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Synergy of PMN-PT with piezoelectric polymer using sugar casting method for sensing applications

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***Abstract*— Sugar casting is a simple and cost-effective direct method of generating polymer foams. By incorporating grains directly into mixtures of polymer and piezoelectric nanoparticles it is possible to create highly compliant materials with excellent piezoelectric properties. In this work, we use the sugar casting method in combination with spin coating to prepare a highly sensitive and flexible 0-3 piezoelectric polymer thin film membranes with a layer thickness of 20 to 190 µm. Porosities and elasticity are tuned by simply adjusting the sugar/polymer mass ratio. The expected outcome of this research was improvements to the piezoelectric voltage, the g_{33} measure, due to the increased compliance of the material, however iezoelectric composite membranes with high concentrations of PMN-PT also demonstrated gains in piezoelectric coupling, the d_{33} measure, when cast with high volume fractions of sugar. A remarkably high d_{33} coefficient of 69 pm/V was measured using the laser vibrometer technique. These innovative materials were developed as broadband ultrasonic sensors for partial discharge detection in undersea cables, however they have potential uses in energy scavenging platforms, biosensors, and acoustic actuators, among others.**

Keywords—piezocomposite; PMN-PT; PZT; ceramic-polymer; UV curing, nanoparticle, spin coating

I. Introduction

Piezoelectric foam composites have key advantages in underwater transducers and medical sensors of low-density, improved acoustic matching with water and tissue and high hydrostatic coefficients [1]. The sensors under development here are intended as a low-cost partial discharge detector for undersea cable condition monitoring. Monitoring partial discharges via acoustic emissions has distinct advantages over inductive or radio frequency techniques in terms of immunity to electromagnet interference, high electrical resistivity and low price. Currently acoustic monitoring of cables is not feasible due to the low sensitivity of acoustic sensors in the 80 – 200 kHz range where the majority of energy is located and the extremely high attenuation of the acoustic signal within the cable foam. Exploring the properties of polymer foam ceramic composites may allow conformal sensors with distinct advantages over PVDF or ceramic-based sensors.

While direct fabrication of piezoelectric foams, for example by mechanical frothing of a ceramic suspension, is simple and low cost the resultant structures remain brittle and will still require shaping, drying and sintering [2]. Composites created by a piezoceramic nanoparticle inclusion are attractive to low frequency applications such as energy harvesting [3] and low frequency hydrophones [4] but have far lower piezoelectric modulus than bulk ceramic. Modification of PZT nanoparticles with surfactants has shown increases in the d_{33} measure to 52 pC/N with relatively low particle loading within a poly-ethalene glycol diacrylate (PEGDA) resin (16% wt/wt) [5] with the same group later showing large gains in the compliance of the piezoelectric materials by adopting a 3D printed lattice structure [6].

In recent years, great progress has been made in making brittle electro ceramics like PZT more flexible by shrinking piezoelectrics and constructing high-density arrays [7]. PZT nanoribbons can be printed on elastomers over wide areas while maintaining effective piezoelectric coefficients of >100 pC/N for energy scavenging devices [8]. Foams, which are generally complete materials with significant vacancy fractions (e.g., 50–80% air), provide a unique way to make materials with identical structure in all dimensions. For piezoelectrics, this usually entails creating ceramic materials using fused-deposition [9] or robocasting [10]. Other techniques, which can then be developed to produce well-controlled porous structures using layer-by-layer or polymeric templating techniques have been reported [11]. PZT foams were discovered to offer stronger piezo-sensitivity, lower acoustic impedance, and higher mechanical flexibility than thin film equivalents, inspiring a variety of applications such as wide-band hydrophones, actuators, and high-temperature filters [12]. Despite the fact that porosity improves many of the electrical and mechanical properties of electro-ceramics, they are still exceedingly brittle and can only be strained a few percent. It was reported that BTO nanoparticles combined with an elastomer such as polydimethylsiloxane (PDMS) and carbon nanotubes (CNTs) to develop highly flexible and efficient energy harvesting piezoelectric materials [13]. CNTs were used in these composites to improve stress transfer from the polymer to the BTO nanoparticles [14].

Here we combine the direct fabrication of wet foams with nanoparticle inclusions to create a porous piezoelectric polymer. Sugar grains are incorporated directly into the photopolymerizable resin along with the ceramic nanoparticle loading, which may then be removed after curing by soaking in water. This simple method leaves a three-dimension network of air passages in the polymer which may be tailored by altering the grain size and loading [16]. Even distributions (1/1/1 by weight) of baking sugar, resin and PMN-PT or PZT nanoparticles are fabricated in this manner and their properties compared to even loadings of resin and piezoceramic without the addition of sugar. Piezocomposites using PZT were found to have a consistent piezoelectric modulus of 33 pm/V while those created with PMN-PT showed a doubling of d_{33} when poled in the porous material.

II. MATERIALS AND METHODS

A commercial photopolymer resin (FormLabs, Somerville, MA) was used as the base monomer in this study. Piezoelectric nanoparticles lead magnesium niobium and lead titanate (PMN-PT, average particle diameter 5 μm) and lead zirconate titanate (PZT, average particle diameter 600 nm) were both acquired from American Elements (USA) and used without further modification.

A. Material formulation

The piezocomposites were all comprised equal parts monomer resin and piezoelectric nanoparticle, with the addition of an equivalent weight of baking sugar for piezoelectric polymer foams (e.g. 1/1/1 resin/PZT/sugar wt/wt/wt for polymer foam feedstock, 1/1 resin/PZT for control feedstock). The mixture was placed in a THINKY AER-250 planetary mixer (Intertronics, Oxfordshire) and mixed for 5 minutes at 2000 rpm before being de-foamed for 3 minutes at 1500 rpm to remove all air bubbles in the composite and ensure a homogeneous mixture.

Thin film samples of the piezocomposites were made using spin coating. Samples were placed on glass slides and spun coated for 15 seconds at 1500 rpm with an Ossila spin coated (Ossila Ltd., Sheffield) to obtain a uniform layer thickness of 80 μm. Spin coated samples were placed under an Intertronics IUV250 hand lamp (Intertronics, Oxfordshire) at an intensity of 15 mW/cm^2 for curing. The presence of oxygen is known to inhibit free-radical polymerization by reacting with the active radicals and degenerating dead chain ends, which we found to have a deleterious effect on the piezoelectric coupling of the resultant polymer. To limit the inhibition effect of oxygen the polymer samples were placed in an airtight zip-lock bag filled with nitrogen gas during the photopolymerization process. This reduces curing times and prevent poorly cured regions with higher ceramic loading. Samples were completely cured in 15 minutes.

After curing the samples were submerged in boiling water at 70ºC for two minutes to effectively remove the sugar. Kapton tape was added to the top and bottom of the samples in preparation for the poling process. The samples were placed in silicon oil heated to a constant temperature of 120ºC under a constant electric field of 14.2 kV/m (4 kV over total sample thickness 280 μm) for 4 hours. Electrodes were formed with silver paint (Sigma-Aldritch, Dorset) applied to the top and bottom surfaces, with electrical connections made using copper tape connected to both sides of each sample.

B. Measurements and characterization

The microstructure of spin coated samples was investigated using X-Ray computer microtomography (μCT). Scans were performed using a Bruker Skyscan 1172 using an SHT 11 Megapixel camera and a Hamamatsu 80 kV (100 μA) source. The sample was mounted vertically on a portion of dental wax and positioned 259.4mm from the source. No filter was applied to the X-Ray source and a voltage of 80 kV was applied for an exposure time of 1050 ms. The images generated were 2664 x 4000 pixels with a resolution of 6.75 μm per pixel. A total of 962 images were taken in 0.2 degree steps around one hemisphere of the sample with the average of 4 frames taken at each rotation step. The images were collected and a volumetric reconstruction of the sample

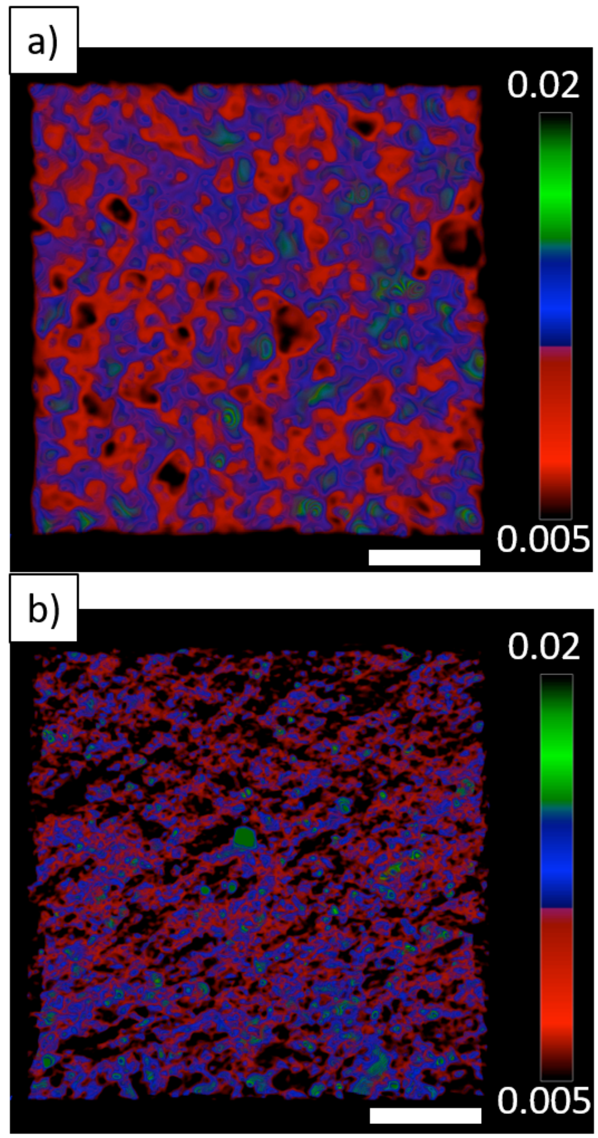

Figure 1: Representative volume elements from X-Ray computer micro tomographic scans. Colour bar represents relative attenuation of X-Rays in this region. (A) Cross section of PMN-PT / monomer / sugar composite before boiling treatment. (B) Sample after boiling showing the greatly increased void fraction.

generated by Bruker's *CTvol* software. The threshold for this attenuation signal was set manually to eliminate speckle around the sample, and then further cleaned with a thresholding mask using Bruker's *CTAn* software.

The piezoelectric modulus of the material is calculated from the inverse effect using a laser Doppler vibrometer (Polytec, MSA100-3D, Waldbronn). A sinusoidal voltage signal of 10 $V_{p\text{-}p}$ is generated by the internal data acquisition board of the laser vibrometer and placed across the axis of charging. The thin film piezocomposite is supported by gluing to a steel block to eliminate any bending modes which may corrupt the measurement. All measurements were averaged over 20 cycles, using complex averaging, and the resultant displacement used to determine the converse piezoelectric modulus. Frequency response data was generated by applying a periodic chirp stimulus from 1 – 50 kHz.

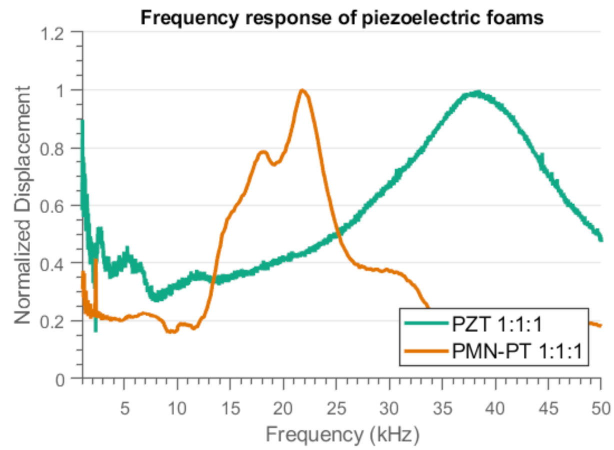

Figure 2: Frequency response of sugar cast samples in response to a periodic chirp between 1 and 50 kHz.

III. RESULTS

A. Morphology

The images produced by the µCT are based on the level of attenuation through the samples, which is dependent on the thickness of the material and its absorption coefficient. Measurements of sample density are therefore relative; however, thresholding can be easily applied by eye such that the air volume is eliminated allowing for visualization of the void fraction of the material. Figure 1 shows 2 mm x 2 mm representative volume elements of cured resin with even mixtures of monomer, sugar and PMN-PT nanoparticles before and after boiling in DI water for 2 minutes.

The colour scale shows the attenuation factor with respect to the maximum radiation dose recorded. In the cross sections the ceramic inclusions can be seen as higher attenuation factor regions dispersed in the polymer matrix, while sugar and polymer are indistinguishable by attenuation. Removal of the sugar by boiling samples at 70 C is shown by the increased void fraction, which may be measured by takeing the 2 mm x 2 mm x 200 µm volume element and applying a binary threshold such that air is excluded. The total volume of all thresholded voxels within this 3D space is subtracted from the total volume to give an estimated void fraction of 4.6% for the sample before boiling and 67.2% for the boiled sample.

B. Piezoelectric properties

The averaged single point measurements of d_{33} for the PZT and PMN-PT nanocomposite samples are given in Table I. Normalised displacement response to the periodic chirps for PZT and PMN-PT sugar cast samples are given in Figure #. The PMN-PT composite responded with a primary resonance at a frequency of 21.56 kHz while the PZT for the same sample thickness and sugar loading responded at 38.17 kHz. The single point scans were made below the relative resonance frequencies to compare the flat-band response as the equivalent to a quasi-static measurement.

TABLE I. D_{33} SINGLE SCAN VALUES OBTAINED BY LDV MEASUREMENTS

Piezocomposite	**d33 measurement**	
	Not sugar cast	***With sugar casting***
PZT / FormLabs resin	33 pm/V	33 pm/V
PMN-PT / FormLabs resin	35 pm/V	69 pm/V

IV. CONCLUSIONS

The sugar templating method is a simple and cost-effective method to produce piezoelectric polymer composite foams, however it would not normally be expected to increase the piezoelectric modulus of the material. The rationale behind creating voids in the material is lowering density, increasing compliance and thereby obtaining higher piezoelectric charge constants (g_{33} measure) and hydrostatic piezoelectric coefficients from the increased bulk compressibility. The results presented are of the phenomenon only, the underlying mechanism behind this increase is not currently clear.

This study looked into and presented innovative piezocomposites made of grey resin combined with Lead Magnesium Niobium Lead (PMN-PT) and PZT nanoparticles. The sugar casting method has allowed similar values of piezoelectric modulus to surface functionalisation methods at low volume fractions of nanocomposite, highly compliant materials while side-stepping the intensive surface-functionalisation. The method allows for considerably finer control of porosity, thinner films, and the possibility of scaling up to produce material to be used for different applications as well as further refinements in the microstructure to potentially increase further the piezoelectric modulus measurement. These foams could find immediate applications in energy scavenging platforms, biosensors, and acoustic transducers due to their tuneable porosity, mechanical flexibility, high surface area, high piezoelectric sensitivity, microstructure and more biocompatible chemical makeup compared to bulk electro ceramics. More research is needed to better understand the dielectric characteristics of these piezocomposites and improve their d_{33} value. The composite presented here is being developed for partial discharge detection by moulding to the cable geometry, which it is hoped will show improved sensitivities over similar PVDF solutions.

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