JOURNAL OF MATERIALS SCIENCE 39 (2004) 6079– 6081 LETTERS

Effect of exposure of piezoelectric paint to water and salt solution

P. N. RAPTIS[†], R. STEPHENSON[‡,§], J. M. HALE[‡], J. R. WHITE[*,§]
[‡] *School of Mechanical and Systems Engineering and* [§] *School of Chemical Engineering and Advanced Materials,*
University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
E-mail: jim.white@ncl.ac.uk

A sprayable piezoelectric paint consisting of piezoelectric particles in an acrylic binder has been developed for vibration monitoring of engineering structures [1]. Many outdoor applications are projected and it is important to know how these novel sensors behave when exposed to rain and other potentially hazardous environmental agents. Natural weathering trials have indicated that prolonged service life can be achieved outdoors [2]. In the experiments reported here, piezoelectric paint sensors were submerged in water for various periods of time up to 24 hr, then removed from the immersion bath and allowed to dry completely. The change in the piezoelectric constant, a measure of sensitivity, was monitored as a function of time during drying out. Additional experiments were conducted using a potassium iodide solution instead of water.

The sensors consisted of lead zirconate-titanate (PZT) particles in an acrylic lacquer [1]. The PZT particles were of the order of 1 μm in diameter and were mixed into the lacquer to form a sprayable paint [1]. The specimens used for the experiments described here were 50–100 μm thick and were prepared by spraying the paint onto thin steel substrates, allowing it to dry for 24 hr, then applying a nickel coating using a proprietary aerosol spray. The nickel formed the upper electrode while the substrate was used as the lower electrode (Fig. 1). Electrical contacts were made to the electrodes using a conductive adhesive. More details of this and of the mixing, spraying, and poling procedures, are given elsewhere [1]. The sensors used in the experiments reported here were aged at room temperature for several months before commencing the exposures to water or salt solution, and can be considered to have reached an equilibrium water level for ambient air prior to commencement of the trials. A poling field of 5–10 kV/mm was applied to sensitize the coating [1].

For each sample, the piezoelectric constant was measured prior to exposure to the environmental trial. This was done using a purpose-built four-point bending jig that bends the sample (substrate plus sensor coating) by the rapid application of a dead-weight load [1]. The output from the sensor was measured by a charge amplifier and recorded by a digital oscilloscope as a millivolt signal. The sensor was a located on the central constant curvature, which was a part of the specimen when the 4-point bending was applied. For this geometry, the piezoelectric constant that determines the size of the signal measured is:

$$d_{31} = \text{(charge per unit area)/(applied stress)}$$

The first subscript “3” indicates the direction of charge displacement measured (which in this case is the through-thickness direction) and the second subscript “1” indicates the direction in which the stress (strain) is applied (parallel to the surface of the sensor here). The piezoelectric constant used by the sensor industry to characterize the sensitivity of monolithic piezoceramic wafers is measured in units of Coulomb/Newton (C/N). To convert the data obtained by the procedure outlined above into this form requires a knowledge of Young’s modulus of the sensor [1]. It is difficult to measure this accurately, but absolute values of d_{31} are not required in order to compare the effects of the conditioning treatments investigated here. Instead, the results have been normalized in terms of the potential recorded for the sensor prior to submerging it in the environmental bath when the standard load was applied in the bending rig. This potential V_0 was of the order of 200 mV, and by normalizing it in this way, the effect of the variations due to differences in sample thickness and other causes are minimized. Thus the results are expressed in terms of $v = V(t)/V_0$, where $V(t)$ is the voltage measured from the time at the termination of a conditioning exposure (time of removal of the specimen from the conditioning bath). Although the control of spraying and testing conditions was not very refined, the range of values for V_0 in the series of samples used in the experiments described here was 150–250 mV with average 190 mV and standard deviation 29 mV.

The trials were conducted as follows. Sensitivity of the sensor was measured and recorded as the initial voltage V_0 . Then the sensor was submerged in deionized water or potassium iodide (KI) solution (3.5% by weight) for a selected period of time, then removed, drained, placed in the bend test rig, and connected to the charge amplifier. Attempts to record a signal within the first few minutes of removal from the conditioning bath failed, the monitoring equipment showing “overload,” indicating a low resistance across the sensor, effectively causing a short circuit between the electrodes. Measurements were made every minute or so until a successful reading was recorded. The time which elapsed while removing the specimen from the conditioning bath and

---

[*] Author to whom all correspondence should be addressed.

0022–2461

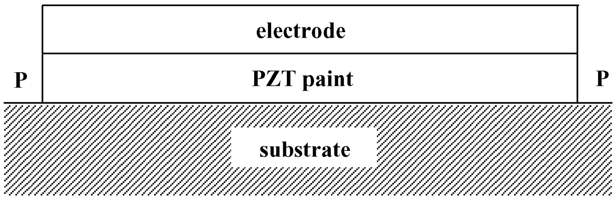

Figure 1 Schematic of piezoelectric paint assembly.

the first successful reading varied from test to test, typically 10–20 min. Longer conditioning times generally required a longer drying out time. Once measurements were possible, readings were taken periodically for a further 30–60 min. The first voltage recorded during the post-conditioning period was significantly higher than V_0 , then the voltage decayed progressively until, at the end of the measurement period, it had fallen to a value close to V_0 and appeared to have stabilized. An example is given in Fig. 2 for a sample in which the specimen was immersed in water for one hour (curve A). V fell almost linearly with time over the 20 min measurement period. On close inspection of the data it is noted that the curve is slightly concave. Similar data are shown in Fig. 2 for a second sample, after immersion for three hours (curve B). The values of V_0 for the samples used for Fig. 2 were 250 mV (A) and 200 mV (B). Some drying out tests were conducted for a prolonged period, which showed that the sensitivity remained almost unchanged once this state had been reached. Sometimes the final value was slightly below V_0 .

When this procedure was followed using KI solution instead of water in the conditioning bath, the first voltage values recorded during drying out were higher than those recorded when deionized water was used (Fig. 3, curve C: this sample had $V_0 = 250$ mV). Curve B for water immersion has been copied in Fig. 3 from Fig. 2 for comparison. Figs B and C were both obtained after 3 hr immersions.

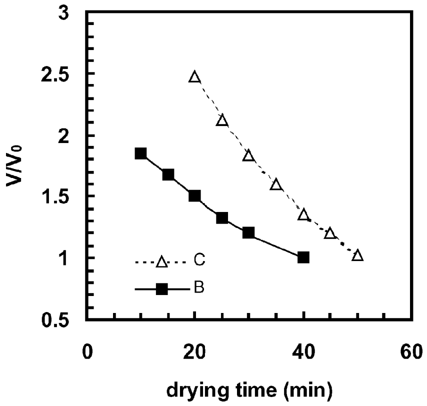

Figure 3 Voltage versus drying time characteristics after immersion for 3 hr in KI (C); and in water (B).

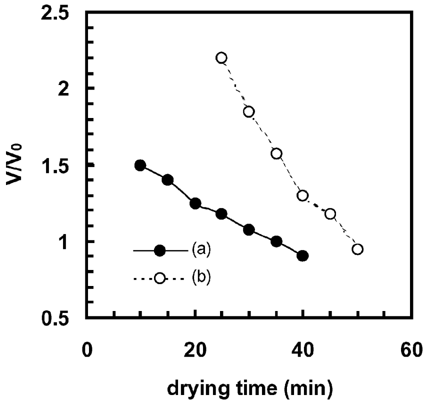

Figure 4 Voltage versus drying time characteristics for a sample first immersed in water for 3 hr then dried out (a) then immersed in KI and dried out again (b).

Some samples were immersed in water, dried out, then immersed in KI and dried out again after the chosen immersion period. Fig. 4 shows the result obtained with a sample that was immersed in water for 3 hr, tested during the subsequent drying out period, then immersed for 3 hr in KI. The piezoelectric sensitivity was measured again during the second drying out period. It is evident that the results obtained with KI show greater sensitivity. The same was true when immersion in KI was performed first, followed by water (Fig. 5). This experiment shows that the most recent immersion fluid had the major controlling influence over the behavior of the sample.

The average ratio of the initial reading to the corresponding V_0 value was approximately 1.7 after a first immersion in water and approximately 2.2 after

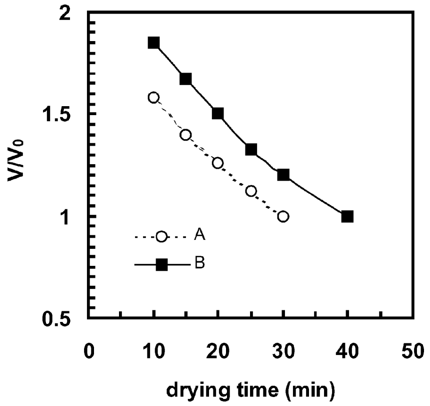

Figure 2 Voltage versus drying time characteristics after immersion in water for A: 1 hr; B: 3 hr.

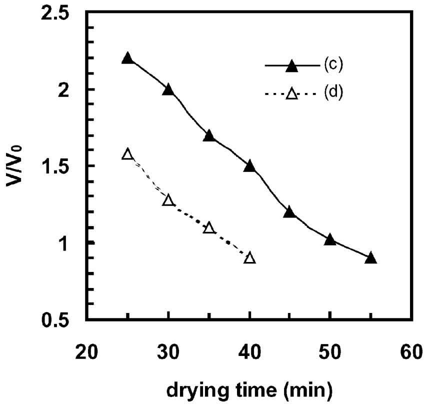

Figure 5 Voltage versus drying time characteristics for a sample first immersed in KI for 3 hr then dried out (c) then immersed in water and dried out again (d).

a first immersion in KI solution. These averages are for a range of immersion periods. There was no marked tendency for the ratio to be higher for the longer immersion periods. It is apparent that ionic conductivity produced by the penetrant enhanced the measured signal, even though a high impedance charge amplifier was employed to measure it. The conductivity of the dielectric is not normally considered when piezoelectric signals are analyzed and this appears to be a new phenomenon that, on one hand, may lead to irreproducibility of measurement, and on the other hand, might lead to the development of enhanced sensitivity if properly understood and controlled.

The data were subjected to further analysis in an attempt to identify the physical mechanism responsible for these observations. Plots were made of V versus $t^{1/2}$ (where t = drying time) for selected experiments. A straight line plot would be consistent with a diffusion-controlled process and might relate to ingress or escape of the penetrant. It is noted in passing that water and KI solution are likely to enter the piezoelectric coating through the edges PP (Fig. 1) rather than through the top surface because the electrode is believed to be relatively impermeable, especially for the relatively short immersion times used here. Although the plots were reasonably linear, it was impossible to confirm whether they were any more linear than the corresponding V versus t plots because of the rather short timespan of the data sets. Similarly, plots of $\log(V - V_0)$ versus t, were not significantly more linear than the other plots tested. This is the relationship which would be obtained if a first order relaxation process dominated the behavior, for which:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -K(V - V_0)$$

This behavior might be expected if a penetrant with limited mobility (say potassium or iodine ions) were to drift in a preferred direction, controlled by molecular relaxation in the surrounding polymer matrix, and accumulate at one of the electrodes.

Therefore at present it is not known what controls the enhanced sensitivity observed in the immersed sensors and further studies of this phenomenon are required.

In conclusion, vibration sensors made from piezoelectric paint that had been immersed in water or KI solution were found to recover functionality after a period of drying out. The initial sensitivity was greater than that prior to immersion and the enhancement was greater when KI solution was used instead of water.

Acknowledgments

The studies described in this paper were supported by a research grant from EPSRC. Morgan Electroceramics are acknowledged for providing PZT materials.

References

1. J. R. WHITE, B. DE POUMEYROL, J. M. HALE and R. STEPHENSON. *J. Mater. Sci.* in press.
2. J. M. HALE, J. R. WHITE, R. STEPHENSON and F. LIU, Submitted for publication.

Received 5 April
and accepted 30 April 2004