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EVALUATION OF SEVERAL COMMERCIAL POLYMERS AS SUPPORT FOR TiO_2 IN PHOTOCATALYTIC APPLICATIONS

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ABSTRACT

This work is aimed to select the best synthetic polymers available in the market with high transmittance in the TiO_2 activation range that can be coated with the semiconductor and withstand the photocatalytic oxidation conditions.

Among eleven commercial organic polymers with different additives and processing techniques, only polypropylene, polystyrene, sheet moulding processed poly (methyl methacrylate) and rigid polyvinyl chloride presented transmittances higher than 80% at 360 nm , which allows irradiation there through. The selected polymers were coated without a calcination step with anatase-TiO_2 obtained by sol-gel. Their weathering was studied during 150 days of exposure to solar radiation, with and without the TiO_2 layer. It was observed that only poly (methyl methacrylate) retains the titania and the good optical and mechanical properties after the natural weathering, and thus is the best candidate for immobilization of TiO_2 for air photocatalytic treatment applications.

Keywords: Photocatalysis; Polymeric substrates; Photo-oxidative degradation; Titanium dioxide.

1. Introduction

The deposition of inorganic thin films on the surface of organic polymers is currently attracting significant attention in several fields. Organic polymers are usually cheap, lightweight and easy to shape, and thus represent an interesting substrate, for instance, to immobilize a semiconductor for heterogeneous photocatalysis applications (Portela *et al*., 2007; Kasanen *et al*., 2011). Titania (titanium dioxide, TiO_2) is the common photocatalyst employed in water and air treatment with this advanced oxidation technology (Laoufi *et al*., 2008, Behnajady *et al*., 2008) and much research work has been devoted to the immobilization thereof, including the deposition on polymeric materials (Herrmann, 2005; Keshmiri *et al*., 2004; Coronado *et al*., 2008). Poly(methyl methacrylate) (PMMA), polystyrene (PS), polyamide (PA), polyethylene (PE) or poly(ethylene terephthalate) (PET) have been coated with titania (Joo *et al*., 2003; Iketani *et al*., 2003; Matsuda *et al*., 2003; Langlet *et al*., 2003; Yang *et al*., 2006; Strohm

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et al., 2003; Matsuzawa *et al*., 2008; Zhiyong *et al*., 2007; Sánchez *et al*., 2006). Many polymers present high transmittance in the TiO_2 activation range (the UV-A region, in the case of the solar spectrum). This property is of high interest for the photocatalytic treatment of water and air, because it allows the irradiation of multiple photocatalytic surfaces in one direction, with one radiation source, and thus to increase the efficiency of the process (Imoberdorf *et al*., 2007; Leung *et al*., 2006). Additionally, some polymers are commercialised in the shape of small-celled honeycomb structures to be used as insulators, which may be useful to obtain adequate flow regimes in photocatalytic reactors (Wong *et al*., 2007). However, the easy thermal- and photo-degradation of polymers, beneficial to obtain self-degrading or self-sterilizing properties, poses a difficulty for the synthesis of durable, UV-transparent and photocatalytically active materials (Espí *et al*., 2007; Shang *et al*., 2003; Kubacka *et al*., 2007; Zhao *et al*., 2007; Cho and Choi, 2001). Many polymers show maximum sensitivity for bond dissociation in the range of 290-400 nm and consequently are photostabilized for commercial use at the expense of their UV transmittance (Feldman, 2002; Allen *et al*., 1998).

The objective of this work is the study of synthetic, commercially available polymers susceptible to be coated with TiO_2 to be used in air photocatalytic treatment taking into account the aforementioned considerations. The materials initially selected are widely used polymers without additives (only the necessary for processing). Additionally, some polymers with additives that improve the physical properties are included in the study: polyvinyl chloride with UV stabilizers and plasticizers, and ethylene-vinyl acetate, the most common greenhouse plastic, with HALS (hindered amine light stabilizer), that slows down the photochemically initiated degradation reactions to provide high solar radiation resistance (Irusta *et al*., 2009). The adhesion of the photocatalyst, the optical properties and the photodegradation of the commercial polymers have been investigated.

Main findings are that sheet moulding-processed PMMA has the best transmittance and degradation resistance among the commercial polymers under study, and therefore could be a good support if the TiO_2 adherence is improved.

2. Materials and methods

2.1. Organic polymers

The commercial materials selected were homopolymer and copolymer blends as listed in Table 1, including polyolefin films used in agriculture, such us polyethylene, ethylene-vinyl acetate copolymer and polypropylene; two types of poly(methyl-methacrylate), processed by sheet moulding and by extrusion; three types of polyvinyl, rigid and flexible polyvinyl chloride and polystyrene; and polycarbonate. The different additives present in some of the samples were: HALS, to prevent photo-oxidation, plasticizers, and other processing additives, such as antioxidants. The polymer samples used in this work were supplied by Repsol Chemicals (polyolefins), Nivic (polystyrene and polycarbonate), Ketersa (acrylic) and Manuplast (PVC), as well as the information concerning the additives included in the table.

2.2. Sol-gel synthesis and TiO_2 coating

A TiO_2 sol was prepared as reported in a previous work, by adding titanium isopropoxide $Ti(i\text{-}OPr)_4$ (Aldrich) to an aqueous solution of nitric acid in the proportion 900:6.5:74 ($H_2O:HNO_3:Ti(i\text{-}OPr)_4$). The solution was stirred during three days until a stable and translucent sol was obtained, and then dialyzed to a final pH of 3.5 using cellulosic membranes (3500 MWCO). Transparent TiO_2 films were deposited on both sides of the polymeric substrates by dip-coating of the samples using a multilayer technique and an immersion rate of 0.8 mm s^{-1}. Each single layer was allowed to dry for 1 hour at 50 °C.

2.3. UV exposure tests

Polymers weathering were investigated using a self-constructed solar exposure chamber. The chamber had a borosilicate glass top, with good transmittance in the solar UV-A range, and lateral openings to permit the natural flow of air. Samples of the selected polymers, with and without TiO_2, were introduced in the chamber, which was placed on the roof of building 42 of Ciemat, in Madrid (40.40° N latitude, 3.67° W longitude). The samples were characterized at 0, 100 and 150 days of exposure to study the photodegradation and the effect of the TiO_2 coating.

Table 1. Synthetic polymers available in the market included in this work

Polymer type	Polymer name	Known additives [a]	Sample name	Thickness (mm)
Polyolefin	Polyethylene (LDPE)	P.A.	PE	0.2
	Ethylene-vinyl acetate copolymer (EVA 4%)	P.A.	EVA	0.2
		P.A.+HALS	EVA-H	0.2
	Polypropylene	P.A.	PP	0.05
Acrylic	Poly(methyl methacrylate)	P.A.	PMMA-SM (sheet moulding)	4
		P.A.	PMMA-EP (extrusion)	3
Polycarbonate	Polycarbonate	P.A.	PC-Ce (cellular configuration)	0.2
		P.A.	PC-C (compact)	2
Polyvinyl	Polyvinyl chloride	P.A.	PVC-R (rigid)	0.2
		UV stabilizers, Plasticizers, P.A.	PVC-F (flexible)	3
	Polystyrene	P.A.	PS	2

[a] P.A: Processing antioxidants, HALS: Hindered Amine Light Stabilizers

2.4. Characterization

The XRD patterns of TiO_2 xerogels obtained drying the sol at 50 °C were recorded on a D5000 diffractometer to analyze the crystallization of TiO_2. The crystalline domain mean size was calculated according to the Sherrer equation. The effective adhesion of the coatings was studied using a Hitachi scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDX); the samples were initially coated with a conductive layer of graphite for the analysis.

The optical properties of the as-prepared and aged samples with and without the photocatalytic coating were measured using a Perkin Elmer Lambda 650S UV–vis spectrophotometer (wavelength interval of 200-800 nm) and a FT-IR Thermo Nicolet 6700 spectrometer with an attenuated total reflection (ATR) accessory with a ZnSe crystal (wavelength interval of 4000-650 cm^{-1}). The spectra were obtained from 64 scans at 4 cm^{-1} resolution. All the samples were previously ultrasonically washed.

Morphological changes in the aging process (i.e. physical changes such as discoloration or cracking) were studied with a stereoscopic light microscope (Nikon Eclipse 80 i).

Finally, to evaluate the effect on the mechanical properties of the polymers the resistance of the samples to tensile stress was measured at room temperature with a Metrotec Hounsfield dynamometer H10KT.

3. Results and discussion

3.1. Polymers selection and characterization of TiO_2 films

With the objective to select the samples with better transmittance in the appropriate region of the spectra, the UV-vis transmittance of the raw materials was measured. For comparative purposes, 360 nm was selected as reference wavelength, because at this value there is significant radiation absorption by crystalline TiO_2 (anatase band gap is 3.2 eV) and it is the maximum radiance value of common UV-A lamps used in photocatalysis (e.g. Philips TL-8W/05) (Serpone, 2006). The measures show that due to the chemical nature of the polymer or its additives, most samples present medium to high radiation absorption at the selected reference wavelength. As shown in Fig.1, PVC-F, PMMA-EP and the polycarbonates transmit less than 6% of incident radiation. A low transmittance is advantageous to avoid the polymer photodegradation, but hinders the radiation harvesting in gas phase photocatalytic degradation processes with stacked units of polymer-supported TiO_2. Only four samples showed a transmittance higher than 80% (Fig. 2), and therefore they were selected for further studies: PP (91%), PS (86%), PMMA-SM (89%) and PVC-R (80%). It is worth remarking that PMMA and PP present similar good transmittance despite the thickness of the former.

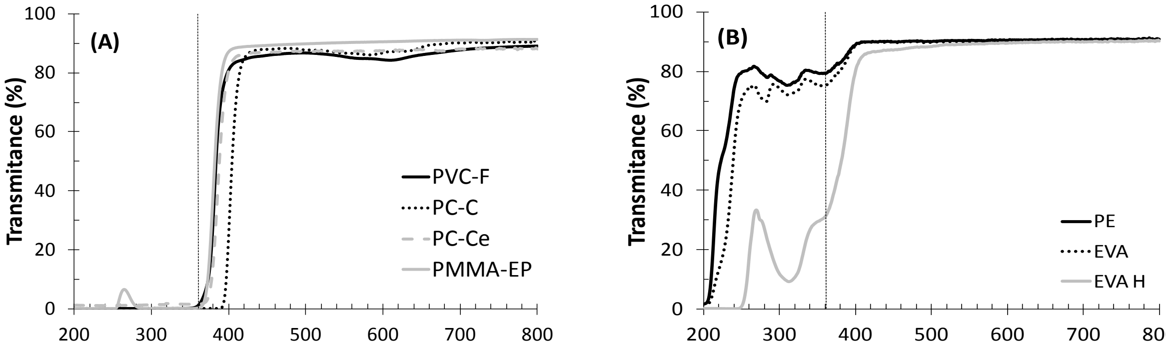


Figure 1. Radiation transmission in the UV-vis. The dotted line at 360 nm indicates the reference value for comparison. (A) low transmittance polymers, (B) medium transmittance polymers

The coating with the TiO_2 sol was performed without any pretreatment of the supports for the sake of simplicity, although the direct deposition of TiO_2 films on plastic substrates poses difficulties (due to low surface energy the film adhesion is poor).

The films were characterized after the deposition of each layer. As expected, the successive layers of TiO_2 made the transmittance in the semiconductor absorption region decline in all the materials studied (Fig. 2), but the transmittance was kept over 65 % in all cases. The decrease was especially important in the polypropylene and poly (methyl methacrylate) samples, with a 17% and 15% loss of transmittance at 360 nm, indicating the higher amount of photocatalyst deposited on these polymers. The effectiveness of the TiO_2 coating was corroborated by EDX analyses (not shown).

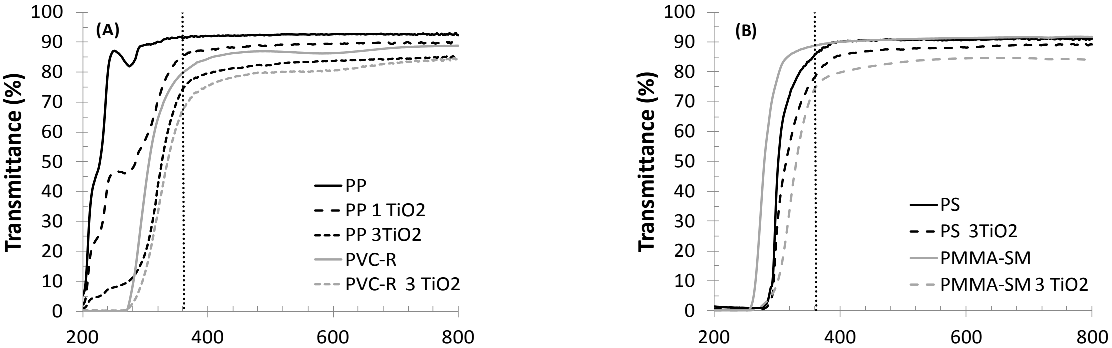


Figure 2. Influence of TiO_2 layers on the UV transmittance of the selected polymers. (A) polypropylene and polyvinyl chloride, (B) polystyrene and poly(methyl) methacrylate)

In order to ascertain the crystallinity of the TiO_2 obtained by sol-gel after drying at 50 °C, the XRD pattern of TiO_2 xerogel was analysed. It showed the typical diffraction peaks of anatase, the main of them at $2\theta = 25.2°$, with a small contribution of brookite, clearly observed in the peak at 30.8 °C (Fig. 3). Therefore, despite the low temperature employed in the drying procedure, compatible with the polymer thermal stability, the TiO_2 film obtained is expected to be photocatalytically active. The size of the crystalline domain was calculated to be 3.9 nm.

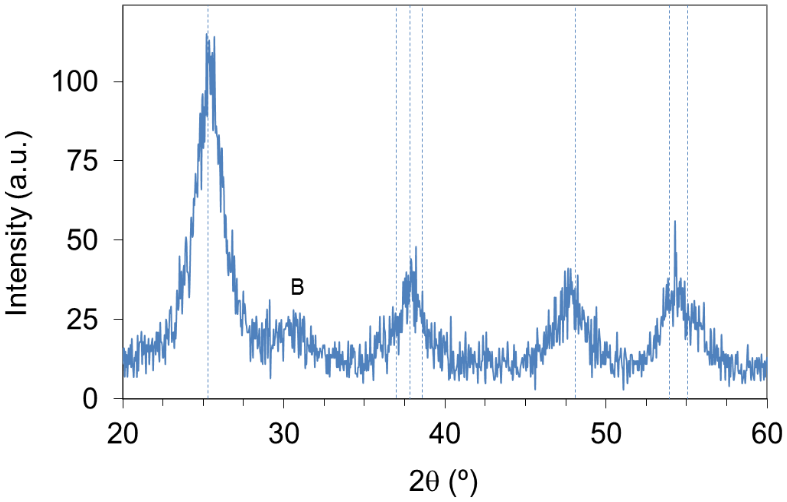


Figure 3. XRD analysis of TiO_2 xerogel dried at 50 °C. The dotted lines indicate the main anatase peaks and "B" the main brookite peak not overlapping with anatase peaks

3.2. Polymer weathering

The selected organic polymers, with and without titania, were placed inside the natural weathering chamber to investigate their degradation, which is produced by a combination of physical and chemical effects related to the UV radiation of the solar spectrum, oxygen and humidity, which are always present in the gas-phase photocatalytic treatments (Hinsken *et al.*, 1991). Although the aging process can be greatly accelerated through the use of accelerated weathering chambers, this option was ruled out, because real outdoor exposure is difficult to reproduce in such conditions (Espí *et al.*, 2007). The representativeness, and therefore the usefulness, of results obtained with accelerated weathering chambers for prediction of durability is discussed (Mallon *et al.*, 2002; Adams, 2000).

The visual observation and the spectroscopic characterization of the samples evidenced their photodegradation. As observed in Fig.4, after a period of 150 days the PVC-R and PS raw samples suffered the highest loss of transmittance at 360 nm, with a decrease of 56% and 81%, respectively. Both materials became coloured and brittle, even more in the case of PVC, with a notable increase in rigidity. On the contrary, PP and PMMA-SM experienced a transmittance decrease of only 5% and 3%, respectively. Nevertheless, both materials suffered fine cracks, and in the case of PP also some colouring. The loss of transmittance for the coated PVC-R and PS samples was similar to that of the uncoated samples, while the TiO_2-coated PP and PMMA-SM samples showed an increase of transmittance of 6% and 10%, respectively, after 150 days of aging, due to the removal of some TiO_2 during the aging process.

The ATR-FTIR analysis of the selected samples helps to understand the phenomena occurring during the aging process Fig. 5. In general, together with the characteristic bands related to the respective polymeric substrates, the spectra of the coated samples show two wide bands at 650-950 cm^{-1} and 2600-3700 cm^{-1} and a single peak at 1635 cm^{-1} that correspond to the TiO_2.

In Fig.5 (A), the typical vibration bands of PVC can be seen. The C-Cl vibration bands are observed in the region below 700 cm^{-1}. Among the main features, methylene asymmetric stretch peaks appear at 2912 cm^{-1}, with a methine C-H stretch peaking at 2970 cm^{-1}. The methylene deformation vibration can be seen at 1434 and 1426 cm^{-1} (Xiao-Jing, 2008). The band at 1730 cm^{-1} could be assigned to the C=O stretching, probably associated to an UV stabilizer (Beltrán, 1995).

After the aging process, the PVC FTIR spectra show little changes. A slightly widening of the carbonyl band in the raw material is observed due to the presence of new oxidized groups resulting from the photodegradation, but there are no changes in the coated sample. The presence of the TiO_2 does not seem to catalyse the degradation process in the conditions of this study, contrary to what was found in previous works using UV-A lamps (Xiao-Jing *et al.*, 2008). After 150 days of aging, coated and uncoated samples of PVC show similar transmittance values: 24% and 26% respectively at 360 nm. The C-H peak intensities decreased after irradiation for both the pristine PVC and PVC-TiO_2 films, and this indicates that C-H bonds are removed by the reaction of hydroxyl groups resulting from photodegradation.

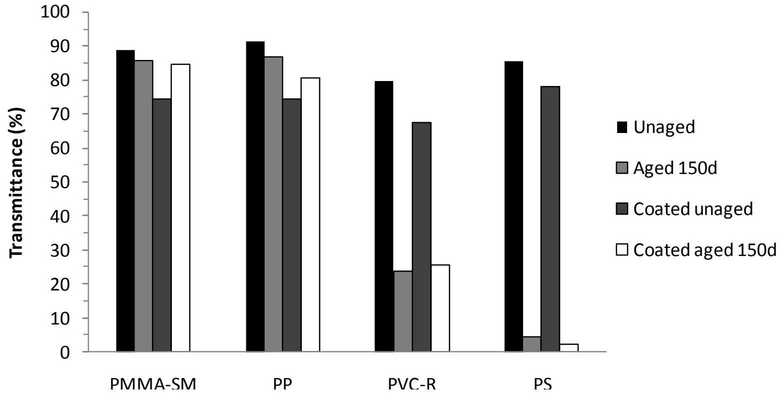
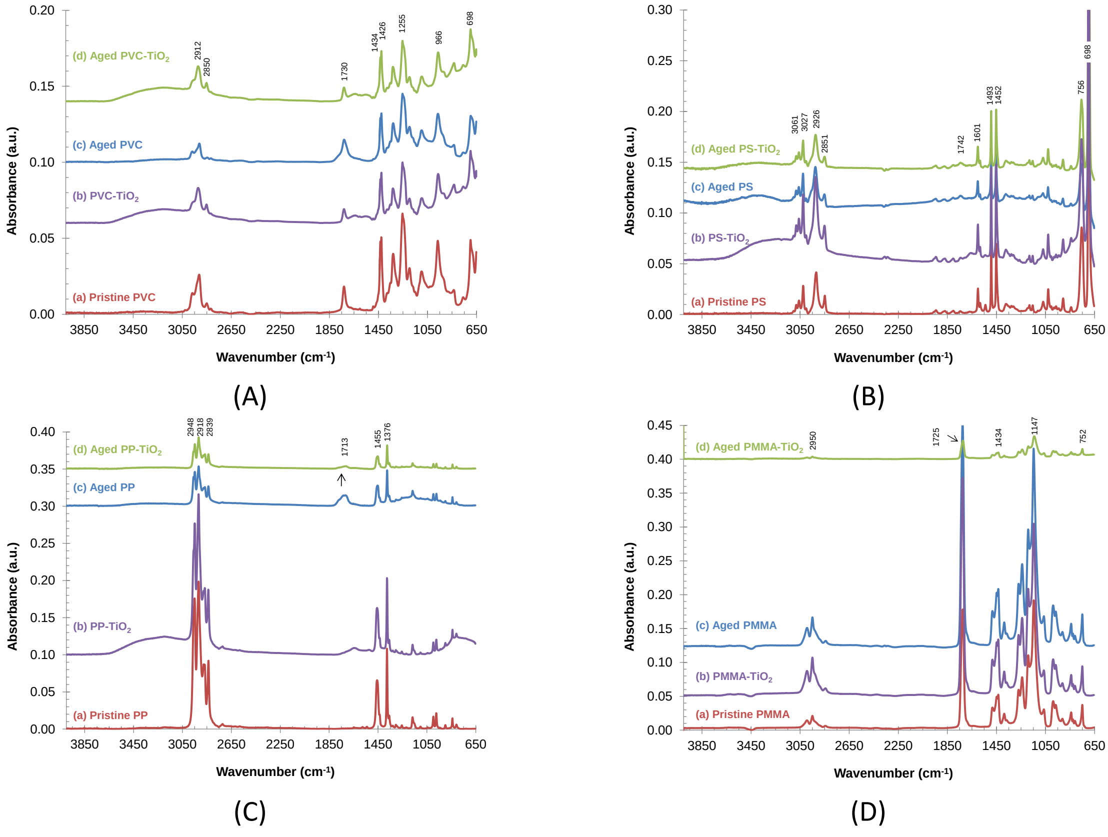


Figure 4. Effect of the natural weathering (150 days) on the transmittance at the reference wavelenght (360 nm) for uncoated samples and samples with three TiO_2 layers

PVC photo-oxidation mechanism is not yet fully understood. According to the literature, two different processes take place: dehydrochlorination reactions, leading to the appearance of conjugated polyene sequences with concomitant evolution of HCl, and photo-oxidative degradation. These processes produce a rapid discoloration that can be clearly seen in coated and uncoated samples after 150 days of aging (Shi *et al.*, 2007).



(A) (B)

(C) (D)

Figure 5. FTIR-ATR spectra of PVC-R (**A**), PS (**B**), PP (**C**) and PMMA-SM (**D**) samples: (a) pristine, (b) coated with TiO_2, (c) aged for 150 days, (d) coated with TiO_2 and aged for 150 days

In polystyrene, the side group on the methylene chain is an aromatic ring, so that the infrared spectrum is a combination of methylene and mono-substituted aromatic ring peaks, as shown in Fig.5 (B). The peaks observed at 2926 and 2851 cm^{-1} correspond to the methylene C-H stretches and those at 3082, 3061 and 3027 cm^{-1} to the aromatic C-H stretches. The out-of-plane C-H bonds of the aromatic ring form intense peaks at 698 and 756 cm^{-1}, while the breathing modes appear at 1601, 1493 and 1452 cm^{-1}.

Surface discoloration in coated and uncoated PS samples revealed the degradation suffered after 150 exposure days. As shown in Fig.5 (B), a new small carbonyl band grew at 1742 cm^{-1} for both samples during the aging process. Additionally, the loss of the TiO_2 thin film can be observed.

According to the literature, the degradation process in polystyrene samples is clearly different to PVC. The aromatic ring of polystyrene is an UV-absorbing group. Therefore, the polymer is sensitive to UV degradation, which, according to the literature, begins with the formation of alkyl and alkyl radicals. Under oxygen-containing atmosphere these are transformed into peroxide radicals with photochemical activity, which shift the absorption edge to the long-wavelength range, leading to the so-called photochain dissociation (Kuzina and Mikhailov, 1998). Only 10% of the radicals are converted by the ordinary hydroperoxide mechanism (Kuzina and Mikhailov, 2001).

Two domains of the infrared spectrum are of interest for the analysis of the PP aging, corresponding to the stretching vibrations of carbonyl (C=O) and hydroxyl groups (-OH). It is reported that the photo-oxidative degradation of polypropylene starts with the formation of alkyl radicals from the polymer chain that continue with the formation of hydroperoxides, which can decompose to produce alkoxy radicals. These radicals produce the abstraction of a hydrogen atom from the polymer backbone. As a consequence of these processes, different carbonyl species are formed and the polymer matrix suffers degradation (Qin *et al.*, 2005; Waldman and De Paoli, 2008). The new absorption band formed at 1713 cm^{-1} in the infrared spectra of the two aged samples in Fig.5 (C) can be assigned to the carbonyl group of carboxylic acid in the dimmer form (Morlat *et al.*, 2004). The shape of the peak suggests the presence of other carbonyl vibrations, for instance of carboxylic acids associated to hydroxyl groups at 1735 cm^{-1}. The wide vibration band slightly appreciated at 3000-3600 cm^{-1} corresponds to the O-H stretching of hydroperoxides and alcohols, with a small contribution of O–H adsorption of carboxylic acids, indicating the very low presence of these compounds (Philippart *et al.*, 1997).

In the spectrum of the coated PP, the strong vibration bands at 650-950 cm^{-1}, 2600-3700 cm^{-1} and 1635 cm^{-1} of TiO_2 almost disappear after the aging process, evidencing the bad adherence of the oxide despite the significant amount of titania initially deposited. The degradation seems lower than in uncoated samples, in spite of the presence of the photocatalyst; the poor film adhesion could induce a protective effect instead of the expected photocatalytic oxidation (Rabek, 1995).

Polymethylmethacrylate is a highly photostable polymer due to its weak absorption of the solar UV radiation (Nagai *et al.*, 2005). The infrared spectra of PMMA samples are shown in Fig.5 (D). The C–H stretching vibration peaks are observed in the region 2800-3100 cm^{-1}. The carbonyl (C=O) vibration of the ester group takes place at 1725 cm^{-1}, while the bands in the range 1050-1300 cm^{-1} are related to the stretching vibration of the C-O-C. The absorption band near 1050 cm^{-1} comes from the C-O stretching vibration coupled to adjacent C-C (Sankar *et al.*, 2004). Despite the reduction in the UV-vis absorbance observed after the impregnation with TiO_2 and the detection of Ti by EDX, the characteristic IR absorption bands of titania are not detected in the coated sample, and thus the amount of photocatalyst deposited must be increased to obtain a photocatalytically active material.

After the natural weathering no changes in the intensity and position of the bands were observed, either related to the carbonyl or to new oxidized groups. The photodegradation effects observed by other authors under UV radiation cannot be detected in the spectra of Fig.5 (D), even for the coated sample, where the poor amount of TiO_2 had no influence in the degradation process (Kaczmarek and Chaberska, 2006). According to the literature, PMMA photodegradation starts with crosslinking processes and chain scission of ester side-groups; the resulting macroradicals may induce oxidation processes that cause also chain scission (Çaykara and Güven, 1999).

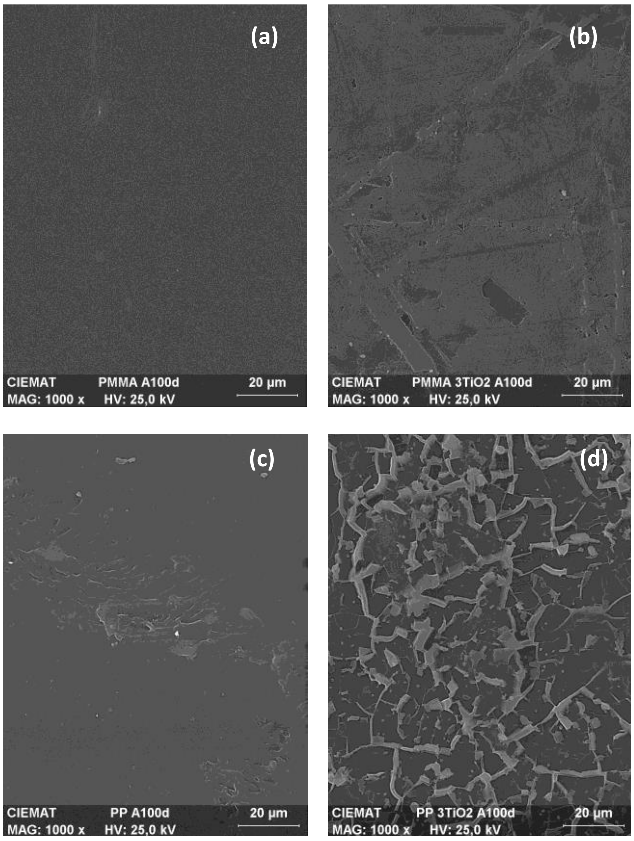


Figure 6. SEM micrographs of PMMA (a and b) and PP (c and d) samples after 100 days of aging, uncoated (left) and coated with three layers of TiO_2 (right)

Fig.6 contains the SEM micrographs of TiO_2-coated PP and PMMA after 100 days of aging. PMMA-SM does not show surface modifications after the natural weathering, while the degradation of PP samples is observed in the roughening of the coated surface and the appearance of cracks (Eve and Mohr, 2009). EDX analysis confirmed the strong loss of TiO_2 in both PMMA and PP samples and the damage of the film homogeneity in the PP aging process.

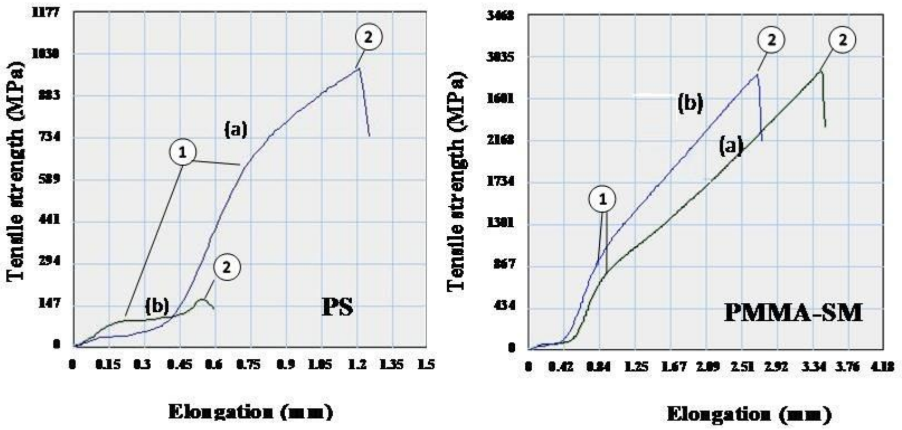


Figure 7. Stress-strain curves for PS and PMMA-SM samples:
(a) pristine, (b) coated, after 150 days of aging. ① Proportional stress limit, ② tensile strain at break

The results of the tensile strain tests of the aged materials confirm that PP and PS suffer more degradation than PMMA-SM. Fig. 7 illustrates the great differences between PS and PMMA-SM samples, especially in tensile strain at break. The aged TiO_2-coated PS sample shows break down before the elastic limit is reached and the crack follows a saw-tooth pattern that evidences internal degradation. On the contrary, the PMMA-SM curves are very similar, though the aged sample shows somewhat less elongation at break than the virgin one. The stress-strain curves of PP (not included) show the typical pattern of a semi-crystalline polymer; aged and pristine PP samples show great differences in elongation at break, and this is an evidence of the degradation process in which fracture strain occurs rapidly (Kontou and Farasoglou, 1998; Severini *et al.*, 1998; Chou *et al.*, 1973).

4. Conclusion

PVC-R, PP, PS and PMMA-SM present good UV transmittance in the TiO_2 activation range, but after natural weathering the transmittance is maintained only by PMMA and PP. The poor transmittance of the extruded PMMA and flexible PVC in the UV region discard these materials as substrates for TiO_2 in photocatalytic applications where the radiation has to pass through several layers of photocatalyst. The natural aging of the selected materials was followed for 150 days of exposure to solar radiation, before and after deposition of a TiO_2 coating. PP is discarded due to the strong photodegradation, evidenced by FTIR-ATR analysis. Sheet moulding-processed PMMA has the best transmittance and photodegradation resistance among the commercial polymers under study, and therefore could be a good support if the TiO_2 adherence is improved. New research is in progress to optimize the deposition of the films to the polymer surface, e.g. by modifying the sol-gel process or the polymer surface, and to test the photocatalytic activity for air treatment of the photocatalyst immobilized on the polymeric substrate.

Acknowledgements

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