SUSTAINABLE PRODUCTION OF PVDF-TrFE/$CoFe_2O_4$-BASED PIEZOELECTRIC NANOCOMPOSITE FILMS FOR WAVE ENERGY HARVESTING APPLICATIONS

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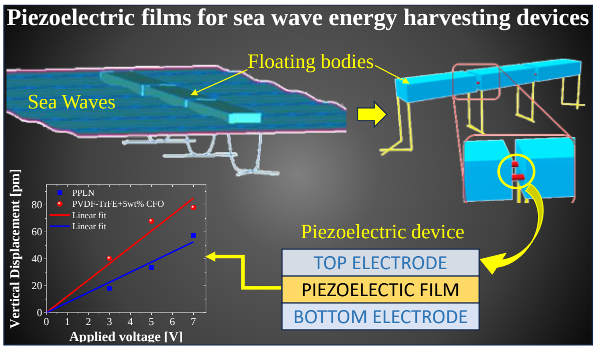

Fig. 1 - Graphical abstract for this research work

Recent advancements have demonstrated the strong potential of piezoelectric devices to convert mechanical energy, such as vibrations and motion, into electrical energy [1]. These devices rely on the piezoelectric effect, which is most effective in materials with high piezoelectric coefficients (d_{33}). Although conventional piezoceramics such as barium titanate, lead zirconate titanate, and lithium niobate exhibit high d_{33} values, they are limited by toxicity, brittleness, and environmental concerns, prompting the search for safer and more flexible alternatives.

Piezoelectric polymers, nanostructures, and nanocomposites have emerged as promising candidates for flexible energy-harvesting applications [2]. Among them, poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFe) stands out for its superior piezoelectric and ferroelectric properties, including high chemical resistance, thermal stability, strong polarization, fast switching behavior, and mechanical flexibility [3]. These properties are closely linked to the material's crystalline structure. PVDF can crystallize in several polymorphs (α, β, γ, δ), with the β-phase being the most electroactive due to its all-trans conformation. Trifluoroethylene (TrFe) enhances β-phase stability, thereby improving overall piezoelectric and ferroelectric performance without compromising flexibility.

The research activity aims to develop a flexible, cost-effective, eco-friendly and highly efficient prototype of a piezoelectric device attached in between floating bodies on sea waves (shown in graphical abstract) capable of converting wave motion into electrical energy. It is mainly designed to offer a sustainable off-grid energy solution for powering remote areas and also to provide a reliable alternative to traditional batteries. However, optimizing the piezoelectric response of PVDF-TrFe requires alignment of molecular dipoles, typically achieved through electrical poling at high voltages (~10^6 V/m) and elevated temperatures (~100–120 °C). However, this process is costly and unsuitable for large-scale production. Alternative techniques, such as mechanical stretching, spin-coating, quenching, and the incorporation of functional fillers have been developed to address these limitations [4]. Notably, nanofillers like graphene nanoplatelets (GNPs) and zinc oxide (ZnO) nanorods have been shown to enhance β-phase content and domain alignment [5]. Moreover, integrating ferromagnetic nanoparticles such as $CoFe_2O_4$ into PVDF-TrFe matrices, combined with spin-coating and magnetic field-assisted alignment, further improves the piezoelectric coefficient by enhancing dipole orientation [6]. Therefore, we fabricated a PVDF-TrFE/$CoFe_2O_4$ polymer nanocomposite film using a sustainable approach with cyclopentanone as the solvent. The resulting film was magnetically poled under optimal conditions, applying a magnetic field of 50 mT for approximately 2 hours at a temperature of 65 °C, as reported in [6]. The piezoelectric coefficient (d_{33}) of the films was then evaluated using piezoresponse force microscopy (PFM). Figure 2a shows the vertical displacement as a function of the applied voltage, along with the corresponding linear fits for both the calibration sample periodically poled lithium niobate (PPLN) and the PVDF-TrFE/$CoFe_2O_4$ nanocomposite. As shown in Figure 2b, the slopes of the linear fits correspond to the piezoelectric coefficients (d_{33}), calculated as 7.5 pm/V and (12.13 ± 0.83) pm/V for PPLN and PVDF-TrFe/$CoFe_2O_4$, respectively. Future work will focus on enhancing the piezoresponse by increasing the concentration of magnetic nanoparticles and optimizing processing parameters to achieve higher d_{33} values, with the goal of developing an efficient wave energy converter for energy harvesting and sensing applications.

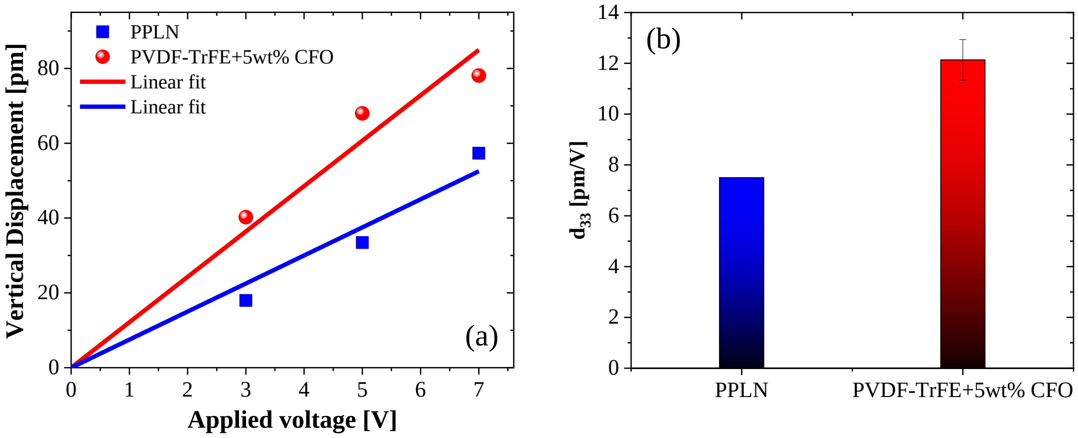

Figure 2. (a) Average amplitude of the vertical displacement measured through PFM as a function of the applied voltage V_{ac} and (b) Measured average piezoelectric coefficient for both PPLN and PVDF-TrFE+5wt% CFO.

The research activity is part of the research line ‘Innovative Materials for the Production of Energy from Wave Motion’, financed within the FP1 flagship project of Rome Technopole code ECS 00000024 funded by the National Recovery and Resilience Plan (PNRR), Mission 4, Component 2, Investment 1.5.

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