can see in Fig. 3 the behavior of this parameter and it can be seen that the elasticity is not strongly affected in this range of ceramic content.

Fig. 1. Stress–Strain behavior of PZT-PANi/PVDF composite with different ceramic content.

Fig. 2. Maximum deformation and stress: (a) Elastic regime and (b) plastic regime.

Stress–Strain analysis is one of the most important and simple test to determine some mechanical properties of the material. The test consists in monitoring the load applied on the sample while it is pulled at a constant speed. The sample size is predetermined by the D882 standard.

A close analysis in the elastic and plastic regimes indicates a decrease in the maximum elastic strain and maximum elastic stress and a decrease in the rupture strain and maximum stress with an increase in the volume fraction of the ceramic phase (Fig. 2). As shown in Fig. 1, the maximum stress and the maximum strain points occur at the limit of elastic and plastic regimes. Although there is maximum stress and deformation decrease, the modulus of elasticity remain almost the same in the volume fraction range studied as can be seen in Fig. 3.

As reported by Yanovsky and Obratsov,¹⁷ also by Nielsen and Landel¹⁸ rupture can occur easily at the ceramic-polymer

Fig. 3. Young's modulus for different concentration of ceramic.

interface due to the fragile physical interactions between the inclusion and the matrix. Fu and co-workers¹⁹ has studied these interactions in different kinds of composite and they called it interfacial adhesion. Thus, an increase in the ceramic phase amount implies in the increase of ceramic–polymer interfaces and consequently the properties related with mechanical stress become poor although the volumetric fraction of the particles does not change significantly the elastic constant of the polymer matrix (Fig. 3). Therefore, the focus on ferroelectric composite is to obtain a sample with good electroactive property with low ceramic content. In this context, the use of PZT coated with conductor polymer is worthwhile because even with low ceramic volume fraction an electrical flux path is created between the particles optimizing the poling process and increasing the piezo and pyroelectric coefficients as reported in previous work.⁶

As stated, the Poon–Shin model has given good results for composite samples with 0–3 connectivity. The values of the dielectric constant of the pure materials (i.e., PZT coated and PVDF) obtained experimentally were used in Eq. (2) to calculate the dielectric constant of the composite samples. Figure 4 shows the applied model for composites with 20 vol. %, 30 vol. % and 40 vol. % of PZT coated with PANi partially protonated. The fitting fails for ceramic concentration above 20 vol. % indicating a mixed connectivity in the composite sample.

Several papers have considered composite samples with 0–3 connectivity, even with a ceramic content up to 50 vol. %. Recently, Ploss *et al.*^{9,11} demonstrated that the Poon–Shin model gives a good fit for the dielectric constant of a composite with a third conductive phase which has been included to reduce the difference of the dielectric permittivity between matrix and the ceramic inclusion. In all these works, the adjustment were done considering a two-phase system consisted of ferroelectric ceramic as inclusion and polymer with conducting particles as matrix. However, as shown in Fig. 4,

Fig. 4. Poon–Shin model for PZT–PAni/PVDF with 20 vol.%, 30 vol.% and 40 vol.% of ceramic.

using the Poon–Shin model, the composite had 0–3 connectivity when the ceramic content was about 20 vol.%. Above this concentration there was no agreement between experimental data of the dielectric constant and the calculated using Eq. (2), indicating that the composite had mixed rather than pure 0–3 connectivity.

In general many authors have considered 0–3 connectivity for composite obtained by the ceramic particles dispersed into polymeric matrix up to 60 vol.% for both, Furukawa's (spherical) and Yamada's (ellipsoidal) models.^{20,21} Also for composite using conducting particles, the crystal model is used to consider 0–3 connectivity for composite with 60 vol.% of inclusions. It is a little hard to accept because there is a tendency of the particles to agglomerate. Although the composition used in the present study is limited and the interval is quite large, the result displayed in Fig. 4 give us an idea that between 20 vol.% and 30 vol.% of inclusions the Poon–Shin model for composite with 0–3 connectivity fit very well. Lower interval was not used because the ceramic particles dispersion cannot be very homogeneous and we

(a)

(b)

(c)

Fig. 5. SEM-FEG images of PZT–PAni/PVDF composite films: (a) 20 vol.%, (b) 30 vol.% and (c) 40 vol.% of ceramic.

could have some region very similar for composites with 20 or 25 vol.%. That way, dielectric measurements of the composite and of its phase analyzed with the Poon–Shin model can evaluate if the connectivity of the composite is only 0–3 in the composition range used here.

Figure 5 shows SEM-FEG images of the composite films with 20%, 30% and 40% volume of ceramic. At the 20 vol.% (Fig. 5(a)) of dispersed particles, the particles showed a random distribution, and they were not self-connected. In contrast, at 30% and 40% volume of ceramic particles, they seemed to be connected, which is more evident at the 40 vol.%.

4. Conclusion

PVDF matrix-based composite films and PZT inclusions with different concentrations were submitted to stress–strain test. The sample became more fragile as the ceramic volume fraction was increased, although no significant change was observed in the modulus of elasticity.

The dielectric constant of composite films with a ceramic volume fraction up to 20 vol.% follows the Poon–Shin model, and the composite can be considered to have 0–3 connectivity. At higher ceramic concentration the Poon–Shin model is not applicable because there are mixed rather than pure 0–3 connectivity. This conclusion is supported by the microscopy images. This work illustrates the possibility of using the Poon–Shin model to study the limit of ceramic content that can be incorporated in a 0–3 composite.

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