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Morphological, Electrical, and Mechanical Characterization of a Sustainable Three-Phase Composite Based on Natural Rubber, Leather Residue, and PZT Particles

Caracterização Morfológica, Elétrica e Mecânica de um Compósito Trifásico Sustentável à Base de Borracha Natural, Resíduo de Couro e Partículas de PZT

Caracterización Morfológica, Eléctrica y Mecánica de un Compuesto Trifásico Sostenible a Base de Caucho Natural, Residuos de Cuero y Partículas de PZT

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Raquel Laina Barbosa dos Santos[1]
ORCID: https://orcid.org/0009-0006-4641-9087
São Paulo State University, Brazil
E-mail: raquel.laina@unesp.br
Hellinton dos Santos[1]
ORCID: https://orcid.org/0000-0003-1420-7646
São Paulo State University, Brazil
E-mail: hellinton.santos@unesp.br
Diego Silva de Melo[1]
ORCID: https://orcid.org/0009-0008-4514-5277
São Paulo State University, Brazil
E-mail: diego.melo@unesp.br
Nuelson Carlitos Gomes[1]
ORCID: https://orcid.org/0009-0005-0833-1298
São Paulo State University, Brazil
E-mail: nuelson.gomes@unesp.br
Carlos Toshiyuki Hiranobe[2]
ORCID: https://orcid.org/0000-0002-5182-2018
São Paulo State University, Brazil
E-mail: carlos.hiranobe@unesp.br
Renivaldo José Santos[2]
ORCID: https://orcid.org/0000-0002-0079-6876
São Paulo State University, Brazil
E-mail: renivaldo.santos@unesp.br
Leandro Ferreira Pinto[2]
ORCID: https://orcid.org/0000-0002-0656-9471
São Paulo State University, Brazil
E-mail: leandro.f.pinto@unesp.br
Michael Jones Silva[2]
ORCID: https://orcid.org/0000-0002-2971-1696
São Paulo State University, Brazil
E-mail: michael.silva@unesp.br

Abstract
The purpose of this study is to evaluate the morphological and electrical properties of a composite made from vulcanized natural rubber (VNR) reinforced with PZT particles and leather residue (LR). The materials were processed using a simple open-roll mixing method, keeping constant proportions of natural rubber and leather residue, while varying the PZT content at 25 and 50 phr. Scanning electron microscopy revealed homogeneous dispersion of both the LR and PZT particles within the VNR matrix, with no visible agglomerations, confirming the effectiveness of the mixing process. Electrical impedance analyses indicated that all composites exhibited frequency-dependent conductivity, a characteristic of disordered solid materials. Samples containing higher PZT concentrations showed increased conductivity at low frequencies, mainly due to dipole movement within the ceramic phase. Dielectric permittivity and capacitance also decreased with increasing frequency, while the composite with 50 phr of PZT presented the highest dielectric constant and energy storage capacity. Mechanical tests demonstrated that the inclusion of LR enhanced tensile strength and reduced elongation at break, acting as a fibrous reinforcement. The addition of

[1] Department of Engineering, School of Engineering, Campus of Ilha Solteira, Sao Paulo State University (UNESP), SP, Brazil.
[2] Department of Engineering, School of Engineering and Sciences, Campus of Rosana, Sao Paulo State University (UNESP), Brazil.

PZT particles increased stiffness, resulting in slightly more brittle behavior. The VNR-LR/PZT three-phase composite with 50 phr PZT achieved the best balance between the mechanical strength and electrical performance. Overall, the results confirm that the developed composite exhibits promising multifunctional behavior suitable for piezoelectric sensing and energy-harvesting applications. Furthermore, the reuse of leather waste provides an environmentally responsible alternative, converting an industrial residue into a functional, high-value material with both technological and ecological benefits.
Keywords: Piezoelectric composites; Natural rubber; Leather residue; PZT; Electrical and mechanical properties.

Resumo
O objetivo deste estudo é avaliar as propriedades morfológicas e elétricas de um compósito feito de borracha natural vulcanizada (VNR) reforçada com partículas de PZT e resíduo de couro (LR). Os materiais foram processados usando um método simples de mistura de rolo paralelos aberto, mantendo proporções constantes de borracha natural e resíduo LR, enquanto variava o teor de PZT em 25 e 50 phr. A microscopia eletrônica de varredura revelou dispersão homogênea de LR e partículas de PZT dentro da matriz de VNR, sem aglomerações visíveis, confirmando a eficácia do processo de mistura. As análises de impedância elétrica indicaram que todos os compósitos exibiram condutividade dependente da frequência, uma característica de materiais sólidos desordenados. Amostras contendo maiores concentrações de PZT mostraram aumento da condutividade em baixas frequências, principalmente devido ao movimento do dipolo dentro da fase cerâmica. A permissividade dielétrica e a capacitância também diminuíram com o aumento da frequência, enquanto o compósito com 50 phr de PZT apresentou a maior constante dielétrica e capacidade de armazenamento de energia. Testes mecânicos demonstraram que a inclusão de LR aumentou a resistência à tração e reduziu o alongamento na ruptura, atuando como um reforço fibroso. A adição de partículas de PZT aumentou a rigidez, resultando em um comportamento ligeiramente mais frágil. O compósito trifásico VNR-LR/PZT com 50 phr PZT alcançou o melhor equilíbrio entre resistência mecânica e desempenho elétrico. No geral, os resultados confirmam que o compósito desenvolvido apresenta um comportamento multifuncional promissor, adequado para aplicações de sensoriamento piezoelétrico e coleta de energia. Além disso, a reutilização de resíduos de couro oferece uma alternativa ambientalmente responsável, convertendo um resíduo industrial em um material funcional e de alto valor, com benefícios tecnológicos e ecológicos.
Palavras-chave: Compósitos piezoelétricos; Borracha natural; Resíduo de couro; PZT; Propriedades elétricas e mecânicas.

Resumen
El propósito de este estudio es evaluar las propiedades morfológicas y eléctricas de un compuesto hecho de caucho natural vulcanizado (VNR) reforzado con partículas de PZT y residuos de cuero (LR). Los materiales se procesaron utilizando un método simple de mezcla de rodillo abierto, manteniendo proporciones constantes de natural caucho y residuos de cuero, mientras que variaba el contenido de PZT a 25 y 50 phr. La microscopía electrónica de barrido reveló una dispersión homogénea tanto de las LR como de las partículas de PZT dentro de la matriz de caucho, sin aglomeraciones visibles, lo que confirma la efectividad del proceso de mezcla. Los análisis de impedancia eléctrica indicaron que todos los compuestos exhibieron conductividad dependiente de la frecuencia, una característica de los materiales sólidos desordenados. Las muestras con mayores concentraciones de PZT mostraron un aumento de la conductividad a bajas frecuencias, principalmente debido al movimiento dipolar dentro de la fase cerámica. La permitividad dieléctrica y la capacitancia también disminuyeron con el aumento de la frecuencia, mientras que el compuesto con 50 phr de PZT presentó la constante dieléctrica y la capacidad de almacenamiento de energía más altas. Las pruebas mecánicas demostraron que la inclusión de residuos de cuero mejoró la resistencia a la tracción y redujo el alargamiento a la rotura, actuando como refuerzo fibroso. La adición de partículas de PZT aumentó la rigidez, lo que resultó en un comportamiento ligeramente más frágil. El compuesto trifásico VNR-LR/PZT con 50 phr PZT logró el mejor equilibrio entre la resistencia mecánica y el rendimiento eléctrico. En general, los resultados confirman que el compuesto desarrollado exhibe un prometedor comportamiento multifuncional, adecuado para aplicaciones de detección piezoeléctrica y captación de energía. Además, la reutilización de residuos de cuero ofrece una alternativa respetuosa con el medio ambiente, convirtiendo un residuo industrial en un material funcional de alto valor con beneficios tanto tecnológicos como ecológicos.
Palabras clave: Compuestos piezoeléctricos; Caucho natural; Residuos de cuero; PZT; Propiedades eléctricas y mecánicas.

1. Introduction

The impact of human activity on the environment has become increasingly significant since the industrial revolution in the late 18th century. As a result of population growth, coupled with the pursuit of comfort and quality of life, environmental problems have arisen that have been discussed by researchers and environmentalists around the world (Azevedo et al., 2023).

Environmental concerns and the potential depletion of natural resources have led society today to seek alternative methods of reducing carbon emissions and, in addition, reintroducing industrial waste to prevent environmental damage or even disposing of it properly in order to prevent pollution (Tyagi et al., 2014; M. Yang et al., 2023). As a result, industrial waste has become a major problem for disposal and recycling in recent years (Abubakar et al., 2022).

Among the industries in the industrial sector, the leather production industry deserves a negative spotlight due to the large quantities of solid waste that are generated by leather processing (Covington & Wise, 2020; Gong et al., 2010). During the manufacturing process, waste is impregnated with basic chromium (III) sulfate (Cr(III)) and when improperly disposed of, this substance can provide ideal conditions for the oxidation of Cr(III), raising its valence to Cr(VI) (Gong et al., 2010). As a result, it is extremely harmful to living beings, especially humans, due to its high toxicity and ease with which it penetrates human cells (Cavalcante et al., 2017; Sivaram & Barik, 2019).

The use of this residue as a low-cost filler and reinforcement in compounds with polymers is an alternative that has been extensively studied (Cavalcante et al., 2017; Ruiz et al., 2015). In this sense, the combination of polymeric matrix and low-cost filler serves as a means of obtaining composite materials (Ghosh & Dwivedi, 2020). A composite is defined as a material composed of two or more components that have compositions, structures, and properties that are specific to each material alone (Freire Filho et al., 2023). It is the objective to combine the specific properties of each phase into a new material, which will have improved properties over the phases that make up the original material. Composite materials formed from polymer matrix and reinforced with piezoelectric ceramic particles stand out within this class (Freire Filho et al., 2023; Katsumi et al., 2011).

The most widely studied polymer/ceramic composites are those with 0-3 connectivity because they are easy to own. However, there are ten different patterns of connectivity that are possible in the production of composites (Patsidis & Psarras, 2008). The ceramic grains in composites with 0-3 connectivity are dispersed within the matrix so that there is no chemical or physical bonding between them. In contrast, the polymer phase forms a network that is connected in three dimensions (Freire Filho et al., 2023). There is a wide range of applications for 0-3 piezoelectric composites, including transducers for medical ultrasound applications, sensors, energy harvesting devices, etc. (Bowen et al., 2016; Jackson et al., 2014; Z. Yang et al., 2015). The most prominent piezoelectric materials are ferroelectric ceramics, including lead zirconate titanate (PZT) (Sampathkumar et al., 2013; Venkatragavaraj et al., 2001). In piezoelectric materials, mechanical deformation results in the generation of electric current and this property is known as piezoelectricity (Arnau & Soares, 2009). The term piezoelectricity refers to the process of converting mechanical energy into electrical energy (or the reverse) (Arnau & Soares, 2009; Furukawa, 1989).

In this context, the purpose of this study is to evaluate the morphological and electrical properties of a composite made from vulcanized natural rubber (VNR) reinforced with PZT particles and leather residue (LR). This study was conducted in order to evaluate the effects of PZT particle and LR dispersion on the morphological, mechanical and electrical properties of the VNR-LR/PZT three-phase composite.

2. Methodology

This study was developed as an experimental laboratory investigation focused on the preparation and characterization of polymer-based composites. Using a methodological approach, morphological, electrical, and mechanical properties of vulcanized natural rubber (VNR) composites reinforced with leather residue (LR) and lead zirconate titanate (PZT) particles were obtained, analyzed, and correlated. Experiments were conducted under controlled conditions in order to ensure reproducibility and reliability of the results, allowing a comprehensive understanding of the processing steps and their effects on the final composite properties.

2.1 Composite Preparation Method

A Brazilian clear crepe natural rubber (CCB) with a Mooney viscosity of 98.0 was purchased from DLP Industria e Comércio de Borracha e Artefatos LTDA in Poloni, Brazil. Vulcanization reagents, including zinc oxide (ZnO, 99.8% purity, from Neon), stearic acid ($C_{18}H_{36}O_2$, 95%, from Êxodo Científica), and sulfur (S_8, 99.5%, from Scientific Exotic), in addition to the accelerators benzoathiazole disulfide/MBTS ($C_{14}H_8N_2S_4$, 99%, from Basile Química) and tetramethylthiuram disulfide/TMTD ($C_6H_{12}N_2S_4$, 99%, from Basile Química), were obtained commercially. The leather residue was collected from the Touro tannery in Presidente Prudente, São Paulo, Brazil. In order to obtain particles smaller than 30 mesh, the waste was ground and sieved. American Piezo Ceramics – APC was provided commercially available PZT ceramic particles in powder form under reference code 855, with the following characteristics: (i) piezoelectric coefficient $d_{33} \approx 630$ pC/N; (ii) piezoelectric voltage constant $g_{33} \approx 21 \times 10^{-3}$ Vm/N; (iii) relative dielectric constant at 1 kHz ≈ 3300; (iv) Curie temperature ≈ 200°C; (v) density ≈ 7.6 g/cm^3.

In Table 1, the names of the curing agents are listed along with their molar masses and their respective chemical formulas. The formulation used to prepare the composites of VNR-LR/PZT is presented in Table 1. In order to obtain the samples, the same procedures and methodologies were used as those proposed by Santos et al., 2015. In order to carry out the entire production process, a parallel cylinder mixer was used, as shown in Figure 1.

Figure 1: Illustration of the parallel roller mixer for sample production.

Source: Authors.

Table 1 presents the values of the components used to obtain samples of neat VNR, VNR-LR composites, and VNR-LR/PZT three-phase composites. In the preparation process, the mass concentrations of VNR (100 phr) and LR (20 phr) were maintained constant, whereas the PZT concentrations were varied in the following proportions: 25 and 50 phr.

For the preparation of the three-phase composite samples, 100 grams of NR were used - as a result, each 1 phr has a mass of 1.0 g. The Brazilian light crepe rubber was first masticated for 10 min in an open cylinder with a friction ratio of 1:1.25. Due to shearing between the polymer chains and the formation of a rubber blanket around the front cylinder, NR's elastic properties are briefly lost. As a result, it would become plastic and have a low viscosity (more elastic), thus facilitating the incorporation and reaction of the filler and activator.

As soon as the NR had been sheared and plasticized, stearic acid was added simultaneously with zinc oxide in order to achieve homogenization. The mixing process was carried out for 20 min. As soon as the rubber compound had been homogenized, it was removed from the mixer and allowed to rest for 24 h in order to enhance the crosslinking process. After the rest period, the NR/ZnO/stearic acid gum was returned to the mixer, along with sulfur, MBTS, and TMTD, and was mixed for another ten minutes. To obtain the samples in the form of a blanket, the pure NR was compressed in a hydraulic press under a pressure of 120 kgf/cm^2 at a temperature of 150°C for 5 min.

The production of the VNR-LR two-phase and VNR-LR/PZT three-phase composites followed the same methodology as the production of the pure blanket, except the LR and PZT were added before the sulfur, MBTS, and TMTD were added. Composite blankets were produced using the same procedure as pure VNR samples.

Table 1: Material and reagents used in the preparation of samples of VNR-LR/PZT composites in phr.

Materials	Neat VNR	VNR-LR	VNR-LR/PZT25	VNR -LR/PZT50
NR	100.00	100.00	100.00	100.00
Zinc oxide	4.00	4.00	4.00	4.00
Stearic acid	2.00	2.00	2.00	2.00
Sulfur	1.50	1.50	1.50	1.50
MBTS	1.00	1.00	1.00	1.00
TMTD	0.50	0.50	0.50	0.50
LR	0.00	20.00	20.00	20.00
PZT	0.00	0.00	25.00	50.00

Source: Authors.

2.2 Characterization

To obtain micrographs of the cryo-fractured surface of the samples, a Zeiss EVO LS15 scanning electron microscope, located at the FEIS-UNESP (campus of Ilha Solteira), was used. In order to conduct morphological analysis, the samples were cleaved with liquid nitrogen in film form. A thin layer of graphite was deposited on the samples using a Sputter Coater after drying in a dynamic vacuum.

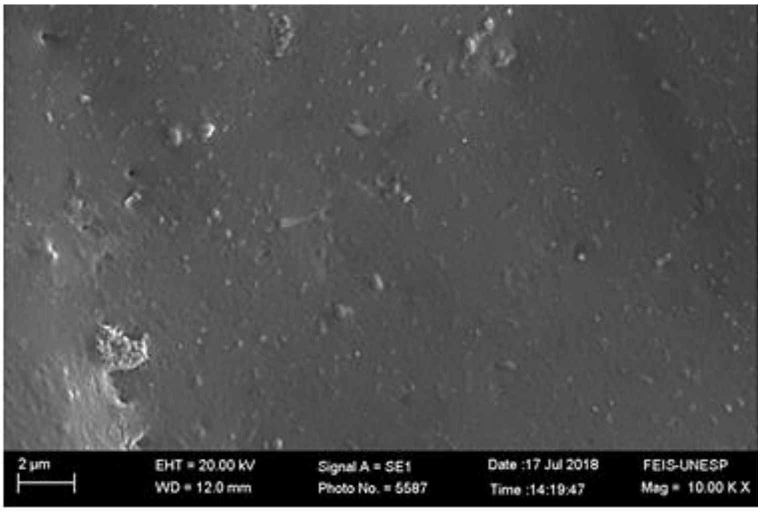
Solartron SI 1260 electrical impedance analyzers were utilized to measure the impedance of all samples (both sides were coated with conductive paint). The accuracy was 0.1%. At room temperature, measurements were conducted between the frequency ranges of 10^{-2} Hz and 10^5 Hz using a 0.5 V voltage. Based on these analyses, the following parameters were determined: real electrical conductivity ($\sigma'(f)$), real dielectric permittivity ($\varepsilon'(f)$), and capacitance modulus. Analyses of electrical impedance were performed in the polymer group of the Physics and Chemistry Department of the Ilha Solteira School of Engineering (FEIS-UNESP).

Mechanical tests (stress-strain mode) were performed using an Instron universal testing machine (model 3639), using a 500 N load cell and crosshead speed of 500 mm min^{-1}. The tests were conducted using Type A specimens (dumbbell-shaped), in accordance with ASTM D412-16.

3. Results and Discussion

Analyses of the morphology of the VNR, VNR-LR and VNR-LR/PZT composite samples were conducted using SEM and are shown in Figures 2-4. As can be seen in Figure 2, the VNR exhibits a smoother surface compared to the other composite samples. It appears that the few particles that are visible are additives and accelerators used in NR vulcanization that did not react with the rubber, according to Santos et al., 2015. The homogeneity on the sample surface indicates that the mixing process in the open cylinder mixer and the NR vulcanization process were efficient. Similar results were observed by Santos et al. 2015, in which the SEM images of pure VNRs showed homogeneous grain distribution similar to Figure 2.

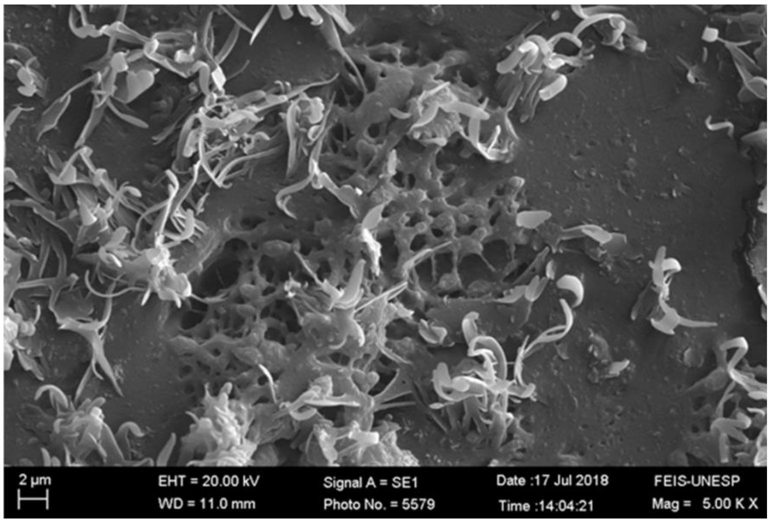
Figure 2: Analyses of the cryofactualized surface of neat VNR by SEM.



Source: Authors.

Figure 3 illustrates the morphological analysis of the cryofactualized surface of the VNR-LR composite. As can be seen in Figure 3, the surface of the VNR-LR composite displays a large amount of LR that appears as if it were composed of fibers. Since LR are composed of several fibrils, or small fibers, this is to be expected, since Santos et al. (2015) points out that LR is a fiber formed by a group of several fibrils. According to the authors, this group is formed during the tanning process, which enhances the mechanical properties of the LR, making it more suitable for industrial use (Cavalcante et al., 2018; Santos et al., 2015).

Figure 3: Analysis of the cryofactualized surface of the VNR-LR composite using SEM.

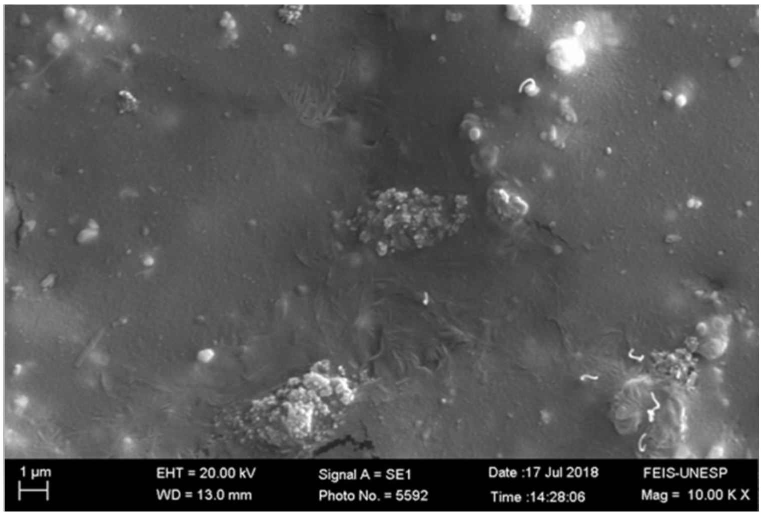


Source: Authors.

The distribution of the LR residue within the composite was homogeneous as shown in Figure 3, demonstrating the efficiency of the open-roll mixing method. As a result of the presence of filler in the polymer matrix, the surface was rougher; this is due to the fact that the surface has irregular characteristics as a result of being a fiber.

Figure 4 illustrates the SEM image of the VNR-LR/PZT three-phase composite at a PZT concentration of 50 phr. According to Figure 3 for the VNR-LR sample, in which there was good dispersion of the LR within the VNR, the same result was also observed for the composite VNR-LR/PZT, where both the PZT and LR particles were well dispersed. Composite materials with a good distribution of PZT particles can exhibit better electrical, dielectric, and piezoelectric properties. Similar behavior was observed in studies reported by Freire Filho et al., 2023 and De Campos Fuzari et al., 2013, in which homogeneous dispersion of PZT particles in different polymer matrixes influenced the final properties of the composites. A similar effect was observed by Sanches et al., 2017 when they examined the synergistic effect of a composite made of polyurethane, PZT, and carbon black

Figure 4: Analysis of the cryofactualized surface of the VNR-LR/PZT three-phase composite at a PZT concentration of 50 phr using SEM.



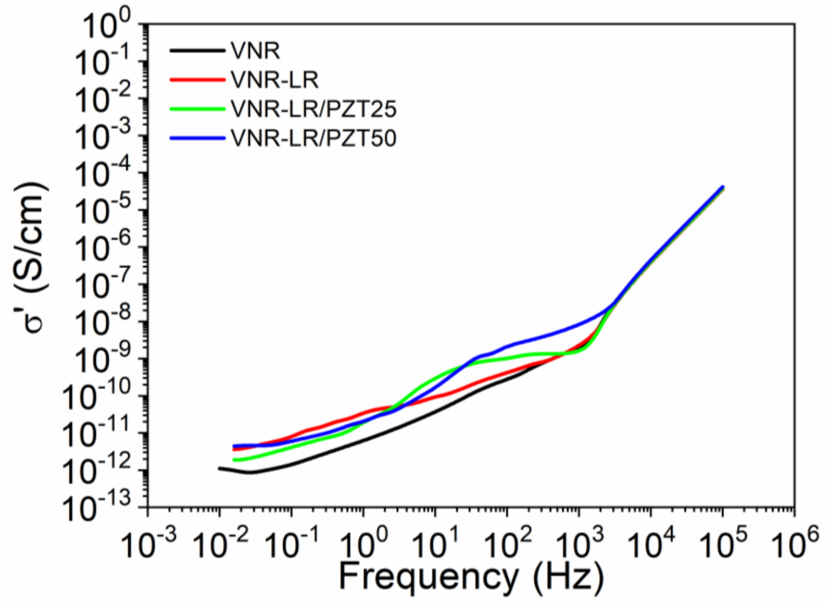
Source: Authors.

Polymer materials and composites based on polymer matrices are regarded as electrically insulating materials since they contain a low concentration of free charge carriers (Rebeque et al., 2019). Due to this, their electrical and dielectric responses are primarily caused by polarization and relaxation phenomena of spatial charges, or dipole movements under the influence of an ac electric field (Rhodes, 2007; Riaz & Ashraf, 2013). When an electric field is applied to a material, these electrical processes occur through dipole orientation effects or the displacement of spatial charges (Callister, 1991; Rebeque et al., 2019).

Meanwhile, ferroelectric ceramics, such as PZT, exhibit spontaneous polarization below the Curie temperature (T_c), which makes them polar and nonlinear dielectric materials. Ceramic materials have a crystalline structure below T_c with permanent dipole moments. When the dipole is exposed to an external electric field, it tends to follow the inversion of the field. As the frequency increases, the material becomes more conductive due to the movement of the dipoles due to the inversion of the direction of the electric field (Callister, 1991).

To evaluate the effect of PZT particle dispersion on the real electrical conductivity ($\sigma'(f)$) of the three-phase composite samples, the impedance technique was utilized, which involved applying an alternating electric field and varying its frequency from 10^{-2} to 10^{5} Hz to evaluate the electrical e dielectric properties. Figure 5 shows the *σ'(f)* as a function of frequency for VNR, VNR-LR, and VNR-LR/PZT samples with PZT concentrations of 25 and 50 phr.

Figure 5: Analysis of real electrical conductivity as a function of electric field frequency for samples of VNR, VNR-LR, and VNR-LR/PZT with 25 and 50 phr of PZT.



Source: Authors.

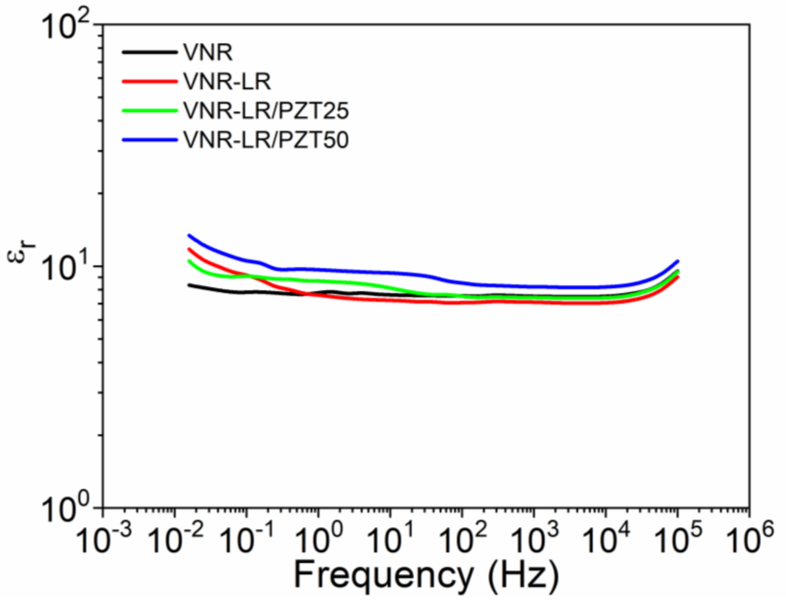
According to Figure 5, the *σ'(f)* is strongly frequency-dependent for neat VNR, VNR-LR, and VNR-LR/PZT composites, as would be expected for disordered solids (Freire Filho et al., 2023; Rebeque et al., 2019). This behavior indicates that all samples become more conductive as the electric field frequency increases, as a result of increasing movement of dipoles or spatial charges within the material as the electric field frequency increases (Freire Filho et al., 2023; Rebeque et al., 2019).

In the low-frequency regime, the samples with a greater concentration of PZT particles presented higher *σ'(f)* values as expected. VNR-LR/PZT25 and VNR-LR/PZT50 have a greater number of electric dipoles as a result of the higher mass fraction of PZT dispersed in the samples (Malmonge et al., 2009). Through dipole movement caused by the inversion of the ac electric field as its frequency increases, these dipoles participate in the conduction process.

According to our previous discussion, all materials are subject to the polarization effect under the action of external ac electric fields, where charges are polarized according to their centers. Positively charged electric charges follow the direction of the electric field vector, whereas negatively charged charges oppose it (Callister, 1991). As a result, the relative dielectric permittivity (ε_r) of a material can be used to represent its ability to be polarized (Callister, 1991). This is a measure of a material's polarizability as a result of the action of an applied electric field, and it is closely related to its ability to store energy.

The capacity to store energy and the ability to polarize are greater in materials with high ε_r value. Figure 6 illustrates that ceramic materials have a higher ε_r value than polymeric materials. According to the results of the experiment, the sample with the highest amount of PZT has a higher permittivity than the other samples.

Figure 6: Analysis of the relative permittivity as a function of frequency for samples VNR, VNR-LR, and VNR-LR/PZT with 25 and 50 phr of PZT.

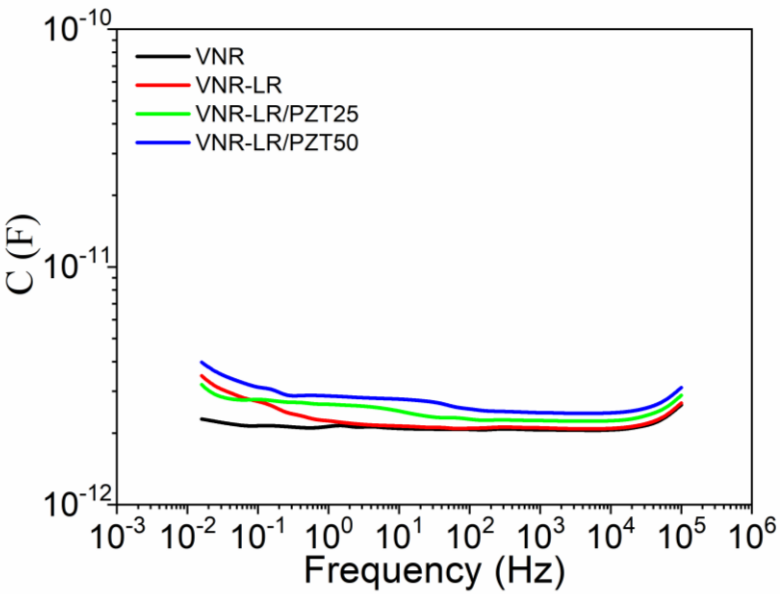


Source: Authors.

In an *ac* electric field, ε_r is frequency-dependent like *σ'(f)* value for all samples. As frequency increases, the number of dipoles that fail to follow the electric field increases, resulting in a decrease in ε_r value (Costa et al., 2020; Freire Filho et al., 2023).

As previously demonstrated, materials with a high ε_r value have a greater capacity for polarization and storage of energy. A capacitance measurement is used to determine the energy storage capacity of electrical samples or devices, resulting from the electric field over the dipoles or the spatial charges trapped at the interfaces (Callister, 1991). As can be seen in Figure 7, the capacitance of the samples was also analyzed.

Figure 7: Capacitance as a function of frequency for samples VNR, VNR-LR, and VNR-LR/PZT for 25 and 50 phr of PZT.



Source: Authors.

Capacitance also exhibits frequency-dependent behavior over the entire range studied. As expected, the VNR-LR/PZT composite with 50 phr of PZT demonstrated a greater energy storage capacity when compared to the VNR-LR/PZT composite with 25 phr of PZT as well as neat VNR and VNR-LR composite. Generally, the decrease in capacitance of all samples with increasing frequency can be attributed to the difficulty of the electric dipoles in following the inversion of ac electric field with increasing frequency (Costa et al., 2020; Freire Filho et al., 2023). A possible explanation for the difficulty of the dipoles following the inversion of ac electric fields as frequency increases is that friction between the dipoles and the crystal lattice within the PZT grains, as well as friction between the spatial charge and the polymer matrix, which results in a decrease in energy storage capacity as frequency increases (Costa et al., 2020; Freire Filho et al., 2023).

Mechanical stress-strain tests demonstrated the synergy between the VNR and LR phases as well as their influence on the mechanical properties of the composite. Table 2 summarizes the mechanical parameters obtained during the stress-strain test, including stress at the break ($\varepsilon_{atbreak}$) and high strain at the break ($\sigma_{atbreak}$), as well as tensile strength at 100% ($\sigma_{100\%}$), 300% ($\sigma_{300\%}$), and 500% ($\sigma_{500\%}$) stress. Table 2 shows that these mechanical parameters are characteristic of elastomeric materials with high $\varepsilon_{atbreak}$ and high $\sigma_{atbreak}$ value. The addition of PZT to the VNR matrix resulted in an increase in material strain, which resulted in a reduction in the deformation of the samples. According to this behavior, the addition of PZT makes the composite stiffer and more brittle, especially in the sample that contains 50 phr of PZT.

Table 2: Mechanical parameters of the stress-train analysis: tensile strength at 100% ($\sigma_{100\%}$), 300% ($\sigma_{300\%}$), and 500% ($\sigma_{500\%}$) stress; strain at the break ($\sigma_{at\ break}$); and the stress at the break ($\varepsilon_{at\ break}$) of neat VNR and VNR-LR/PZT for 25 and 50 phr of PZT.

Samples	σ_{100} (MPa)	σ_{300} (MPa)	σ_{500} (MPa)	$\sigma_{at\ break}$ (MPa)	$\varepsilon_{at\ break}$ (%)
NRV	0.84±0.03	2.28±0.13	3.19±0.24	8.84±1.21	780±32
NRV-LR	2.48±0.21	4.60±0.35	7.94±0.66	8.42±0.73	527±61
NRV-LR/PZT25	2.46±0.07	5.10±0.09	8.86±0.20	9.45±0.77	543±27
NRV-LR/PZT50	2.51±0.09	5.06±0.15	8.72±0.22	8.32±1.0	506±35

Source: Authors.

Finally, the controlled addition of ceramic PZT particles and LR to the VNR matrix proved to be crucial in determining the overall performance of the composite. Based on morphological analyses, both components were dispersed homogeneously within the polymeric phase without evidence of agglomeration. The uniform distribution is crucial, as it enables efficient transfer of electrical charges and mechanical stresses between the different phases, and minimizes the possibility of weak points compromising the structural integrity of the material.

The impedance analysis revealed that all samples exhibited the characteristic behavior of disordered solids, characterized by a strong frequency dependence of $\sigma'(f)$. The increase in PZT content in composite materials improves $\sigma'(f)$ values at low frequencies, directly correlated with the density of active dipoles within the composite. Due to the ferroelectric nature of PZT, these dipoles align and reorient in response to the ac electric field, enhancing charge transport and permittivity. In polymer-based composites containing ceramic inclusions, the restriction of dipole mobility results in a natural decrease in capacitance and dielectric constant at higher frequencies.

Meanwhile, the LR residue acts in a complementary yet distinct manner. LR is composed primarily of collagen fibers, which act as a natural reinforcement within the rubber matrix, improving tensile strength and stiffness while maintaining part of the matrix's elasticity (Araújo et al., 2023; Santos et al., 2015). In addition to anchoring PZT particles during vulcanization, the fibrous structure promotes structural stability by preventing segregation.

As a result of this synergy between PZT and LR phases, the final performance of the composite is directly influenced. An increase in PZT fraction improves dielectric response and energy storage capability, whereas an increase in LR fraction provides mechanical robustness and dimensional stability (Freire Filho et al., 2023; Santos et al., 2015). The combination of these effects produces a balanced multifunctional material suitable for flexible piezoelectric devices, pressure or vibration sensors, and mechanical-to-electric energy harvesting devices.

4. Conclusion

In this study, it has been demonstrated that three-phase VNR/LR/PZT composites may be efficiently produced using an open-roll mixing process. A morphological analysis confirmed that the LR and the PZT particles were uniformly dispersed throughout the VNR matrix, demonstrating the effectiveness of the chosen processing technique.

In terms of electrical characteristics, the composites displayed frequency-dependent conductivity, consistent with disordered solid materials. Besides an increase in PZT content, there was also an increase in conductivity at low frequencies, emphasizing the importance of dipole movement and spatial charge in the conduction process. This effect was also reflected in dielectric and capacitance measurements, which demonstrated greater polarization and energy storage for samples containing higher PZT concentrations, despite the expected reduction at higher frequencies due to dipole relaxation limitations.

Accordingly, leather residue contributed to increased tensile strength by acting as a fibrous reinforcement, while ceramic particles contributed to increased stiffness and a slight reduction in ductility. A composite containing 50 phr of PZT demonstrated the best overall balance between electrical and mechanical properties.

Overall, the VNR/LR/PZT composite system has both desirable structural and functional properties, which indicate its potential use in piezoelectric sensors and energy conversion devices. In addition to its technical relevance, the reuse of leather residue provides an environmentally sustainable alternative, transforming industrial waste into a material with technological and ecological value.

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