Clamping effect on the piezoelectric responses of screen-printed low temperature PZT/Polymer films on flexible substrates

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Abstract. This paper introduces a new flexible PZT/polymer composite material that can be screen-printed onto fabrics and flexible substrates, and investigates the clamping effect of these substrates on the characterization of the piezoelectric material. Experimental results showed that the optimum blend of PZT/polymer binder with a weight ratio of 12:1 which provides a dielectric constant of 146. The measured value of the piezoelectric coefficient d_{33} was found to depend on the substrate used. Measured d_{33clp} values of 70, 40, 36 pC/N were obtained from the optimum formulation printed on Polyester-cotton with an interface layer, Kapton and alumina substrates, respectively. The variation in the measured d_{33clp} values occurs because of the effect of the mechanical boundary conditions of the substrate. The piezoelectric film is mechanically bonded to the surface of the substrate and this constrains the film in the plane of the substrate (the 1-direction). This constraint means that the perpendicular forces (applied in the 3-direction) used to measure d_{33} introduce a strain in the 1-direction that produces a charge of the opposite polarity to that induced by the d_{33} effect. This is due to the negative sign of the d_{31} coefficient and has the effect of reducing the measured d_{33} value. Theoretical and experimental investigations confirm a reduction of 13%, 50% and 55% in the estimated freestanding d_{33fs} values (80 pC/N) on Polyester-cotton, Kapton and alumina substrates, respectively. These results demonstrate the effect of the boundary conditions of the substrate/PZT interface on the piezoelectric response of the PZT/polymer film and in particular the reduced effect of fabric substrates due to their lowered stiffness.

1. Introduction

Mechanical boundary conditions can affect the mechanical performance of the piezoelectric material and its measured piezoelectric response. This paper explores the effect of the substrate mechanical boundary condition on the measured properties of printed polymer piezoelectric films. The magnitude of this effect is dominated by the mechanical properties of the substrate and the influence of three different substrates (textile plus interface layer, Kapton and alumina) is presented. This enables a comparison between rigid ceramic, flexible polymer and flexible textile substrates.

Piezoelectric films act as smart materials that exhibit the ability to convert kinetic energy into electrical energy (the direct effect used in sensors and energy harvesters) and convert applied electric fields into mechanical movement or force (the indirect effect used in actuators) [1, 2]. Piezoelectric ceramic materials such as lead zirconate titanate (PZT) contain individual randomly oriented electric

dipoles. These dipoles can be aligned by applying a sufficient external electric field across the piezoelectric element creating a surface charge which introduces spontaneous polarization [3]. Single crystal materials (e.g. lead magnesium niobate-lead titanate, PMN-PT), ceramics (e.g. lead zirconate titanate, PZT) and polymers (e.g. Polyvinyl fluoride, PVDF) are the most common single-phase piezoelectric materials that are used in sensing and energy harvesting applications [4]. Piezoelectric composites are different type of materials that combine at least two constituents in one material. The most common and easy formulated piezoelectric composite is the 0-3 type which contains piezoelectric ceramic powder mixed and dispersed in polymer or epoxy binder [5, 6]. Polymer piezoelectric composites have many advantages compared to the single phase piezoelectric material such as PVDF. Piezoelectric composites can be screen-printed (PVDF and its co-monomers are not screen-printable) and have higher piezoelectric properties than PVDF (20-30 pC/N) [7].

Many methods have been explored to improve polymer piezoelectric films. For example, binary piezoelectric composites using piezoceramic/piezopolymer have been investigated but the opposite polarity of the materials results in reduced piezoelectric properties [8]. In the case of more straightforward piezoceramic/polymer composites, the effective electric field on the PZT ceramic particles, E_{pz}, should ideally be equal to the external electric field applied, E_{ex} [9]. However, this case does not occur because E_{pz} is determined by the dielectric properties of both the PZT ceramic and the polymer matrix. Therefore, careful selection of both constituents is essential as it affects the polarization process and therefore the piezoelectric properties of the film.

Thick-film technology has been used for over sixty years to produce hybrid circuits [10] typically using screen-printing processes. Screen-printing is suitable for mass production and is capable of printing layers of thickness up to 100 µm [10]. Screen printing can be used to deposit a wide variety of materials that have been mixed into a paste form with suitable viscosity and thixotropic properties [11]. Polymer piezoelectric composites can be mixed into such a paste that can be printed and subsequently cured (e.g. thermal or UV curing). Piezoelectric sensors and actuators have been successfully produced by this fabrication technique [12, 13].

The performance of piezoelectric films can be influenced by the mechanical boundary conditions at the substrate interface that constrains its mechanical movements (e.g. expansion or contraction) when external force is applied [14]. Printing piezoelectric materials on different types of substrates will lead to variations in the boundary conditions that will result in different values of the measured piezoelectric property d_{33}. The d_{33} coefficient can be measured by applying a known force (static or oscillatory) that squeezes the film and substrate. The charge obtained from the test sample is compared to a built-in reference of known properties.

The compressive force through the thickness of the film will cause the film to also expand laterally due to the Poisson's ratio. However, since the film is constrained by the substrate that has different mechanical properties, free expansion is not possible and therefore a d_{31} component is introduced which introduces a charge of opposite polarity. The actual response of the piezoelectric film will change depending on the substrate material and the d_{33} measurements will be different (less than) those of a freestanding sample (i.e. piezoelectric material without substrate).
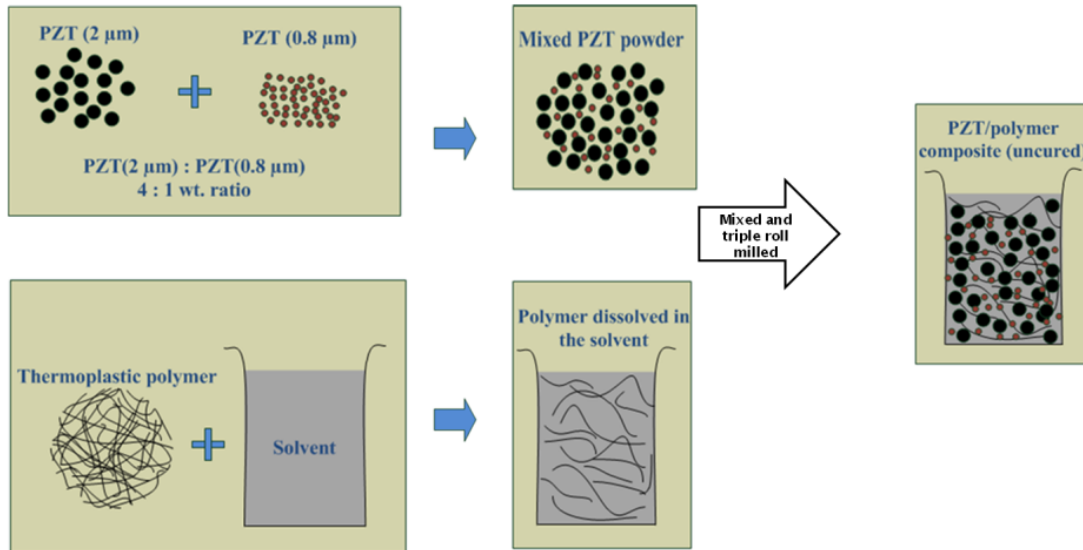
Several studies have been presented to investigate the clamping effect on thin–film piezoelectric films [14, 15]. In addition, Torah et al [16] presented an experimental study on the substrate clamping effect on different high temperature thick-film piezoelectric elements printed only on alumina. In this work, a new flexible low temperature piezoelectric composite with higher piezoelectric properties compared to our previous work version [13, 17] is presented. This material was subsequently printed onto alumina, Kapton and Polyester-cotton substrates to determine the clamping effect from these different substrates. The actual piezoelectric polymer d_{33} coefficient (i.e. equivalent to the freestanding material) is then determined analytically.

2. Experimental Work

2.1. Formulating piezoelectric composite paste

The piezoceramic lead zirconium titanate (PZT) material, type PZT-5H, in a powder form was used as the active material that was dispersed in the polymer matrix forming 0-3 piezoelectric composite. The piezoelectric powder consists of a blend of PZT particles with an average particle size of 2 μm (Pz29, Ferroperm) and 0.8 μm (S-55, Sunnytec). The weight ratio of the 2 μm to 0.8 μm particles was 4:1 which has been previously identified as the optimized combination [13]. The polymer binder was formed from a high dielectric polymer (confidential formulation) that was dissolved in γ-butyrolactone. The PZT powder blend was added to the binder and mixed in a DAC 150 SpeedMixer (Synergy Device Limited) for 2 minutes. The dielectric and piezoelectric properties of the printed paste were investigated for different PZT/polymer weight ratios of 8:1, 10:1, 12:1 and 14:1.

The blended materials were then processed in the triple-roll mill in order to further improve the powder dispersion and remove any air from the paste introduced during mixing. This results in a homogenous paste and a high quality printed film with good mechanical and electrical properties. Figure 1 illustrates the PZT/polymer composite formulation process.
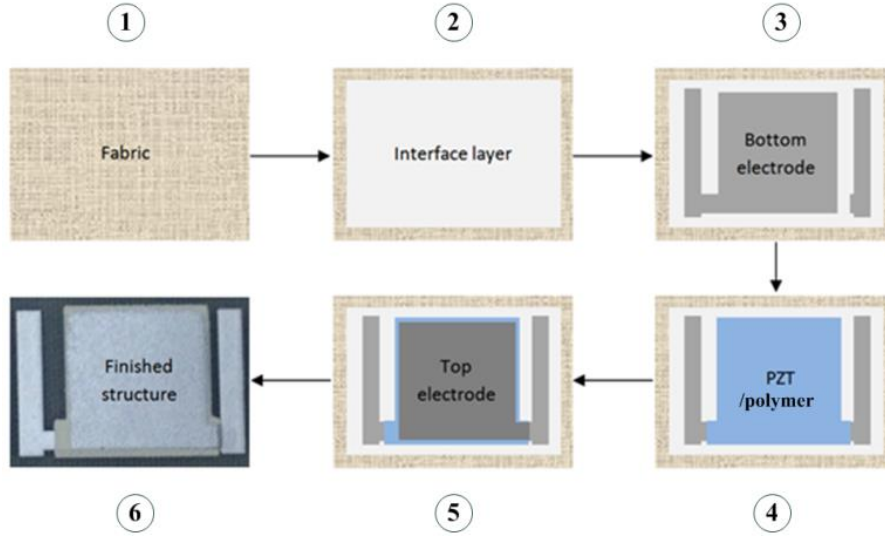

Figure 1: Schematic showing the mixing process of the piezoelectric composite

2.2. Screen-printing the blend and Curing Process

A capacitive structure (shown in Figure 2) was screen-printed on three different substrates, i.e. alumina (630 μm, Hybrid Laser Tech), Kapton polyimide 300HN (75 μm, KATCO) and 300 μm thick woven fabric (Polyester 65%-Cotton 35%) using DEK 248 semi-automatic screen-printer. The PZT/polymer layer was sandwiched between two silver electrodes that were used to enable film poling and perform the dielectric constant and d_{33} measurements.

For the textile substrate, an interface layer was printed onto the Polyester-cotton substrate to provide a smooth surface for subsequent printing. The interface layer was needed to improve the surface roughness of the fabrics that would otherwise prevent the fabrication of consistent working samples. The overall thickness of the Polyester-cotton substrates after printing the interface layer onto it was around 500 μm. The interface layer was not required for the alumina and Kapton substrates. The interface layer was UV cured whilst the other layers were thermally cured in a box oven. Table I shows the curing conditions of each printed films. The curing process of the PZT and top electrode

layers is governed by the requirements of the polymeric binder in the PZT film, hence the lower curing temperature of the top compared to the bottom electrode.
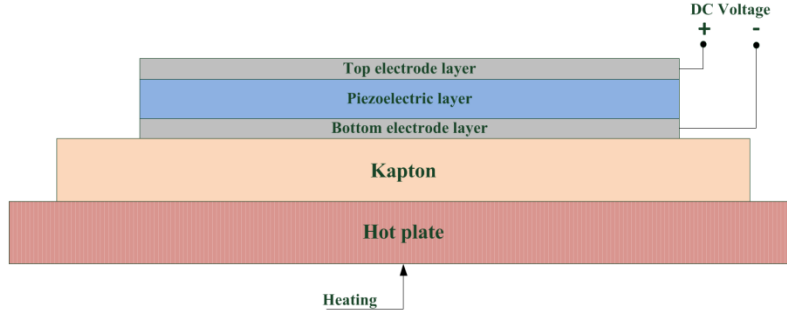

Figure 2: Schematic of the printing process of the capacitive structure printed on Polyester-cotton. The interface layer is only needed in this type of substrates

TABLE I. CURING CONDITIONS OF THE PRINTED MATERIALS

Functional Layer	Materials	Curing Conditions
Interface	Fabink-IF-UV 1039 (1st – 3rd layer) Fabink-IF-UV 1004 (4th layer)	60 s for each layer
PZT/polymer	PZT-5H + polymer binder	8 mins at 90°C
Bottom electrode	DuPont 5000	10 mins at 120°C
Top electrode	DuPont 5000	8 mins at 90°C

2.3. Poling Process of the Materials

As the PZT-5H material in the composite is a ferroelectric ceramic and its piezoelectric properties need to be activated via polarisation. Direct contact poling (DCP) shown in Figure 3 was performed by applying an external electric field at an elevated temperature for a specific period of time. The increased temperature provides the necessary energy to enable the realignment of the dipoles. The existence of the printed electrodes provides a simple setup for direct contact poling and ensures an even distribution of the external electric field across the piezoelectric element. The applied external electric field, E_{ex}, is given by the equation $E_{ex} = V/d$, where V and d are the applied poling voltage and the thickness of the piezoelectric element, respectively.
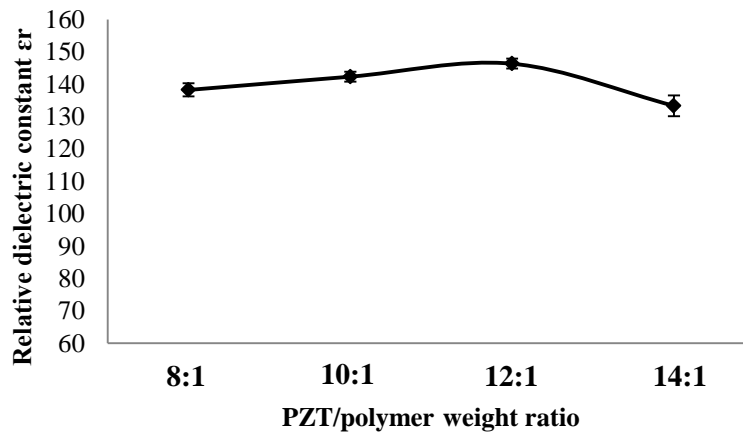
Figure 3: Schematic of the DCP for a capacitive structure printed on Kapton

3. Results and Discussions

3.1. Dielectric Properties of the Piezoelectric Films
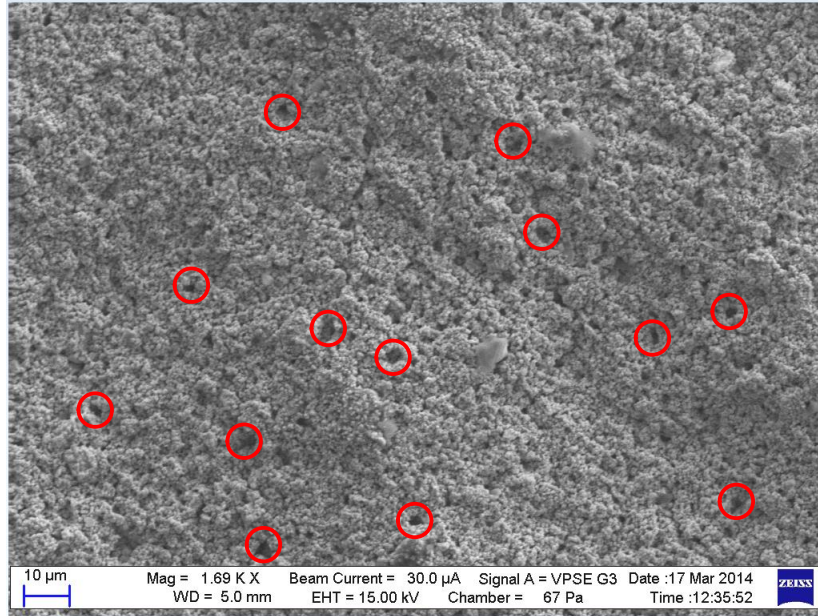
The piezoelectric properties of the film are typically related to its dielectric properties (represented by a dielectric constant). This is because the remnant polarization of the piezoelectric material is dependent on its overall dielectric constant which must be high enough to enable a sufficient effective electric field E_{pz} to be applied to the PZT particles inside the film [9, 18]. Therefore it is essential a polymer binder with good dielectric properties is used. The dielectric constants of the PZT-5H and polymer at 1 kHz are 2900 and 15, respectively. When they are mixed, the total dielectric constant is averaged. However, film porosity and the presence of air void may reduce the overall dielectric properties of the composite.

After measuring the capacitances of the test samples printed on Kapton substrate, the dielectric constants were calculated using the equation $C = (A.\varepsilon_r.\varepsilon_0)/d$, where C is the measured capacitance of the device, A is the area of the electrodes, ε_r is the relative dielectric constant of the material, ε_0 is the permittivity of free space and d is the average thickness of the PZT/polymer film. Figure 4 shows the calculated dielectric constants of the PZT/polymer composites for the different PZT compositions. The optimum PZT/polymer weight ratio of 12:1 gives a maximum dielectric constant of 146 at 1 kHz. Beyond this ratio (threshold point), the number of air voids in the printed film was found to increase and therefore the dielectric constant is reduced.

Figure 4: Dielectric constants (@1kHz) of the PZT/polymer composites at different PZT weight loadings
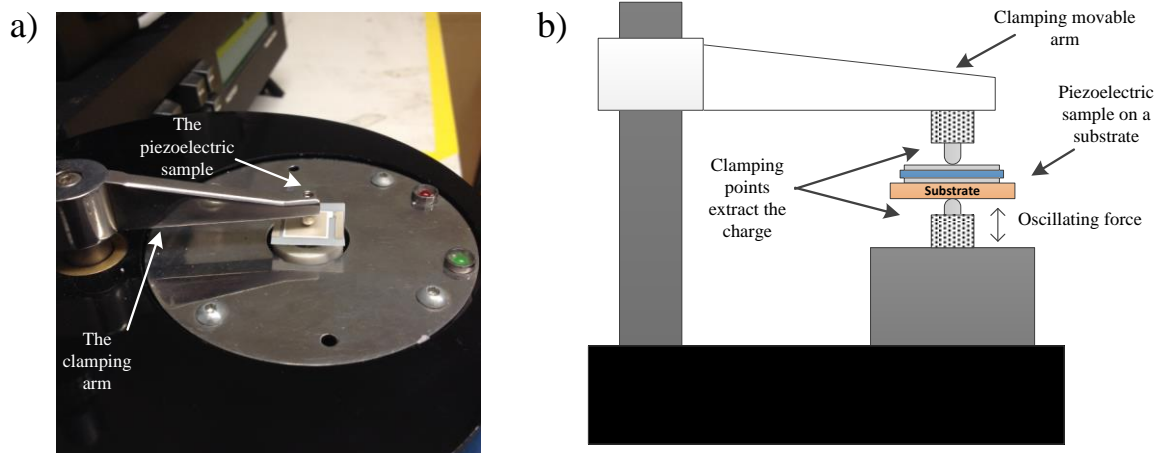
Figure 5 shows an SEM image for the cured PZT/polymer film after printing. The PZT particles are distributed in the polymer matrix which binds the PZT particles together. Also, it shows the air voids and the porosity in the printed film that reduces the dielectric properties.

Figure 5: SEM image of the 12:1 PZT/polymer showing the mixing constituents. Examples of air voids are highlighted by the red circle

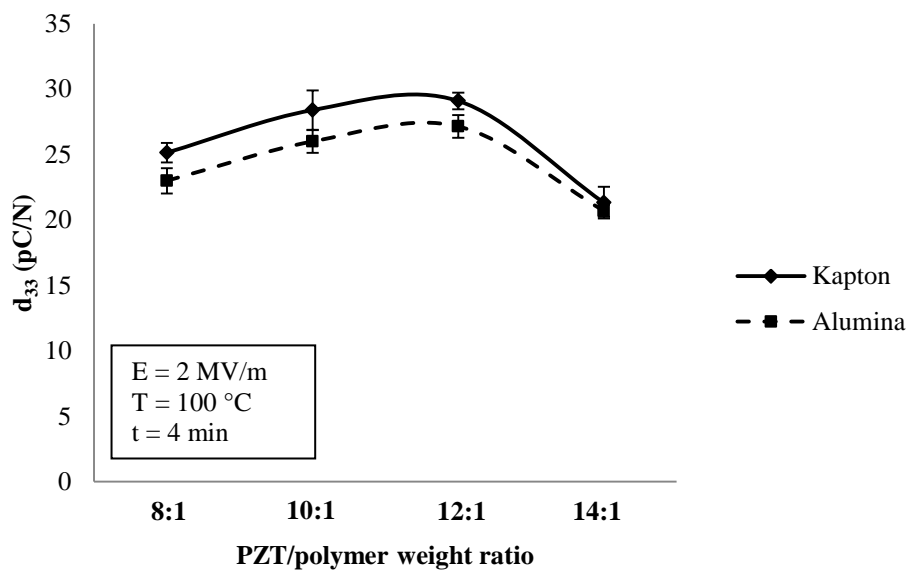### 3.2. Initial d_{33} Measurements of the Materials

The four PZT/polymer compositions with PZT/polymer weight ratios of 8:1, 10:1, 12:1 and 14:1 were printed on alumina, Kapton and Polyester-cotton substrates. They were poled and d_{33} measurements taken. The d_{33} values were measured using the piezometer (PM300, PiezoTest). Figure 6 shows the PM300 piezometer with the actual Polyester-cotton sample under test. Figure 6b schematically illustrates the clamped piezoelectric sample by the two clamping points of the piezometer. It basically works by applying a preset force and a charge is produced by the sample which is measured through a built-in circuit in order to find the piezoelectric coefficient d_{33}.

Figure 6: The PM300 Piezometer used for d_{33} measurements. (a) The actual clamped PZT/polymer film on Polyester-cotton. (b) A schematic illustrates the sample as it is clamped by the piezometer

The initial poling conditions (E = 2 MV/m, T = 100 °C and t = 4 min) were applied to all compositions for devices printed on Kapton and alumina. After poling, for each composition the d_{33} was measured on four samples with five measurements were taken from each sample. Figure 7 shows the average d_{33} of the 20 measurements.

Both the dielectric constant and the initial d_{33} measurements identify the optimum PZT/polymer weight ratio to be 12:1. Figure 7 also shows the results of the clamping effect on the measurements with the alumina results being lower than the Kapton. This is discussed further in section 3.4 having identified the optimum composition; the next task was to optimize the poling conditions for this material on each of the three substrates in order to maximize the d_{33}.
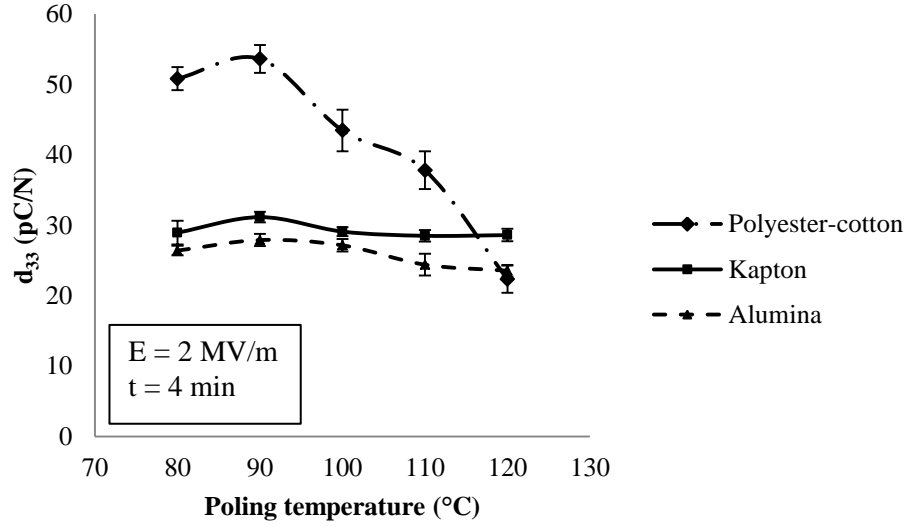

Figure 7: d_{33} measurements with initial poling conditions for devices printed on alumina and Kapton

3.3. Optimizing Poling Conditions of the Selected Materials
In order to maximise the piezoelectric coefficient d_{33}, the poling parameters electric field (E_{ex}), temperature (T) and time (t) were investigated for the alumina, Kapton and textile substrates. Initially, poling temperature was investigated with the other parameters fixed (E_{ex} = 2 MV/m and t = 4 min).

Figure 8 shows the d_{33} values increased with the increasing temperature up to 90 °C and reached a maximum of 28, 31 and 53.6 pC/N for samples printed on alumina, Kapton and Polyester-cotton, respectively. After this optimum temperature, sparks were observed during poling process which indicates the piezoelectric film was breaking down and the electric field was reduced. This explains the reduction in the measured d_{33} values shown in Figure 8.

Figure 8: Optimization of the poling temperature for the d_{33} for devices printed on Polyester-cotton and Kapton

Next poling time was optimised with updated poling conditions of E_{ex} = 2 MV/m and T = 90 °C. Figure 9 shows that the optimum po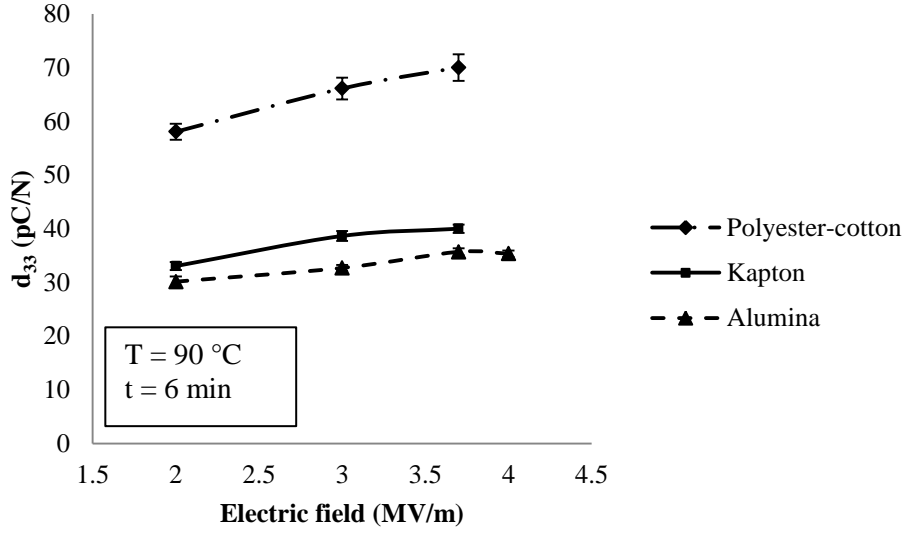ling time was 6 min, which resulted in d_{33} values of 30, 33 and 58 pC/N for samples on alumina, Kapton and Polyester-cotton, respectively. When the poling time was increased over 6 min, the piezoelectric film was again observed to break down and the effective electric field was reduced across the piezoelectric material.

Figure 9: Optimization of the poling time for the d_{33} for devices printed on Polyester-cotton and Kapton

Finally, the applied electric field was optimised with updated poling conditions of t = 6 minutes and T = 90 °C. Figure 10 shows the d_{33} values rise until electric breakdown occurs at around 4 MV/m for Polyester-cotton and Kapton, respectively. The alumina samples were found to survive up to 5 MV/m but no further improvement in measured d_{33} was observed. This confirms the maxium electric field that can be applied for all substrates is 3.7 MV/m and the maximum d_{33} values of 35.8, 40 and 70 were obtained for the alumina, Kapton and Polyester-cotton substrates, respectively.

Figure 10: Optimization of the poling field for the d_{33} for devices printed on alumina, Kapton and Polyester-cotton

The results show that the substrate material does not affect the optimum poling conditions. Table II shows the optimum poling conditions that lead to the best piezoelectric properties and also shows the poling conditions at which the breakdown occurs during poling.

TABLE II.   THE BREAK AND OPTIMUM POLING CONDITIONS OF THE SELECTED MATERIAL ON ALUMINA, KAPTON AND POLYESTER-COTTON

Substrate	Breakdown conditions			Optimum poling conditions		
	T (°C)	t (min)	E (MV/m)	T (°C)	t (min)	E (MV/m)
alumina	120	10	5	90	6	4
Kapton	120	10	4	90	6	3.7
Polyester-cotton	120	10	4	90	6	3.7

3.4. Clamping Effect and d_{33} Measurements
The d_{33} results from the piezoelectric films on different substrates were found to be different under the same poling conditions. This indicates the clamping of the samples has an effect on d_{33} measurements and the magnitude of this effect depends upon mechanical properties of substrate materials. Therefore, it is reasonable to conclude that measuring the d_{33} value on one particular substrate does not reflect the actual d_{33} value of the piezoelectric material. This section will discuss this effect in details and calculate the actual d_{33} value of the proposed PZT/polymer film.

If a compressive force is applied through the thickness of the piezoelectric material, it will also expand laterally in the plane of the substrate but such deformation is restricted by the mechanical boundary conditions with the substrate. For such a constrained piezoelectric film, equation 1 shows the relationship between the measured piezoelectric coefficient d_{33clp} of the PZT/polymer film clamped on the substrate, the freestanding (i.e. without substrate) piezoelectric coefficient d_{33fs} and the freestanding transverse piezoelectric coefficient d_{31fs} of the film [16]. Also, it shows the effect of the mechanical properties of the substrate material on the transverse piezoelectric component d_{31fs} and therefore on the measured piezoelectric coefficient of the film.

$$d_{33clp} = d_{33fs} + 2d_{31fs} \left(\frac{-\left(\frac{v_s}{Y_s}\right) - s_{13}^E}{s_{11}^E + s_{12}^E} \right) \qquad (1)$$

Where, Y_s and v_s are the Young's modulus and the Poisson ratio of the substrate. $s^E{}_{11}$, $s^E{}_{12}$ and $s^E{}_{13}$ are the mechanical compliances of the PZT/polymer film. For anisotropic piezoelectric materials, the ratio between the transverse and longitudinal piezoelectric coefficients is related by the following ratio [19-21]

$$\frac{d_{31}}{d_{33}} = -v_{13} \qquad (2)$$

Assuming our PZT/polymer film is isotropic, from Hook's law, the ratio between the d_{31fs} and d_{33fs} will be as follows

$$\frac{d_{31fs}}{d_{33fs}} = -v_p \qquad (3)$$

And also the mechanical compliance matrix parameters were calculated using the following equations

$$S_{11}^E = \frac{1}{Y_p} \qquad (4)$$

$$S_{12}^E = S_{13}^E = -\left(\frac{v_p}{Y_p}\right) \qquad (5)$$

Where, v_p and Y_p are the Poisson ratio and the Young's modulus of the PZT/polymer film. Substituting equations 3, 4 and 5 into 1 and rearranging it results in

$$d_{33clp} = d_{33fs} \cdot \left[1 - 2.v_p \left(\frac{\left(\frac{v_p}{Y_p}\right) - \left(\frac{v_s}{Y_s}\right)}{\frac{1}{Y_p} - \frac{v_p}{Y_p}} \right) \right] \qquad (6)$$

$$d_{33fs} = \frac{d_{33clp}}{\left[1 - 2.v_p \cdot \left(\frac{\left(\frac{v_p}{Y_p}\right) - \left(\frac{v_s}{Y_s}\right)}{\frac{1}{Y_p} - \frac{v_p}{Y_p}} \right) \right]} \qquad (7)$$

Table III shows the mechanical properties of the substrates and piezoelectric materials. Some of these values were provided by the manufacturers and others were calculated. The Young's modulus of the PZT/polymer film, Y_p, and the Polyester-cotton substrate with interface layer printed were obtained experimentally.

Material	Y	v
alumina [22]	331 GPa [b]	0.25 [b]
Kapton [23]	2.5 GPa [b]	0.34 [b]
Interface+ Polyester-cotton	0.2 GPa [a]	0.44 [c]
PZT-5H [24]	60 GPa [b]	0.34 [b]
Polymer	0.02 MPa [a]	0.48 [a]
PZT/ polymer	131 MPa [a]	0.40 [c]

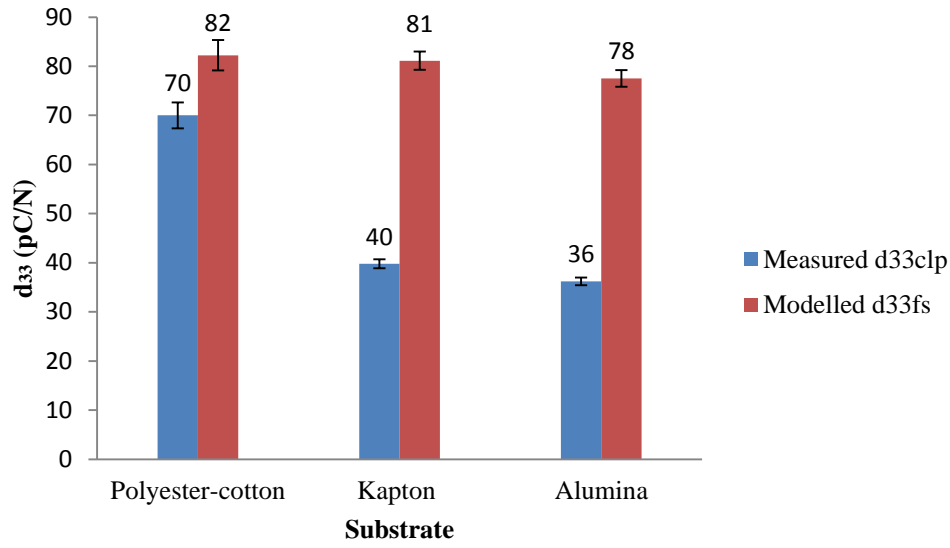[a] measured, [b] provided by the manufacturer and [c] calculated

The Poisson ratios of the materials of the PZT/polymer was calculated using formulas developed by [9] given that Poisson ratios of the two constituents of the PZT/polymer are known with respect to their volume ratio. The Poisson ratio of Polyester-cotton with interface was estimated using the following formula.

$$v_s = v_{fab}V_{fab} + v_{intf}V_{intf} \qquad (8)$$

Where, v_s, v_{fab}, v_{intf} are the Poisson ratios of the entire substrate (interface layer and Polyester-cotton), average Poisson ratio of the Polyester-cotton fabric (=0.42) [25] and Poisson ratio of the interface layer (=0.47) [26], respectively. V_{fab} and V_{intf} are the volume fractions of Polyester-cotton (=0.58) and the interface (=0.42), respectively.
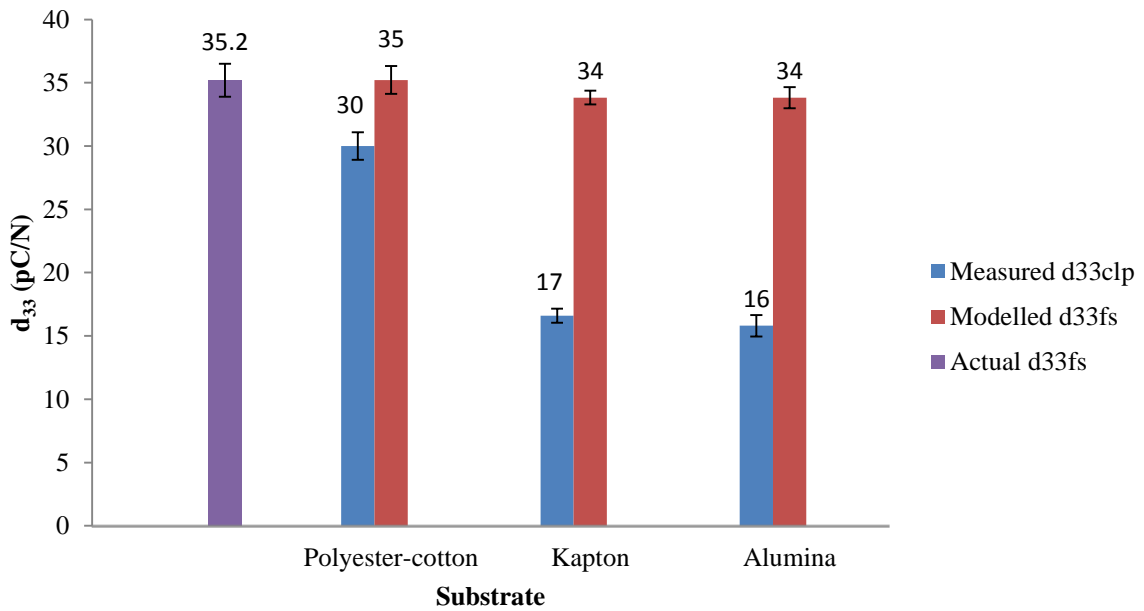
The freestanding piezoelectric coefiicients d_{31fs} was calculated using equation 7 with values listed in table III. Figure 11 shows the measured and corresponding freestanding piezoelectric coefficients of the PZT/polymer films on different substrates. The devices were poled at the same poling conditions E = 3.7 MV/m, T = 90ºC and t = 6 min. The calculated freestanding piezoelectric coefficients, d_{33fs} of PZT/polymer films using different properties of the three substrates were 82 pC/N, 81 pC/N and 78 pC/N. These values are reasonably consistent; there is a maximum difference of 4.8% between them which is due to the variations in measurement of d_{33clp} which is reflected by the standard deviations in the measurements. And if we take an average freestanding d_{33fs} value of 80 pC/N, the measured d_{33} is 13% , 50% and 55% less than the freestanding value for the Polyester-cotton with interface, Kapton and alumina substrates, respectively.

If we suppose that the three substrates are isotopic, the compliance C_s (when a force is applied along 3-direction causing a strain at 1,2-direction) will be $(-v_s/Y_s)$ according to Hook's law. The compliance of the Polyester-cotton with interface, Kapton and alumina substrates are -2×10^{-9}, -1.3×10^{-10} and -7.6×10^{-13} m²/N, respectively. The Kapton is more flexible and has a compliance which is nearly 10^2 times greater than alumina. When applying these compliances values for every substrate on equation 6 and with d_{33fs} value of 80 pC/N , closer constrained d_{33clp} were obtained compared to Polyester-cotton with interface. This is because when a substrate shows a compliance ($\leq -1 \times 10^{-9}$ m²/N), the PZT/polymer will show a very small change in d_{33clp} values. This confirms that the measured d_{33clp} values of the printed PZT/polymer is only related to the compliance C_s of the substrates but not to their flexibility or bendabilty.

Figure 11: d_{33clp} and d_{33fs} for the selected PZT/polymer of Polyester-cotton with interface, Kapton and alumina substrates

To validate the results, freestanding printed piezoelectric films were fabricated. A 500 micron thick piezoelectric film was doctor bladed on a Teflon substrate (TEFLON 200A, KATCO), cured and then peeled from the Teflon producing the freestanding piezoelectric film. DuPont 5000 was coated on both sides of the film producing the capacitive structure for testing. Due to the thickness of the piezoelectric sample and the limitation of the maximum voltage of the power supply (1000 V), a maximum poling field of E = 1MV/m was applied. These poling conditions were also applied to the Polyester-cotton, Kapton and alumina devices to enable comparison with the freestanding structure. The measured and calculated freestanding d_{33fs} values are shown in Figure 12.

Figure 12: Comparisons of measured d_{33fs} of freestanding PZT/polymer film and calculated, d_{33fs} based on measured d_{33clp} of PZT/polymer films on Polyester-cotton with interface layer, Kapton and alumina

The calculated d_{33fs} values of the printed materials on the three substrates show very good agreement with the measured actual d_{33fs} of the freestanding. These results validate the theoretical analysis and the use of equation 7 to calculate the equivalent freestanding d_{33fs}.

4. Conclusion

This paper has introduced a new flexible low temperature 0-3 connectivity type PZT/polymer composite that can be screen-printed onto flexible substrates such as fabrics. The optimum formulation was found to be a PZT to polymer weight ratio of 12:1 that exhibits a relative dielectric constant of 146 at 1kHz and a maximum constraint d_{33clp} of 70, 40 and 36 pC/N when it was printed on Polyester-cotton, Kapton and alumina, respectively. These properties are superior to the PVDF values mentioned in the literature. The change in the measured d_{33clp} for different types of substrate is caused because of the clamping effect at the boundary that constrains the expansion and contraction of the piezoelectric material when a force is applied during measurement. The clamping effect causes a reduction in the measured d_{33clp} but this reduction differs from one substrate to another depending upon its mechanical properties. The theoretical and practical investigations confirmed a reduction on the d_{33clp} values by 13%, 50% and 55% for the Polyester-cotton, Kapton and alumina substrates, respectively. The average d_{33fs} value of the freestanding PZT/polymer material was calculated to be around 80 pC/N. The measured d_{33clp} values on alumina and Kapton where found to be very close despite the compliance of Kapton being 10^2 times greater than alumina. This is because variations in the clamping effect become negligible below a specific compliance (around -1 x 10^{-9} m^2/N) and the printed piezoelectric films only show a slight difference in d_{33clp} values. However, the compliance of the Polyester-cotton with interface is greater than this specific compliance and the measured d_{33clp} is clearly greater.

5. Acknowledgements

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