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Review

Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage

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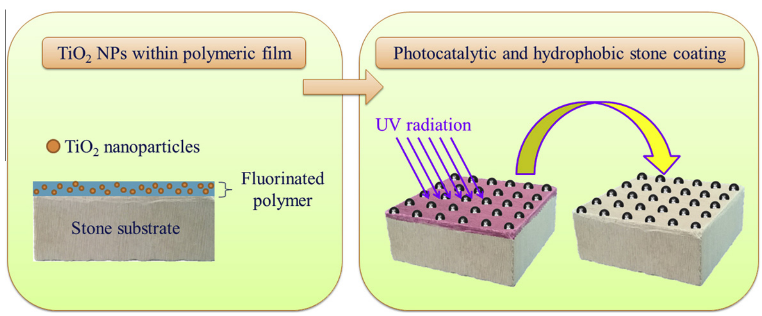
HIGHLIGHTS

- A multifunctional TiO_2 NPs/fluoropolymer product has been successfully developed.
- It meets requirements as self-cleaning and hydrophobic coating for building stone.
- TiO_2 NPs within the fluorinated polymer preserve their photocatalytic activity.
- Hydrophobicity depends on the TiO_2/fluorinated polymer ratio.
- TiO_2/polymer within the composite product needs to be tuned to proper ratios.

GRAPHICAL ABSTRACT



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ABSTRACT

Mixtures based on aqueous solutions of nanostructured TiO_2 and of a fluoropolymer were developed. They were applied on a limestone substrate. The obtained coatings were proved able to provide the functionalization of the stone with simultaneous photocatalytic and hydrophobic properties. They showed a high photodegradation activity ($\geqslant$90%), although with different kinetics, depending on the amounts of nanoparticles within the polymer. Hydrophobic effectiveness was also dependent on the TiO_2 loads; good hydrophobicity was obtained when they were tuned to proper amounts. The addition of TiO_2 to the polymer was found to decrease the color impact of the coatings on the stone surface.

Contents

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1. Introduction

There is growing worldwide interest in the use of titanium dioxide (TiO_2) nanoparticles as an active photocatalytic material. TiO_2 exists in three crystalline phases, namely rutile (the most stable form), anatase, and brookite [1]. Anatase exhibits a higher photocatalytic activity than rutile [2,3], although greater photocatalytic activity has been found for anatase/rutile mixtures than for the single phases [4,5].

TiO_2 has been proposed in various environmental applications such as air purification, waste water treatment, self-sterilization/water disinfection [6,7] and photoinduced hydrophilic coatings with self-cleaning properties [8,9]. A very interesting application of titanium dioxide is in the field of building materials [10]. Whether it is embedded in the bulk of concrete, mortars [11–13], or ceramics [14–16], or perhaps used as an external coating on glass and stone surface [17,18], titanium dioxide can implement these materials with photocatalytic properties. Such properties, which are effective even under weak solar irradiation [10], consist of a self-cleaning ability and an abatement of polluting molecules such as NO_x, SO_x, as well as BTX, with related environmental benefits.

Only in recent years photocatalytic TiO_2 has been addressed for coating of building stones [19–24] and it has been receiving an increasing amount of attention for the conservation of the stone Cultural Heritage. The photocatalytic stone coatings by TiO_2 nanoparticles are very attractive for conservation of buildings because they can preserve the integrity of the stone surface by protecting against the deposition of many organic urban particulates that feed on surface deposits, thus minimizing the maintenance of the building façades by cleaning works. Although photocatalytic TiO_2 is not effective against carbon particulates, which is one of the main sources of the darkening of the building façades, it is indeed very effective in the degradation of uncombusted hydrocarbons, which retain particulate matter at the stone surface in a polluted environment. Moreover, given the extent of stone building heritage, especially within the historic towns, where the natural stone has been the main construction material, photocatalytic stone coatings can provide large environmental benefits due to their depolluting properties.

Photoinduced superhydrophilicity related to photocatalytic TiO_2 [25,26] can be an unwanted aspect in stone coating, even though it is not totally clear if the penetration of the water that is derived from the photoinduced superhydrophilicity on the surface really takes place within the stone [22]. Since water is a preeminent factor of the stone decay [27,28], one of the main conservation needs is the protection against water penetration from the stone surface, and it is commonly ensured by the application of coatings with hydrophobic properties.

In this study, a possible approach has been followed in order to obtain multifunctional products addressing building stone protection. A double component solution was developed by mixing TiO_2 nanoparticles with polymeric materials, which are already well-established as water repellent products for stone and suitably chosen in order to maximize the properties of both the components while minimizing the unwanted aspects. This combination could also improve the retention of TiO_2 nanoparticles on the stone surface. This aspect deserves attention due to the possible release of the nanoparticles to the environment [29–31].

2. Literature survey

Recent studies explored the potential of the use of photocatalytic TiO_2 in composite products, addressing additional properties of interest for stone conservation besides the photocatalytic ones.

Photoactivity of TiO_2 has been demonstrated in association with silica oligomers providing stone strengthening [20]. A new synthesis based on the mixing of titanium and silicon alkoxides in the presence of oxalic acid and organic silica oligomers [32] has been proposed for producing photocatalytic and hydrophobic SiO_2-crystalline TiO_2 nanocomposites. Suitable treatments that combine protection against water penetration and properties of the photocatalytic TiO_2 could simultaneously provide protection of stone artefacts from water decay as well as endow them with advantageous self-cleaning and depolluting properties.

The association of any material with the TiO_2 nanoparticles should take into account that the photocatalytic process can decompose and mineralize a wide range of small organic and inorganic molecules in the solid, liquid, or gaseous phases, as well as polymeric materials [33–37]. On the other hand, the transparent polymeric film should not inhibit the photocatalytic properties of the embedded TiO_2 nanoparticles.

The degradation process of organic molecules involves mainly the breakage of C–H bonds [38]. The incorporation of TiO_2 nanoparticles into a commercial aqueous dispersion of an acrylic polymer has been found to have various problems originating from different stone types, thus hindering the unambiguous evaluation of the polymer's performance as a suitable mixing agent for composite TiO_2-based products [21]. The degradation of coatings obtained by mixing titanium dioxide nanoparticles with Paraloid B72, a well-known acrylic polymer in the restoration field, has been proved and some attempts to slow this process and increase the stability of the films have been made by adding suitable coupling agents [33]. In the present study, a commercial perfluorinated product was chosen in order to prevent the destruction of the polymeric partner. The C–F bond is known to be the strongest chemical bond and it is expected to preserve the polymer chain from mineralization processes promoted by photocatalysis [39]. Fluorinated polymers, which typically have high water-repellent properties, durability, chemical stability, and low chromatic impact on the stone surfaces, are among the most widely used organic materials for stone protection [40–45].

The aim of the present study is to evaluate the mutual influence of the two components within the experimental mixtures and the final properties of the resulting films in terms of both photocatalytic and hydrophobic effectiveness that can improve the performance of the stones within buildings.

3. Material and methods

3.1. Experimental products

A TiO_2 water solution (3% w/w with a mean particle size of 40–50 nm) was provided by Salentec srl. It was synthesized following the procedure described elsewhere [46]. Fluoline PE®, a commercial product suitable for the treatment of