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Piezoelectricity measurements of hybrid films functionalized with ZnO nanostructures and cellulose nanocrystals

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1 Introduction

Piezoelectric energy scavengers for the conversion of mechanical energy (e.g., pressure, bending, stretching and vibrational motions) into electricity, have been manufactured using both polymeric and inorganic materials, as well as their combination [1-3]. It is well known that inorganic materials possess larger piezoelectric coefficients than polymers; however, they exhibit higher stiffness, which makes them less sensitive to small vibrations and more prone to stress failure. On the other hand, polymer-based generators represent a relatively small proportion of the total research due to the involvement of complicated material processing and device fabrication (using precise manipulators), which represent hurdles for scalability and cost. The aim of this work is to develop a novel coating of easy fabrication and low environmental impact that could lead to a real competition in the field of renewable/alternative energy technologies. In particular, two different geometries of ZnO nanoparticles, synthesized on purpose and embedded into a UV-curable acrylic polymer matrix, were selected. The experimental set-up for assessing the piezoelectric behavior of the obtained UV-cured films has been assembled and preliminary results of this behavior are here presented.

2 Materials preparation

Zinc oxide samples were prepared through wet chemistry processes obtaining powders in two different nanoforms shaped like nanosheets and nanoflowers. All ZnO syntheses were carried out using the same precursor, zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$, ≥99.0 %, Sigma-Aldrich), dissolved in water solution and catalyzing the hydrolysis with a proper amount of a weak base (ammonium hydroxide). In particular, nanosheets (ZNS) were prepared adding a proper amount of ammonium hydroxide (28%, Carlo Erba Reagents) to a water solution 0.05 M of $Zn(NO_3)_2 \bullet 6H_2O$, bringing the solution pH to 10. After 1 hour the precipitate was filtered, washed several times with water and diethyl ether, then dried at 100 °C in air overnight and calcinated at 450 °C for 2 h. Nanoflowers (ZNF) were prepared heating a water solution 0.05 M of $Zn(NO_3)_2 \bullet 6H_2O$ at 60 °C, then adding a proper amount of ammonium hydroxide (28%, Carlo Erba Reagents) to reach a pH of 10. After 30 min of thermal treatment at 60 °C, the ZnO precipitate was filtered, washed several times with water and diethyl ether, then dried at 100 °C in air overnight. Field Emission Scanning Electron (FE-SEM) micrographs of ZnO nanostructures were obtained by using a Carl Zeiss Sigma microscope equipped with a Schottky field-emitter (tip made of <100>

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tungsten crystal and a ZrO_2 reservoir) and shown in Fig.1. Cellulose Nanocrystals (CNC) obtained by freeze-dry method were purchased by CelluloseLab.

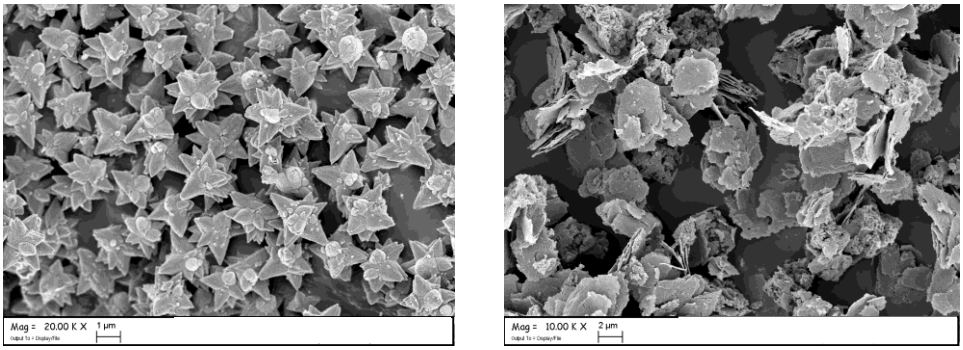

Fig 1. FE-SEM micrographs of ZnO nanostructures: ZNF (left) and ZNS (right)

Nanocomposites were prepared by using a commercial acrylic polymer precursor, namely bis-phenol A ethoxylate diacrylate (Ebecryl 150, hereinafter coded as EB), kindly supplied by Cytec Industries BV (Netherlands). 4% wt. of photoinitiator (Irgacure 1173, 2,2-dimethyl-2-hydroxy acetophenone, from BASF, Italy) was added to the acrylic UV-curable resin; then, the different ZnO nanofillers together with CNC (in equal amount) were dispersed in the obtained UV-curable mixture at 4% wt. and ultrasonicated for 30 min at RT. The obtained dispersions were coated on glass slides, using a wire wound applicator (nominal film thickness: about 200 μm) and then exposed to the UV radiation provided by a F300 S apparatus (Heraeus Noblelight, USA) working in static conditions. The radiation intensity on the sample surface, measured with an UV-meter, was about 800 mW/cm^2; two not consecutive exposures of 15 s were enough for completing the photopolymerization reaction, also in the presence of the different ZnO nanofillers. The obtained UV-cured films were peeled off from the glass slides and cut so that they had all the same final shape, suitable both for obtaining comparable electrical measurements and for the correct insertion into the sample holder mounted on top of the shaker. Finally, an electrically conductive layer was applied to the sample faces, using two different techniques. The first technique exploited a sputtering process where a gold film having a final thickness of about 80 nm was deposited. Conversely, the second technique was based on the application of a conductive paint at room temperature. In order to simplify the whole preparation process, the sputtering technique, used for the initial samples, was then discarded because, as a matter of fact, the conductive painting is a cheaper and faster process that saves much thermal stress to the polymeric samples. The samples, once positioned in the sample holder, had a free square surface of 1 cm^2 that was mechanically stressed to obtain the piezoelectric current generation (Figs. 2, 3). All the materials were tested at 150 (chosen for typical environmental vibration energy harvesting applications), 1000 Hz and the own resonance frequencies. Both materials showed a high piezoelectric activity at frequencies below 10 Hz.

2 Measurement setup

The block diagram of the measurement system for the determination of the piezoelectric characteristics is shown in Fig. 4. The sinusoidal excitation signal is generated by a programmable function generator (1) at the chosen frequencies between 0.1 Hz and 4500 Hz.

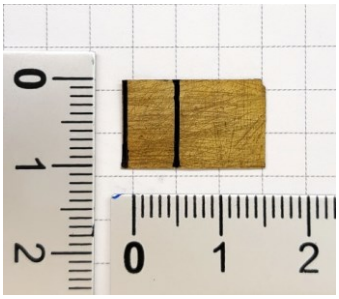

Fig. 2. Sample of bare acrylic polymer (EB) after the gold metallisation process. The rectangular part on the left is clamped into the sample holder.

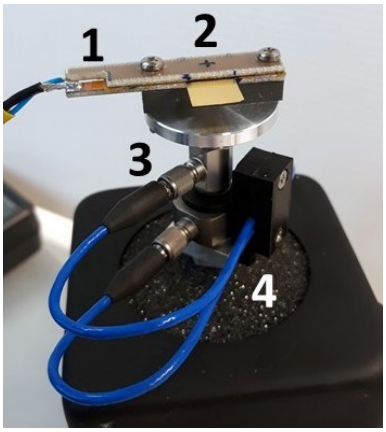

Fig. 3. View of the system used to clamp the sample under test (1, 2) and the two sensors (3, 4)

The generator is connected to an audio frequency amplifier (2), which drives the shaker actuator (3) with a power of about 15 W, enough to move the whole test group (4) consisting of the sample itself, the sample holder and the sensors, in the full frequency range needed. The original excitation signal is also fed both to CH 3 input of the oscilloscope (8) for monitoring and synchronization purpose and to the lock-in amplifier (7) as a reference signal for demodulation. CH 1 input of the oscilloscope is connected to the accelerometer amplifier and conditions the signals from both the accelerometer and the force sensor for the correct measurement.

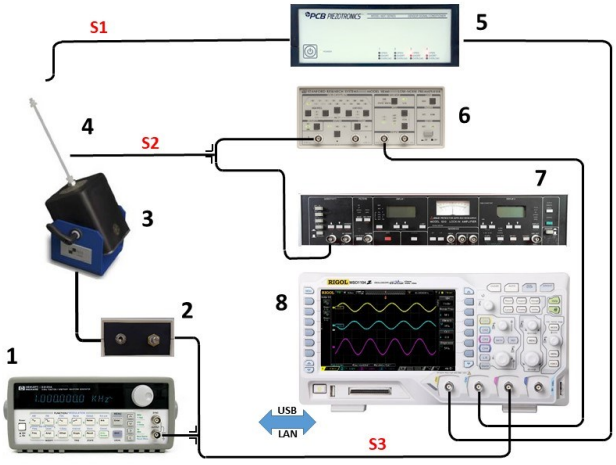

Fig. 4. 1) Function generator; 2) Audio-frequency amplifier; 3) Shaker; 4) Detectors Head and sample holder; 5) Accelerometer amplifier; 6) Low noise amplifier; 7) Lock-in amplifier; 8) oscilloscope.

The piezoelectric signal generated by the polymeric sample is then collected by the conductive paint and connected, through a coaxial cable, to a low noise amplifier (6) equipped with a series of selectable input filters. The output of that amplifier is connected to CH 2 input of the oscilloscope. The characterization with respect to humidity and pressure is carried out at a constant temperature using a commercial air-bath. The thermal characterization can be carried out between 15 and 30 ° C.

3 Measurement results

The piezoelectric response of bare resin, as expected, generates normalized voltages from 150 to 4500 Hz, which is inside to noise limit, without any correlation with the excitation frequency. Conversely, the nanocomposites display enhanced generation properties. More in detail, as shown in Fig.5, the normalized voltage RMS values (for the two samples) at 150, 1000 Hz and resonance frequency are reported. The highest RMS voltage was registered for EB-ZNS in all the range of analyzed frequencies. It is noteworthy that there is no linear increase of the signal produced when acceleration is changed (Fig. 6).

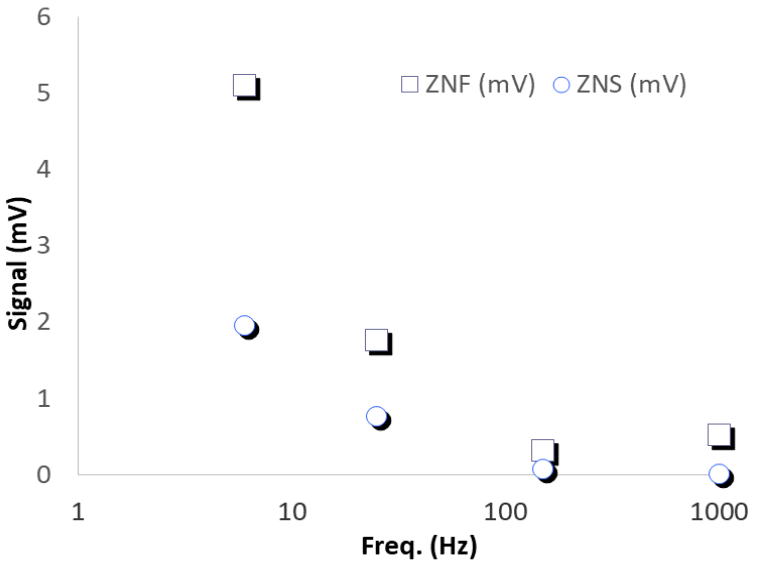

Fig. 5. Normalized voltage RMS values (for the two nanocomposites) at different frequencies.

4 Remarks

The two analyzed systems showed a response in terms of RMS voltage measured as a function of the applied waveform at the frequency used in this work. In particular, the flower-like nanocomposite exhibits the best piezoelectric performance at all the investigated frequencies. The piezoelectric effect of the different ZnO nanostructures (ZNF and ZNS) has to be interpreted on the basis of the possible structure and morphology of the samples and further study are required.

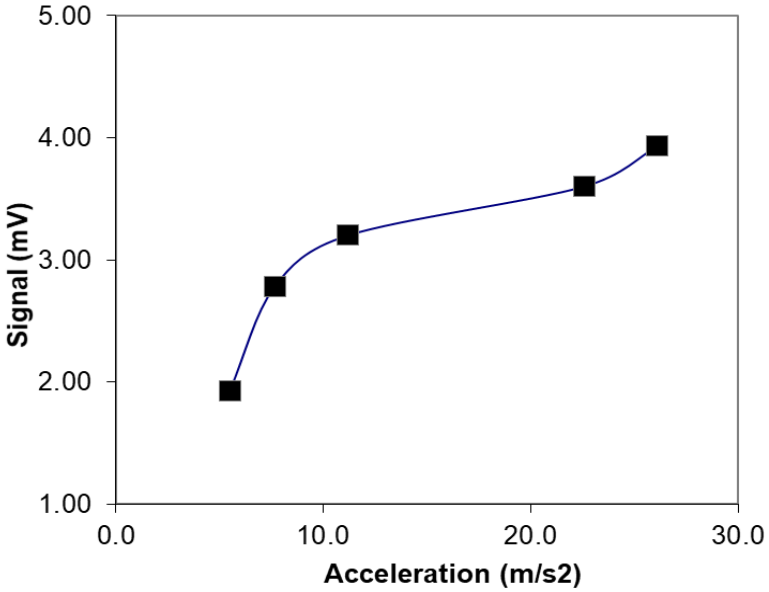

Fig. 6. Signal produced by the sample EB-CNC-ZNS at the frequency of 8 Hz vs. the acceleration value.

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