Synthesis and Characterization of UV-curable nanocellulose/ZnO/AlN acrylic flexible films: thermal, dynamic mechanical and piezoelectric response

SYNTHESIS AND CHARACTERIZATION OF UV-CURABLE NANOCELLULOSE/ZnO/AlN ACRYLIC FLEXIBLE FILMS: THERMAL, DYNAMIC MECHANICAL AND PIEZOELECTRIC RESPONSE

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Introduction

Nowadays, the scientific research is focused, on one hand, on developing devices able to efficiently exploit renewable energy sources and, on the other hand, on encouraging the use of environmentally friendly materials as a sustainable alternative to the traditional ones. Piezoelectric materials fulfill these requirements because, in addition to their utilization as renewable energy sources, they can be deposited on flexible substrates and show cost-effective scalability, which are key elements for the design of innovative devices in the field of green technologies [1]. Among the large variety of solutions aimed at fabricating new flexible piezoelectric materials, composites consisting of piezoelectric ceramic fillers embedded in a polymeric matrix have been proposed. In this context, UV-curable systems have been considered as a particularly suitable matrix to implement new smart composites, thanks to their rapid cure and wide range of properties. UV-curing represents a more economic, faster, and nontoxic method than thermal curing processes. It does not require the use of any solvent, hence reducing volatile compounds emission and resulting environmentally friendly. The UV-cured systems show flexibility, biocompatibility, easiness of processing large areas, simple integration into devices, reduction of device size, improved device reliability, and lower production costs. Several works have been reported in literature about the synthesis of piezoelectric composites for power generation. Recently, nanocellulose has gained great interest among the combinations of materials that can be exploited for fabricating nanocomposites. In spite of its low piezoelectricity, it is often preferred to other piezoelectric fillers with higher piezoelectric response, because of its abundance, low-production cost, biodegradability, and no industrial waste and environmental pollution. In this context, the combination of nanocellulose and ZnO nanostructures has been considered a promising way for the fabrication of self-powered nanogenerators. Indeed, ZnO exhibits interesting complementary properties. It is a semiconductor material with a wide band gap (3.37 eV) and high electron hole binding energy (60 meV), largely used in electronic, optical, laser, and LED devices. Apart from its well-known piezoelectric properties, it is biocompatible; therefore, it can be employed for the design of human and environmentally friendly biomedical engineering systems and green energy production devices [2]. Motivated by the promising results obtained in a previous work [3], a new piezoelectric composite was developed. In particular, the structural, morphological, and piezoelectric properties of new UV-curable systems composed by an acrylic matrix and cellulose nanocrystals alone (EC composite with 4 wt.% of CNCs) and containing also ZnO niddle (ZnN) and flower (ZnF) nanostructures (2 wt.% of CNCs and 2 wt.% of ZnO), were thoroughly investigated. The piezoelectric response of the prepared composites was evaluated by integrating these materials onto rectangular cantilever beams, free on three edges and clamped on a short edge, with 100 nm-thick Al films, sputtered on the top and bottom surfaces, working as electrical contacts. Aiming at improving the piezoelectric generation of the nanocomposites, the integration of a AlN layer onto the top surface of the beam and the anchoring of a proof mass on the beam tip was also evaluated. Also, the root mean square (RMS) open circuit output voltage of all devices was recorded at different applied accelerations.

Results and discussion

The piezoelectric response of the devices at their resonance frequency was measured in the time domain at different acceleration values (namely, 5, 7, and 10 g). The generated open circuit voltages were determined as RMS of the measured output signal and correlated to different experimental parameters, namely: (i) ZnO morphology, (ii) deposition of AlN layer, and (iii) utilization of a proof mass.

(i) All the materials revealed a piezoelectric response, with a resonance frequency of the prepared cantilevers (EC, EC-ZnN, and EC-ZnF) of about 3.3 kHz. Table 1 collects the RMS output voltages generated by the films at their resonance frequency. As expected, the generated output voltage increased with the applied acceleration. The contribution of CNC to voltage generation was quantifiable by the response of the EC sample at different accelerations, as the pure acrylic matrix (EB) did not show any detectable piezoelectric response.

Table 1: RMS output voltage values (mV) of three analyzed samples at different acceleration values.

Type of cantilever	**5 g**	**7 g**	**10 g**
EC	1.06±0.02	1.22±0.03	1.28±0.02
EC-ZnN	1.03±0.02	1.57±0.02	1.78±0.02
EC-ZnF	1.73±0.02	1.78±0.02	2.40±0.02

The piezoelectric response of the composites was enhanced replacing 2 wt.% of CNC with ZnO nanostructures [4]. The composite containing ZnO flowers (i.e. EC-ZnF) was the most promising, in terms of RMS voltage, at different acceleration values.

(ii) A 600 nm-thick AlN thin film was deposited by physical vapor deposition (PVD) on the top side of the different cantilevers before depositing the Al electrode. This additional step on the comprehensive fabrication process was aimed at increasing the piezoelectric performance. The characterization of the composites was performed by applying acceleration values of 5, 7, and 10 g on the rectangular cantilevers within a shaker vibration frequency range between 2.5 and 3.7 kHz. As indicated by the results shown in Figure 1a (representative samples characterized at 10 g acceleration), the highest generation was confirmed at the resonance frequency of 3.3 kHz [4]. This is reasonable, as the nitride film was very thin (600 nm thick), hence it did not affect the beam mass and the effective resonance frequency in a remarkable way. However, the addition of the nitride layer increased the harvested output voltage of all samples, as shown in Figure 1B.

(iii) The addition of the proof mass increased the RMS output voltage [4]. In particular, the deposition of stacked AlN film on either unfilled EC or ZnO-loaded EC, significantly increased the output voltage. This effect was more pronounced at lower acceleration (i.e., 5 g) for EC and EC-ZnN configurations. Higher voltage differences with proof mass insertion were measured in the EC-ZnF sample at low/medium accelerations (5 and 7 g), while at 10 g a smaller signal enhancement was recorded. The best efficiency, in terms of generated RMS open circuit voltage normalized to the acceleration value (mV_{RMS}/g_{max}), was obtained by the EC-ZnF-AlN based beams at 5 g and with proof mass, with a value of 0.650 mV/g versus 0.635 mV/g obtained for the EC-ZnF-AlN based beams, at 5 g and without proof mass.

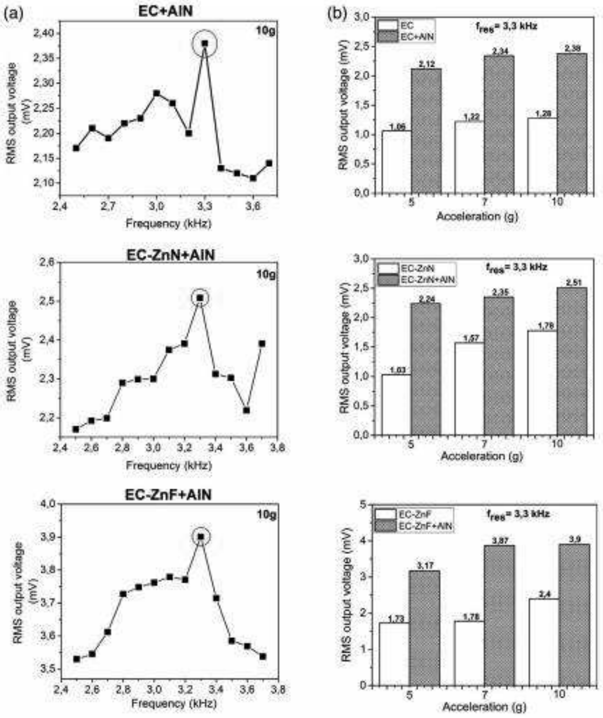

Figure 1: (a) voltage generated at 10 g acceleration for the analyzed films covered by the AlN thin layer; (b) RMS open circuit voltage of all the characterized nanocomposite cantilevers, with and without AlN layer.

Conclusions

A cost-effective fabrication was proposed to develop new piezoelectric vibrational systems, which could be competitive in the field of green energy generation. As initial approach, the synthesized ZnO nanostructures were dispersed into the selected acrylic resin. Aluminum nitride (AlN) film integration on the beam and proof mass insertion at the tip were also investigated in order to increase the piezoelectric response. The incorporation of ZnO nanostructures into the acrylic matrix favored an ordered structural arrangement of the deposited AlN layer, hence improving the piezoelectric response of the resulting nanocomposites. Besides, the addition of the proof mass further increased the RMS output voltage that achieved 4.5 mV for the AlN-coated system containing ZnO nanoflowers.

References

[1] G. Zhang, P. Zhao, X. Zhang, K. Han, T. Zhao, Y. Zhang, C. K. Jeong, S. Jiang, S. Zhang, Q. Wang *Energy Environ. Sci.* 11, 2046 (2018).

[2] F.R. Fan, W. Tang, Z.L. Wang *Adv. Mater.* 28, 4283 (2016).

[3] G. Malucelli, A. Fioravanti, L. Francioso, C. De Pascali, M.A. Signore, M.C. Carotta, A. Bonanno, D. Duraccio, *Prog. Org. Coat.* 109, 45 (2017).

[4] M.A. Signore, C. De Pascali, D. Duraccio, G. Malucelli, A. Fioravanti, E. Melissano M.C. Martucci, M. Masieri, P. Siciliano, L. Francioso. *J Appl Polym Sci.* 138, 49731 (2021).