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Khanbareh, Hamideh; van der Zwaag, Sybrand; Groen, Pim

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In-situ poling and structuring of piezoelectric particulate composites

H Khanbareh^{1,2,3}, S van der Zwaag² and WA Groen^{2,4}

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Abstract

Composites of lead zirconate titanate particles in an epoxy matrix are prepared in the form of 0–3 and quasi 1–3 with different ceramic volume contents from 10% to 50%. Two different processing routes are tested. Firstly a conventional dielectrophoretic structuring is used to induce a chain-like particle configuration, followed by curing the matrix and poling at a high temperature and under a high voltage. Secondly a simultaneous combination of dielectrophoresis and poling is applied at room temperature while the polymer is in the liquid state followed by subsequent curing. This new processing route is practiced in an uncured thermoset system while the polymer matrix still possess a relatively high electrical conductivity. Composites with different degrees of alignment are produced by altering the magnitude of the applied electric field. A significant improvement in piezoelectric properties of quasi 1–3 composites can be achieved by a combination of dielectrophoretic alignment of the ceramic particles and poling process. It has been observed that the degree of structuring as well as the functional properties of the in-situ structured and poled composites enhance significantly compared to those of the conventionally manufactured structured composites. Improving the alignment quality enhances the piezoelectric properties of the particulate composites.

Keywords

Dielectrophoresis, in-situ poling, piezoelectric composites

Introduction

Piezoelectric particulate composites have attracted considerable research interest over the last few years as the inclusions of piezoelectric ceramics in a ductile polymer matrix leads to superior piezoelectric and mechanical properties. In such multiphase composites the volume fraction of the phases, their morphology, the pattern of connectivity as well as the dielectric and electrical properties of the two phases control the overall physical and electromechanical properties. Nine different types of connectivity were distinguished by Newnham (Newnham et al. 1978). The random particle distribution, 0–3 composites with unconnected particles in a fully self-connected matrix, and the fibrous distribution, 1–3 composites with ceramic rods fully aligned and connected in one dimension, present the lower and upper bounds as far as the final properties of the composites are concerned. Structuring equiaxed ceramic particles in a chain form configuration by means of dielectrophoresis (DEP) has been shown to improve the dielectric, piezoelectric and pyroelectric properties of these materials over those of random composites (Bowen et al., 1998; Van den Ende et al., 2010; Khanbareh et al., 2014; Wilson and Whatmore, 2005) When

particle columns are formed, ideally the particles are aligned end-to-end, forming a column-like structure parallel to the applied electric field. Under ideal processing conditions, long particle chain configuration approaches the topology of perfect 1–3 composites. For a given filler concentration the alignment of the particles in the chain-like structure leads to a marked increase in piezoelectric properties while the high mechanical flexibility due to the polymer matrix is maintained (Bowen et al., 1998; Van den Ende et al., 2010; Tang et al., 2012, 2013). The quality of particle alignment is the key parameter in controlling the overall

¹Materials Innovation Institute (M2i), Delft, The Netherlands

²Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, The Netherlands

³Materials and Structures Research Center, Department of Mechanical Engineering, University of Bath, UK

⁴Holst Center, TNO, The Netherlands

Corresponding author:

H Khanbareh, Materials and Structures Research Center, Department of Mechanical Engineering, University of Bath, Claverton Down, BA2 7AY, Bath, UK.

Email: h.khanbareh@bath.ac.uk

properties of the composites (Andrews et al., 2010; Patil et al., 2008; Tang et al., 2013, 2014).

The key parameters controlling the effective properties of the structured composites are the quality of the particle alignment as well as the poling efficiency. Improving the filler orientation while keeping the filler volume fraction low leads to a high electroactive sensitivity, while maintaining the optimum flexibility levels for the composites (Bowen et al., 1998; Van den Ende et al., 2010; Tang et al., 2012, 2013). Enhancing the alignment quality by means of decreasing the interparticle distance has been shown to significantly improve the dielectric, piezoelectric and pyroelectric properties of particulate composites (van den Ende, 2012; Khanbarez et al., 2014). In conventional biphasic ferroelectric ceramic-polymer composites, the polymer phase normally has a lower permittivity and a low conductivity compared to the ceramic particles; thus a high AC field at elevated temperatures for a long period of time is required for efficient poling (Kwok et al., 2007; Lau et al., 2007). Thus the poling process as well as the resulting effective properties of the composites remain a challenge for the manufacturers. Recent investigations have shown that the electrical conductivity of the constituents has a significant effect on the dielectric, piezoelectric and pyroelectric properties of the granular composites (Khanbarez et al., 2015). It has been reported that an enhanced electrical conductivity of the matrix shortens the build-up time of the electric field acting on the ceramic particles. Therefore, for an electrically conductive matrix, efficient poling of the composites is possible at room temperature, with short poling times and relatively low electric fields. The electrical conductivity of thermoset polymer matrices as well as their permittivity decrease upon curing. Thus combining the DEP structuring and DC poling of the composites while the matrix is in the liquid state can improve the poling efficiency of the composites. Moreover the new proposed technique leads to cost effective single-step manufacturing of the composite sensors. In the present work the in-situ dielectrophoretic structuring and poling process of lead zirconate titanate-epoxy composites upon application of AC and DC electric fields is investigated. The effect of processing parameters on the structuring configuration as well as final properties of the composites are demonstrated.

Experimental procedure

Composite manufacturing

Lead zirconate titanate ceramic powder (PZT5A4), received from Morgan Electroceramics UK, was calcined at 1150°C for 1 h to develop a single phase material. The agglomerated powder was then dry-milled using 5 mm zirconium balls for 2 h using a single G90 jar mill. The particle size distribution of milled powder

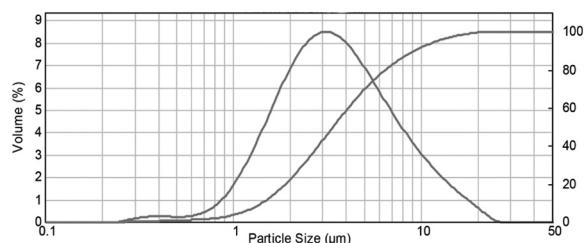


Figure 1. PZT particle size distribution.

in an aqueous solution with 10% isopropyl alcohol measured by a Beckman Coulter LS230 laser diffraction analyzer is shown in Figure 1. The powder was stored in a drying oven at 120°C for 24 h prior to the experiment to avoid moisture adsorption. A two component epoxy system (Epotek 302-3M, Epoxy (diglycidyl ether of bisphenol-A (DGEBA)) resin and poly(oxypropyl)-diamine (POPD) multifunctional aliphatic amine curing agent) was used. Both components were degassed separately in a vacuum oven at RT for 3 h prior to the experiment to avoid air bubble formation. The PZT particles were dispersed in the polymer resin to the specific volume fractions of 10%, 20%, 30%, 40% and 50%; the slurry was degassed for 5 min, then mixed with the hardener, and degassed for another 5 min subsequently. The slurry was then molded. The details of the mold layup are presented elsewhere (Khanbarez et al., 2014). Three sets of samples under specific combinations of AC and DC bias were prepared, as indicated in Table 1. The electric field was applied using a function generator (Agilent, 33210A) coupled to a high voltage amplifier (Radiant Technologies Inc., T6000HVA-2). The optimum frequency level was obtained for the highest phase angle of Lissajous plots for each volume fraction in early stages of the cure that corresponds to the most capacitive system indicating that the polymer has low dielectric loss (Bowen et al., 1997). Although conditions are adequate for alignment, the phase angle never reaches 90°, so losses are still present. Each set was exposed to the specific electric field for 3 h, then cured over night at room temperature in the presence of the electric field. The samples were stored at 100°C for 24 h with their electrodes short circuited prior to the measurements in order to remove the injected charges during the polarization and the trapped charges due to impurities.

The first two sets result in quasi 1–3 composites with different degree of structuring, while set 3 is a 0–3 composite poled while curing. The properties of the obtained composites are compared with those of the reference samples reported by Van den Ende et al. (2010). Those composites were processed at a fixed applied field of $E_{AC} = 1\text{ kV/mm}$ and $f = 4\text{ kHz}$, poled at 10 kV/mm at 100°C in a silicone oil bath for a

Table 1. Different combinations of AC and DC electric fields used for manufacturing of the composites. The AC field magnitudes are reported in peak–peak mode.

Set	E_{AC} (kV/mm)	f_{AC} (kHz)	E_{DC} (kV/mm)
Set 1	1	2	2
Set 2	0.1	2	2
Set 3	0	0	2

duration of 30 min. The microstructures of the samples were observed using a field emission-scanning electron microscope (FE-SEM) (JEOL, JSM-7500F) operated in backscattered electron mode. Samples sectioned parallel to the formed particle chains were embedded into a room temperature curing epoxy and polished with 1 μm diamond paste.

Measurement procedure

The dielectric constant of the composites were determined using the parallel plate capacitor method with an Agilent 4263B LCR meter (Japan) at 1 V and 1 kHz. The curing study of the epoxy polymer as a function of temperature was performed using a broadband spectrometer (Novocontrol) in conjunction with a Cryostat high temperature sample cell and an Agilent E4991A impedance analyzer at 1 V and 1 kHz. The piezoelectric coefficient, d_{33} , measurements were performed with a high precision PM300 Piezometer, Piezosystems, at 110 Hz and a static and dynamic force of 10 N and 0.25 N respectively. At least three samples of each composite were measured. Before performing the d_{33} measurements the samples were grounded with their electrodes shorted at 100°C for 24 h to remove any remaining effects of space charges.

Results and discussion

Microstructure of composites

Figure 2 shows scanning electron microscope images of 20% PZT-epoxy composites prepared by means of conventional method and in-situ structuring and poling as defined in Table 1.

In the random composites the PZT particles are homogeneously distributed in the epoxy matrix. The average particle size matches well with the result of particle size analysis. Chain-like structures along the direction of the electric field are formed during dielectrophoresis. The average orientation of the individual chains can be calculated in terms of \bar{P}_2 as

$$\bar{P}_2 = \frac{3}{2} \overline{\cos^2 \beta} - \frac{1}{2} \quad (1)$$

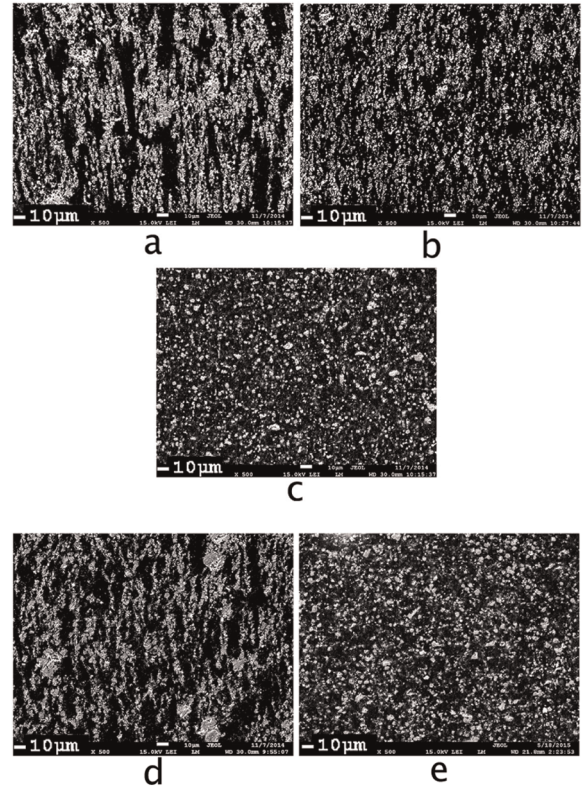


Figure 2. SEM micrographs of 20% PZT-epoxy composites prepared using conventional and in-situ techniques. (a) Set 1; (b) set 2; (c) set 3; (d) structured reference sample; (e) random reference sample.

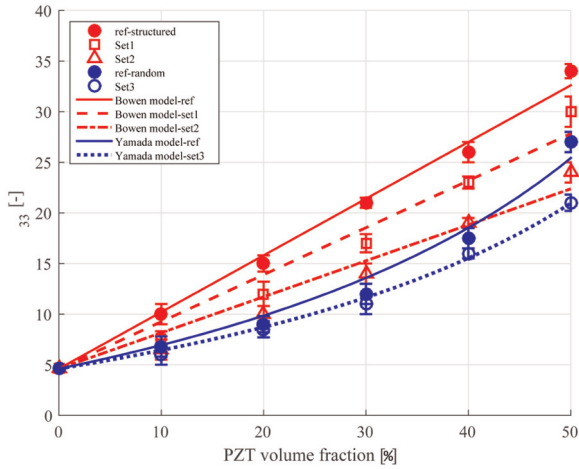
where β is the angle between the dominating dimension of the particle chain and the electric field (Spencer and Moore, 2001). Parameter \bar{P}_2 ranges between 0 for a random microstructure and 1 for a fully aligned situation. The \bar{P}_2 parameter calculated for set 1, set 2 and the reference structured composites are, 0.99, 0.91 and 0.94 respectively. The \bar{P}_2 for set 3 and the reference random composite are 0. A higher degree of orientation is observed for set 1 compared to set 2 as a result of larger driving force acting on the particles in response to a larger imposed electric field (Jones, 2005). The frequency of the electric field, dielectric properties of the matrix and ceramic particles and size of the particles were held constant. It can also be observed that the average chain length is larger for set 1 than for set 2 and the reference structured sample.

Electroactive properties

The dielectric properties of the composites are shown in Figure 3 for PZT volume fractions from 0% to 50%. The model proposed by Yamada et al. (1982) is used to describe the dielectric properties of the random composites.

Table 2. Properties of ceramic and polymer phases at 25°C.

Materials	ϵ at 1 kHz	d_{33} (pC/N)	Y (GPa)
PZT5A4	1850 ^a	460 ^a	70
Epoxy Epotek	4.6	0	1.7

^aMorgan Electro-Ceramics (2015).^bVan den Ende et al. (2010).**Figure 3.** The dielectric constant data for PZT-epoxy composites with their associated models.

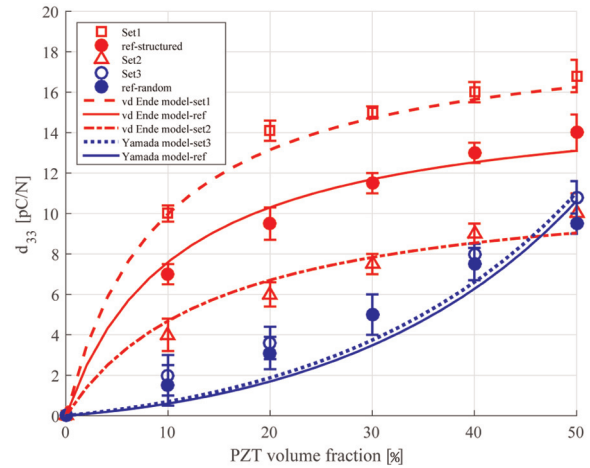
In this model the composite is assumed as a uniform distribution of ellipsoidal particles in an isotropic polymer matrix. The dielectric constant of the composite in the poling direction is given by

$$\epsilon_{\text{random}} = \epsilon_m \left(1 + \frac{n\phi(\epsilon_c - \epsilon_m)}{n\epsilon_m + (\epsilon_c - \epsilon_m)(1 - \phi)} \right) \quad (2)$$

where ϵ is the dielectric constant, and ϕ is the volume fraction of the ceramic phase. The subscripts c , m and random refer to the ceramic, polymer matrix and 0–3 composite properties, respectively and n is the inverse of the depolarization factor for an ellipsoidal particle in the direction of applied electric field. Dielectric properties of the structured composites are fitted to the model proposed by Bowen et al. (1998). In this model the composite contains particles aligned into chain-like structures along a specific direction separated by polymer gaps. The equation for the permittivity for such a composite is

$$\epsilon_{\text{structured}} = \phi_c \left(\frac{R\epsilon_c\epsilon_m}{\epsilon_c + R\epsilon_m} \right) + (1 - \phi_c)\epsilon_m \quad (3)$$

where $\epsilon_{\text{structured}}$ is the dielectric constant of dielectrophoretically structured 1–3 composites and R is the ratio of average particle size to the effective interparticle distance which influences the fraction of the applied electric field acting on the ceramic particles. The input

**Figure 4.** The d_{33} data for PZT-epoxy composites with their associated models.

parameters for both random and structured composite modeling are listed in Table 2. It is assumed that the piezoelectric properties of the particles are equal to the bulk ceramic values, as particle properties could not be measured directly.

The best fit of the experimental data to Yamada's model for both the reference random composite and the in-situ poled random composite was obtained for n is 4.4 which is an indication of particles having an aspect ratio of 1.3 that can be a close approximation to an equiaxed shape. The best fit of the experimental data to Bowen's model for the structured composites of set 1, set 2 and the reference structured sample, was obtained for R values of 11.41, 8.9 and 13 respectively.

The piezoelectric charge coefficients, d_{33} , of the composites are shown in Figure 4 where the experimentally observed d_{33} values of both structured and random composites are plotted in combination with the predictions of associated models. The experimental data for random composites are fitted to the Yamada model Yamada et al. (1982) as shown below. The piezoelectric charge constant, d_{33} , of the composite in the poling direction is given by

$$d_{33\text{random}} = \frac{\phi\alpha n\epsilon_{\text{random}}d_{33c}}{n\epsilon_{\text{random}} + \epsilon_c - \epsilon_{\text{random}}} \quad (4)$$

where α is the poling ratio of the ceramic particles and the other parameters were introduced earlier in equation (2). The analytical model proposed by Van den Ende et al. (2010) is used to describe the piezoelectric behavior of the structured composites. This model, as an extension of Bowen's model (1998), calculates the d_{33} of composites by modeling the particle-matrix alternations in the chains as two capacitors in series in the electrical domain and two springs in series in the mechanical domain. The equation for the d_{33} of a 1–3 composite is given by

Table 3. Comparison of electrical and dielectric properties of cured and uncured epoxy polymer at 1 kHz.

Polymer	Test T ($^{\circ}\text{C}$)	ρ (S/cm)	ϵ
Uncured epoxy	20	1.1×10^{-8}	12
Cured epoxy	100	8×10^{-10}	10.5

$$d_{33\text{structured}} = \frac{(1 + R)^2 \epsilon_m \phi_c d_{33c} Y_c}{\epsilon_c + R \epsilon_m [(1 + R \phi_c) Y_c + (1 - \phi_c) R Y_m]} \quad (5)$$

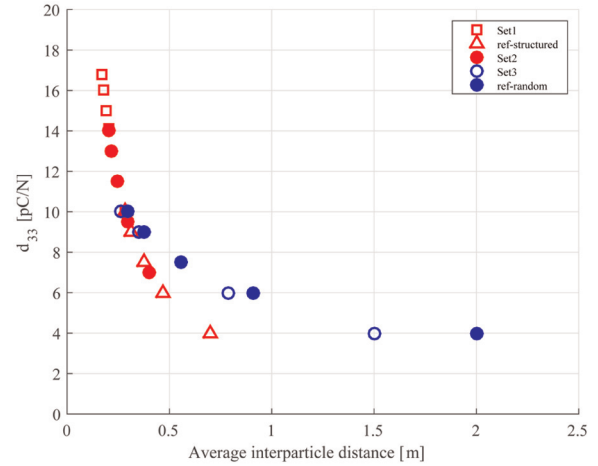
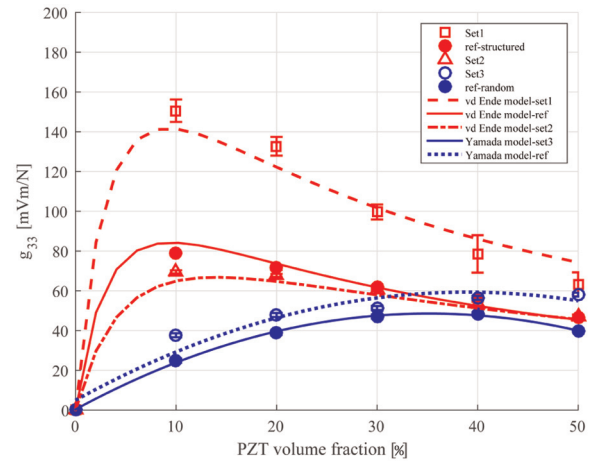
where Y_m and Y_c are elastic moduli of the polymer matrix and that of the ceramic in the direction of chains and R is the ratio of average particle size to the effective interparticle distance in the direction of electric field. The physical parameters for the constituent phases adopted in the theoretical calculations are listed in Table 2.

The best fit of the experimental d_{33} data to Yamada's model was obtained for α is 0.85 and 1 for the reference random composite and the in-situ poled random composite respectively. This is a clear indication of higher poling efficiency for the in-situ poled composites compared to the conventionally poled samples.

The electrical conductivity (ρ) and permittivity (ϵ) of a fully cured epoxy polymer is compared to that of an uncured epoxy in Table 3. The conductivity of the uncured epoxy measured at 20°C is more than an order of magnitude higher than that of the cured epoxy tested at 100°C which is the poling temperature in the conventional method Van den Ende et al. (2010). Higher permittivity of the uncured state also results in enhanced poling efficiency in the uncured matrix. Therefore poling the particulate composites at room temperature is possible at much lower electric fields while the polymer matrix is in the liquid state, possessing relatively high permittivity and electrical conductivity.

The best fit of the experimental data to Bowens's model for the structured composites of set 1, set 2 and the reference structured sample, was obtained for R values of 15.5, 8.1 and 12 respectively. The interparticle distances calculated based on the obtained R values and the measured average particle size, are $0.19 \mu\text{m}$, $0.37 \mu\text{m}$ and $0.28 \mu\text{m}$ for set 1, set 2 and the reference structured sample respectively. A higher degree of perfection during dielectrophoresis is realized for the chains formed in in-situ structured and poled samples, which can also be observed on the SEM microstructures in Figure 2.

The interparticle distance is an important parameter influencing the local electric field acting on the ceramic particles. The interparticle distances at each volume fraction have been estimated independently by fitting the model to the experimental data. The correlation between the d_{33} of the random and structured

**Figure 5.** The d_{33} as a function of interparticle distance for random and structured composites.**Figure 6.** The g_{33} data for PZT-epoxy composites.

composites and their respective average interparticle distance is shown in in Figure 5. The d_{33} values increase as the interparticle distance decreases. The slope seems to be much higher for the DEP structured composites.

The piezoelectric voltage coefficient, g_{33} , calculated by dividing the d_{33} of the composites by their dielectric constant are plotted as a function of PZT volume fraction in Figure 6. The maximum value obtained for the conventionally prepared random composite is 48 mVm/N at a PZT volume fraction of 40%, while for the in-situ poled random composite a maximum value of 58 mVm/N is obtained at a PZT volume fraction of 50%. All sets of structured composites show a comparable behavior as a function of PZT content. The d_{33} increment is higher than that of the dielectric constant, especially at lower volume fractions. Therefore, the voltage coefficient of these composites exhibits a maximum at the low volume fraction of 10% PZT. At higher volume fractions the derivative of d_{33} decreases rapidly to zero

while the derivative of ϵ is constant, so the properties of structured composites degrade rapidly. For the reference structured composite a maximum g_{33} value of 79 mVm/N is obtained. The in-situ structured and poled samples of set 1 and set 2, with high and low degree of chain perfection, show maximum g_{33} values of 151 mVm/N and 69 mVm/N at a PZT volume fraction of 10% respectively. The superior g_{33} values obtained for in-situ structured and poled samples are attributed to higher chain perfection degree and poling efficiency in these composites that lead to higher d_{33} compared to conventionally poled composites. The reason for the model predicting lower g_{33} values for set 1 than the experimentally obtained data is associated with the lower dielectric constant of these samples as a result of the presence of some air bubbles in the polymer matrix.

Conclusions

A significant improvement in piezoelectric properties of quasi 1–3 composites can be achieved via a combination of dielectrophoretic alignment of the ceramic particles and poling process simultaneously while the polymer matrix is still in the liquid state. This new processing route is practiced in a thermoset polymer system during curing while the polymer possesses relatively high permittivity as well as electrical conductivity as compared to a fully cured system. The proposed method offers new avenues in low cost manufacturing of composite pressure sensitive materials for demanding long-term sensor applications.

Declaration of conflicting interests

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