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ABSTRACT

We present a simple, efficient method, which combines uniaxial compression and subsequent poling, to produce piezoelectric polyvinylidene fluoride-based epoxy composites. The values of the piezoelectric factors obtained are slightly higher than those of neat piezoelectric polyvinylidene fluoride. The composites respond rapidly and reach a saturation voltage output, to the application of mechanical stimulus quickly. The composites are promising for the creation of “bulk” piezoelectric devices, different from the usual stretched films, exploiting the physico-chemical α of the epoxy matrix. The piezoelectric factor d_{31} vs the mechanical stimulus for the specimens studied scale according to a double logarithmic representation.

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Polymer-based composites are being investigated widely due to their ceaseless expansion of application potentials. PolyVinylidene DiFluoride (PVDF), in particular, relishes an overgrowing heed ascribed to its remarkable pyroelectric and piezoelectric attributes.^{1–10} Consequently, it serves as a candidate for numerous sensory and actuator devices, mostly in the form of thin stretched β -PVDF films.^{1–6,11} Manufacturing and optimization of such specimens often exhibit various levels of complication and scalability issues,^{6,8,9} which in this work, concurrently with providing longevity and adaptability features, we are attempting to surpass. More specifically, issues in the field of piezoelectric sensors and energy harvesters to be addressed are (i) the development of a simple and inexpensive experimental scheme for achieving the piezoelectric phase, (ii) the efficiency and response of the composite be comparable or better than those of PVDF and composites, and (iii) the optimization of the fraction of PVDF, while the composite shares the advantageous physico-chemical features of its matrix (epoxy). The resulting instances will be easily prepared, moldable, durable, efficiently adhesive to different substrates, noncorrosive, and remarkably sensitive to mechanical stimuli devices. The protocol followed is uncomplicated compared with that commonly reported for receiving the piezoelectric δ -phase for PVDF microstructure;⁹

moreover, it yields bulk specimens of any shape. Furthermore, our experimental configuration permits the determination of an inaccuracy of about 9%, which is better than that reported in published works.

We prepared a test sample of neat PVDF (sample A), an epoxy-based PVDF composite (sample B) and another one, loaded with nanographene platelets (NGPs) (sample C), the mass ratios of which are given in Table I. Mixtures of nonpiezoelectric PVDF powder consist of average molecular weight of $\sim 534\,000$ powder particles with typical size of about $1\ \mu\text{m}$ (Sigma-Aldrich-182702-100G) and commercial two component epoxy (UHU-37376) cured at ambient conditions. Moreover, samples with additional nanographene platelets (NGPs) (Angstrom-N008-P-40) were prepared as well. The distribution of inclusions is dispersed randomly within the epoxy matrix. The diameter of the resulting disk-shaped specimens is typically a few centimeters, and the thickness is typically 1–3 mm. For the transition of the as-received PVDF to one of its piezoelectric phases, we followed a two-stage procedure: The specimens were uniaxially compressed under $10^{10}\ \text{N/m}^2$ by using an Enerpack RC 504 hydraulic press for about 5 s. The force was applied along axis-1 perpendicular to the parallel surfaces of the composite, while the side free surface area of the

TABLE I. Mass fraction of epoxy/PVDF composites and NGP.

Specimen	(Epoxy:PVDF) (w/w)	NGP loading (wt. % of the total mass of the composite)
A	(100:0)	0
B	(95:5)	0
C	(95:5)	1.25

sample was unconfined during deformation; thus, directions perpendicular to axis-1 are indistinguishable and isotropic (axis-3 is labeled any of these axes). The compressed pellets were subsequently polarized within a coronalike schedule; i.e., placed between a couple of parallel spring-loaded platinum electrodes and polarized by an electric field of about 2 MV/m for a time duration of about 5 h. The advantages of the method applied in the present work are the following: (i) while, in the literature, PVDF is available in films that are stretched to become piezoelectric, in the present work, bulk specimens of any size and shape can be formed and (ii) the equipment required to attain the piezoelectric phase is simple and inexpensive.

To ensure that the abovementioned procedure drives PVDF from the nonpiezoelectric α -phase to its piezoelectric one (based on the literature, it is identical to the δ -phase, induced by axial compression⁸), a solid freestanding PVDF pellet (sample A) was formed from its melt and, subsequently, underwent the mechano-electrical scheme described above.

The typical dimensions of the disk-shaped specimens studied are a few centimeters in diameter and about 0.5 mm in thickness. A couple of electrodes permanently silver pasted on the specimen's surface (Fig. 1) was connected to a digital Keithley 617 electrometer. Each device was placed inside a Faraday cage for electromagnetic shielding. Real-time voltage or current was recorded as a function of time, while axial force-stimulus covering three orders of magnitude (i.e., 0.02 N, 0.14 N, 2 N, respectively) could be applied. The sample capacitance was measured directly using a Solartron 1260A impedance analyzer controlled by the Novocontrol[®] WinDETA software.

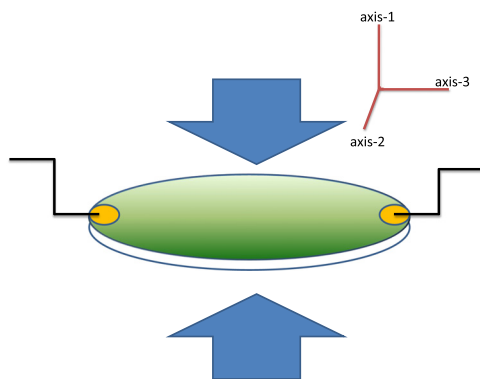


FIG. 1. Experimental configuration for measuring the piezoelectric response. Arrows indicate the mechanical stimuli applied along axis-1 and perpendicular to the parallel surfaces of the composite. Electrodes are silver pasted at both ends along axis-3. Leads from the electrodes are connected to a Keithley 617 electrometer (not depicted).

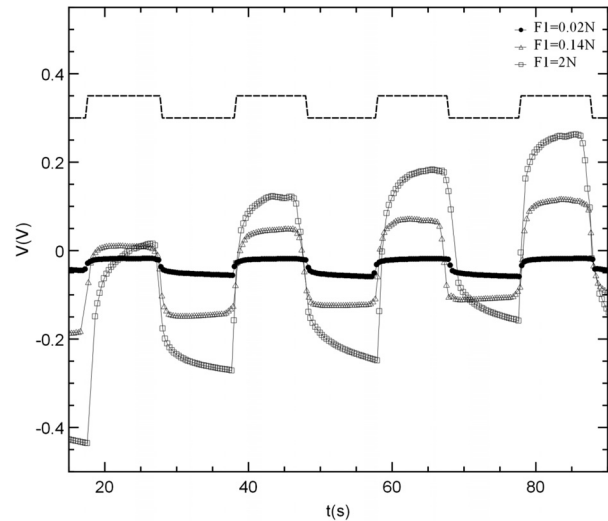


FIG. 2. Voltage output measured between the ends of a diameter for a composite with ~5 wt. % PVDF (specimen B). Dashed line denotes a typical mechanical stimulus (in arbitrary units) as a function of time.

Voltage and current responses to externally applied force for sample B are depicted in Figs. 2 and 3, respectively. The force F_1 was applied perpendicular to the parallel surfaces of the disk-shaped composite (see Fig. 1). Voltage V_3 measured between the electrode is given by:

$$V_3 = \frac{d_{31} \cdot F_1}{C}, \quad (1)$$

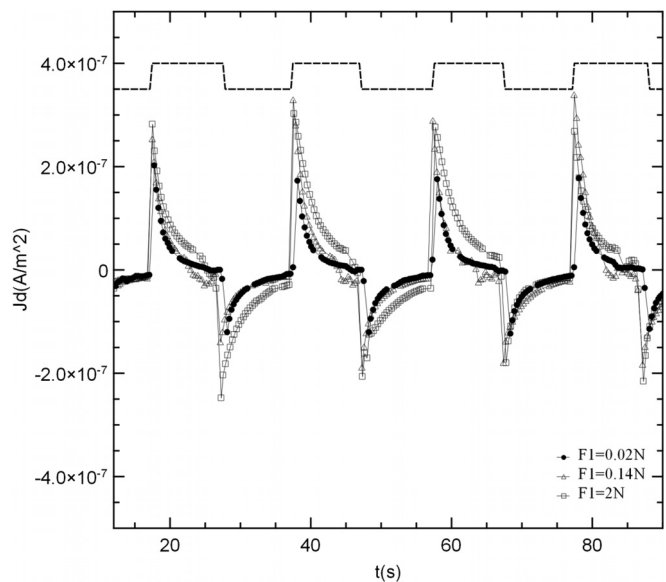


FIG. 3. Current density emitted from a composite loaded with 5 wt. % PVDF (specimen B). The sign reversals are signatures of the application and subsequent switch off of the external mechanical stimuli (schematically depicted by the dashed line), respectively. Current evolution is proportional to the rate of the piezoelectric voltage.

where C denotes the sample's capacitance and d_{31} is the piezoelectric coefficient. We measured both the response and relaxation for 10 s intervals, for rectangular pulses of mechanical stimuli depicted by the dashed line in Figs. 2 and 3.

The piezoelectric coefficient d_{31} is obtained from Eq. (1), whereas V_3 holds its saturation value dictated by the application of F_1 . $d_{31}(F_1)$ data points are plotted in Fig. 4, for the three specimens studied in the present work. The determination of the saturation voltage was obtained from single-pulse stress. However, after thorough experimentation, we led to the conclusion that a time interval between two successive force pulses, such as that depicted by the dashed line in Figs. 2 and 3, was optimally adequate for the specimen relax compared with the timescale of the piezoelectric response; the latter is actually immediate to the external force triggering. We observe that, for all samples, d_{31} is a decreasing function of F_1 , in accordance with the experimental observations and theoretical modeling for heterogeneous piezoelectric composites. The phenomenon was attributed to the distribution of internal stresses to the piezoelectric inclusions, the local change of the topology, and the variable degrees of physical contacting of the piezoelectric domains. The piezoelectric coefficient of neat PVDF is comparable or slightly larger than those reported for its piezoelectric phases developed with experimental schemes different from ours (i.e., uniaxial compression and poling). Moreover, epoxy-based composites exhibit d_{31} values comparable with those of neat PVDF (specimen A), suggesting that, despite their low content in PVDF (5 wt. %), they have equal or slightly better efficiency than neat PVDF. The piezoelectric coefficients were determined with an error of 8% for samples A and B and 6–12% for sample C. A remarkable feat is the high reproducibility of the results, indicative of a stable structure and predictable behavior of the samples.

The $d_{31}(F_1)$ data points collapse on a single master curve when plotted in a double logarithmic diagram (Fig. 5). Regarding the range

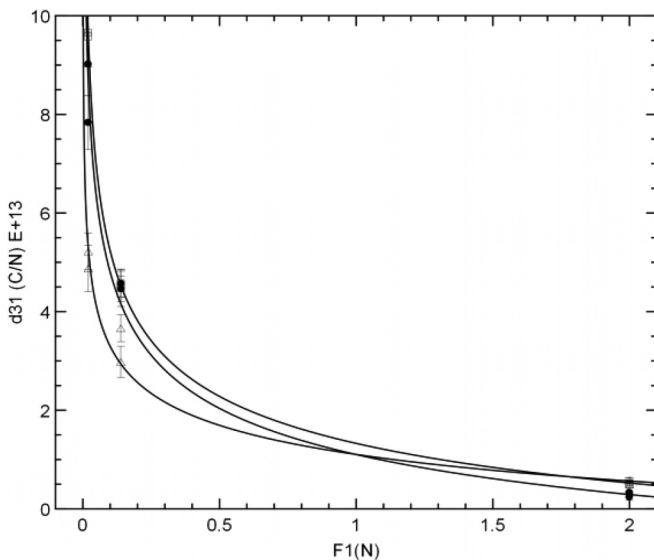


FIG. 4. Piezoelectric coefficients for samples A (circles), B (triangles), and C (squares). Fitting is in the form of $y = ax^b + c$ with factor $R^2 > 0.99$. The samples provide a remarkable performance when 0.02 N is applied and converge while the stimulus strengthens.

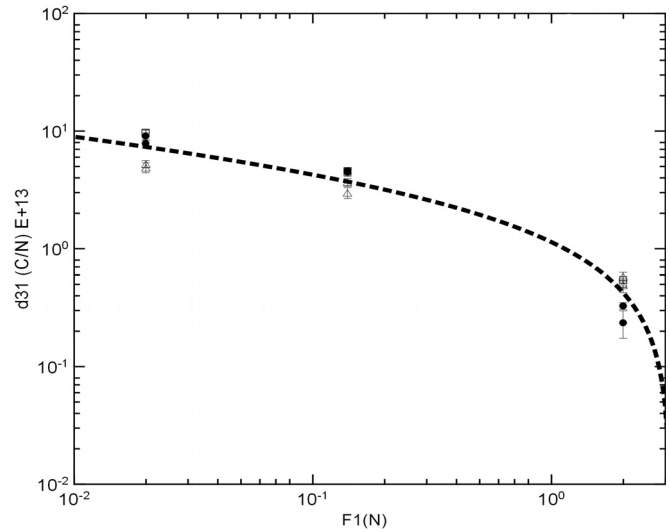


FIG. 5. A master curve (dashed line) given by Eq. (2) matches the entire set of data points with correlation factor $R^2 = 0.975$.

of mechanical modulus investigated in the present work, a universal empirical fitting function is:

$$d_{31}(F_1) = -5 + 6.136 \times F_1^{-0.178} \quad (2)$$

with correlation factor $R^2 > 0.99$. The description of the experimental results through a common function evidences for a common underlying process for electromechanical coupling and a unified scaled behavior of the three different composites.

A functional piezoelectric device is characterized by its ability to require both strong and rapidly produced voltage output signals. A piezoelectric coefficient is a measure of the ratio of the “saturation” voltage over stress and is a measure of the energy conversion. The increase of voltage to saturation upon applying a mechanical stimulus is described by:

$$V(t) \propto \begin{cases} 1 - e^{-\frac{t}{\tau}}, & F \neq 0 \\ e^{-\frac{t}{\tau}}, & F = 0, \end{cases} \quad (3)$$

where τ is a time constant, which tells how fast a saturation voltage value is attained. The values of τ obtained by fitting Eq. (3) to the $V(t)$ data points subsequent to the application of the external force is presented in Fig. 6. At low stress applied, the three specimens share a relatively common short relaxation time (around 2 s) to reach a saturation output. At high stress values, epoxy results in an increase of the relaxation time, while the small amount of NGPs intensifies the latter phenomenon. Among the three specimens, the one with NGPs (sample C) exhibit a retarded response and differences on exerting or removing the force stimulus. The advantages of the methodology used in relation to the current status in the field of piezoelectric sensors and energy harvesting can be summarized as follows: (i) the experimental scheme for achieving the piezoelectric phase is simple and inexpensive, (ii) the efficiency and response of the composite are improved, compared to those reported, (iii) the composite has an optimally low amount of PVDF and shares the advantages of its matrix (epoxy).

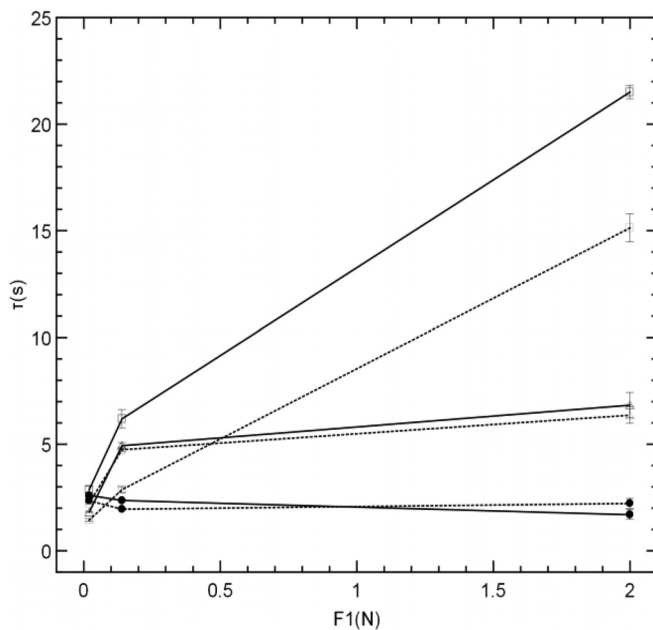


FIG. 6. Time constants for the response to the application and removal of external mechanical stimulus: samples A (circles), B (triangles), and C (squares). Solid and dashed lines connect data points regarding relaxation after force application and removal, respectively.

In the present work, we developed a simple, reliable, and low cost procedure to obtain piezoelectric PVDF and epoxy composites. The piezoelectric d_{31} parameter was determined with high accuracy compared to that usually reported in the literature. Epoxy composites

exhibit equal or slightly stronger piezoelectric factors than neat PVDF, probably stemming from their heterogeneous structure. A universal scaling law has been found for $d_{31}(F_1)$, evidencing for a common electromechanical coupling mechanism underlying the piezoelectric properties of different samples studied in the present work. Rapid response to applied stimulus is observed.

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