



Study of Immobilization of Nano-TiO₂ for Environmental Aspects on Glass by Different Resin Families

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ABSTRACT

TiO₂ and especially its nano-metric structure have many applications for environmental proposes. It can be used in mobilized or immobilized status, but its consumption is less in immobilized form and its process is economical. In addition, the environmental problems would be minimized. There are a few methods for immobilization of nano-TiO₂ inside the process. The sol-gel method is typically applied for immobilization of nano-TiO₂ on Pyrex and quartz glasses, but these two glasses are expensive. To reduce the costs, two different resins have been studied for immobilization of nano-TiO₂ on conventional low cost glasses, but the glass coating and its surface preparation is very critical in order to increase the stability of catalyst and its life time. In this research, the immobilization process of nano-TiO₂ has been studied, and the conditions of process and critical parameters have been delineated. Different experiments have been done to characterize the properties of prepared coating, such as hardness, and water resistance measurements, and differential scanning calorimetry (DSC). Prog. Color Colorants Coat. 4(2011), 1-6. © Institute for Color Science and Technology.

1. Introduction

Development of nano-technology has increased application of nano-powders and it was changed to one of important technologies on industrial wastewater treatment in 1990s. In recent works, catalyst particles have been applied in nano-sized range. The rate of reaction and decolorization has increased significantly by nano-catalysts compared to micro sized.

Dispersed nano-TiO₂ particles have been used in

many wastewater treatment processes, but it would discharge a large amount of suspended particles to environment and requires expensive filtration system to remove nano-particles from treated wastewater. Direct discharge of these nano-particles is so harmful to environment. Therefore, immobilization of these nano-particles on surfaces of treatment system can decrease their harmful effect [1-7].

Nano-particles of TiO₂ are being directly stabilized

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on glassy surfaces of degradation reactor by sol-gel method in the most of immobilization processes [1, 8-12]. In this method, expensive glasses, such as Pyrex and Quartz, should be used. In addition, coating process on non-glass surfaces is very difficult. The coatings are unstable on amorphous glasses (conventional and cheap glasses). Moreover, nano-TiO₂ particles are removed from the glass surface during operational time and it should be recoated after a while.

In the present study, resins are used to stabilize nano-TiO₂ on reactor surfaces, as glue. Two different organic- and inorganic-based resins were applied and their coating properties were compared. This process is more stable than direct deposition method and its regeneration is simpler. Moreover, it can be applied on non-glass surfaces. Other advantages of this method are water and chemical resistant, UV resistant, mechanical stability, chemical inactivity, and cost effective [13]:

Selection of proper substrates and surface pretreatment operation are the most important parts of immobilization of nano-TiO₂ on resin surfaces. In this research, nano-TiO₂ particles have been immobilized on reactor surfaces by mineral and organic resins. Survey of coating and preparation processes were investigated with respect to hardness, water resistant and differential scanning calorimetry (DSC) tests.

2. Experimental

2.1. Materials and equipments

Resins were purchased from Epoxiran and Ciba companies. Their specifications present in Table 1. Nano-TiO₂ (P-25; with mean particle size of 30 nanometers) and hydrochloric acid were supplied from Degussa and Merck, respectively. Coning hardness meter and DSC (Perkin Elmer-Pyris 6) have been applied for characterization of the coatings.

2.2. Nano-TiO₂ immobilization and stabilization

Two different resin families were used to immobilize nano-TiO₂. At the first step, surfaces of conventional glasses, as reactor walls, were coated by the resins, and then pretreatment process was carried out by the solvent. In order to immobilize and stabilize nano-TiO₂, glass surface was washed and activated by dilute hydrochloric acid (HCl), and then pretreated surface was coated by resin. After drying for at least 48 hrs, resin surface pretreatment process was performed at 10, 15, and 20 minutes by different solvents. The exposure time and the amount of solvent are critical in pretreatment process. In short exposure time and insufficient amount of solvent, the surface treatment will not be completed for immobilization of nano-TiO₂. On the other hand, if these two factors are higher than optimized quantities, the resin will decompose.

The degradation reactor is ready to use when the pretreatment process has been completed. Performance of this nano-TiO₂ coated reactor has been investigated for environmental aspects in past articles [1, 2].

Table 1: Specifications of used resins.

Type of resin, %	Unsaturated polyester resin	Silicon resin
Amount of resin, %	77	75
Amount of monomer, solvent, and others	23	25
Amount of polysiloxan in solid resin	-	50
Dynamics viscosity @ 25°C, poise	20-25	-
Kinematics viscosity @ 25°C, cSt	-	4500-5500
Acidic no.	≤ 47	-
Iodine no.		2-4
Color (G33)	≤ 1	-
Sp. Gr.	1.20	1.06
Solubility	Soluble in Styrene monomer completely, Soluble in Xylene, Methyl ethyl ketone and Ethyl acetate partially	Soluble in Aromatics (Toluene and Xylene), Ketone and Esters, Soluble in Alcohol partially, very low soluble in Aliphatic solvents

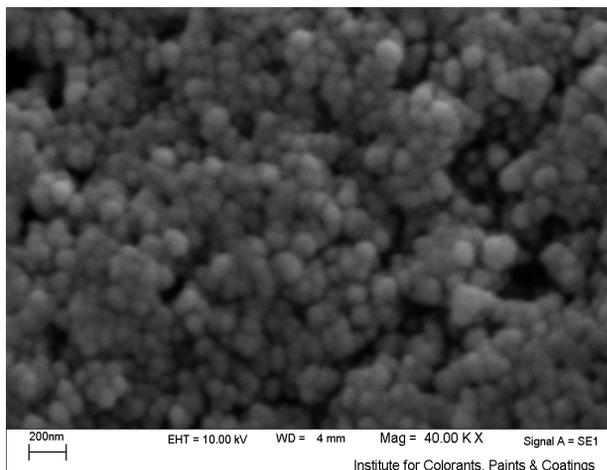


Figure 1: SEM image of nano-TiO₂ on silicon resin coating.

Figure 1 shows the scanning electron microscopy (SEM) image of nano-TiO₂ on silicon resin coating.

3. Results and discussion

Tables 2 and 3 show the response of organic and inorganic resins to solvent exposure, respectively. Surface of catalyst carrier (resin) was placed on exposure to different solvents, such as alcohol, acetone, methyl ethyl ketone and toluene, for 10, 15 and 20 minutes. These tables illustrate that the acetone has the best response after 10 and 20 minutes exposure for organic and inorganic resins, respectively. Represented results in Tables 2 and 3 are qualitative and have been earned by visual experiments, but they have been supported by DSC (Figures 2 and 3), water resistance (Tables 4 and 5) and Conig hardness (Figure 4) tests too.

Figures 2 and 3 present the responses of organic and inorganic resin coatings to DSC instrument between -50 to 200°C after 10, 15 and 20 minutes exposure to solvent, respectively. Graphs presented in these figures show small changes after exposure to solvent. In addition, Figure 3 presents improvement in DSC for inorganic resin coatings after exposure to solvent.

Table 2: Solvent exposure of organic resin during 10, 15 and 20 minutes.

Exposure time, min	Alcohol	Acetone	Methyl ethyl ketone	Toluene
10	No change ¹	Prepared ²	Deformation ⁴	No change ¹
15	No change ¹	Decomposed ³	Scaling ⁵	No change ¹
20	No change ¹	Decomposed ³	Scaling ⁵	No change ¹

¹ No change: Exposure to solvent had no effect on the resin surface.

² Prepared: Surface was suitable for immobilization of nano-TiO₂.

³ Decomposed: Exposure to solvent decomposed the resin surface.

⁴ Deformation: Exposure to solvent deformed the resin surface.

⁵ Scaling: Exposure to solvent caused scaling the resin surface and reduced the binding capability of resin.

Table 3: Solvent exposure of inorganic resin during 10, 15 and 20 minutes.

Exposure time, min	Alcohol	Acetone	Methyl ethyl ketone	Toluene
10	No change ¹	No change ¹	No change ¹	No change ¹
15	No change ¹	No change ¹	No change ¹	No change ¹
20	No change ¹	Prepared ²	Decomposed ³	No change ¹

¹ No change: Exposure to solvent had no effect on the resin surface.

² Prepared: Surface was suitable for immobilization of nano-TiO₂.

³ Decomposed: Exposure to solvent decomposed the resin surface.

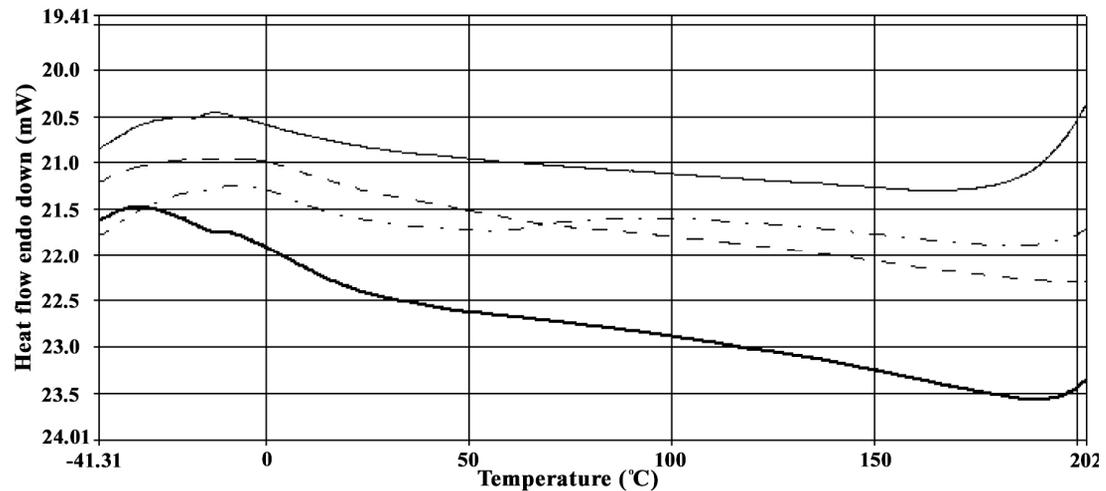


Figure 2: DSC graphs for organic resin coatings after, 0 (—), 10 (- -), 15 (- ·) and 20 (—) minutes exposure time to acetone.

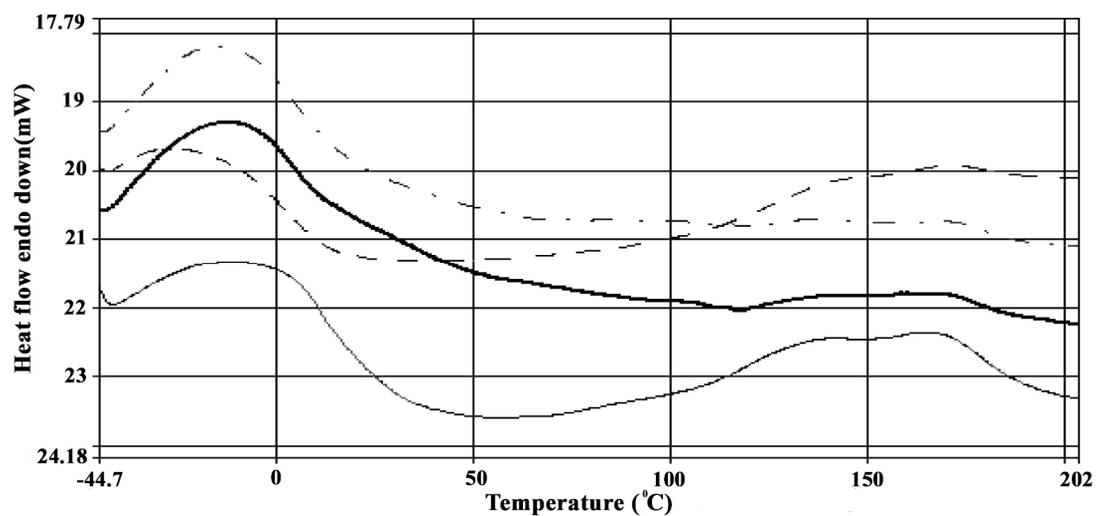


Figure 3: DSC graphs for inorganic resin coatings after, 0 (—), 10 (- -), 15 (- ·) and 20 (—) minutes exposure time to acetone.

For row organic resin the maximum heat flow is 21.35 mW and the minimum is 20.35 mW, but the maximum and minimum are 23.6 mW and 21.3 mW for row inorganic resin, respectively. The difference between maximum and minimum amount is 1 mW and 2.3 mW for row organic and inorganic resins, respectively. But the response of exposed resins is a little different. For 20 minutes exposure time, the differences are 2.15 mW and 2.95 mW, respectively. It means that exposure to solvent has more effect on organic resin (115%) with comparison to inorganic resin (28.3%). Inorganic resin is more resistible to solvent exposure.

Water resistant of prepared coatings has been investigated according to standards ASTM D870-92 [14]. Distilled water has been applied in this test. In this standard, water resistant is tested for submerging of samples after 24, 48 and 72 hours at normal water temperature. The coated samples are checked after each submerging times. Results of water resistant test present at Tables 4 and 5 for exposed organic and inorganic resins to acetone, respectively. Few samples were decomposed. Samples showed scaling feature after 72 hours submerging when the surface was pretreated for more than 15 minutes by acetone.

Table 4: Results of water resistant test for organic resin.

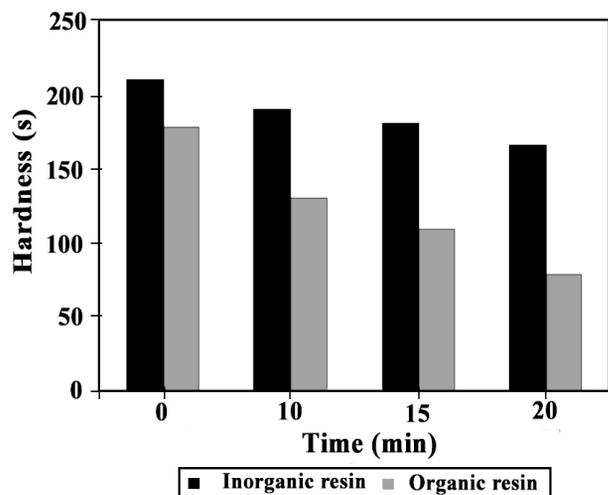
Time, hrs	Scaling	Blister	Cracking	Peeling
24	-	-	-	-
48	-	-	-	-
72	+	-	-	-

⁺ Resin samples with 15 and 20 prepared times were decomposed.

Table 5: Results of water resistant test for inorganic resin.

Time, hrs	Scaling	Blistering	Cracking	Peeling
24	-	-	-	-
48	-	-	-	-
72	-	-	-	-

Results of Conig hardness test (ASTM D2794) have been presented in Figure 4 for organic and inorganic resins at different exposure time to acetone [15]. This Figure shows that coating hardness of organic resin is less than inorganic resin. In addition, pretreatment process has more effect on organic resin than inorganic resin and the trend of hardness reduction is more for exposed organic resin.

**Figure 4:** Conig hardness of organic and inorganic resins at different exposure time to acetone.

4. Conclusions

In this paper, the nano-TiO₂ particles were immobilized and stabilized on surfaces of degradation reactor of colorants by different resins family. Surfaces were coated with resin after preparation by HCl. The resin surfaces were pretreated by exposure to different solvents and nano-TiO₂ particles immobilized on pretreated surfaces. Samples were tested by different coating experiments, such as DSC, water resistant, and hardness.

The experimental results present that the best resin, solvent and exposure time to solvent are inorganic resin, acetone and 10 minutes, respectively.

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