

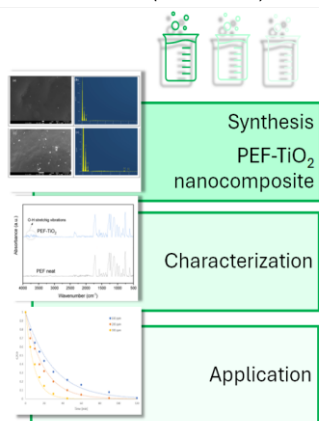
# Biobased Poly(ethylene furanoate) Polyester/TiO<sub>2</sub> Supported Photocatalyst For The Degradation Of Brilliant Green Dye

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The immobilization of photocatalytic nanoparticles is a practical tool to avoid the high-cost post-treatment separation step. In the present study, a polymer supported nanocomposite, consisting of bio-based poly(ethylene furanoate) polyester and TiO<sub>2</sub> nanoparticles, was prepared and evaluated as effective photocatalyst for the degradation of brilliant green dye. The nanocomposite was prepared via in-situ polymerization technique and was systematically characterized combining a range of techniques. The successful polymerization was confirmed by ATR-FTIR spectroscopy, and the molecular weight values were determined indirectly by applying intrinsic viscosity measurements. SEM micrographs revealed that the photocatalytic nanoparticles are well dispersed into the PEF matrix. Photocatalytic degradation of the target dye revealed the efficiency of the nanocomposites in degrading organic pollutants. Finally, the arising transformation products (TPs) were identified by HRMS.

## Introduction

Titanium dioxide (TiO<sub>2</sub>) is well known photocatalyst successfully applied for wastewater treatment, due to its high photocatalytic activity, low cost, nontoxicity and excellent stability under illumination. Usually, TiO<sub>2</sub> nanoparticles are generally used as a slurry system since larger surface area of the catalyst is by this way available, achieving high photocatalytic efficiency. Nevertheless, the filtration to eliminate and recycle the powdered TiO<sub>2</sub> suspended in the treated water increases running cost and induces the secondary pollution, which has become a main limiting factor for practical application. Alternatively, to overcome the drawbacks, many efforts have been devoted to immobilizing TiO<sub>2</sub> nanoparticles on a variety of substrates [1].

Various substrates have been tested for the immobilization of TiO<sub>2</sub> among which polymers have been proved as attractive candidates due to their excellent properties of processibility and low-cost. Bio-based polymers that are either biodegradable or at least partly bio-based, have been recently employed as green alternatives to replace the already used petroleum-based counterparts and minimize by this way their harmful fingerprint [2]. Poly(ethylene furanoate) (PEF) is a recyclable biobased polymer which had received attention from the industry and academia due to its superior thermal properties while the furan ring provides PEF higher polarity, making it more compatible with TiO<sub>2</sub> nanoparticles and therefore more suitable as a support polymer for TiO<sub>2</sub> [3].

Under this light, the main scope of the study was to apply PEF as a substrate for the immobilization of TiO<sub>2</sub>. The objectives were i) to synthesize and characterize the PEF-TiO<sub>2</sub> photocatalyst ii) to evaluate the photocatalytic efficiency of the nanocomposite towards the degradation of the

organic dye brilliant green and ii) to identify the arising TPs.

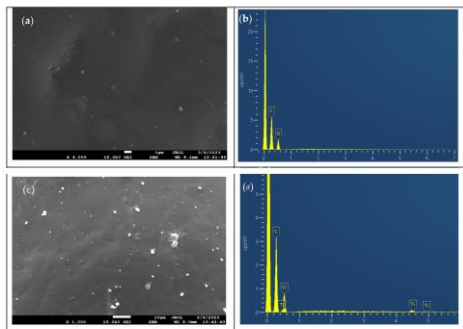
## Material and Methods

2,5-Furandicarboxylic acid (FDCA) and Ethylene glycol (EG) were utilized in a 1:2.1 molar ratio, and 10 wt.% of TiO<sub>2</sub> was incorporated into the reaction flask. The reaction mixture was pre-heated at 170 °C for 30 min, 190°C for 1 h, 200°C for 30 min, and 210°C for 30 min under nitrogen atmosphere. During the second stage, antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) (300 ppm) catalyst was added, and a vacuum (5.0 Pa) was applied slowly for 15 min to initiate the polycondensation process. Finally, the temperature is increased to 250°C for 2h and to 260°C for 2h. The photocatalytic experiments were conducted using a pyrex UV reactor equipped with a high-pressure mercury lamp and a cut-off UV-filter restricting the transmission below 290nm. Analysis of the concentration of the dye was conducted in a UV-Vis spectrometer at 625nm. The arising transformation products were identified using LC-HRMS technique.

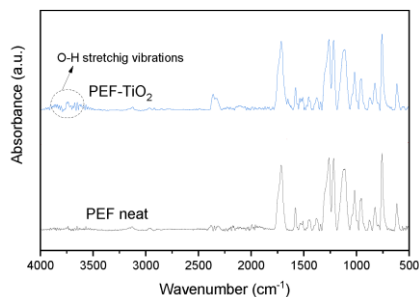
## Results and Discussion

The synthesized photocatalyst was characterized with various techniques such as Scanning Electron Microscopy (SEM), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) and Broadband Dielectric Spectroscopy (BDS). SEM images revealed the presence of very small aggregates on the surface of PEF (Figure 1). However, the fabrication of nanocomposites with a smaller percentage of nanoparticles, by in-situ polymerization inhibits the agglomeration of particles by incorporating evenly distributed nanoparticles into the PEF matrix.

Moreover, EDX spectra analysis confirms that nanoparticles were successfully incorporated into the PEF matrix by in-situ polymerization method. ATR-FTIR analysis showed that PEF-TiO<sub>2</sub> samples show tiny, sharp peaks around 3644–3708 cm<sup>-1</sup>, indicating O–H stretching vibrations, as seen in **Figure 2**.



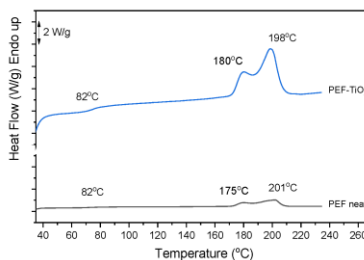
**Figure 1.** SEM micrographs of (a) neat PEF and (c) PEF-TiO<sub>2</sub> nanocomposites. EDX spectrum of (b) neat PEF, (d) PEF-TiO<sub>2</sub> nanocomposites.



**Figure 2.** ATR-FTIR spectra of the neat PEF and PEF-TiO<sub>2</sub> nanocomposites.

**Figure 3** shows the calorimetric data from DSC scans after a one-hour annealing process (170 °C at 20 °C/min). The T<sub>g</sub> of PEF-TiO<sub>2</sub> remains unchanged

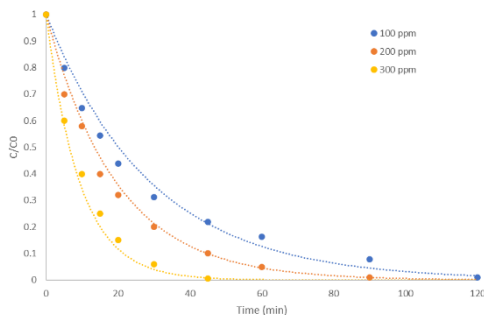
after annealing.



**Figure 3.** DSC scans of neat PEF and PEF-TiO<sub>2</sub> nanocomposite after annealing (1st heating, rate 20 °C/min).

The synthesized photocatalyst was tested in three different concentrations against the photocatalytic degradation of brilliant green dye (**Figure 4**). Obviously, increasing the concentration of the catalyst causes an enhancement of the degradation process leading finally to the complete elimination of the compound within 45 min when using the higher amount of catalyst dose.

**Figure 4.** Photocatalytic degradation of brilliant green in three different concentrations of PEF-TiO<sub>2</sub> nanocomposites



HRMS identification of the TPs revealed that hydroxylation, N-demethylation and dealkylation are the primary degradation pathways.

## Conclusions

TiO<sub>2</sub> nanoparticles were successfully immobilized on biobased PEF polymer. The nanocomposite was able to degrade the target organic dye within 45 min of treatment. Higher doses of the catalyst achieve higher reaction rates. Identification of the arising transformation products showed that brilliant green photocatalytic degradation proceeds through hydroxylation, N-demethylation and dealkylation as basic transformation routes.

## Acknowledgments

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