Piezoelectric composite films for energy harvesting devices

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Abstract

The main aim of this work is the development of novel, flexible, efficient, versatile piezoelectric films of easy fabrication and low impact, which may lead to a real competition in the field of renewable/alternative energy technologies. Among the large variety of solutions, we decided to prepare UV-cured composites made of an acrylic resin (EB) filled with different shaped ZnO structures, synthesized on the purpose, and/or cellulose (pristine form: nanocrystals). More in detail, four different morphologies of ZnO were synthesized, following a facile aqueous sol-gel route, namely: nano-particles (ZNP), bipyramidal (ZBP), flower-like (ZNF) and long needles (ZLN) morphologies. Commercially available cellulose nanocrystals (CNC) were subjected to mechanical treatments by grinding in a mortar (C) or by ball milling (BMC). Films of 150 μm of thickness were obtained with the highest achievable cross-linking density.

For the composites containing ZnO, only EB-ZLN and EB-ZNF showed a uniform distribution and dispersion of the fillers within the polymer matrix, which was maintained also when the filler amount increased. For the composites containing cellulose, ball milling allowed obtaining a better dispersion, as well as a decrease of the size of cellulose domains embedded in the polymer matrix as compared to the composites containing grinded cellulose.

The thermal stability of the composites was not worsened by the presence of the fillers. For ZnO composites, whatever the fillers morphology was, a slight increase in the thermal stability at low temperatures was observed; besides, at higher temperatures, ZnO was found to catalyse the degradation processes. For the cellulose-containing composites (with and without ZnO), ball milled cellulose promoted a higher stability of composite films with respect to those containing grinded cellulose.

In general, the increase of filler content (ZnO, cellulose or ZnO+cellulose) caused an increase of glass transition temperature (Tg) and a decrease of the storage modulus in the glassy state. The composites containing ZnO were stiffer than those containing cellulose; besides, the samples containing grinded cellulose with or without ZnO showed higher Tg values than those containing BMC (being equal the composition).

Then, the piezoelectric response generated by the polymer composites and measured in cooperation with the Institute of Metrological Research (INRIM) of Torino (Italy) and the Institute of Microelectronics and Microsystems (IMM) of the National Research Council (CNR) in Lecce (Italy), was satisfactory in terms of RMS (root mean square) voltage measured as a function of the applied waveform, both at low and at resonance frequency. The highest voltage was registered for EB-ZNF (with and without cellulose) in all the range of analyzed frequencies. This result was explained by the higher probability that the flower-like particles, in the UV-cured films, have a higher number of 0002 planes oriented perpendicularly to the measured solicitation with respect to the other morphologies: indeed, this is due to their peculiar geometry.

Furthermore, the RMS voltage generated at 19 Hz as a function of the acceleration increased with increasing ZFL loading, reaching the maximum value at 20 wt.%, though the increase in RMS voltage was not linearly correlated with the ZFL loading. This finding was not ascribed to the dispersion of filler and to the number of particles on the surface of the composite films, but to the decrease of storage modulus of the composites at high ZFL concentration.

As far as cellulose-containing composites are considered, it worthy to underline that cellulose showed a detrimental effect on the piezoelectric properties of the composite films as compared with ZnO. This is probably due to different factors, including the lower crystallinity of cellulose, as well as the worse interfacial adhesion with the polymer matrix. Besides, though the correlation with the storage modulus was not clearly interpreted, it seems that a lower storage modulus provides lower piezoelectricity. Finally, it was also possible to observe that ball milling process, by enhancing dispersion and distribution of cellulose within the UV-cured acrylic network, improved the piezoelectricity and dielectric values with respect to the composites containing grinded cellulose.

Despite the high gap between the measured voltage values in this PhD thesis and those related to fully inorganic piezoelectric systems (which are 2-3 orders of magnitude higher), the proposed piezoelectric films show two main advantages, i.e. flexibility and cost-effective scalability, which are key elements for the development of innovative devices in the field of green technologies and that suggest to further continue the work on energy harvesting devices.