Biocidal capability optimization in organic-inorganic nanocomposites based on titania

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Optimization of the interfacial agent content in biocidal organic-inorganic nanocomposites is analyzed in terms of their physico-chemical interface characteristics. The balance between the photochemistry (photo-killing) behavior and the thermal properties is achieved in the nanocomposites with an incorporation of 2 wt.-% in inorganic nanoparticles (TiO₂) using a compatibilizer content ranging from 50 to 80 wt.-% with respect to the titania amount.

Introduction

The use of photocatalytic semiconductor oxides emerges as a successful technology to struggle against biological risks in these days that great concerns exist to guarantee the safety of products related to foods/beverages packaging or containers for biomedical/pharmaceutical materials/devices. TiO₂-Anatase is by far the most widely used photocatalyst, being a wide band-gap (3.2 eV) semiconductor that under UV illumination generates energy-rich electron-hole pairs able to degrade cell components of microorganisms rendering innocuous products (1). Moreover, none weakness with respect to the microorganism nature (bacteria, virus, fungus, etc.) is nowadays known. Consequently, its incorporation as a constituent in polymeric multicomponent materials could be a future alternative within goods packaging field.

Isotactic polypropylene (iPP) is one of the most widely utilized polyolefin. Among other applications are included its industrial use as material in areas of food packaging and medical supplies. Its non-polar macromolecular nature does, however, make the incorporation of functionalized oligomers as compatibilizers essential while hosting inorganic components. There are numerous works related to the incorporation of maleic anhydride (MAH) modified PP oligomers (PP-g-MAH) to help dispersion of particles in composites resulting in a greater reinforcement effect of the clays or silica oxide-type materials (2,3).

Vladimirov et al. (4) found that the average size of silica particle aggregates within an iPP matrix increased as silica contents did, whilst they became smaller using higher amounts of PP-g-MAH. Therefore, a crucial task when nanocomposite materials with improved performance are developed is to appropriately choose the characteristics and amounts of the different components.

This work describes optimization of the interfacial agent content required for preparation using a cost-effective melting processing of novel organic-inorganic nanocomposites based on titania and isotactic polypropylene with a very efficient antimicrobial activity towards both gram-negative (*Pseudomonas aeruginosa*) and gram-positive bacteria (*Enterococcus faecalis*). The importance of optimizing the compatibilizer content lies in attaining the perfect TiO_2 -anatase dispersion into the iPP matrix required to exhibit extraordinary biocide characteristics without damaging the mechanical performance of the nanocomposites. An earlier survey clearly demonstrated that the minimum amount of TiO_2 nanoparticles for achieving an effective and entire elimination of micro-organisms in several materials is around 2% in weight (5,6) Therefore, an in-deep study of the biocidal capability of the system as well as its physicochemical background are performed as function of compatibilizer agent incorporation, which allows a continuous-like oxide-polymer contact at interface.

Experimental Section

Nanocomposite preparation: The TiO_2 component (characteristic primary particle size below 10 nm) was prepared using microemulsion synthetic route by addition of titanium (IV) isopropoxide (Aldrich) to an inverse emulsion containing an aqueous phase dispersed in *n*-heptane (Panreac), using Triton X-100 (Aldrich) as surfactant and 1-hexanol (Aldrich) as cosurfactant. The mixture was stirred for 24 h, centrifuged, decanted, rinsed under stirring five consecutive times with methanol (twice), water (twice) and acetone (one) to eliminate any portion from the organic and surfactant media, dried at 110 °C for 24 h and calcined at 500 °C for 2 h. A commercially available metallocene-catalyzed isotactic polypropylene, iPP (Basell Metocene X50081: melt flow index of 60 g/10 min at 230 °C/2.16 kg, ASTM D1238), meeting FDA requirements for food contact (Federal Regulations, 21 CFR 177.1520), was used as polymeric matrix in the preparation of these iPP- TiO_2 nanocomposites. PP-g-MAH, polypropylene wax partially grafted with maleic anhydride, was used as interfacial agent (Licomont® AR 504 fine grain from Clariant) in compositions of 0, 30, 50 and 80 wt.-% with respect to the content of 2 wt.-% in TiO_2 nanoparticles (0, 0.6, 1 and 1.6 overall wt.-% loadings, respectively). The resultant three-component nanocomposites were labeled as iPPxT2 along manuscript, being x the compatibilizer content related to the 2 wt.-% composition in TiO_2 . These biocidal nanocomposites were prepared through a straightforward melt processing in an internal mixer with volumetric capacity of 3 cm³ at 160

°C and at 60 rpm for 5 min, previous TiO₂ sonication in an ultrasonic device to minimize the aggregation of nanoparticles and maximize the performance of resultant nanocomposites. After that, specimens were obtained as films (100 ± 5 µm thickness) by compression molding in a Collin press between hot plates (175 °C) at a pressure of 1.5 MPa for 5 min. A quench was applied to the different films.

Nanocomposites characterization: Transmission electron microscopy was performed at room temperature in a 200 Kv JEM-2000 FX JEOL microscope to analyze material homogeneity. Samples were embedded in Spurr resin (cured at 60 °C for 48 h) to obtain parallel cuts of the films surface in thin sections (80 nm) by ultramicrotomy (Reichert-Jung Ultracut E). Specimens were then picked up on copper grids and coated with a thin layer of carbon graphite (MED 010 Balzers evaporator) to improve heat conduction. The crystalline characteristics of nanocomposites were examined by wide-angle X-ray scattering, WAXS, in reflection mode at room temperature using a Bruker AXS: D8 Advance diffractometer, Cu K α radiation (λ = 1.5418 Å) and a Vantec-1 detector. The scans were collected at a rate of 1°/min between 2 θ values from 5 to 30°. The goniometer was calibrated with a standard of silicon. The X-ray determination of crystallinity degree, f_c^{WAXS} , was performed by subtraction of the amorphous component comparing to a totally amorphous profile from an elastomeric PP sample. Studies at small angle region were performed in the synchrotron beamline A2 at Hasylab (Hamburg, Germany) (λ = 1.50 Å) using a MAR CCD detector at a distance of 230 cm from the sample. SAXS detector was calibrated with the different orders of the long spacing of rat-tail cornea (L=65 nm). The two-dimensional X-ray patterns were processed with the FIT2D program (ESRF) and converted into one-dimensional arrays after normalization for intensity of primary beam and subtraction of scattering of an empty sample.

The phase transitions on heating were analyzed by differential scanning calorimetry measurements performed in a Perkin Elmer DSC/TA7DX calorimeter connected to a cooling system and calibrated with different standards. Samples (~10 mg) were scanned from -50 to 180 °C at 10 °C/min under dry nitrogen (20 cm³/min). Raman and photoluminescence measurements were carried out at room temperature with different laser lines of an Ar+-Kr+ laser: 333 nm+365 nm, and 514 nm. A home-made micro-Raman system was utilized, consisting on a Jobin-Yvon HR 460 monochromator, a N₂ cooled CCD and Kaiser Super-Notch-Plus filters to suppress the elastic scattered light at 514 nm. The excitation light was focused on samples with an Olympus microscope (except for 333 and 365 nm UV laser lines), which was also used to collect the scattered light. Spectra were corrected by the instrumental function recorded with a calibrated white source and a CaF₂ pellet. Raman spectra were normalized using the total intensity of the C-H rocking vibrations.

Microbiological tests: The microorganisms used in this study included two clinical isolates: *Pseudomonas aeruginosa* PAO clinical isolate PBCLOp11 from burn wound infections and *Enterococcus faecalis* clinical isolate brs30 from human biliary, both classified according to 16 S rRNA (unpublished). Bacterial cells were streaked from a glycerol stock onto a LB agar plate, grown overnight at 37 °C (*P. aeruginosa*: OD₆₀₀~ 6.0) (no antibiotics) and subsequently used. To study the antimicrobial activity of films, a suspension containing 10 µl of microbial cells (ca. 10⁹ cfu ml⁻¹) suspended in 1 ml broth solution was made (7). Aliquots of 1 ml from these suspensions were added to a 4 ml quartz cubic cell containing 1 ml of sterilized water and the corresponding film under continuous stirring. The film-cell slurry was placed in the UV spectrometer chamber (UVIKON 930) and irradiated with a UV light at 280 nm for different time periods since TiO₂ appears highly efficient under UV-B and UV-A wavelengths (280-380 nm). Care was put of using a sub-lethal, maximum radiation energy fluence of ca. 1 kJ m⁻² throughout the study. After irradiation and for different time intervals, aliquots of 100 µl were transferred to a 10 ml LB broth test tube. The order of cell dilution at this stage was 10⁻². Loss of viability after each exposure time was determined by the viable count procedure on Luria Bertani agar plates after serial dilution (10⁻² to 10⁻⁵). All plates were incubated at 37 °C for 24 h prior to enumeration. A minimum of three experimental runs was performed to determine antimicrobial activity.

Results and Discussion

Figure 1 presents the TEM micrograph of the iPP80T2, nanocomposite with the highest compatibilizer amount. TiO₂ is well-dispersed within the polymer exhibiting nanometric aggregates ranged from 10 to 200 nm, with an average size (Feret diameter) of 80 nm (± 20 nm). Considering that the titania preparation makes use of an oxide previously calcined at high temperature to ensure the exclusive presence of the anatase polymorph and to strictly control its biocidal capabilities, the nanometric dispersion of the oxide is rather significant. This scenario is quite different to that shown by the specimen iPP0T2 where some micro-sized aggregates can be easily observed (Figure 1).

Figure 2 displays WAXS profiles at room temperature of the iPPxT2 nanocomposites, showing the five main diffractions characteristic of the α modification of iPP at 2θ values of 14.0, 16.8, 18.5, 21.1 and 21.7 degrees and that related to the 101 anatase diffraction at around 25.5°. In addition, the γ iPP modification is partially developed within the nanocomposite iPP30T2 and, consequently, a small peak is seen at about 20° corresponding to its (117) reflection (8). On the other hand, f_c^{WAXS} values are analogous for the different nanocomposites independently of the compatibilizer content (Table 1). The influence of TiO₂ incorporation and interfacial agent composition are clearly noticeable at higher scale on the

SAXS profiles and the long spacing estimated from them (Figure 3). An overlapping of two crystallite size distributions is observed in the iPP0T2, iPP30T2 and iPP50T2 specimens (see inset for iPP50T2) while iPP80T2 exhibits a broad but symmetric and more uniform distribution, fact that seems to indicate an improved interface adhesion between the different components with distinct electron density.

Table 1 also summarizes the characteristic glass and melting transition temperatures, T_g and T_m , respectively. While T_m values determined by DSC appear constant for the different interfacial agent contents, probably due to the crystallite improvement over heating, T_g is shifted to higher temperatures indicating that mobility within amorphous regions is hindered as the compatibilizer amount increases. Assuming an intimate contact between the oxide and the interfacial agent (a direct outcome of the preparation method), data suggest the dominant presence of the inorganic component at the polymer amorphous phase within nanocomposites. The behavior at interface can be also studied by Raman, providing information about the inorganic component state in the nanocomposites. Figure 4 shows the Raman spectra in the selected fitting area for the distinct nanocomposites. The differences found in the stronger E_g anatase peak at ca. $140\text{-}150\text{ cm}^{-1}$, in terms of peak intensity, reveal the effect of the compatibilizer content. Looking at peak height, the highest value corresponds to an interfacial agent content of 50% whereas if peak area is considered the optimal one is 80%. These results indicate differences in scattering events due to subtle interface variation and further suggest the influence of the compatibilizer content in the nanocomposites through its interaction with the TiO_2 nanoparticles.

The study of the UV excitation and de-excitation helps to understand the biocidal capabilities of these nanocomposites. The UV-visible sample spectra are shown in Figure 5A. The iPP spectrum displays a single feature at ca. 220 nm ascribed to chromophores (phenolic antioxidants and/or PP degradation products) coming from its industrial origin, while for nanocomposites, onset of a broad feature occurs in all cases at ca. 380 nm, which is characteristic of the anatase- TiO_2 component (9). No significant dissimilarities are found between the different iPPxTi2 nanocomposites. Considering that creation of electron-hole pairs occurs mainly in the TiO_2 upon UV light absorption with wavelength above ca. 250 nm, radiative de-excitation of these charge carriers can be followed by photoluminescence spectroscopy and potentially informs of charge handling processes on the whole nanocomposite system (10). Figure 5B depicts the photoluminescence spectra of samples showing strong similarities with the one exhibited by iPP. Two broad features are seen at ca. 425, 440 nm, associated with the iPP matrix and the additive presence because of its industrial source (10), respectively. The inclusion of titania within the polymer enhances the

radiative recombination pathway and causes the formation of an additional broad contribution centered at ca. 390-400 nm. This oxide-born feature is practically imperceptible for iPP30T2 but becomes visible for iPP50T2 and more significant for iPP80T2. As anatase-TiO₂ is an indirect band gap semiconductor, band edge luminescence is very difficult to observe due to the inherent low probability of indirect transitions. In nanometric anatase-TiO₂, near band edge luminescence is attributed to oxygen vacancies with two trapped electrons, i.e. F centers (11). These are likely related to surface states that are activated/enhanced only when compatibilizer allows a smooth interface contact between components. We detect charge transfer among components which, according to their band(s) gap and position, may include exciton (from charge originated at the organic component) and/or hole (from the inorganic component) separation, leaving holes into organic-like electronic states and electrons at the inorganic-like electronic states. As UV spectroscopy shown, charge carriers are dominantly generated at the inorganic component for light photons above 250 nm and, according to the photoluminescence results, could subsequently suffer an efficient charge separation process if compared with that occurring in the oxide alone. Therefore, a fraction of holes reaches the nanocomposite surface (from the bulk position of the inorganic component) and is involved in the microorganism photo-killing processes. There is thus an enhancement of light-induced surface charge carrier (e.g. hole) density at the surface of the nanocomposite films as compatibilizer amount increases. The combined SAXS/Raman analysis indicates that the improvement of the organic-inorganic interaction at interface with compatibilizer content is the key of this phenomenon, facilitating the charge separation process for loadings above 50 wt. %.

Moreover, AFM micrographs and EPR measurements with probe molecules (oxygen) (results not shown) do not detect oxide existence at surface, indicating its dominant presence at the bulk of the material, this feature being a direct consequence of the preparation method. Therefore, there is not leaching of the nanocomposite to the aqueous phase when antimicrobial tests are performed.

A preliminary analysis established that titania nanoparticle-polypropylene nanocomposites with different TiO₂ contents possesses an unprecedented power for destruction of regular bacteria, as *B. stearothermophilus*, *E. coli*, *S. aureus* and *P. jadini*, compared with other biocidal agents. The microorganisms here evaluated are *P. aeruginosa* and *E. faecalis*, since both microbes cause infections and serious illness and are widely present in the environment. Furthermore, *P. aeruginosa* is known as one of the most drug and vaccine-resistant microorganism. Moreover, we have used antibiotic-resistant and clinically isolated strains, magnifying the interest of the results. Blank experiments in presence of the iPP matrix demonstrate the relative innocuousness of UV radiation, a maximum of ca. 1.5 log-reductions (see Figure 6). Incorporation of TiO₂ has an important impact on the cell

inactivation exhibited by the nanocomposites with respect to the blank test (measuring UV influence in presence of neat iPP). Accordingly, an initial increase of elimination velocity is clearly observed as well as the further decrease of final log-reduction at the end of the experiments. The behavior of the nanocomposites under the two microorganisms tested shows some similarities. On one hand, the greatest initial reduction rate is observed in samples of the iPP50T2 nanocomposite and, on the other hand, the almost complete cell inactivation of both microorganisms is reached, accounting for a log-reduction of near 9 units, in iPP50T2 and iPP80T2 specimens. Consequently, the loss of effectiveness found in the iPP30T2 seems to be ascribed to the lowest compatibilization level existing in this specimen because of its small interfacial agent content. However, this killing level is commonly understood as being bactericidal and sufficient to maintain an appropriate safety control, helping in eliminating the need for sterilization or other aggressive treatment of foods (12). Moreover, the system does not suffer any appreciable inactivation and could be reused without significant differences with these results.

Evaluation of other biocidal agents permits to appreciate that the present systems display an unprecedented power for bacteria destruction although it has to be considered that in the investigations below discussed the conditions used and initial bacterial population may vary from one study to the other. In relation to *P. aeruginosa*, the maximum (8.0 log-reduction/0.5 h) can be compared with those observed using TiO₂ either as a powder (Degussa P25; 3.5 log-reduction/0.67 h) (13) or supported on Plexiglas (5.4 log-reduction/1 h) (14) and ethylene-vinyl alcohol copolymer (EVOH; 8.3 log-reduction/0.5 h) (5). Comparison with results using Ag-based systems as commercial AgION® coating stain steel (1.6 log-reduction/4 h) (15); AgBr particles coating poly(vinyl pyridine) (max. 4 log-reduction) (16); NO on silica (4 log-reduction/1.5 h) (17); poly(alkylammonium) coatings on polyurethanes (4.4 log-reduction/0.5 h) (18); or simple chemicals like glutaraldehyde, formaldehyde, H₂O₂, phenol, cupric ascorbate or sodium hypochlorite (all below 6 log-reduction/0.5 h) (19) highlights the potential of our systems.

Concerning *E. faecalis*, it is well-known that this Gram positive bacterium can cause life-threatening infections in humans and its thicker and more compact cell wall makes its destruction difficult by far other microorganisms. The obtained results (ca. 9 log-reduction/0.5 h) can be compared with water suspensions of TiO₂ promoted with Pt(IV) salts (ca. 6 log-reduction/0.5 h) (20); TiO₂ supported on EVOH (6.3 log-reduction/0.5 h) (5) or Ni-TiO₂ nanocomposite coatings (2 log-reduction for extended period of times) (21). Other biocidal agents based on chemicals as trichlorosan on styrene-acrylate copolymers (initial rate enhancement below 2 with respect to the copolymer alone) (22); organometallic complexes leading to oxygen radical formation (3.5 log-reduction/4h) (23); or UV-treated Nylon (1.8 log-

reduction/6 h) (24) provide further support to the assertion of the excellent functioning of the organic-inorganic nanocomposite films here described.

Summing up, the influence of PP-g-MAH content in the polymer/oxide crystalline characteristics, evaluated by WAXD and DSC, is rather insignificant for the different nanocomposites. However, the mobility of polymer amorphous regions is hindered leading to a slight improvement in thermal properties as compatibilizer content increases. These latest features seem to indicate a better adhesion at nanoparticle-polymer interfaces with contents of interfacial agent higher than 30% that appears corroborated by an enhancement of structural homogeneity of the interface according to SAXS and Raman. Differences also concern to the extraordinary powerful antimicrobiological activity exhibited by these nanocomposites, which is markedly faster for the iPP50T2 specimen. In relation to the final log-reduction reached, the iPP50T2 and iPP80T2 nanocomposites show analogous values, being higher than those observed in iPP30T2 for the two microorganisms. Photoluminescence measurements support the presence of oxide-born charge carriers in the materials with the two highest PP-g-MAH compositions that efficiently interact and kill pernicious microorganisms and correlate well with the degree of nanoparticle-polymer interface adhesion. To conclude, it can be said that the ideal interfacial agent content for obtaining the most effective nanocomposite ranges from 50 to 80 wt.-%.

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Table 1. Characteristics of polypropylene crystalline phase for the different iPPxT2 nanocomposites and for the iPP homopolymer: f_c^{WAXS} (crystallinity degree determined by WAXS at room temperature); T_g : glass transition temperature; T_m : melting temperature; ΔH_m : melting enthalpy.

Sample ^[a]	T_g (°C)	T_m (°C)	ΔH_m (J/g)	f_c^{WAXS}
iPP	6	139	106	0.70
iPP30T2	5	139	104	0.65
iPP50T2	8	139	104	0.65
iPP80T2	10	139	108	0.65
[a] Standard errors ($\pm$): 1 °C for T_g and T_m ; 4 J/g for ΔH_m ; 7 % for f_c^{WAXS}

Figure 1. TEM micrographs of a) iPP0T2 and b) iPP80T2 nanocomposite.

Figure 2. WAXS profiles at room temperature for the different iPPxT2 nanocomposites.

Figure 3. SAXS profiles at room temperature for iPPxT2 nanocomposites with different compatibilizer contents.

Figure 4. Raman spectra of iPPxT2 nanocomposites with different interfacial agent contents.

Figure 5. A) UV-visible and B) photoluminescence spectra of the reference polypropylene and iPPxT2 nanocomposite films. Excitation energy: 365 nm.

Figure 6. Process come-up logarithmic reduction of microorganism population suspended in LB medium. Survival curves of *P. Aeruginosa* and *E. faecalis* as function of irradiation time for iPP control and iPPxT2 samples.

Table of Contents brief

Extraordinary biocidal properties in iPP-TiO₂ nanocomposites are resulting from good interactions at interface which are favored by an appropriate compatibilizer content choice.