Extrusion of poly(vinylidene fluoride) recycled filaments: effect of the processing cycles on the degree of crystallinity and electroactive phase content

M.P.Silva[1], R.S. Martins[2], H. Carvalho[2], J. M. Nobrega[3] and S. Lanceros-Mendez[1]

Corresponding author: H. Carvalho[2], helder@det.uminho.pt, +351967001699

[1] Centro/Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-058 Braga, Portugal. marco.uminho@gmail.com , lanceros@fisica.uminho.pt

[2] CCTT-Centre for Textile Science and Technology, Dep. de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal, rui.martins@dep.uminho.pt, helder@det.uminho.pt

[3] I3N - Institute of Nanostructures, Nanomodelling and Nanofabrication, Dep. de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal. mnobrega@dep.uminho.pt

Abstract: This study analyses the possibility of reprocessing used poly(vinylidene fluoride), PVDF, maintaining the main properties critical for its use in piezoelectric sensor/actuator applications. The influence of multiple reprocessing cycles of PVDF on crystallinity and ß-phase content fundamental for its electroactive behaviour, was studied. Nine reprocessing cycles were completed and it was found that the material preserved the characteristics required for its use as piezoelectric polymer without significant degradation.

Keywords: ferroelectrics; PVDF; extrusion; phase transformation; recycling; reuse.

Introduction

Poly(vinylidene fluoride), PVDF, is known for its outstanding electroactive properties, non-linear optical susceptibility and an unusually high dielectric constant among polymers [1]. These properties are the basis for its use in various applications, notably in the field of sensor and actuator devices [1-3]. Recently, its use in the preparation of conducting polymeric materials has also been studied [4].

PVDF is a semi-crystalline polymer with at least four crystalline phases, known as α, β, γ and δ[1-3].

The non-polar α-phase is obtained by crystallization from the melt at high or moderate cooling speeds [1-3]. The β-phase is usually obtained by stretching α-PVDF at 80ºC using a stretch ratio (R) between 3 and 5 [5, 6]. The electroactive properties of the material depend on the amount of β-phase content and its microstructural properties. The maximisation of the β-phase content has thus been a research subject of large interest [2, 7-9]. The phase content, microstructure and degree of crystallinity are crucial to the electroactive properties of the material. Therefore, processing conditions heavily influence PVDF final properties [2, 3].

PVDF has unique characteristics that make it a polymer of very high interest, but it also has a relatively high cost. In research work, as well as in industrial production, during ramp-up of the production process, there is a potential for waste of this expensive material. It is uncertain if the electroactive properties and β-phase content of the material are maintained after the polymer waste has been reprocessed; little or no information on this particular aspect can be found in literature, and the product datasheets only refer to the influence of reprocessing on mechanical properties [10].

Considering this, the feasibility of reusing PVDF whilst maintaining all the characteristics, especially the electroactive properties, is investigated in this work. With this purpose, PVDF has been reprocessed a certain number of times through extrusion and temperature-controlled stretching, and the influence of this recycling process on thermal properties, crystallinity and phase content of the material was analysed.

Experimental

Poly(vinylidene fluoride) (PVDF) supplied by Solvay (Solef 1010) was directly extruded in a monofilament production line under the conditions specified in Table 1 and Table 2. Processing parameters were chosen according to previous work that studied the optimized conditions for the production of piezoelectric PVDF filament using the same grade [11]. Figure 1 shows the schematic representation of the experimental setup used to produce the PVDF filament [11].

Table 1 – Processing conditions

Extrusion temperature	225 ºC
Cooling water temperature	30 ºC
Draw ratio	6
Stretching temperature	80 ºC

Table 2 – Different section temperatures in the extrusion process

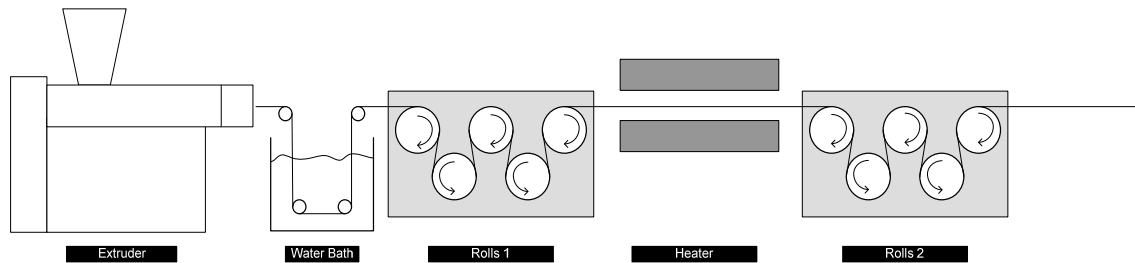| Zone 1 Feed Zone	Zone 2 Compression Zone	Zone 3 Metering Zone	Zone 4 Die
195	205	215	225

Figure 1 - Monofilament prototype extrusion line used to produce the filaments [11].

As illustrated, the material leaves the extruder and is cooled in a water bath. Subsequently, the polymer enters a system of rolls (1) that imposes a certain linear velocity, following another system of rolls (2) that work at a different linear speed. The combination of these two roll systems working at different speeds (V_{roll1} and V_{roll2}) imposes a stretch ratio (R) to the filament quantified by

$$R = \frac{V_{Roll1}}{V_{Roll2}} \tag{1}$$

This process of stretching and heating the material at a controlled temperature and ratio is critical for achieving the required α-phase to β-phase transformation of the material [5, 6].

Nine cycles were performed, using the same extrusion conditions and re-using the same material. Filaments were re-granulated between cycles using an adequate thermoplastics granulator (C F SCHEER & CIE, Model D-7000 Stuttgart 30).

After extrusion, samples were collected and studied by Differential Scanning Calorimetry (DSC) in order to determine the melting temperature and enthalpy. Three samples with weight between 10 and 20 mg were collected for the virgin material and after the 1st, 5th and 9th cycles, and tested using a DSC-7 from Perkin-Elmer. Scans were performed from 30 to 200 ℃, under a dry nitrogen environment at a rate of 10°C/min.A second scan was performed for each sample to eliminate the effect of the thermal history acquired during the reprocessing procedure the material was subjected to. It should be noted that in the second scan the sample crystallizes in the α-phase of the material.

Fourier transformed infrared spectroscopy (FTIR) tests were performed in order to calculate the β-phase content of samples after cycles 1,3,5,7 and 9. Measurements were made with a Perkin-Elmer Spectrum 100 in ATR mode at room temperature. Samples were prepared by pressing together several filaments at a temperature of 80 ℃. Treatment of the samples at this temperature does not affect the β-phase content of the material [12].

Infrared absorption bands at 763 and 840 cm^{-1}, specific to the α- and β-phases [13], respectively, and a procedure similar to that presented in [14] was used. The amount of β-phase is calculated by

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} = \frac{A_\beta}{1.26 A_\alpha + A_\beta} \tag{2}$$

where A_α and A_β are the absorbances at 763 and 840 cm^{-1}, corresponding to the α-and β-phase material; K_α and K_β are the absorption coefficients at the respective wave numbers, and X_α and X_β represent the degree of crystallinity of each phase. The value of K is 7.7×104 and 6.1×104 cm2/mol for α- and β-phase, respectively [14]. The relationship between the β-phase content and the piezoelectric coefficient d_{33} of the material has been previously demonstrated [6].

Results and Discussion

Figure 2 shows one set of DSC scans, and the resulting average melting temperature values for the three samples are shown in Figure 3.
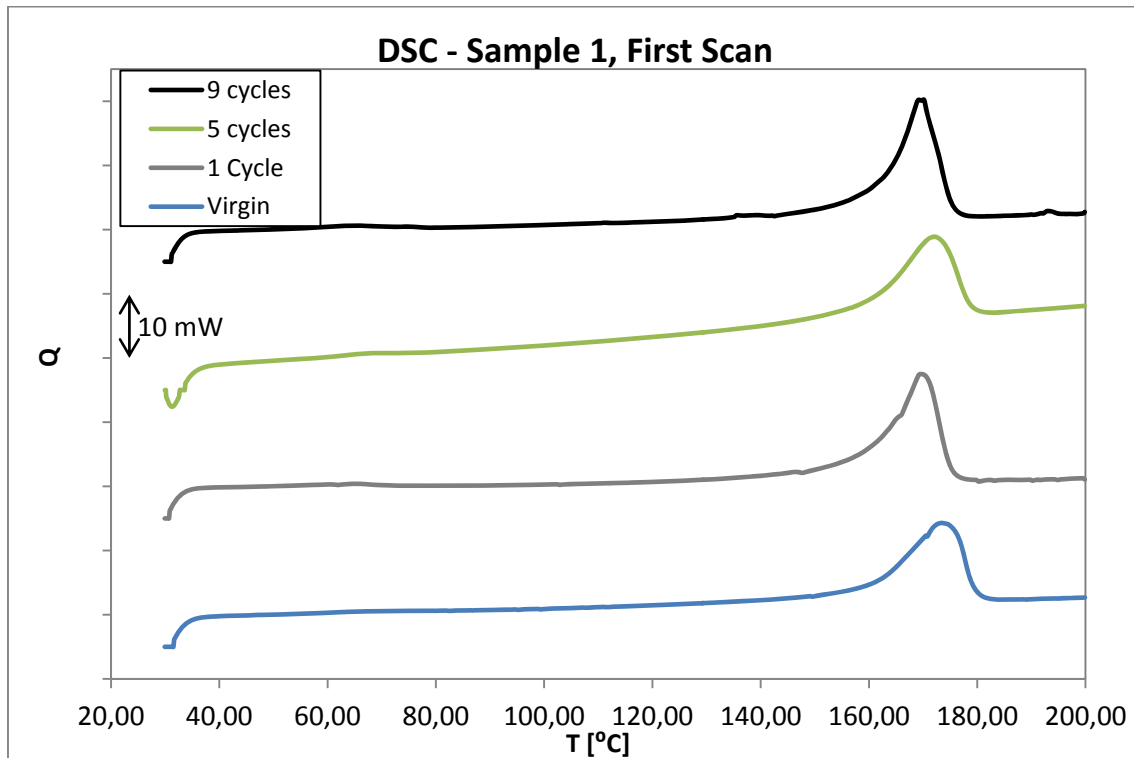

Figure 2 - DSC scans obtained for virgin PVDF and PVDF reprocessed 1, 5 and 9 times, first scan, one sample for each condition
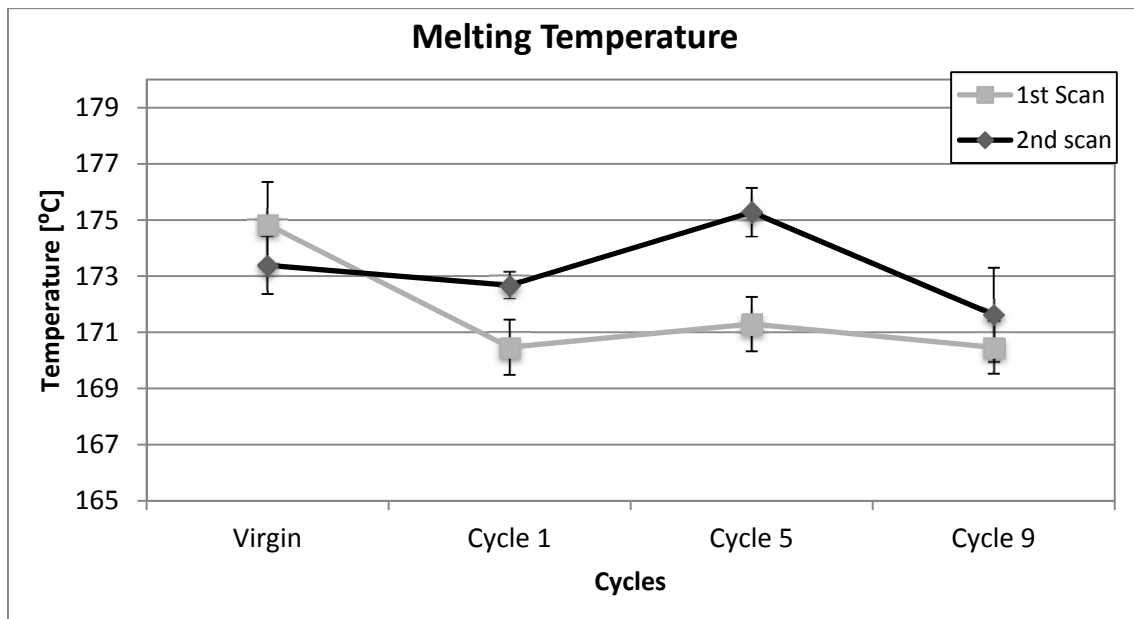
Figure 3 – Average melting temperature values of the samples, with standard-deviation.

The data obtained in the first scan indicates that the melting peak of the sample of virgin polymer is about 175ºC, which is the value supplied by the manufacturer in the datasheet, 4 to 5 ºC higher than the values found for the remaining samples. This slight difference is related to the crystallization after processing. It has to be noted that the virgin sample is analyzed by DSC without undergoing the extrusion/reprocessing process. The process comprises a quick cooling in the water bath, followed by heating to stretch the filament and cooling again, which does not allow the material to crystallize slowly to form larger crystallites, thus reducing its melting peak. After the first scan, all samples are cooled in a more controlled way in the DSC. This eliminates the thermal history of the samples and the melting temperatures become similar, as shown in Figure 3 for the second DSC scan. Although the peak of the sample reprocessed 9 times is lower than the others, no pattern of increase or decrease in melting temperature can be identified, and the difference between values is not significant.

The graph presented in Figure 4 shows the values of enthalpy of fusion normalized to the mass of the samples.
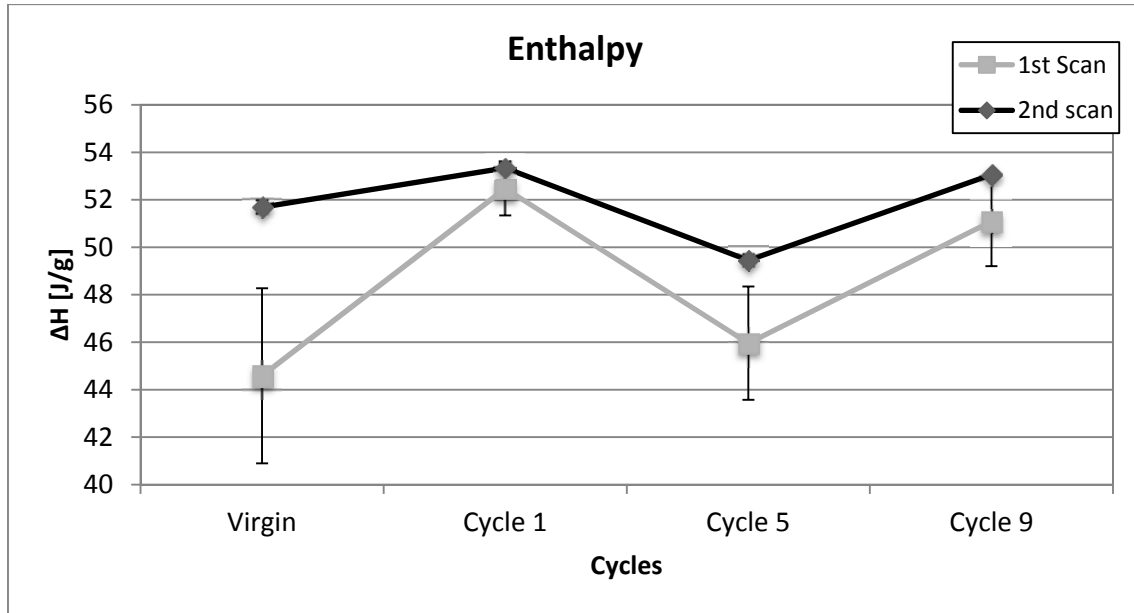
Figure 4 – Average enthalpy values, normalized to sample mass, with standard deviation.

The degree of crystallinity, X_c^m, was calculated by

$$X_c^m = \frac{\Delta H_m}{\Delta H_{100}} \qquad (3)$$

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 the β-PVDF, the letter value is 103.4 J/g [13]. The results are presented in Table 3. No significant differences are observed in the degree of crystallinity of the samples.

Table 3 – Crystalline phase content obtained from the DSC heating scans.

Number of Cycles	$X_c{}^m$(percentage, ± 5%) 1st scan	$X_c{}^m$(percentage, ± 5%) 2nd scan
Virgin	*43*	49
1	*51*	51
5	*44*	47
9	*49*	51

FTIR analysis (figure 5 and table 4) shows that there is no difference in the β-phase content of samples after several reprocessing cycles. It is found that all samples exhibit an extremely high percentage, above 95%, with no significant differences. It is thus confirmed that the amount of β-phase is not affected by reprocessing cycles.
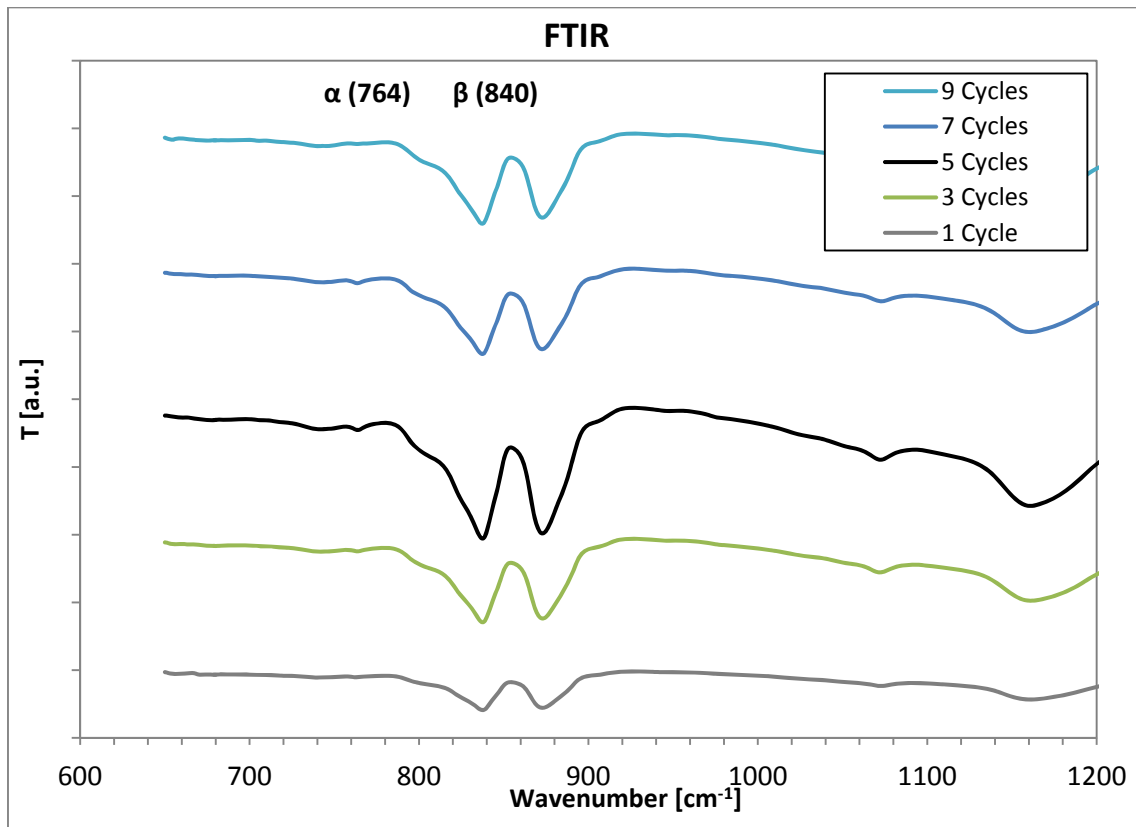
Figure 5 – Room temperature FTIR spectra obtained for β-PVDF after different number of cycles.

Table 4 – β-phase content (%) for the samples after the different processing cycles.

Number of Cycles	β-phase content in percentage(± 7%)
1	97
3	96
5	95
7	95
9	98

Conclusions

PVDF samples were subjected to several consecutive processing cycles in a production line used to produce piezoelectric filament, with the purpose of determining if the properties reling to the electroactive behavior of the material are affected by this reprocessing. It has been found that all of the parameters studied are unaffected or only very slightly affected by up to 9 processing cycles. It can, therefore, be concluded that

cristallinity and β-phase content can be reproduced in subsequent reprocessing cycles, making PVDF recycling feasible regarding its electroactive properties.

Acknowledgements

References

1.   J. Lovinger, Developments in crystalline polymers, Elsevier applied science, London (1982).

2.   S. Bauer, Journal of Applied Physics 80 (1996), p. 5531.

3.   H. S. Nalwa, Ferroelectric Polymers: Chemistry, Physics and Applications Marcel Dekker, Inc, New York (1995).

4.   J. N. Martins, M. Kersch, V. Altstädt, R.V.B. Oliveira, Electrical conductivity of poly(vinylidene fluoride)/polyaniline blends under oscillatory and steady shear conditions, Polymer Testing, Volume 32, Issue 5 (2013), pp. 862-869,

5.   V. Sencadas, R. G. Jr. and S. Lanceros-Mendez, Journal of Macromolecular Science, Part B: Physics 48 (2009), p. 514

6.   J. Gomes, J. Serrado Nunes, V. Sencadas and S. Lanceros-Mendez, Smart Materials and Structures, 19 (6) (2010): 065010.

7.   S. Lanceros-Mendez, J. F. Mano, A. M. Costa and V. H. Schmidt, Journal of Macromolecular Science, Part B: Physics 40 (2001), p. 517

8.   K. Nakamura, D. Sawai, Y. Watanabe, D. Taguchi, Y. Takahashi, T. Furukawa and T. Kanamoto, Journal of Polymer Science Part B: Polymer Physics 41 (2003), p. 1701.

9.   S. Lanceros-Mendez, M. V. Moreira, J. F. Mano, V. H. Schmidt and G. Bohannan, Ferroelectrics 273 (2002), p. 15

10.   Solef PVDF Design & Processing Guide, Solvay Specialty Polymers,(2012) p.38, available at

http://www.solvayplastics.com/sites/solvayplastics/EN/Solvay%20Plastics%20Literature/DPG_Solef_Hylar_EN.pdf, accessed 25/3/2013

11.   Ferreira, P. Costa, H. Carvalho, J.M. Nóbrega, V.Sencadas, S. Lanceros-Mendez,, Extrusion of poly(vinylidene fluoride) filaments: effect of the processing conditions and conductive inner core on the electroactive phase content and mechanical properties, Journal of Polymer Research, Volume 18, Issue 6 (2011), Springer, Netherlands

12.   M.P. Silva, C.M. Costa, V. Sencadas, A.J. Paleo, S. Lanceros-Méndez, Degradation of the dielectric and piezoelectric response of β-poly(vinylidene fluoride) after temperature annealing. Journal of Polymer Research vol. 18, issue 6 (2011), pp. 1451 – 1457

13.   J. F. Mano, A. M. Costa, and V. H. Schmidt, FTIR and DSC studies of mechanically deformed β-PVDF films, vol. 40 (2001), pp. 517–527, 2001.

14.   Salimi and A. A. Yousefi, Analysis Method, Polymer Testing, vol. 22, no. 6 (2003), pp. 699–704, Sep. 2003.