JOURNAL OF MATERIALS SCIENCE 39 (2004) 3105–3114

Piezoelectric paint: Ceramic-polymer composites for vibration sensors

J. R. WHITE*
School of Chemical Engineering & Advanced Materials, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
E-mail: jim.white@ncl.ac.uk

B. DE POUMEYROL, J. M. HALE, R. STEPHENSON
School of Mechanical & Systems Engineering, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK

A piezoelectric ceramic-polymer composite has been developed for use as a novel thick film strain sensor for vibration monitoring of structures. The material is in the form of a paint that can be applied to a wide range of substrates using conventional spraying equipment. The sensor properties depend on the morphology of the composite and on the electrodes that are used to couple it to the charge amplifier. Electrodes of various kinds have been tested. Interaction between the electrode and the piezoelectric paint sometimes occurs (for example, the organic vehicle for spray-coated electrodes may interact with the paint binder). The morphologies of the piezoelectric paint and of the electrode materials have been studied using light optical microscopy and scanning electron microscopy to investigate the effect of different compositions and of different processing conditions (e.g., paint mixing schedule). Preliminary work is reported on the characteristics of the piezoelectric particles and on the effect of heat treatment applied to anneal out defects produced by milling. X-ray analysis and particle size analysis have been used to characterize the changes that take place on heat treatment. X-ray diffractometry has also been used to follow the effect of poling on the paint sensors. At the present state of development, sensors made using the paint have a dynamic range of at least 40–4000 microstrain and a bandwidth of at least 1 Hz–2 kHz, and piezoelectric coefficient d_{31} of approximately 20 pC/N. The sensors are resistant to outdoor exposure and a successful field trial has been conducted. © *2004 Kluwer Academic Publishers*

---

1. Introduction

Piezoelectric ceramics are used as stress sensors and displacement actuators in a wide range of applications. This paper describes the development and characteristics of sprayable piezoelectric paints formed by mixing piezoelectric ceramic particles into an acrylic lacquer. Coatings prepared by spraying such materials onto a substrate can be used as strain-measuring sensors. They conform well to the substrate surface and they can be applied to curved surfaces. The substrate surface should be free from contaminants such as grease but need not be especially smooth. The coatings are deformable so that they follow the deformation of the substrate when it is stressed, giving a signal that is characteristic of the deformation.

The earliest reports concerning the preparation of piezoelectric paints were published by Newnham and co-workers [1, 2]. More recent contributions have been made by Egusa and Iwasawa [3–5] but their composites were based on epoxy resin binder requiring manual spreading, less convenient and less reproducible than a sprayed coating. It should be noted that many problems encountered with the application of piezoelectric paints are shared with other classes of ceramic-polymer ferroelectric composites (reviewed by Dias and Das Gupta [6]) and with thin film piezoelectric microelectromechanical systems (MEMS) (reviewed by Polla and Francis [7]). The first attempt to prepare a sprayable piezoelectric paint was described by Hale and Tuck [8].

The piezoelectric ceramic most commonly used is lead zirconate titanate (PZT). It can be prepared by standard ceramics processing routes, including the sol-gel method. The final step is normally a high temperature sintering operation that results in a polycrystalline monolith (wafer) with randomly oriented crystal domains. The piezoelectric properties follow from the noncentrosymmetric nature of the unit cell in which the body-centred Ti or Zi atom is displaced along the *c*-axis of the crystal. The contribution to the piezoelectric constant of a particular domain depends on the direction

---

*Author to whom all correspondence should be addressed.

the c-axis makes with the principal axes of the ceramic wafer, and also the direction of displacement of the centred atom (i.e., whether the resolved component is parallel or anti-parallel to the through-thickness direction of the wafer). The piezoelectric properties can then be enhanced by "poling," which involves the application of an electric field to alter the orientation distribution of noncentrosymmetric structural elements from random to textured. This can involve reversal of the polarity of domains oriented anti-parallel to the wafer axis or rotation through 90° for those in which the displacement is nearly transverse to the wafer axis. The overall effect depends on the fraction of domains that take up the most favoured polarization open to them and also on the crystal orientation distribution. The latter is fixed in a sintered ceramic wafer (and normally random) but might be altered to a more suitable texture by appropriate processing.

Although monolithic ceramic wafers find many applications both as sensors and as actuators they have some drawbacks. Firstly, they are brittle and have a quite limited deformability. This restricts their use as strain sensors to applications in which the strains to be measured are small and makes them prone to accidental damage. Secondly, they are difficult to attach to a structure in such a way that they deform conformally with it, so that they can act as deformation or vibration monitors. These problems have been addressed by the use of piezoelectric composite materials in the form of thick films. The commonest form consists of finely powdered piezoelectric ceramic particles, usually PZT, in a glass matrix [9]. This works well, but has the drawback that a high temperature cure is required to fuse the glass. This prevents the use of these materials on temperature sensitive substrates such as GRP and on large structures that cannot be placed in an oven. The alternative is to use an organic matrix that cures at ambient temperature by polymerization or crosslinking.

Such binders are tough and deformable and can be applied to structures using adhesives in much the same way as resistance strain gauges, for which the substrate surface must be prepared to a high level of cleanliness. The substrate often requires to be polished and degreased thoroughly before the strain gauge can be attached, an operation that is often very inconvenient in field applications. To obtain a signal from a resistance strain gauge, it should be aligned to a principal strain direction; if the strain field directionality is not known, a strain gauge rosette consisting of three strain gauges should be used, requiring three strain bridge amplifiers and signal processing channels. Since the piezoceramic particles are equiaxed, the composite material is isotropic, and the sensors are insensitive to the direction of in-plane strain, simplifying application, while experience indicates that signal wire attachment is somewhat simpler than with miniature strain gauges. Modifications to the geometry of piezoelectric composite sensors must be made if strain direction information is required; this is not addressed in the current paper.

The objective of the studies reported here was to develop a piezoelectric-polymer composite that can be deposited as a thick film in the form of a paint. It should be suitable for spraying onto a non-ideal surface (i.e., one that does not have to be perfectly smooth and flat) yet which will still form a high quality sensor suitable for vibration monitoring. The kind of application envisaged for such a sensor is in long term monitoring of the health of such structures as buildings, bridges, aerospace vehicles, land vehicles, electricity pylons and oil field derricks.

2. Materials and preparation of piezoelectric paint

2.1. General layout of a paint sensor

Before discussing the materials requirements for the sensors it is important to consider the general layout for a thick film sensor. This is shown in schematic form in Fig. 1. The substrate is the element for which the vibration analysis is required. If the substrate is non-conducting, a conductive electrode must be applied before the piezoelectric paint coating is applied (Fig. 1a). If the substrate is conductive, it may be used as the bottom electrode, and the active piezoelectric coating can be applied directly to it (Fig. 1b). An upper electrode has to be applied on top of the piezoelectric paint layer. Electrical connections are made by connecting single strand 150 μm wire or a slightly thicker multi-strand wire to the conductive layer using a silver-loaded epoxy adhesive (RS Components). It may be necessary to apply a protective coating over the whole assembly, to prevent water ingress, for example.

2.2. General material requirements

For shock and vibration measurement, sensors made from the paint should have a bandwidth (frequency range) covering 10–1000 Hz and a dynamic range (strain amplitude range) up to 10^{-3} (1000 microstrain). The requirements of a piezoelectric paint are thus summarised as follows:

(a) It must be capable of being sprayed using portable equipment;

(b) It must adhere to the structure (substrate) to which it is applied and for which the vibration characteristics are to be monitored;

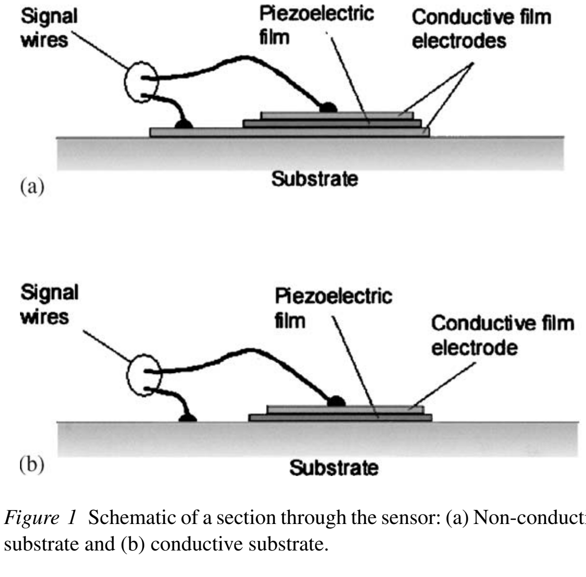

Figure 1 Schematic of a section through the sensor: (a) Non-conductive substrate and (b) conductive substrate.

(c) It must be deformable so that deformation caused by deformation of the substrate does not cause it to detach or crack;

(d) It must generate a piezoelectric charge sufficient to be measured using standard instrumentation;

(e) It must not contain significant residual stresses.

These requirements place limitations on the component parts in turn. Thus the piezoceramic (the active element that is included in the form of small particles within the polymer vehicle) has the following requirements:

(a) Small particle size to allow good sprayability, preferably less than 5 μm;

(b) Low tendency to aggregate in the paint mix, to retain good spraying properties and formation of an homogeneous film;

(c) Strong piezoelectric characteristics ($d_{33} \geq 300$ pC/N, $d_{31} \geq 10$ pC/N);

(d) One domain per particle (ideal—see later discussion).

For the polymer binder the following requirements can be listed:

(a) Good stress transfer to the piezoceramic (PZT) particles;

(b) Good adhesion to the substrate;

(c) Deformable;

(d) Suitable properties in dynamic loading;

(e) Electrically insulating.

For the polymer this implies that it should have a high Young's modulus ($\geq$1 GPa), low stress relaxation during the timescale of the measurement and low loss during dynamic loading.

These requirements have all been met to a greater or lesser extent in the programme upon which this paper is based. The formulation has been developed to a state where a very satisfactory sensor can be prepared fairly routinely, as described below, but it is believed that very significant improvements can be achieved as outlined in a later section.

2.3. PZT particles

The PZT particles used in this study were provided by Morgan Electro Ceramics Ltd. (Southampton). They were in the form of fine particles that were produced by ball milling and were similar to the commercial grade, PZT 5A. The particles as-received from the manufacturer were approximately micron-sized and roughly spherical (Fig. 2). Fig. 3 shows a particle size analysis. In many of the experimental formulations tested in

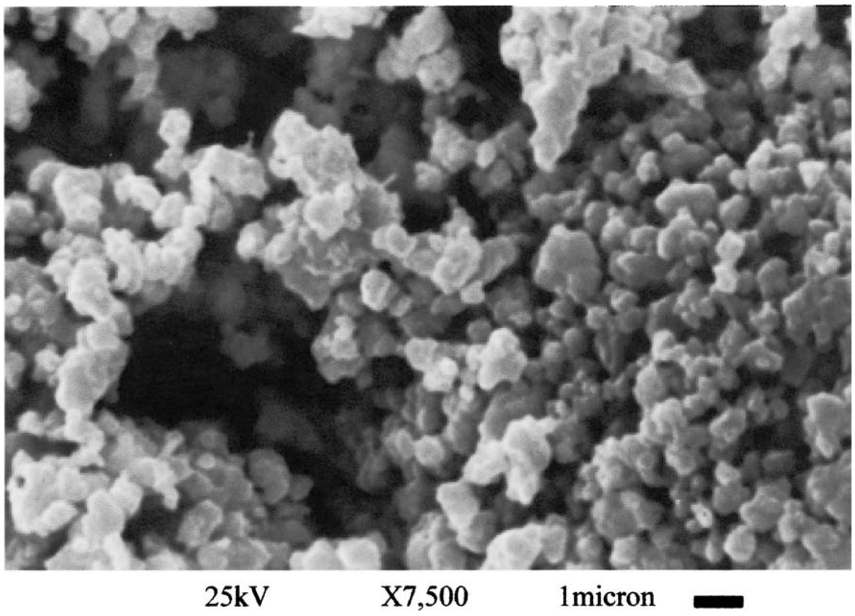

Figure 2 Scanning electron micrograph of PZT particles in the as-received state. The specimen was prepared by spreading the powder onto an adhesive patch on the SEM stub, then applying a sputtered gold coating.

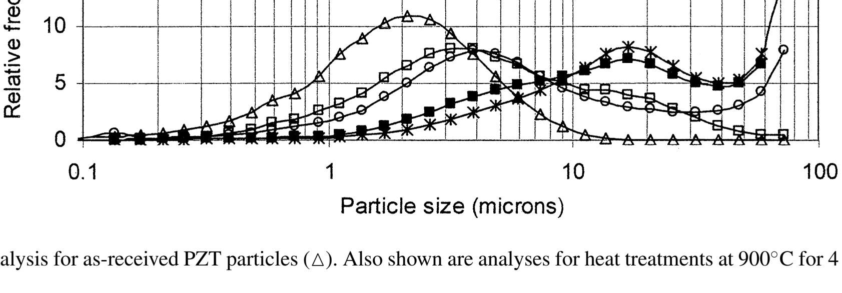

Figure 3 Particle size analysis for as-received PZT particles (△). Also shown are analyses for heat treatments at 900°C for 4 h (□), 10 h (o), 24 h (■) and 50 h (×).

this programme the particles were used in this state. For further study, some were modified by heat treatment (see Section 5). The results of the heat treatments on the particle size distribution are shown in Fig. 3 and will be discussed in Section 5. The particle size distributions were obtained using a Fritsch "Analysette 22" laser particle analyser and a Malvern Instruments laser-based "Mastersizer". The powder samples were dispersed in distilled water using an ultrasonic agitator prior to taking readings.

2.4. Polymer binder

Initial experiments [8] involved a solvent-based lacquer but it was always intended to switch to a non-solvent system for health and environmental concerns. After trials with a small number of different systems, the polymer binder chosen was a water-based acrylic produced by Rohm and Haas and supplied by Aquacryl (Borough Green, Kent). This lacquer is not available commercially.

2.5. Paint preparation

PZT powder-lacquer compositions with weight ratios lying between 1:1 and 4:1 have been tested. The most studied compositions have been those with PZT contents 50, 60, 70 and 80% by weight respectively. Most of the results reported here have been obtained on samples prepared with a weight ratio of PZT:lacquer of 7:3. Various mixing procedures and schedules have been tried, including dispersion using an ultrasonic bath. Trials were made with several types of mixer unit, including some home-made configurations powered by a power drill using a stirrer speed of 1300 rpm, giving a blade tip speed $\sim$2 m s^{-1}. Our current choice is a Silverson L4R High Shear Laboratory Mixer. If the stirring is too vigorous the temperature rises, accelerating polymerization of the binder. This is a quite critical part of the preparation procedure because of the conflict between conditions required to break up agglomerates and to avoid premature polymerization of the binder. For trouble-free spraying and high quality paint films it was found necessary to perform high shear mixing for half an hour prior to coating application. The mixture has a short shelf life; the PZT particles have a tendency to settle out and, possibly, to re-agglomerate. As well as breaking up agglomerates, high shear mixing has been found to be necessary to minimise voiding in the paints (possibly a phenomenon related to agglomeration). The paint mixes with lower PZT contents were found to be more prone to voiding, one of the main reasons for choosing the 70% by weight composition for extensive study. Higher PZT loadings were found to be difficult to handle.

2.6. Spray technique

The sprayability of the paint is one of its key features, but the development of a successful spraying procedure has required much experimentation. Experiments have been conducted using spraying assemblies based on an air-brush spray-head and on an in-house design of hydraulic pressurised spray head. The most successful system tested to date is a miniature DeVilbiss (Bournemouth, UK) 0.8 mm air-atomising spray gun operating at approximately 1.7 bar using a gravity feed paint cup. The coatings described in this paper were prepared using a hand-held spray gun 200 mm from the substrate and were 50–200 μm thick.

The paint is thixotropic under the spraying conditions used, giving an even thickness and smooth finish.

2.7. Application of electrodes

After applying the paint to the surface that is to be the subject of vibration monitoring, an electrode must be applied to the top surface so that the sensor can be connected to the appropriate signal conditioning equipment. In the first experiments, an evaporated gold layer was applied [8]. This was chosen because of its known excellent characteristics for this kind of application, but it is strictly a laboratory method and cannot be easily adapted to field use. When the substrate for which vibration monitoring is required is conductive, the substrate itself can be used as the lower electrode but when it is non-conducting (as in the case of a polymer composite, for example) it is necessary to apply a conductive coating onto it prior to the application of the piezoelectric paint layer. The piezoelectric paint layer is then sandwiched between two electrodes.

The electrodes used in most of the work conducted to date have been made using commercially available products (RS Components) in the form of a conductive nickel coating that has an air-drying acrylic resin binder, and a silver paint. The nickel coating is supplied in aerosol form and can cover complex shapes easily and quickly. It is touch-dry in 10–20 min but it is advisable to let it dry for up to 24 h to obtain full conductive capacity, and this was allowed in the studies reported here. The flexibility of the resulting coating is adequate for the current application. The silver paint has the advantage of containing smaller particles than is the case with the nickel spray, allowing a more homogeneous coating to be produced. It is touch-dry in approximately 10 min and ready to use after 30 min. One disadvantage with the silver paint is that it must be applied with a brush, giving a surface finish that is inevitably inferior to that of the sprayed nickel product. Although the piezoelectric paint has forgiving coating properties, and gives a good top surface when applied to a rough electrode, undulations in the surface of the lower electrode will cause thickness variations in the piezoelectric coating. A second disadvantage is that the adhesion of the silver paint to the substrates tested to date appears to be inferior to that of the nickel coatings and delamination has been found to occur on occasions. There is no particular disadvantage when using silver paint as the top electrode.

The nickel spray has been used to prepare electrodes on glass reinforced polyester and on poly(vinyl chloride) (PVC) surfaces. It has proved to be sufficiently flexible to perform well on these substrates, which are more deformable than the steel substrates used in earlier studies. There is evidence that the nickel coatings interact with the piezoelectric paint (see below), a problem that is particularly troublesome when they are used for the top electrode, and the silver paint is now the preferred option for this application.

2.8. Poling

To increase the piezoelectric coefficient it is necessary to pole the piezoelectric coating by applying a high electric field across the electrodes. This was done using a Brandenburg Model 475R Photomultiplier Power Supply (variable 0–2 kV). After testing the effect of a range of poling fields, the value chosen was 5-10 kV/mm. In PZT wafers, poling is often performed at elevated temperature (say 150°C) to improve efficiency. This is not an option for the paints used in the current work because of the thermal characteristics of the polymeric binder, and we chose to conduct poling at an elevated temperature of ~40–50°C, by placing a 150 W lamp close to the sensor while poling and using a non-contacting thermometer to check the temperature. Our preliminary results indicate that there is some advantage gained by adopting this procedure, and we plan to conduct a systematic study with a range of controlled temperatures in the future, preferably using a polymer binder with higher temperature capability. The poling field is normally applied for between 1 and 5 s. Much longer times, up to 1000 s, have also been tested but do not seem to produce further improvement.

3. Morphological characterization of the paint sensors

3.1. Sample preparation and techniques used

For general morphological assessment of the morphology of the paint and of the electrodes, sections were made for light optical microscopy observation. Sections through the sensors (as prepared on the substrates) were mounted in cold-curing resin and polished using a water-cooled polishing wheel with metallographic grinding paper grade P120, followed by waterproof silicon carbide papers, grades P220, P1200, P2500 and P4000 (five stages).

Scanning electron microscopy (SEM) was used for more detailed examination of the PZT powder. Samples were prepared either by spreading powder onto an adhesive patch on a SEM stub or by fracturing a coating to expose a section in which the PZT particles were dispersed. In either case a gold coating was applied by sputtering to minimise charging problems in the SEM.

X-ray analysis was used to follow the effects of annealing and/or poling on the PZT particles. Paint samples were attached to the sample holder of a Rowland circle diffractometer and scanned through a 2θ range of approximately 43–46° using Cu K_α radiation (wavelength ~ 0.1542 nm).

3.2. Morphology of paint and electrodes

Fig. 4 is a light optical micrograph of a polished section through a paint sensor applied to a steel shim substrate, with an upper electrode of aerosol-sprayed conductive nickel. It is evident that the top surface of the piezoelectric paint is not perfectly flat. It is believed that the polymer binder in the piezoelectric paint is softened by the solvent contained in the nickel coating mixture, and it is suspected that the undulations develop during the application of the electrode. It is also evident that the electrode top surface is even less flat. The homogeneity of the piezoelectric paint is very good. The homogeneity of the nickel coating is quite good, though the larger particles and particle size distribution make it rather less so than the piezoelectric paint. The combination of uneven thickness and large particles (some with diameter significantly greater than 10% of the electrode thickness) makes it likely that conductivity through the electrode will be very uneven across its surface. The morphologies of the piezoelectric paint and the nickel electrode, and the interaction between them, are also shown in Fig. 5, which shows a sensor made on a PVC surface, using nickel electrodes both top and bottom.

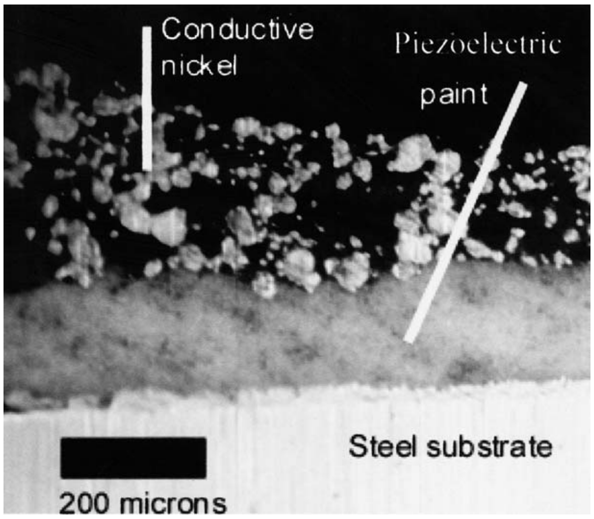

Figure 4 Section of a paint sensor on a steel shim substrate, showing also the conductive nickel electrode.

Fig. 6 shows the effect of using a brushed silver electrode instead of sprayed nickel. The silver paint has much smaller particles but has a much more uneven thickness. It is easy to see that pinholes would be likely with this material. The unevenness is not such a problem if the silver paint is used as the lower electrode, as noted above. The piezoelectric paint layer appears to have thinned in regions where the silver paint is thickest, as would be expected if the solvent for the silver paint binder attacked the binder in the piezoelectric paint. Thus this is a likely source of pinholes in the piezoelectric paint layer that, if present, would be expected to lead to electrical breakdown. It is worth remarking that some interaction between the PZT paint and the electrode is essential if the adhesion between the coatings is to be sufficient, but it seems possible that this could be achieved without the development of undulations at the interface that are as extensive as those observed here.

4. Paint testing and performance

4.1. Signal conditioning

The main component in the signal conditioning apparatus is the charge amplifier. In the experiments reported here a Kistler 5011 unit has been used. It has excellent linearity down to low frequencies (<1 Hz) and sensitivity ranges suitable for piezoelectric paint

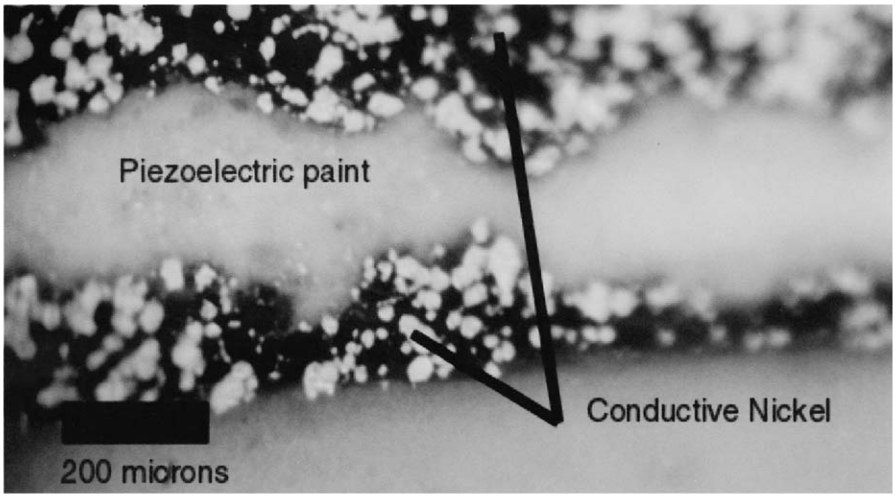

Figure 5 Section of a paint sensor on a PVC substrate, with conductive nickel electrodes both top and bottom.

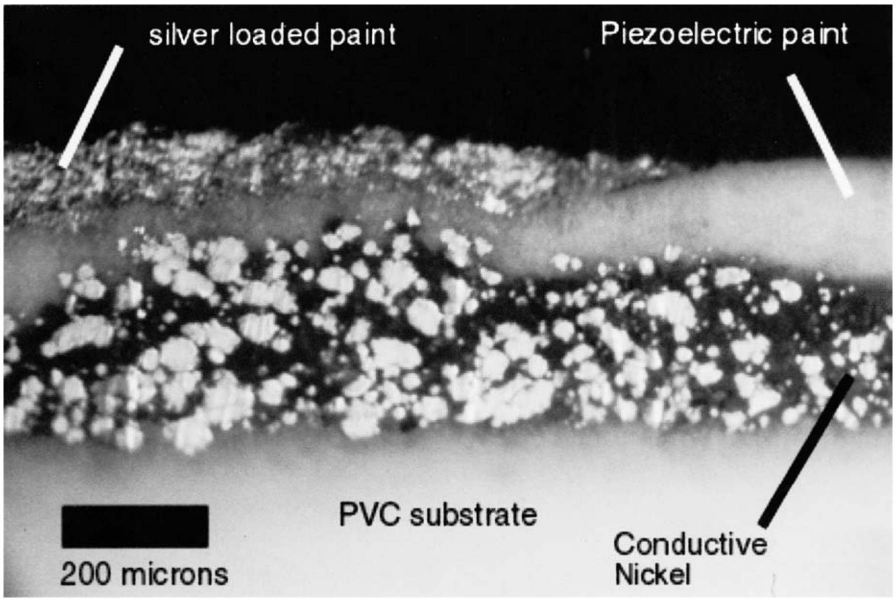

Figure 6 Section of a paint sensor on a PVC substrate, showing also the conductive silver (top) electrode.

sensors. Signals were recorded on a conventional digital oscilloscope.

4.2. Measurement of piezoelectric coefficient d_{31}

For structural vibration measurement, a piezoelectric sensor is used in the "31" mode, in which a charge is generated across the film thickness (the 3-direction) by a stress in the plane of the film (the 1-direction). It was thus desirable to measure the piezoelectric constant d_{31}, the charge per unit area in the 3-direction per unit stress in the plane of the film (1-direction), which is conventionally used to characterize piezoelectric sensor materials in this mode. Although it would be more appropriate to characterize the sensitivity of the sensor in terms of the charge generated by a given amount of strain, a sensitivity defined with reference to stress is required simply to afford comparison with other piezoelectric sensor materials.

Measurement of this quantity is difficult because of the need to know the in-plane stress in the film. To be a good sensor, it is necessary for the film to provide negligible reinforcement of the substrate, and the relatively soft polymer matrix facilitates this. The in-plane strain in the film is the same as the strain at the substrate surface and therefore the same as would be present in the absence of the sensor under the same loading conditions. The sensor deformation is strain controlled and the in-plane stress depends on the Young's modulus of the composite.

The strategy employed to measure d_{31} involved determining first the charge per unit area per unit strain. This was measured by mounting sensors on beams that were subjected to well-controlled bending. The bending strain in the outer fibres of the substrate was obtained directly from measurement of the applied deformation or was calculated from the corresponding applied force using simple bending beam theory. This strain was taken to be the strain in the paint layer applied to this surface. To convert this measured strain to stress, the value of Young's modulus for the paint was required. This was obtained by a separate tensile test on a free film prepared by spraying onto a PTFE substrate. The value of

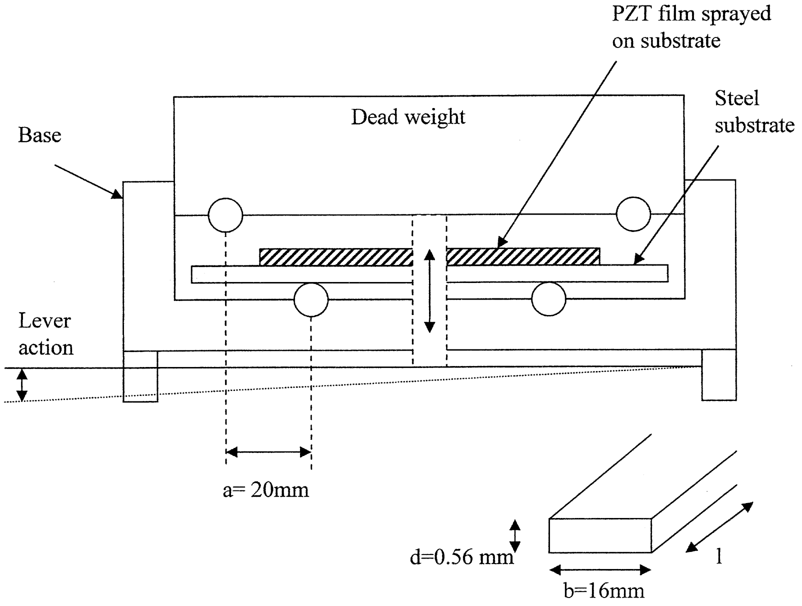

Figure 7 Bending rig for d_{31} measurement. The diagram shows the dead weight in the disengaged state. The lever is used to lower it onto the sample.

d_{31} was calculated from the charge measurement when a chosen strain was applied and the stress deduced from the Young's modulus.

The beam bending measurements were conducted in four point bending using a purpose-built rig (Fig. 7). The test piece was supported on two cylindrical anvils. A heavy bar carrying two more cylindrical anvils was suspended above it. The bar was placed in a guide frame that constrained it to move vertically so that loading was applied symmetrically when the moving anvils made contact with the test piece. A mechanism was provided to lower and raise the bar quickly but without shock. Dead weight loading was employed and no force measurement was required. For symmetrical 4-point loading, as employed here, the bending stress was uniform along the testpiece, and hence the strain and stress was uniform within the sensor film and so the sensor response was independent of position.

The substrates used were spring steel coupons 150 × 16 × 0.56 mm^3. The lower anvils were 120 mm apart and the upper pair 80 mm apart. The mass of the loading bar was 0.806 kg, giving a uniform bending moment of 79.1×10^{-3} Nm over the gauge length. These data were used to determine the strain in the film and hence the stress in the film (see Appendix 1).

The signal from the sensor was of the form shown in Fig. 8. Because of the nature of piezoelectrics and the time constant of the charge amplifier used, a step load input gives an impulse voltage output that decays over a few seconds to zero. Loading and unloading therefore give antisymmetric signals, as shown. On unloading, the assembly vibrates, and this is the source of the ringing observed in Fig. 8. On the other hand, on loading can be done rapidly: the sample is coupled to the loading mass, so that the system to which the sensor is attached has very much more inertia, and gives less ringing and much more reproducible signals.

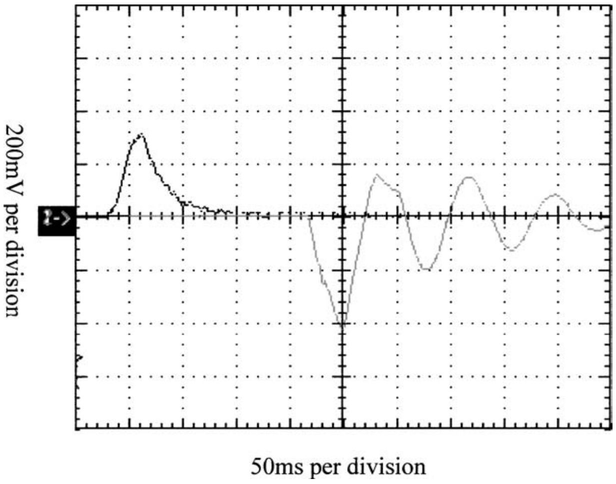

Figure 8 Sensor signals obtained using the d_{31} rig on loading (left hand side) and unloading (right hand side). Note the ringing obtained when unloading.

The values for d_{31} measured by this procedure varied according to the composition of the paint and any conditioning to which it was subjected (including outdoor weathering) as expected. The values for the standard composition, based on the as-received PZT particles, were usually around 20 pC/N. The value for d_{31} for sintered PZT ceramic wafers is of the order of 200 pC/N.

4.3. Measurement of dynamic characteristics of piezoelectric paint sensors

The characteristics of interest in a sensor for vibration measurements are bandwidth (useful frequency range) and dynamic range (useful range of strain amplitudes). These properties were measured for the same sensors as for the d_{31} tests described above, driven in first bending mode vibration. This work is fully described in a previous paper [10]. This showed a bandwidth of 1–2000 Hz and dynamic range of 40–4000 microstrain, which is adequate for most structural monitoring applications. The upper values of both frequency and strain given here were set by the limitations of the measuring techniques, not by the material, and it is likely that the ranges will be extended significantly when tests are made using equipment capable of more extreme measurement.

In order to prove the practical potential of this material, trials were arranged on a new engineering structure (see Appendix 2).

4.4. Weathering characteristics

Preliminary investigations of the weatherability of the sensors have been made by exposing samples on the roof of one of the buildings at the University of Newcastle upon Tyne. They are placed on racks in different locations, with different degrees of shelter from the sun and rain. This is an on-going programme of testing, which involves also laboratory conditioning in aggressive environments, and the results will be published at a later date. At the present time it is sufficient to report that none of the sensors have failed as a result of 12 months exposure outdoors. There has been some change in d_{31}, which has increased somewhat in most cases. This mimics some measurements on samples exposed to water in the laboratory that will be reported separately.

5. Refinement of piezoelectric paint

5.1. PZT particles

The PZT particles as used in this study are normally used as the basis of sintered ceramic parts. Sintering is conducted at high temperatures (>1000°C), required to facilitate the diffusion-controlled processes that are involved in fusing the particles together to form the monolithic sintered structure. This level of atomic mobility will also permit localised defect healing and changes in crystal habit if thermodynamically favoured. Therefore the state of the crystal domains in the sintered ceramic may be quite different from that in the particles used as the active element in the paints that are the subject of this paper. This may place some limitation on the piezoelectric response of the particles and therefore on the paint itself. Fig. 9 shows X-ray diffractometer traces taken from a selection of paints made up using PZT samples with different thermo-mechanical histories. The 2θ range displayed in Fig. 9 includes that in which the 200 and 002 reflections of tetragonal PZT (at ~45° and ~44° respectively) and the 200 reflection of rhombohedral PZT (at ~44.5°) are found. Results for the sintered material, supplied in the form of wafers 200 μm thick, are also shown. It is seen to be predominantly tetragonal, with the 200 peak much stronger than the 002, as expected because of the 200/020 degeneracy in the tetragonal structure, in which the c-direction corresponds to the direction of displacement of the body-centred atom and the charge displacement. The 002 reflection is relatively much stronger in the raw powder though the large breadth of the low angle peak suggests that there may be some rhombohedral material present. The development of a significant rhombohedral component is clear in the sample that was heat treated at 900°C for 5 h whereas 930°C for 24 h produced a significant shift towards the structure found in the sintered wafer,

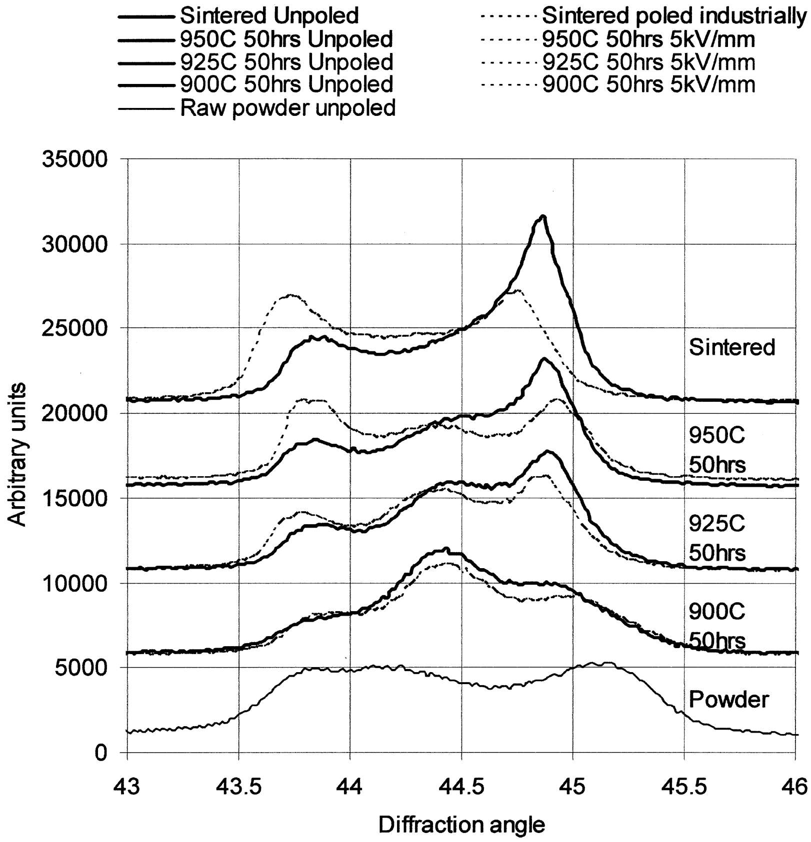

Figure 9 X-ray diffractograms obtained using Cu K_α radiation ($\lambda = 0.1542$ nm) with paints made from PZT in the following forms: (a) as-received ball-milled PZT-5A powder; PZT-5A heat treated for 50 h at (b) 900°C, (c) 925°C, (d) 950°C. Results for a sintered PZT-5A wafer (as provided by Morgan Electroceramics) are also shown. The effect of poling is also shown.

with the 200 and 002 tetragonal peaks clearly resolved and a smaller yet easily recognised rhombohedral peak in between. Even though at these temperatures there is no sign of sintering in the normally accepted sense, the heat treatments produced significant increases in particle size (Fig. 3). The extent of particle size growth was not sufficient to prevent the powders from being sprayed and forming homogeneous coatings with the desired piezoelectric characteristics. It seems likely that the benefits from the reduction in structural defects produced by heat treatment outweighs the disadvantages caused by an increase in particle size and work continues to try to determine the optimal conditions.

The effect of poling can also be followed by X-ray diffraction. Fig. 10 compares a poled PZT-5A wafer with and the as-sintered wafer, confirming that the effect is to produce preferred orientation with (001) tetragonal domains forming preferentially at the expense of (100) oriented domains. This effect can also be seen in the paints, for which the results for poled samples are also shown in Fig. 9.

The X-ray peaks become sharper on annealing (Fig. 9) confirming that annealing has either increased the crystallite size or reduced distortion, or both. If the X-ray line broadening is attributed to the small crystal size effect rather than distortion, the average crystal diameter, L, can be estimated from the Scherrer equation [11]:

$$L = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where K is the Scherrer constant (≈ 1), λ is the X-ray wavelength ($= 0.1542$ nm), B is the line breadth at half peak height (in radians), and θ is the Bragg angle of the peak. For the sharpest peaks (as obtained with the sintered polymer) this leads to an average crystal diameter of approximately 30–40 nm, much smaller than the particle size in the milled samples. It is therefore deduced that there are many domains per particle in the milled powders. Ideally, each particle would have a single domain and, in a coating formed from the paint, the [001] axis of this domain would be oriented normal to the substrate surface for each particle. It is evident that at the current stage of development the paint is far from reaching this ideal; there is therefore much scope to further improve the sensitivity.

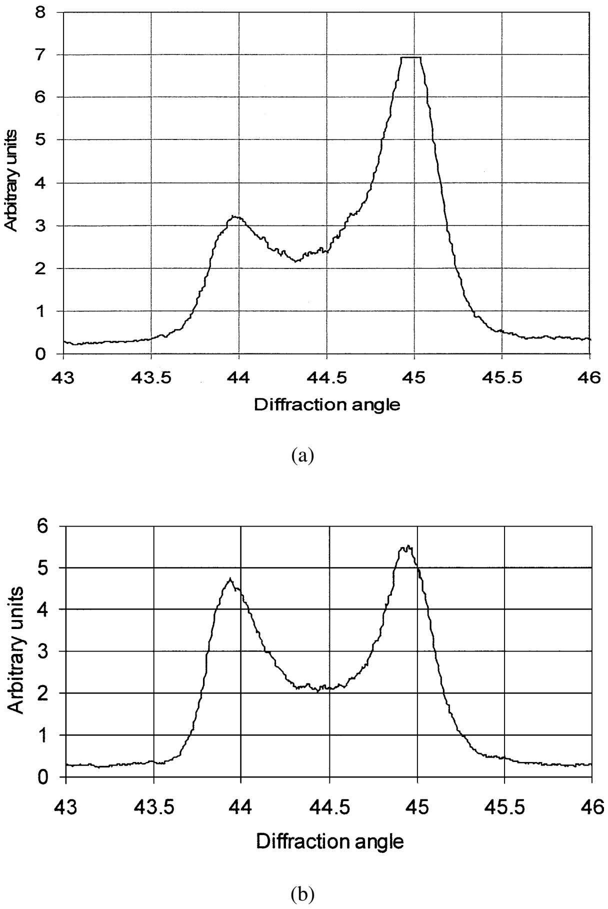

Figure 10 X-ray diffractograms obtained using Cu K_α radiation ($\lambda = 0.1542$ nm) with sintered PZT-5A wafers: (a) before poling and (b) after poling at 60°C for 1 s.

5.2. Polymer binder

Apart from the move from solvent-based lacquers to water-based ones, no attempt has been made to identify polymer binders with improved performance. The lacquer used in the study described above was selected for its rheological properties only. Future plans include experimenting with polymers with higher modulus (to improve stress transfer and therefore to increase the overall value of d_{31} of the paint) and polymers with a higher temperature capability. The latter property is desirable not only because it would permit a higher operating temperature but also because it would permit a higher poling temperature.

6. Conclusions

A viable coating system with piezoelectric properties has been developed for use as a sensor for vibration monitoring. It is suitable for use on surfaces that do not have to be flat or exceptionally smooth. Tests have shown that the dynamic range is at least 40–4000 microstrain and the bandwidth is at least 1 Hz–2 kHz. Measurements have not been made outside of these ranges in the "31" mode and it is expected that sensors based on this paint will have a much broader bandwidth and significantly greater dynamic range. The sensors show promising resistance to outdoor exposure. There are good prospects for making sensors with substantial improvements in the properties and in environmental resistance by judicious choice of materials and processing procedures.

Acknowledgements

The studies described in this paper were supported by a research grant from EPSRC. Morgan Electroceramics are acknowledged for providing PZT materials, for conducting heat treatments and particle size analyses. We are especially indebted to M Thomas and M Williams for making these arrangements and for valuable discussions. Valuable advice, and samples of lacquer, were provided by Aquacryl (J Parker).

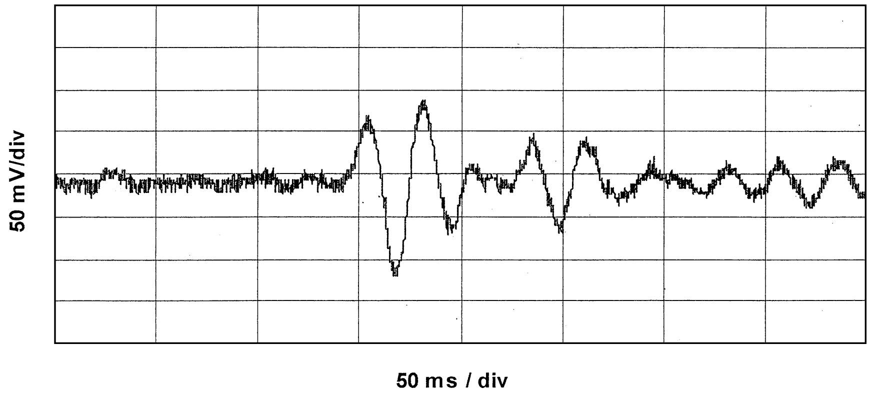

Figure A1 Signal obtained when a pedestrian used the walkway adjacent to the sensor. No other persons were moving on the bridge in the vicinity of the sensor at the time.

Appendix 1: Measurement of d_{31}

The piezoelectric coefficient d_{31} is defined as follows:

$$d_{31} = (\text{short circuit charge per unit area of electrode})/(\text{applied stress}) \qquad \text{(A1)}$$

This is because the electrode effectively defines the area of the sensor. The units normally employed are pC/N.

The charge generated when the sensor is loaded is measured using the charge amplifier and divided by the electrode area to obtain the numerator in Equation A1. The applied strain in the sensor is equal to the strain at the surface of the substrate when the load is applied. In the d_{31} test rig this is easily obtained from the bending moment applied to the test strip and the dimensions of the substrate. To convert this to the stress in the sensor, the Young's modulus of the sensor is required. This was obtained using tensile tests of free-standing films obtained by spraying onto poly(tetrafluoroethylene) (PTFE) substrates and peeling off. The films prepared in this manner were fragile and broke at low load, preventing accurate measurement of their load-deformation behaviour. The value deduced from these measurements was therefore subject to a quite large error: 300 MPa ± 20%.

Because the coating is constrained by the substrate the elastic properties of both substrate and coating must be taken into account when determining the deformation and stresses in the coating. This leads to a factor $(1 - \upsilon_f)/(1 - \upsilon_s)$ where υ_f and υ_s are the Poisson's ratios for the film and substrate respectively. If the Poisson's ratios of the film and substrate are equal, this factor is unity, and it has been neglected in the calculations conducted to date. The Poisson's ratio for the composite will have an upper bound of 0.5 (the value for rubber) but for heavily pigmented materials such as those studied here the value of Poisson's ratio is commonly much closer to 0.3 and therefore close to that of the substrate. It is therefore considered that the major source of error in the measurements of d_{31} made to date result from the uncertainty in the Young's modulus ($\sim \pm 20\%$).

Appendix 2: Field performance

We are fortunate in having been afforded the opportunity to test the piezoelectric paint sensors on a large structure, the Gateshead Millennium Bridge, which has a deck divided for use by pedestrians and cyclists. It spans the River Tyne between Gateshead and Newcastle, and is designed to tilt so that the curved deck forms an arch across the river to allow ships to pass. The bridge is coated with an epoxy-based paint that we were not permitted to remove to expose the steel structure. We were allowed access to the bridge during the installation and commissioning period and installed a sensor on the upstand between the walkway and the cycleway. An enclosure for the sensor and the associated circuitry was used to provide protection from direct exposure to the weather, but no special attempt was made to make to waterproof it or to seal it to the bridge. The sensitivity of the sensor can be gauged by the response to a pedestrian walking across the bridge near to the installation, shown in Fig. A1. The sensor is experimental, and is not part of the regular monitoring and inspection protocol for the bridge, but we were given access to check it one year after installation and found that it was still operating soundly.

References

1. K. A. KLEIN, A. SAFARI, R. E. NEWNHAM and J. RUNT, in Proc. IEEE 6th Int. Symp on Applied Ferroelectrics (ISAF-86), Pennsylvania (1986) p. 285.
2. *Idem.*, *Ferroelectrics* **100** (1989) 255.
3. S. EGUSA and N. IWASAWA, *J. Mater. Sci.* **28** (1993) 1667.
4. *Idem.*, *J. Reinf. Plast. Compos.* **15** (1996) 806.
5. *Idem.*, *Smart Mater. Struct.* **7** (1998) 438.
6. C. J. DIAS and D. K. DAS-GUPTA, *IEEE Trans. Dielectr. Electr. Insul.* **3** (1996) 706.
7. D. L. POLLA and L. F. FRANCIS, *Ann. Rev. Mater. Sci.* **28** (1998) 563.
8. J. M. HALE and J. TUCK, *Proc. I. MechE J. Mech. Eng. Sci.* **C213**(6) (1999) 613.
9. N. M. WHITE and J. D. TURNER, *Measurement Sci. Tech.* **8** (1997) 1.
10. B. DE POUMEYROL, J. R. WHITE, R. STEPHENSON and J. M. HALE, in Proc. Ferroelectrics 2001Conf., Sheffield, April 2001.
11. D. CAMPBELL, R. A. PETHRICK and J. R. WHITE, Polymer Characterization, Stanley Thornes, Cheltenham (2000).

Received 25 February 2003
and accepted 28 January 2004