

Article

Structural Water Content in Pigment-Grade TiO₂ Particles Coated with Al₂O₃ and SiO₂, and Their Effect on Polypropylene Photodegradation

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Abstract: The influence of structural water in alumina (Al₂O₃) and silica (SiO₂) coated titanium dioxide (TiO₂) pigments on the photodegradation behavior of polypropylene (PP) composites was investigated. Four commercial rutile TiO₂ pigments with varying surface inorganic coatings were incorporated into PP plaques and subjected to accelerated UV weathering to simulate outdoor exposure. Photodegradation was assessed through gloss retention measurements, the carbonyl index (CI), and stress at break retention, while pigment morphology and composition were analyzed using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). Surface charge and water content were determined through the zeta potential (ζ), Karl Fischer titration, thermogravimetric analysis (TGA), and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The results showed that low-alumina coating alone led to the lowest photodegradation resistance, the highest CI, and the lowest stress at break retention. In contrast, increasing alumina content enhanced photostability, reaching its maximum for combined alumina–silica coatings, which mitigated electron–hole pair migration. PP composites with high alumina–silica-coated TiO₂ exhibited higher gloss retention (36%) compared to low-alumina samples (21%). Furthermore, statistical analysis using ANOVA revealed significant differences in coating content and ζ potential among the pigment grades. These findings provide novel insights into oxide–water interactions and the impact of structural water on the photodegradation of polymer composites.

Keywords: titanium dioxide; structural water; gloss retention; polypropylene; surface coating; photodegradation; hydroxyl groups



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1. Introduction

Titanium dioxide (titania) is one of the most widely used pigments across various industries due to its low toxicity, chemical stability, high refractive index, and minimal light absorption [1–3]. These properties make it suitable for applications in painting, papermaking, plastics, cosmetics, health care, and pharmaceuticals [4–6]. However, its

use in polymeric systems can be limited by its high photocatalytic activity [7,8]. Under UV irradiation, TiO₂ exhibits significant photocatalytic behavior, leading to the generation of electron–hole pairs. These charge carriers can react with adsorbed molecules, forming hydroxide ions (OH[−]), which are highly reactive radicals capable of degrading organic material [9].

The mechanism of polymer degradation mediated by a photocatalytic process has been extensively studied [10,11]. Research has shown that photogenerated holes migrate to the crystal facets of TiO₂ and react with adsorbed water molecules, leading to the formation of reactive oxygen species (ROS). These ROS have a strong affinity for polymer chains and promote chain scission, resulting in the generation of carboxylic groups at the ends of polymer molecules. Additionally, humidity can more easily permeate the amorphous regions of the polymer, altering its original properties [12]. Consequently, the presence of water near the titanium dioxide surface is a primary factor in the breakdown of polymers through photocatalysis [13–15]. Despite this understanding, few studies have examined the combined effect of adsorbed and structural water in the photodegradation of polymers, resins, or coatings, leaving the role of structural water unclear [16–18].

The modification of TiO₂ particle surfaces to reduce the photodegradation of polymeric materials is an important issue, referred to as passivation. To achieve this, organic molecules and inorganic oxides have been used to decrease the photoactivity of TiO₂ particles. Among these, alumina and silica are the most used and are typically incorporated during TiO₂ pigment fabrication [19,20]. The selection and proportion of inorganic surface coatings applied to TiO₂ pigments are determined by the end-use performance requirements, particularly concerning photostability and environmental exposure. Commercial TiO₂ grades are generally classified into three durability categories: non-durable, semi-durable, and durable, based on their resistance to photocatalytic activity under environmental exposure conditions [21,22].

Non-durable TiO₂ pigments are characterized by minimal surface passivation, typically containing less than 2 wt.% of alumina. These grades are primarily used in indoor applications, such as short-term industrial packaging films for food, where exposure to UV light is negligible. Semi-durable TiO₂ pigments incorporate either additional silica into the low-alumina formulation or may contain only alumina in proportions exceeding 2 wt.%. These pigments are commonly used in interior architectural paints and temporary exterior coatings, but they have limited UV exposure resistance. In contrast, durable TiO₂ pigments are designed for long-term performance in outdoor environments. These grades typically have high combined alumina and silica content, with surface treatments reaching approximately 11 wt.%. This formulation suppresses photocatalytic activity, enhancing pigment stability and minimizing polymer degradation. This grade is extensively used in polyolefin-based systems for automotive components, building materials, agricultural films, outdoor furniture, and automotive coatings, where sustained UV resistance is essential [23].

This study aimed to investigate the role of structural water in the photodegradation behavior of polypropylene plaques containing alumina- and silica-coated TiO₂. To achieve this, PP composites were fabricated and exposed to UV irradiation in a controlled chamber, simulating outdoor weathering. The results indicated a direct correlation between PP gloss retention and TiO₂ coating content. It has been demonstrated that these coatings reduce the reactivity of TiO₂, hindering the photo-oxidation reaction. Since alumina and silica are insulators, it is suggested that any coating blocks the interaction of photogenerated charge carriers with reactant molecules. However, alumina and silica can also promote water adsorption through hydroxylation, which in turn could enhance ROS generation and polymer photodegradation. These opposing mechanisms (i.e., water adsorption and stabilization) compete with each other. This study found a direct correlation between PP gloss retention

and the water content of TiO_2 pigments. This was explained by identifying two types of water: adsorbed water and structural water. The former can be incorporated into the crystal lattice through chemical bonds, and the latter is physically attached to the surface of particles by weak interaction forces. Among the coatings studied, the low-alumina formulation exhibited the lowest structural water content, resulting in the weakest photodegradation resistance. In contrast, increasing the coating content effectively enhanced water retention, acting as a protective barrier against moisture loss while limiting the migration of electron–hole pairs or ROS. These observations suggest a synergistic mechanism in which alumina enhances water adsorption, while silica impedes electron–hole pair migration and the subsequent ROS formation. Overall, this study provides essential insights into the role of alumina and silica coatings on TiO_2 pigments, concerning water adsorption dynamics and their impact on the photodegradation process in polymeric systems.

2. Materials and Methods

Four different grades of commercial rutile TiO_2 samples were used, designated based on their formulated Al_2O_3 – SiO_2 coating content as follows: low alumina (LA, 1.7 wt.%), low alumina with added silica (LA 1.7 wt.% + S 3 wt.%), high alumina (HA, 3.2 wt.%), and high alumina with added silica (HA 3.2 wt.% + S 3.5 wt.%). Commercial polypropylene (PP) with a melt flow index (MFI) of 4 g/10 min, under a load of 2.16 kg at 190 °C, was used for plaque preparation to evaluate photodegradation. The PP was supplied by Greennova (San Luis Potosí, Mexico), and the TiO_2 samples were obtained from Chemours (Altamira, Mexico).

2.1. Polypropylene/ TiO_2 Plaques Fabrication, Degradation, and Mechanical Tests

Polypropylene (PP) was compounded with TiO_2 pigment at 10 wt.% load using hot melt extrusion in a co-rotating twin-screw extruder ZSK-30 (Werner & Pfleiderer, Stuttgart, Germany). The barrel and die section temperatures were maintained at 210 °C and 220 °C, respectively, with an extruder speed of 300 rpm and a length-to-diameter ratio of 24:1. Using this compounded material, PP plaques were fabricated in an injection molding machine (Battenfeld LCMI, Kottlingbrunn, Austria) where the barrel temperature was set at 220 °C, the mold temperature 27 °C, and the injection pressure 8.27 MPa, with a shot volume of 43 cm³. The plaques were produced in dimensions of 60 × 60 × 2 mm, as depicted in Figure 1.

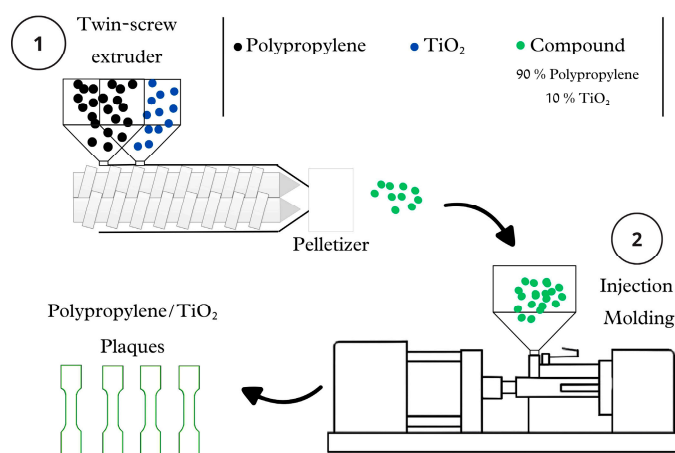


Figure 1. Schematic representation of PP/ TiO_2 plaques fabrication.

Following fabrication, the plaques were exposed to UV radiation in an aging chamber (Q-Panel model with a UVA lamp at 60 °C). The exposure cycle included condensation at 50 °C with deionized water spray and a radiation intensity of 0.8 W/m²/nm at 340 nm.

The plaques were subjected to UV exposure for 0, 300, and 500 h. Durability was assessed by evaluating changes in optical properties, carbonyl index, and stress at break retention.

Gloss retention was measured using a TRI-gloss 4430 gloss meter (Byk Gardner, Geretsried, Germany) following ASTM D2457 standards. The carbonyl index was determined using Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) on a Cary 600 spectrometer (Agilent, Santa Clara, CA, USA) within a spectral range of 1200 to 2000 cm^{-1} and 32 scans per sample. Mechanical properties were evaluated by measuring stress at break retention at different UV weathering times, following ASTM D638 standards, using a universal testing machine (Instron, Norwood, MA, USA) equipped with load cells of 0.1, 5, and 30 kN.

2.2. Characterization of TiO_2 Pigment

The crystalline phase of pigments was determined using X-ray powder diffraction (XRD) with an AXS D8 Advance diffractometer (Bruker, Karlsruhe, Germany) equipped with a Cu tube emitting $\text{K}\alpha$ radiation at 1.5405 Å. The scanning range was set from 20° to 90° (2θ) with a step size of $0.02^\circ/\text{s}$.

Pigment particle size and chemical composition were analyzed using transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) in a JEM-1230 (JEOL, Tokyo, Japan). The zeta potential (ζ) was measured using an analyzer Zen3600 (Malvern Panalytical, Malvern, UK). The sample moisture content was determined using the Karl Fischer titration method with a DL39 titrator (Mettler Toledo, Greifensee, Switzerland).

Thermogravimetric analysis (TGA) was performed using a TGA Q600 (TA Instruments, New Castle, DE, USA) with thermograms recorded at a heating rate of $10^\circ\text{C}/\text{min}$ over a temperature range of 25 – 450°C . DRIFTS spectra were obtained using a Nicolet 6700 infrared spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Samples were placed in a stainless-steel sample cup (10 mm diameter $\times$ 3 mm deep), leveled at the top, and positioned in a Praying Mantis (Harrick Scientific, Pleasantville, NJ, USA). The experimental conditions were set from room temperature to 300°C , with a heating rate of $10^\circ\text{C}/\text{min}$.

2.3. ANOVA Statistical Analysis and Mathematical Modeling

An analysis of variance (ANOVA) was conducted to identify the sources of variance in one or more factors affecting TiO_2 particles. This study aimed to determine whether differences arise from variability between pigment grades or within different samples of a single TiO_2 type. ANOVA evaluates the sources of variation linked to independent variables and examines how these variables interact to influence the properties of the four titania samples.

The analysis tests the null hypothesis (H_0), which states that all population means (μ_i) are equal, against the alternative hypothesis (H_1), which suggests differences among the four TiO_2 samples.

$$H_0 : \mu_1 = \mu_2 = \mu_3 = \mu_4 \quad (1)$$

$$H_1 : \text{at least one is different from the others} \quad (2)$$

The ANOVA table decomposes the variance of the data into two components: the between-group component and the within-group component. The p -value defines the probability that, if the null hypothesis were true, the sampling variation would produce an estimate further from the hypothesized value than the observed estimate. If the p -value is less than 0.05, there is a statistically significant difference between the means of the four variables with a 95.0% confidence level.

To determine which means are significantly different, Fisher's Least Significant Difference (LSD) test is used. This test is applied in the context of analysis of variance when the

p -value suggests rejection of the null hypothesis (H_0), indicating a significant difference between population means. The LSD test helps to identify populations whose means are statistically distinct.

Additionally, the experimental data were fitted to a polynomial mathematical model, correlating various sample properties such as diameter, zeta potential, Al_2O_3 , and SiO_2 composition on the TiO_2 surface, with an adjustment exceeding a 95.0% confidence level. Before conducting ANOVA, the assumption of homogeneity of variances was evaluated using Levene's test. A p -value greater than 0.05 indicates that variances are not significantly different, validating the use of ANOVA. The determined p -values from Levene's test for chemical composition were 0.22 and 0.68 for TiO_2 and Al_2O_3 across the four TiO_2 grades, while for SiO_2 in the LA+S and HA+S samples, the p -value was 0.84. For particle size across the four grades, the p -value from Levene's test was 0.51.

3. Results and Discussion

3.1. Effect of Inorganic Coatings on Photodegradation of Polypropylene/ TiO_2 Plaques

PP plaques extruded with different grades of TiO_2 were irradiated in a UV light aging chamber. Figure 2 illustrates the photodegradative effect on each sample in polypropylene plaques. The optical property was assessed by measuring gloss retention at three different exposure times, with this factor evaluated exclusively for pigmented composites to facilitate comparison.

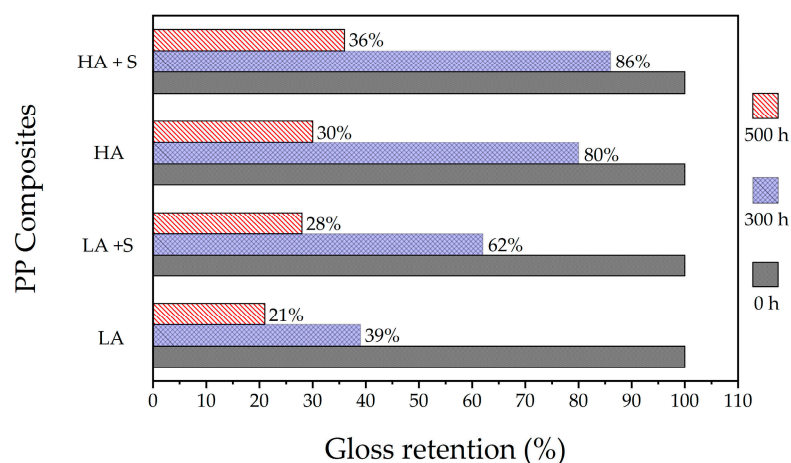


Figure 2. PP plaques gloss retention under UV irradiation with 10 wt.% of TiO_2 as a function of inorganic coatings content.

The surface gloss retention graph indicates that the PP/HA+S plaque maintained the highest gloss retention after 500 h of UV exposure, while the PP/LA plaque exhibited the lowest, with values of 36% and 21%, respectively. A clear trend is observed in gloss retention as a function of Al_2O_3 and SiO_2 surface content. The combination of both oxides appears to exert a synergistic stabilizing effect by inhibiting electron–hole pair separation and suppressing hydroxyl radical formation, which are key drivers of polymer degradation.

Additionally, a direct relationship is noted between gloss retention and moisture content, with the following order: PP/LA > PP/LA+S > PP/HA > PP/HA+S. To explain this effect, an ANOVA analysis was conducted to evaluate the TiO_2 pigment's capability of capturing hydroxyl groups as a function of Al_2O_3 and SiO_2 content. This trend is also observed in the evaluation of mechanical properties, specifically stress at break retention measurements, as a function of TiO_2 coating content.

Stress at break retention of PP/ TiO_2 was used as an indicator of polymeric composite degradation due to UV weathering exposure. Figure 3 illustrates that PP without TiO_2

exhibited the greatest loss of mechanical properties across all three exposure times. In contrast, incorporating TiO_2 into PP enhanced stress at break retention, stabilizing its mechanical properties. The influence of TiO_2 coating on stabilization follows this sequence: $\text{PP/LA} > \text{PP/LA+S} > \text{PP/HA} > \text{PP/HA+S}$.

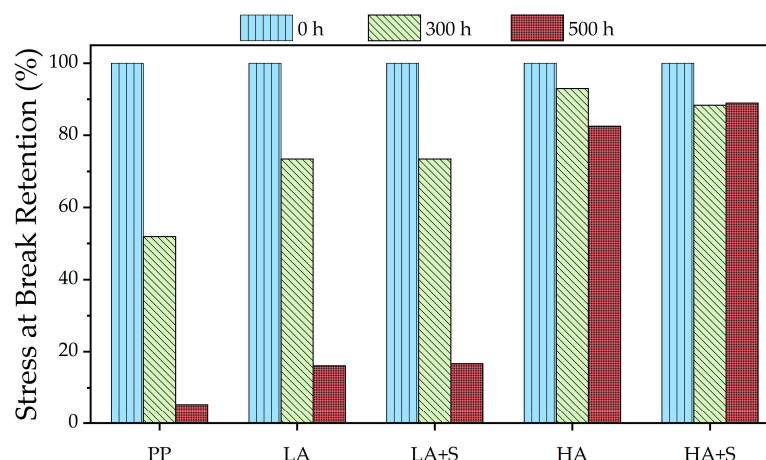


Figure 3. Stress at break retention of PP and PP/ TiO_2 composite as a function of inorganic coating of TiO_2 .

The carbonyl index (CI), measured as an indicator of photodegradation in polymeric materials, was determined by calculating the ratio of the carbonyl band (C=O) at approximately $1700\text{--}1740\text{ cm}^{-1}$ to the CH_3 stretching mode band at around 1455 cm^{-1} as a reference. This method has been established as a reliable indicator of photodegradation in polyolefins [24,25].

Figure 4 presents the carbonyl index as a function of inorganic coating content and exposure time. The results indicate that the incorporation of TiO_2 pigment reduces the photodegradation of polypropylene (PP) to varying degrees, with the extent of stabilization strongly influenced by the surface coating composition. The samples containing LA and LA+S coatings demonstrated enhanced resistance to photodegradation, while the HA-coated pigment provided superior stabilization. The most pronounced protective effect was observed in the pigment with the HA+S surface coating.

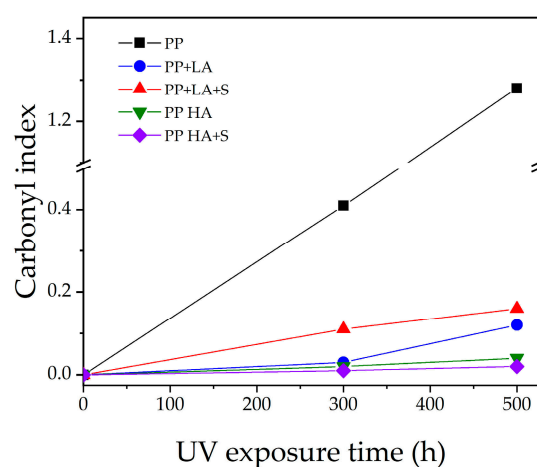


Figure 4. Carbonyl index (CI) as a function of inorganic coatings content at different exposure times.

3.2. Characterization of TiO₂ Pigment and Statistical Analysis

3.2.1. Structural Analysis by X-Ray Diffraction

Figure 5 presents the X-ray diffraction patterns of TiO₂ pigments as a function of inorganic coating content. These diffraction patterns were compared with ICDD PDF 21-1276 and PDF 21-1272, which correspond to rutile and anatase phases, respectively. All samples exhibited the primary peaks of the rutile phase, with Miller indices (110), (101), (200), (111), (210), (211), (220), (002), (310), (112), and (301). No additional peaks associated with other phases were detected.

Although commercial rutile TiO₂ samples often contain anatase impurities, these impurities may be below the detection limit of this technique. Consequently, no significant differences in crystalline structure were observed among the TiO₂ samples, with the surface content of alumina and silica remaining the primary variable factor.

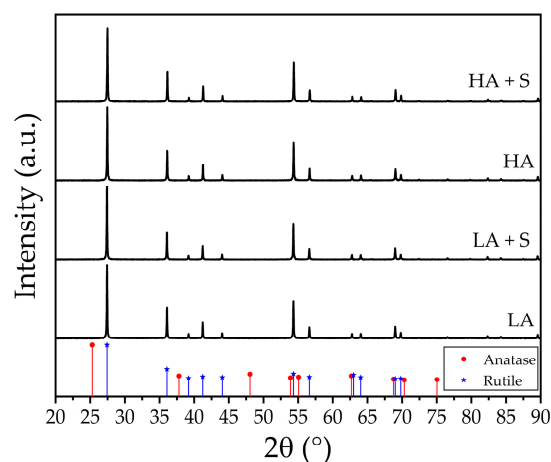


Figure 5. X-ray diffraction patterns of TiO₂ as a function of inorganic coating content. The main diffraction peaks of rutile and anatase are included for comparison.

3.2.2. Coating of TiO₂ Surface

The composition of pigment particles was determined using EDS coupled with TEM during image acquisition. EDS microanalysis spectra were obtained from representative regions of pigment particles, and the elemental concentrations (wt.%) of titanium (Ti), aluminum (Al), and silicon (Si) were converted to their respective oxide forms (i.e., TiO₂, Al₂O₃, and SiO₂) based on their stoichiometric ratios and molar masses. The results, displayed in Table 1, provide a detailed breakdown of the metallic oxide composition of each particle. Figure 6 presents a boxplot illustrating the distribution of three principal oxides identified in the sample particles: TiO₂ (a), alumina (Al₂O₃) (b), and silica (SiO₂) (c). According to the composition analysis, the LA sample exhibited the highest TiO₂ content, suggesting that it may demonstrate greater reactivity compared to the other samples. The statistical significance of these differences was confirmed through ANOVA analysis, as shown in Table 2.

Since the *p*-value is less than 0.05, there is a statistically significant difference between the means of the four variables with a 95.0% confidence level. The LA sample exhibits the lowest alumina content at 1.5 ± 0.3 wt.%, while the LA+S sample contains 2.5 ± 0.5 wt.% of Al₂O₃. The HA and HA+S samples have alumina concentrations of 3.6 ± 0.3 wt.% and 3.8 ± 0.3 wt.%, respectively.

Regarding silica content, the *p*-value is also less than 0.05, indicating that at least one sample has a different concentration. Statistically, the LA+S and HA+S samples show distinct silica content, with compositions of 3.4 ± 0.3 wt.% and 2.5 ± 0.3 wt.%, respectively.

These findings align with the estimated order of magnitude required for silica or alumina to coat the surface [20,26,27].

Table 1. Experimental composition of TiO₂ pigment.

Sample ID	Inorganic Coatings Content Experimental (wt.%)		
	TiO ₂	Al ₂ O ₃	SiO ₂
LA	98.5 ± 0.3	1.5 ± 0.3	/
LA+S	95.0 ± 0.3	2.5 ± 0.5	2.5 ± 0.3
HA	96.4 ± 0.3	3.6 ± 0.3	/
HA+S	92.7 ± 0.6	3.8 ± 0.3	3.4 ± 0.3

/ not reported.

Table 2. ANOVA summary with chemical analyses for the principal components: TiO₂, Al₂O₃, and SiO₂ (^a degree of freedom, ^b Fisher statistic, ^c probability).

	Source	Sum of Squares	d.f. ^a	Mean Squares	F ^b	P ^c
TiO ₂	Between	52.30	3	17.43	110.98	0.0000
	Within (error)	1.26	8	0.16		
	Total	53.55	11			
Al ₂ O ₃	Between	10.35	3	3.45	26.58	0.0000
	Within (error)	1.04	8	0.13		
	Total	11.39	11			
SiO ₂	Between	1.13	1	1.13	14.05	0.0199
	Within (error)	0.32	4	0.08		
	Total	1.46	5			

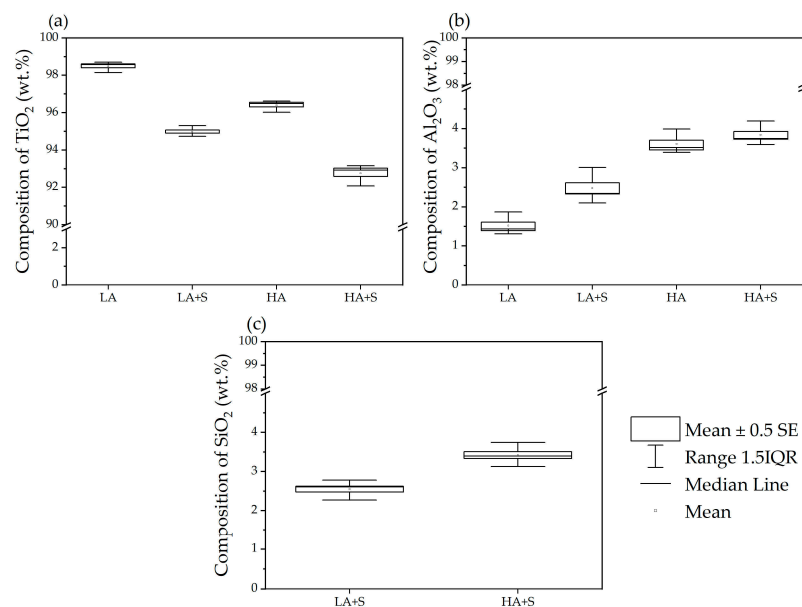


Figure 6. Boxplot of statistical analyses, with chemical composition by EDS, for the three principal oxides in TiO₂ particles: (a) TiO₂ composition; (b) Al₂O₃ composition; (c) SiO₂ composition.

3.2.3. Particle Size

The morphology of the pigment particles was analyzed using TEM, with Figure 7 displaying micrographs as a function of inorganic coating content. In general, faceted particles were observed regardless of the coating composition. Additionally, the average particle size was determined from TEM images for each pigment grade. The HA+S sample

exhibited the largest size, with a diameter of 233 ± 64 nm, while HA had the smallest size at 165 ± 27 nm. The LA and LA+S samples had diameters of 203 ± 40 nm and 199 ± 32 nm, respectively.

Figure 8 presents the LSD test and boxplot of particle size analyses, while Table 3 provides the ANOVA summary. The letters above each boxplot indicate statistically homogeneous groups where treatments sharing a letter are not significantly different. The reported *p*-value in the table exceeds 0.05, indicating that there is no statistically significant difference in the size parameter [28].

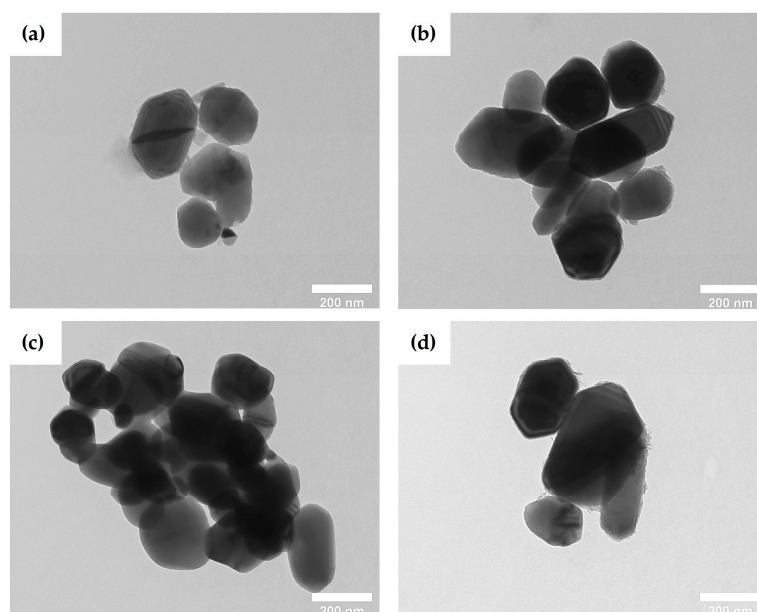


Figure 7. Transmission electron micrographs of TiO₂ particles: (a) LA; (b) LA+S; (c) HA; (d) HA+S.

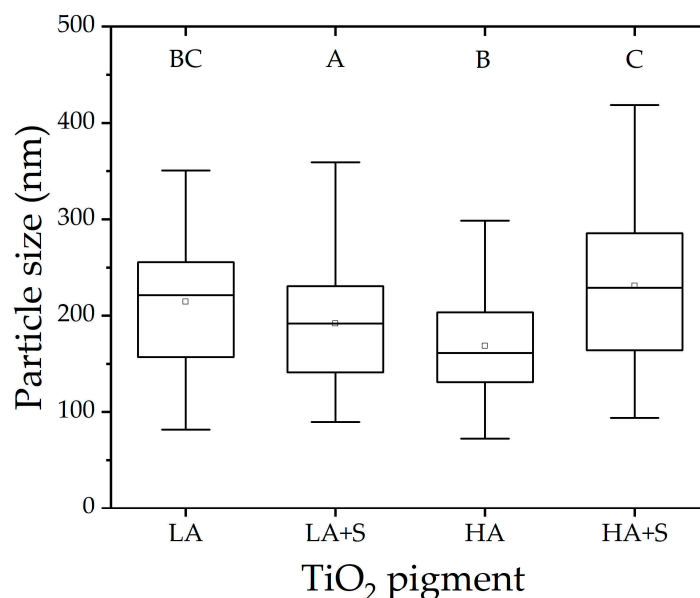


Figure 8. LSD test and boxplot of TiO₂ particle sizes. The letters A, B, and C correspond to model interactions.

Table 3. ANOVA summary table for particle diameters. Here, ANOVA analysis decomposes the data variance into two components: between-group component and within-group component (^a degree of freedom, ^b Fisher statistic, ^c probability).

Source	Sum of Squares	d.f. ^a	Mean Squares	F ^b	P ^c
Between	9409.43	3	3136.48	1.67	0.226
Within (error)	22,579.92	12	1881.66		
Total	31,989.35	15			

3.2.4. Zeta Potential (ζ)

Zeta potential measurements were conducted on aqueous suspensions of TiO₂ at the as-obtained pH of 6.6, achieved by dispersing pigment particles in deionized water. This pH value represents the equilibrium condition of TiO₂ in water as a function of inorganic coatings content. Figure 9 presents the LSD test for zeta potential in TiO₂ particles, while Table 4 displays the ANOVA test results for these zeta potential values. Since the *p*-value is less than 0.05, at least one sample exhibited a statistically different zeta potential value. The LSD test assigned different letters (A, B, C, and D) to each TiO₂ pigment formulation, indicating statistically significant differences among formulations.

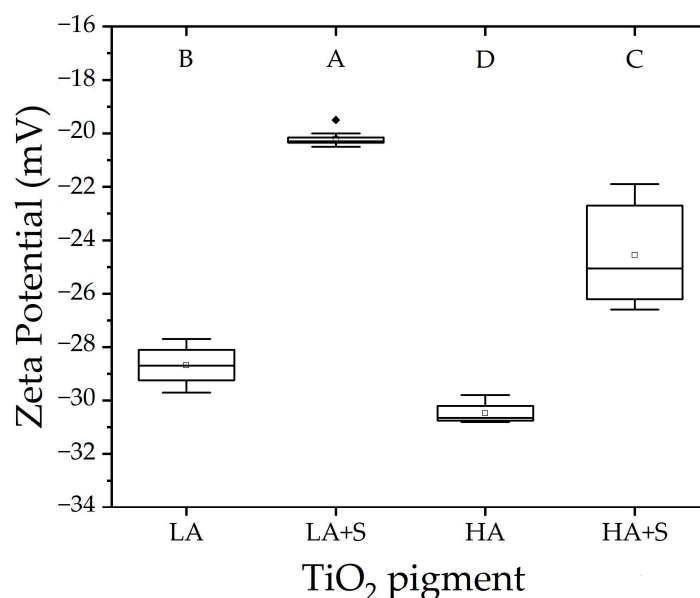


Figure 9. Boxplot of zeta potential and LSD test of TiO₂ samples, at pH 6.6.

Table 4. ANOVA summary table for zeta potential at pH 6.6 (^a degree of freedom, ^b Fisher statistic, ^c probability).

Source	Sum of Squares	d.f. ^a	Mean Squares	F ^b	P ^c
Between	411.47	3	137.16	110.48	0.0000
Within (error)	29.80	24	1.24		
Total	441.26	27			

All samples exhibit statistically distinct zeta potential values. The zeta potential measurements for LA, LA+S, HA, and HA+S were -28.7 ± 0.7 mV, -20.2 ± 0.3 mV, -30.5 ± 0.5 mV, and -24.6 ± 1.9 mV, respectively. Negative values are characteristic of metallic oxides due to the presence of retained -OH groups on their surfaces [29,30].

According to the mathematical model from ANOVA, different average values of zeta potential were fitted to the amount of aluminum and silica. The relationship is expressed by the following equation:

$$Zp = -26.20 - 1.24C_{Al} + 3.56C_{Si} \quad (3)$$

where C_{Al} and C_{Si} represent the percentage compositions of Al_2O_3 and SiO_2 , respectively. A linear model was adjusted with an R-squared value of 0.99 (Figure 10), indicating a strong correlation. These findings suggest that zeta potential is modulated by the composition of inorganic oxides incorporated into TiO_2 particles, which in turn influences the effective charge of the particle surface.

The density of surface hydroxyl groups correlates with zeta potential, and these groups play a crucial role in promoting water adsorption. In this case, the zeta potential, as a function of the composition of inorganic coatings and the measured values, confirms the presence of hydroxyl groups on alumina- and silica-coated TiO_2 surfaces. Silica modifies these surface hydroxyl groups, leading to a less negative surface charge.

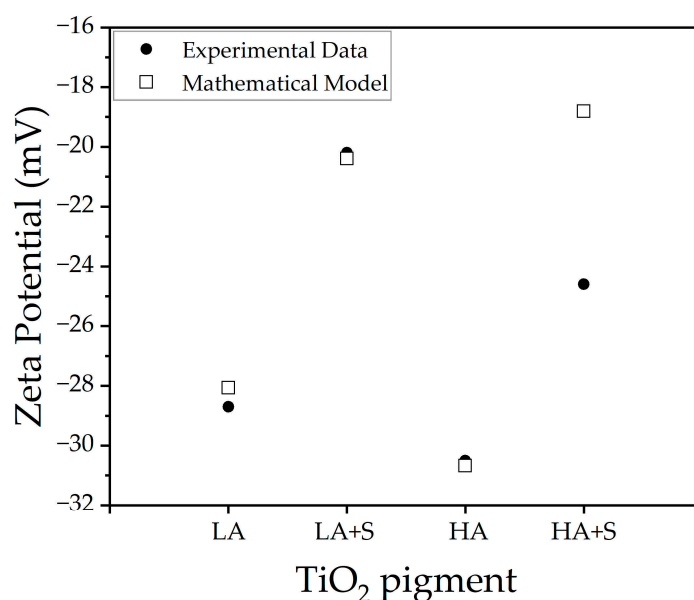


Figure 10. Zeta potential as a function of Al_2O_3 and SiO_2 composition. Experimental data (●) and model fitting (□).

3.2.5. Water Content

Water content plays a crucial role in photodegradation performance, since photocatalytic processes occur in an aqueous environment. Adsorbed water molecules interact with bridging oxygen atoms on the pigment surface through multiple hydrogen bonds, as depicted in Figure 11, enhancing proton transfer and photo-oxidative reactions [16,31]. This interaction facilitates the generation of reactive oxygen species, such as hydroxyl radicals ($\bullet OH$), which subsequently attack the polymer backbone. These free radicals lead to the formation of carboxyl groups in the polymer chains, reducing molecular size and resulting in degradation.

In alumina- and silica-coated TiO_2 , two distinct types of water can exist: physically adsorbed water and structural water [32]. Physically adsorbed water is easily removed upon heating, whereas structural water is more strongly bound. However, the role of structural water in photodegradation remains unestablished. Due to the thermal desorption overlap of physically adsorbed and structural water within the 100–300 °C range, the water determination was not separated.

To quantify total water content regardless of its binding state, the Karl Fischer titration method was employed. The results, presented in Table 5, indicate that the lowest water content was observed in the LA sample (0.11 wt.%), followed by LA+S (0.19 wt.%) and HA (0.45 wt.%). The highest value was recorded for HA+S (0.54 wt.%). Based on these findings, the sequence of overall water loss was as follows: LA < LA+S < HA < HA+S.

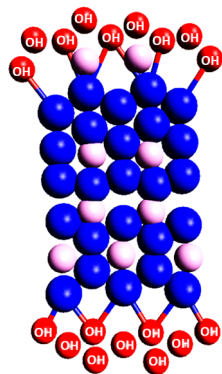


Figure 11. Schematic representation of hydroxyl ions formation on the rutile TiO_2 surface, titanium (blue spheres), oxygen (white spheres).

Table 5. Total water values obtained by the Karl Fischer titration method at $T = 190^\circ\text{C}$.

ID	Moisture (wt.%)
HA+S	0.54
HA	0.45
LA+S	0.19
LA	0.11

These results suggest a direct proportional effect between the percentage of coating on the TiO_2 surface and water content. Furthermore, gloss retention in polypropylene plaques directly correlates with water content. An analysis of TGA supported these findings, and the results are presented as thermograms in Figure 12. In both thermograms shown in Figure 12, the highest weight loss was observed for the HA+S sample. Here, an important point to consider is the presence of hydrous alumina particles, which lowers van der Waals forces between TiO_2 pigment particles, decreasing particle-to-particle attractions by several orders of magnitude. Thus, hydrous aluminum oxide ($\text{Al}(\text{OH})_3$) phases are used to improve dispersibility more effectively than other hydroxides and oxides [33]. Accordingly, the observed weight loss at around 300°C can be attributed to the dehydroxylation of aluminum hydroxide, resulting in the formation of alumina and water [34–36]. The initial step in the thermal decomposition of aluminum hydroxide can be assigned to the diffusion of protons and the reaction with hydroxyl ions (OH^-) to form water [37,38]. This process removes the binding force between subsequent units in the aluminum hydroxide structure. The HA+S sample exhibits the highest weight loss at higher temperatures or prolonged exposure times, consistent with its high alumina and silica content. In contrast, LA shows the lowest weight loss. The TGA results up to 450°C reflect both physically adsorbed and structural water. Compared with the Karl Fischer values, the HA+S sample contains the most significant structural water content. This finding is further corroborated by DRIFTS analysis.

DRIFTS analysis enabled the complementary evaluation of pigments under thermal conditions [34]. The infrared spectra of the four grades of TiO_2 (Figure 13) revealed broad absorption bands between 3700 and 3260 cm^{-1} (O-H stretching) and 1627 – 1640 cm^{-1} (H-O-

H bending), attributed to surface hydroxyl and adsorbed water, respectively. These bands were more intense in the LA and HA samples. In silica-containing samples (LA+S and HA+S), absorption bands between 1047 and 1055 cm^{-1} and between 1230 and 1245 cm^{-1} were observed, suggesting chemical interaction between hydrous silica and TiO_2 surfaces [26,30]. The disruption of Si-O tetrahedral symmetry by Ti atoms leads to IR band splitting or activation of otherwise inactive modes [39]. It is worth noting that the persistence of O-H bands after heating to 300 $^{\circ}\text{C}$ confirms the presence of structural water. Upon heating, band intensity decreased significantly for LA, partially for LA+S, and remained strong in HA+S, suggesting a stabilizing effect of alumina-silica coatings. These results indicate that LA primarily retains physically adsorbed water, while HA and HA+S retain more structural water. In addition, silica enhances water retention, as shown by stronger O-H bands in DRIFTS. Structural water does not participate directly in surface reaction, but hydroxyl coverage governs interfacial interactions, clearly evidenced in the LA sample.

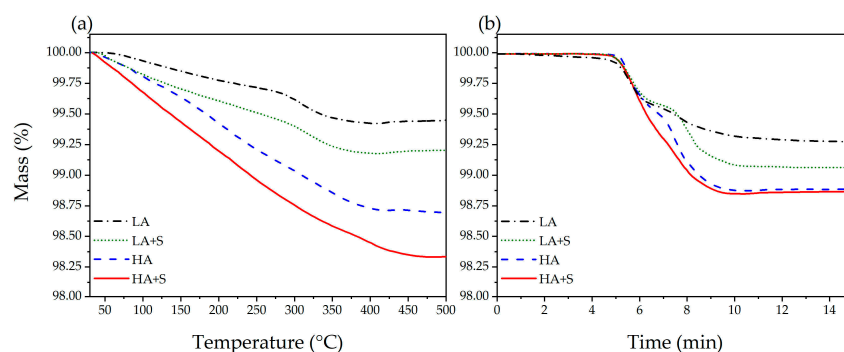


Figure 12. TGA thermograms of TiO_2 pigment of different grades: (a) dynamic analysis at 10 $^{\circ}\text{C}/\text{min}$ of heating rate; (b) isothermal analysis at 300 $^{\circ}\text{C}$.

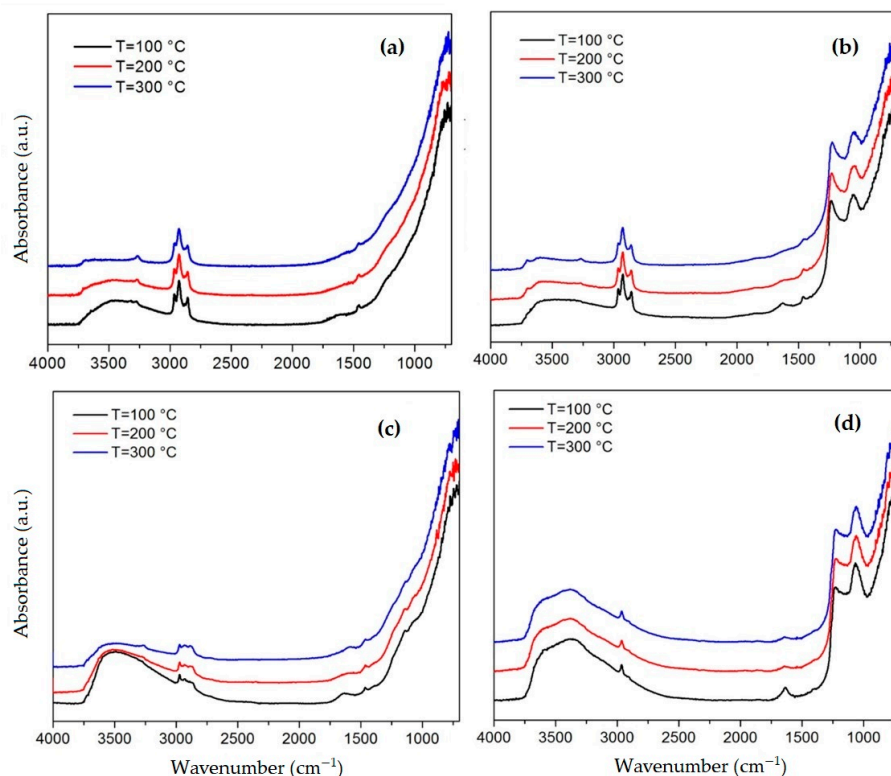


Figure 13. DRIFTS spectrum of each TiO_2 sample at a heating rate of 10 $^{\circ}\text{C}/\text{min}$: (a) LA; (b) LA+S; (c) HA; (d) HA+S.

Based on these findings, structural water on the TiO₂ surface, particularly that associated with the inorganic coatings of Al₂O₃ and SiO₂, appears to contribute to increased UV protection efficiency in polypropylene matrices. The composition and ratio of coating materials determine the density of hydroxyl groups and water retention behavior. This correlation was validated through DRIFTS, Karl Fischer titration, and zeta potential measurements. ANOVA analyses confirmed statistically significant differences between pigment grades. Despite differences in water content and surface properties, the optical performance of the polymer composites indicates a synergistic effect of alumina and silica, enhancing surface passivation and improving resistance to UV-induced degradation, as measured by gloss retention, stress at break retention, and the carbonyl index.

3.3. Water Stabilization Mechanism by Silica on TiO₂ Surfaces

The results of this study provide significant evidence regarding the role of silica in stabilizing adsorbed water on the TiO₂ surface. DRIFTS analyses revealed that silica-containing samples (LA+S and HA+S) exhibit characteristic absorption bands at 1047–1055 cm^{−1}, indicating a chemical interaction between hydrous silica and TiO₂ surfaces [39,40]. This molecular interaction is fundamental to understanding the protection mechanism.

Silica acts as a water stabilizer through several interrelated mechanisms, including hydrogen bond formation, modification of water mobility, physical barrier effects, and passivation of active sites. These mechanisms contribute to enhanced photostability by reducing the likelihood of photocatalytic degradation in polymeric systems.

- **Hydrogen Bond Formation:** The tetrahedral structure of silica, with its surface silanol (Si-OH) groups, offers numerous sites for hydrogen bond formation with water molecules [16]. These bonds are stronger than water-TiO₂ interactions, leading to more stable adsorption.
- **Modification of Water Mobility:** Water adsorbed on the silica surface exhibits reduced mobility compared to water on the alumina surface or pure TiO₂ [17,31]. This decreased mobility restricts the ability of water molecules to participate in photocatalytic reactions.
- **Physical Barrier for Reactive Species Migration:** The silica layer functions as a physical barrier, preventing the migration of photogenerated electron–hole pairs to the surface [19]. This reduction in migration significantly decreases the likelihood of these pairs interacting with water molecules to form reactive oxygen species (ROS).
- **Passivation of Active Sites:** Silica effectively passivates the catalytically active sites on the TiO₂ surface, thereby reducing the pigment's ability to initiate photocatalytic reactions that lead to polymer degradation [8,41].

Zeta potential analysis confirms this mechanism, demonstrating that samples containing silica (LA+S and HA+S) exhibit less negative zeta potential values (-20.2 ± 0.3 mV and -24.6 ± 1.9 mV) compared to samples without silica (LA and HA, with -28.7 ± 0.7 mV and -30.5 ± 0.5 mV, respectively). This shift in zeta potential indicates a significant modification in surface charge, which directly influences the interaction with water molecules [29,30].

The equation derived from the ANOVA model ($Zp = -26.20 - 1.24C_{Al} + 3.56C_{Si}$) quantifies this relationship, revealing that silica's contribution to the zeta potential is approximately 2.3 times greater than that of alumina. This finding suggests that silica has a more pronounced effect on modifying the surface properties of TiO₂, which explains its superior effectiveness in stabilizing adsorbed water [34].

3.4. Practical Implications for Polymer Applications

The findings of this study have significant practical implications for the formulation and application of polypropylene compounds containing TiO₂, providing valuable insights into optimizing their stability and performance.

- Coating optimization for outdoor applications: For polypropylene products designed for outdoor applications, including garden furniture, exterior automotive components, and construction materials, the use of TiO₂ pigments with combined alumina and silica coatings (like the HA+S sample) is recommended to enhance gloss retention and durability [10,27].
- Processing considerations: The presence of silica coatings on TiO₂ particles may influence the rheological properties of the molten polymer during processing [7]. To account for these effects, manufacturers should consider adjusting processing parameters, including melting temperature and extrusion speed.
- Cost–benefit balance: Although TiO₂ pigments with alumina and silica coatings may have a higher initial cost, their significant improvement in durability and gloss retention can lead to lower long-term costs due to extended product life [4].
- Reduction in additional additives: The enhanced UV stability achieved with properly coated TiO₂ pigments may enable a reduction in the amount of additional UV stabilizers in the polymer formulation, potentially streamlining the formulation process and lowering costs [9,12].
- Specific Applications: For applications where gloss retention is essential, such as consumer packaging or decorative pieces, selecting TiO₂ pigments with an optimal balance of alumina and silica coatings can significantly enhance product performance [6].

3.5. Comparison with Previous Studies on TiO₂ Coatings

Our results on the role of alumina and silica coatings on TiO₂ expand the current understanding of UV protection mechanisms in polymeric systems. Previous studies, such as those by Egerton and colleagues, have demonstrated that inorganic coatings reduce the photoactivity of TiO₂ [39]. However, these studies focus primarily on coatings acting as physical barriers that prevent charge carrier migration. Our work adds a new dimension to this understanding by highlighting the critical role of structural and adsorbed water in the photodegradation process.

Unlike earlier research that mainly examined the effect of alumina and silica on TiO₂ particle dispersion and opacity, our study directly links coating composition to water retention and, ultimately, UV protection performance. Guo et al.'s studies on thin Al₂O₃ films for suppressing the photocatalytic activity of TiO₂ showed similar results in reducing photocatalytic activity but did not address the specific mechanism related to water retention [20]. Our findings complement these studies by providing a mechanistic model.

Wang and colleagues investigated TiO₂@SiO₂ nanocomposites for printing pigment applications, demonstrating improvements in dispersibility and optical performance [26]. However, they did not explore the effect on UV durability in polymeric matrices. Our study extends those findings to the context of polypropylene photodegradation.

Perhaps most significantly, our results challenge some conventional assumptions in the literature. While previous studies have suggested that alumina alone is sufficient for passivation, our data indicate that a combination of alumina and silica provides a superior synergistic effect for UV stabilization. This observation has important implications for the formulation of TiO₂ pigments in polymer applications where long-term durability is critical [32,42].

In summary, our research provides a more comprehensive and nuanced understanding of the role of inorganic coatings in modifying the TiO₂ surface for polymer applications,

specifically highlighting the importance of water–oxide interactions in the photodegradation mechanism [15].

4. Conclusions

This study establishes a direct correlation between structural water content in TiO₂ particles and photodegradation resistance of polypropylene composites, yielding several significant findings with important industrial implications. The investigation of four commercial TiO₂ variants with different Al₂O₃ and SiO₂ surface treatments revealed that water–oxide interactions play a crucial and previously underappreciated role in polymer photostability.

Comprehensive characterization through TEM, EDS, zeta potential analysis, and DRIFTS demonstrates that alumina coatings significantly increase water adsorption on TiO₂ surfaces. However, this water becomes a liability for photostability unless stabilized by silica. The sample with low alumina content (LA) exhibited the most severe photodegradation despite showing minimal weight loss during thermal analysis, indicating that its surface hydroxyl groups were particularly susceptible to participating in photocatalytic degradation processes.

Statistical analysis using ANOVA confirmed significant differences in surface properties across the four TiO₂ variants, with zeta potential measurements providing a quantitative indicator of hydroxyl group density. The mathematical model developed ($Zp = -26.20 - 1.24C_{Al} + 3.56C_{Si}$) demonstrates that silica has approximately 2.3 times greater impact on surface charge properties than alumina, which correlates strongly with improved UV protection performance.

The synergistic mechanism revealed in this study operates as follows: alumina coating provides sites for water adsorption through its hydroxyl-rich surface, while silica stabilizes this adsorbed water through stronger hydrogen bonding and simultaneously forms a physical barrier against electron–hole pair migration. This dual protective action results in significantly enhanced gloss and stress at break retention in PP composites containing alumina- and silica-coated TiO₂ (HA+S). This last composite reached maximum properties retention after 500 h of accelerated UV exposure, with 36% gloss retention, the highest stress at break retention, and the lowest carbonyl index.

These findings provide valuable guidance for optimizing TiO₂ surface treatments in polymer applications requiring enhanced weather resistance. For exterior applications, where UV stability is critical, TiO₂ pigments should ideally incorporate balanced aluminum and silicon oxide coatings to maximize photostability. The insights gained about water–oxide interactions may also inform the development of novel stabilization strategies beyond conventional approaches focused solely on electron–hole pair suppression.

Future research directions should explore the long-term stability of these water–oxide interactions under varied environmental conditions, the potential for further optimizing the Al₂O₃:SiO₂ ratio for specific polymer systems, and the extension of these findings to other photocatalytically active pigments and polymeric matrices.

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