

Surface Organic Modification of Titanium Dioxide Fine Particles Through Photo Polymerization

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ABSTRACT: C=C unsaturated groups were chemically inserted onto TiO₂ particles surfaces through chemical reaction of hydroxyl group on the TiO₂ fine particle surface with 2,4-diisocyanatotoluene (TDI) first, and then with 2-hydroxyethyl acrylate (HEA). Finally, TiO₂ fine particles with surface organic modification were made through the free radical copolymerization reaction with *n*-butyl acrylate (BA) monomer under UV irradiation. The structure and properties of unmodified and modified TiO₂ were studied by FT-IR, XPS, TGA, TEM, lipophilic rates, and adhesion properties tests. The results show that the surface of TiO₂ has been successfully introduced with the organic chains through chemical bonding linkage; the surface lipophilic rates of TiO₂ particles

are increased. The dispersion and compatibility of the modified TiO₂ particles in a commercial ink 508C resin greatly improve as compared with that of unmodified TiO₂, and agglomeration of particles obviously reduces. The adhesion strength between the white printing ink made from the modified TiO₂ particles and BOPP is much better than that from the unmodified TiO₂. When the organic rate reached 24.93%, the adhesion strength reaches Grade I. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5286–5292, 2012

Key words: TiO₂ fine particles; 2,4-diisocyanatotoluene; 2-hydroxyethyl acrylate; surface modification; UV-induced polymerization

INTRODUCTION

Titanium dioxide (TiO₂) fine particles with a unique color effect, UV-shielding characteristic, and excellent chemical and thermal stabilities are commonly used in paints and inks based on polymer resin matrix.^{1–4} However, the interfacial interactions between TiO₂ particles and most polymer matrices are poor because of its considerable great surface area and surface energy, so TiO₂ particle is difficult to disperse into polymer matrix during paints and inks preparation, and tends to clump and agglomerate.^{5,6}

Organic modification to TiO₂ surface is a kind of effective way to reduce its surface energy and to improve its dispersion properties in polymer matrices. Enis et al. coated TiO₂ surface with PMMA through *in situ* polymerization of methyl methacrylate (MMA) in toluene solvent initiated by azobisisobutyronitrile (AIBN).⁷ Qiu et al. coated TiO₂ surface with polystyrene (PS) by dispersion polymerization reaction.⁸ However, the polymer components onto TiO₂ surface as above connected with particle surface only by physical force. So they easily disintegrate and shed from the TiO₂ surface during the fur-

ther use under surrounding of shear stress and solvent. Li and Zhu modified the surface of TiO₂ by oleic acid.⁹ Tada et al. prepared surface-grafted TiO₂ with polydimethylsiloxane (PDMS).¹⁰ However, the surface organic rates are relatively low by the above ways, so the compatibility between TiO₂ and polymer matrix can not be improved very well.

In this study, an effective method to realize high organic rates onto TiO₂ particle surface through surface photografting has been reported. First, carbon-carbon unsaturated double bond functional groups (C=C) are covalently inserted onto the TiO₂ surface by chemical reaction, then polymerization reaction is initiated through UV light. This article also explores the application of surface organic modified TiO₂ in ink preparation.

EXPERIMENTAL

Materials

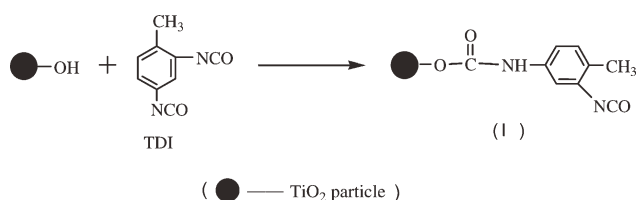
TiO₂ (rutile type), produced by Panzhihua Research Institute in China, was purified at 110°C about 12 h in oven to remove surface water and organic impurities. Alcohol-soluble polyacrylate ink resin (508C, 50% ethanol solution) is produced by Sichuan Center Polymer Materials in China. Biaxially-oriented polypropylene (BOPP) film with single-sided electric spark processing is a commercial products. Acrylic

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hydroxyl (HEA), 2,4-toluene diisocyanate (2,4-TDI), dibutyltin dilaurate (DBTDL), petroleum ether, *p*-benzoquinone, benzoin dimethyl ether, and acetone are analytic quality reagent.

Preparation of surface-modified TiO₂ with TDI (TiO₂-TDI)

About 5.000 g TiO₂ and 100 mL petroleum ether (dried by anhydrous MgSO₄) were added into a 250-mL flask assembled with mechanical agitator (stirring rate: 200 rpm), centigrade thermometer, and reflux condenser. After the mixture was dispersed by ultrasonic dispersion analyzer, a set amount of TDI dissolved with 25 mL petroleum ether and DBTDL (DBTDL/TDI: 1/100 by weight) was added. The reaction was taken under stirring at a set temperature for a given time. The filtrated part of reaction production was thoroughly washed at least two times with petroleum ether, and then extracted with acetone for 12 h in a Soxhlet apparatus to remove the residual TDI and other impurities, at last dried to constant weight in a vacuum oven at 45°C. The surface organic rates can be calculated according to the TiO₂ weight changes of before and after reaction. The 2,4-TDI has two functional NCO groups with one in ortho (-2) and the other in para (-4) positions of methyl group. As the result of the steric effect of methyl group, the reaction rate at 25°C was determined as $k_{\text{para}} = 262$, $k_{\text{ortho}} = 25$, respectively.¹¹ In the other words, the NCO group in the para position is far more reactive than that in the ortho position. Therefore, in excess TiO₂ the reaction was always considered to occur at the para position. Equation (1) is as follows:



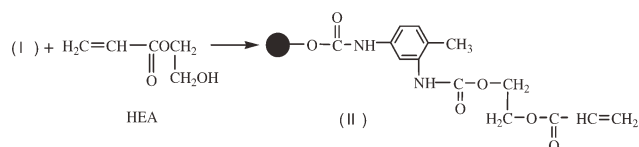
Equation 1 Reaction of hydroxyl in the surface of TiO₂ with para-NCO.

The optimum reaction conditions determined by orthogonal experimental method: reaction time at 6 h, reaction temperature at 60°C, the molar ratio of TDI and TiO₂ at 0.4 : 1, ultrasonic dispersion time at 10 min. Under above condition three times parallel experiment results show that: the average surface organic rate is 9.26%.

Preparation of surface-modified TiO₂-TDI particles with HEA (TiO₂-TDI-HEA)

TiO₂-TDI with the surface organic rates at 9.26% prepared as above, 100 mL petroleum ether (dried by

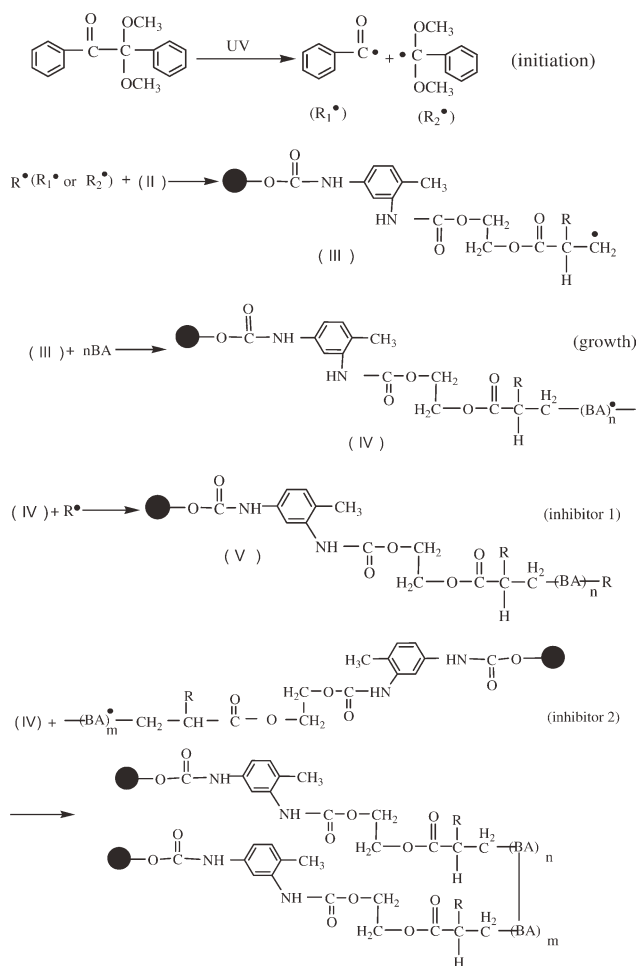
anhydrous MgSO₄), were placed into a 250-mL flask assembled with mechanical agitator (stirring rate: 200 rpm), centigrade thermometer, and reflux condenser. After the mixture was dispersed by ultrasonic dispersion analyzer about 30 min, a set amount of HEA, DBTDL (DBTDL/HEA : 1/100 by weight), and 1,4-benzoquinone (1,4-benzoquinone/HEA : 1/100 by weight) was added. The reaction was taken under stirring at 30°C about 12 h. The filtrated part of reaction production was thoroughly washed at least two times with petroleum ether, and then extracted with acetone for 24 h in a Soxhlet apparatus to remove the residual HEA and other impurities, at last dried to constant weight in a vacuum oven at 45°C. So TiO₂-TDI-HEA particles were obtained, and carbon-carbon unsaturated double bond functional groups (C=C) were covalently inserted onto the TiO₂ surface. Its organic rates (HEA/TiO₂-TDI: 0.20 : 1 by weight) was increased to 15.03% from 9.28%. The chemical reaction in this step can be described as follows:



Equation 2 Reaction of the residual ortho-NCO group of TiO₂-TDI with HEA.

Preparation of surface-grafted TiO₂ with BA monomer initiated by UV light (TiO₂-TDI-HEA-PBA)

A set amounts of BA monomers and benzoin dimethyl ether (benzoin dimethyl ether/BA: 3/100 by weight) as photosensitizers were dissolved in ethanol (BA/ethanol: 0.3, 0.4, and 0.5 g mL⁻¹) to form reaction solution, then homogeneously mixed with 0.100 g TiO₂-TDI-HEA with organic rates 15.03%. The mixture was poured into a culture dish, and vibrating the dish until the mixture was evenly spread in dish bottom, then the dish was sealed with LDPE film and placed into a UV irradiation device designed in our laboratory.¹² The dish was placed 20-cm away from the Ga-I UV lamp with a power of 500 W. After graft-polymerization reaction was carried out for a given time by UV irradiation, the filtrated part of reaction production was thoroughly washed at least two times with anhydrous alcohol, then extracted with anhydrous alcohol for 24 h in a Soxhlet apparatus to remove the residual BA, its homopolymer (PBA), and other impurities, at last dried to a constant weight at 45°C under a vacuum oven to obtain the purified TiO₂-TDI-HEA-PBA. Its graft rate is 9.80%, while total organic rate is 24.93% (BA/ethanol: 0.5 g mL⁻¹, irradiation time at 40 min). The photografting reactions take place as free radical polymerization and can be described as eq. (3):



Equation 3 Free-radical polymerization reaction of TiO_2 -TDI-HEA with butyl acrylate.

Preparation of four kinds of white ink for plastic printing

A 12.5 g TiO_2 , TiO_2 -TDI, TiO_2 -TDI-HEA, and TiO_2 -TDI-HEA-PBA was respectively, mixed with 30.0 g 508C resins and 150.0 g ethanol as diluents, then high-speed dispersing to form the homogeneous mixture, namely white ink for plastic printing. BOPP membrane surface treated by electrical discharge was respectively, printed by four kinds of white ink prepared as above for further tests.

CHARACTERIZATIONS

If no specific notes, all samples used as the further tests were TiO_2 -TDI with organic rates at 9.28%, TiO_2 -TDI-HEA with organic rates at 15.03%, and TiO_2 -TDI-HEA-PBA with organic rates at 24.93%.

The organic rate measurement

The organic rate or graft rate was calculated by the following equation:

$$G = \frac{W_2 - W_1}{W_1} \times 100\%$$

G —the organic rate or the graft rate, wt%

W_1, W_2 —the weights of the TiO_2 particles before and after modified, g

Equation 4 The organic rate or the graft rate.

FT-IR spectrum analysis

FT-IR spectra were taken as a KBr pellets with Nicolet NICOLET 170-SX Fourier Transform Infrared Spectrometer made in USA.

X-ray photoelectron spectroscopy (XPS) characterization

XPS was obtained on a Kratos Xsam 800 spectrometer, using a monochromatic Al $K\alpha$ photo source.

Thermogravimetric analysis (TGA) characterization

TGA measurements were conducted in TA Q600 Thermal Analysis instrument at a heating rate $20,000^\circ\text{C min}^{-1}$. All samples were heated from equilibrium temperature at 30 – 500°C .

Transmission electron microscopy (TEM) observation

The dispersion of TiO_2 particles before and after modified in printing ink solution was observed by a transmission electron microscopy (TEM) using JSM-100CX made in Japan. All surfaces were coated with a thin layer of silver before scanning electron microscopy (SEM) examination.

Lipophilic test

A 0.100 g TiO_2 , TiO_2 -TDI, TiO_2 -TDI-HEA, TiO_2 -TDI-HEA-PBA was respectively, put in four cylinders containing 50 mL distilled water in each one.^{13,14} Then the methanol was slowly added into above cylinders, respectively, until all floating powers were sunk down the bottom of the cylinders and recorded different amount of adding methanol in mL, so lipophilic rate could be calculated as followed:

$$\text{Lipophilic degree} = \frac{a}{a + 50} \times 100\%$$

a — amount of adding methanol in mL

Equation 5 Lipophilic rates of TiO_2 before and after modified.

Adhesive strength test between ink and BOPP film

Adhesive strength test was determined according to GB9286-88 (China).

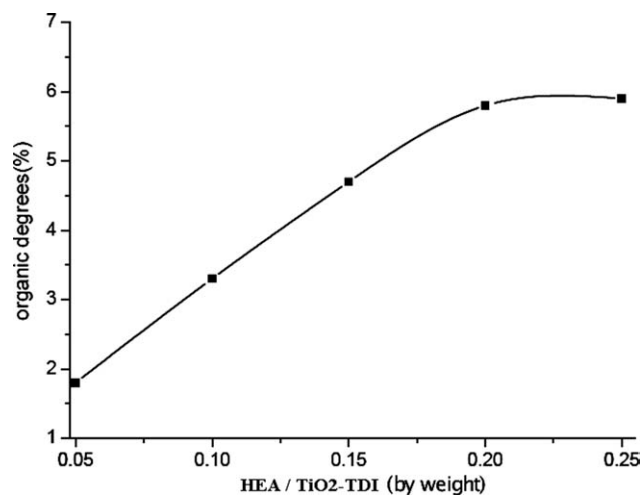


Figure 1 Effect of HEA/TiO₂-TDI (by weight) on organic rates.

RESULTS AND DISCUSSION

The effect of HEA content on organic rate of TiO₂-TDI-HEA

TiO₂-TDI-HEA was prepared by the reaction of TiO₂-TDI (the organic rate at 9.28%) with HEA. Figure 1 shows that the organic rate onto the surface of TiO₂-TDI initial increases with the charge ratio of HEA/TiO₂-TDI, and then tends to level off at the charge ratio about 0.2. That can be explained as the followed theoretical calculation: it is supposed that all TDI connected on TiO₂-TDI surface by chemical bond is generated from para-NCO groups reacting with TDI [shown as Eq. (1)],¹¹ while all TiO₂-TDI-HEA is from the *ortho*-NCO groups of TiO₂-TDI with HEA [shown as Eq. (2)]. TiO₂-TDI with the organic rate at 9.28% has 0.53×10^{-3} mol TDI per gram, in turn theoretical weight reacted with HEA on the surface of TiO₂-TDI-HEA should be 62.0 mg (0.53×10^{-3} mol \times 116.14 \times 10³ mg mol⁻¹). From Figure 1 the organic rate onto

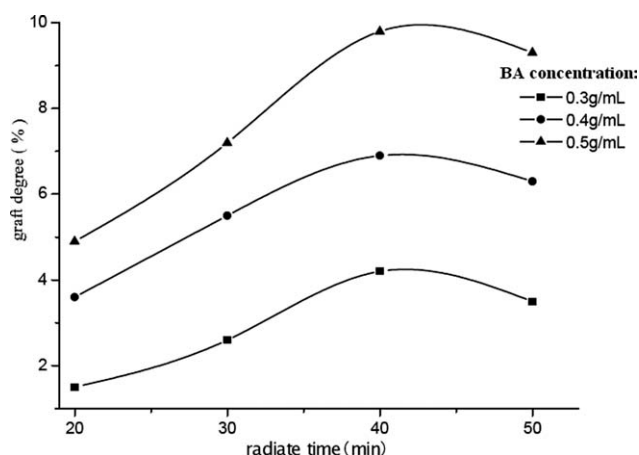


Figure 2 Effect of radiation time and BA concentration on graft rate.

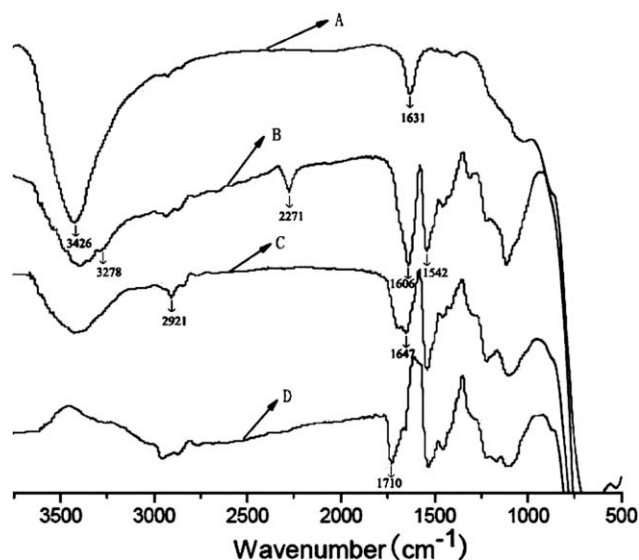


Figure 3 FT-IR spectra of TiO₂ (A), TiO₂-TDI (B), TiO₂-TDI-HEA (C), and TiO₂-TDI-HEA-PBA (D).

the surface of TiO₂-TDI is 5.75% when the charge ratio of HEA/TiO₂-TDI is 0.20, in other word the weight of HEA on TiO₂-TDI surface in per gram is theoretically 57.5 mg, which is corresponded to the theoretical calculation value of 62.0 mg. After that, almost all -NCO groups onto TiO₂ surface had been consumed by the reaction with HEA, so further increase in the charge ratio no more effects the organic rate as shown in Figure 1.

The effect of irradiation time and BA concentration on the graft rate

Figure 2 shows that the graft rate of BA onto TiO₂-TDI-HEA surface initially increases with irradiation time and reaches a maximum after 40 min, then decreases as irradiation time further increases. This may be due to the degradation of the grafted PBA onto the TiO₂-TDI-HEA surface with long time as exposure under UV irradiation. From Figure 2 we can also see that graft rate increases with BA concentration under same irradiation time. When BA concentration is 0.5 g mL⁻¹ (BA/ethanol), graft rate of BA can reach 9.80% (the total organic rate is 24.93%) at irradiation time 40 min.

FTIR spectra

FT-IR spectra of TiO₂ [Curve (A)], TiO₂-TDI [Curve(B)], TiO₂-TDI-HEA [Curve 3(C)], and TiO₂-TDI-

TABLE I
The Relative Strength of Carbonyl Group in the Different Irradiation Time

Irradiation time (min)	0	20	30	40	50
$A_{C=O}/A_{Ti}$	0.089	0.125	0.184	0.220	0.190

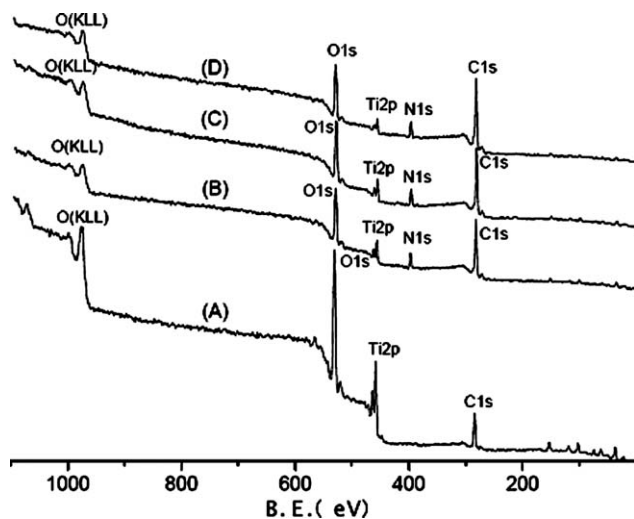


Figure 4 XPS spectra of TiO_2 (A), TiO_2 -TDI (B), TiO_2 -TDI-HEA (C), and TiO_2 -TDI-HEA-PBA (D).

HEA-PBA [Curve (D)] are given in Figure 3, in which Curve (A) shows $-\text{OH}$ absorption peak at $\sim 3426 \text{ cm}^{-1}$ and the peak of bound water on TiO_2 surface at 1631 cm^{-1} .¹⁵ Compared with Curve (A), peak strength at $\sim 3426 \text{ cm}^{-1}$ in curve (B) reduces due to the fact that strong active $-\text{OH}$ group on

TABLE II
Elements Contents on the Surfaces of TiO_2 , TiO_2 -TDI, TiO_2 -TDI-HEA, and TiO_2 -TDI-HEA-PBA

Particle	C (%)	O (%)	Ti (%)	N (%)
TiO_2	30.25	59.43	10.31	0
TiO_2 -TDI	64.23	22.70	4.25	8.81
TiO_2 -TDI-HEA	66.89	20.93	3.48	8.71
TiO_2 -TDI-HEA-PBA	69.24	20.32	2.09	8.35

TiO_2 surface has reacted with $-\text{NCO}$ group in TDI [Eq. (1)]. Some new absorption peaks can be respectively, observed such as antisymmetric stretching vibration peak of ortho- NCO in TDI at ~ 2271 ,¹⁶ stretching vibration peaks of $-\text{NH}-$ at ~ 3278 and $\sim 1302 \text{ cm}^{-1}$, characteristic peaks of benzene at $\sim 1606, 1542 \text{ cm}^{-1}$ in Curve (B), indicating that TDI has been inserted on the TiO_2 surface by chemical bonding linkage. As compared with Curve (B), the peak at $\sim 2271 \text{ cm}^{-1}$ disappears in Curve (C), indicating that the $-\text{NCO}$ in TiO_2 -TDI had completely reacted with HEA, and new functional groups can be observed respectively, such as $\text{C}=\text{C}$ stretching vibration peak at $\sim 1647 \text{ cm}^{-1}$, showing that the carbon-carbon unsaturated $\text{C}=\text{C}$ groups has been successfully introduced onto the particles surface

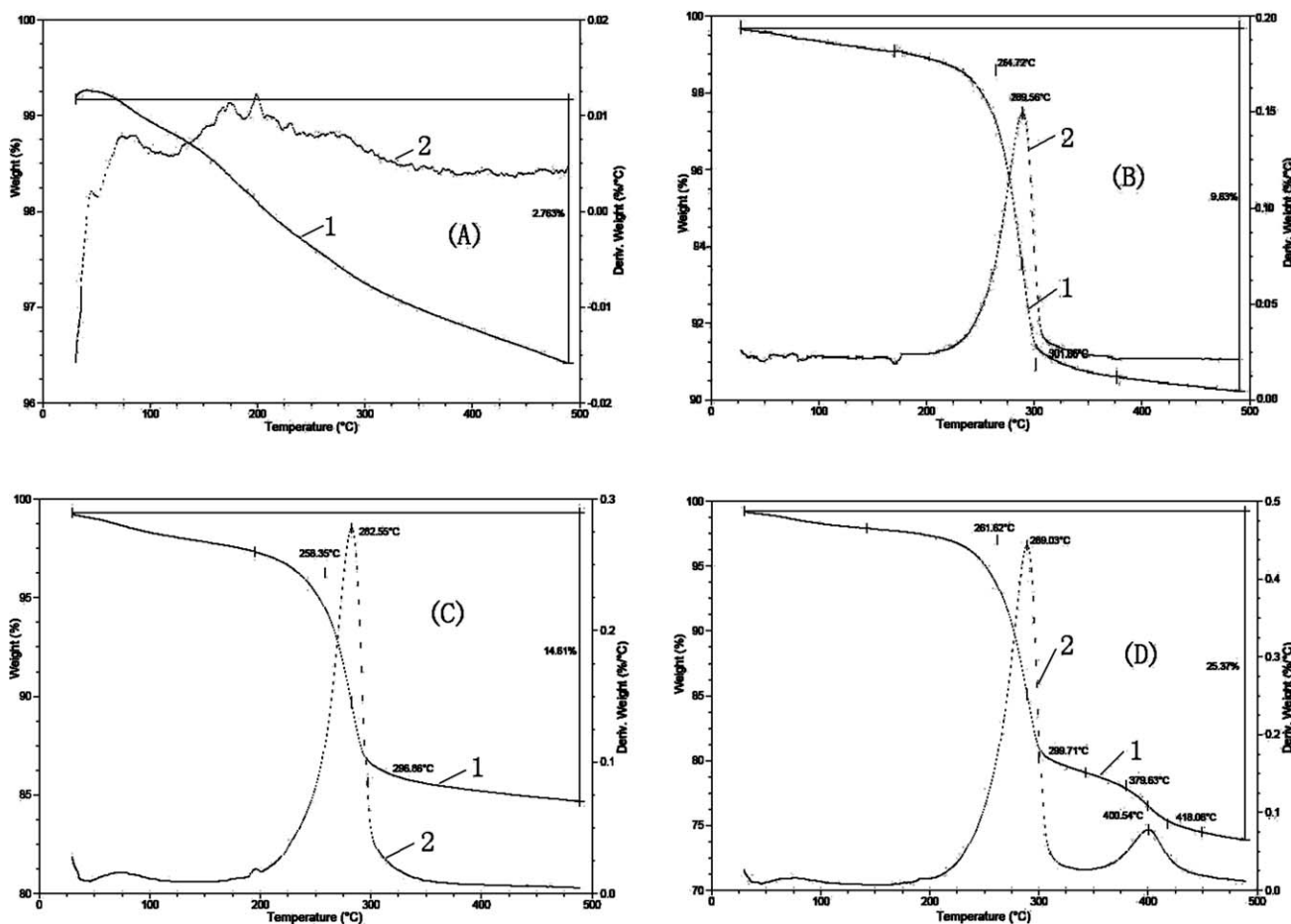


Figure 5 TGA curves of TiO_2 (A), TiO_2 -TDI (B), TiO_2 -TDI-HEA (C), and TiO_2 -TDI-HEA-PBA (D).

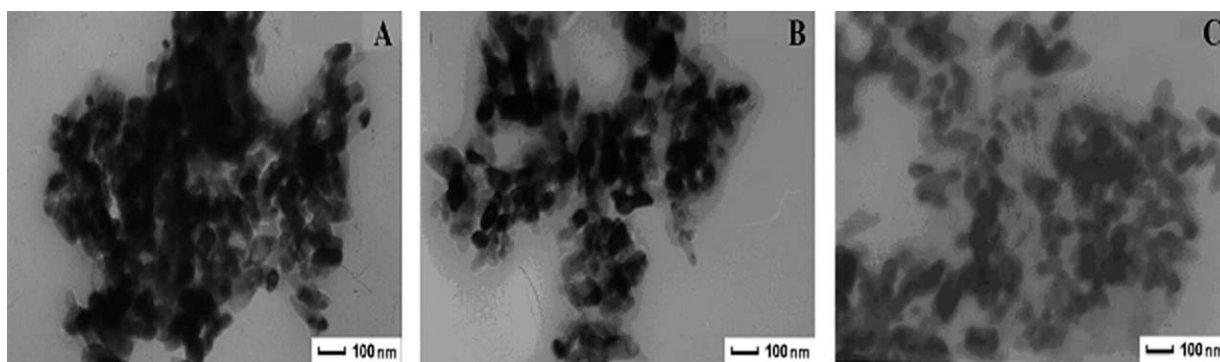


Figure 6 TEM images of white printing ink prepared from TiO₂ (A), TiO₂-TDI-HEA (B), and TiO₂-TDI-HEA-PBA (C) based on 508C resin.

[Eq. (2)]. As compared with Curve (C), the C—H stretching vibration peak at $\sim 2921\text{ cm}^{-1}$ and C=O peak at $\sim 1710\text{ cm}^{-1}$ increase, however, C=C peak reduces in Curve (D), showing that C=C groups have taken part in polymerization reaction with BA monomer initiated by UV light [Eq. (3)]. PBA has formed and covered onto the particles surface by chemical bonds linkage, which can not be removed by the used purification. In conclusion, TDI, HEA, and BA have in turn taken place in chemical reaction and introduced onto TiO₂ surface.

The peak area ratio of C=O group ($\sim 1710\text{ cm}^{-1}$) $A_{\text{C=O}}$ and TiO₂ ($\sim 680\text{ cm}^{-1}$) A_{Ti} on FT-IR spectra of TiO₂-TDI-HEA-PBA prepared under different irradiation time can imply the graft degree. The bigger the ratio is, the more the graft rate is. The data of $A_{\text{C=O}}/A_{\text{Ti}}$ are listed in Table I, in which the graft rate of BA initially increases with irradiation time and reaches a maximum at 40 min, then decreases as irradiation time further increases, corresponding with the test results mentioned in Figure 2.

XPS

Figure 4 shows the XPS of TiO₂ [Curve (A)], TiO₂-TDI [Curve (B)], TiO₂-TDI-HEA [Curve 3(C)], and TiO₂-TDI-HEA-PBA [Curve (D)]. The element contents in percentage on the surfaces of these particles tested are listed in Table II. Figure 4 and Table II show that the contents of C element on the particles surface increase after modified, while the contents of O element and Ti element decrease. This is due to the fact that the original part of O element and Ti element on the TiO₂ particles surfaces have been covered by the organic chain generated on the sur-

face during modifying. Compared Curve (A), a new N element peak can be observed on curve (B), confirming that —NCO group of TDI has reacted with hydroxyl group onto the TiO₂ surface [Eq. (1)]. The N peak strength reduce with the organic modification step by step from Curve (B) to Curve (C), that is because N peak from TDI and —NHCOO— group, has been further covered by HEA and PBA [Eqs. (2) and (3)]. C1s (284.8ev) of raw materials may be caused by the pollution.

TGA curves

Figure 5 shows that TGA curves of TiO₂ [Curve (A)], TiO₂-TDI [Curve (B)], TiO₂-TDI-HEA [Curve 3(C)], and TiO₂-TDI-HEA-PBA [Curve (D)]. In Curve (A), the weight loss rate is 2.76% due to the fact that the fine TiO₂ particle surface might be polluted, or absorb water in air. In Curve (B), the weight loss rate is 9.63%, which might be ascribed to the decomposition¹⁶ of TDI chemically inserted onto TiO₂ particle surface, essentially consistent to the organic rate of TiO₂-TDI (9.28%). In Curve (C), the weight loss rate of TiO₂-TDI-HEA is 14.61%, similar to the organic rate of TiO₂-TDI-HEA at 15.03%. The initial maximum degradation temperature at 258.35°C in Curve (C), lower than that at 264.72°C in Curve (B). In Curve (D), the total weight loss rate of TiO₂-TDI-HEA-PBA is 25.37%, coinciding with the total organic rate onto TiO₂-TDI-HEA-PBA shown as above (24.93%).

TEM observation

Dispersion of fillers in a polymer matrix has significant effects on the properties such as adhesive

TABLE III
Oleophilic Rates of Unmodified TiO₂ and Modified TiO₂ Samples

Sample	TiO ₂	TiO ₂ -TDI	TiO ₂ -TDI-HEA	TiO ₂ -TDI-HEA-PBA
Organic rate (%)	0	9.28	15.03	24.93
Methanol consumption (mL)	0	7.4	9.5	15.4
Oleophilic rates (%)	0	12.89	15.97	23.55

TABLE IV
Adhesion Strength of Various White Printing Inks onto BOPP Film

White printing ink prepared with various TiO ₂	TiO ₂	TiO ₂ -TDI-HEA	TiO ₂ -TDI-HEA-PBA	
Organic rate (%)	0	15.03	21.93	24.93
Scratching lattice level	IV	III	II	I

properties, mechanical properties, shielding action, and so on. However dispersion of inorganic fillers in polymer is not an easy process because of weak interfacial interaction between polymer matrix and fillers, in other words inorganic fillers have a strong tendency to self-agglomerate. Figure 6 shows TEM images of white ink prepared by mixing TiO₂ [Image (A)], TiO₂-TDI-HEA [Image (B)], and TiO₂-TDI-HEA-PBA [Image (C)] with a commercial ink resin named 508C. We can see that most raw TiO₂ particles seriously agglomerate in Image (A), while self-agglomerate tendency reduce in Image (B), owing to that the modified particle surface has been chemically inserted organic components and can increase the interaction between TiO₂ and polymer matrix. From Image (C), it can be inferred that TiO₂-TDI-HEA-PBA particles are uniformly dispersed in the 508C matrix because the composition of TiO₂ surface grafted PBA is similar with that of ink resin, in turn the interfacial interactions with 508C resin further greatly increased. Hence, the modified TiO₂ has the potential application in ink fields.

Lipophilic rate

Table III shows methanol consumption with different TiO₂ sample and corresponding oleophilic rates calculated by Eq. (5). We can see that unmodified TiO₂ is completely hydrophilic as well as water-wetting into the bottom without methanol, while modified TiO₂ can all be wetted with water by adding methanol, and methanol consumption volume needs to be increased with organic rate. The results confirm that TiO₂ particles after surface-organic modified have a changing trend from hydrophilic to hydrophobic particles due to the fact that TiO₂ surface coated organic chains after modification.

Adhesion properties

Three kinds of white printing ink have been prepared by respectively, mixing various TiO₂ with 508C resin as matrix and ethanol as diluents. Table IV shows scratching lattice level test results. According to GB9286-88, the higher the scratching lattice level is, the lower the adhesion strength between prepared

ink and BOPP membrane. Compared with unmodified TiO₂, the adhesion strength of ink prepared with the modified TiO₂ is greatly increased (Table IV), and the adhesion strength increases with organic rate of TiO₂ due to the fact that the compatibility between TiO₂ after surface-linked by organic chain and the polymer resin is improved. As a result that TiO₂ is easily dispersed in the polymer matrix, in turn integrates more closely. The adhesion strength of ink prepared by TiO₂-TDI-HEA-PBA with organic rate at 24.93% onto BOPP membrane arrives to I-level standard, showing an excellent print fastness.

CONCLUSIONS

The surface of TiO₂ particles chemically inserted by C=C unsaturated groups can take the free radical copolymerization reaction with BA monomer under UV irradiation. The PBA prepared are chemically bonded with TiO₂ surface and can not be removed by anhydrous alcohol. The graft rate of BA onto TiO₂-TDI-HEA surface initially increases with irradiation time and reaches a maximum after 40 min, then decreases as irradiation time further increases due to the fact that the graft layer of PBA on the TiO₂ surface degrades. After photografting with BA, the surface lipophilic rates of TiO₂ particles were increased. When the organic rate is 24.93%, the adhesion strength between the white printing ink made from the modified TiO₂ particles and BOPP can reach Grade I.

References

1. Wang, T.; Audebert, R. *J Colloid Interface Sci* 1984, 121, 33.
2. Hua, F. J.; Sun, J.; Gao, L.; Yang, Y. L. *Acta Chim Sin* 2000, 58, 1660 (in Chinese).
3. Chen, J. Y.; Peng, T. Z.; Xiao, Y. F. *Acta Chim Sin* 2003, 61, 1311 (in Chinese).
4. Xiang, L. Q.; Zhao, X. P. *Acta Chim Sin* 2003, 61, 1867 (in Chinese).
5. Wang, W.; Song, M. *Mater Res Bull* 2006, 41, 436.
6. Mao, A. Q.; Song, H. C.; Yang, Y.; Li, F. S. *Paint Coat Ind* 2003, 33, 35 (in Chinese).
7. Džunuzovic, E.; Jeremić, K.; Nedeljković, J. M. *Eur Polym J* 2007, 43, 3719.
8. Qiu, X. Q.; Zhong, J. C.; Long, Z.; Tian, L. H.; Zan, L.; Gong, C. Q.; Luo, Q. R. *Wuhan Univ J (Nat Sci Ed)* 2003, 49, 675 (in Chinese).
9. Li, Z. W.; Zhu, Y. F. *Acta Chim Sin* 2003, 61, 1484 (in Chinese).
10. Tada, H.; Salto Y.; Hirata M. *J Jpn Soc Color Mater* 1991, 64, 12.
11. Wen, Y. C.; Shao, C. C. *J Appl Polym Sci* 1987, 34, 127.
12. Lei, J. X.; Gao, J.; Zhou, R.; Zhang, B. S.; Wang, J. *Polym Int* 2000, 49, 1492.
13. Li, X. E.; Deng, H.; Zhang, F. Y.; et al. *Inorg Chem Ind* 2001, 33, 5 (in Chinese).
14. Zhou, H. M.; Ou, Y.; Lin, J. D. *Chem Res Appl* 2005, 17, 514 (in Chinese).
15. Nakayama, N.; Hayashi T. *Colloids Surfaces* 2008, 317, 543.
16. Zhu, D. Q.; Sheng, Y.; Zhang, W. G.; Li, N. G. *China Plast* 2006, 20, 53 (in Chinese).