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## Extruded expanded polystyrene sheets coated by TiO<sub>2</sub> as new photocatalytic materials for foodstuffs packaging

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### ABSTRACT

Nanostructured, photoactive anatase TiO<sub>2</sub> sol prepared under very mild conditions using titanium tetraisopropoxide as the precursor is used to functionalise extruded expanded polystyrene (XPS) sheets by spray-coating resulting in stable and active materials functionalised by TiO<sub>2</sub> nanoparticles. Photocatalytic tests of these sheets performed in a batch reactor in gas–solid system under UV irradiation show their successful activity in degrading probe molecules (2-propanol, trimethylamine and ethene). Raman spectra ensure the deposition of TiO<sub>2</sub> as crystalline anatase phase on the polymer surface. The presence of TiO<sub>2</sub> with respect to polymer surface can be observed in SEM images coupled to EDAX mapping allowing to monitor the surface morphology and the distribution of TiO<sub>2</sub> particles. Finally thermoforming of these sheets in industrial standard equipment leads to useful containers for foodstuffs.

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### 1. Introduction

Although over the past decade the exploitation of photocatalysis based on the use of a film of titanium dioxide (TiO<sub>2</sub>) in crystalline form has found some practical applications, the preparation of stable crystalline TiO<sub>2</sub> films under mild experimental conditions has not been satisfactorily achieved. Crystalline TiO<sub>2</sub> is an extremely photoactive, stable, non-toxic and inexpensive inorganic semiconductor [1–3].

TiO<sub>2</sub> exhibits the property of degrading organic contaminants under irradiation by ultraviolet light (UV), present either in aqueous solvents or in air. It has been furthermore found that TiO<sub>2</sub> is capable of causing irreparable damage affecting bacterial and fungal cell structures and is thus capable of performing an antimicrobial action [4–6]. Sunlight comprises a small percentage of ultraviolet radiation and TiO<sub>2</sub> films are thus active also under solar irradiation.

A frequent method to produce TiO<sub>2</sub> involves a first step of thermal hydrolysis of an inorganic precursor (typically TiCl<sub>4</sub>) so as to obtain a sol or a gel of hydrated TiO<sub>2</sub> in aqueous solution, from which TiO<sub>2</sub> films are deposited by means of dip coating or spin coating techniques (or other less common methods) and a second step in which the resultant film, upon exposure to a temperature of

350 °C, transforms into a crystalline photoactive phase. However, the application of a TiO<sub>2</sub> film layer onto thermolabile polymers, as for instance expanded polymers forming tubs or containers for foodstuffs, is associated with major technical difficulties and the result obtained by means of known methods is not always satisfactory [7–16].

The expanded polymeric materials are, in fact, intrinsically hydrophobic and are thus not readily wettable with the most conventional sol–gel preparations which give rise to TiO<sub>2</sub>. Furthermore, many polymers tend to undergo changes when the temperature rises, thus preventing sintering of the film deposited in amorphous form. In order to overcome this drawback, sol of commercial crystalline TiO<sub>2</sub> already photocatalytically active are used for deposition onto polymer sheets. However, while on the one hand this solution provides a satisfactory photoactivity, on the other hand the adhesion and uniformity of the TiO<sub>2</sub> on the polymer is rather poor. Alternatively an intermediate layer containing organic and inorganic groups can be deposited between the polymer and TiO<sub>2</sub> or TiO<sub>2</sub> can be modified by attaching hydrophobic aromatic polymer species [10].

In those cases the adhesion of TiO<sub>2</sub> to the polymer can be satisfactory but the photoactivity of the film is usually insufficient. Additionally some additives may induce the instability of the TiO<sub>2</sub> solutions, causing the formation of precipitates, chemical reactions or phase separation [17].

In this work a method to prepare extruded expanded polystyrene (XPS) sheets covered with TiO<sub>2</sub> is reported. The results

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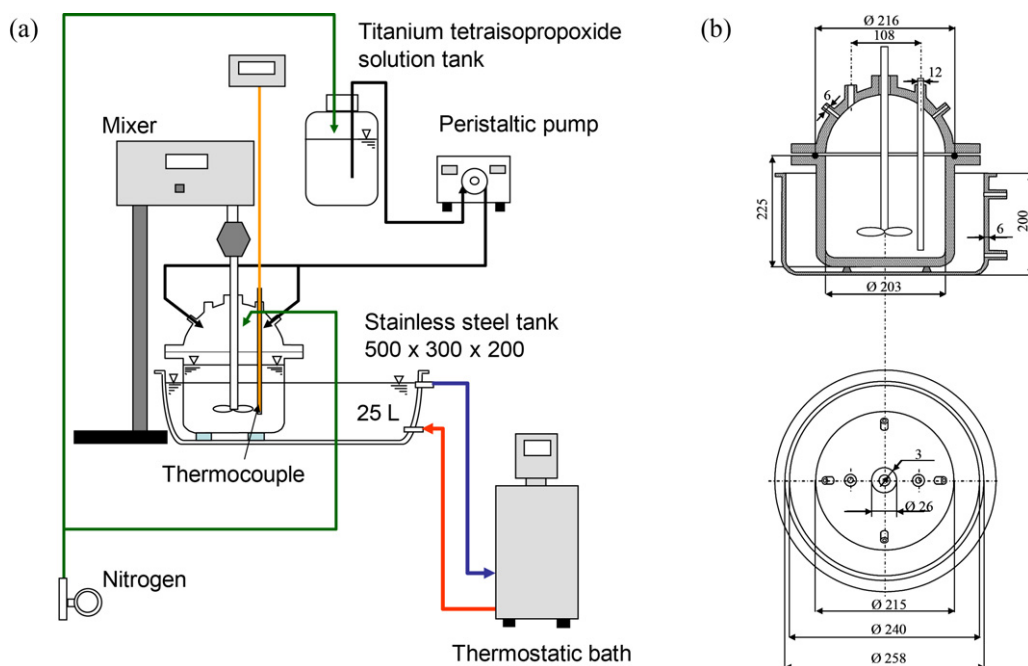


Fig. 1. Reaction set-up (a) and reactor detailed scheme (b) used for the preparation of  $\text{TiO}_2$  sol. Length units are millimetres.

were partially reported in patent EP10425272.1 [18] and in an international conference on Mediterranean feeding [19]. The  $\text{TiO}_2$ -functionalised XPS sheets were used in order to get a thermoformed packaging for foodstuffs. The final photoactivity tests were performed in a batch reactor in gas–solid system by using 2-propanol, trimethylamine and ethene as probe molecules. Notably the Food and Drug Administration (FDA) approves the use of  $\text{TiO}_2$  in packages for foodstuffs (see <http://www.fda.gov>).

## 2. Materials and methods

### 2.1. Preparation of $\text{TiO}_2$ sol

Titanium tetraisopropoxide (TIP) was used as the organic  $\text{TiO}_2$  precursor. An acidic aqueous solution was prepared by mixing 50 mL of  $\text{HNO}_3$  (nitric acid), 200 mL of  $\text{CH}_3\text{COOH}$  (acetic acid) and 4500 mL of  $\text{H}_2\text{O}$ . 250 mL of  $\text{Ti}(\text{OPr})_4$  were added dropwise to this solution under vigorous stirring and nitrogen atmosphere. The 5 L reactor showed in reaction setup reported in Fig. 1 was developed and used for the preparation. The mixture was kept at  $60^\circ\text{C}$  for 16 h in a closed reactor by means of a water bath so as to take the hydrolysis of TIP to completion. The sol, initially whitish, became clear after ca. 0.25 h and was used to cover the polymeric support after 16 h heating at  $60^\circ\text{C}$ . All the used chemicals were purchased by Sigma–Aldrich and used as received.

### 2.2. Preparation and characterisation of $\text{TiO}_2$ -supported XPS sheets by spray-coating

XPS polymer sheets were produced in a plant of Sirap–Gema and were made of extruded expanded polystyrene with substantially closed cells with a thickness of ca. 6 mm. The polystyrene granules were conveyed, melted and plasticised in the extruder. Then a liquid foaming agent (hydrocarbon mix) was injected under pressure into the barrel and in the melt polymer. The polymer was then cooled in a secondary part of the extruder and pumped through a shaping die where the gas expands and creates small bubbles of gas inside the sheets so reducing the density. Finally the sheets were wound in roll stock.

Samples were prepared by using spray-coating method integrated in Sirap–Gema R&D plant, located in Verolanuova (Brescia, Italy). The spray-coating was followed by a thermal treatment at  $50^\circ\text{C}$  for 1.5 h. Spraying cycles were repeated once or twice. Finally the functionalised sheets were used in thermoforming foodstuffs packaging by means of a Sirap–Gema industrial machinery. Generally the polystyrene foam sheet stock in the right thickness and width is heated in a forming temperature range; afterwards stretching of the rubbery sheet into a rigid mold takes place, followed by holding of the stretched plastic sheet against the cold mold walls until it gets rigid; finally the plastic sheet is trimmed in the desired part from the surrounding web. The process was carried out at a temperature of  $200^\circ\text{C}$  making use of vacuum suction. At the end of the process, bare and  $\text{TiO}_2$ -functionalised packaging do not show any significant difference to both the naked eye and the touch.

The resultant  $\text{TiO}_2$  crystalline phase was investigated by Raman spectroscopy measurements by means of a microprobe set-up (ISA–Jobin–Yvon, model Labram), equipped with a CCD detector and a He–Ne laser as excitation source (632.8 nm emission).

Morphology and distribution of  $\text{TiO}_2$  particles on XPS were finally detected by means of a microscope (Philips XL30 ESEM) operating at 25 kV coupled to EDAX detector used for surface mapping.

### 2.3. Photoreactivity set up and procedure

Photoactivity tests were performed by using polymer sheets coated with  $\text{TiO}_2$  in the vapour phase degradation of 2-propanol; trimethylamine and ethene were also used as probe molecules.

The photoactivity tests were carried out using a Pyrex glass gas–solid reactor of cylindrical geometry and having a total volume of approximately 1.0 L; the setup of a similar reactor has been previously showed [20]. It basically consisted of two shells held together by a steel ring and an O-ring gasket was furthermore placed between the parts of the reactor to ensure gas tightness during the photoreaction. The reactor was also provided with an inlet and an outlet orifice fitted with respective opening/closing valves

and an orifice for gas sampling that was performed by means of a 0.5 mL gastight syringe.

In some runs the irradiation source used for the reaction was a 400 W medium pressure mercury lamp. Distilled water continuously flowing between lamp and reactor screened IR radiation thus avoiding an overheating of the reactor and hence the polymer.

In other runs the irradiation source used for the reaction consisted of three external actinic BL TL MINI 15 W/10 Philips fluorescent lamps whose main emission peak (365 nm) is in the near-UV region. The latter runs were performed inside a common domestic refrigerator in refrigeration compartment (at 13 °C) and in the freezer one (at −5 °C).

The gaseous samples were analysed by means of a GC-17A Shimadzu gas chromatograph fitted with an HP-1 methyl siloxane column (30 m × 320 μm × 0.25 μm) from Hewlett-Packard and a flame ionisation detector, using He as carrier gas. Moreover CO<sub>2</sub> has been measured by a Hewlett-Packard 6890 equipped with a Supelco 60/80 Carboxen 1000 column and a thermoconductivity detector (TCD).

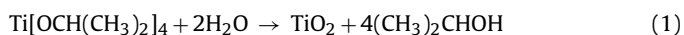
The photoactivity tests on the XPS polymer foodstuff packages coated with TiO<sub>2</sub> were carried out in accordance with the procedure described below.

A sample of TiO<sub>2</sub>-functionalised XPS polymer was cut in round shape (with the same diameter of reactor, i.e. 10 cm) and located on the bottom of the reactor and the reactor was sealed. After saturating the reactor with air, a predetermined quantity of 2-propanol, trimethylamine or ethene was injected through the sampling orifice. After ca. half an hour the lamp was switched on as a constant concentration of the probe molecules was achieved. Subsequently samples were withdrawn from the reactor at predetermined times by means of a gastight syringe and injected into the gas chromatograph.

### 3. Results and discussion

The preparation of TiO<sub>2</sub> sol was performed by means of an appropriate reactor, designed to this aim. The hydrolysis of TIP, i.e. TiO<sub>2</sub> precursor, was performed in nitrogen atmosphere in order to avoid fast hydrolysis caused by air moisture. Moreover a thermostatic bath allowed keeping controlled temperature in order to give rise to anatase phase without causing formation and precipitation of particle agglomerates (see Fig. 1).

The hydrolysis and condensation of TIP with subsequent formation of 2-propanol and TiO<sub>2</sub> are represented by the following overall reaction:



The obtained almost transparent sol was used to coat the XPS polymeric support. Samples were prepared by using spray-coating method followed by a light thermal treatment. Spraying cycles were repeated once or twice. The films thus deposited on XPS exhibited very high stability and uniformity. Finally the functionalised sheets were used in thermoforming foodstuffs packaging by means of a manufacturing process where a plastic sheet was heated and formed to a specific shape in a mold, and finally trimmed to create a functional product. The containers may be obtained by thermoforming the polymer sheet forcing it to assume the desired shape. At the end of the process, bare and TiO<sub>2</sub>-functionalised packaging do not show any significant difference to both the naked eye and the touch.

In order to test the adherence of TiO<sub>2</sub>, the functionalised polymer was immersed in a beaker containing water and subjected to ultrasound treatment and some UV-absorption spectra of the resulting water were recorded after 1 h, using pure water as the reference sample. The absence of UV-absorption indicated the absence

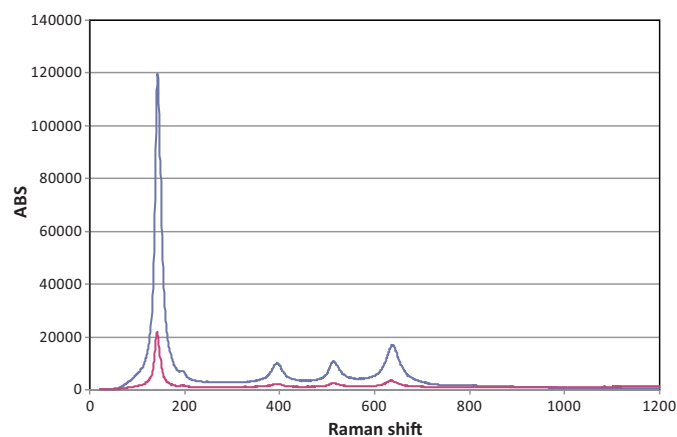


Fig. 2. Raman spectra of XPS polymer sheets coated with TiO<sub>2</sub> film (purple) and TiO<sub>2</sub> anatase reference (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of TiO<sub>2</sub> leaching. The good adherence can be ascribed to the possible insertion of TiO<sub>2</sub> nanoparticles in the huge porosity of XPS and to the acidity of the used sol that could have promoted the grafting of TiO<sub>2</sub> to polystyrene surface. Moreover the final thermoforming process further enhances adhesion that is one of the most desirable features in such a process.

TiO<sub>2</sub> was present in anatase crystalline phase, as proved by Raman spectroscopy, showed in Fig. 2. Purple line represents TiO<sub>2</sub> anatase reference, with characteristic Raman shifts of 144, 396, 513, 640 cm<sup>−1</sup>. The same peaks are present in the red line, thus demonstrating that TiO<sub>2</sub> anatase phase was present in the coating films of the XPS polymer sheets. It is worth noting that other crystalline TiO<sub>2</sub> phases (rutile and brookite) present different characteristic Raman shifts not detected in our samples, whereas no peaks would have been observed for amorphous TiO<sub>2</sub>.

Anatase phase is responsible for the photocatalytic activity of the functionalised polymer, imparting capability of degrading the used probe molecules. This crystalline phase generally is indeed the most active among the various TiO<sub>2</sub> polymorphic forms.

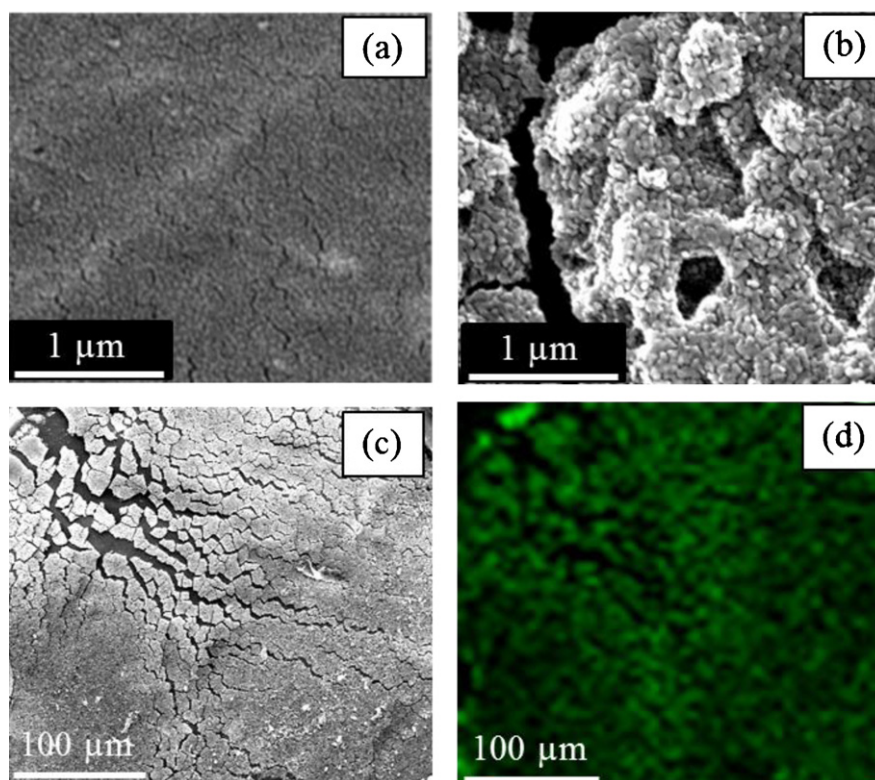
Fig. 3 reports some representative SEM images along with a titanium EDAX mapping (Fig. 3d) of the samples. Homogeneity of the polymer is not high and limited cracks are somehow present due to XPS intrinsic characteristics and mechanical stress caused by thermoforming process.

SEM study indicates that TiO<sub>2</sub> is widely present only in the sample where two spray-coating of TiO<sub>2</sub> were performed; indeed, the sample obtained with only one coating of TiO<sub>2</sub>, not reported for the sake of brevity, shows a morphology very similar to that of the bare XPS substrate. On the contrary, the different morphology observed between the bare XPS substrate (Fig. 3a) and the sample with two coating of TiO<sub>2</sub> (Fig. 3b) is due to the presence of a layer of TiO<sub>2</sub>. In order to qualitatively evaluate the titanium coverage of the surface, Fig. 3d reports the titanium EDAX mapping (highlighted in green colour) carried out on the sample showed in Fig. 3c that reports a picture of the same sample of Fig. 3b but at lower magnification. From this study it is evident that the cracked layer showed in Fig. 3c constitutes TiO<sub>2</sub>. Moreover, it can be seen that TiO<sub>2</sub> is widely present onto the XPS substrate.

The photocatalytic activity was tested as detailed in materials and methods section. Organic pollutants produced by various kinds of food, can be degraded thus avoiding bad smell (see the case of fish producing trimethylamine) or quick ripening of different fruits, for example speeded up by ethene produced by apples.

Before testing the TiO<sub>2</sub>-functionalised polymers in the presence of irradiation, two preliminary tests were performed by using

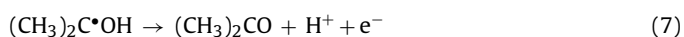
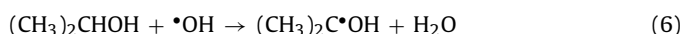




**Fig. 3.** SEM analysis of the thermoformed XPS packaging samples. (a) Unfunctionalised; (b and c) treated by 2 spray-drying cycle; (d) EDAX Ti mapping (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

naked polymer plus light and TiO<sub>2</sub>-functionalised polymer without light. In both cases no reactivity was observed confirming that the contemporary presence of TiO<sub>2</sub> and light is needed in order to degrade molecules. Finally irradiation of TiO<sub>2</sub>-functionalised XPS in the absence of reactants did not produce degradation of polymer since no gaseous product was detected in the gas phase and the white appearance of the polymer remained unchanged.

Fig. 4 shows two runs (concentration vs. time) reporting the outcome of a test of the photocatalytic degradation of 2-propanol on XPS polymer modified by spray-coating of TiO<sub>2</sub> sol repeated once or twice. Eqs. (2)–(7) report photocatalytic oxidation mechanism of 2-propanol to acetone. The latter one is further oxidised to CO<sub>2</sub> (whose concentration has been normalised dividing by 3, i.e. the number of the carbon atoms present in the substrate molecule).



Activity increased by using the twice-covered material due to a more significant presence of photocatalyst. Moving to further coverage showed to be inconvenient since the activity did not increase much and the adhesion of TiO<sub>2</sub> onto the polymer was inadequate.

Fig. 4 also shows the concentration of acetone, the main product of partial oxidation, which is finally degraded to CO<sub>2</sub>. It is worth noting that the produced acetone was present in very low concentrations (lower than 25 µM) and did not produce any change on polymer surface. The formed CO<sub>2</sub> (in this case together with

the acetone) is balanced by the reacted carbon, closing satisfactorily the carbon balance. CO<sub>2</sub> evolution starts from the beginning of irradiation because the oxidised substrate can be alternatively mineralised or partially oxidised to acetone, as commonly observed in photocatalytic oxidations [21].

It is worth noting that the photoactivity of the functionalised polymer was reproducible during different cycles and deactivation phenomena did not occur. This is however typical of TiO<sub>2</sub>-based photocatalysts, since they are stable inorganic materials that do not get easy modifications over time.

The influence of temperature on the photocatalytic process was also studied: the typical refrigerator temperature (13 °C) was indeed used along with the deep-freeze one (−5 °C) and the reactivity obtained in both cases was compared to that characteristic of 20 °C. It should be underlined that the real temperature was increased by ca. 2 °C because of some warming effects caused by irradiation through actinic fluorescent lamps. Fig. 5 shows the experimental runs carried out by using the thermoformed polymer functionalised by two spray-coating cycles. 2-Propanol disappearance rate, as expected, somehow decreases by increasing the reaction temperature due to a worse adsorption of 2-propanol on TiO<sub>2</sub>. It can be however seen that a comparable activity is present at all the used temperatures. These runs have been performed in a real refrigerator, as reported in experimental section. Fig. 6 shows a photo taken during an experimental run inside a refrigerator, whereas the photoactive thermoformed foodstuff packaging is showed in the inset.

The runs ensured that the produced foodstuffs packaging could be used in refrigerators provided of an internal irradiation source.

Additional tests were carried out by using trimethylamine and ethene as the reagents under the same described experimental conditions. These two molecules are produced by fishes (trimethylamine) and some fruits (ethane) and hence the relevance of their degradation is significant for foodstuffs packaging applications.

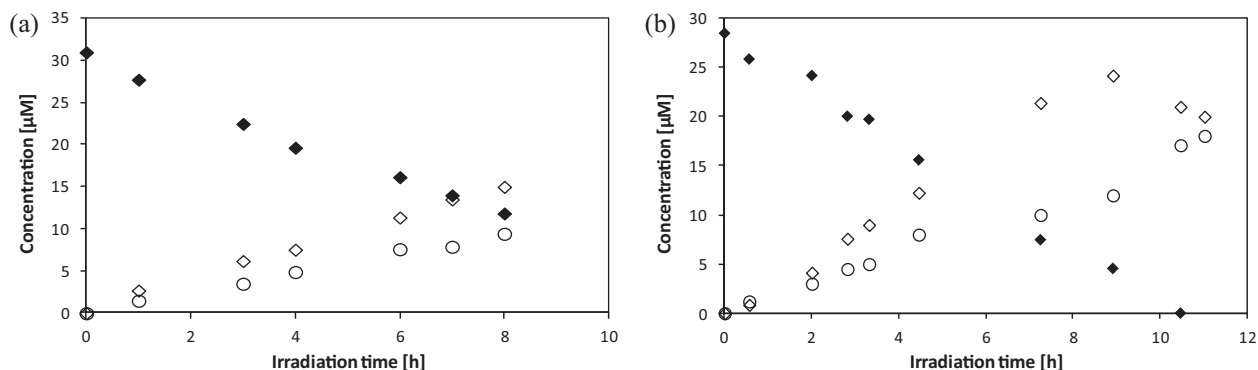


Fig. 4. Photocatalytic runs carried out by using 1-layer (a) and 2-layer (b) functionalised XPS. The concentrations of 2-propanol (◆), acetone (◇) and CO<sub>2</sub> (○) are reported.

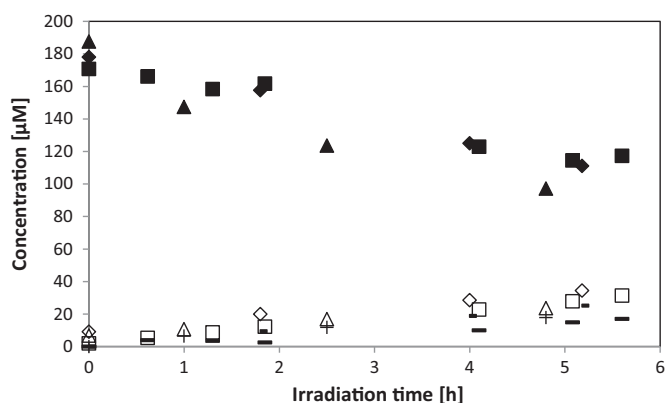


Fig. 5. Photocatalytic runs carried out at different temperatures (at room temperature and inside a refrigerator and in deep-freeze compartment). The concentrations of 2-propanol, acetone and CO<sub>2</sub> are reported at -5°C (▲, △, +), 13°C (◆, ◇, -) and 20°C (■, □, -).

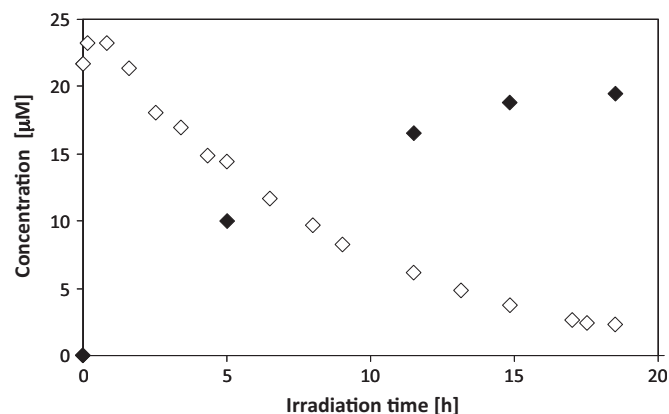


Fig. 7. Photocatalytic run carried out by using 2-layer functionalised XPS. The concentrations of trimethylamine (◇) and CO<sub>2</sub> (◆) are reported vs. irradiation time.

Figs. 7 and 8 show the trends of photocatalytic degradations carried out by using XPS coated by two layers of TiO<sub>2</sub> and the corresponding produced CO<sub>2</sub> (normalised by dividing by 3 or 2, respectively). It can be seen that the reactivity is in both cases comparable to that observed for the degradation of 2-propanol and the coated XPS sheets can be thus fruitfully used to abate molecules produced by foods that are responsible of their deterioration.

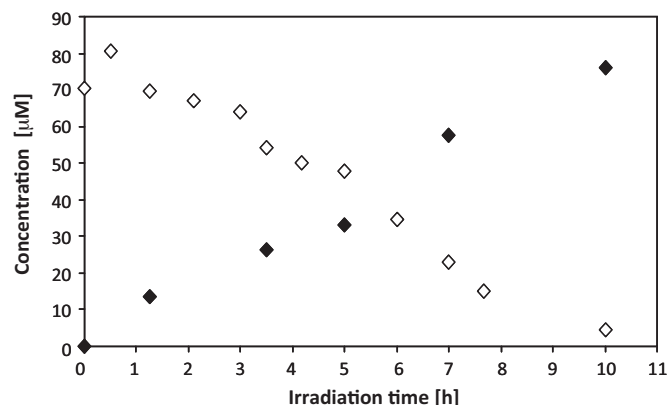


Fig. 8. Photocatalytic run carried out by using 2-layer functionalised XPS. The concentrations of ethene (◇) and CO<sub>2</sub> (◆) are reported vs. irradiation time.

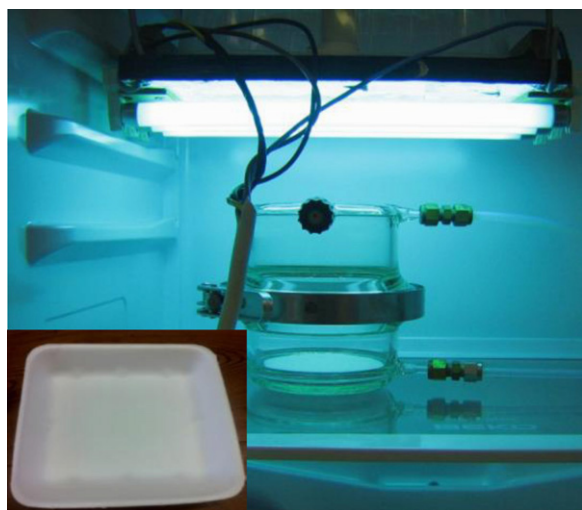


Fig. 6. Photo taken during an experimental run carried out inside a refrigerator and (inset) a photoactive thermoformed foodstuff packaging made of extruded expanded polystyrene (XPS).

#### 4. Conclusions

This work demonstrates the possibility of developing a TiO<sub>2</sub> anatase sol and its deposition by spray-coating on XPS sheets, typically used for foodstuffs packaging. The sol was developed starting from an organic precursor of TiO<sub>2</sub> and without addition of any noxious additive. The new photocatalytically active material has proved to be stable and active towards the degradation of 2-propanol, trimethylamine and ethene without modifying the characteristics of the polymer and without causing leaching of TiO<sub>2</sub> particles. Moreover the reported method has been implemented in the existing industrial equipments by Sirap-Gema used to thermoform foodstuffs packaging polymers and samples of

TiO<sub>2</sub>-functionalised packaging have been produced and tested to demonstrate that an industrial production of this innovative photoactive material is possible.

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