

## Composite Polymeric Films with Photocatalytic Properties

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Polymeric films and in particular polypropylene (PP) films could be selected as excellent substrates for photocatalytic applications based on TiO<sub>2</sub>. However, hydrophobic surface of PP makes very difficult the adhesion of TiO<sub>2</sub> particles on its surface. In this work corona pre-treated PP was used as a support for commercial TiO<sub>2</sub> in order to remove organic dye methylene blue (MB) from aqueous solution under UV irradiation. In details, the pre-treated polypropylene PP films were coated with TiO<sub>2</sub> particles by dip-coating technique. The corona pre-treatment is a practical and effective method to increase the wettability of organic polymers due to the introduction of negative groups (COO<sup>-</sup>, -O-O<sup>-</sup>) onto the surfaces, which results in a better adhesion of the photocatalyst. The obtained coated films were characterized with different techniques and the photocatalytic effect under UV light was analyzed in the degradation of MB dye. The photocatalytic tests were carried out in a batch photoreactor irradiated by a UV lamp (nominal power of 8 W and wavelength emission 365 nm).

The experimental results showed that the coating of TiO<sub>2</sub> onto PP films allowed to achieve a MB discoloration of 47% after about 180 min of UV irradiation. In contrast the unfunctionalized PP film did not show any photocatalytic activity under the same irradiation conditions.

### 1. Introduction

Heterogeneous photocatalysis based on TiO<sub>2</sub> has become an attractive area of research since the discovery of Fujishima and Honda in 1972 (Fujishima and Honda, 1972). In fact the TiO<sub>2</sub> semiconductor thanks to its properties is one of the most efficient photocatalyst (Haider et al., 2019) and it was studied for different kinds of applications, such as air purification, photo-induced hydrophilic, self-cleaning devices, water disinfection, wastewater treatment and production of hydrogen fuel (Nakata and Fujishima, 2012). However, one of the most important drawbacks is that photocatalysts are often used in powder form and need to be separated from the system after the treatment step.

In last years, the immobilization of TiO<sub>2</sub> on different types of supports substrates has been drawing a lot of attention because it eliminates the need of costly post-treatment separation processes (Vaiano et al., 2015). Considering the various substrates that have been tried for supporting TiO<sub>2</sub> based photocatalysts, polymeric substrates seem to be very promising due to their several advantages (Singh et al., 2013).

The methods for anchoring TiO<sub>2</sub> on the support influence the photocatalytic activity of titania depending on the type of substrate and the pollutant to be removed. In particular, the aim of the employed method must not lead to any reduction in the photocatalytic performances of TiO<sub>2</sub>.

Different methods have been reported in the literature, such as sol-gel method (Chen et al., 2008), chemical vapour deposition, thermal treatment method (Fabiya and Skelton, 2000) and so on. The techniques for the immobilization require high temperature calcinations and complex procedures.

The absence of appropriate binding sites on the polymer surface, in addition to their low surface energy leads to lower adhesion of TiO<sub>2</sub> particles and consequently offers difficulty in surface coating.

In fact, it is really hard to obtain a well-adhered and crack-free coating since polymeric substrates are generally relatively hydrophobic (Shimizu et al., 1999).

In this sense, an appropriate surface pre-treatment could improve the adhesion of TiO<sub>2</sub> on the polymeric substrate. For this purpose, different methods have been employed, such as surface etching (Lei et al., 2012) or deposition of intermediate layer (Kasanen et al., 2009). In this contest, the pre-treatment of polymeric surface with plasma technology presents a great potential and it has already been used for anchoring TiO<sub>2</sub> on different types of support. It is well known that the plasma pre-treatments increase the surface tension of materials and, consequently, the attachment of subsequent coatings by wet methods is improved (Singh et al., 2013). The aim of this study was the immobilization of commercial TiO<sub>2</sub> on the polypropylene (PP) film pre-treated with corona discharge at atmospheric pressure. The obtained coated films were characterized with different techniques and the photocatalytic effect under UV light was analyzed in the degradation of model organic pollutant (methylene blue dye, MB) in aqueous solution.

## 2. Experimental

### 2.1 Preparation and characterization of PP\_TiO<sub>2</sub> film

PP film was used for the immobilization of commercial TiO<sub>2</sub> (aeroxide P25), provided by Evonik Industries (average particle size: 25 nm, purity: ≥99.5% trace metals basis, crystalline phase: 80% anatase + 20% rutile). The PP film was provided by Maca srl and it was previously subjected to a corona discharge pretreatment (carried out by Maca srl) in order to increase the hydrophilicity of the PP material. For the preparation of PP film functionalized with TiO<sub>2</sub>, 0.5 g photocatalyst was dispersed in 100 mL of pure ethanol. The suspension was vigorously stirring for 20 minutes. PP film (dimensions: 7.5 cm × 2.4 cm, thickness: 0.01 mm) was then dipped in TiO<sub>2</sub> suspension for 5 min (PP\_TiO<sub>2</sub>\_film) and dried in air for 24 h (Figure 1). The final sample were rinsed with ethanol and dried at room temperature for 24 h. Both unfunctionalized PP and PP\_film\_TiO<sub>2</sub> were characterized from physico-chemical characterization point of view. The surface morphology was analyzed by a ΣIGMA (Zeiss) field emission scanning electron microscope (FESEM) with a nominal resolution of 1.3 nm at 20 kV, The fluorescence spectra were recorded on a fluorescence and absorbance spectrometer, Duetta (Horiba Scientific). Fluorescence emission (FL) spectra give information about electron hole recombination as well as surface defects.

### 2.2 Photocatalytic tests

The photocatalytic tests were carried out with a pyrex reactor (ID= 10 cm, h= 1 cm, V=78 ml) .The photoreactor was irradiated by one UV lamp (Philips, nominal power: 8 W each with main emission at 365 nm). The lamp was positioned at 10 cm on the top of reactor in order to irradiate the volume of the solution uniformly.

The pH of the solutions was not modified and it was about 6.5 for all the photocatalytic tests. The PP\_TiO<sub>2</sub>\_film was dipped in 50 mL of aqueous solution containing 5 mg L<sup>-1</sup> of MB. The system was left in dark conditions for 30 min till dye adsorption/desorption equilibrium. Subsequently, the photocatalytic test under UV or visible light was performed up to 180 min. A volume (1.5 mL) of solution was used at different reaction times in order to measure the MB dye concentration during the experiments. A fluorescence spectrometer Duetta (Horiba Scientific) was used to analyse the MB absorbance at the wavelength of 663 nm.

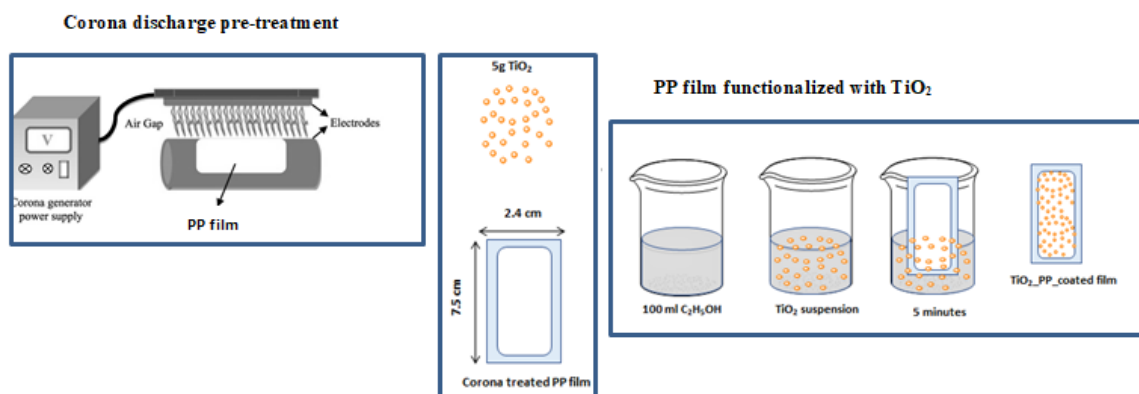


Figure 1: Schematic representation of coating process

### 3. Results and Discussion

#### 3.1 Characterization of the samples

The FL spectra of unfunctionalized PP film (PP\_film) and PP\_TiO<sub>2</sub>\_film were measured with 400 nm excitation wavelength and at 3.1 eV excitation energy (Figure 2). The signals at 430, 440, 456, 482 nm can be assigned to charge transitions from an oxygen vacancy trapped electron, recombination of self-trapped excitons and intrinsic states of TiO<sub>2</sub> (Eswar et al., 2016). In particular, the peaks at around 460 nm and 482 nm originate from oxygen vacancies and surface defects of TiO<sub>2</sub> immobilized on PP film. These charge carriers are generally trapped by oxygen vacancies and surface hydroxyl groups, which contribute in their visible luminescence (D'Amato et al., 2018). Surface morphology of PP film before and after deposition of TiO<sub>2</sub> particles was characterized with FESEM.

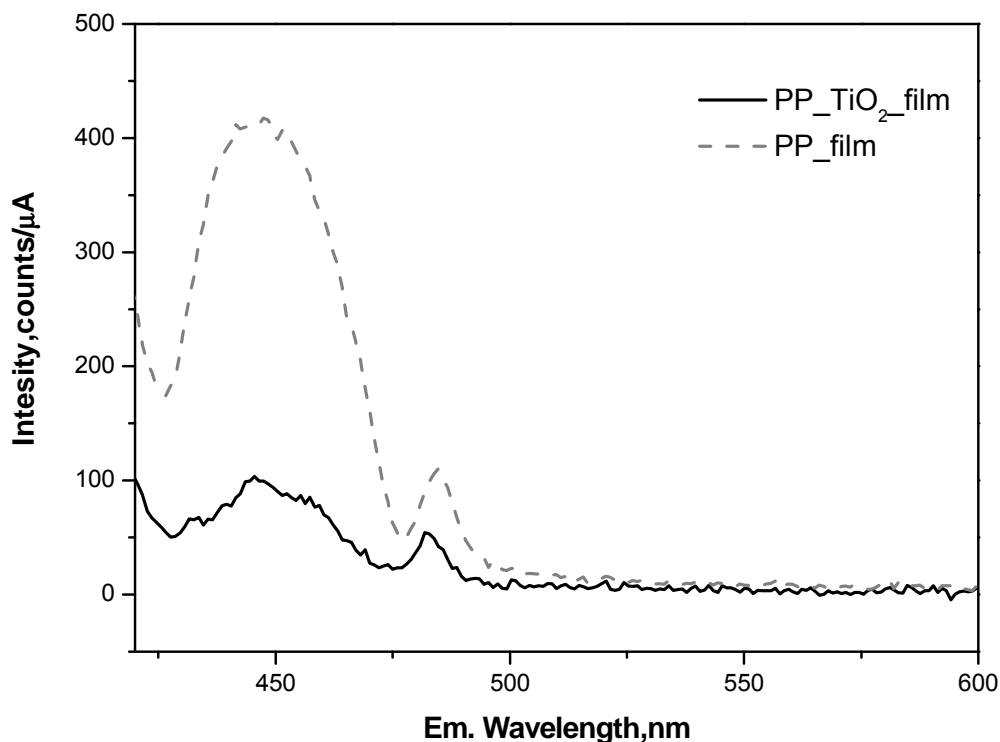


Figure 2: Fluorescence spectra of PP\_film and PP\_TiO<sub>2</sub>\_film

Figure 3 reports typical FESEM micrographs of PP\_film and of the modified sample with the TiO<sub>2</sub> nanoparticles.

For PP\_film a flat surface is observed, while for PP\_TiO<sub>2</sub>\_film, single particles and agglomerates of particles are clearly visible. The morphology studies of PP film functionalized with TiO<sub>2</sub> show the presence (Figure 3b) of both single particles with a diameter of about 25 nm and particles agglomerates with an average diameter of approximately 50-100 nanometres. In fact, corona treatment induces the changes in chemical composition of PP surface by introducing polar functional groups (hydroxyl, carbonyl and carboxyl) (Leroux et al., 2008). Thanks to the formation of polar functional groups on the PP surface. The PP film becomes more accessible to hydrophilic suspension of TiO<sub>2</sub> particles.

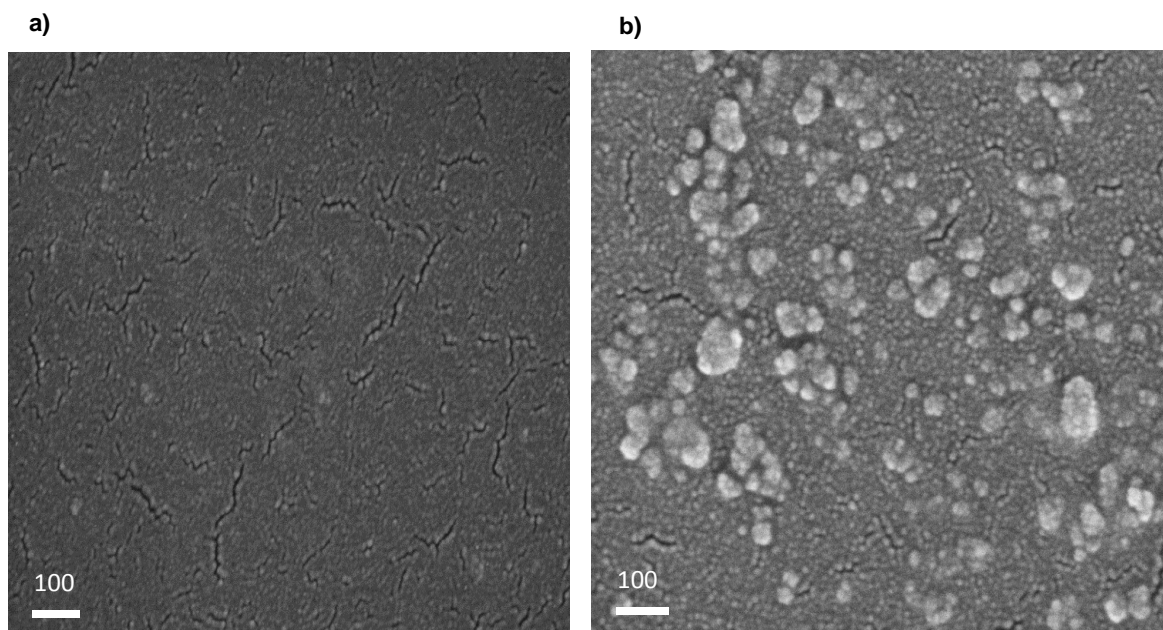


Figure 3: FESEM image of a) PP\_film and b) PP\_TiO<sub>2</sub>\_film

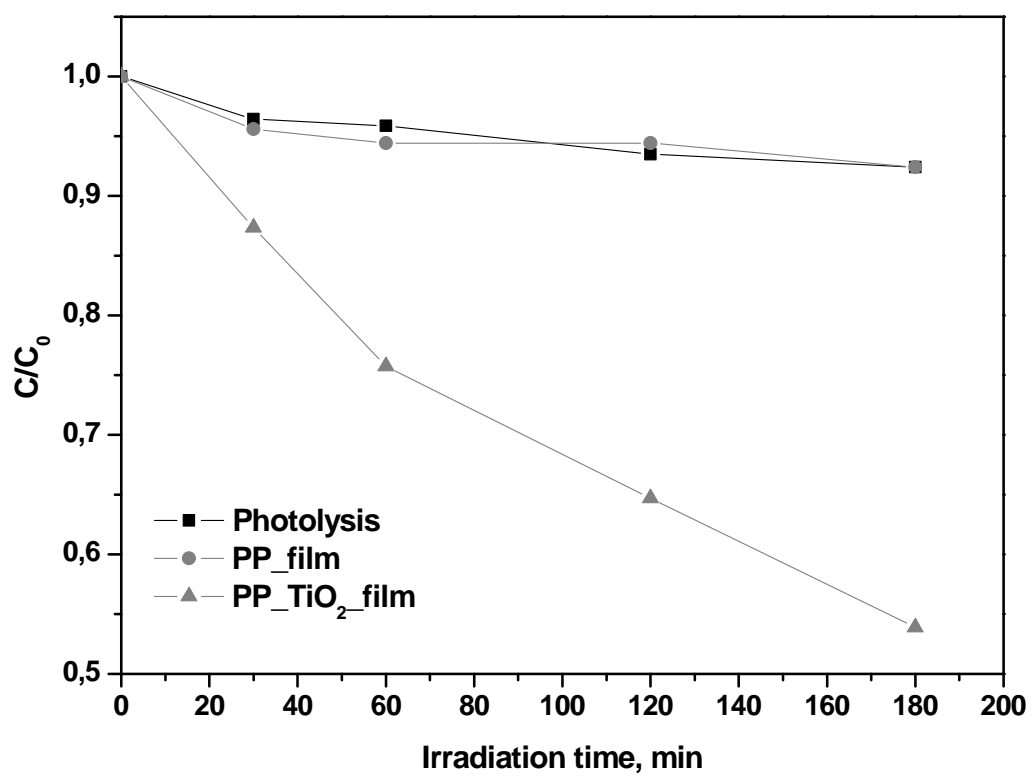


Figure 4: Photocatalytic degradation of MB under UV irradiation

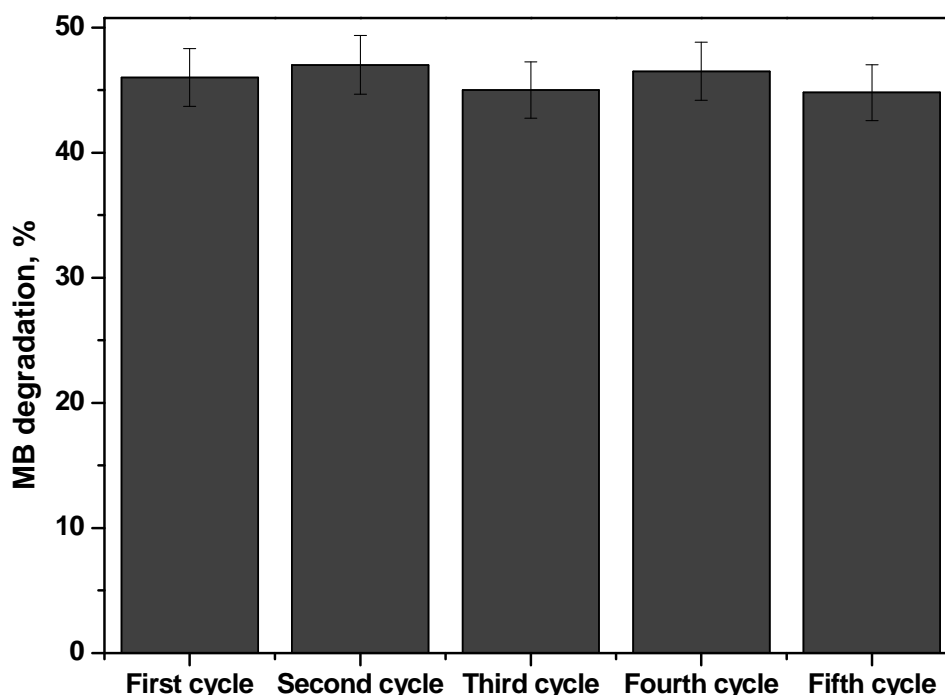


Figure 5: Reuse cycles of PP\_TiO<sub>2</sub>\_film under UV irradiation on the MB degradation after 180 min of irradiation time

### 3.2 Photocatalytic activity results

Before photocatalysis experiments, the stability of MB dye in presence of PP\_film and UV light (photolysis) were investigated.

The aqueous solution of MB was exposed to UV light for 180 min and the change of dye concentration was monitored using UV/VIS spectrophotometer.

About 7% of MB was degraded both in presence of only UV light and irradiated PP\_film (Figure 4).

A different trend was observed using PP\_TiO<sub>2</sub>\_film under UV light. Specifically, PP\_TiO<sub>2</sub>\_film was able to reach 47% of dye degradation after 180 min of UV irradiation.

In order, to investigate the possibility of reusing the PP material modified with TiO<sub>2</sub>, the photocatalytic reaction was repeated five times under the same operating conditions.

The obtained results are presented in Figure 5. As it is possible to observe from the comparison of the first cycle with the fifth cycle, the MB degradation was almost the same in all tests, indicating a good stability of the prepared sample.

## 4. Conclusions

In this work corona pre-treated PP was used as a support for commercial TiO<sub>2</sub> in order to remove organic dye methylene blue (MB) from aqueous solution under UV irradiation.

The obtained coated films were characterized with different techniques that evidenced the presence of TiO<sub>2</sub> particles anchored on PP surface thanks to the formation of polar functional groups on the polymeric surface promoted by corona discharge pretreatment.

The photocatalytic activity results showed that the TiO<sub>2</sub> coated on PP films allowed to achieve a MB degradation of almost 47% after 180 min of UV irradiation time. In contrast the unfunctionalized PP film did not show any photocatalytic activity under the same irradiation conditions.

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