

## STUDY OF THE INCORPORATION OF TiO<sub>2</sub>/Ag NANOPARTICLES IN POLYAMIDE BY CASTING METHOD AIMING FOR BIOCIDIC APPLICATION

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**Abstract** - This study consists in the characterization of polyamide (PA6) films charged with different concentrations of silver nanoparticles deposited in titanium dioxide (TiO<sub>2</sub>) carrier. The silver nanoparticles were synthesized according to the method adapted from Turkevich using a titanium dioxide carrier and inserted, by suspension, in a polyamide solution. The preparation of PA: AgNp films was performed by the *casting* method by the dissolution of PA pellets in formic acid.

The analysis and characterization of the films by the XRD, DSC, TGA and Raman confocal techniques indicated incorporation of nanoparticles into the polymers, a second thermogravimetric decomposition event as the concentration of AgNp-TiO<sub>2</sub> increased and there was no significant change in crystallinity.

**Keywords:** AgNp-TiO<sub>2</sub>, nanosilver, Polyamide 6, nanoparticles, characterization.

### Introduction

Polymers are macromolecular materials, consisting of the bonding of subunits through covalent bonds. By varying the composition of the subunits, it is possible to obtain a great diversity of polymers with the most diverse properties[1]. In addition, it is possible to introduce nanocompounds to improve specific desirable characteristics in the polymer.

With the combination of different areas of science and the emergence of new tools, from the XX century to the present day, the field of nanoscience and interest in the nanoscale has increased. This area is relatively recent because it studies matter on an atomic scale, that is, at values close to 10<sup>-9</sup>m. On this scale, it is common for materials to have different properties and applications than when compared to the macroscopic scale, as quantum mechanics is predominant over classical mechanics [2,3]. However, nanomaterials are commonly used in conjunction with larger, macroscopic materials [2]. Thus, the application of nanoparticles in polymeric compounds can improve their characteristics and commercial uses.

Studies in the literature demonstrate that silver nanoparticles in different forms of nanomaterials have biocidal activity for various bacteria. Due to this property, studies on the application of these nanoparticles in different materials, including polymers are performed [4]. The use of silver nanoparticles (AgNPs) must be accompanied by a carrier, due to its small size and thermodynamic instability. The carrier used in this study, in order to provide stability, was titanium oxide (TiO<sub>2</sub>).

Polyamide (PA) has interest in the plastic engineering due to its high thermal stability. However, there are not many studies about the commodities resulting from the addition of nanosilver in this polymer [5].

In this context, the focus of this study is to incorporate in polyamide, silver nanoparticles in TiO<sub>2</sub>, as carrier, in concentrations of 0.1% and 0.5%. Some characteristics were analyzed from obtained PA films, such as melting temperature, decomposition temperature and crystalline structure.

### Experimental

The synthesis of nanoparticles was based on and adapted from the Turkevich method [6]. The particles of TiO<sub>2</sub> (P25 Degussa Evonik), AgNO<sub>3</sub> (Labsynth), sodium citrate (Labsynth) and PVP (polyvinylpyrrolidone K30 - Labsynth) were used without previous treatment. For the beginning, an AgNO<sub>3</sub> solution ( $2 \times 10^{-2} \text{ molL}^{-1}$ ) was heated to the boiling temperature where sodium citrate ( $13.6 \times 10^{-2} \text{ molL}^{-1}$ ) was added. After 50 min, the PVP solution ( $13.75 \times 10^{-3} \text{ molL}^{-1}$ ) was added. Separately, 1g of TiO<sub>2</sub> was dispersed into 100ml of deionized water by ultrasound for approximately 10 min and then added to the silver solution, resulting in a stabilized suspension of AgNp-TiO<sub>2</sub>. The sample was washed and the solid dried in the stove until the solvent was completely evaporated.

The nanoparticles were incorporated into the polyamide by suspension in acetone (PA - ACS Alphatec) in percentages (% m/m) of PA, shown in Table 1. Also, to reduce the damage caused by oxidation, the antioxidant IRGANOX® 1010 BASF was added to the suspension in the proportion of 1%. The films of PA: AgNp were prepared using the *casting* method, where polyamide-6 (PA6) pellets were dissolved in formic acid (85% P.A - ACS Synth).

**Table 1** – Proportions for the synthesis of the casting film

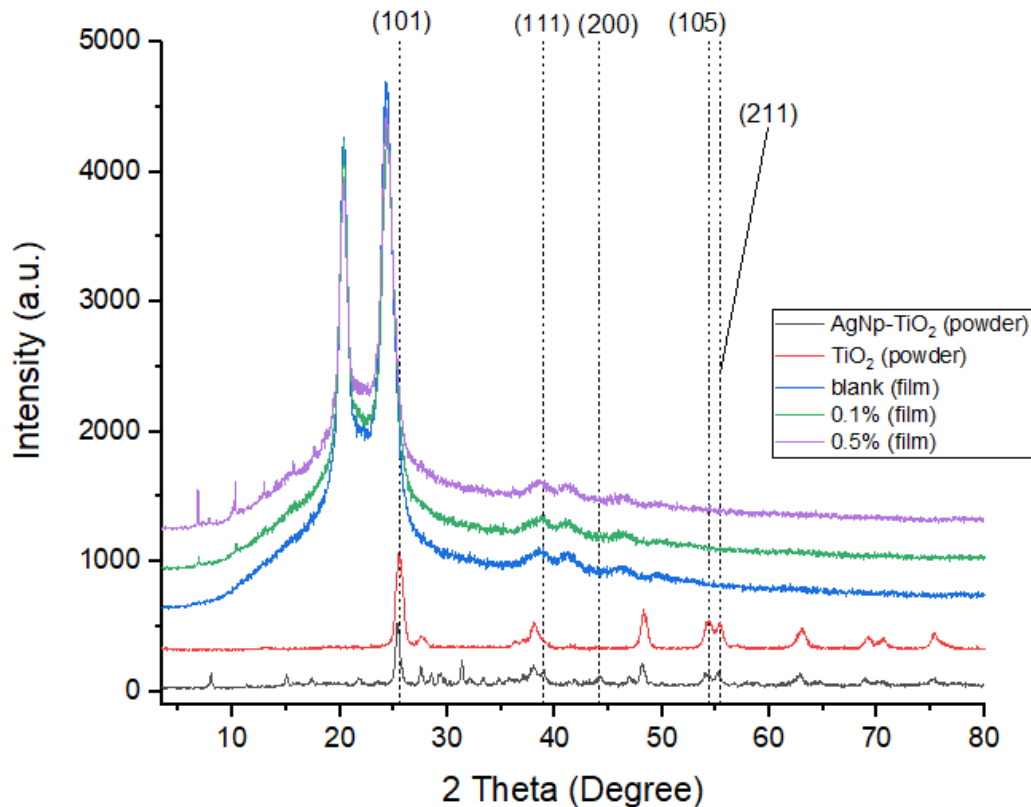
% AgNp-TiO <sub>2</sub>	Mass of PA (g)	% of IRGANOX®
Blank	2.5	1
0.1		
0.5		

The analysis by X-ray diffractometry, XRD, was performed on the Rigaku Mine Flex II equipment. The determination of crystallization with Differential Scanning Calorimetry, DSC, was carried out in the Mettler-Toledo DSC 822 equipment under nitrogen atmosphere. Thermogravimetry (TGA) analysis was performed on the Mettler-Toledo - TGA / SDTA 851 device. The Raman spectroscopy measurements were made with a confocal Raman from HORIBA, model LabRAM HR-SNOM-TERS, using a 633 nm laser as an excitation source and a x100 microscope lens to make the measurements for the three different samples.

### Results and Discussion

The results obtained by XRD (X-Ray Diffraction), shown in Fig.1, were not conclusive to the incorporation of the nanoparticles into the polymer. The typical peaks [7] of TiO<sub>2</sub> [(101), (200), (211)] and nanoparticles of Ag [(111), (200)] coincides with the peaks of the polyamide, and difficult the interpretation of the components. Other peaks present in the AgNP-TiO<sub>2</sub> and TiO<sub>2</sub> samples were not observed in the films. Some peaks observed at around 5-15 degrees exist at 0.1% AgNp-TiO<sub>2</sub> and more intense at 0.5%. However, they were not conclusive as to the presence of nanoparticles, since it was not reported in the literature and therefore it is assumed that if presente they are due to impurities of reactants.

**Figure 1** – XRD patterns of the synthesized AgNp-TiO<sub>2</sub> (powder), TiO<sub>2</sub> (powder) and the films in concentrations of 0.1%, 0.5% and the reference (blank).



The DSC analysis, Table 2, and the DRX peaks showed that the crystallinity of the polyamide did not change significantly after the addition of nanoparticles.

**Table 2** – DSC (Differential Scanning Calorimetry) results

Sample	T <sub>m2</sub> (°C)	T <sub>c</sub> (°C)	ΔH1 (J/g)	ΔH2 (J/g)	X <sub>2</sub> %
blank	220.46	-48.30	50.66	-49.68	26.43
0.1%	219.59	-49.26	50.98	-50.46	26.84
0.5%	220.23	-48.80	49.54	-48.71	26.04

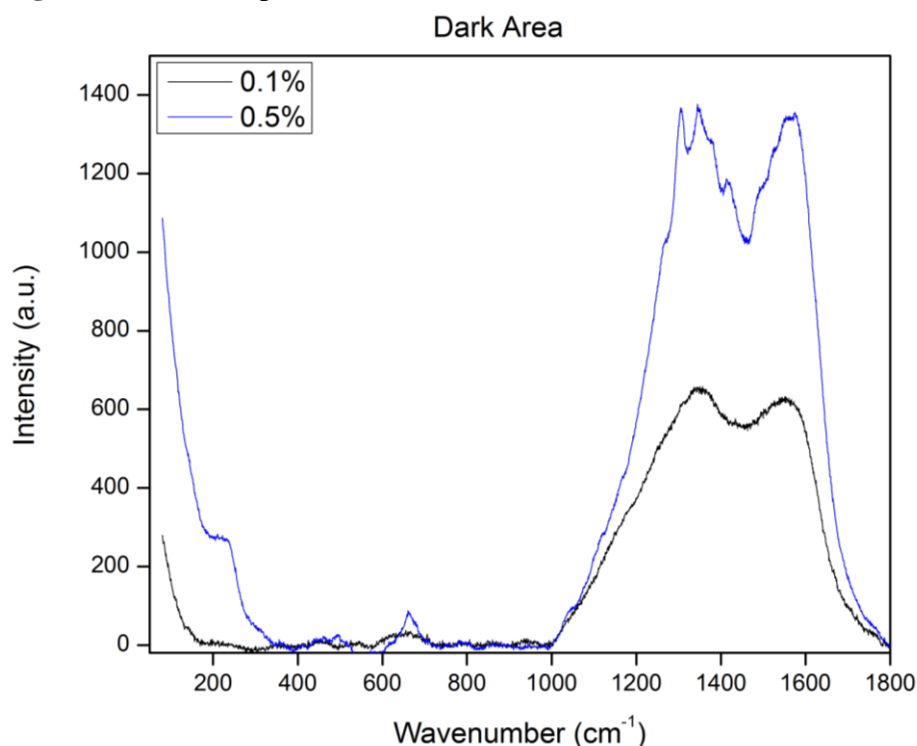
The decomposition occurred in two events in the samples containing the AgNp-TiO<sub>2</sub>, in which the second event presented Δm of decomposition attributed to the presence of the nanoparticles for both of the concentrations of AgNp-TiO<sub>2</sub>, that indicate, probably adsorbed secondary products of the decomposition. It was also observed a decrease in the decomposition temperature as the AgNp-TiO<sub>2</sub> was added, Table 3.

**Table 3** – TGA (Thermogravimetric analysis) results

Sample	T(°C) decomposition	% decomposition 1	% decomposition 2
Blank	373.5	100	-
0.1%	365.7	94.7	5.3
0.5%	359.8	95.6	4.4

For the Raman spectroscopy of 0.1% sample, five measurements were averaged, each taking ten seconds of integration for each point. The results were three different studied areas (black, gray and white). For the white region, it is clear that no silver nanoparticles are embedded, having the same spectrum as the blank surface that was previously measured. For the gray areas, it is possible to verify the existence of silver nanoparticles from the  $240\text{ cm}^{-1}$  and the  $1200\text{ cm}^{-1}$  bands that become more evident according to literature [8,9]. The black areas, however, present the largest amount of silver nanoparticles, having specially the  $1200\text{ cm}^{-1}$  band with a larger signal. In the 0.5% sample, we also took five averaged measurements, with eight seconds of integration time for each measured point. Results are shown in blue in Fig. 2. For this doped amount, the white areas already have a small concentration of silver nanoparticles, differently from the 0.1% previously shown. The  $240\text{ cm}^{-1}$  silver band is clearer in the gray area, while the  $1200\text{ cm}^{-1}$  band is much larger for the black areas.

**Figure 2** – Raman spectra of the 0.1% (black), 0.5% (blue)



## Conclusions

In this work we present the methodology and results about the incorporation of AgNp-TiO<sub>2</sub> particles in the polyamide 6. The results indicated incorporation of nanoparticles. In the future, we intend to study the cause of the presence of peaks at around 5-15 degrees not interpreted yet in the XRD, and also the effects of the biocidal action caused by the incorporation of such nanoparticles into the polymer.

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