Enhancement of Electrical and Optical Properties of Polyvinylidene Fluoride Samples by Cerium Sulfate Addition

E.A. Falcão[1*], M.J.R. Amorim[1,2], E.R. Botero[1], N.L.C. Domingues[1], I.A. Santos[3] and A.W. Rinaldi[3]

[1]Federal University of Grande Dourados (UFGD), Rodovia Dourados-Itahum, km 12, Dourados, ZIP code 79.804-970, MS, Brazil

[2]Federal Institute of Mato Grosso do Sul (IFMS), R. Ângelo Melão, 790, Três Lagoas, ZIP code 79.641-162, MS, Brazil

[3]State University of Maringá (UEM), Av. Colombo 5790, Zona 07, Maringá, ZIP code 87.020-900, PR, Brazil

Abstract: In the present work, polyvinylidene fluoride's (PVDF) electrical and optical properties have been studied as a function of cerium sulfate tetrahydrate called $Ce(SO_4)_2$. Experimental result shows that the relative percentage of β phase ($F_\beta\%$) increases by almost 55 % with $Ce(SO_4)_2$ addition in the polymeric matrix. The dielectric permittivity measurements presented an increase, at 1 KHz, of 62 % up to 0.8 % of $Ce(SO_4)_2$ content. This increase was attributed to the Maxwell-Wagner effect. The UV-Vis measurements presented some changes at the UV region due to $Ce(SO_4)_2$. The fluorescence measurements showed an enhancement in the fluorescence peak of almost 130 % for the PVDF/$Ce(SO_4)_2$ 0.8% and a blue shift of the maximum fluorescence intensity. These results show that PVDF/$Ce(SO_4)_2$ sample is a potential candidate for optical, photonic, electrical, and electronic applications.

Keywords: PVDF, Ferroelectric polymer, Cerium sulfate tetrahydrate, Fluorescence.

1. INTRODUCTION

The interest in obtaining and characterizing the physical properties of multifunctional materials with ferroelectric properties has increased because they can be prepared for different applications and produced on a large scale [1, 2]. Polymeric materials have gained special attention because of their excellent ferroelectric properties and flexibility. Among the ferroelectric polymer materials, polyvinylidene fluoride (PVDF) is one of the most studied due to its excellent piezoelectric and pyroelectric properties compared to other ferroelectric polymer materials. For example, PVDF samples possesses a piezoelectric coefficient (d_{31}) between 20 and 30 pC/N, for polyvinyl fluoride and polyvinyl chloride d_{31} is 1 pC/N and for nylon d_{31} is 3 pC/N. The pyroelectric coefficient (p) for PVDF are between 30 and 40 $\mu C/Km^2$, instead for other ferroelectric polymers p is less than 10 $\mu C/Km^2$ [3]. Ferroelectricity in PVDF is due to its semi-crystalline structure, composed of five different phases known as α, β, γ, δ, and ε [4]. From these phases α is non polar and β, γ, δ, and ε possesses a non-zero dipole moment [5]. However, the formation of these phases is closely related to the synthesis route adopted to prepare the PVDF films [6]. The α and β phases are the most studied for technological applications [7, 8]. When PVDF presents a high percentage of α phase, it is used in mechanical applications. For ferroelectric applications, is required a high percentage of β phase. PVDF is frequently used as a coating to prevent a corrosive attack, sensors, actuators, and memories [9]. Recently PVDF ferroelectric polymers also have attracted interest in the photonics area to be used as a host for rare-earth ions, which enable the use of these materials in optical devices [4, 6, 9]. These studies are interesting from the technological point of view once the insertion of rare earth ions in the polymeric matrix may improve the optical fluorescence of the PVDF [4, 9]. Thus, this work presents the synthesis and characterization of cerium sulfate doped PVDF samples. FT-IR measurements were done to verify the incorporation of cerium sulfate in the polymeric matrix. The dielectric measurements as dielectric permittivity was done to analyze the effects caused by cerium sulfate addition. The UV-Vis measurements were used to determine the optical absorbance. Fluorescence measurements were used to determine the changes caused in the natural fluorescence of PVDF by $Ce(SO_4)_2$ addition. The results of this work show that PVDF/$Ce(SO_4)_2$ is a potential candidate to be used in electro, electronic, optical, and photonic devices.

2. EXPERIMENTAL

To prepare the PVDF composites it was used a stock solution of 75 mg/ml of PVDF dissolute in DMF

---

[*] Address correspondence to this author at the Federal University of Grande Dourados (UFGD), Rodovia Dourados-Itahum, km 12, Dourados, ZIP code 79.804-970, MS, Brazil; E-mail: evaristofalcao@ufgd.edu.br

E-ISSN: 2311-8717/23

(Dimethylformamide**)** and a stock solution of 0.6 mg/ml of $Ce(SO_4)_2.4H_2O$ or $Ce(SO_4)_2$. The stock solutions were prepared using magnetic stirring for 60 min at room temperature. After aliquots of PVDF and $Ce(SO_4)_2$ were added in Petri dishes to obtain concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 wt%. After stirring the mixture, they were dried in an oven at 50° C for 16 h. All samples presented a thickness of 60 ± 0.5 μm.

The Fourier Transform Infrared measurements (FT-IR) were done by equipment JASCO FT/ IR - 4100. To collect the experimental data, it was used 150 scans with a resolution of 2 cm^{-1} in the range 4000-500 cm^{-1}

The fluorescence measurements were performed with the portable Spectrofluorimeter composed of two excitation laser beans operating at 405 nm and 532 nm, a monochromator (USB 2000 FL / Ocean Optics), a fiber-type "Y," and a laptop. This work used a laser of 405 nm of wavelength.

Dielectric measurements were performed using an RLC bridge (Precision LCR – Meter Agilent E4980A) from 500 Hz to 2 MHz.

3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis

Figure **1** is plotted the experimental results of FT-IR for PVDF 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 wt % of cerium sulfate doped samples. These measurements have been done to verify the incorporation and analyze the effects caused by dopant addition in the polymeric matrix. For pure PVDF, the typical absorption peaks at 1402, 976, 855, 795, 766, 615, and 530 cm^{-1} refer to α-phase, the peaks at 1279–1275, 840, 511 cm^{-1} refers to β-phase, the peaks at 834, 812, 778 cm^{-1} belongs to γ-phase. The broadband between 1242 and 1064 cm^{-1} is caused by the C–F stretching and is the PVDF signature [4, 10-12].

Experimental results reveal that $Ce(SO_4)_{22}$ has been incorporated into the PVDF matrix. From Figure **1**, it is possible to observe that $Ce(SO_4)_2$ addition changes the characteristic peaks at 840 cm^{-1} and 764 cm^{-1}, marked by the dotted lines representing β and α phases, respectively. From these peaks, it is possible to calculate the relative percentage of β phase ($F_\beta\%$) using the Salimi and Yousef model, described by Equation 1 [11].

$$(F_\beta\%) = \frac{Abs_\beta}{1{,}26Abs_\alpha + Abs\beta} \tag{1}$$

where A_β and A_α are the areas of FT-IR absorption band at 840 cm^{-1} and 764 cm^{-1}, respectively.

The results (see Figure **2**) show that ($F_\beta\%$) for pure PVDF is 50 % presenting a relative percentage of β phase, and agree with previous work reported in the literature. Gregório obtained the same percentage for his samples [12]. However, the results for doped samples present an increase in the ($F_\beta\%$) as a function of $Ce(SO_4)_2$ content. From pure PVDF to PVDF/

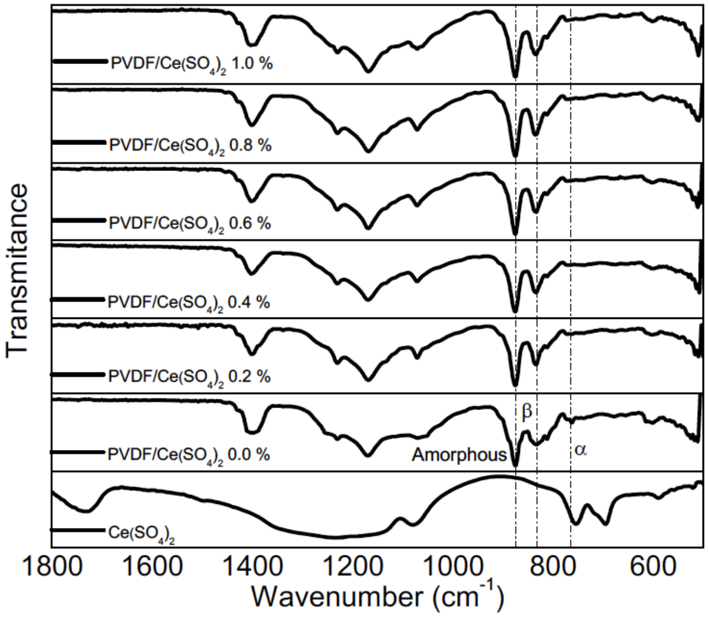

Figure 1: FT-IR measurements in the PVDF/$Ce(SO_4)_2$ doped samples as a function of concentration.

$Ce(SO_4)_2$ 1.0 % the variation is almost 55 %, showing that dopant addition increases the polar phase of pure PVDF. From the literature, Aguiar reported that β phase remains constant with Nd_2O_3 addition [4] and the same behavior has been reported previously for PVDF/Ho doped samples [6].

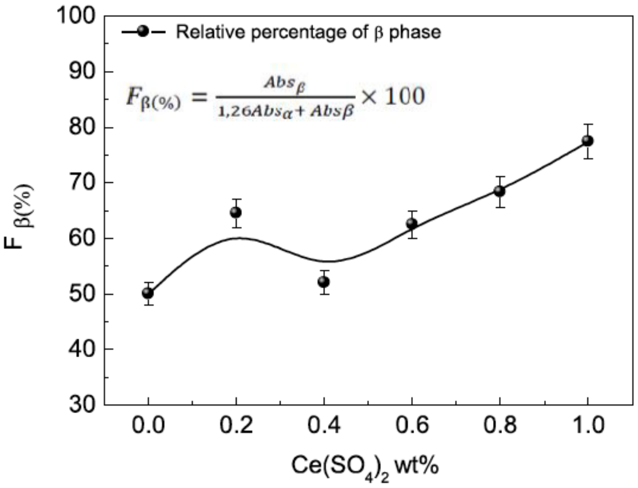

Figure 2: Relative percentage of b phase for PVDF/$Ce(SO_4)_2$ doped samples as a function of concentration.

3.2. Dielectric Characterization

Considering that β is the ferroelectric phase of PVDF and that $Ce(SO_4)_2$ addition increases ($F_\beta\%$). Measurements of the dielectric permittivity (ε') have been done to verify the effects caused by the dopant addition, and the results are displayed in Figure **3**. For pure PVDF, the parameter ε' decreases by almost 63 % with the frequency increase, and for doped samples, 69 %. This behavior is due to a reduction of dipolar contribution at high frequencies [13].

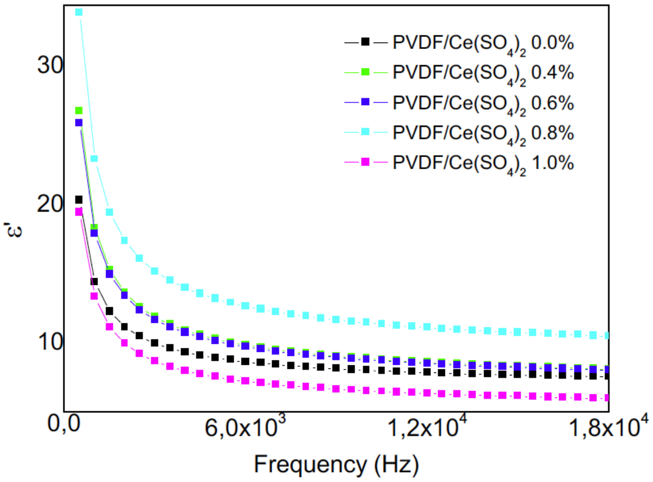

Figure 3: Dielectric permittivity measurements of PVDF/$Ce(SO_4)_2$ doped samples as a function of concentration and frequency up to 18 KHz.

For simplicity, it was chosen the frequency of 1 KHz to analyze ε' measurements, Figure **4**. For pure PVDF at this frequency, the value of ε' is 14.3, Figure **4**(**a**). Campos and coworkers found a value of 13, and Rozana found 10 for 1 KHz, proving that our results agree with those from the literature [14, 15]. The dopant addition increases ε' by almost 62 % at 1 KHz up to the concentration of 0.8 % in the polymeric matrix. Garain reported that the cerium ammonium sulfate (CAS) addition in the PVDF matrix increases ε' from 7.5 to 40.7 at 1KHz [13]. However, for the concentration of 1 % ε' decreases to 13 that is almost 43 %. This behavior indicates a saturation condition that might induce interfacial polarization or defects. However, to affirm it, other studies should be done. To better understand this effect, the values of ε' versus a value ($F_\beta\%$) Figure **4**(**b**). The experimental results reveal the behavior observed in Figure **4**(**a**), proving the saturation condition and that the dopant addition causes this effect.

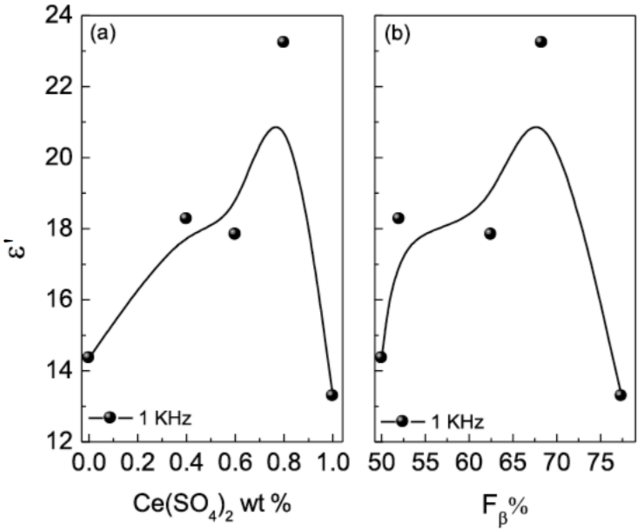

Figure 4: Dielectric permittivity results at 1 KHz as a function of the concentration of $Ce(SO_4)_2$ (**a**), and dielectric permittivity results as a function of ($F_\beta\%$) (**b**).

3.3. Absorption Spectra (UV–Vis)

In the present work, the UV-Vis measurements have been done to analyze the changes caused by $Ce(SO_4)_2$ in the optical absorbance of pure PVDF, and the normalized experimental results are displayed in Figure **5**. As it can be seen, pure PVDF presents an optical absorption band between 250 nm and 400 nm that is attributed to the electronic transition of the fluorocarbons (F–C) [4,17]. As can be seen in the inset of Figure **5**, $Ce(SO_4)_2$ presents characteristic peaks at 225 nm, 240 nm, and 320 nm, values that are close to those reported in the literature. In addition, Basha and coworkers found a peak at 290 nm attributed to electronic transition 5d→4f [18]. $Ce(SO_4)_2$ addition changes the optical absorbance at the UV region of PVDF, appearing as two "shoulders" close to 240 nm and 300 nm. The "shoulder" close to 240 nm increases up to 0,6 % of $Ce(SO_4)_2$ content and decreases for high concentrations.

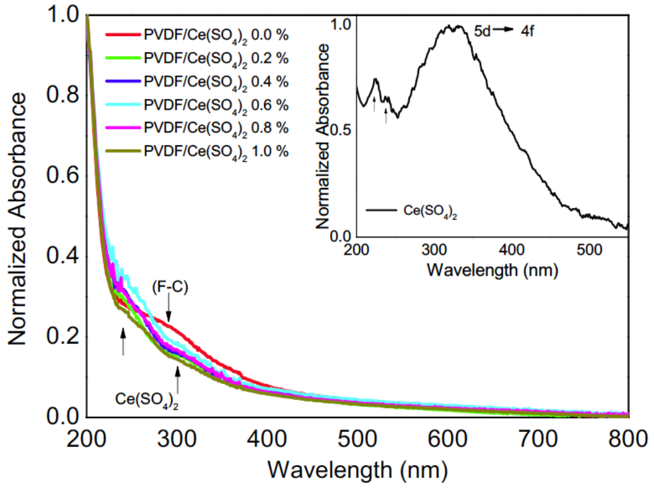

Figure 5: Normalized absorbance measurements of PVDF/ $Ce(SO_4)_2$ as a function of dopant content.

3.4. Fluorescence Measurements

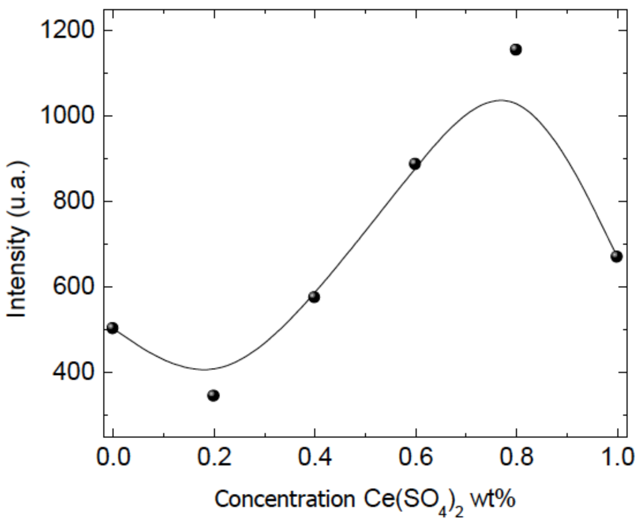

Figura 6: Maximum fluoresce peak of PVDF as a function of $Ce(SO_4)_2$ addition.

In Figure **6**, it was chosen to present only the maximum fluorescence intensity as a function of dopant content to analyze the enhancement in the fluorescence measurements caused by $Ce(SO_4)_2$ addition. For $Ce(SO_4)_2$, the maximum fluorescence intensity is 122, which is a low fluorescence compared with other materials. The pure PVDF sample presents a maximum fluorescence intensity of 500. When 0,2 % of dopant is added, the maximum fluorescence peak decreases to 345. For high concentrations of $Ce(SO_4)_2$, the maximum fluorescence peak is 1154 for PVDF/$Ce(SO_4)_2$ 0,8%, and for PVDF/$Ce(SO_4)_2$, 1.0 % decreases to 670. The observed increase confirms the enhancement caused by $Ce(SO_4)_2$ addition, and the decrease indicates a saturation condition where the sample loses energy by a non-radiative process, decreasing the fluorescence.

Figure **7** presents the normalized fluorescence spectra for all samples. The $Ce(SO_4)_2$ sample presents a bandwidth at half height of the order of 95 nm with a maximum fluorescence peak at 560 nm. For pure PVDF, the bandwidth at half height is approximately 120 nm and a peak at 530 nm. Abdelaziz reports that the maximum fluorescence intensity occurs at 550 nm for PVDF/PMMA and might be associated with the physical rotation of the polar group (CH_2–CF_2) of PVDF [16].

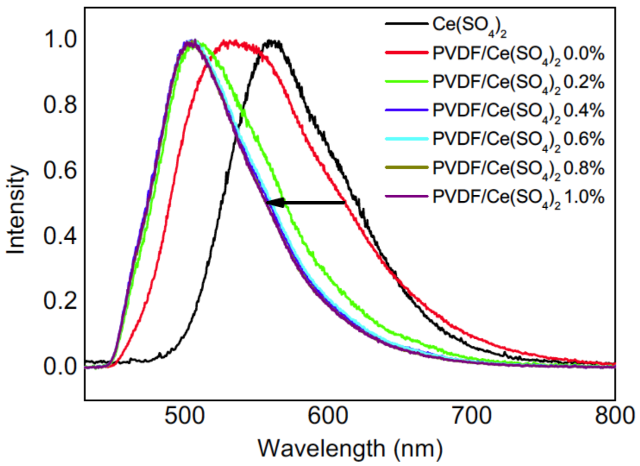

Figure 7: Normalized fluorescence spectra for PVDF/$Ce(SO_4)_2$ in different concentrations.

In Figure **7** can be observed that the $Ce(SO_4)_2$ insertion in the PVDF matrix causes a blue shift of approximately 28 nm in the fluorescence peak of PVDF from 531 nm to 503 nm. As can be seen, adding just 0.2% $Ce(SO_4)_2$ is sufficient to shift the maximum intensity peak to the blue region and stabilize at high concentrations. This effect may be associated with how $Ce(SO_4)_2$ binds to the PVDF matrix. However, other studies must be done to understand the phenomenology of this effect. Although the Ce^{4+} does not present fluorescence at this oxidation state, adding it with sulfate induces significant changes in the fluorescence spectra. This effect might be associated with SO_4^{2-}. The results reveal that PVDF/$Ce(SO_4)_2$

sample is a potential candidate for electrical, optical, and photonic applications

CONCLUSION

The relative percentage of β phase and dielectric properties of PVDF/$Ce(SO_4)_2$ doped samples were studied as a function of dopant content. The experimental results have shown that $Ce(SO_4)_2$ addition induces significant changes in the relative percentage of β phase, presenting an increase of almost 55 %. The dielectric permittivity measurements presented an increase, at 1 KHz, of 62 % for 0.8 % of $Ce(SO_4)_2$ content and for 1.0% decreases close to the value of pure PVDF. This effect might indicate a saturation condition and be attributed to the interfacial polarization or Maxwell-Wagner effect. Thus, from the technological point of view, our results reveal that $Ce(SO_4)_2$ insertion enhances the polar phase and dielectric properties of the PVDF matrix, and there is a limit to this. The UV-Vis measurements presented the same behavior observed in the dielectric measurements. Fluorescence measurements showed an increase in the maximum fluorescence peak of 130 % PVDF/$Ce(SO_4)_2$ 0.8%, and a blue shift. Our results also reveal that adding $Ce(SO_4)_2$ in the PVDF matrix enhances pure PVDF's optical and electrical properties. In conclusion, the experimental results showed that PVDF/$Ce(SO_4)_2$ is a potential candidate for optical, photonic, electrical, and electronic applications.

ACKNOWLEDGEMENTS

The authors are thankful to the Brazilian Agencies, CAPES, CNPQ (process: 483683/2010-8, 208232/2014-1), FINEP (contract: 04.13.0448.00/2013), Araucária Foundation, and FUNDECT, for the financial support of this work.

REFERENCES

[1] W. Koechner, M. B, Solid State Laser Engineering, Springer Series in Optical Sciences Vol. 1, edited by D.L. MacAdam, 4th ed. (Springer, Berlin, 1996). https://link.springer.com/book/10.1007/0-387-29338-8.

[2] W. Ma, L. E. Cross, Tunable Electric-Field-Induced Piezoelectricity in High Strain Relaxor Ferroelectric P(VDF-TrFE) Copolymer, J. Phys.: Condens. Matter 2005; 17: 1011-1018. http://dx.doi.org/10.1088/0953-8984/17/6/019

[3] A. J. Lovinger, Ferroelectric Polymer, Science 220 [4602] 1983; 1115-1121. https://doi.org/10.1126/science.220.4602.1115

[4] L.W. Aguiar, E.R. Botero, C.T. Carvalho, A.R.L. Caires, C.T.P. da Silva, A.W. Rinaldi, R. Guo, A.S. Bhalla, E.A. Falcao, Study of the changes in the polar phase and optical properties of poly (vinylidene fluoride) matrix by neodymium compound addition, Mat. Tod. Com. 2020; 25: 101274. https://doi.org/10.1016/j.mtcomm.2020.101274

[5] B. Mohammadi, A. A. Yousefi, S. M. Bellah, Effect of Tensile Strain Rate and Elongation on Crystalline Structure and Piezoelectric Properties ff PVDF Thin Films, Polymer Testing 2007; 26: 42-50. http://dx.doi.org/10.1016%2Fj.polymertesting.2006.08.003

[6] B. C. F. Farinelli, M. S. Silva, E. R. Botero, C. T. Carvalho, A. R. L. Caires, R. Guo, A. S. Bhalla, E. A. Falcão, Study of the effects of holmium and 2- aminoterephthalate additions on the optical properties of polyvinylidene fluoride, Integrated Ferroelectrics, 2016; 174(1): 167-173. https://doi.org/10.1080/10584587.2016.1195629

[7] A. Moslehyani, A. F. Ismail, M. H. D. Othman, T. Matsuura, Design and Performance Study of Hybrid Photocatalytic Reactor-PVDF/ MWCNT Nanocomposite Membrane System for Treatment of Petroleum Refinery Wastewater, Desalination 2015; 363. https://doi.org/10.1016/j.desal.2015.01.044

[8] P. Anithakumari, B. P. Mandal, E. Abdelhamid, R. Naik, A. K. Tyagi, Enhancementof Dielectric, Ferroelectric And Magneto-Dielectric Properties in PVDF–$BaFe_{12}O_{19}$ Composites: A Step Towards Miniaturizated Electronic Devices, RSC Adv. 2016; 6: 16073-16080. https://doi.org/10.1039/C5RA27023E

[9] E. A. Falcao, L. W. Aguiar, R. Guo, A. S. Bhalla, Optical absorption of Nd_2O_3-Doped polyvinylidene fluoride films, Mat. Chem. and Phys. 2021; 258: 123904 https://doi.org/10.1016/j.matchemphys.2020.123904

[10] Y. Bormashenki, Vibrational spectrum of PVDF and its interpretation, Polym. Test., 2004; 23: 791-796. https://doi.org/10.1016/j.polymertesting.2004.04.001

[11] A. Salimi, A.A. Yousefi, Analisis method: FTIR Studies of β-phase crystal formation in stretched PVDF films, Polym. Test. 2003; 22: 699-704. https://doi.org/10.1016/S0142-9418(03)00003-5

[12] R. Gregorio, M. Cestari, Effect of crystallization temperature on the crystalline phase content and morphology of poly(vinylidene Fluoride), J. Polym. Sci. Part B: Polym. Phys. 1994; 32: 859-870. https://doi.org/10.1002/polb.1994.090320509

[13] S. Garain, S. Sen, K. Henkel, D. Schmeißer, D. Mandal, Enhancement of Electroactive β-phase and Superior Dielectric Properties in Cerium Based Poly(vinylidene fluoride) Composite Films, Mat. Today: Proc. 2018; 5(3): 10084-10090. https://doi.org/10.1016/j.matpr.2017.11.003]

[14] J. S. C. Campos, G. A. Santarine, Laser pulse energy detector, Eclética Quimica 1997; 22 . https://doi.org/10.1590/S0100-46701997000100009

[15] M. D. Rozana, A. N. Arshadl, M.H. Wahidl, Z. Habibah, L.N. Ismail, M. N. Sarip, M. Rusop, Dielectric constant of PVDF/MgO nanocomposites thin films; IEEE Symp. on Busi., Eng. and Ind. Appl. 2012; 18-22. https://doi.org/10.1109/ISBEIA.2012.6422866

[16] M. Abdelaziz, Investigations on optical and dielectric properties of PVDF/PMMA blend doped with mixed samarium and nickel chlorides, J Mater Sci: Mater Electron 2013; 24: 2727-2736. https://doi.org/10.1007/s10854-013-1162-x

[17] B. Ahmed, S.K. Raghuvanshi, N.P. Sharma, J.B.M. Krishna, M.A. Wahab, 1.25mev gamma irradiated induced physical and chemical changesin poly vinylidene fluoride (PVDF) polymer, Prog. Nanotechnol. Nanomater. 2013; 2: 42-46. http://dx.doi.org/10.1016/j.nimb.2009.08.026

[18] M. A. F. Basha, Spectroscopic, Magnetic, and Optical Characterization of Nanocomposite Films of

Polyvinylpyrrolidone Doped with Cerium Disulphate; J. of App. Pol., 2011; 122: 2121-2129. https://doi.org/10.1002/app.34295

Received on 10-04-2023 Accepted on 13-05-2023 Published on 21-06-2023

DOI: https://doi.org/10.12974/2311-8717.2023.11.02