

Preliminary Studies of MWCNT/PVDF Polymer Composites

Esther Lorrayne M. Pereira, Adriana Souza M. Batista, Fabíola A. S. Ribeiro, Adelina P. Santos, Clascídia A. Furtado, Luiz O. Faria

Abstract—The combination of multi-walled carbon nanotubes (MWCNTs) with polymers offers an attractive route to reinforce the macromolecular compounds as well as the introduction of new properties based on morphological modifications or electronic interactions between the two constituents. As they are only a few nanometers in dimension, it offers ultra-large interfacial area per volume between the nano-element and polymer matrix. Nevertheless, the use of MWCNTs as a rough material in different applications has been largely limited by their poor processability, insolubility, and infusibility. Studies concerning the nanofiller reinforced polymer composites are justified in an attempt to overcome these limitations. This work presents one preliminary study of MWCNTs dispersion into the PVDF homopolymer. For preparation, the composite components were diluted in *n,n*-dimethylacetamide (DMAc) with mechanical agitation assistance. After complete dilution, followed by slow evaporation of the solvent at 60°C, the samples were dried. Films of about 80 μm were obtained. FTIR and UV-Vis spectroscopic techniques were used to characterize the nanocomposites. The appearance of absorption bands in the FTIR spectra of nanofilled samples, when compared to the spectrum of pristine PVDF samples, are discussed and compared with the UV-Vis measurements.

Keywords—Composites materials, FTIR, MWNTs, PVDF, UV-Vis.

I. INTRODUCTION

POLY(vinylidene fluoride) (PVDF) homopolymers, whose main chain is formed by the repetition of $-(CF_2-CH_2)_n-$ monomers, are used in a diverse range of industries where their unique set of properties which includes high purity, chemical resistance, abrasion resistance, fire resistance, weatherability to UV and humidity, mechanical strength, flexibility, impact resistance, thermal stability, and ease of processing, is required. PVDF exhibits polymorphism of several crystalline phases and shows at least five possible types of crystal phase, the so-called nonpolar α -phase, polar β -phase, and γ , δ , and ϵ -phase. The most common polymorph of PVDF is the α -phase, having a monoclinic unit cell with TG^+TG^- chain conformation. The β -phase is the more attractive and desirable among the PVDF phases, with conformational

Esther Lorrayne M. Pereira, and Adriana Souza M. Batista are with the Universidade Federal de Minas, Belo Horizonte, MG 31270-970 Brasil (phone: 55-31-3409-6666, 31-55-3409-9770; fax: 55-31-3409-6660, 31-55-3409-9770; e-mail: esther_machado@outlook.com.br, adriananuclear@yahoo.com.br).

Fabíola A. S. Ribeiro, Adelina P. Santos, Clascídia A. Furtado, and Luiz O. Faria are with Serviço de Nanotecnologia e Materiais Nucleares, Belo Horizonte, MG 31270-901 Brasil, on leave from the Centro de Desenvolvimento da Tecnologia Nuclear, Minas Gerais, Brasil (e-mail: farialo@cdtn.br).

sequences of *TTT* (all trans) [1]. In this conformation, PVDF is ferroelectric, i.e. it simultaneously presents piezo and pyroelectricity, which render them application as sensors and actuators.

Ever since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [2], the use of CNTs as a nano-filler for polymers has been receiving increasing attention. Two forms of CNTs exist: single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). SWCNTs comprise a single sheet of graphite rolled into a cylinder; multiwalled carbon nanotubes (MWCNT) consist of concentric cylinders around a hollow center with constant wall to wall separation of 0.34 nm [3].

Nanoparticles with their nanometer size, high surface area, and the associated performance of interfaces can be used as structure and morphology directors in the nanocomposites production. Incorporation of nanoparticles into various polymers to produce composites has been extensively utilized in an attempt to enhance the mechanical, physical, and thermal properties of polymer [4]. In recent years, some investigations have been pursued on of PVDF/nanoparticle composites, which main motivation is related to the control of the crystalline phase, thereby conferring to the resulted material desirable features. In this context, some composites of PVDF with SiO₂, among others, have been studied [5]. Other authors have studied pristine MWCNTs and zirconia-coated multiwalled carbon nanotubes (ZrO₂/MWCNTs) by isothermal hydrolysis. The traditional chemical precipitation method have been used to disperse the nanofillers into the PVDF matrix by solution mixing in *N,N*-dimethylformamide (DMF). Due to the improved dispersion of the coated nanotubes, the incorporation of 3 wt % of ZrO₂-coated MWCNTs leads to an increase of the thermal stability and dielectric properties and decrease of the peak heat-release rate [6]. Also, very recently, nanocomposites made of P(VDF-TrFE) copolymers and ZrO₂ nanoparticles encapsulated with methyl methacrylate (MMA) have been proposed as X-rays attenuator protective clothes [7].

In this work, a preliminary study of MWCNTs dispersion in PVDF/ZrO₂ mixture is presented. The PVDF/ZrO₂-MWCNT films were studied by FTIR and UV-Vis spectroscopic techniques.

II. EXPERIMENTAL

PVDF homopolymers were supplied by ATOCHEM (France). Nanocomposites were produced by mixing solved PVDF in DMAc with ZrO₂ dispersed in an aqueous solution,

by mechanical agitation assistance. MWCNTs dispersed into DMAC were added to PVDF/ZrO₂ solution in three proportions: 0.5, 1.0 and 1.5 mg of MWCNT for 250 ml of the PVDF and 2.0 mg of ZrO₂ nanoparticles.

In Fig. 1 (a) we present samples with high concentrations of nanotubos but with poor dispersion into the PVDF matrix. After overcoming the dispersing difficulties, we show in Fig. 1 (b) the sample with a better dispersion of carbon nanotubes, obtained by the conventional casting technique (slow evaporation at 60°C).



(a)



(b)

Fig. 1 (a) Samples of PVDF/ZrO₂/MWCNT (1.0 mg and 1.5 mg respectively), before casting, (b) sample of PVDF/ZrO₂/MWCNT (0.5 mg) obtained by the conventional casting technique (slow evaporation at 60°C)

Optical transmission measurements were taken in a Shimadzu UV-2401 PC spectrometer, for wavelengths ranging from 190 to 900 nm. Lorentzian (Amplitude) lines were then used to perform the deconvolution of the optical absorption peaks, each one fitted as in (1):

$$y = \frac{a_0}{1 + \left(\frac{x - a_1}{a_2}\right)^2} \quad (1)$$

where a_0 = amplitude, a_1 = center and a_2 = width

After deconvolution using the software "Peak Fit", we try to correlate the individual peaks to those reported in literature.

FTIR spectra were collected with 32 scans each, in a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000 cm⁻¹.

III. RESULTS AND DISCUSSION

UV-Vis spectroscopy was used to examine the presence of the MWCNTs in the PVDF/ZrO₂ matrix. It has been reported that two wide absorption bands, attributed to MWCNTs, appear at 235 and 255nm [8]. Because of their proximity, these two bands look like a unique wide absorption peak. UV-Vis absorbance spectra of pure PVDF and PVDF/ZrO₂ and PVDF/ZrO₂/MWCNTs composite samples are shown in Fig. 2. In the spectra collected for samples fulfilled with MWCNT it is possible to see the appearing of a wide peak, starting around 220nm and ending at 275nm, which is in agreement with data reported in literature [9]. Note that the peak intensities increase for increasing MWCNT concentrations.

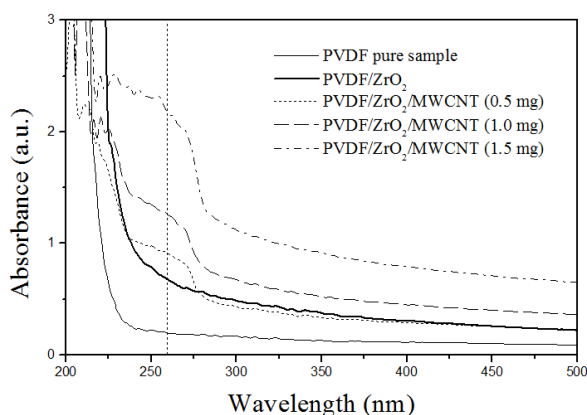


Fig. 2 UV-Vis spectra for PVDF pure sample, PVDF/ZrO₂ and PVDF/ZrO₂/MWCNTs composites with 0.5, 1.0 and 1.5 mg of MWCNTs

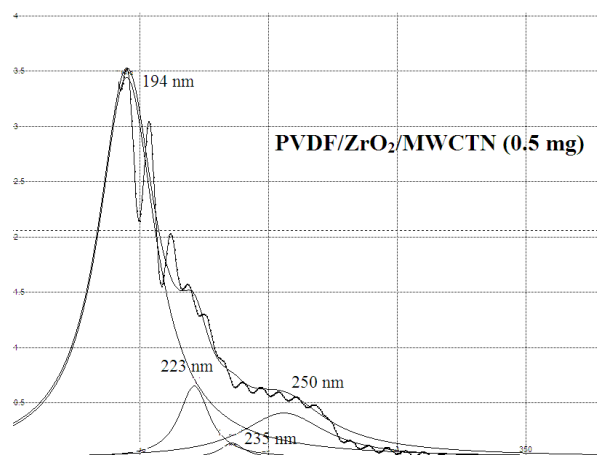


Fig. 3 UV-Vis spectra of the PVDF/ZrO₂/MWCNTs (0.5 mg) and absorption peaks at 194, 223, 235 and 255 nm, obtained after peak fitting

Lorentzian lines were then used to peak fit the spectra. The individual peaks could be used to better explain the experimental spectra (Fig. 3). In fact, the absorption peaks attributed to conjugated C=C bonds that appear at 194 nm and 223 nm have been reported to correspond to singlet and

doublet of conjugated C=C bonds, respectively, in PVDF radio-induced chains defects [10].

The FTIR spectra of pure PVDF, PVDF/ZrO₂ and PVDF/ZrO₂/MWCNTs (1.0 mg) composite samples are shown in Fig. 4. FTIR is considered elsewhere a good technique for unambiguous identification of the PVDF crystalline structure.

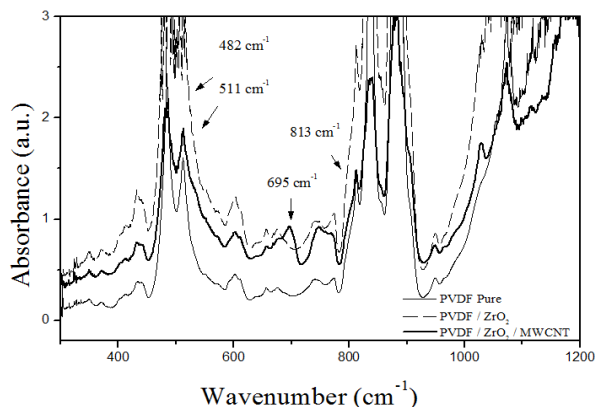


Fig. 4 FTIR spectra of PVDF pure sample, PVDF/ZrO₂ and PVDF/ZrO₂/MWCNTs composites with 1.0 mg of the MWCNTs

According to literature, the bands at 532, 615, 764, 796, 855, 876, 976 and 1218 cm⁻¹ are assigned to TG+ TG⁻ chain conformation characteristic of the PVDF α -phase while bands at 510, 840, 1274 and 1284 cm⁻¹ are related to the TT trans sequence (β -phase). Absorption bands at 813 and 482 and 511 cm⁻¹ are assigned to γ -phase, which is thought to be a mixture of α and β -phase [8]. Based on this observation, the appearance of absorption bands at 482, 511 and 813 cm⁻¹, indicative of the γ -phase, and also the bands attributed to both α and β -phases, as seen in Fig. 4, suggests that the samples are in the γ -phase.

With the addition of the MWCNTs, the band intensity at 695 cm⁻¹ becomes stronger. Otherwise, the bands not common to PVDF could be attributed to the presence of aldehydes groups, which in this case is -C-C-CHO- bonds [11]. In fact, the first vibrational calculation of the IR active modes in SWCNTs reported in literature includes an absorption band localized at 682 cm⁻¹[11].

The Powder Diffraction File, International Center for Diffraction Data (ICDD) data base reports four crystalline phases for PVDF: form I (β -phase), form II (α -phase) and two forms III (γ -phase) with different parameters. The diffraction patterns for each of the forms were simulated theoretically according to this information and are shown in Fig. 5 films [12].

The experimental X-ray diffractograms are shown in Fig. 6. In the XRD diffractograms for pure PVDF (bottom) we see the 110, 020 and 100 reflection planes at $2\theta = 20.14^\circ$, 18.4° and 17.88° , respectively, which are attributed to the α -phase. Also, the small peak around 40° belongs to this same phase. From the diffractograms for PVDF/ZrO₂/MWCNT composites (upper) we see that the PVDF crystalline phase is not changed and that the crystalline order is decreased for

higher contents of MWCNTs. On the other hand, back in the FTIR analyses, new absorption bands can be seen in the samples with MWCNTs, centered at 2852 and 2928 cm⁻¹, as shown in Fig. 7. They are attributed to the CH stretching modes. The bands at 2981 and 3023 cm⁻¹ are attributed to the CH₂ symmetric and asymmetric stretching vibrations, also present in the PVDF pure samples. However, the new absorptions at 2852 and 2928 cm⁻¹ may be due to the presence of MWCNTs in the PVDF matrix. In fact, M. Zhang et al., (2003) observed these bands in as grown MWCNT samples and have attributed them to C-Hx stretching vibrations of chemisorbed hydrogen of various types presents in carbon films [13].

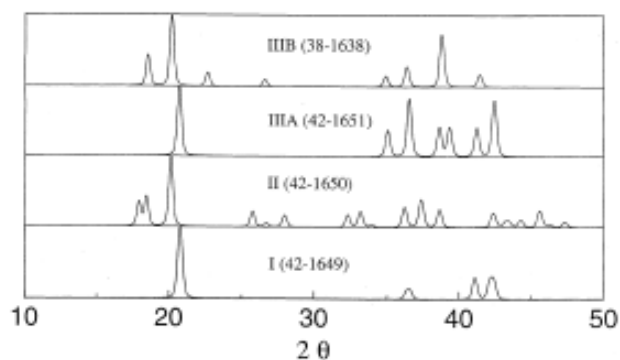


Fig. 5 Theoretical simulations of X-ray spectra for the four known phases of PVDF [11]

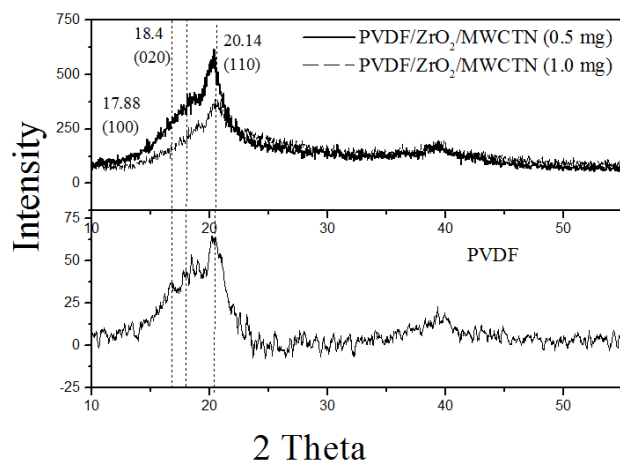


Fig. 6 X-rays diffractograms for samples of PVDF whit PVDF/ZrO₂/MWCNT (0.5 mg) and PVDF/ZrO₂/MWCNT (1.0 mg)

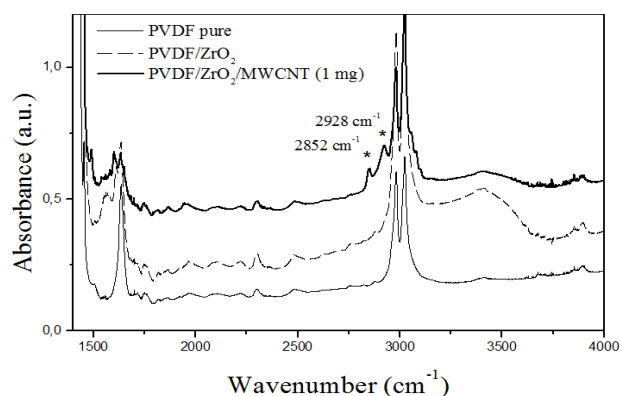


Fig. 7 FTIR spectra of the PVDF pure sample, PVDF/ZrO₂ and PVDF/ZrO₂/MWNTs with 1.0 mg of the MWNTs

IV. CONCLUSIONS

PVDF pure samples, PVDF/ZrO₂ and PVDF/ZrO₂/MWCNTs were produced and characterized by UV-Vis and FTIR spectroscopic techniques. It was observed that the samples crystallized in the PVDF γ -phase. The FTIR analyses reveal the presence of new absorbance bands at 2852 and 2928 cm⁻¹ in the nanocomposite that are attributed to C–Hx stretching vibrations of chemisorbed hydrogen of various types, present in the as grow MWCNTs. DRX data revealed that the addition of ZrO₂ and MWCNT to the PVDF matrix does not change the crystalline phase. However, the crystalline order decreases as the amount of MWCNT increases in the composite.

ACKNOWLEDGMENT

Financial support from Conselho Nacional de Pesquisa e Desenvolvimento Científico (CNPq) and Fundação de Amparo a Pesquisa do Estado de Minas Gerais (FAPEMIG) are acknowledged.

REFERENCES

- [1] C. Xing, L. Zhao, J. You, W. Dong, X. Cao, Y. Li, "Impact of ionic liquid-modified multiwalled carbon nanotubes on the crystallization behavior of poly(vinylidene fluoride)", in *The Journal Physical Chemistry*, vol. 116, 2012, pp. 8312-8320.
- [2] S. Iijima, "Helical microtubules of graphitic carbon" in *Nature*, vol. 354, 1991, pp. 56-58.
- [3] W. Huang, K. Edenzon, L. Fernandez, S. Razmpour, J. Woodbum, P. Cebe, "Nanocomposites of poly(vinylidene fluoride) with multiwalled carbon nanotubes", in *Journal Applied Polymer Science*, vol. 113, 2010, pp. 3238-3248.
- [4] L. He, Q. Xu, C. Hua, R. Song, "Effect of multi-walled carbon nanotubes on crystallization, thermal, and mechanical properties of poly(vinylidene fluoride)" in *Polymer Composites*, 2010, pp. 921-926.
- [5] R. Song, D.B. Yang, L.H. He, in *Journal Materials Science*, vol. 42, 2007, pp. 8408-8417.
- [6] K. Pal, D.J. Kang, Z.X. Zhang, J.K. Kim, "Synergistic effect of zirconia-coated carbon nanotubes on crystalline structure of polyvinylidene fluoride nanocomposites: electrical properties and flame-retardant behavior" in *Langmuir*, vol. 26 (5), 2010, pp. 3609-3614.
- [7] C.C.P. Fontainha, A. T. Baptista-Neto, A. P. Santos, L. O. Faria, "P(VDF-TrFE)/ZrO₂ Polymer-Composites for X-ray Shielding" in *Material Research*, 2015 (in print).
- [8] Xuelian Cheng, Jun Zhong, Jie Meng, Man Yang, Fumin Jia, Zhen Xu, Hua Kong, and Haiyan Xu "Characterization of Multiwalled Carbon Nanotubes Dispersing in Water and Association with Biological Effects"

Journal of Nanomaterials. Volume 2011 (2011), Article ID 938491
<http://dx.doi.org/10.1155/2011/938491>

- [9] L. He, J. Sun, X. Wang, L. Yao, J. Li, R. Song, Y. Hao, Y. He, W. Huang, "Enhancement of β -crystalline phase of poly(vinylidene fluoride) in the presence of hyperbranched copolymer wrapped multiwalled carbon nanotubes" in *Journal of Colloid and Interface Science*, vol. 363, 2011, pp. 122-128.
- [10] A. S. Medeiros, L. O. Faria, "High gamma dose response of poly(vinylidene fluoride) copolymers", in *Nuclear Instruments and Methods in Physics Research, Section B, Beam Interactions with Materials and Atoms (Print)*, v. 268, 2010, pp. 2740 – 2743.
- [11] S. Lefrant, M. Baibarac, I. Baltog, "Raman and FTIR spectroscopy as valuable tools for the characterization of polymer and carbon nanotube based composites", in *Journal Materials Chemistry*, vol. 19, 2009, pp. 5690-5704.
- [12] E. Adem, J. Rickards, G. Burillo, L. Cota, M. Avalos-Borja, "Changes in poly-vinylidene fluoride produced by electron irradiation" in *Radiation Physics and Chemistry*, vol. 54, 1999, pp. 637-641.
- [13] M. Zhang, M. Yudasaka, S. Bandow, S. Iijima, *Chem. Phys. Lett.*, vol. 369, 2003, pp. 680.