A comprehensive study of the piezoelectric response of PVDF-based composites submitted to large bendings for energy harvesting

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Flexibility and robustness have made the PVDF-based polymers worldwide studied piezomaterials for the design of novel autonomous piezogenerators. The race to achieve the best piezoperformances with PVDF and/or relatives is on.
To better understand how material modifications act on the figure of merit of the piezoelectricity in polymers is at the heart of the project.
In the framework of energy harvesting, our first consideration is that there is a huge difference of piezoelectric generator functioning between polymer films and solid crystals. In the case of polymers, the optimal piezoelectric response imposes the large deformation regime. Starting from the linear Curie's constitutive equations, we have developed an analytical model to describe the piezoelectric response of a flexible piezomaterial under the assumption of a large bending and elongation regime. This model demonstrates a non-linear piezoelectric response with the applied pressure. The piezoelectric response should follow a power 2/3 of the mechanical excitation. To experimentally achieve a large bending regime with flexible piezopolymers, our newly mounted experimental set-up was adapted to a bulge testing configuration. Coupled with a sinusoidal mechanical excitation, it enabled us to confront theoretical results with experimental measurements.
The developed model takes into account relevant intrinsic parameters such as the permittivity ε, Poisson's ratio v, Young's modulus E and the piezoelectric constant d. All of these parameters can be experimentally tuned playing on the synthesis of PVDF-based piezocomposites. Notably, by changing inorganic fillers inside the piezoPVDF matrix, one may expect to drastically change at minima ε.
Mixing Swift-Heavy Ions (SHI) irradiations and Materials Science engineering on thin piezoPVDF films (dozens of microns) enables to multiply the elaboration of various PVDF-based composites. From nanoporous PVDF matrices obtained after ion-track-etching, it was thus possible to fill the etched ion-tracks with, not only, inorganic nano-objects such as Ni nanowires (NWs) and piezoelectric ZnO NWs, but also, hybrid nano-objects such as MOF. These new composites were characterized by FTIR, UV-visible spectrometry, SEM, TEM, AFM and dielectric permittivity measurements. A special focus will be made on ZnO/PVDF composite membranes for which the beneficial effect of hydrothermal process on the morphology and piezoelectric performance was demonstrated. The maxima of the output powers were predicted using our analytical model. Optimal power values, with and without ZnO, were 1.9 $\mu W.cm^{-2}$ 1.2 $\mu W.cm^{-2}$, respectively. It corresponds to a 60 ± 10% improvement in presence of these ZnO NWs of high aspect-ratio for a low mechanical excitation frequency of 26 Hz. An unexpected result was that the main driven parameter for piezoelectric improvement in such composite may be not the ε but the resulted piezoelectric constant *d.*
A validation of our analytical model by experiments studying independently pure piezoPVDF film as reference and Swift-Heavy-Ion (SHI) nanostructured PVDF-based composites will be presented.