

# Improving the dielectric and piezoelectric properties of screen-printed Low temperature PZT/polymer composite using cold isostatic pressing

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**Abstract.** This paper reports an improvement in dielectric and piezoelectric properties of screen-printed PZT/polymer films for flexible electronics applications using Cold Isostatic Pressing (CIP). The investigation involved half and fully cured PZT/polymer composite pastes with weight ratio of 12:1 to investigate the effect of the CIP process on the piezoelectric and dielectric properties. It was observed that the highest dielectric and piezoelectric properties are achieved at pressures of 5 and 10 MPa for half and fully cured films respectively. The relative dielectric constants were 300 and 245 measured at 1 kHz for the half and fully cured samples. Using unoptimised poling conditions, the initial  $d_{33}$  values were 30 and 35 pC/N for the half and fully cured films, respectively. The fully cured sample was then poled using optimized conditions and demonstrated a  $d_{33}$  of approximately 44 pC/N which is an increase of 7% compared with non-CIP processed materials.

## 1. Introduction

Many researchers exploit the piezoelectric effect in energy harvesting, sensing and actuating applications. Piezoelectric materials can be used in energy harvesting and sensing by applying a mechanical force (e.g. squashing or compression) to the material which produces a charge and voltage across the material (i.e. the direct effect). It can be also exploited inversely in actuating systems by applying a voltage across the material which results in a change in its geometry (i.e. the inverse effect).

Piezoelectric materials can be found in four forms: single crystal materials, ceramics, polymers and composites. Ceramic piezoelectric materials (e.g. lead zirconate titanate PZT, Barium titanate  $\text{BaTiO}_3$ ) are brittle but offer high  $d_{33}$  (350-560 pC/N) and high dielectric constants (2900). Piezoelectric polymers such as PVDF provide relatively low  $d_{33}$  (20-30 pC/N) [1], low dielectric constants ( $\sim 8$  at 1kHz) [2] but they have good mechanical flexibility. Relatively high  $d_{33}$ ,  $\epsilon_r$  and mechanical flexibility can be provided by piezoelectric composite materials which are a mixture of piezoelectric ceramic powders and a polymer matrix. The polymer used can itself be piezoelectric [3] or alternatively standard non-piezoelectric materials can be employed [4, 5]. Using piezoelectric polymers such as PVDF can be problematic since it has positive piezoelectric coefficients and if mixed with PZT (which has negative coefficients) can reduce the overall  $d_{33}$  of the composite material [3]. Using piezoelectric composites instead of piezoelectric polymers gives the advantage of producing a material with a higher piezoelectric coefficient  $d_{33}$  and dielectric constant  $\epsilon_r$  values [4, 5], improved electromechanical coupling coefficient [6] and greater opportunity for use in mass production because of the lower price of its ingredients compared to PVDF and its copolymers counterparts. However, piezoelectric

composites suffer from porosity and air voids that affect its dielectric and piezoelectric properties. This porosity increases when increasing the weight percentages of the ceramic phase above 50% [7]. It occurs during the curing and evaporation of the solvent phase in the composite after printing as the solvent is only dissolved in the polymer phase. During evaporation, the solvent leaves pores in the polymer which then become filled with air.

Thick film deposition such as screen-printing can produce films with typical thickness between 1-100  $\mu\text{m}$  [8]. However, some other reviews state that this range can be shifted to higher thicknesses 10-200  $\mu\text{m}$  [9]. The use of screen-printing can offer mass production, simplicity and a high range of ceramic loadings in the composite (e.g. < 90%).

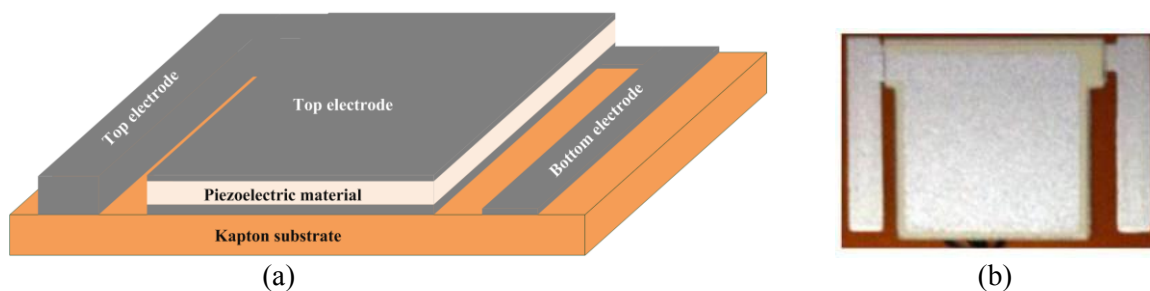
Applying high pressure to the printed film can densify the material and reduce the number and size of the air voids. *Cold Isostatic Pressing* (CIP) is a technique that applies a homogenous and continuous (i.e. depending on the holding time) force across the surface of the material at room temperature. CIP can also be used to process complicated shapes and structures without deformation [10].

This paper presents an evaluation of the effect of CIP on screen-printed composite PZT/polymer films by measuring the effect it has on the mechanical, dielectric and piezoelectric properties of the printed material.

## 2. Experimental

### 2.1. Paste Formulation and Screen-printing

The 0-3 type PZT/polymer composite material consists of three constituents, PZT-5H powder, thermoplastic polymer and solvent. The PZT powder was a mixture of 2  $\mu\text{m}$  (Pz29, Ferroperm Piezoceramics) and 0.8  $\mu\text{m}$  (Pzt-S-55, Sunnytec) particles with a weight ratio of 4:1. The thermoplastic polymer was dissolved in a solvent to convert it from a solid to liquid phase. Then, the PZT and the polymer were blended together with a weight ratio of 12:1. A triple roll mill was employed to disperse the PZT particles inside the polymer producing a homogeneous paste. This provides a screen-printable paste without lumps that has consistent and repeatable mechanical piezoelectric and dielectric properties. The material was screen-printed using a DEK 248 screen-printer between two electrodes on Kapton polyimide 300 HN substrate (75  $\mu\text{m}$  thickness). This printing formed the capacitive structure shown in Figure 1.



**Figure 1:** Printed capacitive structure. (a) Schematic of the capacitive structure. (b) Top view of the screen-printed printed device

### 2.2. Curing printed materials

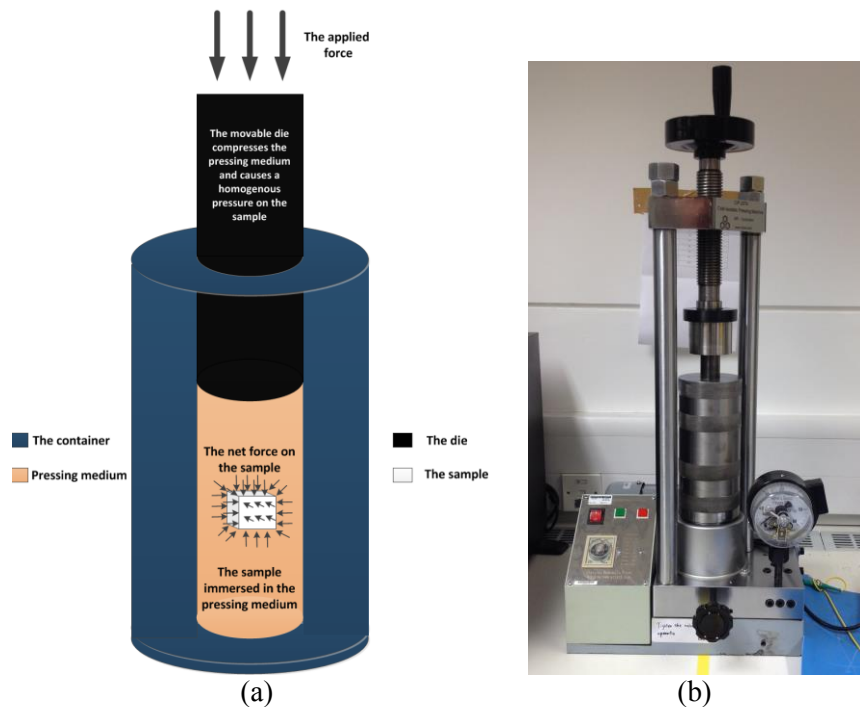
A silver-polymer paste (DuPont 5000) was used for printing the bottom and top electrodes. The curing conditions of the composite films were governed by the curing requirements of the polymer matrix. The screen-printed materials were cured in a box oven. Bottom electrode was cured at 120  $^{\circ}\text{C}$  for 10 min. The PZT/polymer composite and top electrode films were cured at 90  $^{\circ}\text{C}$  for 8 min. Although both the top and bottom electrode are formed from the same material, the top electrode was cured at lower curing temperature so that it does not over-cure and affect the piezoelectric film, which might lead to a variation in the properties of the printed composite.

### 2.3. Initial Dielectric and Piezoelectric Properties before CIP

Poling ferroelectric materials such as PZT is an important phase to activate its piezoelectric behaviour. The poling process was conducted by applying an external electric field concurrently with elevated temperatures for a specific time. A variety of poling methods can activate the piezoelectric properties of the material. Direct contact poling method was used in this investigation. Electrodes offer a basic setup to ensure an even distributed electric field across piezoelectric material. The applied electric field is given by  $E = V/d$ , where  $V$ ,  $d$  and  $E$  are the applied voltage, the thickness of the piezoelectric material and external electric field applied. It was essential to take reference  $d_{33}$  and  $\epsilon_r$  measurements in order to identify if CIP leads to any improvement in these properties. The  $d_{33}$  and dielectric constant measurements were performed using piezometer (PM35, PiezoTest) and Precision Impedance Analyser (WAYNE KERR, UK) respectively. The capacitances of the devices were obtained from the impedance analyser. Then, the dielectric constants were calculated with the aid of the following equation  $c = (A \cdot \epsilon_r \cdot \epsilon_0) / d$ , where  $A$  is the area of the electrodes,  $\epsilon_r$  is the relative permittivity or the dielectric constant of the material,  $\epsilon_0$  is the permittivity of free space and  $d$  is the average thickness of the piezoelectric film.

### 2.4. Cold Isostatic Pressing (CIP) Process

The CIP process was performed using Cold Isostatic Pressing Machine (CIP-20TA, MTI Corporation) shown in Figure 2. The sample is placed in the cylindrical chamber that is filled with pressing medium as shown schematically in Figure 2a. The die is pushed by an external force through the hole from the top of the cylindrical chamber pressurizing the hydraulic fluid which then applies a homogenous pressure across the sample. The compression can be applied continuously for the duration of the holding time.



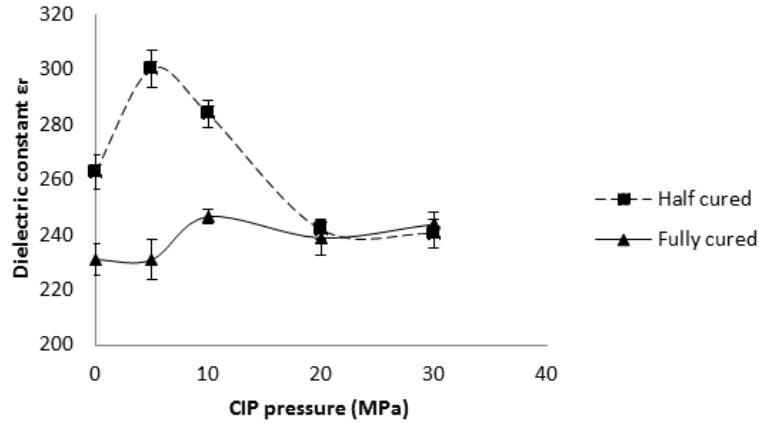
**Figure 2:** A schematic shows the CIP process (a). Actual CIP machine (b)

## 3. Results and Discussion

### 3.1. Dielectric Constants after Applying CIP

After applying CIP on two devices at different pressures, 5 dielectric constant readings were taken for each device giving a total of 10 measurements at every pressure point. The overall dielectric constant of the half cured sample is greater than the fully cured ones because of incomplete evaporation of the

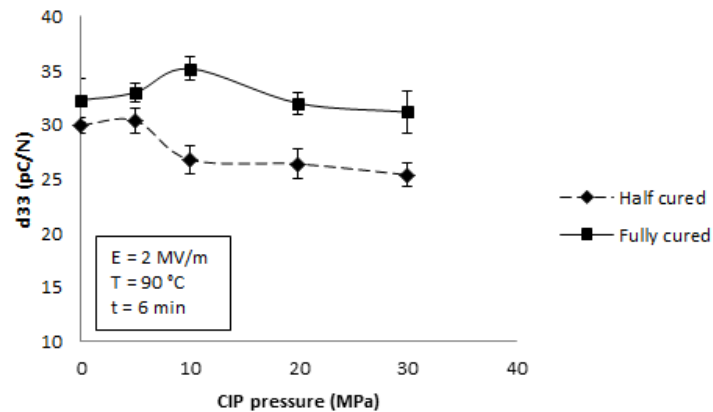
solvent. Once the solvent is fully evaporated and voids are left (i.e. because of the poor cross linking of the polymer), these voids are filled with air and the dielectric constant is reduced. Figure 3 shows that the dielectric constant increases to 300 and 245 with applied CIP pressures up to 5 and 10 MPa for the half and fully cured samples respectively. After 5 MPa, further increases in CIP pressure actually reduce the dielectric constant of the half cured sample whilst the fully cured sample remains fairly constant after 10 MPa.



**Figure 3:** Effect of the applied pressure on the dielectric constant (at 1 kHz) for half and fully cured samples

### 3.2. Piezoelectric Coefficient $d_{33}$ after Applying CIP

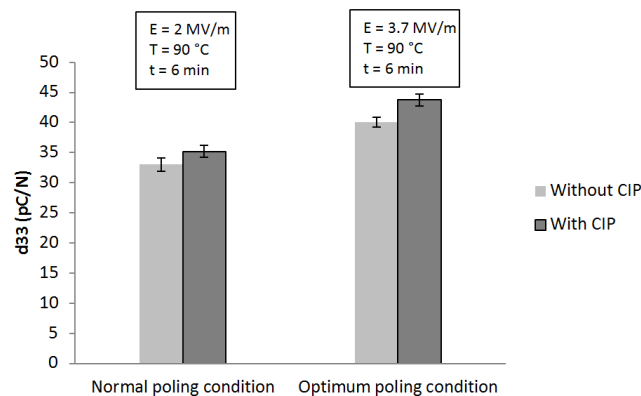
Two devices were used for every pressure point and five  $d_{33}$  measurements were taken for every device giving 10 measurements in total. Half cured samples were put in the oven for complete curing before the poling process. Similarly, the  $d_{33}$  values were improved by increasing the CIP on the samples reaching their maximum values 30 and 35 pC/N at pressures 5 and 10 MPa for the half cured and cured samples, respectively. Above these pressures, the CIP negatively affected the piezoelectric properties of the film for both the half cured and fully cured materials.



**Figure 4:** Effect of the applied pressure on the  $d_{33}$  values for half and fully cured samples

### 3.3. $d_{33}$ Values at Optimum Poling Conditions

CIP improved the piezoelectric properties of the cured samples by 6 and 7% for samples poled at with normal and optimum poling condition, respectively. Figure 5 shows the maximum  $d_{33}$  achieved is 44 pC/N obtained at optimum poling conditions ( $E = 3.7 \text{ MV/m}$ ,  $T = 90 \text{ }^\circ\text{C}$  and  $t = 6 \text{ min}$ ).



**Figure 5:**  $d_{33}$  values comparisons between PZT/polymer films with and without 10 MPa CIP at normal and optimum poling conditions

#### 4. Conclusion

CIP process does improve the dielectric and piezoelectric properties of PZT/polymer films. This paper has confirmed this improvement but there is a limit to the pressure that should be applied (i.e. there is an optimum pressure that can be applied in order to maximise the properties of the material). After applying a CIP pressure of 10 MPa, the PZT/polymer film showed a maximum  $d_{33}$  of 44 pC/N with an increase of 7% compared to films without CIP.

#### 5. Acknowledgment

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