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Piezoelectric paints: preparation and application as built-in vibration sensors of structural materials

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Piezoelectric paints were prepared using lead zirconate titanate (PZT) ceramic powder as a pigment and epoxy resin as a binder. The obtained paints were spread on the surface of an aluminium beam and cured at room temperature, thus forming the final thin films having thicknesses of 35–81 μm and PZT volume fractions of 25%–53%. The thin films were then poled under electric fields of up to 350 kV cm^{-1} at room temperature, and the resulting piezoelectric activity was evaluated from vibration measurements on the aluminium beam. Although not strictly quantitative, the piezoelectric activity of the thin film showed a tendency to increase with an increase in the film thickness and the PZT volume fraction. From the standpoint of the thin film application as built-in vibration sensors, the piezoelectric activity was confirmed to be high enough to determine the natural frequencies and mode shapes of the aluminium beam.

1. Introduction

Piezoelectric materials have become increasingly important as sensors and actuators in their applications to the emerging technology of intelligent material systems and structures [1–7]. In such applications, piezoelectric sensors and actuators are embedded within some host materials or bonded to the material surface, thus imparting the vibration sensing and control capabilities to the conventional host materials. Usually, piezoelectric materials such as lead zirconate titanate (PZT) ceramics and polyvinylidene fluoride (PVDF) films are used for this purpose.

Piezoelectric paints spread on the surface of structural materials may also be used as a built-in vibration sensor, if such paints are successfully prepared. The advantages of such a paint sensor over the PZT and PVDF sensors will be the capability of large-area coverage and the applicability to any surface shape of structural materials. The absence of a bonding layer of adhesives between the sensor and the structural materials may be another advantage of the paint sensor from a viewpoint of sensors integrated into structural materials.

The principle that piezoelectric paints can, indeed, be prepared has already been demonstrated by Hanner *et al.* [8]. At present, however, no study has been reported on the application of such paints as built-in vibration sensors of structural materials. In the present work, we tried to prepare piezoelectric paints whose piezoelectric activity is high enough for vibration sensor applications. The paints were prepared using PZT ceramic powder as a pigment and epoxy resin as a binder. The obtained paints were spread on the surface of aluminium beams and cured at room temperature. The final thin films were then poled under electric fields of up to 350 kV cm^{-1} at room temperature, thus making the thin films piezoelectrically active.

The present paper mainly describes the effects of the film thickness and the PZT volume fraction on the piezoelectric activity, and, also the applicability of the piezoelectric paints as built-in vibration sensors capable of determining the natural frequencies and mode shapes of structural materials.

2. Experimental procedure

2.1. Preparation of paints

Epoxy resin Epikoto 1001 (diglycidyl ether of bisphenol A with an average molecular weight of ~ 1000) was obtained from Yuka Shell Epoxy K. K. PZT ceramic powder PE-60A was obtained from Fuji Titanium Industry Co. Ltd. A prescribed amount of the PZT powder was added to a 30 wt % epoxy solution in xylene, and was stirred for 30 min in a Red Devil paint shaker. To this epoxy solution, polyamide as epoxy hardener was added with stirring in such a way that the ratio of the active hydrogen of the hardener to the epoxide group of the epoxy resin was 1 : 1 by mole.

The paint thus obtained was spread with a paint brush on one surface of a 3 mm thick aluminium beam

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of 30 mm width and 500 mm length, and was dried in air at room temperature for at least 3 days. Then the surface of the final thin film was polished lightly with sandpaper. The thickness of the film was measured with a Fisherscope Multi-650C of Helmut Fischer GmbH and Co.

2.2 Poling and vibration measurements

Electrodes and leads were printed on the thin film using a Mitani MEC-4000 screen printer, a screen mask with a pattern shown in Fig. 1, and Fujikura XA-208 silver paint as printing ink. The electrodes and leads thus printed were cured at 150 °C for 30 min. The thin film was then poled using the printed electrodes as the first electrode and the aluminium beam as the second electrode. The poling was carried out in air at room temperature with a Fluke 415B high-voltage power supply.

The piezoelectric activity of the thin film was evaluated from vibration measurements on the aluminium beam with a strain gauge bonded to the opposite side of the beam. The vibration measurements were performed using the experimental apparatus shown schematically in Fig. 2. The clamped portion of the beam was electrically insulated using 3M 5413 Kapton film tape. A periodic noise signal generated by a Hewlett-Packard 3582A dual-channel FFT analyser was used to drive a Brüel and Kjær 4809 exciter. The strain-gauge signal and the thin-film signal were connected to the input channels A and B of the FFT analyser, respectively. Data thus obtained were transmitted from the FFT analyser to a personal computer over the HP-IB (IEEE-488) bus. Then, the transfer function from the strain-gauge signal to the thin-film signal was computed so as to refer to the ratio of the charge per unit film area to the strain developed along the beam direction. The ratio thus determined was taken as the piezoelectric activity of the thin film.

3. Results and discussion

3.1. Determination procedure of piezoelectric activity

A typical example of the vibration measurement for piezoelectric activity determination is shown in Fig. 3 for a 75 μm thick film having a PZT volume fraction of 53%. This thin film was poled at 200 kV cm^{-1} for 30 min using the printed electrode 3 (Fig. 1). In this figure, the frequency spectrum of the thin-film signal is

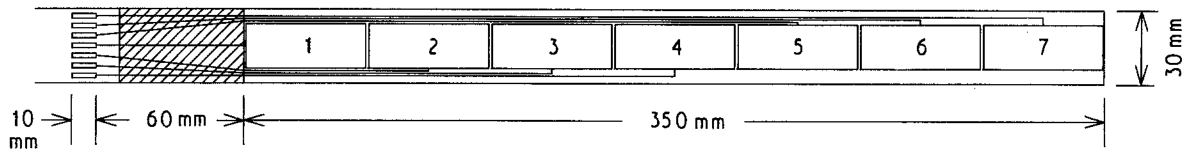

Figure 1 Configuration of silver ink electrodes and leads printed on the piezoelectric thin film formed on an aluminium beam of 30 mm width, 500 mm length, and 3 mm thickness. The length and width of each electrode are 49 and 18 mm, respectively, and the width of the leads is 0.5 mm. The shaded area represents a portion which is wrapped in an electrically insulating material. The aluminium beam is clamped at this portion in vibration measurements.

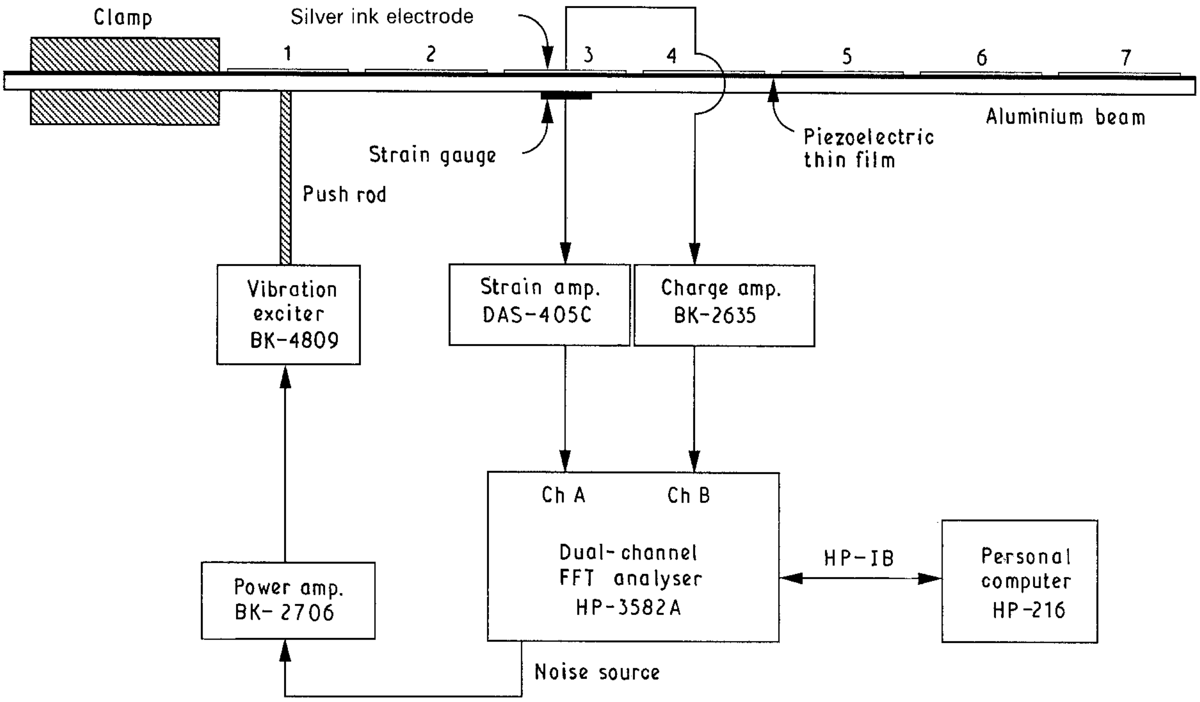

Figure 2 Experimental apparatus for evaluating the piezoelectric activity of the thin film formed on one surface of an aluminium beam.

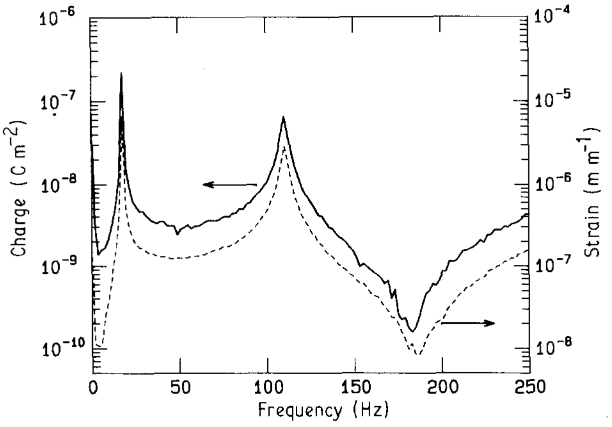

Figure 3 Frequency spectra of vibration signals from (—) a piezoelectric thin film formed on one surface of an aluminium beam, and (···) a strain gauge bonded to the opposite side of the beam. See the text for the preparation formula of this film and the poling conditions.

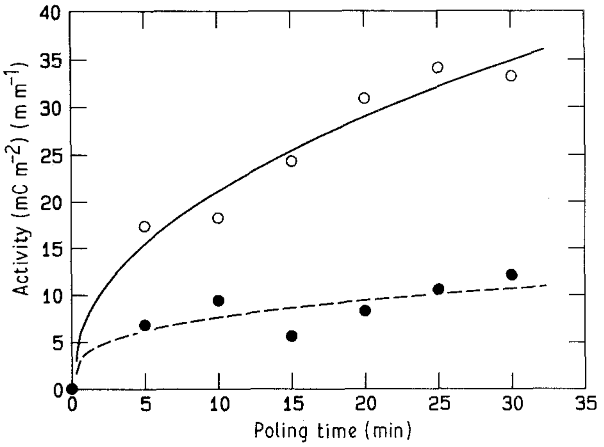

Figure 4 Plot of the piezoelectric activity after poling at (○) 200 and (●) 133 kV cm^{-1} against the poling time for a 75 μm thick film having a PZT volume fraction of 53%.

scaled so as to refer to the amount of charge per unit film area. It is seen that the frequency spectra of the charge signal and the strain signal include the first two natural frequencies at 18 and 112 Hz in the frequency range 0–250 Hz. It is also seen that the spectrum shapes for the charge and strain signals are similar to each other, thus indicating that the transfer function from the strain signal to the charge signal is independent of frequency, at least in this frequency range. In the present work, the piezoelectric activity of the thin film was determined from the magnitude of the transfer function at the first natural frequency.

The piezoelectric activity thus determined is plotted in Fig. 4 as a function of the poling time for a 75 μm thick film having a PZT volume fraction of 53%. This thin film was poled at electric fields of 133 and 200 kV cm^{-1} using the printed electrode 3 (Fig. 1). The piezoelectric activity is seen to increase steadily with increasing poling time for both electric fields. At 200 kV cm^{-1} in particular, the piezoelectric activity appears to continue increasing even after the poling time of 30 min, thus indicating that a duration of 30 min is insufficient to achieve a saturation poling of the thin film. This observation is compatible with the experimental results of Furukawa *et al.* [9] that although pure PZT ceramics undergo the complete polarization reversal almost instantaneously, PZT particles dispersed in a polymer matrix take more than 3 h to reach an equilibrium state of the polarization reversal even at the poling temperature of 100 °C.

Fig. 4 shows that the piezoelectric activity increases with an increase in the poling field, thus giving an expectation that a poling field higher than 200 kV cm^{-1} leads to a further increase in the piezoelectric activity. Increasing the poling field, however, was ultimately limited by dielectric breakdown of the thin film. In the present work, for this reason, the evaluation of piezoelectric activity of a thin film was made by a procedure similar to that described by Hanner *et al.* [8]. We applied the poling voltage stepwise with an increment of 0.1 kV, and allowed the thin film to remain at a particular voltage for 5 min. Then the vibration measurement for piezoelectric activity determination was carried out, followed by the 0.1 kV increase in the poling voltage. This procedure was repeated until the poling voltage was reached at the dielectric breakdown strength of the thin film. Unless otherwise noted in the text, the piezoelectric activity evaluation was made using the printed electrode 3 (see Fig. 1).

It should be pointed out here that a duration of 5 min at each poling voltage is perhaps insufficient to achieve an equilibrium state of poling, as seen from the plot of piezoelectric activity against poling time in Fig. 4. The piezoelectric activity evaluated by the above-mentioned procedure, therefore, is merely a rough estimate and should be used for qualitative purposes only.

3.2. Effect of film thickness

The effect of film thickness on the piezoelectric activity was studied for thin films having thicknesses of 81, 49, and 35 μm. The PZT volume fraction was 53% for all of these films. The maximum poling field applied without causing dielectric breakdown was approximately 290, 290, and 340 kV cm^{-1} for the 81, 49, and 35 μm thick films, respectively, thus suggesting that the film thickness has essentially no influence on the dielectric breakdown strength of the thin film.

The piezoelectric activity of the thin film is plotted in Fig. 5 as a function of poling field. It is seen that the piezoelectric activity increases steadily with increasing poling field for all the thin films. It is also seen that dielectric breakdown always occurs before the piezoelectric activity reaches a saturation value. Comparison of the 81, 49, and 35 μm thick films, on the other hand, shows that the piezoelectric activity at each poling field increases with an increase in the film thickness. In this connection, it should be noted that the total time spent in poling until dielectric breakdown occurred was 115, 70, and 60 min for these

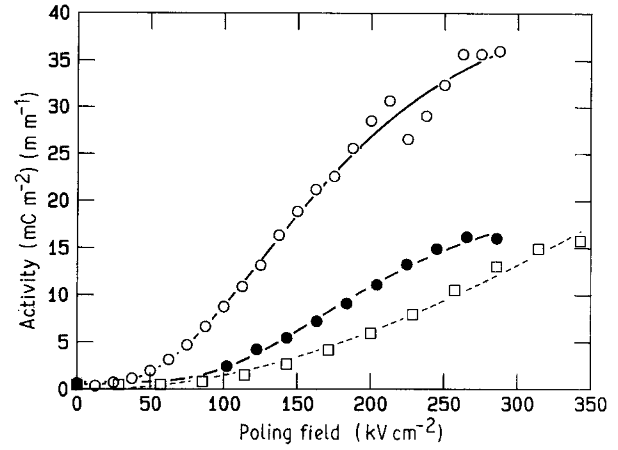

Figure 5 Plot of the piezoelectric activity against the poling field for thin films having thicknesses of (○) 81, (●) 49 and (□) 35 μm. The PZT volume fraction is 53% for all of these films. See the text for the poling conditions.

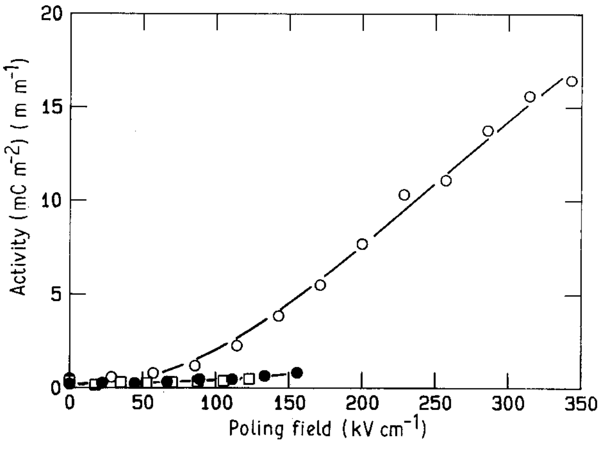

Figure 6 Plot of the piezoelectric activity against the poling field for thin films having PZT volume fractions of (○) 53%, (●) 35% and (□) 30%. See the text for the thickness of these films and the poling conditions.

films, respectively. Then it is possible that this difference in the total poling time is responsible, at least in part, for the film-thickness dependence of the piezoelectric activity in Fig. 5. It is also possible that such a film-thickness dependence is inherently associated with inhomogeneous microstructure of the thin film made up of PZT particles and epoxy resin. At present, however, no evidence supporting these speculations is available. Further studies are therefore required for a detailed discussion of this point.

3.3. Effect of PZT volume fraction

The effect of PZT volume fraction, V_{PZT}, on the piezoelectric activity was studied for thin films having V_{PZT} values of 53%, 35%, 30%, and 25%. The thickness of these films was 35, 45, 37, and 53 μm, respectively. The maximum poling field applied without causing dielectric breakdown was approximately 340, 160, 120, and 60 kV cm^{-1} for V_{PZT} values of 53%, 35%, 30%, and 25%, respectively, thus showing a marked tendency for the dielectric breakdown strength of the thin film to increase with an increase in the PZT volume fraction.

The piezoelectric activity of the thin film is plotted in Fig. 6 as a function of poling field for the thin films having V_{PZT} values of 53%, 35%, and 30%. It is seen that the maximum piezoelectric activity obtained just before dielectric breakdown is quite low for V_{PZT} values of 35% and 30% compared with a V_{PZT} of 53%, thus strongly suggesting that a thin film having a low V_{PZT} value is hardly poled under the present poling conditions.

Fig. 7 is a scanning electron micrograph showing the transverse microstructure of a thin film having a PZT volume fraction of 53%. It is seen that the size of PZT particles ranges from ~ 0.5 to ~ 1.5 μm. It is also seen that a major fraction of the PZT particles is in contact with each other in such a way that the PZT phase is practically self-connected in three dimensions [10]. For thin films having PZT volume fractions lower than 35%, on the other hand, the scanning electron micrographs showed that the PZT particles are isolated from one another by the continuous phase of epoxy resin. According to the calculation results given by Sa-Gong *et al.* [11], the electric field acting on such isolated PZT particles is reduced to as low as about 1/100 of the externally applied electric field, as a result of much lower dielectric constants of polymers compared to PZT. Accordingly the low piezoelectric activity for the thin films having PZT volume fractions lower than 35% (Fig. 6) is most likely ascribed to a significantly reduced electric field in the PZT particles during the poling.

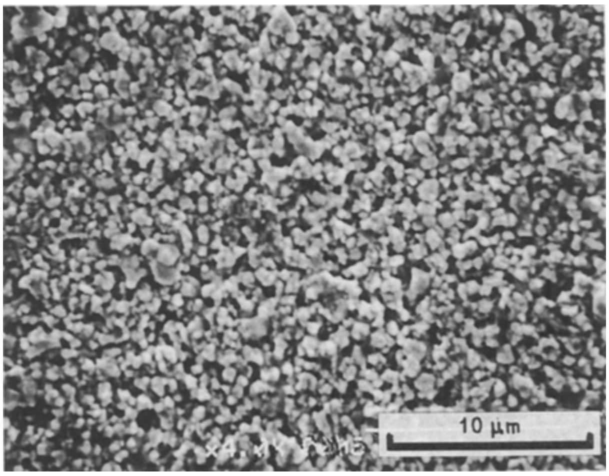

Figure 7 Scanning electron micrograph showing the transverse microstructure of a 75 μm thick film having a PZT volume fraction of 53%.

For the thin film having a PZT volume fraction of 53%, on the other hand, Fig. 7 shows that a major fraction of the PZT particles is in contact with each other, thus forming a continuous chain of PZT particles reaching from one electrode to the other. According to the experimental results of Furukawa *et al.* [9], such a chain of PZT particles appears to be poled much more easily compared with PZT particles isolated from one another, thus leading to the high piezoelectric activity for the thin film having a PZT volume fraction of 53% (Fig. 6). It will be reasonable to conclude, therefore, that the effect of PZT volume fraction on the piezoelectric activity should be interpreted primarily in terms of the connectivity of the PZT phase in the thin film.

3.4. Application as built-in vibration sensors

As one application of the piezoelectric paints prepared here, we tried to determine the vibration mode shapes of a cantilever beam using a piezoelectric thin film formed on the beam surface. Electrodes and leads were printed on the thin film in exactly the same way as described in the experimental section. The thin film was then poled under identical poling conditions for all the printed electrodes, 1–7 (Fig. 1). The sensitivity of the thin film as a vibration sensor was determined in exactly the same way as described above for the piezoelectric activity of the thin film. The experimental apparatus and procedures for vibration measurements were essentially the same as shown in Fig. 2, except that a Brüel and Kjær 8001 force transducer was used instead of a strain gauge. The force transducer was fixed between the vibration exciter and the aluminium beam, and was connected to the input channel A of the FFT analyser.

The determination of vibration mode shapes of a cantilever beam was tried by using a 46 μm thick film having a PZT volume fraction of 53%. This thin film was poled at 170 kV cm^{-1} for 30 min, resulting in a sensitivity of 9.0 (mC m^{-2})/(m m^{-1}) as a vibration sensor. A set of transfer function measurements were carried out for the printed electrodes 1–7, with an identical excitation force applied at a point of the electrode 1 (see Figs 1 and 2). The measured transfer function from the force-transducer signal to the thin-film signal was computed so as to refer to the ratio of the strain at each electrode to the excitation force. Then, the modal strain shapes of the cantilever beam were obtained by the so-called quadrature response method [12], i.e. by plotting the imaginary part of the strain-to-force ratio against the distance from the clamped end of the beam to the centre of each electrode. The modal strain shapes thus obtained are shown in Fig. 8 for the first three modes at 18, 112 and 315 Hz.

The transverse displacement of a uniform cantilever beam, ϕ, can be calculated by double integration of the following equation with respect to the longitudinal coordinate of the beam, x

$$\mathrm{d}^2\phi/\mathrm{d}x^2 = -\varepsilon/\eta \qquad (1)$$

where ε is the strain at the beam surface and η is the half-thickness of the beam [13]. The numerical integration of the strain data shown in Fig. 8, however, was found not to yield reliable results for the modal displacement shapes, especially for higher modes.

In the present work, for this reason, we assume the following equation as the modal displacement-shape function, $\phi(x)$

$$\begin{aligned}\phi(x) &= A_1\cos(\lambda x/L) + A_2\cosh(\lambda x/L)\\ &\quad + A_3\sin(\lambda x/L) + A_4\sinh(\lambda x/L) \qquad (2)\end{aligned}$$

where A_1, A_2, A_3, A_4 and λ are constants for each mode, and L is the length of the beam [14]. Double differentiation of this equation by x and substitution of the result into Equation 1 gives the following equation as the modal strain-shape function, $\varepsilon(x)$

$$\begin{aligned}\varepsilon(x) &= \eta(\lambda/L)^2[A_1\cos(\lambda x/L) - A_2\cosh(\lambda x/L)\\ &\quad + A_3\sin(\lambda x/L) - A_4\sinh(\lambda x/L)] \qquad (3)\end{aligned}$$

This equation is fitted to the strain data in Fig. 8 by using the non-linear least squares method referred to as the Marquardt method, thus giving the numerical values of A_1, A_2, A_3, A_4 and λ for each mode. These numerical values are then used to calculate the modal displacement shapes from Equation 2.

The modal displacement shapes thus determined are shown in Fig. 9 by the solid, broken, and dotted curves for the first, second, and third modes of the

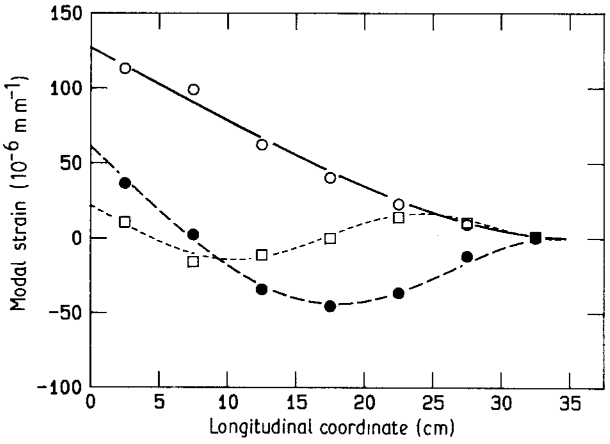

Figure 8 Modal strain shapes of a cantilever beam for the (○) first (18 Hz), (●) second (112 Hz) and (□) third (315 Hz) modes determined by a piezoelectric thin film formed on the beam surface. See the text for the preparation formula of this film and the poling conditions. (—, - - -, ···) The results of fitting Equation 3 to the data points ○, ● and □, respectively (see text).

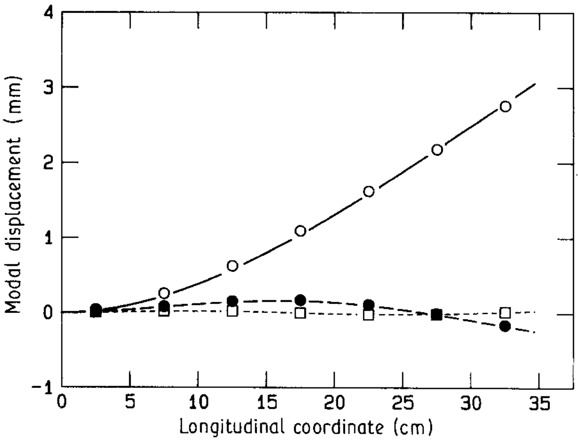

Figure 9 Modal displacement shapes of a cantilever beam for the (—) first (18 Hz), (- - - -) second (112 Hz) and (···) third (315 Hz) modes determined by a piezoelectric thin film formed on the beam surface. See the text for the calculation procedures of these shapes. (○, ●, □) The modal displacements for the first three modes determined by a laser Doppler vibrometer.

cantilever beam, respectively. In this figure, the corresponding modal displacements determined by a Graphtec AT3100 laser Doppler vibrometer are also shown. It is seen that the modal displacements determined by a piezoelectric thin film and a laser Doppler vibrometer agree closely with each other for each mode, thus demonstrating that the piezoelectric thin film prepared here is quite promising as a built-in vibration modal sensor.

4. Conclusion

The present work has shown that a paint made up of PZT ceramic powder and epoxy resin forms a thin film whose piezoelectric activity is high enough for vibration sensor applications. Although not strictly quantitative, the piezoelectric activity was shown to have a tendency to increase with an increase in the film thickness and the PZT volume fraction. It was also demonstrated that the piezoelectric thin film is quite promising as a built-in vibration sensor capable of determining the natural frequencies and mode shapes of structural materials.

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References

1. N. W. HAGOOD, E. F. CRAWLEY, J. de LUIS and E. H. ANDERSON, in "Proceedings of the Smart Materials, Structures, and Mathematical Issues", edited by C. A. Rogers (Technomic, Lancaster, 1989) p. 80.
2. S. HANAGUD, M. W. OBAL and A. G. CALISE, *ibid.*, p. 69.
3. E. F. CRAWLEY and E. H. ANDERSON, *J. Intell. Mater. Syst. Struct.* **1** (1990) 4.
4. R. IKEGAMI, D. G. WILSON, J. R. ANDERSON and G. J. JULIEN, *ibid.* **1** (1990) 189.
5. E. GARCIA and D. J. INMAN, *ibid.* **1** (1990) 261.
6. S. POH and A. BAZ, *ibid.* **1** (1990) 273.
7. C. R. FULLER, G. P. GIBBS and R. J. SILCOX, *ibid.* **1** (1990) 235.
8. K. A. HANNER, A. SAFARI, R. E. NEWNHAM and J. RUNT, *Ferroelectrics* **100** (1989) 255.
9. T. FURUKAWA, K. SUZUKI and M. DATE, *ibid.* **68** (1986) 33.
10. R. E. NEWNHAM, L. J. BOWEN, K. A. KLICKER and L. E. CROSS, *Mater. Eng.* **2** (1980) 93.
11. G. SA-GONG, A. SAFARI, S. J. JANG and R. E. NEWNHAM, *Ferroelect. Lett.* **5** (1986) 131.
12. D. L. BROWN, R. J. ALLEMANG, R. ZIMMERMAN and M. MERGEAY, SAE Technical Paper Series 790221 (1979).
13. S. H. CRANDALL, N. C. DAHL and T. J. LARDNER, in "An Introduction to the Mechanics of Solids" (McGraw-Hill, New York, 1972) p. 628.
14. R. D. BLEVINS, in "Formulas for Natural Frequency and Mode Shape" (Krieger, Malabar, FL, 1979) p. 492.

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