Evaluation of performance of polyamide/lead zirconate titanate composite for energy harvesters and actuators

Rida Farhan, Mohamed Rguiti, Adil Eddiai, M'hammed Mazroui, Mounir Meddad, Christian Courtois

HAL Id: hal-03080537
https://hal-uphf.archives-ouvertes.fr/hal-03080537

Submitted on 31 Aug 2022

Evaluation of performance of polyamide/lead zirconate titanate composite for energy harvesters and actuators

R Farhan[1], M Rguiti[2], A Eddiai[1], M Mazroui[1], M Meddad[2] and C Courtois[3]

By means of experimental tools, we have studied the effect of lead zirconate titanate volume fraction introduced in polyamide-6/lead zirconate titanate composites on dielectric, piezoelectric, mechanical, and structural properties. As the first result, we found that the insertion of lead zirconate titanate particles makes the dielectric permittivity of the polyamide-6 matrix increases from 10 to 95.8. The dielectric property studies reveal that under an electrical field of 1 kV the remnant polarization is also increased from 0.17 to 0.4, this behavior is related to both the increase of volume fraction of lead zirconate titanate from 20% to 40% and the piezoelectric coefficient changes proportionally with that of volume fraction of lead zirconate titanate. Furthermore, piezoelectric activity increases with lead zirconate titanate particle size at a range where there is a lower order of magnitude. Finally, the uniform dispersion of the ceramic lead zirconate titanate particles in polyamide matrix has been confirmed by scanning electron microscopy analysis. The performances reached by polyamide-6/lead zirconate titanate composites open new horizons for energy harvesting and actuators.

Keywords: Polyamide-6, lead zirconate titanate, piezoelectric properties, energy harvesting, actuator

Introduction

With the growth of microelectronic and mechanical systems (MEMS) production in the last decade, the requisition of wearable electronics and cordless detectors is increasing.[1] Moreover, great advances in the domain of smart materials, because of their sensor and actuator capabilities, have given rise to research into the power harvesting capabilities of these materials. Recently, has been used for diverse applications like sensor[2] for improving performance. Assuring the mobility of various devices energetic autonomy on behalf of exploration and conversion of environmental energy sources such as solar, thermal, and vibrations,[3,4] became increasingly a challenging for scientific community. Investigations show that piezoelectric composites are reliable energy conversion purpose due to their flexibility, processability, and optical quality even at higher thicknesses. Piezoelectric composites are formed using particulate piezoelectric ceramic phase dispersed inside a polymer matrix. Composites prepared in such manner are also possible candidates for sensors devices.[5,6] Composite materials are an interesting technology as use of nano-seized fillers allows great structural improvements in comparison to micro-reinforcement polymer materials, which fits well to industrial aims to produce lighter, thinner, and stronger structures at reduced cost.[7] The nano-sized fillers increase the area of contact between the matrix and the fillers, thus reduce the concentration of stress forces. Ferroelectric

[1]Laboratory of Physics of Condensed Matter (LPMC), Faculty of Sciences Ben M'Sik Hassan II University, Morocco
[2]LAS Laboratory of Setif, Mohamed el Bachir el Ibrahimi BBA University, Algeria
[3]Univ. Valenciennes, EA 2443—LMCPA—Laboratoire des Matériaux Céramiques et Procédés Associés, France

Corresponding author:
Rida Farhan, Laboratory of Physics of Condensed Matter (LPMC), Faculty of Sciences Ben M'Sik Hassan II University, Av Driss El Harti Sidi Othmane, Casablanca 7955, Morocco.
Email: farhan.lpmc@gmail.com

polymers such as polyvinylidene fluoride (PVDF), polyamide-6 (PA6), and polyamide-11 (PA11) display good electromechanical coupling coefficients and high ductility.[8,9] Though, one of the most exploited ferroelectric materials is the lead zirconate titanate (PZT) particles. Due to its excellent piezoelectric properties, it is often used in sensors.[10–12] However, vibratory harvesting application of PZT is hindered due to lack of flexibility. Yet, the piezoelectric responses of the polarization fields are higher 10 times than those used for polishing inorganic ceramics such as lead zirconate titanate (PZT).[13,14] Furthermore, has a high electromechanical property over a wide range of temperature. To take advantage of both, composites are prepared, where ferroelectric ceramic were introduced into a polymer matrix.[15–17] So as to keep the mechanical properties of the polymer for a higher volume fraction of inorganic particles, micronic fillers were substituted by submicronic ones.[18–21] Depending on the final mechanical properties required, other solutions are proposed to provide a soft piezoelectric material by introducing a piezoelectric structural fiber into a polymeric matrix.[22,23] There have been many studies into the behavior of piezoelectric materials and their application in the development of piezoelectric devices. Eddiai et al.,[24] Guyomar et al.,[25] Shinde et al.[26] have developed expressions to predict the dielectric, piezoelectric, elastic constants, and modulus for binary systems such as poly(vinylidene-fluoride)/PZT. Recently, this material is described as a highly dielectric compound, applicable in electrical energy harvesting. PA11, polyurethane, and PVDF are known to be semicrystalline polymers, with excellent dielectric, mechanical and piezoelectric properties. Therefore, we have developed new series of piezoelectric a 0–3 connectivity composites (PA6/PZT) by incorporating PZT into a matrix of PA6 that is able to realize composites with high dielectric permittivity and piezoelectric coefficient. The purpose of this work is to investigate the potential of piezoelectric composite for actuator and energy-harvesting applications. Polymeric composites gain increasing interest in materials research and practice applications due to their excellent properties of piezoelectric ceramic. A new composite with high dielectric constant has been developed by incorporating PA matrix through microparticles of ceramic PZT. A structural, electrical, and mechanical characterization of PA6/PZT composite has been performed in order to evaluate their potential for good application in sensing and actuator area. The obtained results show that the incorporation of the PZT particles increases significantly the intrinsic parameters of our composites. Finally, these augmentations make this composite as potential candidates for energy harvesting.

The paper is organized as follows. In the next section, we present the preparation method of polymer materials. The obtained experimental results and their discussion are given in the Results and discussion section. Finally, the last section briefly concludes the paper in which we mention the main findings of our experimental study.

Experimental procedure

Materials

The PA6 was chosen as polymer matrix for its good mechanical properties particularly its high tensile strength. We notice that most of PA tend to be semi-crystalline and overall is very rough material with good thermal and chemical resistance.

PZT is characterized by a very high constant dielectric, high charge coefficient, and high electromechanical coupling coefficient. The PZT particles were provided by Ferropem (Denmark) with an average diameter of $1 \mu m$. Bulk ceramic exhibits a Curie temperature of $235°C$ and a piezoelectric coefficient d_{33} of 600 pC/N (given by the manufacturer in the bulky state). The former X-ray diffraction measurement has shown the ferroelectric properties of these inorganic fillers in a way the can acquire piezoelectric after a poling step.[20]

Composite processing

The composite PA6/PZT was prepared in laboratory by solutions casting. The PA6 granules were first dissolved in formic acid at $120°C$. Particles were dissolved in solvent using an ultrasonic probe. Thereafter, the dispersed microscale PZT particles were mixed with the polymer solution; they were agitated at a rotational speed of $100 r/min$ for $15 min$. The films were manually placed on a glass plate and dried in the oven at $40°C$.

Results and discussion

Material properties

Figure 1 shows the permittivity versus frequency for a filled PA6/PZT. We have calculated the dielectric constants of the obtained samples from the capacitance at room temperature by using a Hewlett Packard 4274 A multi-frequency LCR meter. We observed a large decrease of the dielectric constant around 30 Hz for 20%, 30%, and 40% of PA6/PZT composites when the frequency increased. This behavior is due to the loss of one of the polarization contributions (interfacial polarization) of the dielectric constant.[27] Considering the value of the frequency, this decrease could be actually attributed to the loss of the space charges inducing
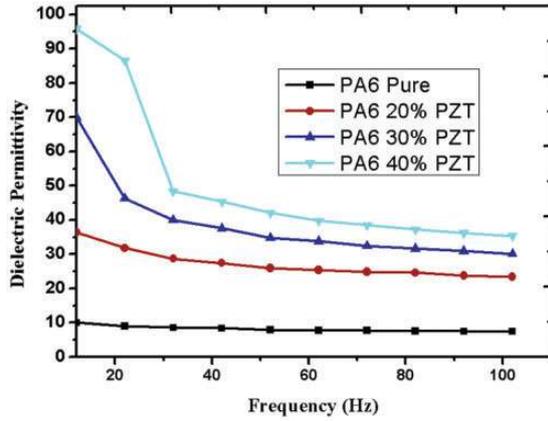
Figure 1. Dielectric permittivity of composites with different volume fractions as a function of frequency.

Figure 2. Losses as a function of the frequency for the filled PA6.

an interfacial polarization contribution. Furthermore, we could neglect the contribution of the space charge for frequencies higher than some tens of Hertz. For pure PA6, the dielectric permittivity remained constant in the considered frequency range.

With 40% of microscale PZT particles, the dielectric permittivity of PA6 pure increases up from above 10 to 95.8. PZT content in PA6 raises the dielectric constant and also dielectric loss value of PA6 as displays the dielectric study of the composite system. However, high content of ceramic in PA6 leads to agglomeration of ceramic particles in polymer matrix, which introduces void and pores in the composite film (as shown in SEM Figure 6) and thus deteriorate the dielectric behavior.

The frequency dependence of the loss tangent for the filled PA (20%, 30%, and 40% by volume) and pure PA is shown in Figure 2. At lower frequencies, an important increase is observed in the loss tangent. While for higher frequencies from 50 Hz to 100 Hz, the value of the tangent loss for the filled PA was practically constant over the considered frequency range.

Piezoelectric coefficient

A polarization step is required in order to make the composites piezoelectric. It is governed by three parameters: the value of applied electric field, the time, and the temperature of polarization. The coercive field in PA6 is 30 times higher than that of PZT, which has been polarized in this study. In order to keep away from breakdown situations under strong field, the composite materials are immersed in a castor oil bath with the dielectric permittivity greater than to that of the air. In order to optimize the polarisation parameter, it is necessary to study the piezoelectric coefficient d_{33} of the PA6/PZT composite with a thickness of 60 μm and PZT contents of 20%, 30%, and 40% vol. Figure 3
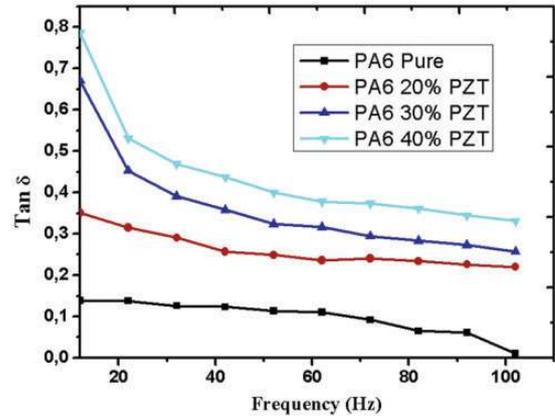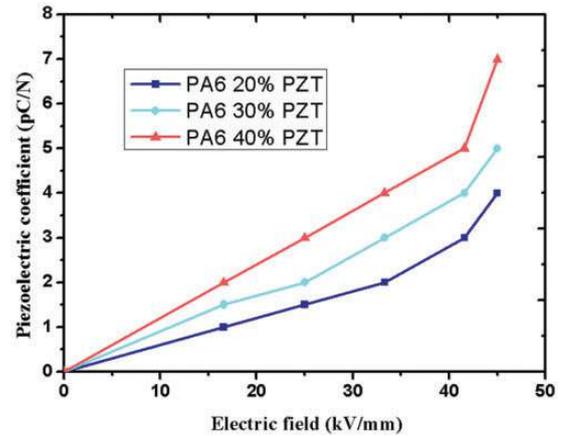

Figure 3. Piezoelectric coefficient d_{33} of 20% PA6/PZT, 30% PA6/PZT, and 40% PA6/PZT composites as a function of electric field.

describes the piezoelectric coefficient d_{33} of filled PA as a function of electric field, during the poling process. It is obvious that the piezoelectric activity appears at 16.6 kV/mm and reaches a maximum of 45 kV/mm. The coefficient d_{33} increases with the volume fraction of PZT: the composite loaded at 40% of PZT induces a maximum d_{33} increase of 7 pC/N for a poling field of 45 kV mm^{-1}. While the composite loaded at 20% vol is characterized by a coefficient of 4 pC/N; at 30% by volume, the coefficient d_{33} is equal to 5 pC/N for the same value of electric field.

The piezoelectric coefficient values are directly related to the amount of the piezoelectric phase introduced in the composite. The SEM images showed a wide particle size distribution. At room temperature, the better piezoelectric coefficient is obtained with the PA6/PZT as shown in Table 1. Compared to the PA11/PZT[20] composite, the d_{33} coefficient is increased by a factor of 2.6.

Table 1. Comparison of piezoelectric coefficients d_{33} of 30% PA6/PZT and 30% PA11/PZT composites at 26°C.

Composite	PA6/PZT	PA11/PZT[20]
d_{33}(pC/N)	7	2.7

PA6: polyamide-6; PZT: lead zirconate titanate.
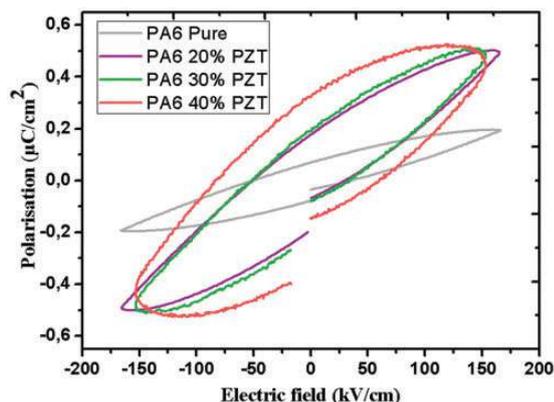
Figure 4. Hysteresis loops of the composites with different PZT volume fractions at 80 Hz.

Figure 5. Remanent polarization (Pr) as a function of the PZT volume fraction.

This result indicates that the polarization of ceramic particles is enhanced at high dielectric permittivity of the polymer matrix. This result brings the conclusion that the polarization of ceramic particles is more efficient in case of an intrinsically high dielectric permittivity of the polymer matrix. Another phenomenon is susceptible to play a role in these results, a homogeneous distribution of electrical dipoles from the PA6/PZT compared to the one induced by the PA11/PZT.

Hysteresis loop analysis

In order to measure the electrical properties, gold electrodes were deposited on the samples and then the poling process was performed in silicone oil at 166.6 kV/cm for the DC electric field. The hysteresis loops were getting by Radiant Precision Workstation ferroelectric testing system. Figure 4 shows the filled PA6/PZT hysteresis loops for various volume fractions. For comparison, the hysteresis loop of the pure polymer was also plotted. The results obtained show that below a low electric field, the PA6 has to make a hysteresis loop. PA6/PZT 20 vol%, PA6/PZT 30 vol%, and PA6/PZT 40% have the polarization saturation higher than the pure PA6.

Under an electrical field of 1 kV, the lower remnant polarization of filled PA film ($0.17\,\mu C/cm^2$) may be affected by the random distribution of PZT (Figure 5). The higher remnant polarization ($0.4\,\mu C/cm^2$) in our composites (20%, 30%, and 40% of PZT) can be attributed 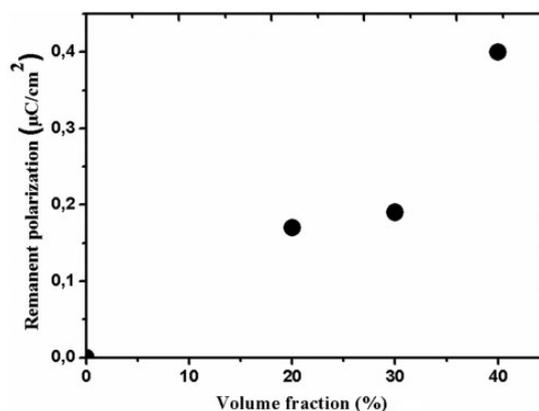to the enhanced polarization from the dipole–dipole interaction of directly filled powders as well as fracture free and defect free composite formation in the polymer film.

Scanning electron microscopy

The microstructure and the morphology of the samples were characterized using scanning electron microscopy (SEM, Hitachi S-3500N). The samples were sputtered with a thin layer of carbon prior to SEM analysis at magnifications from 5× and imaging was conducted at a voltage of 0 kV. SEM was used to study PZT dispersion in the PA matrix. To have elaboration conditions similar to that of various composites, the dispersion of the microscale particles of ceramics PZT in the PA6 was carried out for duration and a rotation speed of the screws of 15 min and 7 r/min, respectively. The compounds that have loaded at 20%, 30%, and 40% by volume, were prepared by solutions casting, are shown in Figure 6.

The surface microstructure of 20%, 30%, and 40% composites show that the PZT particles are distributed throughout PA6 matrix. For 20% and 30% PA6/PZT films, dispersion of PZT is found identical with very few pores as compare to other composition (40% PA6/PZT). It could be seen that the ceramic incorporation dispersed homogeneously over the polymer matrix and there are no large agglomerations of ceramic powder. Nevertheless, higher volume of PZT in composition shows agglomeration with important number of void; it causes reduction in dielectric constant and hence increases in dielectric loss.

Mechanical testing

Principle and experimental setup. Rectangular test samples (20×36 mm^2) were cut from our composites. Then,
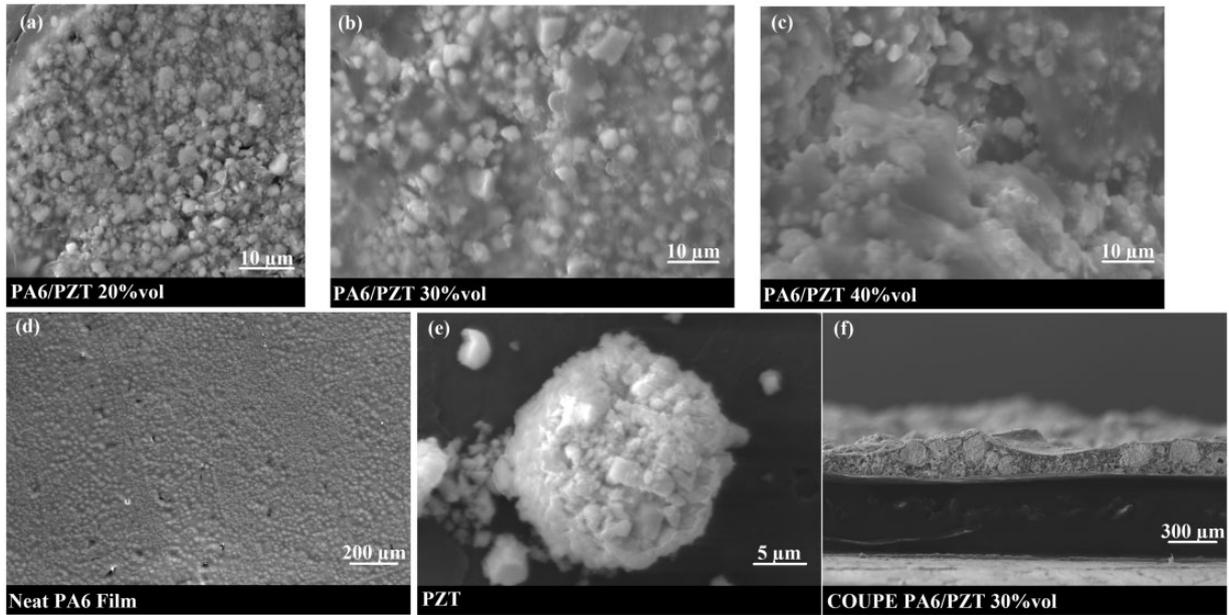
Figure 6. SEM image of (a) 20% PA6/PZT, (b) 30% PA6/PZT, (c) 40% PA6/PZT, (d) neat PA6 film, (e) SEM micrograph of PZT powder, and (f) layer thickness of composite 30% PA6/PZT.
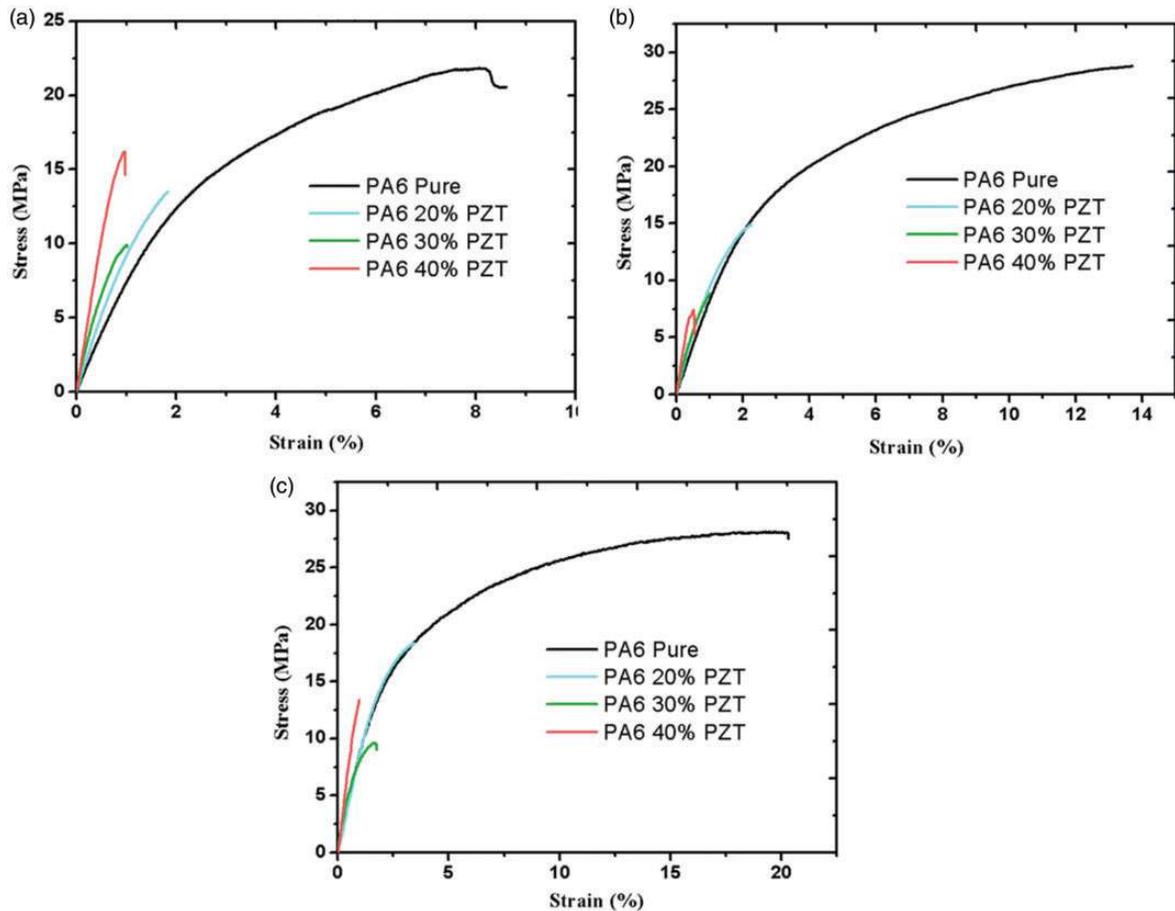

Figure 7. Stress–strain curves of the composites at different volume fractions with different velocities (a) 2 mm min^{-1}, (b) 5 mm min^{-1}, and (c) 10 mm min^{-1}.

longitudinal traction was performed at 25°C using testometric traction machine at the max capacity 3 kN. We have made our tests by placing the sample between two self-locked jaws where the superior one is movable. For recording stress–strain measurements, an extensional rate of 2, 5, and 10 mm min⁻¹ was used. When the specimens are geometrically similar, the comparative survey between different produced composites would be possible. The important information that can be got from this kind of study is that the stress result is equal to our measured force over the surface of the section. Another point, which must be taken in consideration is the awareness of the initial length of the sample as well as the elongation applied; allow the strain of the sample. The hook's law is an accurate approximation to describe the perfectly flexible solids. In this law, the stress and the deformation are proportional and related by Young's modulus. The polymer retrieves its main extension when the value of the imposed deformation is reduced to zero. Beyond the elastic domain, the strain of the polymer becomes viscoelastic then plastic.[28,29]

Experimental setup of traction.

Longitudinal traction. In this work, tensile properties of PA6/PZT composites were investigated. Stress–strain curves of PA6/PZT composites are reported in Figure 7 with different velocity. Equal diameters, the composites loaded at 20%, 30%, and 40% by volume are compared with PA6. The tests of these various composites were done with the same experimental tools used for the pure PA6 tests. On the other hand, we have used three different velocities for the traction

Table 2. Tensile properties of the different composites at room temperature with velocity 2 mm min⁻¹.

Composite	Maximal force (N)	Strain (%)	Stress (MPa)	Y (MPa)
PA6 pure	21.5	8.6	20.5	675.2
PA6 20% PZT	16.1	1.8	13.4	990.3
PA6 30% PZT	11.8	1.01	9.7	1356.2
PA6 40% PZT	19.4	0.9	14.6	2091.4

PA6: polyamide-6; PZT: lead zirconate titanate.

test such as 2, 5, and 10 mm min⁻¹ to exhibit the impact of the velocity along the tests.

In general, tensile modulus increases with PZT volume fraction: the composites are reinforced. For different filled composites and for a speed traction 2, 5, and 10 mm min⁻¹ the maximum stress is close to the PA6 one for volume fraction at 20% and 30% (between 9 MPa and 16 MPa) and the rupture arrives above 1.5% of strain. At 40% of the volume, the tensile stress is at 8.8 MPa for the deformations less than 0.4%. We clearly see that the choice of the filler integrated to the PA6, is an important factor and have a great effect on the mechanical properties of the composites concerning the strain at break, two behaviors arise. The composites loaded at 20%, 30%, and neat PA6 present a ductile behavior since a plastic deformation remains above 0.5% strain. The composites loaded at 40% are characterized by a fragile behavior. We clearly observe in these figures, that the performance of tensile stress versus tensile strain is linear up to 3 MPa, and there is no major effect of the extensional rate on stress levels of PA6/PZT composites charged at 20%, 30%, and 40% by volume under 5 MPa. Results of the tensile tests for different composites are presented in Table 2. For different speeds, the obtained results clearly show that the addition of the particles in the starting matrices has an important influence on Young's modulus and on the surface, which describes the mechanical losses. This slight increase makes it possible to keep the flexibility of the elastomers for a good performance on actuation and to take advantage of the elevation of the relative permittivity by the incorporation of the particles for energy recovery.

Conclusion

By putting submicronic ferroelectric particles (PZT) into a semicrystalline thermoplastic matrix (PA6), a new composite has been elaborated by solution casting. In parallel, the dielectric and mechanical properties of the composites with different volumes were evaluated, where the dielectric ones are modified by the presence of PZT. The ferroelectric properties of the

composite depend on the dielectric permittivity of the organic phase. Due to the insertion of PZT particles, the dielectric permittivity and the loss indices of the PA6 matrix have been increased. Furthermore, the piezoelectric coefficient increases with the content of the ceramic particles.

According to the SEM images, PZT particles are perfectly dispersed in the polymer matrix at a micronic scale and that the PA6/PZT composites have aggregates only up to 40% by volumes. On the other hand, the hysteresis loops of these composites exhibit a dependence on the ceramic volume fraction. In addition, a larger remnant polarization and coercive field have been obtained when the volume fraction increases from 20 vol% to 40 vol% of PZT. Finally, this work opens opportunities to improve thermoplastic-based composite with an excellent enhancement of the polymer dielectric permittivity.

Future works will concern the effect of the size of the particles PZT to increase the permittivity of the composite and consequently its capabilities to harvest electrical energy on mechanical vibrations.

Declaration of Conflicting Interests

Funding

ORCID iD

Rida Farhan ⓘ http://orcid.org/0000-0002-5160-3173

References

1. Amirtharajah R and Chandrakasan AP. Self-powered low power signal processing. In *IEEE symposium VLSI circuits-digest of technical papers*. Kyoto, Japan, 13–15 June, 1997, pp. 25–26.
2. Lallart M, Cottinet P, Lebrun L, et al. Evaluation of energy harvesting performance of electrostrictive polymer and carbon-filled terpolymer composites. *J Appl Phys* 2010; 108: 034901.
3. Krikke J. T-Engine: Japan's Ubiquitous Computing Architecture is ready for prime time. *IEEE Pervasive Comput* 2005; 4: 4.
4. Lallart M, Guyomar D, Jayet Y, et al. Synchronized switch harvesting applied to self-powered smart systems: Piezoactive microgenerators for autonomous wireless receivers. *Sensors and Actuators A* 2008; 147: 263–272.
5. Wenger MF, Blanas P, Shuford RJ, et al. Acoustic emission signal detection by ceramic/polymer composite piezoelectrics embedded in glass-epoxy laminates. *Polym Eng Sci* 1996; 36: 2945–2954.
6. Badcock RA and Birt EA. The use of 0-3 piezocomposite embedded Lamb wave sensors for detection of damage in advanced fibre composites. *Smart Mater Struct* 2000; 9: 291–297.
7. Jagur-Grodzinski J. Nanostructured polyolefins/clay composites: role of the molecular interaction at the interface. *Polym Adv Technol* 2006; 17: 395–418.
8. Ibos L, Bernès A and Lacabanne C. Annealing or storage influence on pyroelectricity of ferroelectric PVDF and P(VDF-TrFE) copolymer. *Ferroelectrics* 2005; 320: 15–21.
9. Teyssèdre G and Lacabanne C. Study of the thermal and dielectric behavior of P(VDF-TrFE) copolymers in relation with their electroactive properties. *Ferroelectrics* 1995; 171: 125–144.
10. Sakamoto WK, Marin-Franch P and Das-Gupta DK. Characterization and application of PZT/PU and graphite doped PZT/PU composite. *Sensors Actuat A Phys* 2002; 100: 165–174.
11. Fan H and Kim HE. Perovskite stabilization and electromechanical properties of polycrystalline lead zinc niobate-lead zirconate titanate. *J Appl Phys* 2002; 91: 317–322.
12. Sodano HA, Inman DJ and Park G. Generation and storage of electricity from power harvesting devices. *J Intell Mater Syst Struct* 2005; 16: 67–75.
13. Kamel TM, Kools FXNM and de With G. Poling of soft piezoceramic PZT. *J Eur Ceram Soc* 2007; 27: 2471–2479.
14. Nayak B, Mansingh A and Machwe MK. Dielectric studies of PZT-polymer composites. *J Mater Sci* 1990; 25: 749–752.
15. Van Den Ende DA, Bory BF, Groen WA, et al. Improving the d_{33} and g33 properties of 0-3 piezoelectric composites by dielectrophoresis. *J Appl Phys* 2010; 107: 0–8.
16. Li K, Wang H and Ding A. Polyamide-11/lead zirconate titanates-a novel composite material with high dielectric properties. *Polym Sci Ser B* 2010; 52: 438–442.
17. Furukawa T, Fujino K and Fukada E. Electromechanical properties in the composites of epoxy resin and PZT ceramics. *Jpn J Appl Phys* 1976; 15: 2119–2129.
18. Sharma SK, Gaur H, Kulkarni M, et al. PZT-PDMS composite for active damping of vibrations. *Compos Sci Technol* 2013; 77: 42–51.
19. David C, Capsal J-F, Laffont L, et al. Piezoelectric properties of polyamide 11/NaNbO3 nanowire composites. *J Phys D Appl Phys* 2012; 45: 415305.
20. Carponcin D, Dantras E, Dandurand J, et al. Electrical and piezoelectric behavior of polyamide/PZT/CNT multifunctional nanocomposites. *Adv Eng Mater* 2014; 16: 1018–1025.
21. Capsal JF, Dantras E, Dandurand J, et al. Electroactive influence of ferroelectric nanofillers on polyamide 11 matrix properties. *J Non Cryst Solids* 2007; 353: 4437–4442.
22. Lin Y and Sodano HA. Fabrication and electromechanical characterization of a piezoelectric structural fiber for multifunctional composites. *Adv Funct Mater* 2009; 19: 592–598.

23. Lin Y, Shaffer JW and Sodano Ha. Electrolytic deposition of PZT on carbon fibers for fabricating multifunctional composites. *Smart Mater Struct* 2010; 19: 1–8.
24. Eddiai A, Meddad M, Mazroui M, et al. Strain effects on an electrostrictive polymer composite for power harvesting: experiments and modeling. *Polym Adv Technol* 2016; 27: 677–684.
25. Guyomar D, Cottinet P-J, Lebrun L, et al. The compressive electrical field electrostrictive coefficient M_{33} of electroactive polymer composites and its saturation versus electrical field, polymer thickness, frequency, and fillers. *Polym Adv Technol* 2012; 23: 946.
26. Shinde AV, Pande SA, Joshi SS, et al. Novel ceramic-polyamide nanocomposites approach to make flexible film of PZT ceramics: structural and dielectric study. *Ferroelectrics* 2016; 502: 187–196.
27. Mitchell BS. *An introduction to materials engineering and science for chemical and materials engineers*. New Jersey: John Wiley & Sons, 2004, pp.179–83.
28. Gendre L, Abhyankar H, Njuguna J, et al. Mechanical properties of three-phase polyamide 6 nanocomposites. In *Proceedings of the 11th International Conference on Manufacturing Research (ICMR2013)*. Cranfield University, UK, 1920 September, 2013, pp. 375–380.
29. Regrain C, Laiarinandrasana L and Toillon S. Experimental and numerical study of creep and creep rupture behavior of PA6. *Eng Fract Mech* 2009; 76: 2656–2665.