Improved piezoelectric properties of PLA/PZT hybrid composite films

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Abstract. Piezoelectric polymer-ceramic composites are promising materials for Sensing, Wireless electronics and actuating applications. We report the fabrication of highly piezoelectric biocompatible films containing lead zirconate titanate (PZT) ferroelectric ceramic particles dispersed in poly lactic acid (PLA) with different volume fractions using a solvent cast technique. The properties of the piezoelectric polymer-ceramic films were investigated by Fourier transform infrared spectrometry (FTIR) and field emission scanning electron microscopy (FE-SEM). In the FTIR spectra appear a large number of absorption bands which are attributed to the phases from PLA matrix confirming the total embedding of PZT filler into the matrix. The SEM results showed a good distribution of fillers in the matrix. We find that the added PZT imposes a significant effect on the α-β phase transformation. Our finding can lead to extraordinary enhancement of piezoelectric properties for the PLA/PZT composite films.

Keywords: Piezoelectric polymer-ceramic, PLA, PZT, solvent cast technique.

1. Introduction
Polylactic acid (PLA) remains the leader of electroactive polymers which are used in 43% of the scientific work in the field of recovery and conversion of electromechanical energy [1-6]. This polymer has the advantage of having a better mechanical strength, thermal and ease of implementation compared to other polymers [7]. Although it can present three primary crystalline phases (α, β and γ) according to its conformation in helices and symmetries of different lattices. These forms appear under thermal or mechanical constraints, the β phase is the most common and interesting one since it is the only one that can present a strong piezoelectric response in the PLA.

Adding fillers to prepared PLA polymer composites represents a practical way to enhance β-phase content in PLA films. In the few decades, several nanofillers, such as carbon nanotube (CNT), graphene oxide and graphene, were used as improving agents of the β –phase [8–10]. Recently, there have been
many studies to directly relate the phase variation induced by carbon nano-fillers with enhanced piezoelectric properties. For example, Wu et al. [8] added the CNF and CNT into PVDF to improve the piezoelectricity of PVDF. It was observed that the fraction of \( \beta \) -phase improved significantly in CNT or CNF films, which was confirmed by X-ray diffraction (XRD). Lee et al. [11] PVDF/CNT composite films were prepared by solution blending method. It was confirmed by FTIR that the \( \beta \) -phase improved with the presence of CNT.

To the best of our knowledge, there is no work about the preparation of PLA/PZT films by the solvent cast method. Thus, in the present work, the PLA/PZT composite were prepared using this technique with different volume fractions. These samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM). We added micro particles into polylactic acid (PLA) to prepare composite films of exceptional piezoelectricity. Based on the survey on crystal structures, we clarified the roles played by PZT in phase transformation.

2. Experimental

2.1 Materials

PLA (Nature Works Ingeo 3100 HP) with a melt flow index of 24 g/10 min (at 210°C and 2.16 kg) was used as matrix of the composite.

Lead zirconate titanate (PZT) was supplied by Ferropem (Denmark) with an average diameter between 1 and 10 \( \mu \)m. This micro particles exhibit a curie temperature of 235 \(^\circ\)C and a piezoelectric coefficient \( d_{33} \) of 600 pC/N.

2.2 Preparation of the PLA / PZT composites

PLA/PZT composites is prepared by the solvent cast method. A measured quantity of PLA is dissolved in THF (Tetrahydrofuran) by stirring and heating in the microwave oven until it dissolves. The PZT is dispersed completely in the polymer PLA solution. The prepared solution PLA/PZT/THF is spread at room temperature on a glass plate using a stainless steel and is then heated in the oven at 66 \(^\circ\)C for 15 min. When the solvent evaporates completely, PLA/PZT composite films are obtained. The process is repeated with different volume fractions (ranging from 0.1, 0.3, 0.5, 0.8, 1 to 2wt.%).

2.3 Characterization of PLA/PZT composites

The chemical structure analysis of micro particles, PLA and its composites, was performed using a Fourier transformation infrared spectrometer (FT-IR, Nicolet iS10, spectra from 500 to 4000 cm\(^{-1}\)). The morphological observations of PLA/PZT composites were performed with scanning electron microscopy (SEM, SH-5000P-EDS), operating at an acceleration voltage of 15 kV. The samples’ surfaces were coated under vacuum with carbon for SEM observation.

3. Results and discussion

3.1 SEM analysis of PLA/PZT composite films

Figure 1 shows the surface morphology of PLA/PZT composites with 0.5 and 1 volume fraction. Furthermore, on the level of 200 micrometers, the composites display an homogeneous and identical microstructure. When looking at the 1% volume fraction PZT image, it becomes apparent that the microstructure is also homogeneous at the micrometer level. The analysis of microstructure of the 1% volume fraction PZT composite indicates the good adhesion of polymer matrix with the particles of PZT ceramic. We conclude that the ceramic particles are homogeneously dispersed in the polymer matrix and are adhering well to it.
Figure 1. SEM micrographs of thin films hybrids nanocomposites of (A) PLA neat, (B) PLA/0.5 wt % PZT, (C) PLA/1wt % PZT.

Thus, we conclude the presence of uniform micro particles dispersion without agglomeration in the polymer matrix for lower filler volume fraction.

3.2 FT-IR analysis of PLA/PZT composites films

The samples were characterized by FTIR, and the corresponding spectra in the 800-1500 cm\(^{-1}\) region are presented in figure 2. From this figure, it is obvious that PZT effect the phase transformation significantly in initial crystallization process. Indeed, an appearance of the piezoelectric \(\beta\) crystalline phase at 1212 is 872 cm\(^{-1}\) was observed in all PLA / PZT nanocomposite films with different volume fractions of PZT ceramic, which remains important in energy harvesting. Consequently, the addition of a small percent of PZT micro fillers (0.1 wt %) in the PLA matrix, it was possible to obtain the \(\beta\)-phase in the crystallization.

Figure 2. FTIR analysis of PLA/PZT nanocomposite.
We can see that the crystalline phase of the resulting polymer matrix is not disturbed during the addition of PZT ceramic. We can say that we combined in these film nanocomposites, the flexibility of a polymer matrix with the piezoelectric character of the ceramic particle of PZT. Also, the absorption peak intensities of charge materials increase proportionally with the charge content volume in the PLA. This indicates that both polymer matrix and the charge materials have retained their original chemical composition after the dispersion process.

4. Conclusion
PLA polymer and PZT fillers can be mixed in conditions which enables the formation of a homogeneous solution in THF, resulting in the formation of a stable solution at room temperature. By casting solutions of PLA and PLA-PZT mixture on glass plates, high quality and flexible PZT-filled PVDF nanocomposite films have been produced. Due to the high compatibility between PZT and PLA, PZT fillers are well dispersed and distributed within the PLA matrix.

The properties of the piezoceramic filler before and after dispersion in solvent and embedding into the PVDF polymer matrix were investigated. The FTIR spectrum indicated the total embedding of PZT filler into the matrix, by keeping the absorption bands characteristics for the α – phase of PLA. It was observed in the SEM images that the PZT filler kept their morphology and their size at the same nanometric range after its incorporation in PVDF matrix.

It was observed that PZT influenced the phase formation significantly during the preparation. The properties enhancements are directly related to the strong and specific interfacial interaction that results in the adsorption of macromolecular chains of PLA onto the PZT surface.

The PLA/PZT composites open new opportunities to develop thin films for technological applications such as: energy harvesting, sensors and actuators.

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