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Lead zirconate (PbZrO$_3$) embedded in natural rubber as electroactive elastomer composites

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Perovskite lead zirconate (PbZrO$_3$) was synthesized in an orthorhombic form at a temperature below the Curie temperature, T_C. The orthorhombic form is a noncentrosymmetric structure which is capable of spontaneous polarization. Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) patterns confirm the successful synthesis of the lead zirconate; and scanning electron microscopy (SEM) micrographs indicate that PbZrO$_3$ particles are moderately dispersed in the natural rubber (NR) matrix. Without an electrical field, the particles merely act as a ferroelectric filler, which can absorb and store additional stress. Under an electrical field, particle-induced dipole moments are generated, leading to interparticle interaction and a substantial increase in the storage modulus. At a small amount of lead zirconate particulates present in the natural rubber matrix, at a volume fraction of 0.007306, the electrical conductivity increases dramatically by nearly two orders of magnitude at the electrical frequency of 500 kHz.

Keywords: Natural rubber; perovskite lead zirconate; actuator sensors; smart engineering devices.

1. Introduction

Lead zirconate (PbZrO$_3$) is an inorganic and anti-ferroelectric material containing Pb^{2+}, Zr^{4+}, and O^{2-} ions within the unit cell with the Curie temperature ($T_C$) approximately at 230°C. The antiferroelectric materials may phase transform to ferroelectric materials when induced by electrical field. The advantages of lead zirconate are a material for high displacement electromechanical actuator and energy storage applications due to the spontaneous

polarizations consisting of: orientation polarization (Debye polarization), and ionic and electronic polarizations (Wagner polarization). Lead zirconate can be prepared by many methods such as sol–gel, conventional process, wet chemical precipitation, and microemulsion.[1,2]

Composite materials are made of a filler or dispersed phase (either particles, flakes, or fibers) embedded in a matrix phase made of polymer, metal, and ceramic materials. Combining a ferroelectric ceramic and a polymer host to form a flexible ferroelectric composite has been the subject of interest in recent years in view of the greater flexibility allowed by these materials to suit particular property requirements such as mechanical, electrical, thermal and/or a coupling between these properties. The characteristics of the ceramic powder depend not only on their composition and their crystal structure but also on the microstructure, including grain size, grain boundary, pore size, crystalline, polarization, and phase transformation which can affect various properties.[3]

The objective in this work was to investigate an uncrosslinked natural rubber (NR) matrix embedded with a dielectric material ($PbZrO_3$) under the effect of volume fraction. The electrical properties, dielectric constant (ε), and electrical conductivity (σ) of the soft composite materials consisting of lead zirconate particles and the NR swollen in a hexane (C_6H_{14}) medium are reported here. It is known that NR containing nonpolar molecules tends to be soluble and swollen in the nonpolar solvents such as carbon tetrachloride, diethyl ether, and benzene, as shown in Scheme 1.[3,4]

Here we have also made detailed investigations by scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), and X-ray diffraction (XRD) to confirm the electrical properties and results. Lead zirconate ($PbZrO_3$) and NR (Standard Thai Rubber 5L, STR 5L) composite materials can be used as biomimetic actuators, artificial muscles, and smart engineering devices such as active engine mounts, shock absorbers, clutches, brakes, damping devices, hydraulic valves, and robotic controlling systems.[3–12]
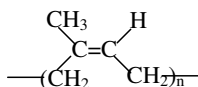
Scheme 1.   Polyisoprene structure.

2.   Experimental Procedure

2.1.   *Materials*

The production process of pure perovskite lead zirconate ($PbZrO_3$) was successfully synthesized via the sol–gel process.[13–15] Lead glycolate and sodium tris (glycozirconate) were used as the starting precursors. The obtained molar ratio (Pb:Zr) of $PbZrO_3$ was 0.9805:1 and in the orthorhombic form when the lead zirconate powder was calcined at 300°C for 1 h, a temperature close to the Curie temperature (T_C). The lead zirconate synthesized possesses high dielectric constant and high electrical conductivity values of 9.248 and 5.84×10^{-7} $(\Omega \cdot m)^{-1}$, respectively, as measured at 27°C and 500 kHz. The density of the calcined lead zirconate powder is $7.50\,g/cm^3$. The average particle diameter of the $PbZrO_3$ is approximately 16.724 ± 0.026 microns.

The NR (STR5L) was supplied by Union Rubber Product Corporation Co., Ltd., Thailand. The NR is an uncrosslinked rubber type in an extra light color slab suitable for producing rubber bands, cut thread, baby bottle nipples, extruded hoses, footwear, and medical applications. The density, impurity content, Mooney viscosity, initial plasticity, and the plasticity retention of the natural rubber (NR-STR 5L) are $0.92\,g/cm^3$, 0.004 % by weight, 62.8, 32.0, and 81.3, respectively.

Hexane (High Performance Liquid Chromatography, HPLC grade) medium was obtained from Lab-Scan Co., Ltd., Thailand. It was used for the swelling of the uncrosslinked NR. The dielectric constant and density of acetone are 2.00, and $0.655\,g/cm^3$, respectively.

2.2.   *Instruments*

(1) FTIR were recorded on a Perkin Elmer, model Spectrum One spectrometer with a spectral resolution of $4\,cm^{-1}$. The samples were measured by single-crystal potassium bromide, KBr.
(2) XRD was taken and analyzed using a Bruker AXS analyzer (D8 Discover) with VANTEC-1 Detector. Samples were analyzed using a double-crystal wide-angle goniometer. Peak positions were consistent with those of the International Center for Diffraction Data Standard (JCPDS) patterns to identify crystalline phases and phase transformation via the Bragg equation: $\lambda = 2d\sin\Theta$.

(3) SEM: Micrographs were obtained using a scanning electron microscope (SEM, JEOL-5200).

(4) Electrical properties were measured and obtained using an impedance analyzer (HP, model 16451B) with an LCR meter (HP, model 4284A), in the frequency range of 1 to 1000 kHz. The samples were prepared according to ASTM B263-94 for the electrical properties measurement. Pellet samples were prepared as thin discs having a diameter of 38 mm and a thickness of 0.50 mm. In our experiment, the electrical properties were measured at frequencies from 10^3 to 10^6 Hz with an AC electrical field of 2 A at the volume fraction defined in Eq. (1) as follows:

$$\chi_\beta = \frac{\nu_{\text{disperse}}}{\nu_{\text{total}}}. \qquad (1)$$

The electrical resistivity of the composite materials was converted to electrical conductivity using the resistivity-mixture rule, Eqs. (2) and (3), as follows:

$$\rho_{\text{eff}} = \frac{RA}{L} = \frac{1}{\sigma} = \chi_\alpha \rho_\alpha + \chi_\beta \rho_\beta, \qquad (2)$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}, \qquad (3)$$

where ρ_{eff} is the effective resistivity ($\Omega \cdot$ m), R is the resistance (Ω), A is the cross-sectional area of the discs (m^2), L is the total length or thickness (m), χ_α is the volume fraction of the continuous phase, χ_β is the volume fraction of the dispersed phase, ρ_α is the resistivity of the continuous phase, ρ_β is the resistivity of the dispersed phase, ε_r is the relative dielectric constant, ε_0 is the permittivity in a vacuum 8.854×10^{-12} (F/m), σ is the electrical conductivity $(\Omega \cdot$ m$)^{-1}$, and ε is the permittivity of the samples (F/m).

2.3. *Sample preparation of soft composite materials*

Natural rubber (STR5L) samples, consisting of nonpolar molecules, were dissolved and swollen in the 20% V/V hexane medium. The suspensions were homogeneously mixed by using a magnetic stirrer at room temperature for 24 h. Lead zirconate particles were added into the suspensions at the volume fractions of 0.000000 (STR5L/PZ_0), 0.000037 (STR5L/PZ_1), 0.000074 (STR5L/PZ_2), 0.00368 (STR5L/PZ_3), 0.003667 (STR5L/PZ_4),

0.007306 (STR5L/PZ_5), and 0.035494 (STR5L/PZ_6). The suspensions were then poured into petri dishes, covered with glass plates to avoid dust and bubbles, and allowed to dry slowly at room temperature overnight. The dried samples obtained display the colors varying between light yellow to dark yellow, depending on the volume fraction of lead zirconate embedded in NR.

3. Results and Discussion

3.1. *Characterization of natural rubber (NR-STR 5L)/lead zirconate (PbZrO₃) composite materials*

The FTIR spectra of lead zirconate (PbZrO₃), NR, and NR-STR5L/PbZrO₃ composite materials are shown in Fig. 1 and the peaks are tabulated in Table 1. The characteristic peaks of NR-STR5L/PbZrO₃ are at: 3459 cm$^{-1}\nu$(O–H); 3036 and 3282 cm$^{-1}\nu$(C–H); 2852, 2915, and 2960 cm$^{-1}\nu$(CH$_2$); 1663 and 1710 cm$^{-1}\nu$(C=C); 1546 cm^{-1} of CH$_3$ asymmetry; 1375 and 1448 cm^{-1}(CH$_3$ of O–CH$_2$CH$_3$ and C–O stretching); 1241 and 1287 cm$^{-1}\nu$(C–O–C); 1128 cm^{-1}(R–CO–R); 990 and 1053 cm$^{-1}\nu$(Zr–O–C); 884 cm^{-1}(C–O–Pb and C–O–O–C); and 691 cm$^{-1}\nu$(Pb–O) and ν(Pb–O–Zr). The FTIR spectra are consistent with the earlier results obtained by Jha and Bhowmick.[16,17]

A broad XRD characteristic peak of pure natural rubber (NR-STR 5L) shows that it is amorphous. The X-ray characteristic diffraction diagrams of the NR-STR5L/PbZrO₃ composites show patterns of
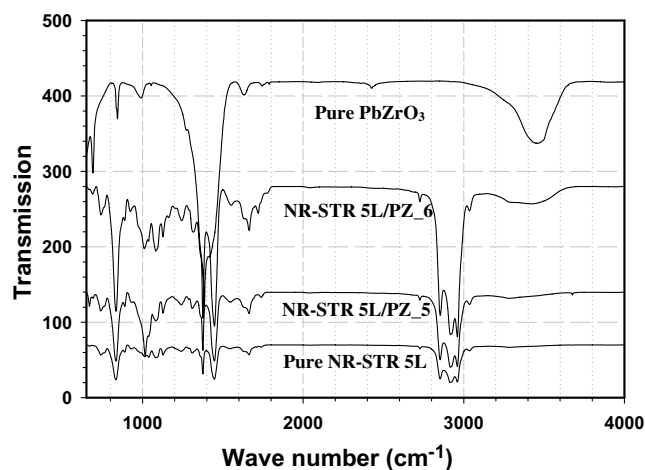

Fig. 1. FTIR spectra of natural rubber (NR-STR 5L), lead zirconate (PbZrO₃), NR-STR5L/PZ_5, and NR-STR5L/PZ_6 composite materials.

Table 1. FTIR spectra of natural rubber (NR-STR 5L), lead zirconate (PbZrO$_3$), and NR-STR 5L/PbZrO$_3$ composite materials.

Wave number (cm^{-1})	Functional group
3282, 3459 (CAS7732-18-5); (CAS78-79-5)	OH stretching of PbZrO$_3$ added NR
3036 (CAS78-79-5)	–C–H and =CH stretching vibration of isoprene
2852, 2915, 2960 (CAS78-79-5)	–CH$_2$ stretching vibration of C–CH$_2$CH$_3$
1663, 1710 (CAS78-79-4)	>C=C stretching for carbon double bonds
1448 (CAS78-79-5); (CAS110-54-3); (CAS73513-42-5)	–CH$_3$ asymmetric deformation
1375 (CAS78-79-5)	–CH$_3$ deformation of O–CH$_2$CH$_3$
1241, 1287 (CAS110-54-3)	Asymmetric C–O–C stretching vibration
1128	R–CO–R symmetric stretching
990, 1053 (CAS110-54-3)	Zr–O–C
884	C–O–Pb and C–O–O–C
691	Pb–O and Pb–O–Zr stretching

Table 2. Electrical properties of NR-STR5L/PbZrO$_3$ composites measured at $27 \pm 1°$C, and 500 kHz.

Code	Mass of PbZrO$_3$ (300°C_1 h) (g)	Mass of STR5L (g)	Volume fraction of PbZrO$_3$	Dielectric constant at 500 kHz	Electrical conductivity at 500 kHz $(\Omega \cdot m)^{-1}$	Upper bound of σ $(\Omega \cdot m)^{-1}$	Lower bound of σ $(\Omega \cdot m)^{-1}$
PbZrO$_3$	1.0000	0.00000	1.000000	9.248	5.8400E-07	5.84E-07	2.76E-15
NR-STR5L/PZ_0	0.0000	3.00000	0.000000	0.718	4.7300E-09	4.75E-09	4.73E-09
NR-STR5L/PZ_1	0.0009	3.00000	0.000037	1.062	4.7793E-09	6.14E-09	4.734E-09
NR-STR5L/PZ_2	0.0018	3.00000	0.000074	1.601	5.7783E-09	7.55E-09	4.747E-09
NR-STR5L/PZ_3	0.0090	3.00000	0.000368	1.355	6.6959E-09	1.86E-08	4.752E-09
NR-STR5L/PZ_4	0.0900	3.00000	0.003667	1.243	1.0119E-08	1.19E-07	4.756E-09
NR-STR5L/PZ_5	0.1800	3.00000	0.007306	1.597	4.4283E-08	1.95E-07	4.760E-09
NR-STR5L/PZ_6	0.9000	3.00000	0.035494	1.661	3.0066E-08	4.16E-7	4.900E-09

Note: Density of NR − STR5L = 0.92 g/cm^3, Density of PbZrO$_3$ powder = 7.50 g/cm^3.

the amorphous phase mixed with the crystalline phases, with the peaks at 28.500, 29.305, 30.850, 34.550, and 45.45 (as shown in Fig. 2), indicating the orthorhombic form. These peaks resemble those recorded by the JCPDS numbers 35-739, 77-856, and 75-1607.

The microstructures of pure natural rubber (NR-STR5L), lead zirconate (PbZrO$_3$), NR-STR5L/PZ_5, and NR-STR5L/PZ_6, as obtained by SEM, are shown in Fig. 3. Figure 3(a) is a micrograph of the natural rubber (NR-STR5L). The average particle diameter of PbZrO$_3$ is approximately 16.724 $\pm$ 0.026 microns[10–12] as shown in Fig. 3(b); it is irregular in shape. Figure 3(c) shows a uniform dispersion of the doped PbZrO$_3$ particles at a volume fraction of 0.007306 embedded within the natural rubber matrix (NR-STR5L/PZ_5). The NR-STR5L/PZ_6 composite sample suggests a nonuniform dispersion or agglomeration of lead zirconate particles at a high volume fraction of 0.035494, in the NR, as shown in Fig. 3(d).
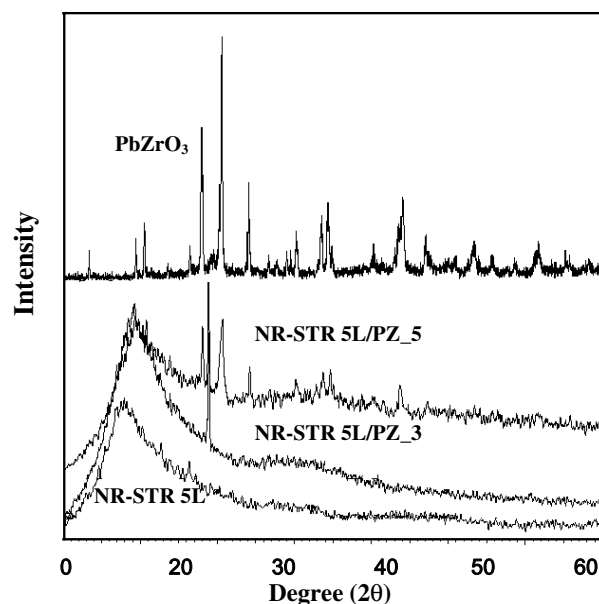

Fig. 2. XRD patterns of natural rubber (NR-STR 5L), lead zirconate (PbZrO$_3$), NR-STR5L/PZ_3, and NR-STR5L/PZ_5 composite materials.
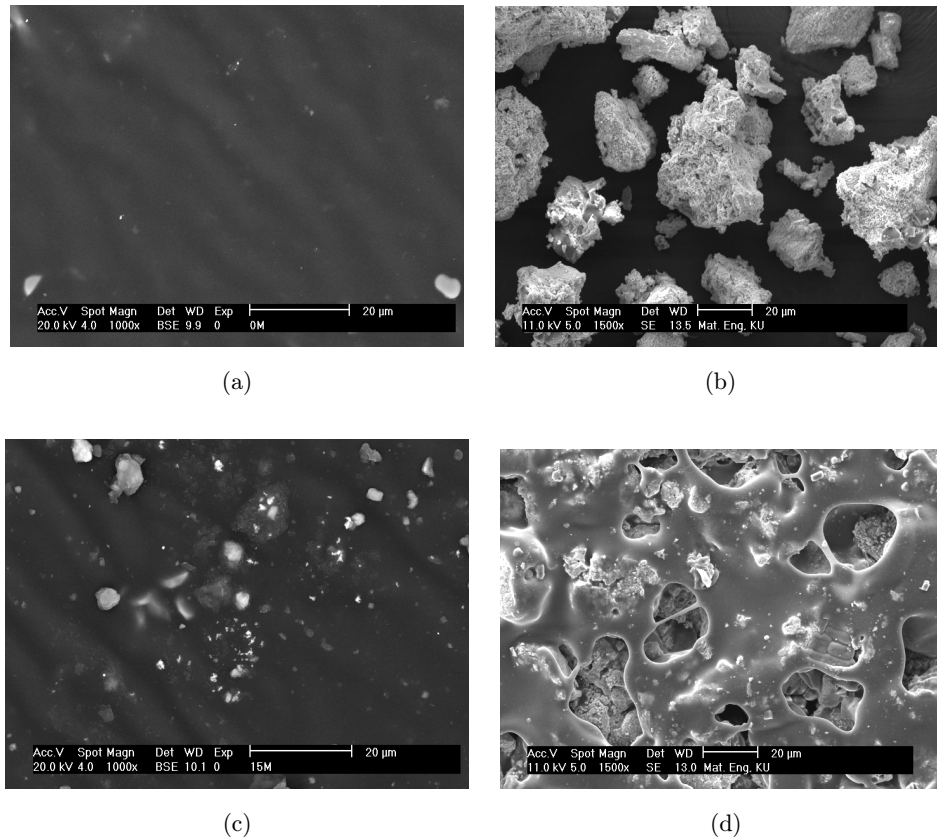
Fig. 3. SEM micrographs of: (a) natural rubber (NR-STR 5L), (b) lead zirconate (PbZrO₃), (c) NR-STR5L/PZ_5 and (d) NR-STR5L/PZ_6.

3.2. Electrical properties of natural rubber (NR-STR 5L)/lead zirconate (PbZrO₃)

The electrical properties of the NR, dielectric material (PbZrO₃), and composite materials (NR-STR5L/PbZrO₃) were measured using the impedance analyzer with an AC field at 500 kHz, as tabulated in Table 2. The dielectric constant values are 0.718, 9.248, and 1.597 for NR-STR5L, PbZrO₃, and NR-STR5L/PZ_5, respectively. The electrical conductivities of NR-STR5L, PbZrO₃, and NR-STR5L/PZ_5 are 4.7300×10^{-9}, 5.8400×10^{-7}, and 4.4283×10^{-8} $(\Omega \cdot m)^{-1}$, respectively. The variation of dielectric constant with frequency from 0.5 to 1000 kHz of the natural rubber (NR-STR5L), PbZrO₃, and NR-STR5L/PZ_5 suggests the electronic, ionic, and orientation polarizations of the Pb^{2+}, Zr^{4+}, and O^{2-} ions within the unit cell, as shown in Fig. 4.

The electrical conductivity of the composites versus volume fraction is consistent with the mixture rule, as shown in Fig. 5.[8] The mixture rule

depends on composition, crystal structure, degrees of crystallization, polarization, and morphology, which includes grain size, grain boundary, and pore size of lead zirconate particles.[3,4]
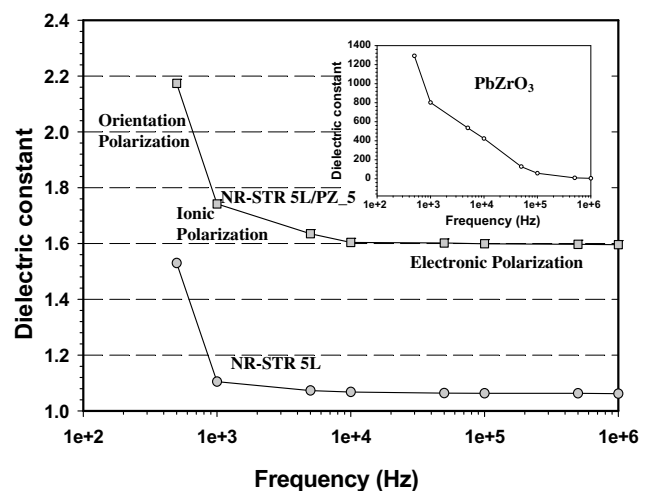

Fig. 4. Dependence of dielectric constant on frequency of NR-STR5L/PbZrO₃ composite materials.
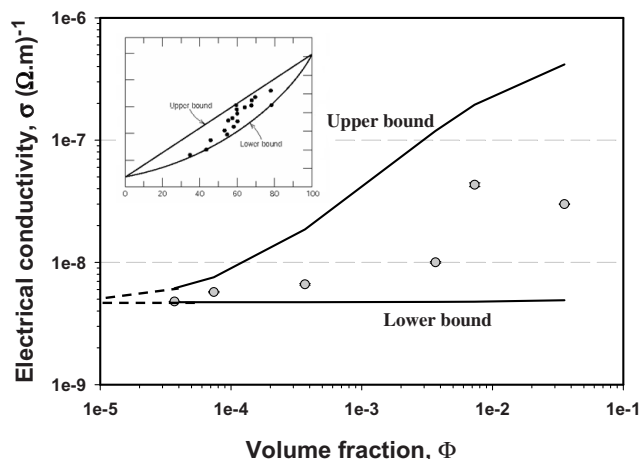
Fig. 5. Electrical conductivity versus volume fraction of NR-STR5L/PZ_5 composite compared to the upper bound and lower bound limitation of the mixture rule.

3.3. *Electrorheological properties of natural rubber (NR-STR5L)/lead zirconate (PbZrO₃): Time dependence, effects of particulate volume fraction, and electrical field strength*

The G' temporal characteristics of the samples were recorded in the linear viscoelastic regime at electrical field strengths of 1 and 2 kV/mm, and at the frequency of 1 rad/s. Figure 6 shows the G' temporal characteristics of the dried pure natural rubber (NR-STR 5L/PZ_0) and the composite
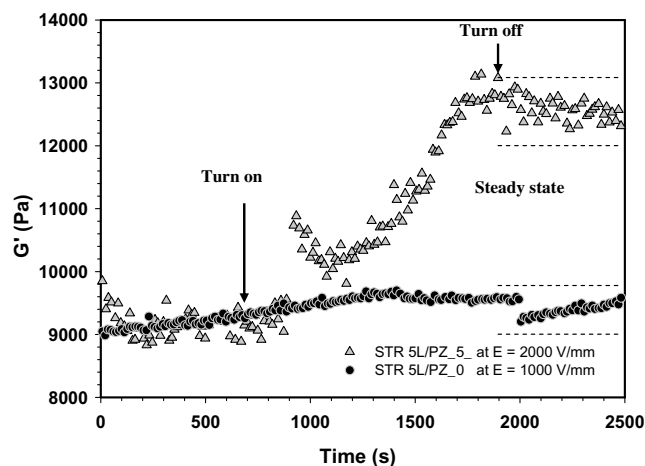

Fig. 6. Temporal response of the storage modulus of NR-STR 5L/PZ_0 and NR-STR 5L/PZ_5 composites at electrical field strength of 1.0 and 2.0 kV/mm, frequency 1.0 rad/s, strain 0.1%, and at 27°C.

sample (NR-STR 5L/PZ_5) under the time sweep tests, in which an electrical field is turned on and off. After an initial period with the electrical field on at the electrical field strength 1 kV/mm, the temporal characteristic of the NR-STR 5L/PZ_0 appears to increase from 9.4 kPa and subsequently reach a steady state value of 9.6 kPa. It decreases slightly as the electric field is turned off. While the temporal characteristic of the NR-STR 5L/PZ_5 composite increases abruptly from 9.4 to 12.6 kPa; and then it decreases slowly as the electrical field is turned off; however it does not recover its original value. This behavior indicates that there are some irreversible interactions, possibly due to the dipole bonding between small lead zirconate particles at this volume concentration and some residual dipole moments remaining.

4. Conclusion

Pure perovskite lead zirconate (PbZrO₃) of the orthorhombic form can be used as a filler, not only to reinforce the external energy within a NR matrix but also to improve the electrical and electromechanical properties of the composite materials. Lead zirconate (PbZrO₃) exhibits a dielectric behavior, which can show spontaneous polarizations (electronic, ionic, and orientation) in the positions of Pb^{2+}, Zr^{4+}, and O^{2-} ions as well as possess the noncentrosymmetric structure. The electrical properties — dielectric constant and electrical conductivity — of the most active sample, NR-STR5L/PZ_5, at a small volume fraction of PbZrO₃ (0.007306), are 1.597 and $4.4283 \times 10^{-8} (\Omega \cdot m)^{-1}$, respectively, measured at an AC electrical field at 500 kHz and at 27°C. The NR-STR5L/PZ_5 is demonstrated here as a potential of composite material suitable for use as biomimetic actuators, sensors, artificial muscles, vibration isolators, and smart engineering devices.

Acknowledgments

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