Polymer Testing 32 (2013) 1041–1044

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material properties

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

M.P. Silva [a], R.S. Martins [b], H. Carvalho [b,*], J.M. Nobrega [c], S. Lanceros-Mendez [a]

[a] Centro/Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-058 Braga, Portugal
[b] CCTT – Centre for Textile Science and Technology, Dep. de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[c] I3N – Institute of Nanostructures, Nanomodelling and Nanofabrication, Dep. de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

ARTICLE INFO

Article history:
Received 12 April 2013
Accepted 24 May 2013

Keywords:
Ferroelectrics
PVDF
Extrusion
Phase transformation
Recycling
Reuse

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.

1. Introduction

Poly(vinylidene fluoride), PVDF, is known among polymers for its outstanding electroactive properties, nonlinear optical susceptibility and an unusually high dielectric constant [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 nonpolar 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 80 °C 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, therefore, been a research subject of great 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

* Corresponding author. Tel.: +351 967001699.
E-mail addresses: marco.uminho@gmail.com (M.P. Silva), rui.martins@dep.uminho.pt (R.S. Martins), helder@det.uminho.pt (H. Carvalho), mnobrega@dep.uminho.pt (J.M. Nobrega), lanceros@fisica.uminho.pt (S. Lanceros-Mendez).

0142-9418/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymertesting.2013.05.010

Table 1
Processing conditions.

Extrusion temperature	225 °C
Cooling water temperature	30 °C
Draw ratio	6
Stretching temperature	80 °C

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

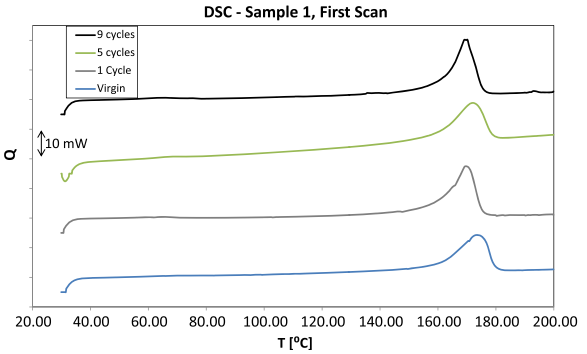

Fig. 2. DSC scans obtained for virgin PVDF and PVDF reprocessed 1, 5 and 9 times, first scan, one sample for each condition.

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.

2. Experimental

Poly(vinylidene fluoride) (PVDF) supplied by Solvay (Solef 1010) was directly extruded in a monofilament production line under the conditions specified in Tables 1 and 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]. Fig. 1 shows the schematic representation of the experimental setup used to produce the PVDF filament [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, followed by 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

$$R = \frac{V_{Roll1}}{V_{Roll2}} \quad (1)$$

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 suitable 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 °C, 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 °C. Treatment of the samples at this temperature does not affect the β-phase content of the material [12].

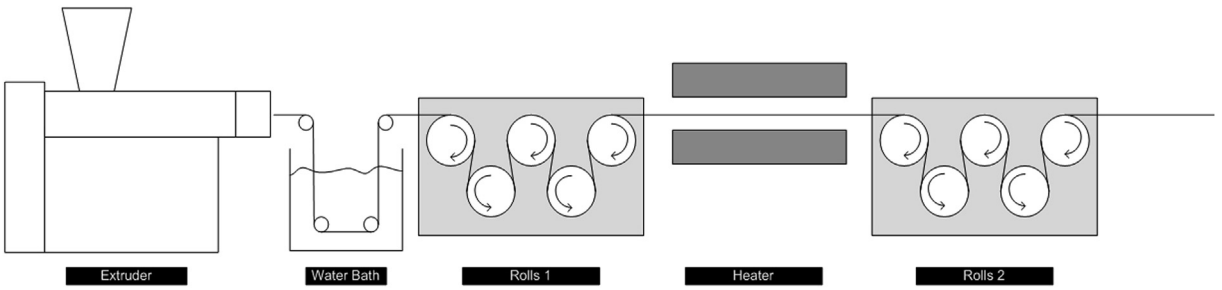

Fig. 1. Monofilament prototype extrusion line used to produce the filaments [11].