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Original Research

Development of multi-functional nano-paint for energy harvesting applications

Bir B. Bohara, Ashok K. Batra*

Department of Physics, Chemistry and Mathematics (Materials Science Group), College of Engineering, Technology and Physical Sciences, Alabama A&M University, Normal (Huntsville), AL 35762, United States

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ABSTRACT

The multi-functionality of lead magnesium niobate-lead titanate/paint (PMN-PT/paint) nanocomposite films for energy harvesting via piezoelectric and pyroelectric effects is described. PMN-PT/paint films have been fabricated by a conventional paint-brushing technique to provide a low-cost, low-temperature and low–energy route to create multi-functional films. The properties investigated included dielectric constants, ε' and ε'', as a function of temperature, frequency and composition. From these parameters, it is indicated that the dielectric constants and AC conductivity (σ_{AC}) increase with an increase of filler content and temperature, implying an improvement of the functionality of the films. The results revealed that σ_{AC} obeyed the relation $\sigma_{AC} = A\omega^s$, and exponent s, was found to decrease by increasing the temperature. The correlated barrier hopping was the dominant conduction mechanism in the nanocomposite films. The efforts were made to investigate the performance of nanocomposite films to mechanical vibrations and thermal variations. A cantilever system was designed and examined to assess its performance as energy harvesters. The highest output voltage and power for a PMN-PT/paint based harvester with a broad frequency response operating in the -31-piezoelectric mode were 65 mV and 1 nW, respectively. Voltage and power were shown to be enhanced by application of thermal variations. Thus, films could be utilized for combined energy harvesting via piezoelectric and pyroelectric characteristics.

1. Introduction

Recently, nanocomposites composed of ceramic particles and polymer matrices have been fabricated as a means of engineering the dielectric, pyroelectric and piezoelectric properties, and their energy storage capacity for use in variety of sensor and energy harvesting devices [1–9]. The reduction in size of high performance electronic devices requires integration of passive components such as resistors and capacitors in the integrated circuits. Thus, fabrication of films with high dielectric constant (ε') is essential and important for the integration of the passive components. Ferroelectric ceramic lead zirconate titanate and barium titanate are candidates for such high-k capacitor materials. These materials require high temperature processing; however, this is not compatible for embedding the capacitors in printed circuit boards. Several researchers, including the authors of the present study, have investigated the pyroelectric, piezoelectric, and other physical properties of 0–3 polymer-composite films fabricated by low temperature solution casting method [9]. Wen and Chung investigated the pyroelectric behavior of cement-based materials and demonstrated that the steel/carbon-nanofibers increase the dielectric properties of cement composites [10]. In 2009, Batra et al. investigated pyroelectric polymer composites whereby silver nano-particles were embedded in a P(VDF-TrFE)/lithium tantalate composite and indicated an enhancement in pyroelectric performance as compared with pristine P(VDF-TrFE) [11].

According to the recent literature, limited work has examined in detail to their dielectric behavior and transport mechanism of charge carriers under the influence of temperature and frequency of applied electric signal for synthetic paint/electro-ceramic composites from viewpoint of their use in embedded capacitors. These electric phenomena are important to understand the potential of the materials for storage mechanical and poling behavior of composites to create a piezoelectric or pyroelectric response. For example, the accumulation and de-trapping of electric charges resulting from mechanical or thermal load can be responsible for the failure of these materials. Different composites of lead zirconate titanate (PZT), barium titanate (BT) and barium strontium titanate (BST) with various types of polymers such as polyvinylidene di-fluoride (PVDF), polyvinyl chloride (PVC), polyvinyl alcohol (PVA) and copolymers have been widely studied and reported in the literature [5]. However, to the best of author's knowledge, no work is reported on the dielectric behavior of nanocomposite films

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* Corresponding author.
E-mail address: ashok.batra@aamu.edu (A.K. Batra).

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Table 1
A list of composite films fabricated with various wt% of PMN-PT nanoparticles.

Nanocomposite films	Mass of paint (g)	Mass of PMN-PT (g)	PMN-PT wt%
MP-1	20.0 +/− 0.2	0.5 +/− 0.05	2.50
MP-3	20.0+/− 0.2	1.0+/− 0.05	4.78
MP-5	20.0+/− 0.2	1.5+/− 0.05	7.00
MP-7	20.0+/− 0.2	2.0+/− 0.05	8.98

based on electro-active materials in paint. In the present work, synthetic paint is used as a vehicle for an active multi-functional component to create a thick film composite. A conductive silver paint is then used for electrodes and the dielectric and ac conductivity in a large domain of temperature and frequency is characterized in detail, including ac conduction mechanisms. The composite lead magnesium niobate-lead titanate (PMN-PT/paint) films were fabricated with nano-sized PMN-PT particles of a range of contents by an efficient and cost-effective conventional brush coating technique on a flexible copper substrate that also acted as a lower electrode. PMN-PT has been selected because of its high dielectric constant at room temperature ($\varepsilon' \sim 4645$) [12]. In the present paper, the PMN-PT/paint composite films were also investigated to determine their functionality for use in energy harvesting devices and the performance of a paint based energy harvester via both pyroelectric and piezoelectric effects. The films were found to be multi-functional and due to their flexibility, can be used in piezoelectric touch/tactile sensors including in numerous scientific and medical instruments, high-k capacitors, in addition to piezoelectric/pyroelectric energy harvesting.

2. Experimental details

The 0–3 connectivity composite films were fabricated using a conventional brush technique. The first step was the preparation of a 'die-mix' which involved mixing a suitable amount of modified nano-PMN-PT powder (approx. 100 nm) in a commercial synthetic paint (topside paint) at room temperature which was made from a modified alkyd and was durable in extreme weather conditions. An alkyd was polyester modified by the addition of fatty acids and other components, and derived from polyols and a dicarboxylic acid or carboxylic acid anhydride. The paint seemed to be a polar functional dielectric with inorganic constituents in addition to the other components stated above. This mixture (die-mix) was ultrasonically agitated/mechanically stirred, for an hour, to break-up the agglomerates. The films fabricated with various wt% of nano-sized PMN-PT (approx. 100 nm) powder in the paint are tabulated in Table 1 along with designated sample name.

The films were coated by an artist brush on to a pre-cleaned flexible copper substrate. The painted films were dried and cured in air for one week. The flow chart depicting protocol for the fabrication of nano-composite films is shown in Fig. 1. After poling, the upper silver electrode was deposited on the film using a shadow mask for testing with copper as the lower electrode. The samples were poled at 4 kV for 30 min using a corona-poling set-up.

After the poling process, the samples were short circuited and annealed at 50 °C for 1 h to remove any extrinsic charges. A real part (ε'), imaginary part (ε'') of the dielectric constant and AC conductivity (σ_{AC}) were determined as:

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon'' = \varepsilon' tan\delta \tag{2}$$

$$\sigma_{AC} = \varepsilon_0 \omega \varepsilon'' \tag{3}$$

where C_p is the parallel capacitance of the sample at the chosen signal frequency ω, $tan\delta$ is the dielectric loss, A is the electrode area of silver electrode, d is the thickness of the sample, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum. Isothermal runs were carried out for frequency domain 1 kHz to 1 MHz and different temperature varying from room temperature to 80 °C. The details of the instrumentation and procedure used for measurements are described in our earlier publications [5–8].

3. Results and discussion

3.1. Dielectric behavior of PMN-PT/paint nano-composites

The dielectric constants of composites depend not only on the dielectric constant of each phase in the composites but also their shape, size, porosity, interphase polarizability and interphase/ceramic volume fractions [5]. Fig. 2(a–b) shows the dielectric constant ε', and the dielectric loss ε'' of the PMN-PT/paint composite films, respectively. The parameters (ε', ε'') increase with the increase in temperature and weight % of PMN-PT nanoparticles in the paint. This is to be expected in ferroelectric PMN-PT, since real permittivity of PMN-PT is $\varepsilon' \sim 4645$.

An increase in PMN-PT loading in the composite film increases the interfacial area between the particles and paint phase. As a result, the effect of interfacial polarization on the dielectric constants (ε', ε'') can be significant. Thus, an increase of dielectric parameters with PMN-PT loading is observed. The bar-chart clearly illustrates the comparison of dielectric constant (ε') and dielectric loss (ε'') at 45 °C in Fig. 3a & b, respectively. The introduction of PMN-PT nanoparticles having a permittivity higher than the paint matrix increases the effective permittivity of the paint composites, mainly due to the influence of filler permittivity. A slight reduction in MP-7 (8.9 wt%) as compared to MP-5 (7.0 wt%) sample is possible if its bulk polarization mechanisms are

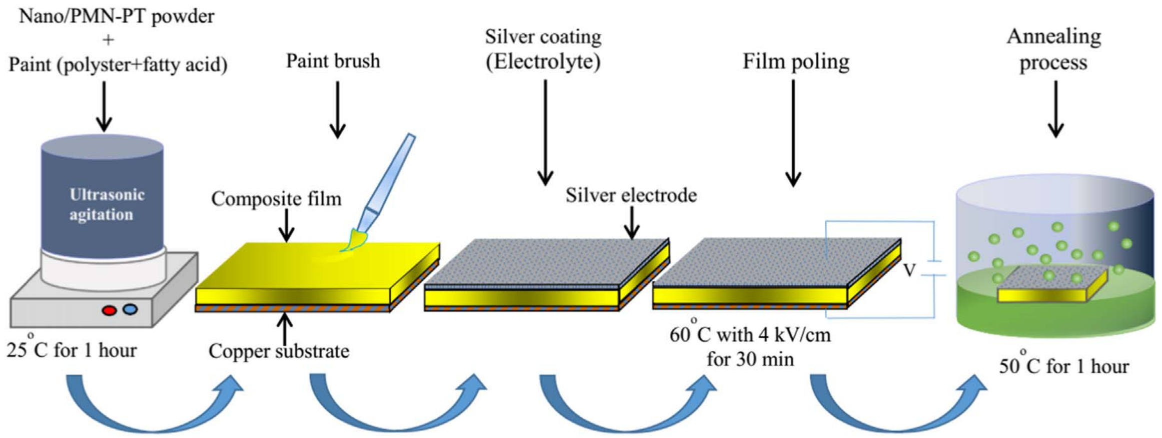

Fig. 1. Fabrication of films protocol adopted for fabrication of PMN-PT/paint samples.