



**HAL**  
open science

## Enhanced Dielectric Properties of Recycled PLA/BaTiO<sub>3</sub> Nanocomposites: Towards Sustainable Capacitor Applications

Keerati Meeporn, Hayri Okcu, Liam Johnston, Gwenn Morvezen, Benjamin Borgnic, Sebastien Flury, David Muñoz-Rojas, Vincent H Mareau, Alain Sylvestre

### ► To cite this version:

Keerati Meeporn, Hayri Okcu, Liam Johnston, Gwenn Morvezen, Benjamin Borgnic, et al.. Enhanced Dielectric Properties of Recycled PLA/BaTiO<sub>3</sub> Nanocomposites: Towards Sustainable Capacitor Applications. The International Conference of Dielectrics (IEEE-ICD 2024), IEEE, Jun 2024, Toulouse, France. hal-04655351

**HAL Id: hal-04655351**

**<https://cnrs.hal.science/hal-04655351>**

Submitted on 22 Jul 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Enhanced Dielectric Properties of Recycled PLA/BaTiO<sub>3</sub> Nanocomposites: Towards Sustainable Capacitor Applications

Keerati Meeporn<sup>1</sup>, Hayri Okcu<sup>2</sup>, Liam Johnston<sup>2</sup>, Gwenn Morvezen<sup>1</sup>, Benjamin Borgnic<sup>2</sup>, Sebastien Flury<sup>1</sup>, David Muñoz-Rojas<sup>2</sup>, Vincent H. Mareau<sup>3</sup>, Alain Sylvestre<sup>1\*</sup>

<sup>1</sup>University Grenoble Alpes, CNRS, Grenoble INP, G2Elab, Grenoble 38000, France

<sup>2</sup>University Grenoble Alpes, CNRS, Grenoble INP, LMGP, 38000 Grenoble, France

<sup>3</sup>University Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, 38000 Grenoble, France

\*alain.sylvestre@g2elab.grenoble-inp.fr

**Abstract**—Recycled polylactic acid (R-PLA)/BaTiO<sub>3</sub> nanocomposite films were successfully prepared using solution blending and hot-pressing methods. The dielectric properties of the R-PLA nanocomposites with different volume fractions of BaTiO<sub>3</sub> nanoparticles (nBT) were investigated using dielectric spectroscopy and compared to fresh commercial polylactic acid (C-PLA) nanocomposites. R-PLA nanocomposites exhibited promising dielectric properties with high permittivity and low loss tangent, comparable to those of C-PLA nanocomposites. At 1 kHz, both pure C-PLA and R-PLA exhibited a consistent permittivity value of 4. Additionally, they demonstrated promising permittivity values of 10 when filled with nBT at a volume fraction ( $f_{nBT}$ ) of 0.20. Interestingly, at 1 kHz, the R-PLA nanocomposite exhibited a lower loss tangent (0.009) compared to the C-PLA (0.013), indicating its potential for improved dielectric performance in capacitor applications and highlighting the viability of plastic waste derived from recycled PLA as a promising alternative in the dielectric fields.

**Keywords**—recycled PLA, biodegradable and sustainable polymer, dielectric nanocomposite, high permittivity, low loss tangent

## I. INTRODUCTION

Dielectric polymer composites with high permittivity are rapidly emerging as indispensable materials for advanced electronic devices and energy systems [1]. These materials are crucial in a variety of applications, including capacitive energy storage, energy harvesting, high-power electronics, solid-state cooling devices, electric circuits, as well as actuators and sensors [2-3]. Unfortunately, the current commercial dielectric polymers such as biaxially oriented polypropylene (BOPP), biaxially oriented polyethylene terephthalate (BOPET), and polyvinylidene fluoride (PVDF), which are widely used as polymer matrices in ongoing dielectric polymer composites research in laboratories, are derived from petroleum, a non-renewable resource that is non-biodegradable [1]. This contributes to the accumulation of electronic waste and has a negative impact on the environment, which is a critical and rapidly growing problem.

Polylactic acid (PLA) is a recyclable, biodegradable, and bio-based polymer derived from lactic acid, a linear aliphatic thermoplastic polyester with notable mechanical and processing properties. PLA offers great promise in a wide range of commodity applications including biomedical implants, commodity packages, textile products, *etc.* [4-5].

In this context, lead-free barium titanate (BaTiO<sub>3</sub>), having exceptional dielectric properties such as high permittivity and low dielectric loss as well as eco-friendly composition, has been extensively investigated as a filler in polymer composites for potential applications in energy storage [6-7].

In this study, fresh and recycled PLA were used as matrices separately, with BaTiO<sub>3</sub> nanoparticles (nBT) serving as fillers for the fabrication of nanocomposites through a simple and scalable process. The morphology, thermal and dielectric properties of the resultant nanocomposites were investigated. In addition to enhancing the dielectric properties of the fresh PLA through the nanocomposites with BaTiO<sub>3</sub>, we demonstrate the potential of plastic waste derived from recycled PLA to promote circularity and sustainable development goals.

## II. EXPERIMENTAL

### A. Fabrication of the nanocomposite films

Commercial fresh PLA (C-PLA) with a nominal granule size of 3 mm was purchased from Merck, while recycled PLA (R-PLA) was sourced from wastes generated by 3D printing. nBT with a diameter of 100 nm were purchased from US Research Nanomaterials Inc., and N,N-dimethylformamide (DMF,  $\geq 99.8\%$ ) was procured from Carl Roth.

C-PLA and R-PLA were separately dissolved in DMF and stirred for 1 h. Subsequently, nBT were dispersed in DMF using an ultrasonicator for 1 h to achieve dispersion. The dispersed nBT were then added to the C-PLA and R-PLA solutions separately and stirred for 2 h, followed by drying in a fume hood overnight. The dried mixture was ground and shaped into pellets before the film preparation using hot-pressing at 200 °C and 2 bars of pressure. Both C-PLA and R-PLA nanocomposite films were prepared with different volume fractions of nBT ( $f_{nBT} = 0, 0.05, 0.10, \text{ and } 0.20$ ).

### B. Characterization of the dielectric properties

The dielectric properties of the nanocomposite films were investigated using a Novocontrol Technologies Alpha-A high-performance frequency analyzer under nitrogen gas at frequencies ranging from 10<sup>0</sup> to 10<sup>6</sup> Hz and at temperatures ranging from -60 °C to 90 °C. The temperature was controlled using a Linkam T95-HS instrument. Prior to the dielectric investigation, gold electrodes were deposited on both sides of the nanocomposite samples using a Quorum Q150TES sputter coater.

---

This work was supported by the Fédération Micro et Nanotechnologies (FMNT) through the OPE)N(RA functional characterization platform.

### III. RESULTS AND DISCUSSION

Fig. 1a shows SEM images depicting the morphology of nBT nanoparticles and the fractured surfaces of C-PLA/nBT and R-PLA/nBT nanocomposites with  $f_{\text{nBT}} = 0.20$ . Spherical nBT fillers are randomly dispersed within both C-PLA and R-PLA matrices. Fig. 1b displays DTA curves of both nanocomposites with  $f_{\text{nBT}} = 0$  and 0.20. All samples exhibit similar thermal behavior, with a curing step around 60 °C, an exothermic peak at approximately 110 °C, and an endothermic peak at about 165 °C, corresponding to glass transition, crystallization, and melting, respectively [8-9].

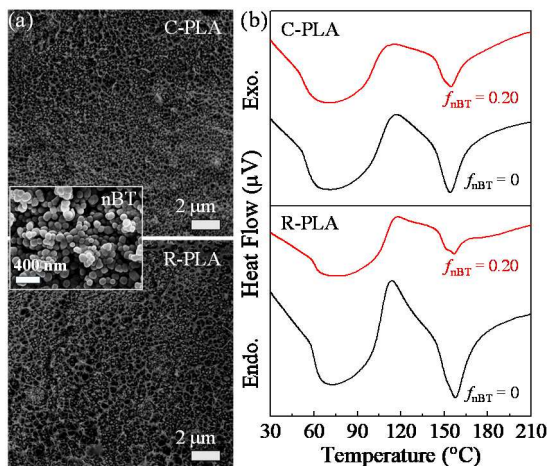


Fig. 1 (a) SEM images of nBT nanoparticles and the fractured surfaces of C-PLA/nBT and R-PLA/nBT nanocomposites with  $f_{\text{nBT}} = 0.20$ . (b) DTA curves of C-PLA/nBT and R-PLA/nBT nanocomposites with  $f_{\text{nBT}} = 0$  and 0.20.

The permittivity of a material reflects its ability to store energy, such as charges, when subjected to an electric field. In contrast, the dielectric loss tangent quantifies the ratio of dissipated energy to stored energy by a dielectric under cyclic field conditions [4]. Fig. 2 shows the frequency dependence of permittivity, loss tangent and conductivity of C-PLA/nBT nanocomposites at different  $f_{\text{nBT}}$ . All nanocomposites exhibit a weak frequency dependence of permittivity (Fig. 2a). Compared with pure C-PLA, all the nanocomposites exhibit enhanced permittivity, and the permittivity gradually increases with the increase of nBT nanoparticles loading. At room temperature and 1 kHz the permittivity of the nanocomposites with  $f_{\text{nBT}} = 0, 0.05, 0.10,$  and  $0.20$  are 4, 6, 8, and 10, respectively, while the loss tangent values (Fig. 2b) are 0.007, 0.009, 0.01, and 0.01, respectively. The increase in permittivity is attributed to the electric field enhancement in the polymer matrix, induced by the large permittivity mismatch between nBT and PLA [10], while the increase in loss tangent is primarily due to interfacial incompatibility between nBT and PLA [11]. The conductivity increases linearly with the increase in frequency (Fig. 2c), and it remains lower than  $10^{-11}$  S/cm at 1 kHz, even when  $f_{\text{nBT}} = 0.20$ , contributing to the insulating nature of PLA and the absence of an nBT network in the nanocomposites [12]. Promisingly, the frequency dependence of dielectric properties in R-PLA/nBT shows a similar trend to that of C-PLA/nBT, as depicted in Fig. 3a-c. R-PLA nanocomposites exhibit permittivity values comparable to those of pure C-PLA and nanocomposites. Notably, R-PLA nanocomposites with  $f_{\text{nBT}} = 0.20$  demonstrate lower loss tangent (0.009) and conductivity ( $5.16 \times 10^{-11}$  S/cm), highlighting the potential of recycled PLA to match the properties of fresh commercial PLA for dielectric applications.

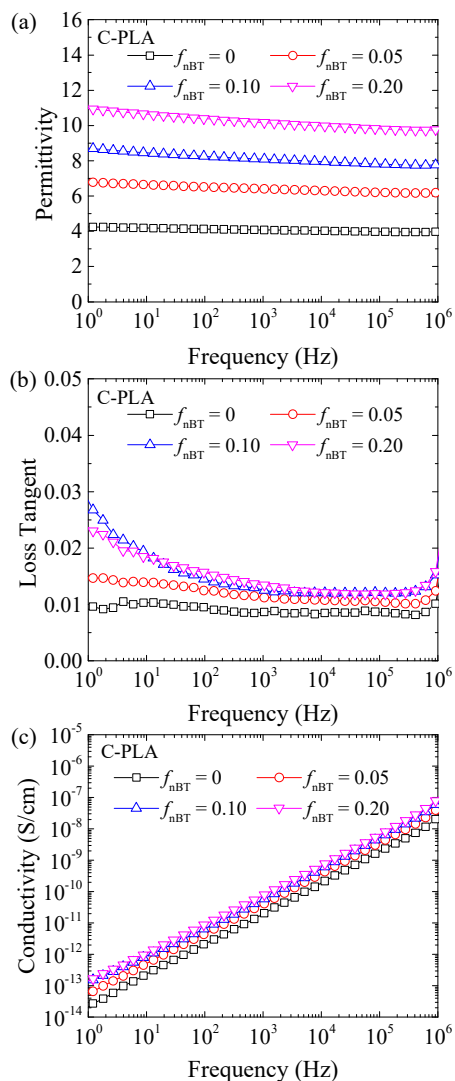


Fig. 2 Frequency dependence of (a) permittivity, (b) loss tangent and (c) conductivity of C-PLA/nBT nanocomposites at room temperature.

The temperature dependence of the dielectric properties at 1 kHz of the C-PLA/nBT and R-PLA/nBT nanocomposites is shown in Fig. 4 and Fig. 5, respectively. For the C-PLA/nBT nanocomposites, both permittivity and loss tangent values exhibit a weak temperature dependence between -60 °C and 40 °C. However, above 40 °C, the increase in loss tangent values becomes more pronounced as shown in Fig. 4a-b. At lower temperatures, the loss tangent values remain relatively low and stable, indicating minimal dissipation of energy within the nanocomposites. However, as the temperature increases, the loss tangent values show an increasing trend for all volume fractions of nBT, indicating a rise in energy dissipation within the nanocomposites at higher temperatures. This increase becomes more pronounced at elevated temperatures (above 40 °C), suggesting a more significant loss of energy within the nanocomposites as the temperature rises further. Additionally, higher volume fractions of nBT generally correspond to higher permittivity and loss tangent values across all temperature ranges. Interestingly, the R-PLA nanocomposites demonstrate a relatively weak temperature dependence of permittivity values throughout the range of -60 °C to 60 °C and maintain lower loss tangent values above 40 °C, as shown in Fig. 5a-b. R-PLA/nBT nanocomposites generally demonstrate higher permittivity and slightly lower loss tangent values compared

to C-PLA/nBT nanocomposites, especially at lower temperatures. Overall, R-PLA/nBT nanocomposites exhibit better dielectric properties, particularly at high temperatures, making them promising for applications requiring stable performance across varying temperature ranges.

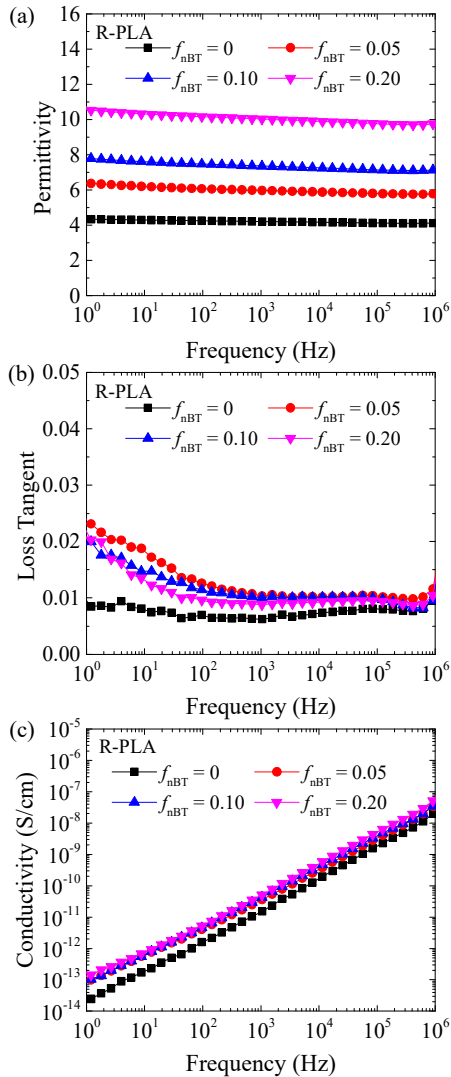


Fig. 3 Frequency dependence of (a) permittivity, (b) loss tangent and (c) conductivity of R-PLA/nBT nanocomposites at room temperature.

The temperature-dependent permittivity and loss tangent as a function of frequency for R-PLA/nBT nanocomposites with  $f_{nBT} = 0$  and  $0.20$  are shown in Fig. 6 and 7, respectively. The temperature effects on the dielectric response of the  $f_{nBT} = 0$  sample are divided into two regimes: below  $60\text{ }^{\circ}\text{C}$  and  $\geq 60\text{ }^{\circ}\text{C}$ . At low temperatures, both permittivity and loss tangent exhibit weak frequency dependence. Conversely, at temperatures  $\geq 60\text{ }^{\circ}\text{C}$ , permittivity increases rapidly with decreasing frequency from  $10^1$  to  $10^0$  Hz, corresponding to an increase in loss tangent. Additionally, at  $90\text{ }^{\circ}\text{C}$ , a clearer loss tangent peak appears at  $10^5$  Hz, indicating decreased permittivity due to relaxation polarization, as shown in Fig. 6a-b. The interpretation of these experimental observations focuses on the changes in molecular dynamics with increasing temperature. PLA has a glass transition temperature of approximately  $60\text{ }^{\circ}\text{C}$ , as confirmed by the DTA result mentioned above. Below this temperature, in the glassy state, the molecule chains of the PLA matrix experience restricted motion, resulting in minimal relaxation polarization within the tested frequency range, thereby maintaining a stable

dielectric response in this region. However, in the high-elastic state above  $60\text{ }^{\circ}\text{C}$ , molecule chain stretching and turning become more facile. Polar chemical bonds such as carbonyl and C–O bonds promote orientation polarization, which is generally non-elastic. This phenomenon leads to a rapid increase in dielectric loss and instability of the permittivity [13]. The temperature effects on the dielectric response of the  $f_{nBT} = 0.20$  sample exhibit similar behavior to that of the  $f_{nBT} = 0$  sample, as illustrated in Fig. 7a-b. However, at  $90\text{ }^{\circ}\text{C}$ , the intensity of the loss tangent peak at  $10^5$  Hz appears to be lower, which may be attributed to the beneficial thermal stability of nBT fillers.

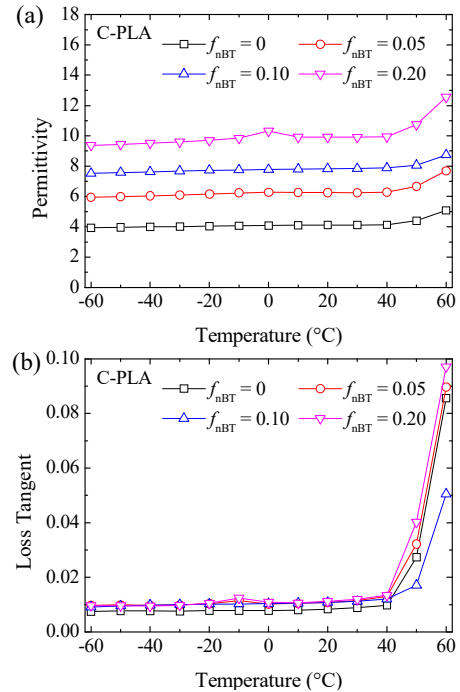


Fig. 4 Temperature dependence of (a) permittivity and (b) loss tangent of C-PLA/nBT nanocomposites with various volume fraction of nBT ( $f_{nBT}$ ).

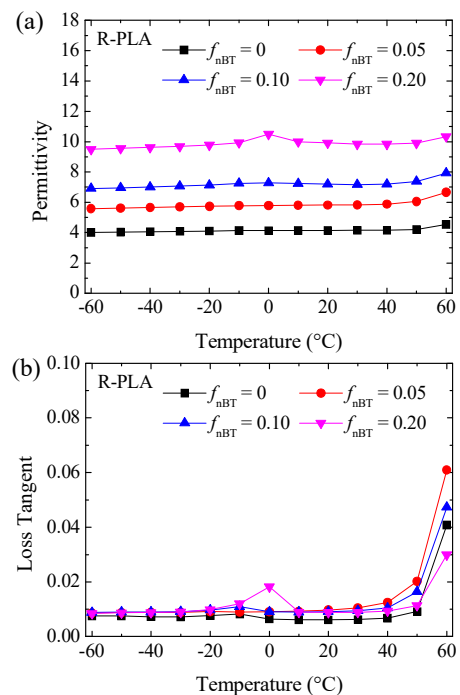


Fig. 5 Temperature dependence of (a) permittivity and (b) loss tangent of R-PLA/nBT nanocomposites with various volume fraction of nBT ( $f_{nBT}$ ).

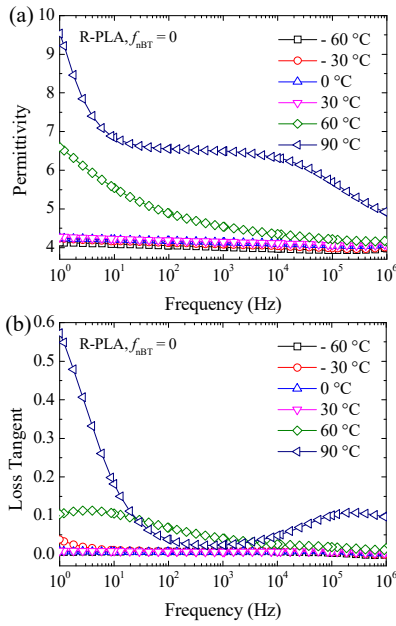


Fig. 6 Temperature-dependent (a) permittivity and (b) loss tangent as a function of frequency for R-PLA/nBT nanocomposites with  $f_{nBT} = 0$ .

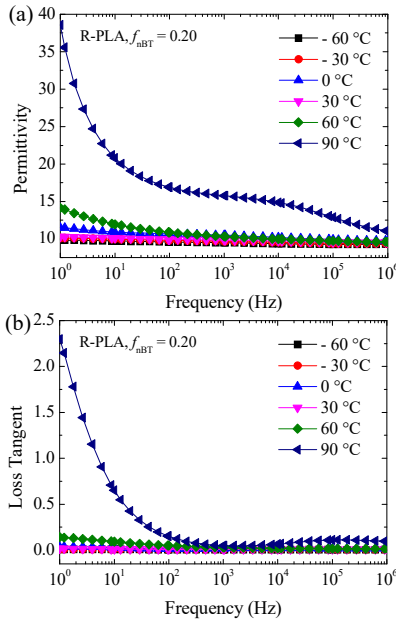


Fig. 7 Temperature-dependent (a) permittivity and (b) loss tangent as a function of frequency for R-PLA/nBT nanocomposites with  $f_{nBT} = 0.20$ .

#### IV. CONCLUSIONS

This study presents an investigation of the dielectric properties of recycled polylactic acid (R-PLA)/BaTiO<sub>3</sub> nanocomposite films with varying volume fractions of BaTiO<sub>3</sub> nanoparticles (nBT). The dielectric response of R-PLA nanocomposites was compared to that of fresh commercial polylactic acid (C-PLA) nanocomposites, demonstrating promising dielectric properties with high permittivity and low loss tangent. The R-PLA nanocomposites exhibited stable dielectric performances across a wide temperature range, showing weak frequency dependence at low temperatures and increased permittivity and loss tangent at higher temperatures. Notably, R-PLA/nBT nanocomposites exhibited better dielectric properties than C-PLA/nBT nanocomposites, particularly at elevated temperatures,

making them promising candidates for applications requiring stable performance in varying thermal environments. Overall, this research highlights the potential of utilizing recycled PLA as a sustainable alternative in dielectric applications, contributing to circularity and sustainable development goals. Further studies could explore optimization strategies to enhance the dielectric performance of R-PLA/nBT nanocomposites for specific application requirements.

#### ACKNOWLEDGMENT

This work was supported by the Fédération Micro et Nanotechnologies (FMNT) through the OPEJN(RA) functional characterization platform. The authors appreciate the facility and technical support for electrical measurements and recycled PLA sourcing from Mr. Christophe Pollet and Mr. Enzo Cuilla at the Laboratoire de Génie Electrique de Grenoble (G2Elab), as well as the facility and technical support for DTA analysis from Dr. Isabelle Gélard at the Laboratoire des Matériaux et du Génie Physique (LMGP).

#### REFERENCES

- [1] H. Luo et al., "Progress on Polymer Dielectrics for Electrostatic Capacitors Application," *Adv. Sci.*, vol. 9, no. 29, pp. 1–25, 2022.
- [2] H. Wu et al., "Polymer-/Ceramic-based Dielectric Composites for Energy Storage and Conversion," *Energy Environ. Mater.*, vol. 5, no. 2, pp. 486–514, 2022.
- [3] H. Tao et al., "Progress in preparation, processing, and application of high dielectric polypropylene matrix composite materials," *Polym. Compos.*, no. December 2023, pp. 1–20, 2024.
- [4] Y. Fan, X. Huang, G. Wang, and P. Jiang, "Core-Shell Structured Biopolymer@BaTiO<sub>3</sub> Nanoparticles for Biopolymer Nanocomposites with Significantly Enhanced Dielectric Properties and Energy Storage Capability," *J. Phys. Chem. C*, vol. 119, no. 49, pp. 27330–27339, 2015.
- [5] H. Tu et al., "High strength and biodegradable dielectric film with synergistic alignment of chitosan nanofibrous networks and BNNSs," *Carbohydr. Polym.*, vol. 299, pp. 120234, 2023.
- [6] F. Ram, P. Kaviraj, R. Pramanik, A. Krishnan, K. Shanmuganathan, and A. Arockiarajan, "PVDF/BaTiO<sub>3</sub> films with nanocellulose impregnation: Investigation of structural, morphological and mechanical properties," *J. Alloys Compd.*, vol. 823, p. 153701, 2020.
- [7] Y. B. Adediji, A. M. Adeyinka, D. I. Yahya, and O. V. Mbelu, "A review of energy storage applications of lead-free BaTiO<sub>3</sub>-based dielectric ceramic capacitors," *Energy, Ecol. Environ.*, vol. 8, no. 5, pp. 401–419, 2023.
- [8] J. Suder, Z. Bobovsky, M. Safar, J. Mlotek, M. Vocetka, and Z. Zeman, "Experimental analysis of temperature resistance of 3d printed PLA components," *MM Sci. J.*, pp. 4322–4327, 2021.
- [9] G. Cicala, D. Giordano, C. Tosto, G. Filippone, A. Recca, and I. Blanco, "Polylactide (PLA) Filaments a Biobased Solution for Additive Manufacturing: Correlating Rheology and Thermomechanical Properties with Printing Quality" *Materials.*, vol. 11, pp. 1191, 2018.
- [10] J. D. Badia, L. Monreal, V. Sáenz De Juano-Arbona, and A. Ribes-Greus, "Dielectric spectroscopy of recycled polylactide," *Polym. Degrad. Stab.*, vol. 107, pp. 21–27, 2014.
- [11] W. Wu, X. Huang, S. Li, P. Jiang, and T. Toshikatsu, "Novel three-dimensional zinc oxide superstructures for high dielectric constant polymer composites capable of withstanding high electric field," *J. Phys. Chem. C*, vol. 116, no. 47, pp. 24887–24895, 2012.
- [12] S. Luo, S. Yu, R. Sun, and C. P. Wong, "Nano Ag-deposited BaTiO<sub>3</sub> hybrid particles as fillers for polymeric dielectric composites: Toward high dielectric constant and suppressed Loss," *ACS Appl. Mater. Interfaces*, vol. 6, no. 1, pp. 176–182, 2014.
- [13] G. Q. Su, W. D. Li, H. J. Liu, F. Wang, Y. Liu, and G. J. Zhang, "Dielectric and Thermal Properties of Polylactic Acid/Barium Titanate Composites," *7th IEEE Int. Conf. High Volt. Eng. Appl. ICHVE 2020 - Proc.*, 2020.