# *Rapid Method for Preparing Polymeric Piezoelectric Films*

## INTRODUCTION

To date, the best polymeric material for preparation of piezoelectric films is poly(vinylidene fluoride) ($PVF_2$). The conventional method for preparing piezoelectric films is comprised of (1) orienting the film by uniaxial stretching at elevated temperature, (2) electroding the film by vacuum metallization, and (3) poling the film with a high dc electric field at elevated temperature followed by cooling with the dc potential maintained across the film. Piezoelectric activity increases up to a point as the degree of stretching is increased during film processing[1]; further, increasing the poling electric field strength and duration of poling also enhances piezoelectric activity within limits. However, the maximum electric field strength that can be applied during poling is dependent upon the dielectric breakdown strength of the film at the poling temperature and freedom of the film from defects. Experience at the Southwest Research Institute with the conventional poling method indicates that dielectric failure occurs frequently, even when the applied electric field is well below the reported dielectric strength of the film, especially during prolonged exposure.

Southgate[2] developed a room temperature poling procedure for producing pyroelectric films from $PVF_2$, and others have reported successful use of similar procedures for preparation of piezoelectric films. In this room temperature procedure, an electrode on one side of the film is grounded while the other side is exposed for a few seconds to a high-voltage dc corona discharge from a point source about 1 cm from the film. This procedure was adapted by the authors to a rapid method of preparing piezoelectric film samples for laboratory studies, and a parametric study of the process was conducted.

## EXPERIMENTAL

$PVF_2$ film, identified as Kureha KF 50, was purchased from Kureha Chemical Industry Company, Ltd.; this unoriented film was 50 $\mu$m thick. $PVF_2$ film, 150 $\mu$m thick, was obtained from Westlake Plastics Co., silver powder was supplied by E. I. duPont de Nemours and Co. and acrylic multipolymer (GMS 378) was obtained from the Rohm and Haas Co.

### Preparation of Conductive Paint

The special electrically conductive paint used as the electrode material was prepared by dispersing 18.0 g of silver powder in 2.5 g of acrylic multipolymer and diluting the mixture with butyl acetate to obtain a sprayable consistency. The degree of dilution required depends upon the type of spray gun and air pressure used; in this work, an air brush operated at about 140 kPa (20 psi) air pressure was utilized.

### Preparation of Piezoelectric Films

Samples of 50-$\mu$m thick $PVF_2$ film were stretched 3.6–4.0 times original length at 130°C and then allowed to cool to room temperature (25°C) under tension. The degree of stretching was determined by measuring the distance between two marks which were 1 cm apart on the unstretched film; this measurement was made after tension had been relieved and the film had relaxed.

A 25.4 × 25.4-mm conductive paint electrode was sprayed on one side of the stretched film using a mask to prevent overspray and to produce uniform electrode size. The relaxed film was then corona poled by placing the electroded side against a grounded plate and applying a high dc voltage to a pinpoint placed about 0.9 cm above the film. Generally, the poling voltage was applied for 30 sec, although shorter times appeared to be satisfactory. Poling temperatures ranging from 25 to 150°C were used. After corona poling, a second electrode was sprayed on the unelectroded side using the previously described technique; prior to spraying, the mask was located so that the second electrode was aligned with the first one.

Commercial conductive paint preparations produced electrode layers which were stiff enough

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Table I
Piezoelectric Film Properties

| Specimen No. | Relaxed elongation[a] | Film thickness ($\mu$m) | Poling temperature (°C) | Poling voltage (kV at 0.9 cm) | $d_{31}$ (pC/N) |
|---|---|---|---|---|---|
| 7-8 | 3.7× | 16 | 25 | 15 | 15.4 |
| 8-1 | 3.7× | 16 | 25 | 20 | 17.6 |
| 8-5 | 3.7× | 16 | 70 | 10 | 22.4 |
| 9-1 | 3.7× | 16 | 100 | 10 | 20.8 |
| 9-3 | 3.8× | 16 | 100 | 10 | 22.7 |
| 9-4 | 3.7× | 17 | 130 | 10 | 9.1 |
| 9-5[b] | 3.7× | 17 | 100 | 10 | 17.4 |
| 9-6[b] | 3.7× | 16 | 150 | 10 | 0 |

[a] Stretched at 130°C.
[b] Cooled to room temperature with voltage applied.

to alter results of the $d_{31}$ measurement substantially and, hence, were not usable. However, the previously described special conductive paint formulation produced low-stiffness electrode coatings which had negligible effect on measured $d_{31}$ values. Adhesion of the special conductive paint to the polymeric film surface was good, and no evidence of flaking or cracking associated with film flexure was observed.

Electrical connection to the conductive coating was made with pressure contacts or conductive epoxy adhesive; the conductive paint electrode is not solderable. Although surface resistivity of the conductive coating was not determined quantitatively, qualitative measurements performed on each sample indicated that resistivity was quite low and entirely satisfactory for termination of a high-impedance piezoelectric material. Film thickness was not measured; adequacy of an applied electrode was determined by the aforementioned qualitative resistance measurement.

## DISCUSSION AND RESULTS

The piezoelectric constant $d_{31}$ was used as a measure of piezoelectric activity of the films produced.

Corona poling at room temperature (25°C) produced films with $d_{31}$ values in the range of 15–18 pC/N. The maximum poling voltage which could be used without dielectric breakdown was about 8 kV. However, it was found that a piece of 150-$\mu$m $PVF_2$ film placed over the film being poled had little, if any, effect on the final piezoelectric activity, and this arrangement facilitated use of voltages as high as 20 kV without dielectric breakdown.

Poling at temperatures of 70 and 100°C using a $PVF_2$ film cover with a 10-kV poling potential resulted in $d_{31}$ constants in the range of 21–23 pC/N. Higher poling temperatures, 130 and 150°C, produced films with lower piezoelectric activity (Table I). In most of the described experiments utilizing elevated temperatures, the hot film was removed from the corona discharge and cooled rapidly to room temperature; cooling to room temperature in the corona discharge yielded $d_{31}$ values comparable to those obtained with room temperature poling.

## CONCLUSIONS

Corona poling is a rapid method for preparing polymeric piezoelectric films. Additionally, use of electrically conductive paint electrodes greatly accelerates film preparation by eliminating the time-consuming and costly vacuum deposition process. Using corona poling and conductive paint electrodes, $PVF_2$ samples having $d_{31}$ values comparable to those obtained by the conventional poling procedure were prepared with much shorter processing time and substantially higher yield.

## References

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