

Degradation of the dielectric and piezoelectric response of β -poly(vinylidene fluoride) after temperature annealing

M. P. Silva¹, C. M. Costa², V. Sencadas¹, A. J. Paleo³ and S. Lanceros-Méndez^{1,*}

¹ *Centro/Departamento de Física da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*

² *CeNTI - Centre for Nanotechnology and Smart Materials, Rua Fernando Mesquita 2785, 4760-034 Vila Nova de Famalicão, Portugal*

³ *IPC – Institute for Polymers and Composites, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal*

*Corresponding author: lanceros@fisica.uminho.pt

PACS: 77.65.Bn; 77.80.Dj; 77.84.Jd; 61.41.+e

Keywords: PVDF, electroactive polymers, ferroelectric, piezoelectric

1. Abstract:

The effect of annealing temperature and time on the dielectric and piezoelectric response of poly(vinylidene fluoride), PVDF, has been studied. The observed decrease in the value of the dielectric, ϵ' , and piezoelectric, d_{33} , constants is related to depoling of the material and not to variations of the degree of crystallinity or the electroactive β -phase content. In a general way, the dielectric and piezoelectric responses decrease strongly in the first four hours at a given temperature, in particular for temperatures higher than 80 °C, reaching stable values for longer annealing times. For most applications, the temperature of 100 °C will set the limit of suitable performance. Nevertheless, the material still retains stable piezoelectric response of ~ 4 pC/N after reaching temperatures of 140 °C. The mechanisms behind the observed behavior have been discussed.

2. Introduction

Electroactive polymers (EAP) are an interesting group of materials due to their use as smart materials and structures, in particular as sensors and actuators [1-2]. The main types of electroactive polymers include piezoelectric and ferroelectric polymers, dielectric EAPs, electrostrictive graft elastomers, ionic gels, ionomeric polymer-metal composites (IPMCs) and conductive polymers (CPs) and carbon nanotubes (CNTs) [1]. The three first types are under the category of field-activated EAPs. The remaining ones are defined as ionic EAPs [1].

The advantages of field-activated EAPs compared to ionic EAPs are their rapid response (ms) and relatively large induced actuation forces [1, 3]. This class shows actuation strains over 300%, forces from 0.1 to 25 MPa and a consumed power from 10 to 150 V/ μm [4-5].

The most important piezoelectric polymer is poly(vinylidene fluoride), PVDF, and its copolymers, as they show quite high piezoelectric coefficient among polymer materials (d_{33} from -18 to -32 pC/N, depending on material processing and poling conditions) [6-10].

PVDF can show four crystalline phases: α , β , δ , γ . The most important phase for the use as smart material is the β -phase, as it exhibits the largest electroactive properties [6-7]. These properties are related to the phase content, morphology and crystallinity [8-9]. The β -phase can be obtained by mechanical stretching of α -phase films at suitable temperatures [9-11] or directly from solution at $T < 70^\circ\text{C}$ [7]. Before application, the samples must be poled. The poling process consists on the application of an electric field of several MV/cm [7] in order to achieve a biased distribution of the polarization in space toward the direction of the applied electric field [6, 7, 13].

In order to develop suitable applications, the precise knowledge of the limits of operation of the materials is an essential factor. The piezoelectric response of PVDF can be affected by temperature, radiation (UV, γ -, X-ray, energetic particles), chemical attack and time [14-16].

Celina *et al* [14] studied the operation limits of PVDF for space applications. It was concluded that PVDF shows good retention of the piezoelectric properties during γ -

irradiation. It was observed that thermal exposure is a major reason for changes in the piezoelectric properties, leading to new physical equilibrium of the poled domains. Oxygen exposure results in significant erosive damage of thin layers, but bulk piezoelectric properties in the remaining material are retained. Botelho *et al*, studied the thermal degradation of the β -phase of PVDF in relationship with the processing conditions [15]. The same authors evaluated the stability of the β -phase of PVDF against UV radiation. The results obtained showed that, even when some minor degradation takes place that influences the electrical, mechanical and electromechanical responses of the material, this polymer shows very good stability against UV radiation [16].

In this work the variation of the room temperature dielectric and piezoelectric response of PVDF as a function of annealing temperature and time has been studied. This is important in order to establish the performance limits of the material for specific applications as well as in order to understand the mechanisms involved in the decrease of the electroactive response. In order to do this, several samples of poled β -PVDF were subjected to thermal treatment at different temperatures for different periods of time. The dielectric constant (ϵ') and piezoelectric coefficients (d_{33}) were then measured and related to changes in the degree of crystallinity and β -phase content obtained from differential scanning calorimetry (DSC) and infrared spectroscopy (FTIR), respectively. Degree of crystallinity and β -phase content were selected as they are, together with dipole orientation through poling, the main contributions to the electroactive response of the material.

3. Theoretical considerations

The crystal polarization and the temperature dependence of the piezoelectric response of β -PVDF have been calculated by Carbeck et al [17, 18]. The β -phase is a polar phase with two identical chemical repeat units CH_2CF_2 per unit cell in an orthorhombic cell. The polarization can be written by [17]:

$$P_3 = \frac{2\mu}{V} , \quad (1)$$

where μ is the magnitude of the repeat unit dipole moment parallel to the 3 axis and V is the unit cell volume. The total repeat unit dipole within the crystal is represented as [17, 18]:

$$\mu = \mu^{sc} \langle \cos \varphi \rangle + \alpha E_{loc} , \quad (2)$$

where μ^{sc} is the dipole of each repeat unit of a single chain in vacuum, $\langle \cos \varphi \rangle$ is the attenuation due to thermal oscillations, α is the repeat unit polarizability along the 3 axis and E_{loc} is the local electric field. From equations 1 and 2, the crystal polarization parallel to the 3 axis is obtained:

$$P_3 = \frac{2}{V} (\mu = \mu^{sc} \langle \cos \varphi \rangle + \alpha E_{loc}) . \quad (3)$$

The piezoelectric coefficients, d_{3i} are defined by

$$d_{3i} = \left(\frac{\partial P_3}{\partial \sigma_i} \right)_{T,E} . \quad (4)$$

Substituting equation 3 in equation 4, the expression for d_{3i} is obtained:

$$d_{3i} = \frac{2\mu^{sc}}{V} \left(\frac{\partial \langle \cos \varphi \rangle}{\partial \sigma_i} \right) + \frac{2}{V} \left(\frac{\partial \Delta \mu}{\partial \sigma_i} \right) - P_3 \sum_j S_{ij} , \quad (5)$$

where σ_i is the stress, S_{ij} are the elastic compliance constants and $\Delta \mu = \alpha E_{loc}$.

The piezoelectric coefficient d_{33} has been determined as -20 pC/N based on X-ray diffraction studies and a point charge model [19], through values from -18 to -32 pC/N are found in the literature [7, 10], depending on processing and poling conditions.

The theoretical work by Carbeck et al. [16, 17] allows to conclude that:

- Increasing temperature causes an increase in the volume of the unit cell and therefore a decrease in polarization.
- Increasing temperature increases the magnitude of the oscillation, $\langle \cos \varphi \rangle$, which decreases the polarization.
- The temperature dependencies of d_{3i} are significant and determined by the temperature dependence of the elastic compliance constants and the variation of the polarizability and the attenuation of the repeat unit dipole due to thermal oscillations with applied stress.

On the other hand this model does not consider possible variations of the degree of crystallinity and electroactive β -phase of the samples, which will also influence the electroactive response of the material [10].

In the present work, the variations of the room temperature d_{33} piezoelectric and dielectric constants with different temperature and time thermal treatments have been investigated. In particular, it has been addresses whether the annealing temperature dependence is also related to possible variations of the degree of crystallinity and β -phase content of the samples.

4. Experimental

Poled β -PVDF films with a thickness of 28 μm were supplied by *Measurements Specialties*, Inc. (Fairfield, NJ, USA). The samples were cut in squares of 15 mm, placed inside an oven THSME-600 hot-stage from *Linkam* and annealed at several temperatures (60, 80, 100, 120 and 140°C) for different times (1, 4, 6, 12 and 24 hours). After the annealing procedure, the samples were removed from the oven and characterized, at room temperature, by Fourier Transformed Infrared spectroscopy, FTIR (*Bomen* spectrophotometer, 20 scans, from 4000 to 400 cm^{-1} , resolution of 4 cm^{-1}) in order to evaluate the β -phase content of the annealed samples.

The thermal behavior of the samples and the degree of crystallinity was evaluated by Differential Scanning Calorimetry (*Perkin-Elmer* Diamond series apparatus) at a heating rate of 10°C.min⁻¹. PVDF samples were cut into small pieces and placed into 40 μl aluminum pans. All experiments were performed under a nitrogen purge with a constant flow rate of 20mL.min⁻¹. The error associated to the calculation of the degree of crystallinity is ~6%.

Dielectric measurements were performed using a *Quadtech* 1920 LCR precision meter. The capacity and the dielectric losses ($\tan \delta$) were obtained at room temperature in the frequency range of 20 Hz to 1 MHz with as applied voltage of 0.5 V. Circular aluminum electrodes of 5 mm diameter were vacuum evaporated onto both sides of each sample. The real part of the dielectric function (ϵ') was calculated from the value of the capacity and the geometry of the sample. The error associated to the dielectric measurements is ~2%.

The piezoelectric response (d_{33}) of the samples was measured with a Wide Range d_{33} -meter (Model 8000, *APC Int. Ltd.*). The error associated to the piezoelectric measurements is ~4%.

5. Results

In the following, the effect of annealing temperature and time on the electroactive phase content, degree of crystallinity, dielectric and piezoelectric response will be presented.

5.1. Electroactive β -phase content

In order to determine the β -phase content present in each sample, infrared absorption bands at 764 and 840 cm^{-1} , characteristics of the α - and β -phases [20], respectively and a procedure similar to the one presented in [8, 21] was used. The amount of β -phase is calculated by

$$F(\beta) = \frac{X_{\beta}}{X_{\alpha} + X_{\beta}} = \frac{A_{\beta}}{(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}} = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}}, \quad (6)$$

where, A_{α} and A_{β} are the absorbencies at 766 and 840 cm^{-1} , corresponding to the α - and β -phase material; K_{α} and K_{β} are the absorption coefficient at the respective wave numbers and X_{α} and X_{β} represent the degree of crystallinity of each phase. The value of K is 7.7×10^4 and 6.1×10^4 cm^2/mol , respectively for α - and β -phase [21].

The room temperature infrared spectra of β -PVDF after thermal annealing at a temperature of 60°C for different times are represented in figure 1, left. In a similar way, the spectra taken after 24 h annealing at different temperatures are represented in figure 1, right.

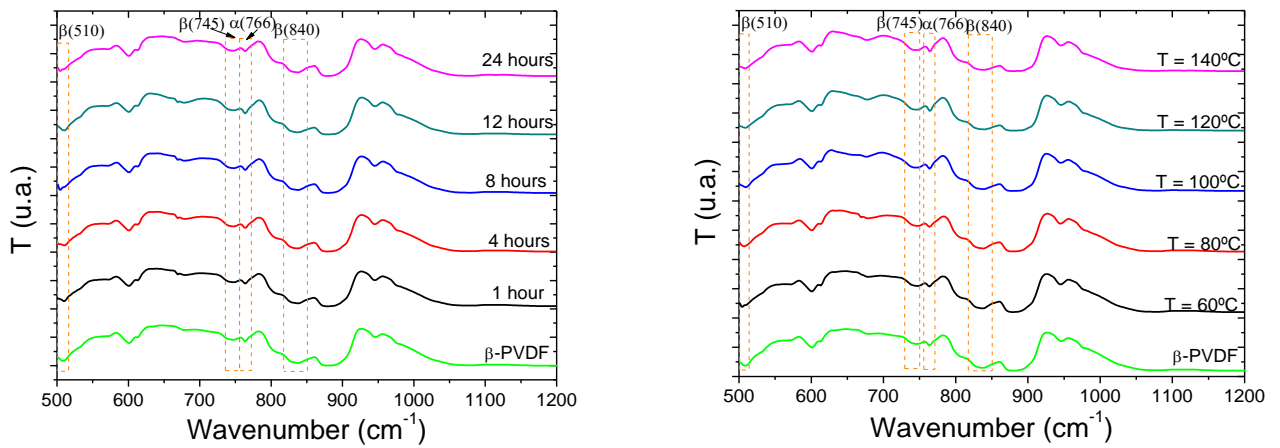


Figure 1 – Room temperature FTIR spectra obtained for β -PVDF after annealing at a temperature of 60°C for different times (left) and after annealing at different temperatures for 24h (right).

Figure 1 shows that the modes associated to the β -phase are observed for the samples after all temperature and time treatments. No substantial β - to α -phase transformation is induced. The β -phase content in each sample was calculated using equation 6 and it is presented in Table 1.

Table 1 – β -phase content (%) for the samples after the different temperature and time annealing procedures.

β-phase content (%)					
Time (h) / T ($^\circ\text{C}$)	60 $^\circ\text{C}$	80 $^\circ\text{C}$	100 $^\circ\text{C}$	120 $^\circ\text{C}$	140 $^\circ\text{C}$
1 h	96.3	96.7	95.9	96.1	95.2
4 h	96.1	96.4	96.7	96.0	96.1

6 h	96.2	96.4	95.6	95.9	95.9
12 h	96.1	96.4	95.8	96.7	96.2
24 h	96.5	96.6	96.4	96.3	96.0

It is confirmed that thermal annealing for temperatures up to 140 °C for 24 h does not induce any phase transformation in the samples, being the β -phase content for all samples, within experimental error, the same as for the sample previous to the temperature treatments (~96.4 %). The main effect of annealing is expected to be at the lamella level. In particular, lamella thickening occurs for the higher annealing temperatures [22]. During this process mainly disordered structures are developed, with no significant effect on the phase content: the phase transformation is suppressed due to the restriction of the polymer chain motions due to the existence of the high-order structures. These results support the results found in [22] in contradiction to earlier reports indicating that the β -phase of PVDF thermodynamically transform into the α -phase during the annealing process [23].

5.2. Degree of crystallinity

The melting behavior of the samples and the degree of crystallinity were investigated by differential scanning calorimetry (DSC). Figure 2 shows the DSC heating scans for different annealing conditions.

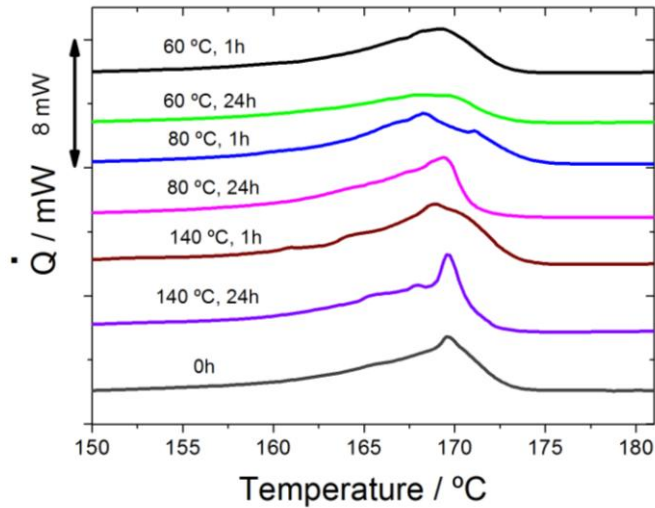


Figure 2 – DSC scans obtained for β -PVDF after different annealing temperatures and times.

The degree of crystallinity, X_c^m , was calculated by equation 7:

$$X_c^m = \frac{\Delta H_m}{\Delta H_{100}} \quad (7)$$

where ΔH_m is the melting enthalpy of the sample and ΔH_{100} is the melting enthalpy for a 100% crystalline sample of pure PVDF. For β -PVDF, the value is 103.4 J/g [24]. The results are presented in Table 2.

From figure 2 and table 2 it can be concluded that, within experimental error, no significant variations of the melting, T_m , temperatures or the degree of crystallinity are induced in the samples by the thermal annealing procedures. A general trend of increasing crystallinity with increasing annealing temperature and time is observed. The observed double endotherm and the increase of crystallinity can be attributed to the increase of lamellae thickness during the annealing process [25]. The thickening is attributed to Ostwald's ripening accompanied by interlamella diffusion of the polymer chains [26]. On the other hand, a high content of chain defects also prevent ordered lamellar thickening and the main effect of annealing is just the crystallization of thin lamellae from a portion of polymer which did not crystallize during the quenching from the melt. The variations of crystallinity obtained in this way are therefore small [27].

Table 2 –Parameters obtained from the DSC heating scans of the samples after the different annealing procedures: ΔH_m : heat of fusion; X_c^m : degree of crystallinity, calculated from equation 7

T (°C)	Annealing Time (h)	ΔH_m (J.g ⁻¹)	X_c^m (%)
60	1	57.2	55.3
	12	53.1	52.6
	24	55.0	53.2
80	1	51.1	51.3
	12	52.1	50.4
	24	58.6	56.6
140	1	58.4	56.5
	12	55.6	53.8
	24	61.8	59.8

5.3. Dielectric response

The evolution of the dielectric constant as a function of annealing time and temperature is represented in figure 3. The dielectric constant is presented at a frequency of 1 kHz. The value of the dielectric constant for β -PVDF without thermal annealing is ~13. For the lower annealing temperatures, the behavior of the dielectric constant over annealing time is characterized by stable values. On the other hand, annealing temperatures higher than 80 °C induce a decrease of the dielectric constant with increasing annealing time for times up to 4 hours, remaining stable or even slightly increasing for higher annealing times. Considering the dielectric constant at a given time, the value steadily decreases with increasing annealing temperature. The value of the dielectric loss ($\tan \delta$) is practically constant for all samples ranging from 0.020 to 0.028. As phase content and degree of crystallinity are practically constant, the behavior

of the dielectric constant is related to the depoling effect with increasing temperature and the consequent decrease of the value of the polarizations along the 3 axis (equation 3) as found in the work of Carbeck *et al* [17, 18]. These results are in agreement with previous results obtained in poled and non-poled samples [28].

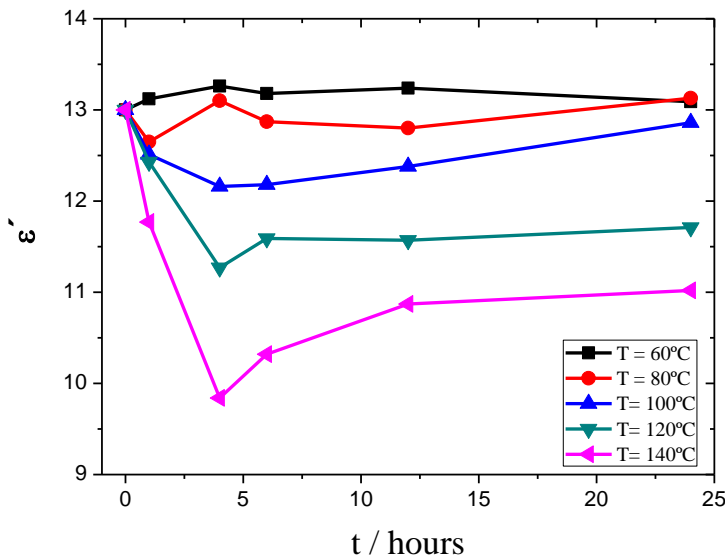


Figure 3 – Dielectric constant for β -PVDF at 1 kHz at different annealing times and temperatures.

5.4. Piezoelectric d_{33} response

Figure 4 shows the evolution of the piezoelectric coefficient d_{33} at room temperature after annealing at different temperatures for different periods of time.

As observed previously for the dielectric constant (figure 3), the d_{33} value suffers a decrease for annealing treatments up to 4 hours for each annealing temperature, reaching then an stable value for larger annealing times.

As expected, the decrease of the d_{33} value as a function of annealing temperature is non-linear, being larger for higher annealing temperatures and occurs for shorter annealing times. In particular, the decrease of d_{33} is particularly strong for temperature higher than 100 °C. The theoretical considerations (equation 5) [17, 18] indicate that the decrease of the piezoelectric response is mainly due to depoling induced by the increase of

molecular mobility with temperature. In this case, the performance of the material is severely hindered after the material has reached temperatures higher than 100 °C. Nevertheless, the piezoelectric response is still maintained at values of ~ - 4 pC/N and stable when the material has reached temperatures up to 140 °C, ~ 30 °C below the melting temperature.

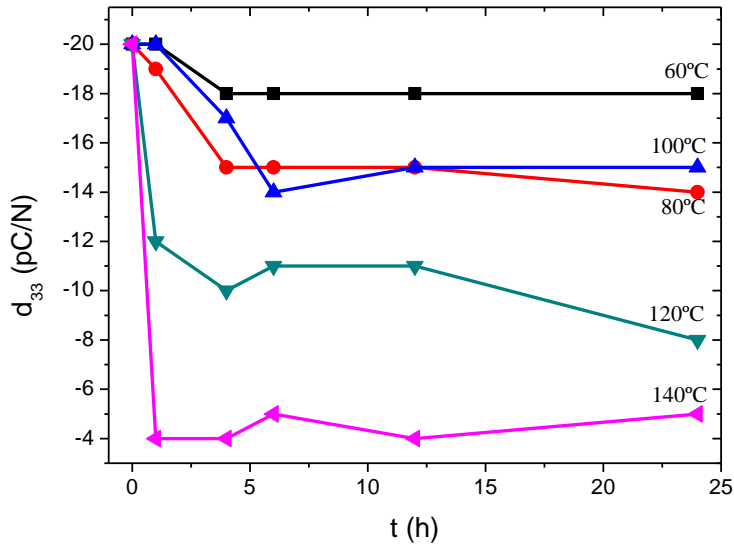


Figure 4 – d_{33} coefficient for β -PVDF after annealing at different temperatures for different periods of time.

6. Discussion

It is considered that there two kinds of relaxation mechanisms are activated during annealing of the PVDF films: Relaxation originating from the formation of disorder structures, such as deflection of polymer chains, which is likely to occur up to ~100_°C [22] and shrinkage and lamella thickening at temperatures higher than 100 °C [24, 29, 30, 31]. It is important to notice that the β -phase films are prepared by mechanically stretching α -phase PVDF [30, 31] in order to achieve the α to β -phase transformation. In this way, residual stress has been introduced into the films that will be slowly released during the low temperature annealing process but that the samples will suffer strong shrinking when the annealing temperature is larger than the processing stretching temperature. Once this is achieved, the sample will suffer a strong decrease in the sample dimensions.

In [10] it is demonstrated the dependence between the β -phase content and the piezoelectric response of PVDF. In the present case there are no variations of the phase content and the crystallinity increases slightly with increasing annealing time and temperature. Increasing crystallinity should lead to larger electroactive response as it is the crystalline part the main responsible for this response [32]. On the other hand, the decrease of the electrical and electroactive properties of the material with increasing annealing temperature is non linear, indicating that more than one activation process are necessary to explain observed behavior, i.e. confirming the existence of the aforementioned relaxation mechanisms.

In this way, the model of Carbeck *et al* [17, 18] is a good base for the explanation of the loss of electroactive properties of the material with increasing temperature as mainly considers the depoling of the material and the variations of the mechanical characteristics of the polymer with increasing temperature. On the other hand, more work is needed in order to understand how the two relaxation mechanisms specifically lead to the loss of the electroactive properties in the observed non-linear way.

7. Conclusion

This work shows how annealing temperature and time influence the dielectric and piezoelectric response of PVDF. This issue is relevant as the material has interesting properties for applications, such as sensors and actuators, in which may be subjected to different temperatures during long time periods.

The variations observed in the dielectric and electroactive response are not related to variations in the degree of crystallinity or β -phase content.

The observed variations are mainly related to depoling effects due to increasing molecular mobility with increasing temperature, shrinkage of the samples and lamella thickening. The decrease in the values of the dielectric and piezoelectric response is achieved during the first one to four hours in which the material is subjected at a given temperature, reaching stable values for higher times.

For most applications on the field of sensor and actuators, the temperature of 100 °C will set the limit of suitable performance. Nevertheless, the material still retains stable piezoelectric response after reaching temperatures of 140 °C, with a value of ~ 4 pC/N, which is still high for polymer systems.

Acknowledgements

The authors thank the Portuguese Foundation for Science and Technology (FCT) for financial support under grants PTDC/CTM/73030/2006 and NANO/NMed-SD/0156/2007. V.S. thanks the FCT for the SFRH/BPD/63148/2009 grant.

References

1. Bar-Cohen, Y. and Q. Zhang, *Electroactive Polymer Actuators and Sensors*, in *MRS Bulletin*. 2008. p. 5.
2. Vinogradov, A., et al., *State-of-the-Art Developments in the Field of Electroactive Polymers*. Mater. Res. Soc. Symp. Proc., 2006. **889**: p. 6.
3. Cheng, Z. and Q. Zhang, *Field-Activated Electroactive Polymers*, in *MRS Bulletin*. 2008. p. 5.
4. Shankar, R., T.K. Ghosh, and R.J. Spontak, *Dielectric elastomers as next-generation polymeric actuators*. Soft Matter, 2007. **3**: p. 14.
5. O'Halloran, A., F. O'Malley, and P. McHugh, *A review on dielectric elastomer actuators, technology, applications and challenges*. Journal of Applied Physics, 2008. **104**(071101): p. 10.
6. Schwartz, M., *Encyclopedia of Smart Materials*. 2002, New York: John Wiley and Sons, Inc.
7. Nalwa, H.S., *Ferroelectric polymers: chemistry, physics and applications*. 1995, New York: Marcel Dekker.
8. Gregorio Jr, R. and E.M. Ueno, *Effect of crystalline phase, orientation and temperature on the dielectric properties of poly(vinylidene fluoride) (PVDF)*. Journal of Materials Science, 1999. **34**(18): p. 4489-4500.
9. Sencadas, V., Lanceros-Mendez S., Gregorio Filho, R, Pouzada, A.S., *α - To - β transformation on PVDF films obtained by uniaxial stretch*. Materials Science Forum, 2006. **514 – 516**: p. 872, 2006
10. Gomes J, Serrado Nunes J, Sencadas V and Lanceros-Mendez S, Influence of the β -phase content and degree of crystallinity on the piezo- and ferroelectric properties of Poly(Vinylidene Fluoride), Smart Materials and Structures, 2010. 19 (6): 065010.
11. Sencadas, V., R. Gregorio Jr, and S. Lanceros-Méndez, *α to β phase transformation and microstructural changes of PVDF films induced by uniaxial stretch*. Journal of Macromolecular Science, Part B: Physics, 2009. **48**(3): p. 514-525.
12. Sencadas, V., R. Gregorio Filho, and S. Lanceros-Mendez, *Processing and characterization of a novel nonporous poly(vinylidene fluoride) films in the β -phase*. Journal of Non-Crystalline Solids, 2006. **352**(21-22): p. 2226-2229.
13. Costa, C.M., et al., *Microscopic origin of the high-strain mechanical response of poled and non-poled poly(vinylidene fluoride) in the β -phase*. Journal of Non-Crystalline Solids, 2008. **354**(32): p. 3871-3876.
14. Celina, M.C., et al., *Piezoelectric PVDF Materials Performance and Operation Limits in Space Environments*. Mater. Res. Soc. Symp. Proc., 2005. **851**: p. 12.
15. Botelho, G., et al., *Relationship between processing conditions, defects and thermal degradation of poly(vinylidene fluoride) in the β -phase*. Journal of Non-Crystalline Solids, 2008. **354**(1): p. 72-78.

16. Botelho, G., et al., *Performance of electroactive poly(vinylidene fluoride) against UV radiation*. Polymer Testing, 2008. **27**(7): p. 818-822.
17. Carbeck, J.D. and G.C. Rutledge, *Temperature dependent elastic, piezoelectric and pyroelectric properties of β -poly(vinylidene fluoride) from molecular simulation*. Polymer, 1996. **37**(22): p. 5089-5097.
18. Carbeck, J.D., D.J. Lacks, and G.C. Rutledge, *A model of crystal polarization in β -poly(vinylidene fluoride)*. The Journal of Chemical Physics, 1995. **103**(23): p. 10347-10355.
19. Tashiro, K., et al., *Calculation of Elastic and Piezoelectric Constants of Polymer Crystals by a Point Charge Model: Application to Poly(vinylidene fluoride) Form I*. Macromolecules, 1980. **13**(3): p. 691-698.
20. Lanceros-Méndez, S., et al., *FTIR and DSC studies of mechanically deformed β -PVDF films*. Journal of Macromolecular Science - Physics, 2001. **40 B**(3-4): p. 517-527.
21. Salimi, A. and A.A. Yousefi, *FTIR studies of β -phase crystal formation in stretched PVDF films*. Polymer Testing, 2003. **22**(6): p. 699-704.
22. Inoue, M., Tada, Y., Suganuma K, Ishiguro, H., *Variations in polymeric structure of ferroelectric poly(vinylidene fluoride) films during annealing at various temperatures*. Journal of Applied Polymer Science, 2009. **111**(6): p. 2837–2843.
23. Kochervinskii, V. V. *Piezoelectricity in crystallizing ferroelectric polymers: Poly(vinylidene fluoride) and its copolymers (A review)* Crystallogr Rep, 2003. **48**: 649-675.
24. Sencadas, V., S. Lanceros-Mendez, and J.F. Mano, *Characterization of poled and non-poled β -PVDF films using thermal analysis techniques*. Thermochimica Acta, 2004. **424**(1-2): p. 201-207.
25. Marega, C., Marigo, A. *Influence of annealing and chain defects on the melting behaviour of poly(vinylidene fluoride)*. European Polymer Journal, 2003. **39**(8): p. 1713-1720
26. Hikosaka, M, Rastogi, S., Keller, A., Kawabata, H. J. *Investigations on the crystallization of polyethylene under high pressure: Role of mobile phases, lamellar thickening growth, phase transformations, and morphology*. Macromol Sci Pt B Physics, 1992. **31**(1): 87-131.
27. Nakagawa, K., Ishida, Y. *Annealing effects in poly(vinylidene fluoride) as revealed by specific volume measurements, differential scanning calorimetry, and electron microscopy*. Journal of Polymer Science: Polymer Physics Edition, 1973. **11**(11): p. 2153–2171.
28. Sencadas, V., et al., *Poling of β -poly(vinylidene fluoride): Dielectric and IR spectroscopy studies*. E-Polymers, 2005. Art 002: p. 1-12.
29. Sencadas, V., Barbosa, R., Lanceros-Mendez, S., Mano, J.F. *Mechanical Characterization and Influence of the High Temperature Shrinkage of β -PVDF Films on its Electromechanical Properties*, Ferroelectrics, 2003. **294**: p. 61-71

30. Blyler, L. L. Jr., Johnson, G. E., Hylton, M. *Characterization of biaxially-oriented polyvinylidene fluoride-film for transducer applications*. *Ferroelectrics*, 1980. **28**: p. 303-306.
31. Johnson, G. E., Blyler, L. L. Jr., Crane, G. R., Gieniewski, C. *Thermal piezoelectric stability of poled uniaxially-and biaxially-oriented poly(vinylidene fluoride)*. *Ferroelectrics*, 1981. **32**: p. 43-47.
32. Vinson, J.H., Jungnickel, B.J. *Structure and stress dependence of pyroelectricity in poly(vinylidene fluoride)*. *Ferroelectrics*, 1998. **216**: p. 63-81.