Characterization of (0-3) piezocomposite materials for transducer applications

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***Abstract*— In this study, we have developed and characterized two different (0-3) piezoelectric composite materials with potential to be used in sensing applications. The composite materials were made using Polydimethylsiloxane (PDMS) as the polymer matrix with Barium Titanate ($BaTiO_3$), and Lead Zirconate Titanate (PZT51) as the dielectric fillers. Thin film samples of the (0-3) piezocomposites were prepared using a solution mixing and spin coating method to produce composites with (0-3) connectivity pattern and layer thickness of 100 µm. The microstructure of the piezocomposites were analyzed using a scanning electron microscope to determine the connectivity structure and homogeneity of the piezocomposites. The mechanical properties of the composites were determined using the method of Oliver and Pharr. FTIR analysis was used to determine the effects of the fillers on the structure of the piezocomposite. The average piezoelectric d_{33} coefficient of the piezocomposites were also measured using the laser vibrometer technique and determined to be 30 pm/V for the piezocomposite consisting of Barium Titanate ($BaTiO_3$) and 32 pm/V for the piezocomposite consisting of Lead Zirconate Titanate (PZT51).**

Keywords*— Piezoelectric; Ceramic-Polymer; Spin coating; UV curable; Composite; FTIR; XRD; SEM

I. INTRODUCTION

Recently, there has been a growing need to develop advanced functional materials to produce highly functioning transducers. To meet such needs, the functional materials should be able to perform different functions such as sensing and actuation simultaneously within a given system. Materials which exhibit piezoelectric properties have been used in transducer technology by harnessing the sensing and actuation function of such materials. Much research has gone into developing a class of highly functional materials based on the piezoelectric effect. These piezocomposite materials comprise of a piezoelectric ceramic mixed with a polymer to produce a combination which offers much promise in the manufacturing of sensing and actuating devices due to the combined properties of each constituent material such as the piezoelectric properties of the ceramic and the mechanical flexibility of the polymer. Some of these can be integrated with metals or polymer composites for structural health monitoring (SHM), and in producing electromechanical transducers such as pressure sensors, hydrophones, and vibration sensors [1,2]. A piezocomposite consists of two phases and can be classified according to the way both phases are connected dimensionally e.g. (1-, 2-, or 3-) into 10 structures; 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3 [3]. Although each structure provides different advantages, one structure which offers much promise is the (0-3).

In a composite with (0−3) connectivity, a ceramic filler is mixed with a three-dimensionally connected polymer phase. These composites can be used to easily fabricate large flexible thin sheets, produce applications in large scale and shaped to conform to variety of shapes [2]. Composites with (0−3) structure were first discovered by Kitayama Pauer and Sugawara [4-5], this was achieved using PZT as the filler material and polyurethane as the matrix. These early (0−3) composites were reported to have low d_{33} values [6]. Different materials such as $PBTiO_3$ ceramic and eccogel polymers, PT-BF powder, have been used to fabricate these piezocomposites [7]. Several types of flexible piezoelectric composites consisting of $PbTiO_3$ powder and chloroprene rubber, $BaTiO_3$ and Norlands Polymer have been developed [8-10], obtaining d_{33} in the range of 1.2 to 3.8 pm/V.

In this paper, we focus on the development and characterization of a (0-3) piezocomposite with Barium Titanate (BT) and PZT as the filler materials and PDMS as the polymer matrix.

II. MATERIALS AND METHODS

The materials used in this experiment include commercially available Polydimethylsiloxane (PDMS), Sylgard 184, Silicon elastomer curing agent (Sigma-Aldrich), silver paint, $BaTIO_3$ 500 nm nanoparticles (US research nanomaterials INC, USA) and Lead Zirconate Titanate (PZT51) 5µm (Changsha Easchem Co. Limited, China).

A. Material Synthesis and Screen Printing

The fabrication process is carried out in two steps. The first step involved synthesizing the Polymers. Silicon elastomer curing agent was mixed with Silicon elastomer at a ratio 1:9. Silicon elastomer curing agent is needed to start the polymerization process when exposed to high temperature. The mixture was put in a THINKY AER-250 mechanical mixer and mixed for 3 min at 1500 rpm and de-foamed for 2min at 1200 rpm. The process removed all air bubbles within the mixture and ensured proper mix between the filler and matrix. A PDMS mixture with viscosity of 3500 cP was obtained.

The second step involved making the (0-3) piezocomposites with the polymer synthesized above. 60%

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w/w BT was added to 40% w/w PDMS and 60% w/w PZT 51 was added to 40% w/w PDMS. Both composites were prepared separately and mixed in a THINKY AER-250 mechanical mixer for 3 min at 1500 rpm and de-foamed for 2 min at 1200 rpm. This process was repeated twice and sonicated for 30 mins. Thin film samples of each piezocomposite were obtained using a spin coating technique. Samples were spin coated using an Ossila spin coater at 2000 rpm for 10 s to give a layer thickness of 100 µm. Although efforts were made to obtain a uniform thickness layer all through, this was unachievable due to the filler particle sizes used and the goal to have thin film samples of approximately 80 - 100 µm. The piezocomposite samples were cured under high temperature at 150 ºC for 2 h using an oven (Heraeus thermo scientific).

Finally, thin film samples of sizes 3 cm by 2cm were cut out and silver paint coated on both sides of the piezocomposites. All samples were polarized in silicon oil heated to a constant temperature of 100 ºC under a voltage of up to 9 kV for 2 h.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Morphology

The microstructure of each piezocomposite sample was investigated using a table-top scanning electron microscope at an accelerating voltage of 15 kV (SEM, Hitachi TM1000, Krefeld, Germany). In Fig. 1(a), the cross-section area of the composite with PZT and PDMS is shown. Thick clusters of the filler is observed with non-uniform dispersion. This result shows a poor degree of bonding and poor adhesion between the PZT filler and PDMS which also indicates that the filler may be inter-connected giving rise to a non (0-3) structure. This could be as a result of the high PZT wt. % used, the particle size (~5 µm) and the solution mixing method used in preparing the composite. In Fig 1(b). The micrograph confirms the (0-3) structure of the composite and shows a higher degree of dispersion than the PZT composite. Here, the BT filler is seen to be densely and uniformly and more homogenous with no apparent agglomeration. Although, some spaces were observed (arrows) in the composite, this is possibly due to the mechanical mixing technique used.

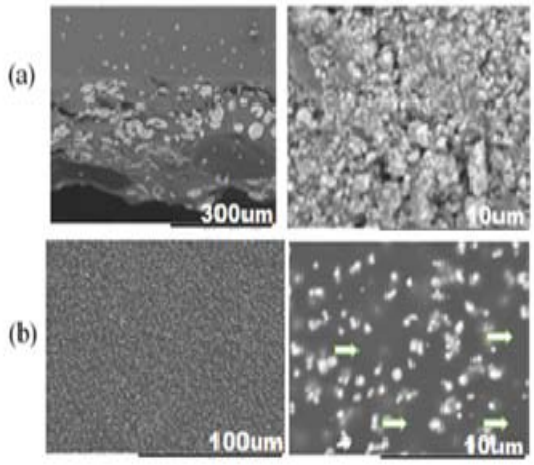

Fig. 1(a). Shows the scanning electron micrographs of the surface area of the composite material containing 60 wt.% PZT and 40 wt.% PDMS. (b). Shows the scanning electron micrographs of the surface area of the composite material containing 60 wt.% BT nanoparticles and 40 wt.% PDMS.

B. FTIR Analysis

FTIR spectra of the composite material were obtained using a Tensor II Bench ATR-IR (Bruker). Each spectrum was background subtracted. The samples were scanned in an inert atmosphere over a wave number range of 4000-400 cm^{-1} with a resolution better than 0.01 cm^{-1}.

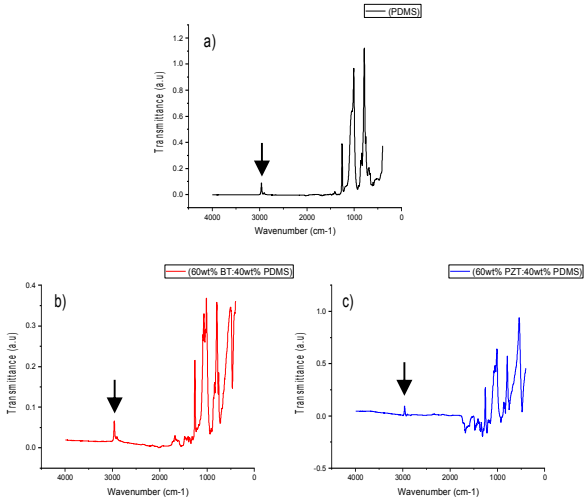

Fig. 2. Shows the FTIR spectra of piezocomposite with PDMS. a) shows the FTIR of pure PDMS; b) indicates the FTIR spectra of PDMS combined with 60% wt of BT and c) reveals the spectra for PDMS combined with 60% PZT nanoparticles.

Fig. 2(a) shows only PDMS and exhibits IR peaks at 789–796 cm^{-1} (−CH_3 rocking and Si-C stretching in Si-CH_3), 1020–1074 cm^{-1} (Si-O-Si stretching), 1260–1259 cm^{-1} (CH_3 deformation in Si-CH_3), and 2950–2960 cm^{-1} (asymmetric CH_3 stretching in Si-CH_3). When the BT and PZT nanoparticles are combined with PDMS (Fig. 2b and 2c), the characteristic peaks of PDMS are maintained and the fingerprint region shows extra signals, which represent the bonds between the piezocomposite and the polymer. The combination between nanoparticles and polymer does not alter the structure of PDMS.

C. XRD Analysis

XRD analysis was performed using a Bruker D2 Phaser diffractometer at ambient temperature with an operating voltage of 30 kV and an operating current of 10 mA. The detection was ensured by 10.5 mm Ni low Beta filter, 2.5° Soller Slits and LynxEye 1D Detector.

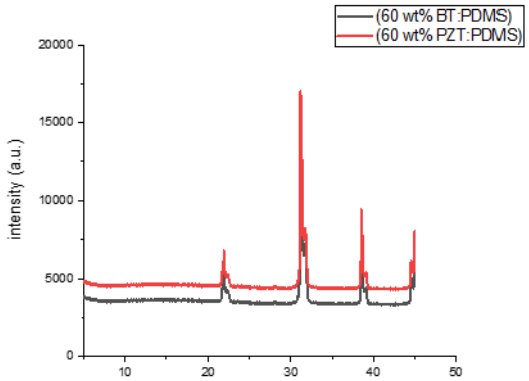

Fig. 3. Shows the XRD pattern for two piezocomposite samples. The red signal represents a sample with 60% wt. of PZT while the black spectra indicates a sample formed of 60% of BT.

D. Piezoelectric properties

The piezoelectric properties of the (0-3) piezocomposites were investigated using a microscanning laser Doppler vibrometer (Polytec MSA100-3D, Waldbronn, Germany) technique [13]. The composites were glued firmly on a metal block to prevent bending of the substrate. A sinusoidal AC voltage of 10V was applied across the axis of charging and the resulting displacement along the poling axis was measured.

The d_{33} coefficient of the (0-3) piezocomposites consisting of BT and PZT filler particles in PDMS was investigated using the direct displacement mode of the laser vibrometer. The result obtained under single point scans is shown in Fig. 4. The mechanical displacement of each piezocomposite is observed with BT: PDMS having a thickness resonance frequency at 15 kHz while the piezocomposite with PZT: PDMS exhibited maximum displacements at 6 kHz, and 11 kHz respectively. A full surface scan with a grid of 1000 scan points was performed below each resonant frequency obtained during the single point scan to obtain a more accurate result. The piezocomposite BT: PDMS gave an average d_{33} of 30 pm/V, while the piezocomposite with PZT: PDMS exhibited an average d_{33} of 32 pm/V.

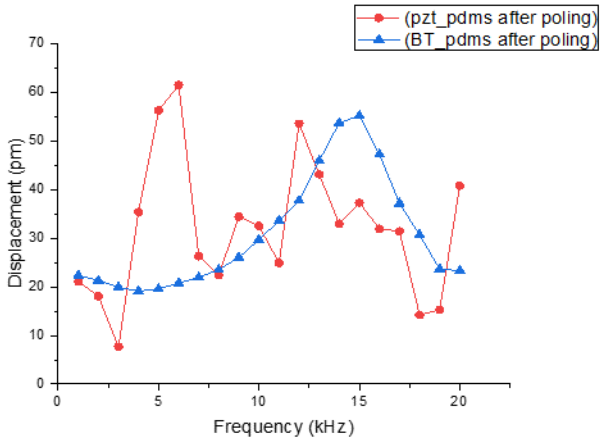

Fig. 4. Shows the magnitude of mechanical displacement as a function of a driving sinusoidal voltage of 10 Vp-p delivered over a frequency range between 1 and 20 kHz.

E. Mechanical Properties

The mechanical properties of the piezocomposites consisting of BT and PZT as fillers were investigated using the method of Oliver and Pharr. Indentation modulus of the samples was evaluated using an MFT-3D Nanoindenter. A maximum load of 460µN was applied to the samples and a 6 x 6 array of indentations separated by 15 µm was carried out to a fixed depth of 1 µm in order to reduce influence from neighboring indentations and to avoid the substrates influence on the mechanical properties. Indentation modulus (n = 36) was measured and shown in table 1.

Table 1. Average indentation modulus E obtained.

Piezocomposites	Average Indentation modulus (MPa)
PDMS: BT	19.95±2.20
PDMS: PZT	26.08±9.50

IV. CONCLUSIONS

Different piezocomposite materials comprising of piezoceramic fillers in polymer matrix is presented in this work. The piezocomposites are designed with a (0-3) structure and fabricated using $BaTiO_3$, PZT nanoparticles, and PDMS as polymer matrix. The piezocomposites were characterized using different techniques to determine the structural, piezoelectric and mechanical properties of the material. The structural analysis of the composite revealed that the polymer matrix with BT fillers closely exhibits the (0-3) structure while that consisting of PZT revealed a composite with more than one connectivity pattern, a combination of a (0-3) structure and non (0-3) structure. This could be as a result of the size of the PZT nanoparticle, the high 60 % w/w ratio and the solution mixing technique used. Both XRD and FTIR analysis showed that both BT and PZT fillers did not alter the structure of PDMS.

Furthermore, the 3D LDV experiments showed the piezoelectric nature of both piezocomposite samples. It was observed that at higher frequencies (6 kHz, 1 kHz, and 15 kHz) all the samples vibrate with higher amplitudes which could be due to the samples having a uniform thickness and homogeneity across different regions or different regions having agglomeration of nanoparticles as observed in the SEM micrographs. The mechanical properties of the composite material were tested using the nanoindentation method, the indentation modulus obtained showed the material exhibits plastic behavior which could be due to high BT and PZT loading. The thin and flexible structure of this piezocomposites coupled with the piezoelectric properties shows that this material offers promise as a functional material which can be used in sensing applications. Although, further work is required to investigate the dielectric properties of these piezocomposites and to further enhance their d_{33} value.

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