Consideration of roles of commercial TiO₂ pigments in aromatic polyurethane coating via the photodegradation of dimethyl toluene-2,4-dicarbamate in non-aqueous solution

Shuolin Zhou · Qiong Xu · Jiafu Xiao · Wenzhou Zhong · Ningya Yu · Steven Robert Kirk · Tao Shu · Dulin Yin

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Abstract Dimethyl toluene-2,4-dicarbamate (2,4-TDC) was selected as a model compound for aromatic polyurethane to investigate the photo-chemical behavior of commercial TiO₂ pigments in non-aqueous solution. The UV–Visible spectrometry analysis results showed that the UV-shielding ability of the rutile TiO₂ pigment was better than that of the anatase TiO₂ pigment. Photodegradation experiments suggested that the photodegradation of 2,4-TDC was retarded by rutile TiO₂ pigment, while accelerated by anatase TiO₂ pigment. With the help of the degradation intermediates during the photodegradation process and calculated data, such as point charges and bond length, the preliminary photodegradation mechanism of 2,4-TDC was also briefly elucidated, including the addition of hydroxyl radicals and the cleavage of the carbamate side chain. Additionally, the photodegradation of 2,4-TDC was used to evaluate the photoreactivity of TiO₂ pigments, this is proved to an efficient approach with potential application in industry.

Keywords Titanium dioxide pigment · Polyurethane · Dimethyl toluene-2,4dicarbamate · Photodegradation · Mechanism

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S. Zhou · Q. Xu (\boxtimes) · J. Xiao · W. Zhong · N. Yu · S. R. Kirk · T. Shu · D. Yin (\boxtimes) National and Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of Resource Fine-Processing and Advanced Materials of Hunan Province and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, People's Republic of China e-mail: xuqiong139@126.com

Introduction

Polyurethane (PU), a polymer connected by the –NHCOO– group, is a well-known coating material which is used in a large variety of commercial and technical applications owing to its excellent adhesion, low temperature flexibility and good chemical, mechanical and physical properties [1, 2]. The aromatic types are, however, very sensitive to exposure to UV light, which greatly affects their optical and mechanical properties and thus restricts the scope of application [3]. In order to suppress degradation and prolong the service life, UV absorbers should be added into the polymer, which can protect the backbone resin against photodegradation reactions.

Inorganic materials have been used as the UV absorbers in PU polymers due to their significant UV-protective properties, the most common of which are TiO₂, ZnO and CeO₂ [4-7]. TiO₂, as a white pigment, is widely used in various applications in our daily life such as paints, coatings and plastics due to its outstanding covering power and UV absorption performance. In recent years, TiO₂ pigment has gradually replaced other materials owing to the higher light scattering and lower cost than other metal oxides, while also being transparent and colorless [8, 9]. TiO₂ is, however, a semiconductor oxide, thus showing photocatalytic activity upon UV radiation absorption, which causes severe damage to most polymers via a photochemical reaction [10-12]. In order to suppress the photoreactivity of titanium dioxide while maintaining its UV-shielding performance, inert oxides such as SiO₂, Al₂O₃, ZrO₂ and CeO₂ have usually been applied as coatings on titanium dioxide surfaces [13-15]. Unfortunately, the photoreactivity of titanium dioxide pigment is still one of the most important influential factors in degradation of coatings [16, 17]. It is therfore necessary to understand the role of TiO₂ pigments in the process of PU degradation.

Previous studies have focused on some physical property of the polymer such as weight loss, discoloration, and gloss retention, for evaluating the performance of titanium dioxide pigments through artificial weathering tests or outdoor exposure tests [18–20]. Changes in these physical properties, however, often take hundreds or thousands of hours to become apparent and also are easily influenced by operating conditions. FT-IR spectroscopy has been used to monitor the evolution of CO_2 during the photodegradation of coating films pigmented with TiO_2 [17, 21]. This method is also somewhat tedious and time-consuming. Furthermore, the abovementioned studies were not readily able to identify the intermediate products and



Fig. 1 Typical structures of aromatic polyurethane and 2,4-TDC model compound

deduce reaction mechanisms. This task can be greatly simplified by using the liquid phase; for example, *n*-hexane was used as reaction medium for its inertness under UV illumination [22].

Dimethyl toluene-2,4-dicarbamate (2,4-TDC) is considered to be an important unit of aromatic PU. The typical chemical structures of PU and 2,4-TDC are shown in Fig. 1, and the photochemistry performance of PU was revealed by that of 2,4-TDC. In this work, 2,4-TDC was chosen as a model compound for aromatic PU, and the photodegradation of 2,4-TDC was investigated in the solution of *n*-hexane. Commercial TiO₂ pigments were used and characterized by UV–Vis spectroscopy and FT-IR spectroscopy. Moreover, the change of concentration of 2,4-TDC was conveniently monitored by HPLC. Based on the identified intermediates and theoretical data, the preliminary degradation mechanism of 2,4-TDC was also elucidated in order to understand the degradation of PU materials containing TiO₂ pigments.

Materials and methods

Chemicals and reagents

The toluene-2,4-diisocyanate (purity >99 %) was obtained from Aladdin Reagent and used as received without further purification. Methanol and tetrahydrofuran (THF) were purchased from Sigma (HPLC grade). Petroleum ether and *n*-hexane were analytical grade reagents. Water used in the laboratory was prepared by a Millipore Milli-Q ultrapure water-purification system. A variety of TiO₂ pigments (P1–P4) with different properties are listed in Table 1.

Synthesis of 2,4-TDC

2,4-TDC was prepared in our laboratory as follows: toluene-2,4-diisocyanate (0.037 mol) was slowly dropped into a three-necked flask which contained 0.075 mol of methanol and 10 ml of petroleum ether at room temperature. There was a drying tube of calcium chloride on the flask to protect against moisture. The resulting product was then recrystallized with ethyl alcohol (95 %) to get the desired product. The purity of 2,4-TDC was 99 % analyzed by HPLC.

TiO₂ pigment characterization

The UV–Vis transmittance spectra of TiO_2 pigments were obtained on a Hitachi U-3010 spectrophotometer with an integrating sphere. The spectra were measured with a scan step of 0.5 nm in the range 200–800 nm with BaSO₄ used as the reference under ambient conditions. The FT-IR spectra of the samples were collected by the KBr pellet technique on a Nicolet 370 Fourier-transform infrared spectrophotometer in the range 500–4,000 cm⁻¹.

TiO ₂ pigment	Composite	Production process	Applications
P1 ^a	TiO ₂ (anatase, >98 %) Al/Si coating	Sulfate process	Paints, fiber, rubber, metallurgy, etc.
P2 ^a	TiO ₂ (rutile, uncoated)	Sulfate process	-
P3 ^a	TiO ₂ (rutile, >92 %) Al/Si coating	Sulfate process	Coatings, rubber, plastic, etc.
P4 ^b	TiO ₂ (rutile, >93 %) Al/Si and organic coating	Chloride process	Coatings, rubber, plastic, etc.

Table 1 Main characterization of commercial TiO₂ pigments

^a Hunan Zhuzhou Chemical

^b DuPont

Irradiation procedures

The experimental device of the photochemical reaction is schematically shown in Fig. 2. The photodegradation of 2,4-TDC was carried out in a quartz reactor (total volume ca. 70 ml) with a rubber stopper to avoid solvent evaporation. The light source was a 300-W medium-pressure mercury lamp ($\lambda_{max} = 365$ nm; Philips) with a double-walled cooling-water jacket housed in one side of the reactor to provide the irradiation. The distance between light source and photo reactor was 22 cm.

Tetrahydrofuran (THF) was used as a co-solvent to enhance solubility of 2,4-TDC in *n*-hexane. A volume of 35 ml of solvent (THF: *n*-hexane = 3:7, ν/ν) solution containing 100 µmol 1⁻¹ of 2,4-TDC was added to the quartz reactor with 35 mg of TiO₂ pigment powder. The suspension was then dispersed by ultrasonic treatment for 5 min. Before exposure to UV radiation, the suspension was stirred in the dark for 30 min. During the photodegradation process about 2 ml of the reaction solution was obtained at regular intervals, centrifuged and filtered through 0.22-µm Millipore membrane filter to remove TiO₂ particles. The initial concentration (*C*₀) and the reaction concentration of 2,4-TDC at reaction time *t* (*C*_t) were analyzed by HPLC. The photodegradation experiments were conducted three times in identical conditions, and the maximum relative error in the measured concentrations was <5 %. All experiments were performed at 298 K.

Analyses

The concentration of 2,4-TDC was monitored by an Agilent 1200 series HPLC equipped with a Venusil XBP C18 column (l = 250 mm, i.d. = 4.6 mm, particles = 5 µm). The mobile phase was composed of 50 % methanol and 50 % water with a flow rate of 0.8 ml min⁻¹. The detection wavelength was 232 nm.

Degradation intermediates were identified by HPLC–MS using a Shimadzu HPLC system with a Venusil XBP C18 column, SIL-HT autosampler, LC-10 AT vacuum pump and API 3000 mass analyzer. HPLC separations were performed at 0.4 ml min⁻¹ and 50 % H₂O and 50 % CH₃OH. An electrospray interface (ESI)



Fig. 2 Schematic diagram of the experimental device

was used for the MS measurements in positive ionization mode and full scan acquisition between m/z 50–300.

Theoretical calculations

Theoretical calculations were carried out using the Gaussian 09 program (Gaussian) with the optimal conformation having a minimum energy obtained at the B3LYP/6-31+G (d, p) level [23]. The point charges (PC) were calculated with the help of natural bond orbital (NBO) to predict the chemisorption position of 2,4-TDC onto the surface of TiO₂ pigment.

Results and discussion

UV-Vis spectra analysis

The UV–Vis spectra of 2,4-TDC and the TiO_2 pigments are shown in Fig. 3. The increase in transmittance in the UV region (280-400 nm) suggests the decrease of UV-shielding ability. The transparency of TiO₂ pigments was about 6-22 % in the region of 280-400 nm due to their absorbance and UV scattering ability, while the transparency of 2,4-TDC solid powder was nearly close to 100 % in the region of 300-400 nm. It can be concluded that TiO₂ pigments have the ability to provide UV protection in the PU coating. The UV-shielding ability of P3 pigment decreased slightly as compared to that of the original P2. This may occur because amorphous Al₂O₃ and SiO₂ on the TiO₂ particles surface can decrease the scattering coefficient, thus decreasing the UV-shielding ability [24]. Additionally, the UV-shielding ability of the rutile TiO_2 pigment was better than that of the anatase TiO_2 pigment because the former absorbed UV light up to 400 nm, while the latter only showed significant absorption up to 380 nm. Importantly, the rutile phase pigment was likely to show much lower apparent photoreactivity than the anatase phase pigment under the UV irradiation [17, 25], suggesting that the rutile-based pigment can be used as stabilizer and effective UV absorber in the polymer coatings.



Fig. 3 UV-Vis spectra of 2,4-TDC and TiO₂ (P1-P4) particles

FT-IR analysis

FT-IR spectroscopy was applied to characterize TiO₂ surface groups. FT-IR spectra of TiO₂ samples are displayed in Fig. 4. The wide peak at 500–800 cm⁻¹ corresponds to the Ti–O–Ti bending mode of TiO₂. All samples except P2 have bands at 1,080 cm⁻¹ and 1,600 cm⁻¹ which are the characteristics of SiO₂ and Al₂O₃, respectively [26]. The broader band at 3,460 cm⁻¹ is attributed to the stretching vibration and bending vibration of hydroxyl groups on TiO₂ [27, 28]. Another peak at 1,630 cm⁻¹ is attributed to the bending vibration of H–O–H on absorbed water [29]. In Fig. 4, it is clearly shown that the hydroxyl groups on TiO₂ pigments surface are abundant. At the beginning of photocatalytic degradation reaction induced by TiO₂ particles, the photogenerated holes (h⁺) would oxidize hydroxyl groups or the water molecules absorbed on TiO₂ surface to ·OH radicals [28]. ·OH radicals are believed to be highly reactive in the decomposition of organic molecules. The TiO₂ particles are therefore likely to participate in the degradation of organic substrate to a certain extent under UV irradiation if the surface of the TiO₂ particles is not coated properly.

Photoreactivity index

Figure 5 shows the typical kinetic curves of photodegradation of 2,4-TDC in the presence of different TiO_2 pigments. It is shown that 2,4-TDC was easily decomposed under UV irradiation in the absence of TiO_2 pigment, while the rutile-based TiO_2 pigments (P2–P4) retarded the photodegradation of 2,4-TDC to various degrees. The results indicated that 2,4-TDC was susceptible to be degraded, which was consistent with the characteristic of PU materials [3, 6, 30]. On the other hand, the rutile TiO_2 pigments can effectively shield and absorb UV light, thus inhibiting



Fig. 4 FT-IR spectra of TiO₂ (P1–P4) particles



Fig. 5 The curves of photodegradation of 2,4-TDC as a function of irradiation time in the presence of P4 (*filled square*), P3 (*filled circle*), P2 (*filled triangle*), no TiO₂ pigments (*inverted triangle*), P1 (*filled diamond*). Reaction conditions: initial concentration of 2,4-TDC, 100 μ mol l⁻¹; TiO₂ pigment dosage, 1.0 g l⁻¹; THF: *n*-hexane = 3:7 (*v*/*v*)

or reducing the degradation rate of 2,4-TDC. Furthermore, the rutile-based TiO₂ pigments coated by inert inorganic oxides (usually SiO₂ and Al₂O₃) showed more a significant inhibitory effect on the degradation of 2,4-TDC compared with naked rutile titanium dioxide. The reason for this phenomenon is that silica oxide and alumina oxide on the TiO₂ surface can further prevent the adsorbed organic moieties interacting with photoactive species. On the contrary, it is observed that the degradation rate of 2,4-TDC was enhanced in the solvent system of THF and *n*-hexane after 90 min irradiation using 1.0 g 1^{-1} of TiO₂ pigment P1. This indicated

TiO ₂ pigment	First order rate constant (min ⁻¹)	Standard deviation values R	Photoreactivity index (%)
_	0.0260	0.9998	_
P1	0.0391	0.9962	100
P2	0.0205	0.9966	52.4
P3	0.0164	0.9988	41.9
P4	0.0098	0.9941	25.1

Table 2 The photodegradation rate of 2,4-TDC using different commercial TiO₂ pigments

that the TiO_2 pigment P1, in the form of anatase, has a significant photoreactivity under UV irradiation in spite of the surface treatment. Compared with the results obtained from P1 and P3, it can be deduced that the crystal form of TiO_2 was a predominant factor affecting its photoreactivity.

The photodegradation of 2,4-TDC follows a pseudo-first-order kinetic equation, which is confirmed by the linear behavior of $-\ln(C_t/C_0)$ as a function of irradiation time, as shown in Fig. S1. The kinetic parameters are listed in Table 2. The degradation rates can be used to compare the photoreactivity of TiO₂ pigments. The TiO₂ pigment P4 was found to give the lowest rate of degradation, suggesting that appropriate inorganic coating in combination with organic surface treatment can effectively reduce the photoreactivity of titanium dioxide particles to an extremely low level. Moreover, the photoreactivity of the commercial TiO₂ pigments decreases in the order P1 > P3 > P4 which correlates with the corresponding increasing order of their UV-shielding ability. From these results, it can be seen that the rutile TiO₂ pigment can act as a UV stabilizer, whereas the anatase TiO₂ pigment (P1) operates primarily as a photosensitiser.

Photodegradation mechanism

In order to understand the degradation of PU coatings containing TiO₂ pigment under outdoor exposure, the photodegradation mechanism of 2,4-TDC was also elucidated by HPLC–MS combined with theoretical calculation of PC and bond length [31, 32]. The experiments were conducted using 100 μ mol l⁻¹ solutions of the parent compounds in the presence of TiO₂ pigment P1 under UV light irradiation, and the main degradation intermediates were identified. Six degradation intermediates were detected during the photodegradation process. The total ion chromatogram of the degradation products and their corresponding mass spectra are given in Figs. S2 and S3, respectively. The molecular ions and corresponding molecular structures are listed in Table 3.

The degradation intermediate (I) with m/z = 209 may be attributed to the loss of $-OCH_3$ from the carbamate group of the side chain. The degradation intermediate (II) with m/z = 151 may be generated from (I) by further loss of $-COOCH_3$ during the photodegradation process. The species with m/z = 253, labeled as intermediate (III), may be attributed to the oxidation of methyl group on the aromatic ring. The degradation intermediate (IV) with m/z = 256 was found, corresponding to addition

Compound	Retention time (min)	EI-MS ([M+H] ⁺)	Chemical formula
I	40.21	209	
Π	5.51	151	HN-CH
III	3.84	253	
IV	29.30	255	
V	7.04	197	
VI	7.50	139	
			OH

of 16 mass units to the parent molecule, which may be attributed to a monohydroxylated intermediate. In addition, intermediates (V) and (VI) may originate from the intermediate (IV) that loses one and two $-COOCH_3$ fragments during the photodegradation process, respectively. Wang et al. [33] have proposed a mechanism of the photochemical degradation of PU included the re-reactions of radical groups formed in the scission reactions. However, the degradation intermediates formed from the re-reactions of radical groups was not detected in our work, probably due to their low concentrations.

TiO₂ was stimulated under UV light irradiation at a wavelength of 365 nm to generate photoholes, which would immediately attack the parent molecule that absorbed on the TiO₂ pigment surface [34, 35]. The exact structures of the degradation intermediates, however, remain unconfirmed. The theoretical atomic PC of 2,4-TDC were therefore computed to explain the chemisorption pattern onto the TiO₂ pigment, and the corresponding data are listed in Table 4, from which it can be seen that the relatively more negative PC were found at C8 (-0.724), N7 (-0.655) and O11 (-0.652), while a more positive charge was found at C10 (0.934). The results indicated that the methyl group and its adjacent side chain (NHCOOCH₃) on the aromatic ring are the most likely to be adsorbed onto the TiO₂ surface and attacked by photoholes [31, 36]. As illustrated in Fig. 6, at the initial photodegradation stage, the intermediate (I) may be generated through the scission of C–O bond by direct UV photolysis, or h⁺ attack, or their combination on the TiO₂ pigment surface. Subsequently, the intermediate (II) may also result from

Table 4 Point charges and bond length on atoms of 2,4-TDC at the B3LYP/6-31+G(d, p) level



Atom label	Point charges	Bond	Bond length
C1	-0.294	C1–C2	1.4047
C2	0.166	C2–C3	1.3986
C3	-0.286	C3–C4	1.3959
C4	-0.207	C4–C5	1.3951
C5	-0.089	C5-C6	1.4170
C6	0.174	C6-C1	1.3974
N7	-0.655	N7-C6	1.4135
C8	-0.724	C8–C5	1.5110
N9	-0.652	N9-C2	1.4133
C10	0.934	C10-N7	1.3758
011	-0.652	O11-C10	1.2211
012	-0.574	O12-C10	1.3504
C13	-0.338	C13-O12	1.4426
C14	0.932	C14-N9	1.3739
015	-0.655	O15-C14	1.2216
016	-0.572	O14–O16	1.3504
C17	-0.337	O16-C17	1.4414

the cleavage of the carbamate bond (C-N) in a similar way. These two types of scissions were consistent with previously reported results [33, 37]. The presence of hydroxyl groups and adsorbed water molecules on the surface of TiO₂ particles (Fig. 4) suggests that TiO₂ particles may be stimulated by absorbing UV light to generate OH radicals. Firstly, OH radicals (oxidation potential: 2.8 V) are stronger oxidants which can oxidize organics by the abstraction of protons generating organic radicals (\mathbf{R}), which can be further oxidized. Accordingly, we assume that the intermediate (III) may be attributed to the oxidation of methyl on the aromatic ring during the photocatalytic degradation process, because it was not found under UV irradiation without TiO₂ pigment. Moreover, the C8–C5 bond (1.5510 Å; see Table 4) is longer than the other C-C bonds (ca. 1.4 Å), which indicates that this bond may be weaker than other C-C bonds. As a result, the methyl group on the aromatic ring seems more easily removed in the subsequent reaction. Secondly, OH radicals exhibited a high activity and can indirectly react with the parent molecular in addition reactions. 2,4-TDC may undergo addition of a hydroxyl radical to give a hydroxyl added intermediate (IV). This species may then undergo a stepwise scission under these reaction conditions to give the observed hydroxylation



Fig. 6 Proposed pathways of photodegradation of 2,4-TDC

intermediates (V and VI). These results indicate that ·OH plays an important and decisive role in the photocatalytic process.

Based on the results of the present study, a possible degradation pathway involving the direct photolysis and photocatalysis degradation of 2,4-TDC in the presence of anatase TiO_2 pigment is proposed in Fig. 6. This synergistic effect causes 2,4-TDC to degrade more easily. It is therefore believed that the aromatic PU containing highly photoreactive anatase TiO_2 particles will possess a series of unfavorable properties, such as surface gloss loss, color change, chalking, and cracking.

Conclusions

In summary, a simple method was developed to assess the photoreactivity of TiO_2 pigments in non-aqueous solution, which in turn has implications for the application performance of TiO_2 pigments in PU coatings. The rutile TiO_2 pigment, along with high UV opacity and low photoreactivity as a UV stabilizer, retards the photodegradation of 2,4-TDC, whereas anatase TiO_2 pigment operates primarily as an effective photocatalyst for accelerating the rate of photodegradation. On the basis of the intermediates identified, the mechanism of photodegradation of 2,4-TDC was proposed, thus giving important insight into the possible pathways of photodegradation of aromatic PU coatings containing high-active TiO_2 particles.

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