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Review article

Piezoceramic-polymer and piezoceramic-cement composites: A brief review

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Abstract

The physical properties of piezoceramic-polymers and lead-based or lead-free - Portland cement or geopolymer are described as part of this brief review. The connectivities such as 0-3, 1-3, 2-2 and 3-3 were employed to fabricate the composites. Their physical properties such as dielectric, coupling constant, acoustic impedance etc. were measured. The acoustic impedance obtained from the PZT-epoxy resin (0-3/1-3 connectivity) showed quite low. This can be further developed to match with water or human tissue for both hydrophone and medical applications. The properties of the composites containing lead-based or lead-free cement or geopolymer were also revealed. The results prove that these composites have a high potential to be employed as green building materials and smart concrete sensors in the future. A thin film of piezopolymer-metal oxide composite could also be developed to perform energy harvesting properties.

1. Introduction

For many years, lead zirconate titanate (PZT) has been in widespread use as a piezoelectric ceramic [1]. Due to PZT's high electromechanical coupling coefficients (higher than other piezoelectric materials), PZT ceramics are endowed with a high electrical-mechanical energy conversion and vice versa [1]. As a result, they are employed as transducer materials, and have found a wide range of applications, such as sensors, igniters, actuators, etc. [2]. The properties of these materials, both electrical and mechanical, have been well documented so that it is possible to predict their performance within any transducer structure. However, PZT ceramics are hard and brittle, so they might not be flexible enough to be adapted for curved surfaces. For some applications, the properties of this piezoelectric ceramic are not ideal and may probably be detrimental to the required design performance. The concept of combining suitable mechanical and electrical properties in a composite material has proved extremely useful. The composite materials can be fabricated to have properties superior to those of the individual components. In addition, the properties of a composite material depend not only on the volume fractions of the individual phase, but also on their connectivity. In this article, we shall review the properties of the composite materials between PZT and other materials such as polymer, and cements. The properties of these composites in some interesting connectivities will also be discussed.

2. Piezoelectric-polymer composites

The main objective of composite technology is to design materials with optimum properties for a given application that often cannot be obtained in single phase materials. For example, in an electromechanical transducer, the objectives may be to maximize the piezoelectric properties to obtain a good acoustic matching with water, and also to make the transducer mechanically flexible enough to suit a curved surface. These requirements mostly cannot be available with a single phase material. Therefore, we may have to select the desirable properties by combining two or more phases that do not ordinarily appear together in nature. Properties such as mechanical, thermal electrical, etc. in composite technology are determined by the choice of component-phases, their relative amounts and the manner in which they are interconnected, which is termed "connectivity". The concept of connectivity was first applied to piezoelectric composites by Newnham [3]. Connectivity describes the configurational pattern of each component of a composite material. In a composite, a component may be self-connected in zero, one, two or three dimensions. In the case of a 2-phase composite, there are ten connectivities: 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 2-3, and 3-3 [3]. In addition, there are 20 connectivities for composites of 3 phases and 35 for composites of 4 phases.

Connectivity is the most important parameter in composites designed to become piezoelectric transducers or pyroelectric detectors. Piezoceramic-polymer composites have been studied and have the potential for being employed in a number of applications such as hydrophones or ultrasonic transmitters. In order to maximize the performance of an acoustic transducer, it is necessary to control the parameters such as thickness mode electro-mechanical coupling coefficient, k_t, the characteristic acoustic impedance, Z, relative permittivity, ε_r, and

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mechanical quality factor, Q_m. The ideal characteristics of a piezoelectric composite for operating in water or in contact with human tissue would be $k_t = 1$, a "Z" matching the acoustic impedance of human tissue or water (about 1.5 Mrayls [4]) and a permittivity close to that required for proper interfacing with the electrical circuit.

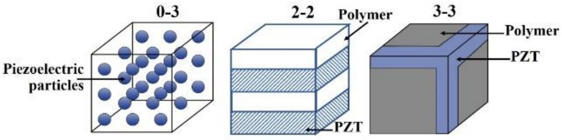

Figure 1. Some connectivity structures for a diphasic solid adapted from Lee et al. [5].

However, it is difficult to optimize both k_t and Z simultaneously to achieve acoustic matching with a single quarter wave layer made from a common low impedance matching material such as epoxy. The main area of recent research in piezoceramic-polymer composites has focused in particular on composites having 0-3, 1-3, 2-2 and 3-3 connectivities. The simplest type of composite, a 0-3 type, consists of a polymer matrix loaded with piezoceramic powder. In many respects a 0-3 composite is similar in structure to PVDF insofar as both consist of a crystalline phase embedded in an amorphous matrix. Among the 10 connectivities, 0-3, 2-2, 1-3 and 3-3 are considerably not very difficult to prepare. The schematic pictures of some connectivities are presented in Figure 1. All the pictures were adapted from Lee et al. [5]. Matrix face is mainly polymer, where PZT is the filler phase. Among these composites, the connectivity of the 0-3 piezoceramic-polymer is considered to be rather uncomplicated. The 0-3 composite structure exhibits a relatively large g_h [4], but a low d_h. The main advantage offered by the 0-3 composites is the ease of fabrication in the form of thin sheets, large extruded sections and in fiber form. Moreover, these could be mass-produced for use in underwater acoustics for large area hydrophones and sonar applications [4]. Nhuapeng and Tunkasiri [6] presented the electrical and piezoelectric properties of 0-3 PZT and polyester resin. The average PZT particle size employed in the experiment was 160 µm. The highest percentage they loaded in the resin was 60%, since if the content is higher than this, the particles may contact each other. However, van der Ende et al. [7] showed that different calcining temperature of PZT powders embedded in liquid crystalline thermosetting (LCT) matrix polymer in 0-3 connectivity could develop high performance of the composites. A maximum voltage constant (g_{33}) was obtained for a composite 40% (by volume) of PZT powder. Figure 2 shows a micrograph (backscattered electron imaging, BEI) of PZT-LCT composite containing PZT calcined at 1100 °C. In the 1-3 piezoceramic-polymer composite, the ceramic phase is self-connected in one dimension. The rod shape is suitable for this idea since it extends through the thickness of a polymer which is self-connected in all 3 dimensions. Some interesting properties of the composites, such as the coupling constant, k_t, mechanical quality factor, Q_m, and acoustic impedance (Z) were presented, and the details of this work can be found in [6]. For the 2-2 connectivity, there are two different model structures. Each structure consists of alternating layers of ceramic and polymer oriented parallel to the electrodes as in the series model, or perpendicular to the electrodes as in the parallel model, whose schematic pictures were drawn and presented in Figure 3. In recent decades, large numbers of (0-3) ceramic-polymer composites have been introduced for telecommunication microelectronic and microwave substrate applications [8].

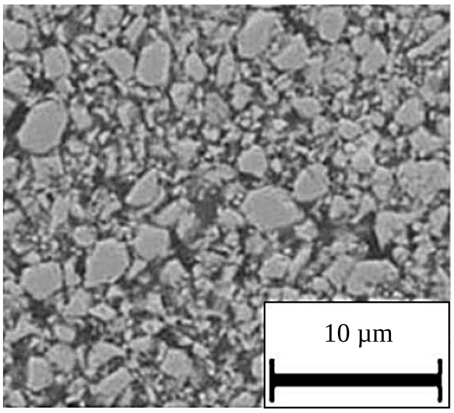

Figure 2. Micrograph (BEI) of cross section of PZT-LCT composite containing powder obtained from PZT calcined at 1100°C. The picture was adapted from van den Ende et al. [7].

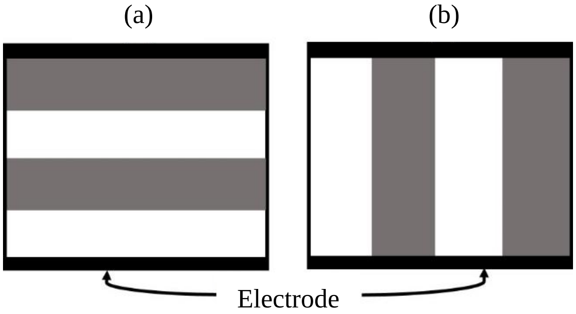

Figure 3. Series (a) and parallel (b) models for lamella diphasic solids.

Piezoceramic-polymer composites having (1-3) type connectivity with a scale size appropriate for high frequency > 1 MHz transducers were carried out by Tontrakoon et al. [9]. This type of composite is rather easy to obtain homogeneity. Besides, it offers many attractive properties such as pulse-echo transducers and medical imaging technologies [10]. The composite consists of PZT rods embedded in a polymer matrix. The PZT rods were accessed by extrusion of PZT paste (stearic acid is a particular lubricant), dried and sintered at a low temperature. Glass former together with excess PbO during sintering were employed in order to obtain both low temperature sintering and the suppression of PbO volatilization. To reduce the sintering temperature, many sintering aids such as a lithium/bismuth-based glass former were mixed in the calcined powder. The amount of lithium carbonate ($LiCO_3$) and bismuth oxide (Bi_2O_3) and other sintering aids can be found in [9]. The PZT rods were aligned in a jar, in which the epoxy resin was poured. After curing, 1-3 composite discs were obtained by slicing in a perpendicular direction to the rod. The details of the experiment can be seen in [9]. Examples of the 1-3 composite sample were drawn and shown in Figure 4. The drawing was adapted from that of Lee et al. [5].

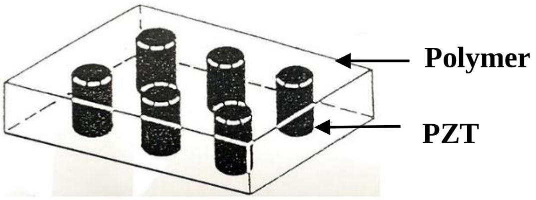

Figure 4. Schematic photograph of 1-3 connectivity with the rods surrounded by rectangular polymer matrix adapted from Lee et al. [5].

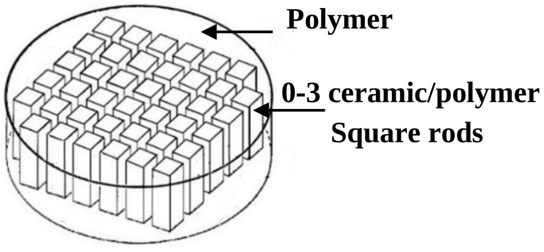

Figure 5. Schematic photograph of (0-3) and (1-3) combined piezocomposite sample, where polymer matrix filled in the spaces to form 1-3 connectivity with 0-3 ceramic/polymer square rods, adapted from Lee et al. [5].

In order to obtain an acoustic impedance (Z) that is low enough to transmit through the media like water or human tissue. The Z value obtained from Nhuapeng's and Tunkasiri's work is about 6 M rays, which is still too high for comparison to that of human tissue or water (1.5 Mrayls [4]). Thamjaree et al. fabricated the combined 0-3 and 1-3 connectivity PZT/epoxy resin composites [10]. The schematic drawing of (0-3) and (1-3) combined piezocomposite was shown in Figure 5 [5].

First, a disc of 0-3 piezocomposite was prepared and the dice and fill method [11] was employed to produce the spaces for filling the polymer. Then, the spaces were filled with epoxy resin to form 1-3 connectivity with 0-3 ceramic/polymer rectangular rods. The details of the preparation can be found in the reference [10]. The properties such as d_{33}, K_p, ε_r and Z were measured. A low acoustic impedance (Z ~ 4 Mrayls) was obtained, which is rather low and very close to that of human tissue and water. Both 1-3 and combination of (0-3)/(1-3) PZT-rod/polymer composites prove that there are promising configurations. The advantages of these composites are their high coupling factors, mechanical flexibility and low acoustic impedance, which can be further developed to match water or human tissue. Piezoelectric ceramic-polymer composites with 3-3 connectivity in which the two phases formed interpenetrating 3-dimensional networks to give two interlocking skeletons an intimate contact with one another. Patterns of this type often occur in living systems such as coral, porous ceramic and wood. The 3-3 composite was designed to take maximum advantage of the useful properties of each phase.

Coral was actually used as the starting material to provide the first 3-3 composite in what was known as the "replamine" or "lost wax" process. The coral was first impregnated with wax, and then leached out by acid. The wax former was then impregnated with PZT slip, and afterwards fired to remove the wax and sinter the PZT. The PZT coral structure was finally filled with a suitable polymer. A simple method was to mix PZT powder with plastic spheres together with a binder. On firing, the plastic spheres were removed to leave a sintered 3-3 porous PZT ceramic which was then infilled with a suitable polymer. The 3-3 composite offers a low density, and as a result, it improved acoustic impedance which matches water, low relative permittivity, large "g" coefficient

Figure 6. Picture of porous PZT, whose holes are to be filled with a polymer, forming a 3-3 connectivity.

Figure 6 presents a porous PZT ceramic after the plastic spheres were removed. The model of composites of 3-3 type was also presented by Lewis et al. [12], (similar to that in Figure 1) to determine the important factors influencing high piezoelectric sensitivity at a different arrangement. The porous PZT ceramic in which the porosity was impregnated with air or polymer. It showed a large number of the pore/polymer with different volume fractions whose expected properties can be evaluated due to the differences in pore arrangement between each model.

3. Piezoceramic and cement, fly ash geo-polymer composites.

The ongoing research which receives great attention at the moment are piezoceramic mixed with cement, fly ash and geopolymer in some connectivities. These new types of composites offer various piezoelectric properties. For example, PZT mixed with Portland cement offer the acoustic impedance (z) close to that of the conventional concrete materials with good compatibility. This new composite material is very important in developing as a composite for using in smart structures, which can act as a sensor to measure the vibration generated by the structure. Both lead-based and lead-free piezoelectrics have been employed to mix with cement because of their promising applications in civil engineering structures such as sensors and actuators. Hunpratub et al. [13] studied the lead-free ($Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$, BCTZO)-Portland cement (PLC) composites, mixing in (0-3) connectivity. The effect of particle size of BCTZO on the dielectric (ε_r) and piezoelectric properties of the composites was investigated. Dielectric properties of 0-3 BCTZO/high calcium fly ash geopolymer composites was also studied by Hunpratub et al. [14]. The samples were fabricated by normal mixing of geopolymer paste and BCTZO. The dielectric of the composites was measured at the frequency of 10^3 Hz, and it was concluded that this was due to spaces charge polarization mechanism. Portland cement (PLC) is mainly employed as the matrix for both lead-based and lead-free ceramic composites. They are mainly fabricated in (0-3) connectivity. Many papers revealed their physical properties, morphology, grain size, domain configuration etc. Chaipanich and his group have worked on properties of piezoceramics-PLC and fly ash composites, such as morphology and domain configuration of lead magnesium niobate titanate (PMNT)-PLC [15], compressive strength and microstructure of PZT-PLC [16], microstructure and electrical properties of BT-PLC [17]. Study of microstructure and electrical properties of BZT- Portland fly ash [18] was carried out.

Other connectivities such as (1-3), have been studied. For example, Rainyoi et al. [19] worked on acoustic and other properties of (1-3) connectivity BT-PLC. Potong et al. [20] studied dielectric and piezoelectric properties of (1-3) of BZT-PLC, and Rainyoi worked on the electro-mechanical coupling coefficient of (1-3) connectivity BT-PLC [21] composites. Dielectric and piezoelectric properties of 2-2 connectivity of PZT-PLC were studied by Chaipanich et al. [22] who obtained the considerably high d_{33} values of 99 pC/N and 113 pC/N of the composites at PZT volume content of 60% and 70%, respectively. Performance of 2-2 connectivity of barium zirconate titanate-PLC composites was also studied by Potong et al. [23]. The dielectric constant, piezoelectric coefficient and piezoelectric voltage were measured and compared to the values calculated from the theoretical models. The results were found to fit with that of the parallel model. Properties of 2-2 connectivity cement/polymer-based piezocomposites with varied piezoelectric phase distribution were studied by Dongyu et al. [24] who found that the piezoelectric composites show potential applications in the fabrication of ultrasonic transducers.

Gowdhaman et al. [25] employed a hot press technique to fabricate ceramic-polymer composites of 0-3 connectivity. They obtained the increase of piezoelectric strain and dielectric properties, depending on the volume fraction of PZT. Jaitanong et al. [26] studied the ordinary Portland cement (OPC), fly ash (FA) and lead strontium zirconate titanate (PSrZT) ceramic composite. They found that a limit of about 5.0 volume% was optimum for enhancing the dielectric and ferroelectric properties.

Dash et al. [27] studied the PVDF-$BiFeO_3$ composite in 0-3 connectivity and found that the composites showed much improved dielectric properties, which could be suitable candidates for capacitor application. Other composites such as hydroxylated bismuth ferrite-poly (vinylidene fluoride-co-hexafluoropropylene) could give high dielectric which can be used for energy storage devices [28]. Some piezoelectric polymer composites can be developed to be employed as energy harvesting materials. Phooplub and Muensit [29] demonstrated successfully that the piezoelectric film-poly (vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) incorporated with zinc oxide (ZnO) nanorods could have uses in micropower energy harvesting. Therefore, other piezo-ceramic composites could be further developed to be employed as energy harvesting materials.

4. Conclusions

Recent developments on the piezoceramics-polymer, or Portland cement including geopolymer composites have been revealed. Both lead-based and lead-free piezoelectrics were employed to mix with the polymer in various connectivities such as 0-3, 1-3, 2-2 and 3-3. These connectivities were employed due to the fact that they are rather uncomplicated for fabrication.

Work on piezoceramics-polymer is mainly to improve the physical properties for example coupling constant and the acoustic impedance in order to match with those of human tissue or water for medical uses and hydrophone. Piezoceramics (both lead-based and lead-free piezoelectrics)-Portland cement or geopolymer composites work is widely used in the construction industry, such as sensors in structure health monitoring application. The cement-based composites (piezoceramic-cement or geopolymer) can be further developed to be used as green building materials and as sensors in smart concrete structures. Work on energy harvesting properties employing thin film of piezopolymer-metal oxide composite was also successfully carried out.

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