

Article

Synthesis of Transparent ZnO–TiO₂ and Its Nanocomposites for Ultraviolet Protection of a Polyethylene Terephthalate (PET) Film

Daejeong Yang, Adam Gopal Ramu and Dongjin Choi * 

School of Materials Science and Engineering, Hongik University, 2639, Sejong-ro, Jochiwon-eup, Sejong City 30016, Republic of Korea

* Correspondence: djchoi@hongik.ac.kr; Tel.: +82-44-860-2525

Abstract: The goal of this research was to investigate the effects of ZnO–TiO₂ and its nanocomposites, on the physical, mechanical, and ultraviolet protection of polyethylene terephthalate (PET). Exposure to ultraviolet (UV) rays is a major cause of the degradation of the quality and optical properties of materials in addition to skin cancer; therefore, research on UV-blocking materials that are safe and have fewer side effects than currently available products is being actively conducted. In this study, a material with UV-blocking capability was synthesized while ensuring the transparency of ZnO and TiO₂. ZnO–TiO₂ and its various composites were successfully synthesized via a hydrothermal method followed by ball milling and their properties were systematically analyzed by using scanning electron microscopy, X-ray diffractometry, Fourier-transform infrared spectroscopy, and water contact angle measurements. Furthermore, a simple dip-coating method was employed to prepare transparent polyethylene terephthalate (PET) films coated with the composites, which were subsequently investigated for UV-blocking properties by exposing them to UV irradiation. The hydroxyl groups of ZnO and TiO₂, as representative inorganic sunblock components, were removed by using 3-chloropropyl trimethoxy silane as a coupling agent to improve their wettability in an organic solvent as well as their dispersibility and stability. The addition of a small amount of Tinuvin[®] allowed the hybrid organic and inorganic components to exhibit transparent UV-blocking characteristics, with a UV transmittance of ≤20% and 90% visible transmittance. These results, thus, serve as a basis for contributing to applications in the field of packaging, health, and hygiene industries.

Keywords: UV protection; ZnO; TiO₂; transparency; polyethylene terephthalate film; transmittance



Citation: Yang, D.; Ramu, A.G.; Choi, D. Synthesis of Transparent ZnO–TiO₂ and Its Nanocomposites for Ultraviolet Protection of a Polyethylene Terephthalate (PET) Film. *Catalysts* **2022**, *12*, 1590. <https://doi.org/10.3390/catal12121590>

Academic Editor: Kangle Lv

Received: 8 November 2022

Accepted: 5 December 2022

Published: 6 December 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Because of its great transparency, strength in mechanical use, and outstanding barrier qualities, polyethylene terephthalate (PET) is commonly used for packing liquids and freshly cut fruit. Because PET is highly transparent to both visible and ultraviolet (UV) light, it can be mixed with low molecular weight, UV-absorbing compounds to lessen the nutrient deterioration that occurs when food is exposed to UV light. UV rays break the chemical bonds of synthetic resins via photolysis, leaving them with cracks or discoloration resulting in a decline in their physical properties, such as impact and tensile strengths [1,2]. The properties of synthetic resins, such as polyethylene and polypropylene, can be degraded by their exposure to light, so UV protection (organic sunscreen and inorganic sunblock) is used to prevent their deterioration (decomposition and discoloration). The primary cause for the aging of synthetic resins is the UV rays of sunlight; thus, their weather and light resistances can be improved by the addition of sunscreen or sunblock. Organic sunscreen absorbs UV energy that has reached the surface of a material and often blocks UV-B (280–320 nm) radiation, whereas inorganic sunblock physically scatters UV rays and mainly employs ZnO and TiO₂ for this purpose, making it effective in blocking UV-A (320–400 nm) radiation, but it is not easy to ensure transparency, as shown in Figure 1A [3,4]. Among the organic ultraviolet absorbers, benzotriazole, which has a good absorption effect of

near-UV, light stabilizer, and synergistic effect, is the most widely used, and benzophenone, cyanoacrylate, and triazine are used according to characteristics (Figure 1B); therefore, both the blocking agents are used together to effectively defend against UV rays.

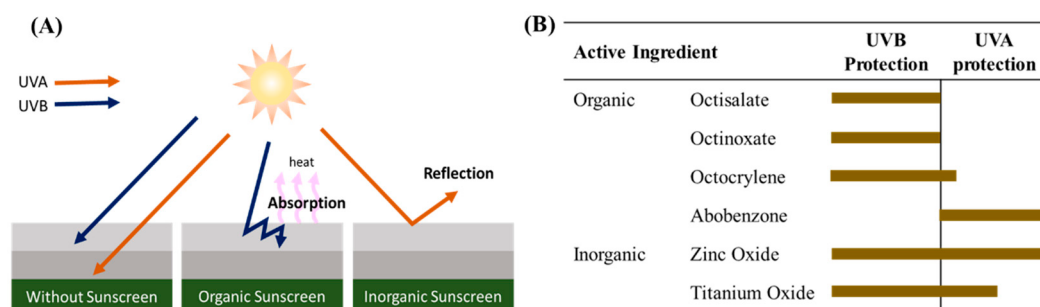


Figure 1. (A) Schematic illustration of the way in which organic and inorganic sunscreens protect against ultraviolet (UV) radiation and (B) the active ingredients for protection against UV-A (320–400 nm) and UV-B (280–320 nm) rays.

Plants create their own sunscreen, such as sinapoyl malate, to prevent the UV rays of the sun from damaging their DNA and hindering their growth. Sinapoyl malate has a ring structure similar to those of common sunscreen components. Stavros et al. found that when oxybenzone molecules—an organic sunscreen—absorb light and become excited, 90% of them decompose and emit heat, but 10% remain excited without breaking; this is similar to a phosphorescence phenomenon, in which light is applied to an object, and is then removed for a long time. By manipulating the rotation area or vibrating the material to convert the excess energy into heat, the material can be returned to a stable ground state [5].

A UV absorber is a synthetic resin additive that selectively absorbs UV energy and converts it into thermal energy; benzotriazole is mainly used for this because it has the best UV absorption ability and does not stain synthetic resins, thereby giving rise to color stability over a long period of time. A representative product for this purpose is Tinuvin. It has already been reported that standard Tinuvin® UV absorbers are used in food and packaging containers available in the market, with no known health issues associated with their use [6]. The requirements of a UV absorber are good light absorption in the UV absorption wavelength range (280–400 nm), thermal and chemical stability, low volatility, excellent compatibility with the target substance, light stability of the absorbent itself, transparency, odorlessness, nontoxicity, and a small amount for effective use. A UV absorber absorbs light in the 250–400 nm wavelength range and converts it into thermal energy.

ZnO, which has excellent UV-A and UV-B properties, and TiO₂, which is more specialized in blocking UV-B, are white powders used in medicines, pigments, and cosmetic raw materials. ZnO is a UV protection material recognized by the U.S. Food and Drug Administration for its stability and effectiveness and is widely used in antibacterial products due to its ecofriendliness, excellent thermal stability, low toxicity to the human body, and strong resistance to bacteria and fungi [7]. In addition, TiO₂ has the ability to absorb light to induce photo-oxidation–reduction reactions via an electron transition and photocatalytically degrade bacteria and organic matter; therefore, it is used to develop antibacterial functional packaging materials to maintain food quality and prevent its decay [8]. Studies have reported that fine nanosized TiO₂ particles show high scattering of UV rays, making TiO₂ an excellent material for use in UV protection applications [9]. Diaz–Visurraga et al. found that chitosan films with 17–170 nm-sized TiO₂ exhibit increased light absorption toward both UV-A and UV-B, thereby showing superior UV protection compared to non-doped films [10]. To ensure transparency, as well as UV protection for maintaining the quality of products, nanoparticles with size <100 nm must be uniformly dispersed [11]. The factor that determines visible light transmittance and UV protection properties is the size of the dispersed particles; nanoparticle materials have very good reactivity properties

because of their high specific surface area [12]. In addition, Sabzi et al. demonstrated that TiO_2 , which was surface-treated with the coupling agent amino propyl dimethoxy silane to efficiently disperse nanosized TiO_2 , has an improved UV protection effect compared with its pretreatment state [13]. In this study, we developed a coating material that is transparent and exhibits guaranteed UV protection via two synthesis methods by using ZnO, TiO_2 , and Tinuvin; it was confirmed that the silane-based coupling coating suppresses the photocatalytic activity of ZnO and TiO_2 , thereby improving their dispersibility and safety.

2. Results and Discussion

As the size of ZnO and TiO_2 particles decreases, the transparency of the visible light region increases; hence, these materials were synthesized under two sets of synthesis conditions, and their particle shapes were observed by using SEM analysis, with the results shown in Figure 2. As can be observed in Figure 2A, the ZnO– TiO_2 –TEA sample exhibits a wirelike structure with a size of several nanometers (195–252 nm). To widen the surface area of ZnO, the nanotetrapod approach can be considered [14,15]. In comparison, the ZnO– TiO_2 nanocomposite exhibits the particles like structures with a size of several hundred nanometers (61–124 nm), as shown in Figure 2B. Figure 2C shows the morphology of a ZnO– TiO_2 –silane composite, which confirms that the ZnO– TiO_2 surface was completely coated with silane; moreover, EDX spectroscopy and elemental mapping results confirmed the presence of Si in the composites.

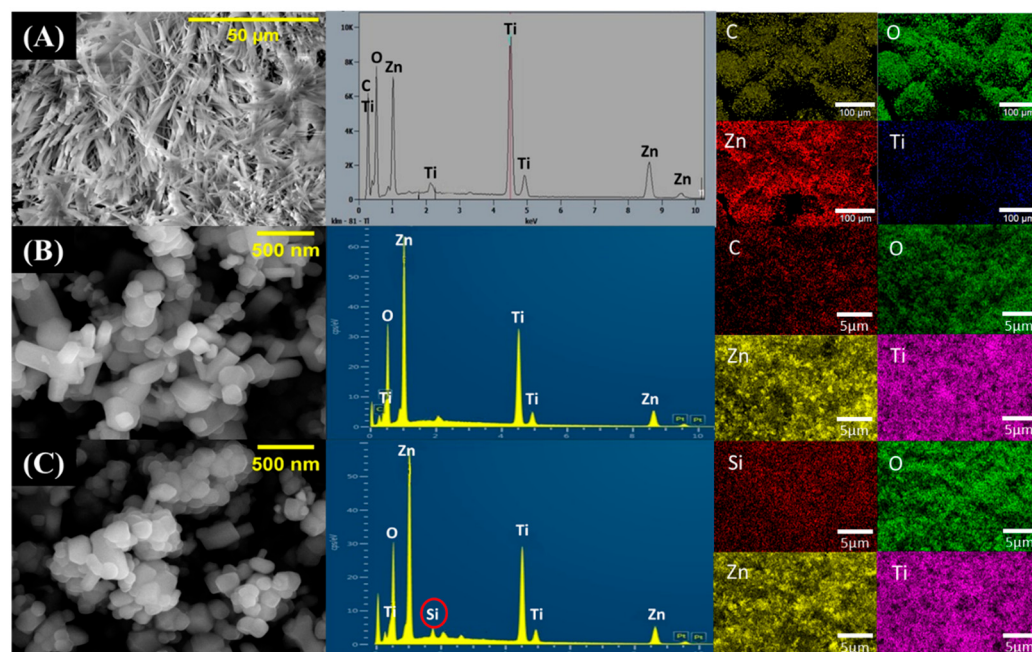


Figure 2. Scanning electron microscopy images and energy-dispersive X-ray spectra of (A) ZnO– TiO_2 –TEA, (B) ZnO– TiO_2 , and (C) ZnO– TiO_2 –silane.

As shown in Figure 3A, all of the samples were synthesized ZnO particles with a hexagonal wurtzite crystal structure with XRD peaks of (2θ , reflection plane) = (31.8° , (100)), (34.5° , (002)), (36.3° , (101)), (47.5° , (102)) and (56.6° , (110)) and were uniformly distributed with TiO_2 in three different phases. The prominent peak of TiO_2 was consistent with the anatase TiO_2 phase ($2\theta = 25^\circ$, (101)), and crystals of the rutile ($2\theta = 27.5^\circ$, (100)) and brookite ($2\theta = 31^\circ$, (120)) TiO_2 phases were also observed. In the case of TiO_2 , the average particle size of the samples was estimated by applying the value of the main XRD peak centered at approximately 25° to the Debye–Scherrer equation ($D = 0.9\lambda/(\beta\cos\theta)$) [16]. In this equation, D is the average crystallite size, the constant with a value of 0.9 is the shape factor, λ is the wavelength of the incident X-rays ($1.5406 \text{ \AA}$), β is the full width at half maximum, and θ is

the diffraction angle of the maximum peak. The average crystallite sizes of ZnO and TiO₂ are 75.45 and 68.24 nm, respectively.

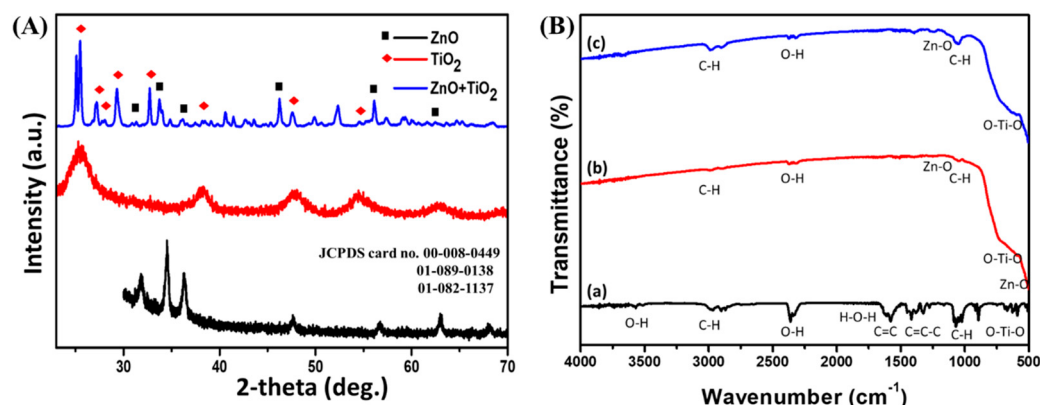


Figure 3. (A) X-ray diffraction patterns of ZnO–TiO₂, ZnO, and TiO₂ and (B) Fourier-transform infrared spectra of (a) ZnO–TiO₂–TEA, (b) ZnO–TiO₂ and (c) ZnO–TiO₂–silane.

Figure 3B shows the FTIR spectra in the wavenumber range of 500–4000 cm^{−1} of the samples for (a) ZnO–TiO₂–TEA, (b) ZnO–TiO₂ and (c) ZnO–TiO₂–silane. Intense and weak bands appearing below 1000 cm^{−1} are due to O–Ti–O bonding [17]. The sample of Figure 3B(b,c) shows stronger O–Ti–O bonding at a wavenumber of 563 cm^{−1} than Figure 3B(a). The peaks for C–H at 1000–1100 and 2898 cm^{−1} are due to the absorption of alkane functional groups [18]. The function of C=C and C=C–C vibrations can be observed at 1635 and 1447 cm^{−1}, respectively [19]. The peaks at 1627 and 2370 cm^{−1} correspond to the H–O–H vibrations in absorbed water molecules [20]. The sample of ZnO–TiO₂–TEA exhibits a more intense absorption hydroxyl peak (–OH) than that of ZnO–TiO₂.

Figure 4 shows the dependence of the spectroscopic characteristics of ZnO–TiO₂–TEA and ZnO–TiO₂ on the silane coupling agent and Tinuvin. The silane coupling agent blocks UV-A transmittance by increasing the absorption in the UV-A region, whereas, Tinuvin increases the absorption in both the UV-A and UV-B regions, thereby significantly lowering the transmittance for all UV regions, e.g., lowering it to 20% for UV-A. Samples obtained via the synthesis of ZnO–TiO₂–TEA exhibit a transmittance of ≤2% in both the UV-A and UV-B regions, but it is difficult to ensure transparency as the transmittance is limited to 25% for visible light. Samples using Tinuvin, ZnO, and TiO₂ entirely block UV-B, 80% UV-A, and 80% visible light, thereby ensuring their transparency. In addition, it can be seen that the sample treated with a silane coupling exhibits excellent UV-blocking of the ZnO and TiO₂ photocatalysts when exposed to UV rays, as shown in the spectra in Figure 4C. The easiest way to protect against UV rays is to increase the concentration of UV blockers. This is because according to the Beer–Lambert law $A = -\log(T) = \log\frac{P_0}{P} = \epsilon bc$ (A : absorbance, T : transmittance, P_0 : incident radiant power, P : transmitted radiant powder, ϵ : molar absorptivity, b : path length of sample, c : concentration of absorber) [21], the greater the thickness and concentration of UV blockers is, the higher is the absorption rate of light; however, if the concentration increases, it is difficult to ensure transmittance to visible light, and the material becomes harmful to skin. Therefore, the use of small amounts of ZnO, TiO₂, and Tinuvin serves as an environmentally friendly and transparent sunscreen.

2.1. Mechanism for Silane Coupling ZnO–TiO₂ UV Blocker

Surface modification allows changes to be made to a material and control of its surface properties to improve its limitations. Figure 5 shows the contact angles before and after the silane coupling of the ZnO and TiO₂ powders, as well as the optical microscope images at 40× magnification. Moreover, the samples were coated with PET film, and optical microscopy images at 10 and 40× magnifications and contact angle measurements of the films were obtained. The contact angle of the powder changed from superhydrophilic at <2° to hydrophobic at 134° ± 2.1° by surface treatment via silane coupling. The effect of the

silane coating on the powder is noticeable, but when a film is incorporated, the effect of the film on the contact angle is unclear. Optical microscopy was used to observe the powder distribution on a film to observe the silane coating effect. The film using the silane-coated sample was very evenly dispersed, whereas, the film using the non-silane-coated sample featured lumps of powder.

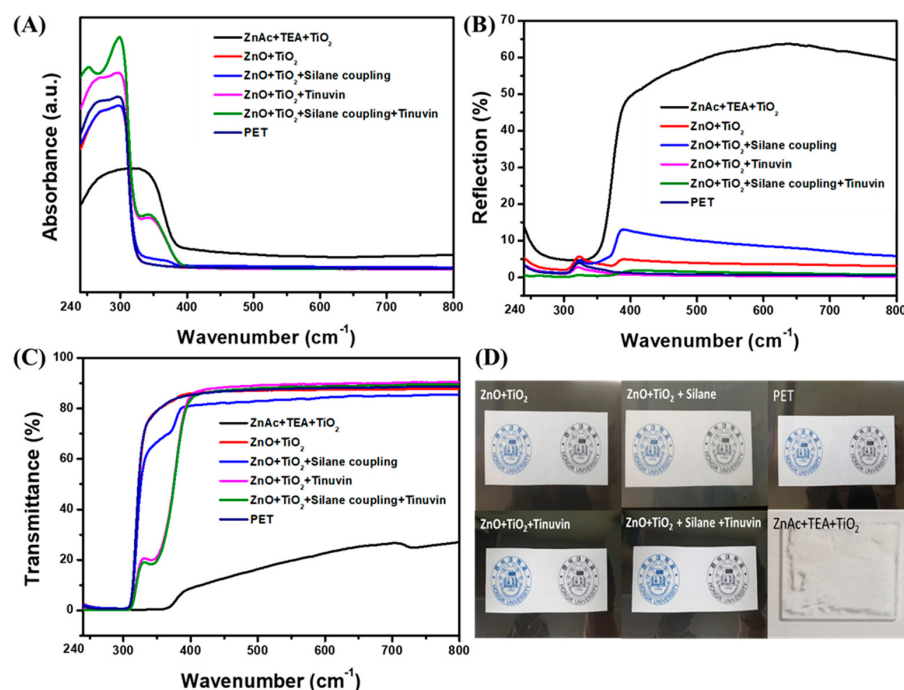


Figure 4. (A–C) UV-vis spectra of ZnO-TiO₂ thin films with the different compositions ZnO-TiO₂-TEA, ZnO-TiO₂, ZnO-TiO₂-silane, ZnO-TiO₂-Tinuvlin and ZnO-TiO₂-silane-Tinuvlin. (D) microscopy images of the transmittance of each sample.

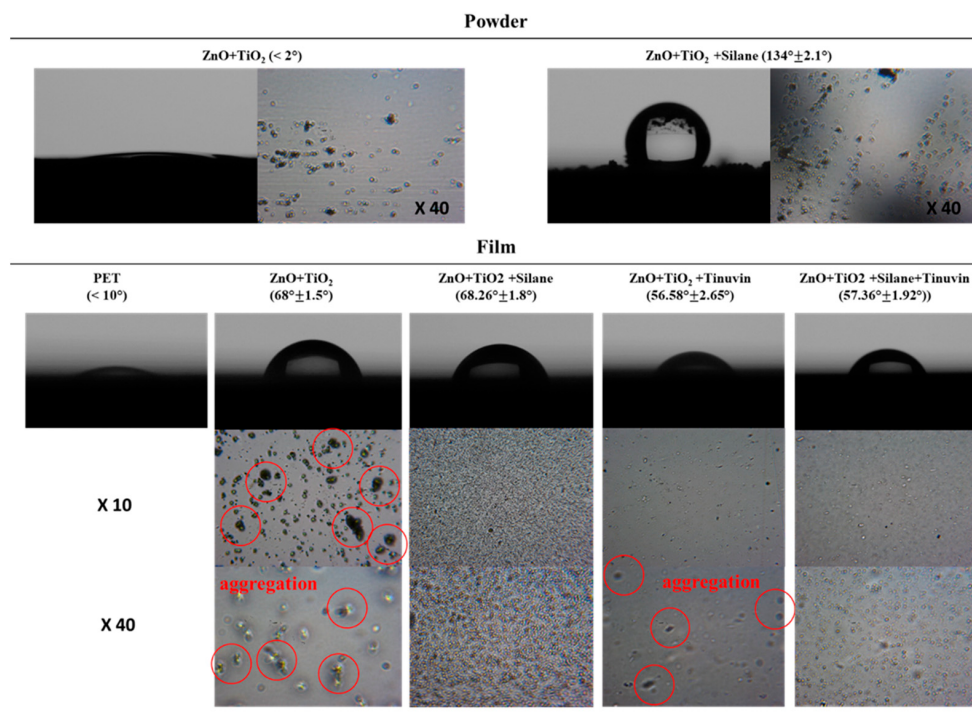


Figure 5. Contact angles and optical microscopy of powders and films with and without silane coupling agent.

Electrons (e^-) and holes (h^+) generate on the surface of ZnO and TiO_2 under UV radiation when used as photocatalysts; the e^- reacts with oxygen on the photocatalyst surface to form O_2^- . The h^+ reacts with moisture in the air to form hydroxyl radicals ($^{\bullet}\text{OH}$) which can oxidize and decompose powerful organic substances, such as odorous compounds, viruses, and bacteria, by converting them into H_2O and CO_2 [22]. However, due to their superhydrophilicity, the hydroxyl groups aggregate and clump together; therefore, to improve the dispersibility of the pigment, it is surface-treated with a coupling agent, which improves the wettability of the organic solvent by removing hydroxyl groups, as shown in Figure 6.

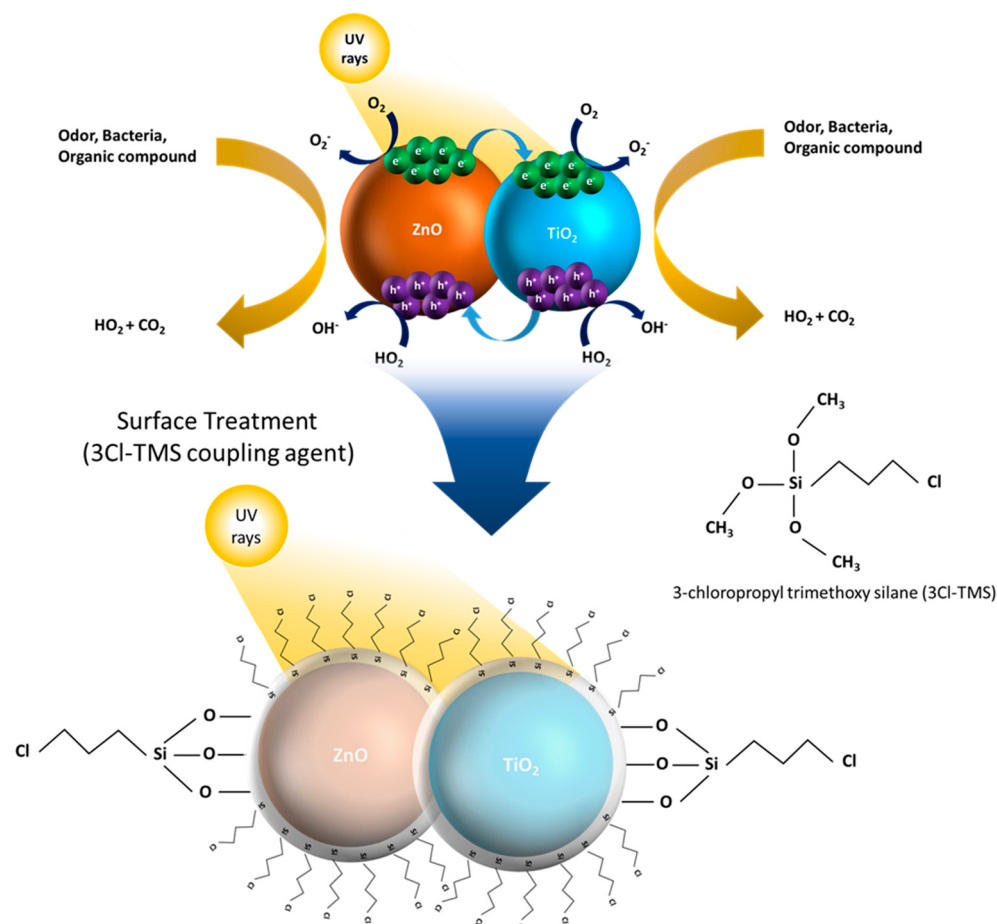


Figure 6. Mechanism for the treatment with 3Cl-TMS coupling agent of ZnO– TiO_2 .

2.2. Mechanism of Tinuvin UV Absorber

Polymer degradation is inhibited in the field of polymer science by screening out incident UV radiation with UV absorbers [23]. Tinuvin is one of many benzotriazoles, which also include UV absorption properties and exceptional photostability, that are used as UV absorbers. By being exposed to UV radiation, the derivatives induce excited-state intramolecular proton transfer (ESIPT) and produce zwitterionic structures that aid in nonradiative deactivation as shown in Figure 7 [24]. Because there is a deactivation pathway that passes through the conical junction, the internal conversion following ESIPT occurs very quickly, making it challenging to deconstruct these derivatives during the limited lifetimes of the excited states [25]. Damage-causing UV light is preferentially absorbed by UV absorbers made of benzotriazoles, and through ESIPT-based nonradiative deactivation, it is then released as thermal energy. Metal-free organic dyes can benefit from the idea of UV absorbers stabilizing and protecting macromolecules.

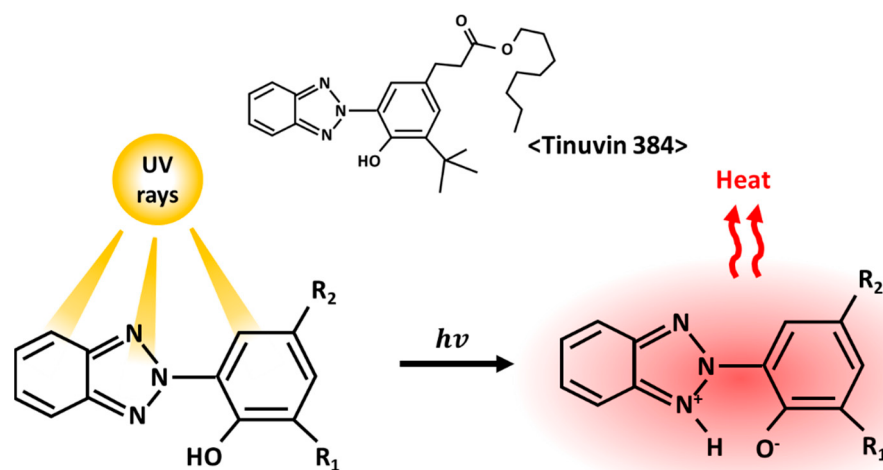


Figure 7. Mechanism of Tinuvin UV absorber.

3. Materials and Methods

3.1. Materials

ZnAc (zinc acetate dihydrate, $\text{Zn}[\text{C}_2\text{H}_3\text{O}_2]_2 \cdot 2\text{H}_2\text{O}$, 99.5%), ZnO (zinc oxide, 99.5%), and TiO_2 (titanium oxide, 99.5%) powders were purchased from Daejung Chemical & Material Co. Ltd., Republic of Korea and used to synthesize UV-blocking agents. Pure ethanol and TEA (triethanolamine, $\text{C}_6\text{H}_{15}\text{NO}_3$) were used as a solvent and stabilizer, respectively. For the surface modification of ZnO and TiO_2 powders, 3CI-TMS (3-chloropropyl trimethoxy silane, $\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, 97%, Sigma-Aldrich, Merck Korea, Seoul, Republic of Korea) was used as a silane coupling agent and MEK (methyl ethyl ketone, $\text{C}_4\text{H}_8\text{O}$, 99%, Daejung, Republic of Korea) was used as a solvent. Propylene glycol monomethyl ether acetate (PGMEA, $\text{C}_6\text{H}_{12}\text{O}_3$, Sigma-Aldrich) was used without purification as a dispersion solvent. The polyethylene terephthalate (PET) film is a thermoplastic polymer that can be amorphous, crystalline, or a mixture of both depending on how it is processed. The PET film used as a substrate was purchased as a commercial A4-sized film with the dimensions 210×297 mm and a thickness of 100 μm from the LamiAce company, Seoul, Republic of Korea.

3.2. Synthesis and Surface Treatment Method

Synthesis of ZnO– TiO_2 –TEA: A mixture of ZnAc and TEA was prepared in a ZnAc:TEA molar ratio 5:2 [26]. TEA was mixed in a reaction vessel with 40 mL of ethanol and stirred by using a magnetic stirrer before the addition of ZnAc and further stirring of the resulting mixture at 50–60 $^\circ\text{C}$ for 30 min. TiO_2 equal to Zn molar ratio of ZnAc was mixed and stirred for 15 min, to which 10 mL of deionized water was added and stirred for 30 min. PET film was washed in a sonicator for 10 min in a mixture of ethanol and acetone; this film was then coated via dipping method, and dried in an oven at 60 $^\circ\text{C}$ for 6 h.

Synthesis of ZnO– TiO_2 : ZnO and TiO_2 powders were mixed in a mass ratio of 1:1 and ground by a ball milling, which was performed at 175 rpm for 4 h, where, in addition to the powders, the ball mill was filled with an appropriate amount of alumina balls and ethanol. After the completion of the milling and removal of the alumina balls, the sample was washed with ethanol and covered with aluminum foil to prevent it being contaminated with impurities, before being left to air dry for a day to allow evaporation of the ethanol. The resulting powder was then dried in the oven at 80 $^\circ\text{C}$ for 3 h.

Silane coating: MEK (300 mL) and 3CI-TMS (9 g) were introduced into a 500 mL reaction vessel, which was well sealed to prevent solvent evaporation and ingress of impurities before being sonicated for 30 min. ZnO and TiO_2 samples (60 g) obtained via the ZnO– TiO_2 synthesis were added to the above solution, and the mixture was stirred uniformly and slowly at room temperature (20–25 $^\circ\text{C}$) for 6 h. When the stirring was

completed, the remaining impurities and unreacted substances were removed by washing with ethanol, and then the product was dried in the oven at 70 °C for 24 h to obtain ZnO–TiO₂–silane.

Tinuvin mixing: The ZnO–TiO₂ composite was mixed in 9:1 ratio with PGMEA, to which 5% wt thermosetting coating solution based on the composite weight was added and coated on the PET film. Similarly, the ZnO–TiO₂–silane–Tinuvin composite was synthesized via the addition of ZnO–TiO₂–silane.

3.3. Measurement and Characteristic Analysis

The crystal phase and morphology of the samples were compared and analyzed by using an X-ray diffraction (XRD; D8 ADVANCE, Bruker, Billerica, MA, USA) and field emission scanning electron microscopy (FE-SEM; Merlin Compact, Carl Zeiss, Jena, Thuringia, Germany), respectively. The structure and surface characteristics of the surface-modified samples were analyzed by using Fourier-transform infrared (FTIR; Spectrum X, Perkin Elmer, Waltham, MA, USA) and energy-dispersive X-ray (EDX; Aztec Energy X-MaxN, Oxford instruments, Abingdon, Oxfordshire, England) spectrometers. In addition, the spectroscopic characteristics of the dispersed film coatings were obtained by using a diffusion reflectance ultraviolet-visible-near-infrared (UV–vis–NIR) spectrometer (SolidSpec-3700, Shimadzu, Kyoto, Kansai, Japan). The contact angles of the film and powder were measured by using a contact angle goniometer (L2004A1, Ossila, Sheffield, South Yorkshire, UK), and the powder dispersibility of the film was measured by using a microscope (LCD MICRO 5MP, Bresser, Rhede, North Rhine-Westphalia, Germany).

4. Conclusions

ZnO–TiO₂ and its various composites were successfully synthesized by using a hydrothermal method followed by ball milling, and their properties were systematically analyzed by using SEM, XRD, FTIR spectroscopy, and water contact angle measurements. In addition, a simple dip-coating method was employed to prepare transparent PET films, which were subsequently exposed to UV irradiation. ZnO and TiO₂ have photocatalytic properties, so when exposed to light, they generate hydroxyl groups and cause oxidation. A coating was applied via silane coupling to overcome the limitations of the use of ZnO and TiO₂ due to their white cast color and photocatalytic properties. Silane coupling agents were used to disperse and stabilize the inorganic ZnO and TiO₂ sunscreen via a wetting method. This improved the wettability of the organic solvent by chemically treating and removing the hydroxyl radicals of the powder components. Silane coating was confirmed to play a key role in the dispersal and stabilization of the sunscreen by optical microscopy. The addition of a small amount of Tinuvin allowed the hybrid organic and inorganic systems to attain transparent UV-blocking characteristics, with a UV transmittance of <20% and 90% visible transmittance.

Author Contributions: D.Y., conceptualization, investigation, writing—original draft; A.G.R., instrument sources, investigation, data curation, visualization; D.C., conceptualization, supervision, writing—original draft, supervision, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Social Economy Innovation Growth Project (P0017637) funded by the government (Ministry of Trade, Industry and Energy). This work was supported by the 2022 Hongik University Innovation Support Program Fund.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shanky, B. Minimal processing and preservation of fruits and vegetables by active packaging. *Int. J. Herb. Med.* **2013**, *1*, 131–138.
2. Kumar, S.; Boro, J.C.; Ray, D.; Mukherjee, A.; Dutta, J. Bionanocomposite films of agar incorporated with ZnO nanoparticles as an active packaging material for shelf life extension of green grape. *Heliyon* **2019**, *5*, e01867. [[CrossRef](#)] [[PubMed](#)]

3. Lee, H.D.; Kim, J.M.; Son, D.H.; Lee, S.H.; Park, S.S. Preparation of ZnO Nano Powder and High-transparent UV Shielding Dispersion Sol. *Appl. Chem. Eng.* **2013**, *24*, 391–395.
4. Iijima, M.; Tsukada, M.; Kamiya, H. Effect of particle size on surface modification of silica nanoparticles by using silane coupling agents and their dispersion stability in methylethylketone. *J. Colloid Interface Sci.* **2007**, *307*, 418–424. [\[CrossRef\]](#)
5. Baker, L.A.; Stavros, V.G. Observing and understanding the ultrafast photochemistry in small molecules: Applications to sunscreens. *Sci. Prog.* **2016**, *99*, 282–311. [\[CrossRef\]](#)
6. Choi, H.; Choi, J.C.; Bae, I.; Lee, C.; Park, S.J.; Kim, M. Simultaneous Determination of UV Absorbers Migrated from Polyethylene and Polypropylene Food Packaging Materials into Food Simulants by HPLC-UVD. *J. Food Saf.* **2017**, *32*, 434–442. [\[CrossRef\]](#)
7. Trandafilović, L.V.; Božanić, D.K.; Dimitrijević-Branković, S.; Luyt, A.S.; Djoković, V. Fabrication and antibacterial properties of ZnO-alginate nanocomposites. *Carbohydr. Polym.* **2012**, *88*, 263–269. [\[CrossRef\]](#)
8. Roy, S.; Rhim, J.W. Preparation of carrageenanbased functional nanocomposite films incorporated with melanin nanoparticles. *Colloids Surf. B* **2019**, *176*, 317–324. [\[CrossRef\]](#)
9. Siddiquey, I.A.; Ukaji, E.; Furusawa, T.; Sato, M.; Suzuki, N. The effects of organic surface treatment by methacryloxypropyltrimethoxysilane on the photostability of TiO₂. *Mater. Chem. Phys.* **2007**, *105*, 162–168. [\[CrossRef\]](#)
10. Díaz-Visurraga, J.; Meléndrez, M.F.; Garcia, A.; Paulraj, M.; Cárdenas, G. Semitransparent chitosan-TiO₂ nanotubes composite film for food package applications. *J. Appl. Polym. Sci.* **2010**, *116*, 3503–3515.
11. Schilling, K.; Bradford, B.; Castelli, D.; Dufour, E.; Nash, J.F.; Pape, W.; Schulte, S.; Tooley, I.; Bosch, V.D.J.; Schellauf, F. Human safety review of “nano” titanium dioxide and zinc oxide. *Photochem. Photobiol. Sci.* **2010**, *9*, 495–509. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Sarsar, V.; Selwal, K.K.; Selwal, M.K. Nanosilver: Potent antimicrobial agent and its biosynthesis. *Afr. J. Adv. Biotechnol.* **2014**, *13*, 546–554.
13. Sabzi, M.; Mirabedini, S.M.; Zohuriaan-Mehr, J.; Atai, M. Surface modification of TiO₂ nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating. *Prog. Org. Coat.* **2009**, *65*, 222–228. [\[CrossRef\]](#)
14. Yang, D.; Gopal, R.A.; Lkhagva, T.; Choi, D. Oxidizing agent impacting on growth of ZnO tetrapod nanostructures and its characterization. *Environ. Res.* **2021**, *197*, 111032. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Ramu, A.G.; Yang, D.J.; Al Olayan, E.M.; AlAmri, O.D.; Aloufi, A.S.; Almushawwah, J.O.; Choi, D. Synthesis of hierarchically structured T-ZnO-rGO-PEI composite and their catalytic removal of colour and colourless phenolic compounds. *Chemosphere* **2021**, *267*, 129245. [\[CrossRef\]](#)
16. Yang, D.; Ramu, A.G.; Lee, Y.; Kim, S.; Jeon, H.; Sathishkumar, V.E.; Amal, M.A.M.; Wedad, A.A.; Algarni, T.; Choi, D. Fabrication of ZnO nanorods based gas sensor pattern by photolithography and lift off techniques. *J. King Saud Univ.-Sci.* **2021**, *33*, 101397. [\[CrossRef\]](#)
17. Johra, F.T.; Jung, W.G. RGO–TiO₂–ZnO composites: Synthesis, characterization, and application to photocatalysis. *Appl. Catal. A Gen.* **2015**, *491*, 52–57. [\[CrossRef\]](#)
18. Munguti, L.; Dejene, F. Influence of annealing temperature on structural, optical and photocatalytic properties of ZnO–TiO₂ composites for application in dye removal in water. *Nano-Struct. Nano-Objects* **2020**, *24*, 100594. [\[CrossRef\]](#)
19. Suganthi, N.; Thangavel, S.; Kannan, K. Hibiscus subdariffa leaf extract mediated 2-D fern-like ZnO/TiO₂ hierarchical nanoleaf for photocatalytic degradation. *FlatChem* **2020**, *24*, 100197. [\[CrossRef\]](#)
20. Moghaddas, S.M.T.H.; Elahi, B.; Javanbakht, V. Biosynthesis of pure zinc oxide nanoparticles using Quince seed mucilage for photocatalytic dye degradation. *J. Alloys Compd.* **2020**, *821*, 153519. [\[CrossRef\]](#)
21. Mayerhöfer, T.G.; Pahlow, S.; Popp, J. The Bouguer-Beer-Lambert law: Shining light on the obscure. *Chemphyschem* **2020**, *21*, 2029–2046. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Khan, M.Z.; Baheti, V.; Ashraf, M.; Hussain, T.; Ali, A.; Javid, A.; Rehman, A. Development of UV protective, superhydrophobic and antibacterial textiles using ZnO and TiO₂ nanoparticles. *Fibers Polym.* **2018**, *19*, 1647–1654. [\[CrossRef\]](#)
23. Xie, F.; Zhang, T.; Bryant, P.; Kurusingal, V.; Colwell, J.M.; Laycock, B. Degradation and stabilization of polyurethane elastomers. *Prog. Polym. Sci.* **2019**, *90*, 211–268.
24. Uesaka, T.; Ishitani, T.; Shimeno, T.; Suzuki, N.; Yagi, S.; Maeda, T. Synthesis and photophysical properties of photostable 1, 8-naphthalimide dyes incorporating benzotriazole-based UV absorbers. *RSC Adv.* **2022**, *12*, 17350–17361. [\[CrossRef\]](#)
25. Pijeu, S.; Foster, D.; Hohenstein, E.G. Excited-state dynamics of a benzotriazole photostabilizer: 2-(2'-hydroxy-5'-methylphenyl)benzotriazole. *J. Phys. Chem. A* **2017**, *121*, 6377–6387. [\[CrossRef\]](#)
26. Ghamsari, M.S.; Alamdari, S.; Han, W.; Park, H.H. Impact of nanostructured thin ZnO film in ultraviolet protection. *Int. J. Nanomed.* **2017**, *12*, 207. [\[CrossRef\]](#)