

Original Paper

A TiO₂/polyurethane Composite for Photodegradation of Formaldehyde via Covalently Incorporation of Amino-functionalized TiO₂

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Abstract

In this study, a TiO₂/polyurethane composite (PU-TiO₂) for photodegradation of formaldehyde was prepared based on TiO₂ amino-functionalized with 3-aminopropyltriethoxysilane (APTS). FTIR, XPS, TG and TEM measurements demonstrated the successful amino-functionalization of TiO₂ by APTS. Then the NH₂-TiO₂ were incorporated into polyurethane (PU) through urea linkages, and the thermal stability, mechanical properties as well as degradation efficiency of PU-TiO₂ were investigated. PU-TiO₂ possessed good thermal stability both in the storage and application. Compared with PU physically blended with TiO₂, PU-TiO₂ showed improved compatibility between PU and NH₂-TiO₂, evidenced by the enhanced mechanical properties. Most importantly, PU-TiO₂ presented a good photoactivity for the degradation of formaldehyde.

Keywords

TiO₂/polyurethane, photodegradation, formaldehyde, amino-functionalized

1 Introduction

With the improvement of living standards, people have paid more attention to safe and environmentally friendly interior decoration. As a significant volatile organic compound, formaldehyde (HCHO) is a kind of colorless gas with strong pungent smell and has been considered one of the most important indoor air pollutants (Diao et al., 2020; Ren et al., 2021; Ullah et al., 2021). Normally, it emits from widely used building and decorative materials in airtight buildings, such as interior walls and furniture coatings (Sahrin et al., 2021). Formaldehyde of high concentration is severely harmful to human immune system as well as nervous system. Even low-dose formaldehyde can cause chronic respiratory

diseases (Liu et al., 2020; Shao et al., 2019; Yang et al., 2019). Therefore, it is urgent to develop a non-toxic, efficient and environmentally friendly method to degrade the indoor formaldehyde.

To satisfy the stringent environmental regulations, a great deal of work has been done to abate the indoor concentrations of formaldehyde. Particularly, since the UV-irradiation-induced redox chemistry on TiO_2 was firstly reported by Fujishima (Fujishima et al., 2000), photocatalytic technology has been rapidly developed as a sustainable method for reducing formaldehyde (Li & Ma, 2021; Wang et al., 2021; Zhang et al., 2019). Formaldehyde can be oxidized into CO_2 over catalysts at room temperature than thermal oxidation (Dou et al., 2019; Huang et al., 2019; Liu et al., 2020). Among photocatalysis, nano titanium dioxide (TiO_2) attracts considerable attention because of its low cost, nontoxicity, long-term photostability and obvious degradation effect on a variety of organic compounds (Chen et al., 2019; Chen et al., 2021; Li et al., 2020; Sun et al., 2020). Recently, researchers attempted to incorporate TiO_2 into polymer matrices, so as to prepare the coating materials with self-photocatalysis to degrade formaldehyde. For example, a study was carried out on the preparation of a poly(vinyl chloride)- TiO_2 composite (Cho & Choi, 2001). Results showed that the photocatalytic degradation in the solid polymer matrix proceeded much faster than the degradation under air, and the composite has an application prospect as a photodegradable product. In another research, Mofokeng and coworkers (Mofokeng & Luyt, 2015), melt-mixed poly(lactic acid) /poly(hydroxybutyrate-co-valerate) blends and nanocomposites with small amounts of TiO_2 nanoparticles. The presence of TiO_2 nanoparticles not only improved the thermal stability of both polymers in the blend but also realized catalysis in the degradation process.

In the past few years, directly blending TiO_2 into polymers has proved to be an efficient method to fabricate coating materials with the ability of photodegradation. However, once used for a long time, TiO_2 is easy to fall off from the matrixes, thereby losing photocatalysis. In addition, due to the incompatibility between inorganics and organics, TiO_2 will negatively affect the initial properties of polymers, such as mechanical properties (Tsui et al., 2005; Xie et al., 2004). Consequently, this has recently drawn significant commercial and academic attention to chemically combine TiO_2 with organic matrixes. Among coating materials, polyurethane (PU) is regarded as the promising candidate, owing to its excellent abrasion resistance, appealing mechanical strength, corrosion resistance, toughness, and process ability (Dall Agnol et al., 2021; Nowak et al., 2021; Paraskar & Kulkarni, 2020; Zhou et al., 2020). To the best of our knowledge, up to date, there has been no reports of coating materials, which are chemically connected of TiO_2 with solvent-free polyurethanes for photodegradation of formaldehyde.

In this study, 3-aminopropyltriethoxysilane (APTS) was selected to amino-functionalize TiO_2 , based on the chemical structure feature of polyurethane. Then the amino-functionalized TiO_2 ($\text{NH}_2\text{-TiO}_2$) was covalently bonded to polyurethane utilizing urea linkages. Results demonstrated that the prepared PU- TiO_2 showed good activity for the degradation of formaldehyde, especially under the illumination of 365 nm light.

2. Experimental

2.1 Materials

Ethanol, triethylamine, 3-aminopropyltriethoxysilane (APTS), 1, 6-diisocyanatohexane (H_{12} MDI), isophorone diisocyanate (IPDI), bismuth neodecanoate, 1,3-butanediol (1, 3-BDO), 1, 4-butanediol (1, 4-BDO) and ditinbutyl dilaurate (DBTDL) were purchased from Aladdin Industrial Corporation (Shanghai, China). Poly (propylene glycol) with a molecular weight of 2000 (PPG220) and 1000 (PPG210) were obtained from Kelong Chemical Co. Ltd. (Chengdu, China) and dried at 120 °C under high vacuum (0.5mmHg) for 12 h before use. TiO_2 with average particle sizes of 50 nm, which is anatase, was provided by Macklin Biochemical Co., Ltd. (Shanghai, China). Distilled water was self-prepared.

2.2 Amino-functionalization of TiO_2

Firstly, 95g ethanol, 5g deionized water, and 1g APTS were added into a three-neck flask equipped with a thermometer, mechanical stirrer, and condenser, followed by magnetic stirring at room temperature for 5 minutes to form a homogeneous solution. Secondly, 2g TiO_2 as well as 2 drops of triethylamine as catalyst were added and dispersed well by ultrasonic wave. The system was refluxed and stirred for 4 h after the temperature rose to 80 °C in an oil bath. After cooling down to room temperature, the mixture was filtered and washed several times with anhydrous ethanol, and then dried at 60 °C in an oven until the quality of the product did not change. The reaction route for amino-functionalization of NH_2-TiO_2 is depicted in Scheme 1(a).

2.3 Preparation of pre-PU

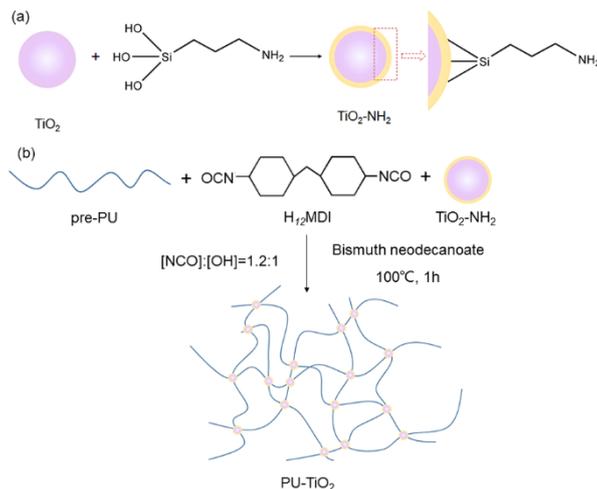
IPDI, PPG220, PPG210, 1, 4-BDO, and 1 drop of DBTDL (molar ratio of IPDI: PPG 220: PPG 210: 1, 4-BDO = 9: 2: 1: 2, molar ratio of NCO: OH= 1.8: 1) were poured into the four-necked flask equipped with a mechanical stirrer, thermometer, and condenser. The mixture was stirred under a nitrogen atmosphere at 85 °C for 2 h. After that, the system was cooled to 50 °C. Then calculating the amount of 1, 3-BDO (molar ratio of IPDI: 1, 3-BDO = 9: 8) was added to the flask. Successively, the mixture was heated to 60 °C for 1 h. Finally, the temperature rose to 80 °C, and the pre-PU was obtained after the reaction lasted for another 20 minutes.

2.4 Preparation of PU- TiO_2

At first, appropriate quantities of pre-PU, H_{12} MDI (molar ratio of NCO:OH=1.2:1) and NH_2-TiO_2 were mixed uniformly with the presence of bismuth neodecanoate. Then it was transferred onto a polytetrafluoroethylene plate, and the average thickness of the films was 0.5 mm. Next, the polytetrafluoroethylene plate was put into an oven and cured at 90 °C for 6 h to form PU- TiO_2 . The curing process is presented in 1(b). Samples here are abbreviated as PU- TiO_2 -x. The corresponding weight percentage of NH_2-TiO_2 in PU- TiO_2 -3, PU- TiO_2 -6, PU- TiO_2 -9, and PU- TiO_2 -12 are 3%, 6%, 9%, and 12%, respectively.

For comparison, PU/ TiO_2 s were prepared in the same procedure except that the NH_2-TiO_2 was replaced by the equal quality of functionalized TiO_2 . The pure PU without TiO_2 was prepared via the same

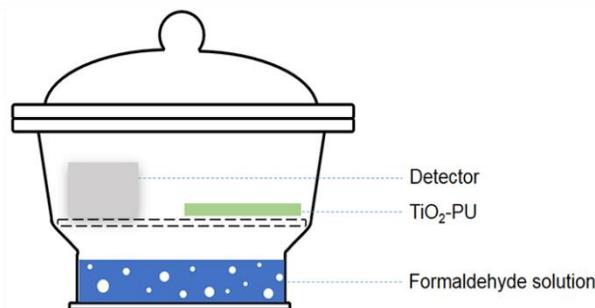
synthetic process. It is noteworthy that $-\text{NH}_2$ in $\text{NH}_2\text{-TiO}_2$ hardly influences the ratio of final polyurethane, because the amount is rather small. So the amount of the other materials remains unchanged.



**Scheme 1 (a). Amino-functionalization Procedure of TiO_2 and Diagram for Surface of $\text{NH}_2\text{-TiO}_2$;
(b) Schematic of the Incorporation of $\text{NH}_2\text{-TiO}_2$ into PU-TiO_2**

2.4 Measurements

Fourier transform infrared (FTIR) spectra were acquired by a Nicolet IS10 FTIR spectrometer (ThermoFisher Scientific, United States) in the range from 400 to 4000 cm^{-1} after 32 scans at 2 cm^{-1} resolution. X-ray photoelectron spectroscopy (XPS) was utilized by a Thermo ESCALAB 250XI spectrometer (ThermoFisher Scientific, United States), with Al $K\alpha$ excitation radiation under ultrahigh-vacuum conditions. A transmission electron microscopy (TEM) was used to study the morphology of $\text{TiO}_2\text{-NH}_2$, and was studied by a transmission electron microscopy (FEI Themis Z, United States). Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere at constant heating to detect the presence of organic matter on the surface of the $\text{TiO}_2\text{-NH}_2$, as well as the thermal stability of PU films. A scanning electron microscope (SEM, Hitachi Model S520, Japan) was employed to observe the cross-section morphologies of PU/TiO_2 and PU-TiO_2 . Dumbbell-shaped polyurethane films of 50-mm length and 10-mm neck width were measured in tension mode with a universal material testing machine (model tensiTECH) supplied by Tech-Pro Inc. (Woodstock, USA) with a cross-head speed of 10 mm/min at $25\text{ }^\circ\text{C}$. Each sample was measured five times to get the average values. The degradation efficiency of formaldehyde was tested in a closed dryer, and the glass joint is sealed with vaseline to ensure that internal air leakage of the dryer is not allowed. A formaldehyde concentration detector and tested samples were placed on the isolation plate inside the dryer. Formaldehyde solution was poured into the bottom of the dryer. A 20W UV lamp was placed on top of the dryer. The specific experimental device is shown in Scheme 2.



Scheme 2. Apparatus for Measuring Concentration of Formaldehyde

3. Results and Discussion

3.1 Structure Characterization of $\text{NH}_2\text{-TiO}_2$

Figure 1(a) presents FTIR spectra of TiO_2 and $\text{NH}_2\text{-TiO}_2$. As for TiO_2 before amino-functionalization, there is a characteristic absorption peak assigned to hydroxyl groups ($-\text{OH}$) at 3358 cm^{-1} , which provided reaction sites for silanol groups ($-\text{Si-OH}$) of APTS. This offered a theoretical possibility that the inorganic parts and the organic parts can be connected by chemical bonds. After amino-functionalization, new peaks at 2923 cm^{-1} , 1114 cm^{-1} , 1031 cm^{-1} appeared, attributed to the stretching vibration of $-\text{CH}_2-$, Si-O and C-N , respectively. Furthermore, the absorption peak at 3423 cm^{-1} , belonged to the stretching vibration of amino group ($-\text{NH}_2$) derived from APTS. All these peaks showed the successful amino-functionalization of TiO_2 by APTS.

XPS was utilized to analyze the elements of sample surface. Figure 1(b) shows the XPS spectra of TiO_2 and $\text{NH}_2\text{-TiO}_2$. The detailed data for surface elemental compositions are summarized in Table 1. From the spectrum of TiO_2 , we can see peaks at 529.9 eV and 490.0 eV , owing to $\text{O } 2s$ and $\text{Ti } 2p$, respectively. As for the spectrum of $\text{NH}_2\text{-TiO}_2$, new peaks at 101.9 eV and 399.8 eV were assigned to $\text{Si } 2p$ and $\text{N } 1s$ from APTS. Moreover, it can be seen from the data in Table 1 that the content of C and O all decreased significantly after NH_2 -functionalization of TiO_2 . Si was obviously detected on the surface of $\text{NH}_2\text{-TiO}_2$. All these changes further verified the surface of TiO_2 was well encapsulated.

To further confirm the amino-functionalization of TiO_2 , the thermal stability was discussed by thermogravimetric analysis (TGA) analysis. Figure 1 (c) provides TGA curves of TiO_2 and $\text{NH}_2\text{-TiO}_2$. Figure 1 (d) presents differential thermogravimetric (DTG) curves of $\text{NH}_2\text{-TiO}_2$. As pure inorganic materials, TiO_2 hardly decomposed under high temperature, except for the removal of hydroxyl groups on the surface and evaporation of the absorbed water. Interestingly, an evident weight loss of $\text{NH}_2\text{-TiO}_2$ was found from $50\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$. According to the DTG curves, the decomposition process can be described as two steps. From $50\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$, the weight loss mainly resulted from the removal of hydroxyl groups and the absorbed water. The second step ($300\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$) corresponded to the organic component originating from APTS.

TEM was performed to observe the morphologies of TiO_2 and $\text{NH}_2\text{-TiO}_2$, as displayed in Figure 1(e) and (f), respectively. The average particle size was found to be 50 nm . The particles of TiO_2 were

smooth and clean. Nevertheless, a layer of coating was noticed in the TEM image of $\text{NH}_2\text{-TiO}_2$, which was due to the grafting of APTS. Taken together, these results all suggested the successful amino-functionalization of TiO_2 by APTS.

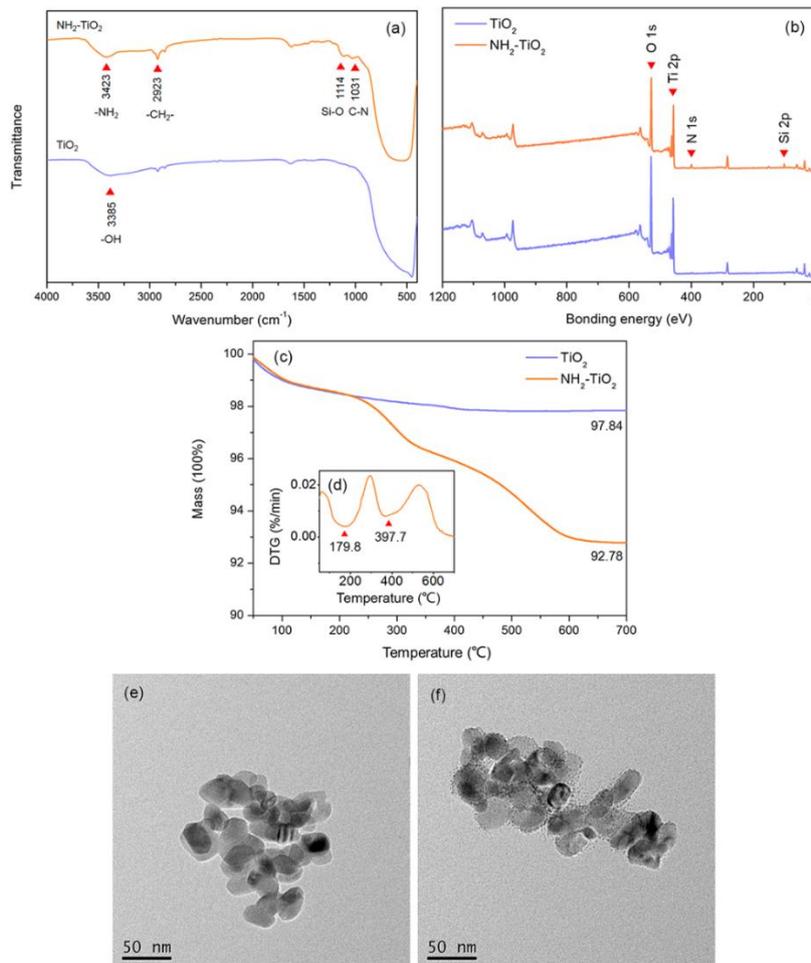


Figure 1 (a). FTIR Spectra of TiO_2 and $\text{NH}_2\text{-TiO}_2$; (b) XPS Spectra of TiO_2 and $\text{NH}_2\text{-TiO}_2$; (c) TGA Curves of TiO_2 and $\text{NH}_2\text{-TiO}_2$; (d) DTG Curve of $\text{NH}_2\text{-TiO}_2$; (e) TEM Images of (a) TiO_2 and (b) $\text{NH}_2\text{-TiO}_2$

Table 1. Surface Elemental Composition of TiO_2 and $\text{NH}_2\text{-TiO}_2$

Samples	C (%)	O (%)	Si (%)
TiO_2	27.33	72.67	/
$\text{NH}_2\text{-TiO}_2$	25.94	68.24	5.82

3.2 Thermal Stability

Thermal stability is an important parameter for materials applied as coating materials. PU- TiO_2 -9 was

selected as a representative example to study thermal stability. As shown in Figure 2, the full lines describe the TGA curves of PU/TiO₂ and PU-TiO₂, while the broken lines present the DTG curves of PU/TiO₂ and PU-TiO₂. The correlational results are summarised in Table 2. On the whole, PU/TiO₂ and PU-TiO₂ exhibited similar TGA and DTG curves. According to the detailed data in Table 2, the thermal stability of PU-TiO₂ was slightly higher than that of PU/TiO₂. The DTG curves showed the typical three steps of polyurethane in thermal degradation. The first step occurred under 300 °C and was related to the evaporation of water (Kopczyńska & Datta, 2016). The temperature of initial decomposition (temperature taken at the 5 wt.% of weight loss, T_{5%}) for PU/TiO₂ and PU-TiO₂ was 298.4 and 300.2 °C, respectively. The second step was ascribed to the decomposition of hard segments, i.e. urethane groups (Caminoa et al., 2001). The third step was attributed to the soft segments (ether or ester bond) (Deshpande & Rezac, 2001). T_{max1} and T_{max2} of PU-TiO₂ were both higher than those of and PU/TiO₂. Because of the amino groups on the surface of NH₂-TiO₂, PU-TiO₂ was crosslinked, and the network structure resulted in the present higher thermotolerance (Chiou & Schoen, 2010; Guo et al., 2012). Thus, PU-TiO₂ has good thermal stability in storage and application.

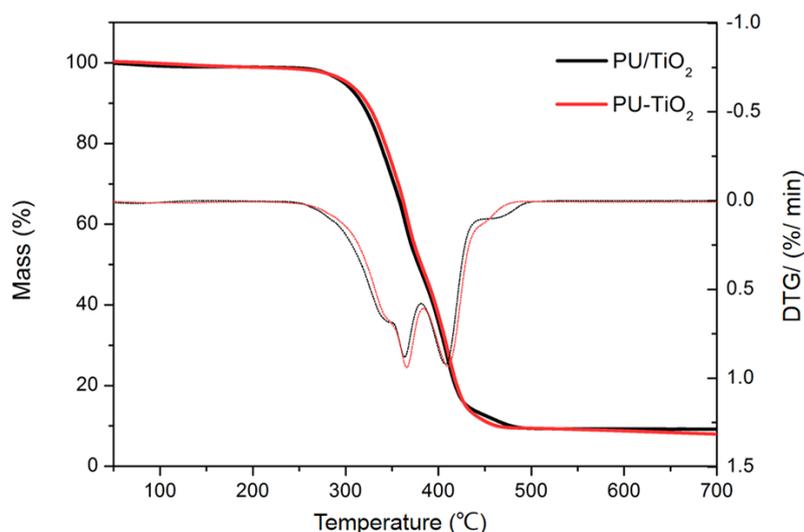


Figure 2. TGA (Full Line) and DTG (Broken Line) Curves of PU/TiO₂ and PU-TiO₂

Table 2. TGA and DTG Results for PU/TiO₂ and PU-TiO₂

Samples	T _{5%} ^a / °C	T _{max1} ^b / °C	T _{max2} ^c / °C
PU/TiO ₂	298.4	381.5	407.6
PU-TiO ₂	300.2	384.1	410.3

^a Temperature at 5 wt% weight loss; ^b Temperature at the max rate of step 2 weight loss; ^c Temperature at the max rate of step 3 weight loss

3.3 Mechanical Properties

In order to explore the effect of TiO₂ on the mechanical properties of polyurethane, tensile tests were conducted. Table 3 listed the tensile strength and elongation at the break of PU, PU-TiO₂s as well as PU/TiO₂s. PU-TiO₂-3 possessed higher tensile strength and elongation at break than pure PU. These enhanced mechanical properties were contributed to the incorporation of nano amino-functionalized TiO₂ particles into polyurethane matrices (Wacharawichanant et al., 2011). NH₂-TiO₂ promoted the crosslinking of polyurethane to some extent. PU-TiO₂-6 presented higher tensile strength but lower elongation at break than PU. Although TiO₂ can enhance the tensile strength of polymers, the intrinsic stiffness of the inorganic fillers inevitably has negative effects on the elongation at break (Tian et al., 2016). Compared to PU-TiO₂-6, PU-TiO₂-9 and PU-TiO₂-12 had inferior tensile strength. On the one hand, the excess mass of inorganic fillers destroyed the integrality of polymer matrices. On the other hand, the higher cross-linking density also restricted polymer chain mobility.

Table 3. Data of Tensile Strength and Elongation at Break

	Tensile strength (MPa)	Elongation at break (%)
PU	3.03±0.21	549.51±13.49
PU-TiO ₂ -3	5.41±0.37	602.39±18.63
PU-TiO ₂ -6	5.39±0.27	266.60±12.43
PU-TiO ₂ -9	2.62±0.11	263.57±15.12
PU-TiO ₂ -12	1.54±0.07	265.33±14.90
PU/TiO ₂ -3	5.25±0.25	542.40±19.31
PU/TiO ₂ -6	5.16±0.29	235.32±14.82
PU/TiO ₂ -9	2.39±0.17	225.74±12.86
PU/TiO ₂ -12	1.42±0.11	228.64±15.24

In general, PU-TiO₂s showed slightly higher tensile strength and elongation at break than that of PU/TiO₂s, in consequence of the enhanced organophilicity by the NH₂-functionalization on the surface of the TiO₂. In theory, the mechanical performances of materials were related to filler distribution (Sabzi et al., 2009). The good compatibility between nanoparticles and polymer molecules were bound to enhance the mechanical properties of polymers. Thereby, SEM images of PU-TiO₂ and PU/TiO₂ were acquired for the distribution of inorganics (Figure 3). As can be seen from Figure 3 (a), TiO₂ was distinctly aggregated. Nevertheless, NH₂-TiO₂ adhered well to the PU matrix and presented an unclear interface, which manifested that the organic part and -NH₂ on the surface of the TiO₂ were able to improve their compatibility with the polymer resin.

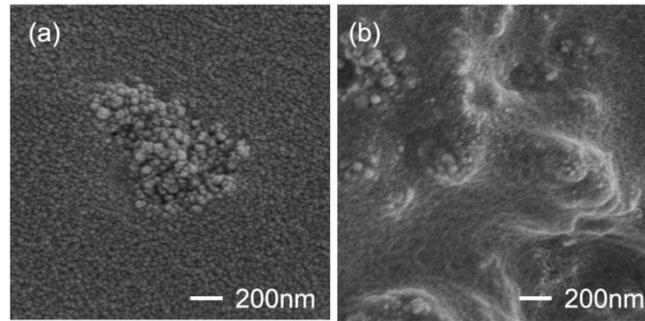


Figure 3. SEM Micrographs of (a) PU/TiO₂; (b) PU-TiO₂

3.4 Degradation of Formaldehyde

Figure 4 (a) shows the formaldehyde photodegradation percentage by PU and PU-TiO₂s under daylight. No obvious photolysis was observed when just the pure PU was used. At the same time, PU-TiO₂s appeared good activity for the degradation of formaldehyde. Additionally, the degradation efficiency increased with the content of TiO₂ in PU increased. After about 240 min, the degradation of formaldehyde reached equilibration.

PU-TiO₂-6 was chosen as a representative sample to investigate the effect of illumination on the degradation efficiency of formaldehyde. Figure 4 (b) compares the formaldehyde photodegradation percentage by PU-TiO₂-6 under different light illumination conditions. It was found that UV irradiation could improve the activity of photodegradation significantly. Particularly, PU-TiO₂-6 exhibited a higher degradation percentage under 365 nm irradiation than that under 298 nm. Energy from 365 nm UV light can induce TiO₂ to produce more electron-hole pairs (Tian et al., 2015). Consequently, more H₂O and O₂ can react with formaldehyde absorbed on the surface, and the catalytic activity was enhanced.

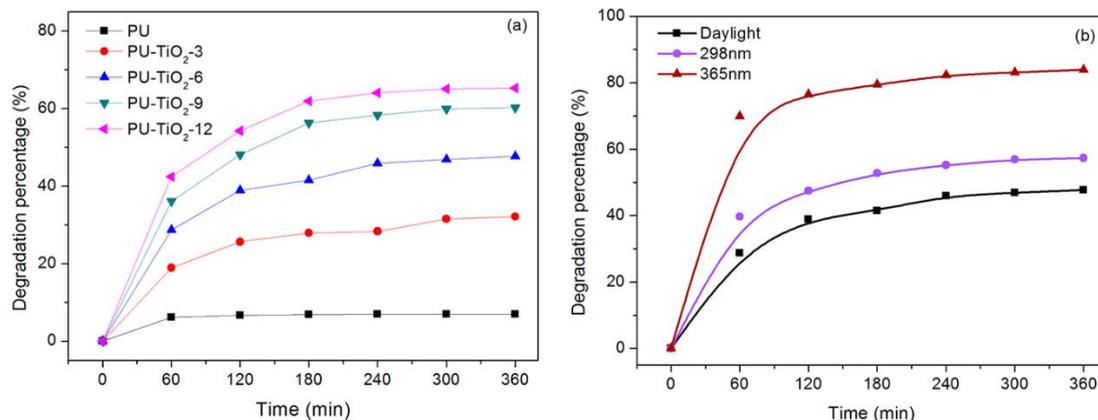


Figure 4 (a). Formaldehyde Photodegradation Percentage by PU and PU-TiO₂s under Daylight; (b) Formaldehyde Photodegradation Percentage by PU-TiO₂-6 under Different Light Illumination Conditions

4. Conclusion

In this study, we prepared a TiO₂/ polyurethane composite (PU- TiO₂) via covalent incorporating of TiO₂, which was amino-functionalized by 3-aminopropyltriethoxysilane. The thermal stability of PU-TiO₂ was slightly higher than that of the blend samples, owing to the crosslinked polymer chains caused by amino groups on the surface of NH₂-TiO₂. Tensile tests and SEM micrographs surely confirmed that NH₂-TiO₂ showed much better compatibility with PU matrix compared with unfunctionalized TiO₂. Besides, PU-TiO₂ presented good activity for the degradation of formaldehyde, especially under the illumination of 365 nm light. The degradation efficiency increased with the increasing content of TiO₂ in PU. The prepared PU-TiO₂ has great potential in coatings to be expected as film-forming materials.

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