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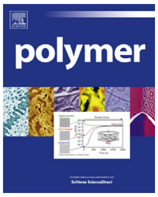

Achieving β-phase poly(vinylidene fluoride) from melt cooling: Effect of surface functionalized carbon nanotubes

Kai Ke [a,b], Petra Pötschke [a,*], Dieter Jehnichen [a], Dieter Fischer [a], Brigitte Voit [a,b]

[a] *Leibniz Institute of Polymer Research Dresden (IPF), Hohe Str. 6, 01069 Dresden, Germany*
[b] *Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden, Germany*

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) based nanocomposites with different surface-functionalized multi-walled carbon nanotubes (MWCNTs) were prepared by melt mixing in a small scale compounder. With the incorporation of commercial functionalized MWCNTs, the β-phase in PVDF can be directly achieved from melt cooling, as verified by results of Fourier transform infrared spectrum and X-ray diffraction. Interestingly, nanocomposites with amino group functionalized MWCNTs showed the highest percentage of β-phase (17.4%) formation in PVDF, followed by those with hydroxyl groups (11.6%) and unmodified MWCNTs (9.4%). However, the nanocomposites containing MWCNTs with carboxyl groups which were thought to be able to well interact with the dipoles on PVDF chains have the lowest amount of β-phase, i.e. 4.7%. The analysis on the mechanism of the influence of surface functionalization of MWCNTs on the formation of β-phase in PVDF shows that the combined effects of the dispersion of MWCNTs and the nanotube–polymer interactions account for the formation of the β-phase in PVDF.

1. Introduction

Owing to the high mechanical strength and excellent resistance to acid and alkali environment, poly(vinylidene fluoride) (PVDF) has been widely used in chemical engineering field like pipes, valves and membranes, etc. Due to the piezo- and pyro-electricity in the crystalline form of β-phase [1,2], PVDF stands out the other polymeric materials for the application of sensors and actuators, and its excellent dielectric and ferroelectric performance in contrast to other polymers endows promising applications in energy storage materials [3,4]. In general, PVDF exhibits at least four crystalline phases, e.g. non-polar α-phase, and the polar β-, γ- and δ-phases [5]. The most common one is the non-polar α-phase which is generally obtained when PVDF is cooled from the melt, while only the polar β-phase is piezo-, pyro- and ferroelectric. To date, a variety of approaches has been developed to induce the formation of the β-phase in PVDF [6–20]. Among them incorporating nanoparticles into PVDF is considered as one of the most facile ways, in which the formation of β-phase generally depends on three types of effects: 1) the interaction between surfaces of the nanoparticles, such as organically modified nanoclay (OMNC) [8–12] and ferrite nanoparticles [13,14], and the dipoles on PVDF chains; 2) the epitaxial theory interpreted as the zigzag conformations on surfaces of carbon nanotubes (CNTs) inducing the formation of all-trans PVDF chains [15–17]; 3) the cooperation effect of nanoparticles and static electric field polarization and mechanical stretching [18–22]. For instance, originally Priya et al. [8] found that commercial OMNC can induce the formation of β-phase PVDF through a melt intercalation only at high concentrations. Giannelis et al. [9] confirmed this and suggested that there are similar lattices between nanoclay and β-phase PVDF and the large flat surface of nanoclay is conducive to interact with PVDF and stabilizes the β-phase of PVDF. Patro's group [10] achieved around 90% β-phase in PVDF using 1 wt. % nanoclay modified with the cation exchange reaction designed by their group, and found that they are much more effective for inducing the formation of β-phase and toughness improvement in contrast to commercially available OMNC and unmodified nanoclay. Afterwards, aiming to obtain high fraction of β-phase PVDF with a low concentration of exfoliated OMNC, some efforts were exerted by Dillon's [11] and Buckley's [12] groups through a solution mixing route, which can strengthen the nanoparticle–polymer interaction by promoting the dispersion of the nanoparticles and benefits the formation of β-phase PVDF by means of crystallizing in a solution system. Consequently, solution mixing was frequently used to prepare carbon nanotube (CNT) filled PVDF nanocomposites with the aim of forming β-phase PVDF. Three types of influences facilitating the formation of β-phase in PVDF via a solution mixing route were proposed: 1) the epitaxy of

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* Corresponding author.
E-mail address: poe@ipfdd.de (P. Pötschke).

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PVDF chains on the surface of CNTs with the zigzag conformations [15–17]; 2) the influence of solvents [23], phase separation methods [24] and crystallization temperatures of the samples prepared by solution mixing [25]; 3) the stretching and polarization of polymer chains during electrospinning [21,22]. However, it seems not yet possible to obtain a large amount of β-phase in PVDF directly by cooling the melt after melt mixing. Although in literature it has been referred to that trace amounts of β-phase PVDF can be formed in PVDF/CNT nanocomposites by melt mixing [26,27] and melt spinning [28], the adsorption bands in Fourier transform infrared (FTIR) spectroscopy or patterns in X-ray diffraction (XRD) are too weak to effectively prove the existence of β-phase or quantifying the amount of β-phase. As a consequence, naturally no discussion about the content of β-phase based on bands in the FTIR spectroscopy or patterns in XRD results has been done in literature [26–28]. Quite recently, Xing et al. [29] found that the addition of 2 wt. % multi-walled CNTs (MWCNTs) induced the formation of 6.1% β-phase in PVDF which is the highest value calculated from FTIR results at this moment when the sample obtained by melt mixing was cooled from the melt after hot pressing, while nearly 100% β-phase was achieved when MWCNTs modified with the ionic liquid ($[BMIM]^+[PF_6]^-$) were introduced. They suggested that the incorporation of the ionic liquid improved the dispersion of MWCNTs and the imidazolium cations in the ionic liquid interacted with $-CF_2$ bonds of PVDF, and accordingly the nucleation of β-phase PVDF was effectively promoted. Besides MWCNTs modified with ionic liquid, MWCNTs modified by poly(methyl methacrylate) [26] and ester groups (e.g. $-COOC_2H_5$) [30] were also used to fabricate PVDF/CNT nanocomposites via a solution method, in which the fraction of β-phase was greatly dependent on the modification of MWCNTs and their dispersion in the matrix. However, these studies contain no comparison with commercially available modified nanotubes so that the influence of functionalization of MWCNTs on the formation of β-phase is still unknown. From a perspective of commercial applications, melt processing is the most suitable way for the fabrication of polymer nanocomposites. Therefore, it is highly favorable to fabricate β-phase PVDF/CNT nanocomposites through a melt mixing route. This is a facile and versatile processing route that can effectively promote the potential applications of piezoelectric PVDF/CNT nanocomposites as smart devices like sensors and actuators.

In this work, PVDF/CNT nanocomposites with a variety of commercial functionalized MWCNTs were prepared by melt-mixing using a small scale compounder. With the incorporation of functionalized MWCNTs, the β-phase PVDF was achieved directly through a melt mixing route, which provides a new and facile way to fabricate piezoelectric PVDF nanocomposites. Besides, the effect of commercial functionalized MWCNTs with different chemical groups on the formation of the β-phase in PVDF was systemically investigated, which can serve as a basis for the optimization of choosing appropriate MWCNTs for fabricating piezoelectric PVDF nanocomposites. Moreover, the reasons for the β-phase formation and the factors determining the amount of β-phase in PVDF nanocomposites filled with differently functionalized MWCNTs were analyzed by studying the relationship between the surface functionalization of MWCNTs and their dispersion in PVDF.

2. Experimental

2.1. Materials and sample preparation

PVDF pellets (Kynar 720, Arkema) with a weight average molecular weight of 455,800 g/mol and a polydispersity of 6.08 were used. Four types of short thin multi-walled carbon nanotubes with a length of ∼1 μm and an average outside diameter of 9.5 nm, belonging to the NC3150 series, were purchased from Nanocyl, S.A., Belgium. The as-received commercial nanotubes were non-functionalized (NC3150), abbreviated as u-CNT, and those functionalized with carboxyl (NC3151), amino (NC3152) and hydroxyl (NC3153) groups, which correspondingly have the abbreviations of c-CNT, a-CNT and h-CNT, respectively. The XPS results as given in Ref. [31] indicate that the contents of carboxyl, amino and hydroxyl groups in c-CNT, a-CNT and h-CNT are ∼3%, ∼0.5% and ∼1.2%, respectively.

The nanocomposites based on PVDF and four types of MWCNTs were fabricated using a twin-screw micro-compounder (DSM Xplore, capacity 15 cm^3, The Netherlands) under conditions of 210 °C, 200 rpm and 10 min. Before compounding, PVDF pellets and MWCNT powder, being dried in a vacuum oven at 80 °C for 12 h, were premixed in a glass by shaking and the mixtures were fed in the hopper of the compounder. The obtained samples were named according to their compositions, e.g. the nanocomposite containing 0.5 wt. % unmodified carbon nanotubes was named as PVDF-0.5% u-CNT. The reference sample namely pure PVDF prepared with the same way was named as PVDF. It is noteworthy that the strands were cooled to room temperature after being extruded from the die (2 mm diameter) and there was no additional treatment for them.

In order to investigate the crystalline structure and physical properties of the nanocomposites, i.e. FTIR, X-ray diffraction, Raman spectroscopy, tensile testing and electrical conductivity measurements, the obtained extruded strands were cut into small pieces and compression molded (200 °C, 50 kN, 2.5 min) into circular plates (60 mm diameter, 0.5 mm thickness) using a hot press (Model-PW40EH, Paul-Otto Weber GmbH, Germany). After that the samples were cooled with a simple cooling instrument structured with two aluminum plates connected to the water pipes directly and cut or punched into the required sample sizes for the aforementioned measurements.

2.2. Characterization

The attenuated total reflection FTIR spectra of the samples were investigated by the Tensor 27 (Bruker, GmbH) Fourier transform infrared spectrometer in the range between 4000 cm^{-1} and 550 cm^{-1}. In order to describe the contribution of the nanotubes with different surface functionalization to the formation of β-phase quantitatively, the relative percentage of β-phase ($F_{(\beta)}$) in the whole crystalline phase is calculated according the following equation [6,26,32]:

$$F_{(\beta)} = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \times 100\% \tag{1}$$

in which X_β and X_α are crystalline mass fractions of α- and β-phase and A_α and A_β correspond to the absorbance of vibration bands at 762 and 839 cm^{-1}, respectively. At least three positions on the films were investigated by FTIR so that the standard deviation can be obtained.

The X-ray diffraction patterns of the samples were studied at room temperature using a 2-circle diffractometer (XRD 3003 T/T, GE Sensing & Inspection Technologies GmbH), and data between $2\theta = 5–45°$ were recorded. The diffraction was performed with Cu-Kα radiation ($\lambda = 0.1542$ nm) generated with 40 kV and 30 mA. Additionally, the percent of β-phase was calculated by integrating the areas of the original curves in the region of $2\theta = 10–30°$ and the fitting curve (ANALYZE software, GE Sensing & Inspection Technologies GmbH) of each peak in this region. The ratio of intensity of β- to α-phase and the fraction of β-phase area in the whole area of the crystalline phase, which were abbreviated as I_β/I_α and X_β respectively, were also calculated based on the fitting XRD results.

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