Research Article

Surface Modification of nTiO₂/Ag Hybrid Nanoparticles Using Microwave-Assisted Polymerization in the Presence of Bis(2-hydroxyethyl) Terephthalate

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Titanium dioxide doped silver (nTiO₂/Ag) nanoparticles were surface-modified by microwave-assisted polymerization of 2-bis-(hydroxyethyl) terephthalate (BHET). The modified and unmodified nanoparticles were analyzed by FTIR, XRD, TGA, and TEM. A thin layer of grafted PET on the surface of the nanoparticles was observed and quantified by TGA giving a value of 40 wt-%. XRD and electron diffraction analyses showed traces of AgO₂ after the modification. The bactericide activity of modified and unmodified nanoparticles was evaluated; the presence of the thin layer of *grafted*-PET on the nTiO₂/Ag did not change significantly the bactericide activity, showing an excellent performance similar to unmodified nanoparticles.

1. Introduction

Considering the increase of microorganisms resistant to multiple antibiotics and increased costs of health care, several studies have focused on the development of new materials that act efficiently against these microorganisms [1].

Recent investigations have been focused on the use of nanocomposites based on titanium dioxide nanoparticles (TiO₂ NPs) doped with silver Ag nanoparticles (Ag NPs) in a polymer matrix since this combination of nanoscale materials maximizes antimicrobial activity and photocatalytic degradation of organic molecules [2, 3]. The synergy shown by these nanoparticles (NPs) comes as a result of the good separation of electron-hole pairs during excitation of doped TiO₂ NPs with Ag NPs, exposed to visible radiation [4, 5]. Sung-Suh et al. [6], in 2004, studied the degradation of rhodamine B dye in aqueous suspensions of TiO₂ NPs and nTiO₂/Ag, finding a 30% increase in the degradation of rhodamine B, using the nAg/TiO₂. On the other hand, Seery et al. [7] conducted similar work in which they increased the

concentration of Ag NPs deposited in TiO₂ NPs finding further degradation of rhodamine B, by increasing the concentration of Ag NPs. Meanwhile, Quiñones-Jurado et al. [8] synthesized Ag NPs supported on TiO₂ NPs and evaluated the bactericidal activity in three different bacteria (*E. coli*, *S. aureus*, and *Salmonella* sp.) finding less sensitivity for *S. aureus*, Gram (+). These authors concluded that this behavior is due to a higher content of peptidoglycan in the cell wall. However, there are certain disadvantages in using NPs, such as aggregation and uncontrolled release of toxic reactive species, making it very difficult to use them safely in a wide range of applications. However, NPs can be incorporated into polymer matrix leading to a new generation of antimicrobial agents with potential use in areas such as medicine, food packaging, and textile fibers. In this context, Dastjerdi et al. [9] obtained filament yarns based on polypropylene (PP)/(nTiO₂/Ag), in order to evaluate the antimicrobial activity by varying the concentration from 0.2 to 1 wt-% of NPs. These authors found that 0.75 wt-% of NPs is the optimal bactericidal content and increasing the content

up to 1 wt-% of NPs they observed a significant reduction in the antimicrobial activity because of the NPs agglomeration. Liu et al. [10] studied the antibacterial activity of glass coated with films of nTiO_2/Ag on *E. coli*. These authors found that films with nTiO_2/Ag not only have antimicrobial activity but also increase photocatalysis. It was concluded that the nTiO_2/Ag film could be used in antibacterial surfaces, self-cleaning, and photocatalysis. In 2010, Dastjerdi et al. [11] coated PET based textile fibers with polysiloxane, polysiloxane/ TiO_2 NPs, and polysiloxane/ TiO_2 NPs/Ag NPs, in order to evaluate the antibacterial performance, antistain properties, photodegradability, and durability. It was found that, incorporating 300 ppm of Ag NPs and 2.5 wt-% of TiO_2 NPs in polysiloxanes, the antibacterial properties increased up to 90%, compared to fibers treated with polysiloxane/ TiO_2 NPs and polysiloxane.

However, this functionality of a nanocomposite depends largely on the dispersion and compatibility of NPs in the polymer matrix, which, in turn, depends on the preparation processes [12]. This is the main reason to study the synthesis and processing of nanocomposites and the relationship with their final properties. Due to this, in recent years the modification of NPs has been investigated, looking to improve compatibility between NPs and a polymer matrix, which results in an improvement of the distribution and dispersion of these in the polymer [13, 14]. For example, Cheng et al. [12] conducted studies on the surface modification of nTiO_2/Ag by grafting 3-aminopropyltriethoxysilane (APS), finding that the APS is chemically bonded to the surface of the NPs with a coating thickness of 25 nm. Subsequently, such modified NPs were mixed in PVC to prepare nanocomposites where dispersion and antibacterial properties were evaluated, concluding that the surface modification provides a higher affinity and dispersion between NPs and PVC. Furthermore, such modification did not affect the antimicrobial properties evaluated for *E. coli* and *S. Aureus*.

Moreover, surface modification of NPs by microwave-assisted polymerization is an attractive alternative since it can be controlled and has a low negative impact on environment. With the microwave-assisted polymerization of a given monomer it is possible to coat NPs surface with a polymer layer [15, 16]. Such modified NPs can be easily homogeneously dispersed and distributed in a polymer matrix to produce a functional nanocomposite [15]. Rodríguez-Tobías et al. [17] modified the surface of zinc oxide NPs (ZnO NPs) with polylactic acid (PLA), synthesized by microwaves. The authors proposed grafting mechanisms, between ZnO NPs and the PLA, establishing the existence of different reactions that explain the formation of the hybrid system (ZnO -graft-PLA). J. Zhu and Y. Zhu [18] obtained polyacrylamide-(PAM-) metal ($M = \text{Ag}, \text{Pt}, \text{Cu}$) nanocomposites, through in situ microwave-assisted polymerization, finding a homogeneous dispersion of metal NPs in the PAM matrix. Zhang et al. [19] synthesized cellulose and Ag NPs nanocomposites using microwaves, by reducing silver nitrate in ethylene glycol (EG) finding that Ag NPs are homogeneously dispersed in the cellulose matrix, having good antimicrobial activity.

TABLE 1: Components for the synthesis of PET and surface modification of nTiO_2/Ag .

Sample	BHET (g)	Sb_2O_3 (g)	nTiO_2/Ag (g)
PET	4.998	0.002	—
nTiO_2/Ag -PET	4.898	0.002	0.1

The aim of this study is to determine the effect of the surface modification of nTiO_2/Ag hybrid NPs, using microwave-assisted polymerization in the presence of BHET, on the morphology, physicochemical properties, and antimicrobial activity.

2. Experimental

2.1. Materials. nTiO_2/Ag nanoparticles were provided by A. Schulman de México, SA de CV, with a purity of 99.8% and an average particle size of 30 nm. For microwave-assisted synthesis of PET on the NPs surface, bis(2-hydroxyethyl) terephthalate (BHET) and antimony oxide (Sb_2O_3) as catalyst were used, both reagents from Sigma-Aldrich, with purity of 99.99%. Chloroform (CHCl_3), 1,1,1,3,3,3-hexafluoro-2-propanol (HFP, $\geq 99\%$), and PTFE membranes from Sigma-Aldrich were used to separate modified nTiO_2/Ag -grafted-PET from PET not linked or free PET (PET^b). For antimicrobial trials, trypticase soy broth and trypticase soy agar from Becton Dickinson de Mexico, SA de CV, was used and two bacterial species were selected, Gram-negative (*E. coli*) ATCC # 25922 and Gram-positive (*S. aureus*) ATCC # 6538.

2.2. Gas Phase Deagglomeration of nTiO_2/Ag by Ultrasonic Waves. Prior to the modification, nTiO_2/Ag agglomerates were placed in a beaker where they were broken using ultrasonic waves generated by an "Ultrasonic Processor" Cole-Palmer, model CV33, with a power of 750 W and a frequency of 20 KHz. This deagglomeration treatment in air (gas phase) with ultrasound was performed in batches of 2 g of treated NPs. The treatment conditions were as follows: amplitude of 80% and magnetic stirring of 30 rpm at room temperature (25°C) for 30 min.

2.3. Synthesis of PET and Surface Modification of nTiO_2/Ag . The synthesis of a standard PET and surface modification of the nanoparticles with catalyst (Sb_2O_3) were performed using a microwave focused/monomodal radiation, model Anton Parr Monowave 300. For the synthesis of PET 4.998 g of BHET and 0.002 g of Sb_2O_3 were added. Furthermore, for surface modification of nanoparticles (nTiO_2/Ag) 4.898 g of BHET, 0.1 g of previously deagglomerated nTiO_2/Ag , and 0.002 g of catalyst were added (see Table 1). At heating step, the temperature is increased from room temperature to the reaction temperature of 280°C in 10 min. Once the reaction temperature was reached, it was maintained for 40 min and at a stirring rate of 600 rpm. All reactions were carried out under nitrogen atmosphere.

FIGURE 1: Process for $n\text{TiO}_2/\text{Ag}$ -grafted-PET nanocomposites preparation using microwave-assisted.

2.4. Separation of Nanoparticles Modified with PET. To separate the $n\text{TiO}_2/\text{Ag}$ -grafted-PET, the material obtained from the synthesis of BHET with $n\text{TiO}_2/\text{Ag}$ was dissolved in chloroform and HFP using a ratio of 10:1, at room temperature, with magnetic stirring for 3 h. Then, the solution was filtered using a PTFE membrane. The product of this filtration was a transparent liquid, which was precipitated in methanol to recover PET^b.

The material, retained by the membrane, was recovered and dispersed in chloroform and HFP in a ratio of 10:1 in order to be filtered again. The same procedure was repeated three times to ensure the proper separation of the components. Finally, the $n\text{TiO}_2/\text{Ag}$ -grafted-PET nanohybrid which was retained on the membrane was dried at 80°C for 12 h. In Figure 1, the synthesis of $n\text{TiO}_2/\text{Ag}$ -grafted-PET hybrid is presented as well as the separation method for NPs modified with PET.

2.5. Characterization Techniques. The obtained materials were further characterized by different techniques:

2.5.1. Size Exclusion Chromatography (SEC). In order to determine the molecular weight distribution of the reference PET and PET^b, size exclusion chromatography was used.

Alliance GPC 2000 Series equipment was used. Prior to the analysis, the samples were dissolved in chloroform (CHCl_3) and HFP (10:1) in a ratio of 1 mg/mL, followed by filtration using a 0.02 μm filter. Chromatographic grade chloroform was used as a transport solvent at a temperature of 40°C.

2.5.2. Fourier Transform Infrared (FTIR) Spectroscopy. PET and $n\text{TiO}_2/\text{Ag}$ -grafted-PET nanohybrid were characterized by FTIR in order to determine the chemical functional groups of the samples. An infrared spectrophotometer Thermo Nicolet MAGNA 550 at 100 scans with a resolution of 16 cm^{-1} was used.

2.5.3. X-Ray Diffraction (XRD). The crystalline structure of modified NPs was studied by XRD. A Siemens diffractometer model D-5000, operated at a voltage of 35 kV and a current of 25 mA with $\text{CuK}\alpha$ radiation of 1.54056 Å, was used. The scanning range in 2θ was 20–80° at a rate of 0.02°/s.

2.5.4. Thermogravimetric Analysis (TGA). In order to determine the amount of PET grafted on the nanoparticles surface, thermogravimetric analysis was conducted on TA instruments model Q500. The heating rate used was 10°C/min.

TABLE 2: Distribution of molecular weights of reference PET and PET^b obtained during surface modification of nTiO₂/Ag.

Sample	Mn (g/mol)	Mw (g/mol)	Đ	Conversion%
PET	922	1128	1.22	39
PET ^b	1013	1219	1.20	24

from room temperature to 600°C in an inert atmosphere of nitrogen.

2.5.5. Antimicrobial Activity (AA). To carry out the evaluation of the antimicrobial activity of the obtained nanohybrid a standard method was applied, known as normalized contact method established by the Japanese Industrial Standard (JIS) Z 2801. In order to determine the effect of the PET grafted on nTiO₂/Ag (nTiO₂/Ag-grafted-PET) on the antimicrobial activity under aseptic conditions, the NPs were inoculated with cultures of clinical importance to immediately undergo an incubation step during the period specified in the standard, 24 h. The antimicrobial activity is determined based on inhibition percent of the organism at the end of the exposure time.

For the antimicrobial activity evaluation *E. coli* and *S. aureus* were used as test organisms. The tests were carried out using sterile vials with 5 mL capacity, to which specific concentrations (2500, 1500, 900, 540, 324, 194, 116, and 69 ppm in 300,000 colony forming units, CFU/mL) were added during 24 h at 37°C. After completion of the exposure period, the sample vials were removed from the incubator and aliquots of said vials were taken and plated on agar. After the incubation period, the count of CFU/mL was made. This method can determine the minimum inhibitory concentration (MIC), that is, the lowest concentration of bactericidal agent, which inhibits the growth of microorganisms in a dilution series.

3. Results

3.1. Synthesis of PET and Surface Modification of nTiO₂/Ag. Molecular weight characterization and conversion of microwave-assisted polymerization of BHET and BHET in presence of nTiO₂/Ag are shown in Table 2. A low value of average molecular weight (Mn) was observed in all cases, which was attributed to the presence of ethylene glycol in the system as a result of the polymerization of BHET, which hinders the PET chain grow. A further increase in molecular weight can be obtained by removing the ethylene glycol produced during polymerization of BHET and by the solid-state polymerization (SSP) [20, 21]. Polydispersity was similar for both cases.

On the other hand, a decrease in conversion was observed when using nTiO₂/Ag, possibly due to reversible reactions, since it is reported that the formation of terephthalic acid (TPA) and EG from BHET is catalytic to the metal oxides used as catalysts for the synthesis of PET. Moreover, this reaction is magnified in the presence of protons and hydroxyl groups present in the ethylene glycol produced during polymerization [21].

FIGURE 2: FT-IR of (a) nTiO₂/Ag, (b) PET^b, and (c) nTiO₂/Ag-grafted-PET.

3.2. Surface Modification of nTiO₂/Ag. The modified nTiO₂/Ag and unbounded PET were analyzed by FTIR. In Figure 2(a) the characteristic fingerprints of TiO₂ are shown, a broad signal around 3200 cm⁻¹ and another signal at 1625 cm⁻¹ attributed to vibration by stretching of the hydroxyl group (Ti-OH), associated with the water absorbed physically on the surface of TiO₂. The signal at 550 cm⁻¹ attributed to the vibration of the links Ti-O is also observed [22]. No signals attributed to silver nanoparticles (Ag NPs) were observed because these are constituted of Ag⁰.

In the spectrum of Figure 2(b), the characteristics signals of PET are observed at 1721 cm⁻¹ (C=O), 1245 cm⁻¹ (C-C-O), and 1100 cm⁻¹ (O-C-C) corresponding to the stretching of the aromatic ester group. Finally, in the spectrum of Figure 2(c), corresponding to the nTiO₂/Ag-grafted-PET nanohybrid, a set of characteristic signals of nTiO₂/Ag and PET is observed, which shows qualitatively that nTiO₂/Ag were surface-modified with PET.

In Figure 3(a), an image acquired by TEM of nTiO₂/Ag native nanoparticles is shown, where it can be observed that Ag NPs has a quasi-spherical form and average diameter of 5 nm, over the TiO₂ NPs surface, which poses an average diameter of 30 nm. Figure 3(b) shows an image acquired by high resolution (HRTEM) corresponding to the same NPs (nTiO₂/Ag), in which different areas were selected, aiming to obtain the fast Fourier transform (FFT) patterns, finding an interplanar distance (*d*) of 0.32 nm, and it corresponds to the tetragonal crystal structure centered on the body of anatase morphology in the TiO₂ (1,0,1). An interplanar distance *d* = 0.24 nm attributed to the cubic structure centered in the faces (ccf) of the Ag NPs (1,1,1) is also observed. These results are supported by Su et al. [23] who synthesized Ag NPs and TiO₂ NPs, finding that the presence of these interplanar distances corresponds to the fact that Ag NPs are attached to TiO₂ NPs.

Figures 3(c) and 3(d) show images of the surface modified nTiO₂/Ag, in which a thin layer of PET of about 3 nm is observed on the surface of the nTiO₂/Ag, demonstrating that

FIGURE 3: TEM micrographs of $n\text{TiO}_2/\text{Ag}$ (a, b) and $n\text{TiO}_2/\text{Ag-grafted-PET}$ (c, d).

the polymer is deposited on the surface of the nanoparticles during microwave-assisted polymerization. Furthermore, the overall FFT (Figure 3(d)) was obtained to determine the crystal structure of modified nanoparticles, finding the interplanar distances that are attributed to $n\text{TiO}_2/n\text{Ag}$.

On the other hand, diffraction pattern of $n\text{TiO}_2/\text{Ag}$ (see Figure 4) shows diffraction peaks centered at $2\theta = 25.3^\circ, 37.8^\circ, 38.6^\circ, 54.0^\circ, 55.17^\circ, 62.21^\circ$, and 68.93° , corresponding to the characteristics signal of the crystalline tetragonal structure centered on the body of Anatase TiO_2 in (1,0,1), (1,0,3), (1,1,2), (1,0,5), (2,1,1), (2,1,3), and (1,1,6), respectively. These signals are equal to the data reported in the JCPDS (Joint Committee on Powder Diffraction Standards) number 21-1272. However, a small population of TiO_2 attributed to the rutile phase $2\theta = 27.4^\circ, 41.2^\circ$, and 64.0° corresponding to the (1,1,0), (1,1,1), and (3,1,0) planes, respectively, was also observed as reported in JCPDS number 76-1940. Two characteristic peaks of Ag at $2\theta = 38.3^\circ$ and 44.17° were observed, corresponding to the characteristics peaks of the cubic structure centered in the

face of silver in (1,1,1) and (2,0,0). XRD results corroborate the findings obtained by HRTEM analysis.

On the other hand, in the diffraction pattern obtained from the $n\text{TiO}_2/\text{Ag-grafted-PET}$, new diffraction peaks are shown besides the ones observed for the unmodified material. For example, diffraction peaks centered at $2\theta = 32.1^\circ, 46.7^\circ$, and 58.1° were further observed and attributed to the oxidation of Ag [24]. Silver oxidation is probably due to oxygen ions and radicals generated during the microwave-assisted polymerization, modifying the structure of Ag NPs, leading to the formation of silver oxide. Diffraction peaks of PET were not found (see Figure 4(c)), possibly because grafted PET on nanoparticles surface is in amorphous phase.

To quantify the amount of PET grafted on the surface of the $n\text{TiO}_2/\text{Ag}$ after microwave-assisted polymerization, thermogravimetric analysis was performed. In Figure 5(a), the curve for $n\text{TiO}_2/\text{Ag}$ shows a high thermal stability of the nanoparticles during TGA test. Meanwhile, in the curve corresponding to the PET^b, it shows a 9 wt-% loss at a

FIGURE 4: Diffractograms of references (a) Ag, (b) TiO_2 -antasa, and (c) TiO_2 -rutilo and diffractograms of (d) nTiO_2/Ag and (e) $\text{nTiO}_2/\text{Ag-grafted-PET}$.

temperature of 253°C , which is associated with the thermal decomposition of the dimers [25] of BHET; subsequently at 420°C a 84 wt-% loss is observed and attributed to the thermal decomposition of PET [26] produced by the microwave-assisted polymerization of BHET.

In the $\text{nTiO}_2/\text{Ag-grafted-PET}$ thermal curve (see Figure 5(a)), three important events were observed:

- (1) A 6 wt-% loss at a temperature of 216°C associated with the decomposition of residual monomer BHET.
- (2) Two losses of 40 wt-% at 373 and 415°C being observed, associated with the decomposition of PET; one of them corresponds to the PET grafted on the surface of the nanoparticles (Figures 5(a) and 5(b)) and the other corresponds to traces of PET^b .
- (3) Finally, a residue of 50 wt-%, corresponding to the nTiO_2/Ag .

These results indicate that the presence of nTiO_2/Ag caused significant changes during polymerization of BHET; it diminishes the conversion in the reaction and molecular weight distribution, evidenced by the presence of the BHET monomer.

As mentioned above the antimicrobial tests were carried out by the standard method known as normalized contact method established by the Japanese Industrial Standard (JIS) Z 2801. In order to determine the effect of $\text{nTiO}_2/\text{Ag-grafted-PET}$ on antimicrobial activity on *E. coli* and *S. aureus* starting from a nanoparticles concentration of 2500, 1500, 900, 540, 324, 194, 116, and 69 ppm, in the control samples an average of 39,000 UFU/mL in *E. coli* and 73,000 UFU/mL *S. aureus* was obtained. Subsequently, serial dilutions were performed with corresponding counts.

In Table 3 the results of antibacterial analysis are shown. For *E. coli*, no growth was observed in either of the two nanoparticles. However, for *S. aureus* the MIC (minimum inhibitory concentration) was found at 194 ppm. These results are attributed to two main factors:

- (1) A lower concentration of reactive oxygen species (ROS) that cause damage to the genetic material of microorganisms, this being due to the PET based coating.
- (2) The difference in the composition of the cell wall between the Gram (+) and Gram (−) bacteria [19].

Gram (+) bacteria such as *S. aureus* have a cell wall of an average thickness of 80 nm composed mainly of peptidoglycan, which confers structural rigidity to the bacteria. Furthermore, the cell wall of Gram (−) bacteria, such as *E. coli*, consists of a very thin layer of peptidoglycan into the periplasmic space of about 20 nm, plus an outer membrane composed mainly of lipids, proteins, and lipopolysaccharides (LPS) which are responsible for increasing the negative charge of the cell membrane, making them more susceptible to nanoparticles. Differences in the composition of the cell wall of Gram (+) and Gram (−) bacteria are presented in Figure 6.

Differences in the composition of the cell wall of microorganisms have resulted in variations in the antimicrobial effect by contact with metal NPs. Similar reports were made by Quiñones-Jurado et al. [8], who found that the antimicrobial activity of the nTiO_2/Ag is lower in *S. aureus* than in *E. coli*, associating this behavior with the composition of Gram (+) bacteria which provides greater protection when interacting with NPs. In the same sense, Kim et al. [3] studied the antimicrobial activity of nAg in *S. aureus* and *E. coli*, finding that the Gram (+) bacteria *S. aureus* in contact with silver NPs are less susceptible, because of the protection conferred by peptidoglycan in the bacterial wall.

4. Conclusions

Microwave-assisted polymerization is a useful technique for introducing a polymeric grafting based on PET on the surface of nTiO_2/Ag . The presence of the PET grafted on the nanoparticles was confirmed by FTIR analysis, XRD, TEM, and TGA. Finally, the antimicrobial analysis found a MIC of 194 ppm, for *S. aureus* in the presence of $\text{nTiO}_2/\text{Ag-grafted-PET}$, was associated with two factors: (i) lower concentration of reactive oxygen species (ROS) that cause damage to the genetic material of microorganisms, this being due to the grafted PET, and (ii) the difference in the composition of the cell wall between Gram (+) and Gram (−) bacteria. However, they are still getting good bactericidal properties. This gives rise to a new generation of antimicrobial agents with potential uses in areas such as medicine, food packaging, and textile.

Competing Interests

The authors declare that they have no competing interests.

FIGURE 5: TGA curves (a) weight loss percentage and (b) derived weight loss percentage of PET^b and nTiO₂/Ag-grafted-PET.

FIGURE 6: Structural differences between Gram-negative bacteria (*E. coli*) and Gram-positive ones (*S. aureus*).

TABLE 3: Antibacterial analysis of nTiO₂/Ag and nTiO₂/Ag-grafted-PET with *E. coli* and *S. aureus*.

Content of nTiO ₂ /Ag (ppm)	<i>E. coli</i> (UFC/mL)	<i>S. aureus</i> (UFC/mL)	Content of nTiO ₂ /Ag-grafted-PET (ppm)	<i>E. coli</i> (UFC/mL)	<i>S. aureus</i> (UFC/mL)
2500	—	—	2500	—	—
1500	—	—	1500	—	—
900	—	—	900	—	—
540	—	—	540	—	—
324	—	—	324	—	—
194	—	—	194	—	32
116	—	—	116	—	98
69	—	—	69	—	Countless

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