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Flexible, printed, Pb-free piezo-composites for haptic feedback systems

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While most of the work on piezoelectric composites focuses on methods to reduce the dielectric constant of the composite (for better sensor and energy harvesting performance), for haptic feedback and actuator applications the opposite is desirable. We present here a study of the effect of adding a second ceramic phase ($BaTiO_3$ nanoparticles) to composites of $(K_{0.5}N_{0.5})_{1-x}Li_xNbO_3$ (x = 0.03) in PVDF-TrFE-CFE in order to increase the dielectric constant of the composite. Adding small amounts of these nanoparticles to the composites results in an increase in the dielectric constant and, at high total ceramic loadings, an increase in the density of the composite. Furthermore, while adding larger amounts of nanoparticles leads to agglomeration and reduced densities, it also allows access to higher loadings of ceramic than normally attainable.

Keywords—Composite, dielectric constant, haptic, actuator

I. INTRODUCTION

Haptic feedback is typically thought of as the creation of a sensation of touch where none exists. It is an increasingly important domain of material applications that can be used to ease the interactions between humans and machines in many instances[1,2]. While older applications, such as braille keyboards [3], are clearly important for the users that rely on them, with the advent of smartphones and the replacement of keyboards with touch screens haptic systems are becoming more and more important.

Piezoelectric materials, which convert electrical to mechanical energy, and vice versa, are ideally suited for these applications [4]. For the majority of commercial piezoelectric applications piezoelectric ceramics are used. In particular $Pb_{1-x}Zr_xTiO_3$ (PZT) has been the ceramic of choice due to the system's excellent piezoelectric properties [5]. However, given the high lead content in these ceramics, there has been a serious push in the research on piezoelectric materials towards lead free systems in recent years. Following the discovery of attractive piezoelectric properties in the Li, Ta and Sb doped $(K_{0.5}Na_{0.5})NbO_3$ system (KNLN) grown and textured using template crystals by Saito et al. [6] particular focus has been paid to the KNLN system for a lead free replacement. The other drawback of using piezoceramics is, of course, the inherent brittleness of ceramic materials. For piezoelectric applications that require flexibility we currently use piezoelectric polymers such as polyvinylidene fluoride (PVDF) and its co-polymer with trifluoroethylene (PVDF-TrFE) [7]. While these systems allow the application of piezoelectrics to flexible systems and are also lead free, they require very high electrical fields in order to pole (over 70 kV mm-1 for PVDF [8]) and have lower thermal stability than the ceramic systems. Thus, in order to combine the best of the properties of ceramics and polymers we work on polymer-ceramic composites where the ceramic is the piezoelectrically-active phase and the polymer matrix confers flexibility to the system [9–11]. To ensure that our composites will be easy to scale industrially, simplicity is desired as much as possible. Therefore, in this work we have studied so-called "random" composites or "0-3" composites where the 0 indicates the dimensionality of the filler connectivity and the 3 that of the matrix.

There are two main problems currently facing piezoelectric composites for their application as actuators: their low stiffness and dielectric constant, leading to a reduction in the sensation that can be produced in a haptic interface based on these materials. To increase the dielectric constant of the matrix we have chosen to work the the PVDF terpolymer PVDF-TrFE-CFE which has a dielectric constant of 50, the highest of any commercially available polymer. In our current work we present a method of further improving the composite's dielectric constant through the inclusion of a second ceramic phase with small particle size, namely barium titanate nanoparticles. We will discuss the effect that this has on the density of the composites as well as the dielectric constant.

II. EXPERIMENTAL

A. KNLN3 Synthesis

$(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$ (x = 0.03) (KNLN3) powder is prepared from a stoichiometric mixture of Na_2CO_3, K_2CO_3, Li_2CO_3 (reagent grade, purity > 99.0 %) and Nb_2O_5 (99.99 % trace metals basis) supplied by Sigma-Aldrich. The powders are calcined at 1050 °C for 3 hours (heating at 5 °C min^{-1}) to form the KNLN3 ceramic. After handmilling and XRD to check phase purity the powder is ball milled for 1 hour in cyclohexane, then calcined a second time at 925 °C for 10 hours (heating at 1 °C min^{-1}) to ensure the starting powders have fully reacted and to remove any small fragments formed during milling that may lead to agglomeration in the final composite. Phase purity of the powders is checked by X-ray diffraction analysis using a Rigaku miniflex600 table top diffractometer and Cu Kα radiation. Rietveld refinement of the

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resulting diffraction pattern (using the fullprof software suite [12]) confirms the presence of single phase KNLN3 with a good fit of the data (R-Bragg = 5.4 %).

B. *Composite Synthesis*

To produce the composites a solution of polyvinylidene difluoride with tri-fluoroethylene and chlorofluoroethylene co-polymers (PVDF-TrFE-CFE) (obtained from Piezotech Arkema) in dimethylformamide (DMF) is prepared. For low volume fractions of filler (< 40 V%) a 20 wt% PVDF-TrFE-CFE in DMF solution is used and for higher volume fractions a 15 wt % solution is used. This is done to keep the final film thicknesses as close as possible. The KNLN3 particles are mixed into this solution using a Hauschild DAC 150 FVZ planetary speed mixer at 750 rpm for 5 minutes. $BaTiO_3$ (BT) powder (HP-250, 250 nm) from Inframat Advanced Materials is then mixed into the solution by the same method. After degassing the resulting mixture for several minutes in a vacuum pot, the composite is cast using the doctor blade technique with a cast height of 1mm. Cast composites are dried in a vacuum oven at 70 °C for 1 hour before annealing at 110 °C for 2 hours. Once annealing is finished a number of discs (12 mm diameter) are cut from the composite for electrical testing. Gold electrodes are sputtered onto the composite discs using a Quorum Q300T sputter coater. The electrical properties of the discs are measured using an Agilent 4263B LCR meter.

Scanning Electron Microscope (SEM) images were taken using a Jeol JSM-7500F field emission scanning electron microscope. Prior to SEM measurements a thin (15 nm) layer of gold is deposited on the sample using the sputter coater described above. In order to examine the cross sections of the composites they are first frozen in liquid N_2 and then cracked.

III. RESULTS AND DISCUSSION

A. *Microstructure*

Fig. 1 (a-c) show the SEM images of the cross sections of three composites with a total ceramic loading of 50 V%. In Fig. 1, a) we see that the KNLN3 particles are well dispersed in the polymer matrix. However, a small amount of porosity can be clearly seen between the particles. This may be due to small cracks from the sample preparation for these cross-section images or it may be intrinsic to the sample. Image b) shows that the mixture of 40 V% KNLN3 with 10 V% BT leads to a well dispersed composite with no visible porosity present. Finally, in image c) substantial porosity can be observed as well as a region near the top of the image that shows agglomeration between the BT nanoparticles. When the total ceramic content increases to 60 V% (Fig. 1 d) and e)) the changes become much more pronounced. The 60 V% KNLN3 composite in image d) shows significant porosity throughout the sample while the same ceramic loading replacing 10 V% KNLN3 with BT only shows a small amount of porosity and no visible agglomeration of the nanoparticles.

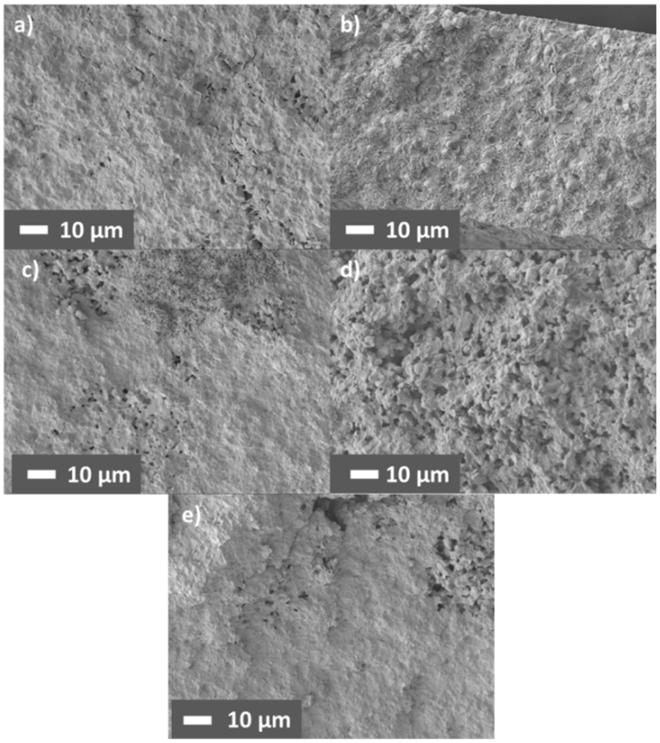

Fig. 1 SEM images of the cross sections of random composites with ceramic loading: a) 50 V% KNLN3, b) 40 V% KNLN3 and 10 V% BT, c) 30 V% KNLN3 and 20 V% BT, d) 60 V% KNLN3 and, e) 50 V% KNLN3 with 10 V% BT.

Thus the replacement of KNLN3 by a small amount of BT nanoparticles leads to a noticeable improvement in the density of the sample without increasing the agglomeration. However, from Fig. 1 c) it can be seen that adding too much of the nano-BT leads to the opposite effect with evidence of increased porosity due to agglomeration of the BT nanoparticles as also evident in Fig. 2 which plots the relative densities of the composites against their ceramic loadings.

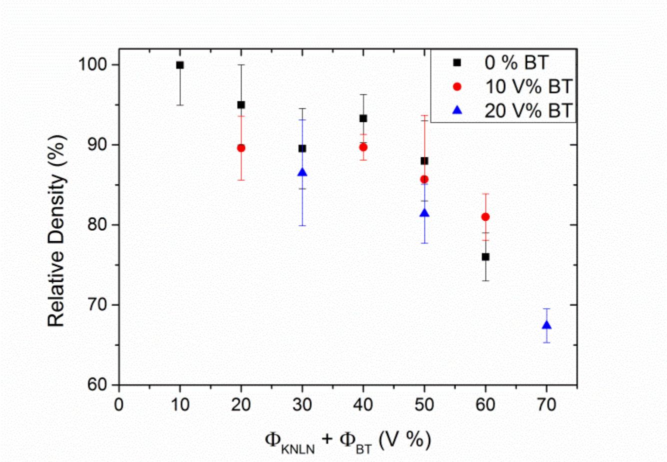

Fig. 2 plot of the relative densities of the composites against their total ceramic loading for the 0, 10 and 20 V% BT nanoparticle composites.

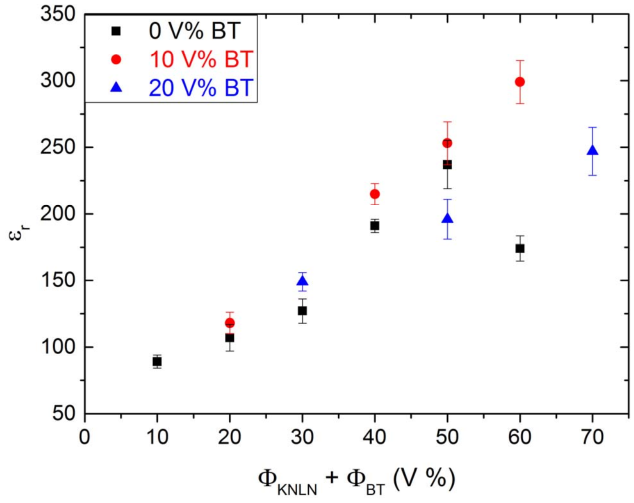

Fig. 3 Plot of the dielectric constants of the prepared composites against total ceramic KNLN3 + BT content.

The microstructural SEM findings are thus in line with the measured densities of the composites.We see that for lower loadings of ceramic the addition of nanoparticles slightly reduces the relative density, however at higher loadings the presence of 10 V% BT nanoparticles leads to higher densities than the same loading of only KNLN3. Finally, by replacing 20 V% of the KNLN3 with BT we were able to access higher total loadings (Φ = 70 V%) than is normally possible with KNLN3 alone. Above 60 V% the composites with only KNLN3 are too fragile to remove from the substrate.

B. Dielectric properties

It has been well documented that, for ceramic-polymer composites, the dielectric constant of the matrix dominates the dielectric constant of the entire composite. Furthermore, as total ceramic loading increases the dielectric constant of the composite approaches that of the bulk ceramic. Therefore, in Fig. 2 it is unsurprising that the dielectric constant of the composites increases with increasing ceramic loadingregardless of the BT loading. However, while the dielectric constant of the matrix may dominate, the ceramic still plays a role. For lower volume fractions, replacing either 10 or 20 V% of KNLN3 ($\varepsilon_r \approx 400$) with BT nanoparticles ($\varepsilon_r \approx 3000$ [13]) causes a noticeable increase in the dielectric constant of the composite. This is despite the fact that the the density of the KNLN3+BT composites is lower than the pure KNLN3 composites at low ceramic loadings (Fig. 1, f). For the composites with only KNLN3, ε_r drops off above 50 V% due to a sharp increase in the porosity. Meanwhile, the same loading with 10 V% BT continues the trend of increasing ε_r. If the amount of BT is increased to 20 V% however we see that the dielectric constants are lower than the fully KNLN3 composite for 50 V%. Lastly, replacing 20 V% KNLN3 by BT allows the creation of composites with 70 V% ceramic loading. Such high ceramic loadings were not able to be achieved for the KNLN3 only composites and the 60 V% KNLN3 10 V% BT composites as they are too fragile to remove from the substrate or study.

IV. CONCLUSIONS

In conclusion, we present here a series of so-called "tri-phase" composites of KNLN3 and BT in PVDF TrFE-CFE. Replacing small amounts (10 V%) of KNLN3 with BT leads to an increase in the dielectric constant and density of the composite. Adding larger amounts of BT (20 V%) initially improves the properties for low total ceramic loadings, however at higher loadings a reduction in ε_r is observed. Notably, while the addition of 20 V% BT reduces the density and ε_r it does allow access to higher ceramic loadings than were typically available from KNLN3 alone or KNLN3 with 10 V% BT. This technique represents an interesting avenue to study composites with very high ceramic loadings for possible actuator and haptic applications.

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