

PRESSURE INDUCED PIEZOELECTRIC β -PHASE CRYSTALLIZATION IN SCREEN PRINTED POLYMER THICK FILMS

K. Arshak, C. Ryan, M. Campion

Electronic & Computer Engineering Department, University of Limerick, Limerick, Ireland.

Abstract

In this work, a novel method of producing thick film piezoelectric polymer film has been used based on the use of pressure during crystallisation. This method induces the desired piezoelectric β - phase in Polyvinylidene Fluoride (PVDF). The screen printing technique was used to fabricate the films on 96% alumina substrates. Various characteristics have been studied, including the thermal and structural properties of the polymeric films.

Introduction

Thick film technology developed as a means of producing hybrid circuits. This technology normally involved cermet based pastes screen printed onto flat ceramic substrates and then fired at temperatures in the region of 900 °C. Polymer thick film technology refers to pastes based on polymers, and sometimes organic semiconductors, which are cured at more modest temperatures (<250 °C). These polymer thick film devices find uses as piezoresistors in strain gauge applications, dielectrics and as conductors. The majority of research into thick film sensors has dealt with the application of cermet thick-film paste systems, with little research being carried out into the development of new polymer thick film materials, in particular piezoelectric polymer thick film materials, for sensor applications [1, 2]. The low cost of thick film technology is an attractive alternative for the realisation of these devices. The main interest in piezoelectric polymers has centred on Polyvinylidene Fluoride (PVDF) and some of its copolymers, most importantly a copolymer of PVDF with TrFE (Trifluoroethylene). PVDF is a semicrystalline ferroelectric polymer, which can crystallise into four different crystal forms, α , β , γ and δ , depending upon the crystallisation conditions. The most common form is the α -phase, which is non-polar. The α -phase can be transformed to the desired highly polar β -phase by mechanical deformation. This normally involves stretching the crystallised film but this method is incompatible with thick film technology. The use of pressure has already been reported to successfully transform the α -phase to the β -phase [1]. PVDF has found applications in the areas of ultrasonic transducers, optic modulation, speakers and surface acoustic wave devices [2, 3]. Due to its low acoustic impedance, it has been used in hydrophones and biomedical applications [4]. In this work a piezoelectric thick film paste has been developed for potential use as a surface acoustic wave device.

Experimental Procedure

The thick film polymer paste was developed in house. The electrodes were fabricated from DuPont conductor 4929. All layers were printed using a DEK 1202 automatic screen printer, with 325 mesh stainless steel screens at an angle of 45° to the frame. The emulsion thickness of the screens used for the electrodes and the polymer were 25 μm and 50 μm respectively giving cured thickness' of 18-20 μm and ~30 μm . The polymer paste was printed and dried repeatedly up to a thickness of approximately 150 μm . The PVDF polymer paste was fabricated using standard cermet techniques. The PVDF powder, with average particle sizes of 5 μm , acts as both the permanent binder and the functional material resulting in a thick film of PVDF after processing. Ethyl Cellulose and terpineol- α were used as the temporary binder and solvent respectively. The printed films had an effective area of 10x10 mm². The polymer layer was extended 5 mm beyond the periphery of the underlying electrode to ensure no shorting occurs between the bottom and top electrodes. The substrate used was 96% alumina with thickness of 0.625 mm.

As-printed films were dried for 30 minutes at 100 °C, then they were placed in a thermal chamber capable of withstanding a pressure of up to 200 bar. The samples were heated in this chamber up to their melting point and the pressure was applied afterwards. After a certain time, the temperature was ramped down with the pressure still applied until it was well below the glass transition temperature of the sample. Once the sample was well below T_g the pressure was removed. In order to optimise the process the pressure applied and the thermal procedure employed were varied.

Results and Discussion

X-Ray Analysis

Unoriented films and films cured using the pressure process described earlier, were examined by XRD to determine if the piezoelectric β -phase was formed within the material. Fig. 1 shows the XRD plot of a sample of PVDF powder. As expected the film is predominantly α - phase. The main peaks, with their 'hkl' values in brackets, associated with α - phase are at 2θ values of 17.9°[100], 18.4°[020], 20.1°[110], 26.7°[021], 33.2°[130] and 38.6°[131]. The peaks corresponding to the different polymorphic phases are identified from established data [5]. The 'hkl' values for the crystalline structure of this phase have been inserted at their appropriate 2θ peaks. An asterisk beside 'hkl' value denotes a peak and is attributed to the β - phase.

An increase in the pressure to 100 bar results in a shift towards the β -phase as shown in Fig. 2. The two maximum peaks are at 2θ angles of 20.08 and 20.98, whereas previously the maximum peak had a 2θ value of 18.68. This second peak, at 20.98, corresponds to [110] β -phase. The α - phase peaks, [100], [130] and [131] have disappeared. Two new peaks have also appeared. These have been attributed to [310] and [130] β - phase. The two main peaks are again at [110] α - phase and [110] β - phase. The emergence of the peaks [110], [310] and [130] due to the β - phase is very promising. This β -phase is the desired highly piezoelectric phase as discussed earlier.

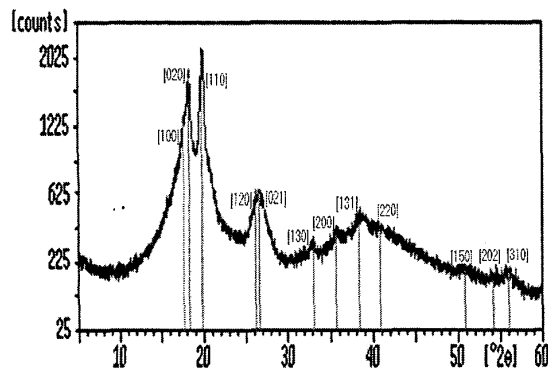


Fig. 1. XRD plot of PVDF powder.

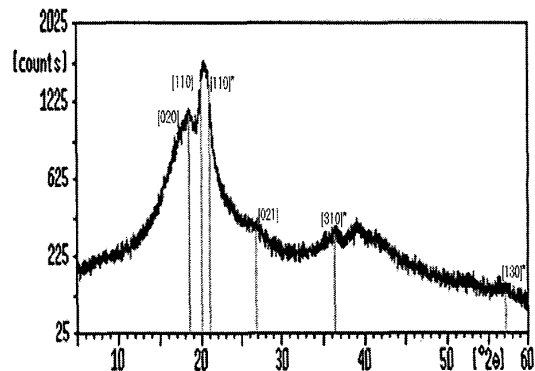


Fig. 2. XRD plot of PVDF crystallised under 100 bar.

DSC Analysis

Fig. 3 – Fig.5 show the plots obtained from the thermal investigation carried out using DSC analysis. They show all the important temperature transitions such as Glass transition (T_g), melting temperature onset (T_{onset}) and the melting temperature max (T_{max}). Other important information which can be obtained from these plots, is the thermal energy required (ΔH_m) to destroy or melt (during the heating ramp), the existence crystal structure (which is in α phase), compared to the thermal energy required (ΔH_r) to create or form (during the cooling ramp), the recrystallisation structure (which is also in α phase). The ΔH_r is always analysed during the second test run of each sample. The percentage crystalline recovered (%) is a relative indication of whether a net loss or a net gain is obtained during the cooling ramp compared to the heating ramp and is given by: $\% = (\Delta H_r / \Delta H_m) * 100$.

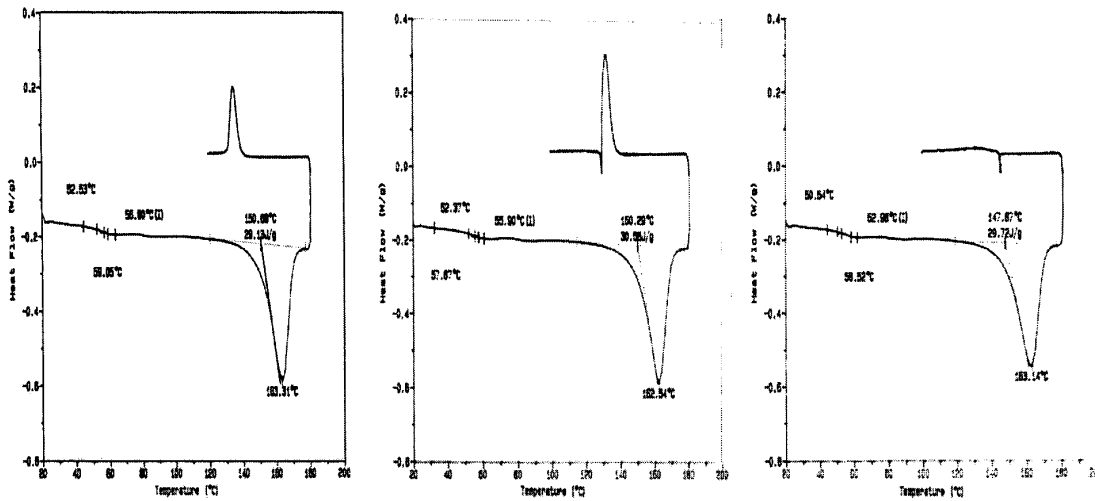


Fig. 3. DSC plot of sample PVDF8. Fig. 4. DSC plot of sample PVDF11. Fig. 5. DSC plot of sample PVDF13.

Fig. 3 shows DSC plot of sample PVDF8 that was held at the maximum temperature of 180 °C for 5 min. The cooling ramp rate was varied in the range of 0.5 to 5 °C/min. It was found that the cooling ramp rate of 1.5 °C/min results in a net gain of 18% in crystallinity for PVDF8 sample, that is the largest percentage of crystallinity recovered. For samples PVDF9 and PVDF10, the cooling ramp rate was further changed to 2 and 2.5 °C/min respectively. This had the effect of reducing the net crystallinity gain to 10.4% and -4.4% (i.e. a net loss).

Fig. 4 shows DSC plot of sample PVDF11, for which during the cooling ramp the temperature is held constant at 130 °C for 30 min before continuing the cooling ramp to 100°C. For PVDF12 and PVDF13 the intermediate temperature was 145 °C for periods of 30 min and 1 hour respectively. Samples PVDF11-PVDF13 show net gains in crystallinity of 11%, 15.5% and 5.8% respectively.

It was found that on average, the glass transition temperature (T_g) was equal to 55.67 °C. It was also found that the polymer granular material will start to melt at the temperature (T_{onset}) equal to 149.89 °C and that the max melting temperature is at (T_{max}) equal to 163.14 °C. During the cooling ramp, the re-crystallisation starts at a temperature of ~145 °C and is completed at a temperature of ~125 °C. These last two temperature figures are read directly off the PVDF8 DSC plot (Fig. 3).

Microscopy Investigation

Fig. 6 – Fig. 9 show the effect of varying temperature, time and pressure on the structural changes of the formed films. Fig. 6 shows the film formed at 170 °C for 30 min at atmospheric pressure. The presence of ‘islands’ can clearly be seen. This is where the solvent has dried off leaving gaps between these islands of the thick film material [6].

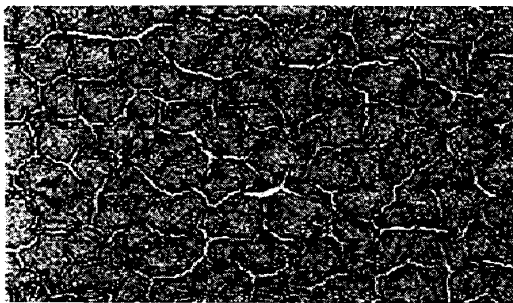


Fig. 6. Film cured at 170 °C for 30 min at atmospheric pressure.

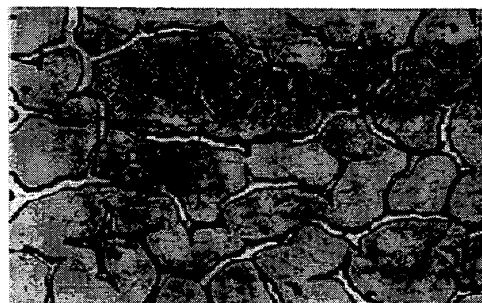


Fig. 7. Film cured at 170 °C for 30 min at a pressure of 8 bar

Fig. 7 shows the film formed at 170 °C for 30 min. at a pressure of 8 bar. The islands have become less numerous but are bigger. Fig. 8 and Fig. 9 show films formed at 100 and 120 bar respectively. Both processes were at 165 °C for 5 minutes. These images show excellently formed films. The lack of islands and spaces in between them is a very desirable feature in thick films. These spaces can contribute to premature shorting in the poling process.

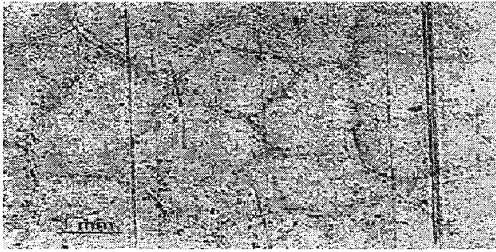


Fig. 8. Film cured at 165 °C for 5 min at a pressure of 100 bar.

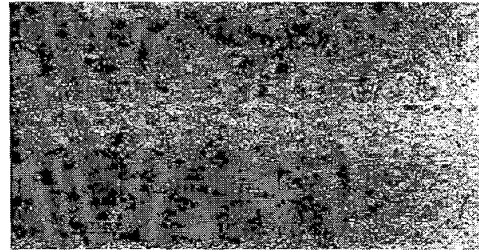


Fig. 9. Film cured at 165 °C for 5 min at a pressure of 120 bar.

Electrical Properties

Fig. 10 and Fig. 11 show the magnitude and phase of the electrical impedance respectively. The magnitude and phase presented are in excellent agreement with the results reported by Toda and Ikenohira [7]. The magnitude of the impedance decreases in the form of a hyperbolic curve, similar to the impedance behaviour of a capacitor. There is no minimum peak present as is expected from a piezoelectric material, thus indicating the lack of a resonant frequency. The phase associated with the impedance is negative and has a constant value of about -83° .

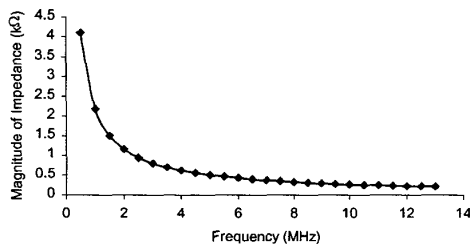


Fig. 10. Electrical impedance Z vs. frequency.

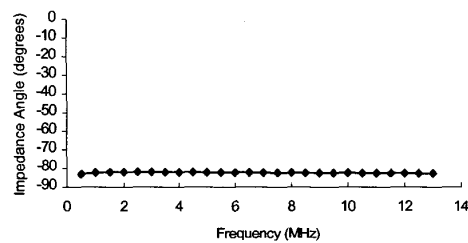


Fig. 11. Phase angle of impedance φ_Z , vs. frequency.

Conclusions

A new thick film polymer based on PVDF polymer was presented. DSC was used to determine the exact T_g and T_m of the polymer. These were found to be 55.7 °C and 163 °C respectively. The effect of the temperature on the crystallinity was also noted. A maximum net gain in crystallinity of 18.17 % was observed. A new process to cure the polymer incorporating the use of pressure was designed. Using XRD and microscopic techniques, effects of changing the temperature and the pressure of the curing process in the formed films was observed. The samples formed using this process were also analysed using wide-angle XRD. For samples formed under pressures of 100 and 120 a definite shift towards the desired piezoelectric β -phase was observed. Structural studies on the films were made using a microscope. It was found that with increasing pressure the films become more continuous structured.

References.

- [1] E. Procter, and J.T. Strong, 1982, *Capacitance strain gauges*, Elsevier applied science (1989), pp. 291-325.
- [2] R. Puers, *Sensors and Actuators A* (1993), 93-105.
- [3] K.I. Arshak, D. Collins, and F. Ansari, *International Journal of Electronics* (1994), 387-399.
- [4] S. Middelhoek and J. Van der Spiegel, *Sensors and Actuators...* (Switzerland: Elsevier Sequoia 1987).
- [5] J. Pople, *BSSM strain measurement reference book* (1979).
- [6] B. Jaffe, R.S. Roth, and S. Marzullo, *Piezoelectricity*, American Institute of Physics (1992), 159-174.
- [7] K. Toda, and K. Ikenohira, *J.Appl. Phys.*, (1980), 5657-5660.