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Influence of $NiFe_2O_4$ on β Phase Formation in PVDF Composites

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ABSTRACT: *This work presents a systematic study on the influence of the synthesis conditions in nickel ferrite ($NiFe_2O_4$) doped polyvinylidene fluoride (PVDF) composites films. The synthesis of nickel ferrite was performed by the Pechini method by different thermal treatment conditions. The $NiFe_2O_4$ powders were characterized by X-ray diffraction (XRD) to check the phases and estimate the particle size. Variables such as concentration and particle size of $NiFe_2O_4$, time, and temperature of solvent removal were controlled during the synthesis of the composite. The composites samples were prepared by the solid-state solutions method and were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), which estimated the relative percentages of β phases and the identification of the incorporation of dopant ($NiFe_2O_4$) in the polymer matrix (PVDF). Also, to verify the inclusion of $NiFe_2O_4$ nanoparticles in the polymer, the samples were characterized by optical microscopy.*

Keywords: *PVDF, β phase, Nickel Ferrite, Pechini synthesis, Nanoparticles.*

I. INTRODUCTION

The technological development and recent increases in scientific research are responsible for the production and use of new materials in the manufacturing of technological devices construction [1]. In this way, polymeric materials such as polycarbonate (PC), polypropylene (PP) and polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), among others, are progressively replacing the traditional materials used in engineerings, such as steel and aluminum, since they have higher corrosion resistance, low price and the possibility of recycling [2-4].

The wide use of polymer materials is, mainly, due to its low cost and good mechanical properties due to its molecular mobility, which is influenced by the chemical nature of the macromolecules, the molecular mass, the presence or absence of branching and crosslinking, the degree of crystallinity, the presence or absence of plasticizer, filler, additives, orientation and other aspects related to the thermal history of the particular sample [5-6]. Even though there are many polymer materials, poly(vinylidene fluoride) has advantages because of its high electroactive nature, high flexibility and is easy to process in the form of films with desired shapeand size. Its high permittivity, relatively low dissipation factor, and high dielectric breakdown have made this polymer a suitable candidate for capacitor dielectric in hight energy density storage applications [7,8]. PVDF is a semi-crystalline polymer that exists in different polymorphsα, β, γ, δ, and ε. Among which β phase is electroactive with all- Trans TTTT conformation exhibiting high piezo-, pyro-, ferro-, and dielectric performances [9,10].

The polyvinylidene fluoride (PVDF), which has been extensively studied due to its attractive pyro and piezoelectric properties (when present predominantly in the β phase) as well as its flexibility, excellent

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processability, chemical stability and mechanical strength [11]. It combines the characteristics of plastic with those of a piezoelectric and pyroelectric element and presents an excellent combination of processability and mechanical strength. This facilitates large-scale production giving it some advantages over conventional ceramic materials [12-13].

For years, the effect of the work of different sizes, shapes, and the surface of ferromagnetic nanoparticles ($CoFe_2O_4$, $NiFe_2O_4$, $Ni_{0,5}Zn_{0,5}Fe_2O_4$) within the PVDF matrix was also studied to improve the electroactive phase of the flexible artificial multiferroic composite [14-17]. In this work, we present the result of the influence of doped ferrite on PVDF, analyzing thestructural formation of the polymeric matrix.

II. MATERIALS AND METHODS

1.1 Nickel Ferrite Synthesis

The synthesis of nanoparticles of Nickel Ferrite ($NiFe_2O_4$) was based on the Pechini method [18-20], which consists of obtaining polyester from citrates. After the synthesis of the citrate solution, a polyalcohol, such as ethyleneglycol, is added to promote polymerization. To perform the synthesis of the nickel ferrite, 30.06 g of citric acid ($C_6H_8O_7$) was solubilized in 120 ml of ethanol (C_2H_8O) under stirring at room temperature. The precursors were added to the solution, with the 3.87 grams nickel chloride II being hexahydrate ($NiCl_2$ $6H_2O$) and the 9.29 grams iron nitrate III nonahydrate ($Fe(NO_3)_3$ $9H_2O$). For the best solubilization of the precursors, 4 drops of nitric acid (HNO_3) were added until the solution became slightly acidic, at approximately pH = 6. The solution was stirred at 70 ºC for 20 minutes. To this solution was added 17.5 ml of ethyleneglycol ($C_2H_6(OH)_2$). Until its saturation, at approximately 80ºC, when the gel is formed. The calcining of the gel occurred after 4 hours at a temperature of 380 ºC. After calcining, thermal treatment was done at different temperatures (400ºC, 500ºC, 600ºC, and 700ºC), for 4 hours. The $NiFe_2O_4$ were structurally analyzed by X-Ray Diffraction (XRD), and its particle size were also estimated.

1.2 Formation of Polymer Composites

Nickel-ferrite PVDF composites were synthesized from the PVDF dissolved in N, N- Dimethylformamide (DMF) under slow stirring at the rate of 40 mg of PVDF/ml of DMF. Doping was performed from 4.0 mg, 8.0 mg, and 12.0 mg of $NiFe_2O_4$/ml of DMF. After homogenization of both solutions, they were mixed at constant agitation (Biomixer, QL 901) for 2 minutes at room temperature. The final solutions was dried at different controlled temperatures and times. The PVDF composites were characterized by the techniques of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and Optical microscopy (OM).

1.3 Experimental Techniques

For X-ray diffraction measurements were used XRD – 7000 patterns obtained using CuKα1 radiation (λ=1.541 Å), in the range of 20 to 60 degrees with steps of 2 degrees per minute at room temperature. The particle size was estimated using the Debye-Scherrer equation [21], assuming a spherical form of the $NiFe_2O_4$ nanocrystals. The width of the diffraction peak is given by the convolution of a family peak considering also instrumental parameters to this process [22].

The FT-IR spectra were obtained at the Jasco FT-IR- 4100, at room temperature, directlyin the films. For these analyzes, were used measurements of 128 cycles with a resolution of 2.0 cm^{-1} in the region of 4000 to 400 cm^{-1}. This technique was also used to evaluate the incorporation of the dopants in the polymer matrix and the structural changes caused by the addition of dopants in the polymer film, besides quantifying the β phase relation in the film.[23].

Optical microscopy measurements were performed at room temperature using an Opton optical microscope, model Tim 108. The area corresponding to polymer and nickel ferrite in each film were estimated using the Image Pro Plus (version 6.0). The porosity was expressed by thevalues of the relative area of the pores on the surface of the film [24].

III. RESULTS AND DISCUSSION

3.1 Characterization of Nickel Ferrite

Figure 1 shows the X-ray diffraction patterns of a-400ºC; b-600ºC and c-700ºC thermaltreated $NiFe_2O_4$, respectively. In all patterns the characteristic peaks of the crystallography planeof the spinel phase of $NiFe_2O_4$ are observed, in approximately in 30º, 35º, 37º, 43º, 53º and 57º, referring to the crystallographic planes (220), (311), (222), (400), (422) and (511), respectively. The most intense peak relative to the plane (311) is characteristic of the inverse spinel structure (JCPDS 10-0325). As the thermal treatment temperature increases peaks of $NiFe_2O_3$ become more tight and intense evident, revealing a better crystallization of the sample.

Also, as a small amount of spurious phase of iron trioxide (Fe2O3), (JCPDS 01-089-0598)was observed in all samples. The presence of iron trioxide shows the temperature during the calcining process was not enough to favor ferrite formation [25-28].

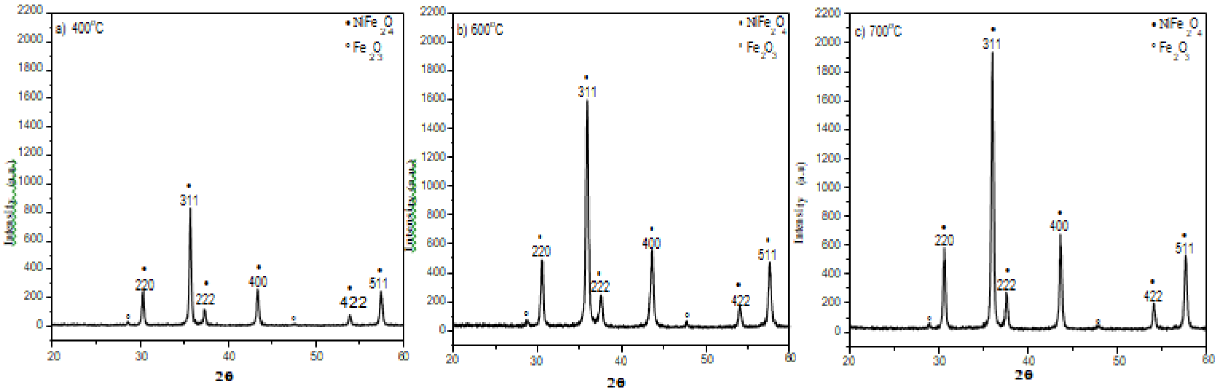

Figure 1: X-ray diffraction $NiFe_2O_4$ at different temperatures of thermal treatment.

The Scherrer equation was used to estimate the crystalline size of the ferrite particles. The results are shown in Table 1. The samples have crystalline size directly proportional to the thermal treatment temperature since the thermal energy favors the growth of the grains [28].

Table 1: The average particle size as a function of the heat treatment temperature, estimated using the Scherrer equation.

Thermal treatment	Estimated particle size
400ºC	24 nm
600ºC	26 nm
700ºC	27 nm

3.2 Structural Characterization of PVDF

PVDF polymers have different crystalline forms, among them the alpha (α), beta (β), gamma (γ) and delta (δ) forms can be identified and even quantified by Fourier Transform by Infrared (FT-IR). Figure 2 shows the spectrum of the pure PVDF obtained by dissolving the PVDF powder in DMF, drying at 50 ºC for 6 hours. Figure 2 shows the absorption bands characteristic of the crystalline phase α at 1182, 975,795, 612 cm^{-1}, and the absorption attributedto the β phase at 1401, 1064, 879, and 840 cm^{-1}. In the bands corresponding to the amorphous part of the PVDF (600 and 880 cm^{-1}) small peaks are observed, since they are overlapped by the 612 cm^{-1} (α) and 879 cm^{-1}(β) bands. The characteristic phase γ was not observed in the absorption region, however, the band observed at 840 cm^{-1} is common for both the β phase and the γ phase. The absorption attributed to the δ phase was not observed. [29-33]

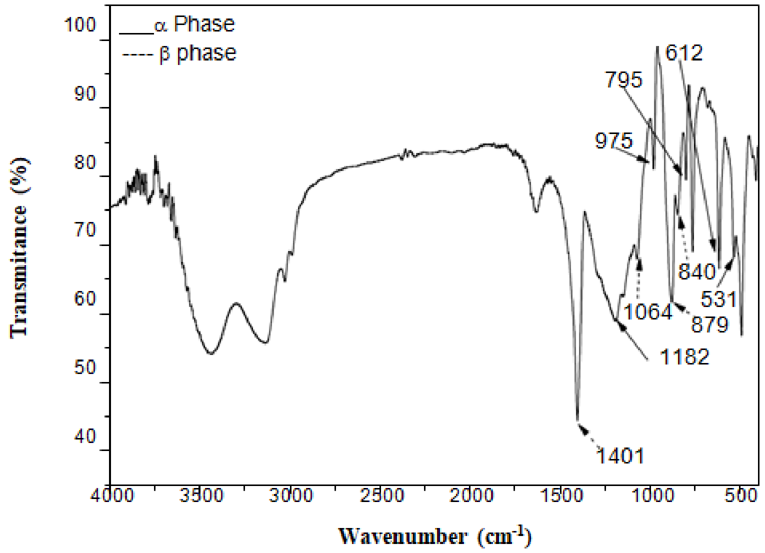

Figure 2: FTIR spectra of pure PVDF samples

To observe the relationship between the formation of the β phase and the synthesis parameters, the intensity of peaks around 763 and 840 cm^{-1} of the FTIR spectra were used to evaluate the relative amount of β phase, according to the reference protocol [33]. In Figure 3, the influence of drying time at a constant temperature of 50 ºC was observed. The highest form of theβ phase was 86 % with a drying time of 16 hours and the lower formation of the β phase was 70% with the drying time of 23 hours. The drying of 6 hours and 10 hours remained as intermediates.So, 16 hours of drying time at 50 ºC can be used as a default for this system.

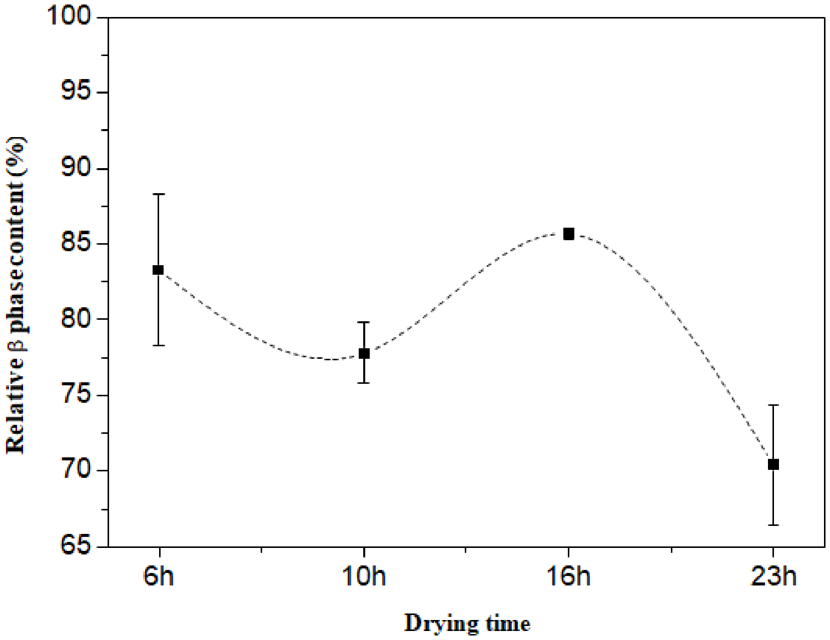

Figure 3: Fraction of β phase in pure PVDF films as a function of drying times at atemperature of 50ºC

3.3 Characterization of Composites

Regarding the percentage of β phase in nickel ferrite doped samples figure 4 shows the amount of β phase as a function of estimated ferrite particle size for different weight % of nickel ferrite added in PVDF polymers. The higher amounts of β phase (higher than 90%) are observed for the smaller sizes of doping particles, regardless of the amount of ferrite added. The amount of dopant added only has significant influences for higher particle sizes (higher than 27 nm).

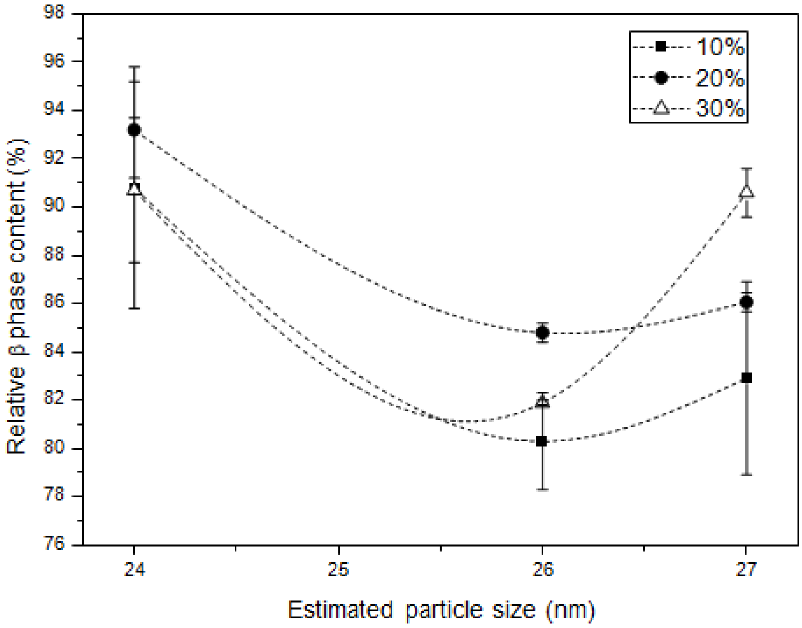

Figure 4: Fraction of β phase in PVDF composites as a function of doping particle sizes fordifferent concentrations of dopants

From microscope images of composites, the two phases can e identified: nickel ferrite (darker phase) and PVDF (lighter phase), as shown in figure 5 for the composite doped with 24nm$NiFe_2O_4$ particles. The images showed a small porosity of the films, resulting in the formation of magnetoelectric composites with higher interaction between polymer and nickel ferrite [34]. Alsois possible to see the formation of spherical particles of PVDF, as predictable.

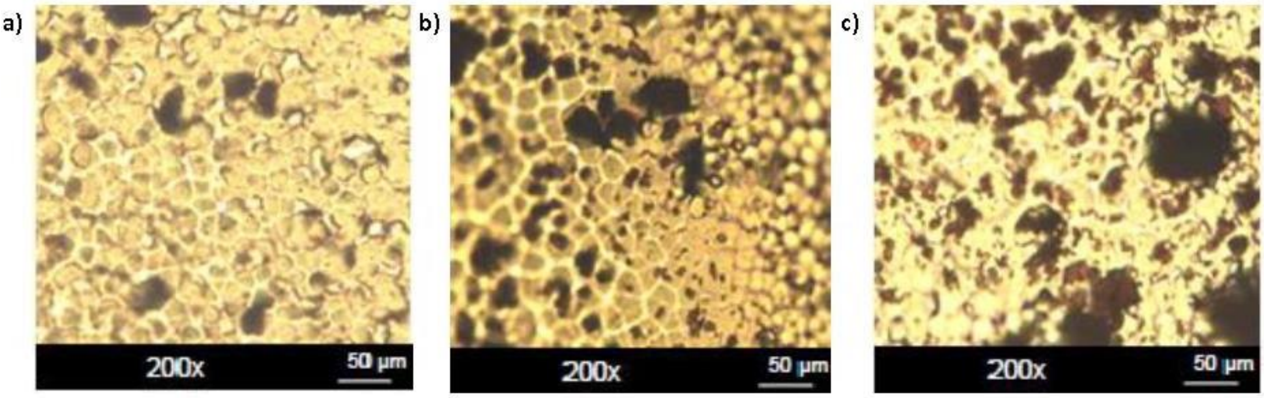

Figure 5: Images from optical microscope of Nickel Ferrite doped PVDF composites a) 10wt.% b) 20wt.% c) 30wt.% of $NiFe_2O_4$.

IV. CONCLUSIONS

The experimental results of the X-ray diffraction of $NiFe_2O_4$, shown a high crystallinity of the samples even for low temperatures of thermal treatment, and also a nanometric size of the particles. From FTIR characterization it was possible to detect separately the α as well as β phases of the polymer. Using the intensities of the absorbance peaks the relative amount of those crystalline phases is evaluated. It was observed the drying time favoring the majority formation of the α phase. Looking to the composites, it was verified that a smaller size of dopant, increasesthe amount of β phase even for a higher concentration of then. And as the dopant particle sizes increase the amount of dopant into the composite has significant influences on the crystalline phase formation.

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