



Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications



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ABSTRACT

Poly(vinylidene fluoride), PVDF, and its copolymers are the family of polymers with the highest dielectric constant and electroactive response, including piezoelectric, pyroelectric and ferroelectric effects. The electroactive properties are increasingly important in a wide range of applications such as in biomedicine, energy generation and storage, monitoring and control, and include the development of sensors and actuators, separator and filtration membranes and smart scaffolds, among others. For many of these applications the polymer should be in one of its electroactive phases. This review presents the developments and summarizes the main characteristics of the electroactive phases of PVDF and copolymers, indicates the different processing strategies as well as the way in which the phase content is identified and quantified. Additionally, recent advances in the development of electroactive composites allowing novel effects, such as magnetoelectric responses, and opening new applications areas are presented. Finally, some of the more interesting potential applications and processing challenges are discussed.

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Abbreviations: DMAc, N,N-dimethylacetamide; DSC, differential scanning calorimetry; FE, ferroelectric; FTIR, Fourier transformed infrared spectroscopy; ME, magnetoelectric; PAN, poly(acrylonitrile); pDDA, amphiphilic poly(N-dodecylacrylamide); PE, paraelectric; PLLA, polylactic acid; PLGA, poly(lactic-glycolic acid); PMMA, poly(methyl methacrylate); PVDF, poly(vinylidene fluoride); P(VDF-CTFE), poly(vinylidene fluoride-chlorotrifluoroethylene); P(VDF-HFP), poly(vinylidene fluoride-co-hexafluoropropene); P(VDF-TrFE), poly(vinylidene fluoride-trifluoroethylene); P(VDF-TrFE-CTFE), poly(vinylidene fluoride/trifluoroethylene/chlorotrifluoroethylene); PZT, lead zirconate titanate; PVC, poly(vinyl chloride); PEMFC, proton exchange membrane fuel cells; T_c , Curie temperature; T_m , melting temperature; XRD, X-ray diffraction.

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1. Introduction

Electroactive polymers are among the most interesting classes of polymers used as smart materials in various and numerous applications, such as sensors, actuators, energy harvesting and as biomaterials in the biomedical field, among others [1]. Amid the few polymers presenting piezo, pyro or ferroelectricity, such as Nylon-11 [2], polylactic acid (PLLA) [3] and poly(lactic-co-glycolic acid) (PLGA) [4], poly(vinylidene fluoride) (PVDF) and its copolymers have the best all-around electroactive properties, being therefore the polymer of choice for the increasing number of possible applications [5–8]. This semi-crystalline polymer shows a complex structure and can present five distinct crystalline phases related to different chain conformations designed as all trans (TTT) planar zigzag for the β -phase, TGTG' (trans-gauche-trans-gauche) for the α and δ phases and T₃GT₃G' for γ and ε phases [7,9,10]. Fig. 1 shows the most investigated and used for applications PVDF phases: α , β and γ -phases.

Many of the interesting properties of PVDF, in particular those related with its use as sensor or actuator, are related to the strong electrical dipole moment of the PVDF monomer unit ($5\text{--}8 \times 10^{-30}$ C m) which is due to the electronegativity of fluorine atoms as compared to those of hydrogen and carbon atoms [7,11]. In this way, each chain possesses a dipole moment perpendicular to the polymer chain. The monomer units and therefore the dipolar

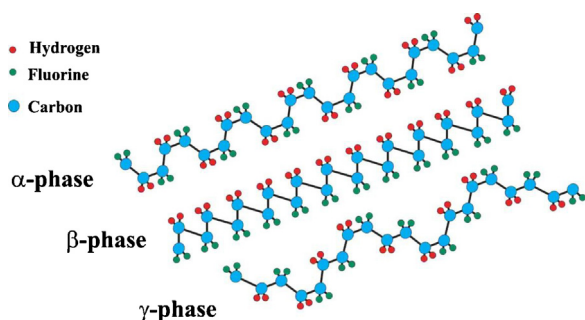


Fig. 1. Schematic representation of the chain conformation for the α , β and γ phases of PVDF.

moments are then packed in a morphology which can show an overall dipolar contribution per unit cell as in the polar β , γ and δ phases. Here, the β -phase is the one with the highest dipolar moment per unit cell (8×10^{-30} C m) when compared to the other two phases [12]. The α and ε phases are non-polar due to antiparallel packing of the dipoles within the unit cell [7,13,14]. Since the β and γ phases are the most electrically active phases, their promotion within the material is an on-going pursuit [15] due to the strong interest in application areas such as sensors, actuators, batteries, filters, chemical warfare protection, magnetoelectric, and, more recently, in the biomedical field [16–19].

Different strategies have been therefore developed to obtain the electroactive phases of PVDF, mainly focusing on the development of specific processing procedures and the inclusion of specific fillers. Another important issue is that some of the reported results regarding the identification and quantification of both γ and β -phases are contradictory: due to the similarity of the β and γ -phase specific conformations, their characteristic Fourier transformed infrared spectroscopy, FTIR, bands and X-ray diffraction peaks typically used for the identification of the phases either coincide or are very close to each other, making difficult to distinguish among both phases [20–22].

Due to the increasing interest and large potential of this electroactive polymer, this review is focused on the determination of each electroactive phase, the strategies used to obtain them, and the additional effects of fillers, together with the use of some of them as PVDF nucleating agents. Finally, some of the most interesting and challenging applications will be outlined.

2. Identification and quantification of the electroactive β and γ -phases of poly(vinylidene fluoride)

The two phases of PVDF firstly discovered were the β and α -phase, which are clearly identified by, for example, FTIR and X-ray diffraction [23]. However, the third discovered phase γ -phase has caused some confusion in its identification and has been mistakenly reported as the β -phase [22]. These mistakes persisted for a long time

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