Preparation and properties of waterborne epoxy coatings modified by TiO$_2$ transparent emulsion

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ABSTRACT

TiO$_2$ transparent emulsion were prepared by using normal temperature hydrolysis and added into the waterborne epoxy coatings, the properties of coating films including hardness, adhesion, flexibility, impact resistance were characterized. The visible-light photocatalytic activities of different contents of TiO$_2$ transparent emulsion in the samples were evaluated using the degradation of rhodamine B. The result shows that waterborne epoxy coatings doping TiO$_2$ have the photocatalytic performance and have the optimal weight ratio (W(TiO$_2$)/W(waterborne epoxy coatings) = 2 %), the properties of the films are still unchanged, which it may be actual applied.

EXPERIMENTAL

Materials

Tetrabutyl titanate (Ti(OBu)$_4$), Rhodamine B, Acetic Acid (CH$_3$COOH), ethanol (CH$_3$CH$_2$OH), triethylene tetramine (TETA) are all analytically puregrade and supplied by the Tianjin Chemical Reagent Co. China. Liquid epoxy resin (E-51) and Self-emulsified Waterborne Epoxy Curing Agent are all supplied by the Hebei Chenyang coating Co. China.

Apparatus and procedure
D-7401 type electric mixer agitator and 85-1 the isothermal magnetic stirrer (Sino-foreign joint venture in Shenzhen Co. China); QHQ-A-type pencil hardness tester, QFH-A-type film cross-cut, The QTX film elastic, The QCJ film impactor (Tianjin Expo Albert the Bose Instrument Co, China); 722N visible spectrophotometer (Shanghai Jingke Co. China).

**Preparation of TiO$_2$ transparent emulsion at room temperature**

(A) Ti(OBu)$_4$ is slowly dropped into anhydrous ethanol stirring on the isothermal magnetic stirrer $\left( \frac{V(\text{Ti(OBu)}_4)}{V(\text{ethanol})} = 1:8 \right)$.

(B) Deionized water and acetic acid (HAC) are added to the anhydrous ethanol $\left( \frac{V(\text{water})}{V(\text{HAC})} = 2:1:4 \right)$, mixing evenly.

The solution of B was slowly dropped into A at 1 drop/s, and go on stirring for 1h after dropping, then TiO$_2$ transparent emulsion is made.

**Synthesis of Self-emulsified Waterborne Epoxy Curing Agent**

TETA (n(TETA) : n (Phenyl Glycidyl Ether) = 3:1) is added to the reaction vessel with condensation and stirring device, slowly adding Phenyl Glycidyl Ether using a funnel under 60°C and react for 2h, and slowly adding epoxy resin (n(epoxy resin E-51) : n (Phenyl Glycidyl Ether) = 1:1) under 40°C, heated to 90°C and reacted for 1h; dropping slowly proper amount of acetic acid and reacting for 1h, adding slowly proper amount of water in 90°C, the curing agent is dissolved in water to obtain the 60% solid content self-emulsifying waterborne epoxy resin curing agent.

**Preparation of Waterborne Epoxy Coatings Modified by TiO$_2$ Transparent Emulsion**

TiO$_2$ transparent emulsion were added into self-emulsified waterborne epoxy curing agent firstly, According to the weight ratio of TiO$_2$ transparent emulsion to Waterborne Epoxy Coatings is 0%, 2%, 4%, 6%, 8%, w/w respectively, then mixed with the liquid epoxy resin (E-51) $\left( \frac{W(\text{E-51})}{W(\text{the mixture})} = 1:1 \right)$ by electric mixer agitator. The mixture is Waterborne Epoxy Coatings Modified by TiO$_2$ transparent emulsion.

**Characterization of Curing System**

The mixture were respectively coated on the tinplate at 120mm $\times$ 50 mm $\times$ 1mm, The properties of coating films including hardness (The national standard of the people’s Republic: GB/T6739-2006), adhesion (GB/T1720-79), flexibility (GB/T6742-2007), impact resistance (GB/T 1732-93) were characterized.

The visible-light photocatalytic activities of different contents of TiO$_2$ transparent emulsion in the samples were evaluated by degrading 7mg/L Rhodamine B. The tinplate coating the mixtures were completely immersed in Rhodamine B solution for 2.5h under natural light. The samples were removed, absorbance (A) of the remaining solution were measured by visiblespectrophotometer (552 nm). Then degradation rate is:

$$\text{degradation rate} \% = \left( \frac{A_0 - A}{A_0} \right) \times 100\%$$

$A_0$: The absorbance of the blank sample; $A$: The absorbance of the sample with TiO$_2$.

The properties of coating films after dry were characterized again.

**RESULTS AND DISCUSSION**

**The properties of coating films**

TABLE 1 is the physical property of waterborne epoxy coatings modified by TiO$_2$ transparent emulsion, As seen from TABLE 1, the Pencil hardness increased a little and adhesion, flexibility, impact resistance decrease with increasing the TiO$_2$ transparent emulsion, the result is why the hardness of the TiO$_2$ is large and

<table>
<thead>
<tr>
<th>Contents of TiO$_2$</th>
<th>Appearance</th>
<th>Pencil hardness</th>
<th>Adhesion</th>
<th>Flexibility /mm</th>
<th>Impact resistance/ N·cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>Transparent,glossy</td>
<td>4H</td>
<td>1</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>2%</td>
<td>Transparent,glossy</td>
<td>5H</td>
<td>1</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>4%</td>
<td>Transparent,glossy</td>
<td>5H</td>
<td>1</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>6%</td>
<td>Transparent,glossy</td>
<td>5H</td>
<td>2</td>
<td>1.5</td>
<td>40</td>
</tr>
<tr>
<td>8%</td>
<td>Transparent,glossy</td>
<td>5H</td>
<td>2</td>
<td>3.0</td>
<td>30</td>
</tr>
</tbody>
</table>
will be self congregation and appear phase separation with increasing the TiO$_2$ transparent emulsion$^{[9]}$, the coating with TiO$_2$ will be brittle. So 2% w/w of TiO$_2$ transparent emulsion is better from the coating performance.

**Photocatalytic effect of rhodamine B with different contents of TiO$_2$**

The visible-light photocatalytic activities of different contents of TiO$_2$ transparent emulsion were investigated, using the degradation of rhodamine B. The results can be seen in Figure 1. Figure 1 shows the degradation rate increased with increasing the amount of TiO$_2$ transparent emulsion. It indicated that TiO$_2$ transparent emulsion was well dispersed in the waterborne epoxy coatings layer to improve photocatalytic activities of coating$^{[9]}$. But when the contents of TiO$_2$ is about more than 6%, the photocatalytic activity was a little change, this is because it is suggested that agglomerated particles reduced the photocatalytic activity$^{[10]}$. The mechanism of film expect to be investigated.

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**REFERENCES**


**CONCLUSIONS**

Waterborne epoxy coatings modified TiO$_2$ transparent emulsion was prepared by adding different amount of TiO$_2$ transparent emulsion into self-emulsified waterborne epoxy curing agent, then mixed with the liquid epoxy resin, and made the cure coating. The film physical and photocatalytic properties were characted. The results showed that adding TiO$_2$ transparent emulsion can improve the photocatalytic properties of the coating, and be an optimum content (about 2%) considering physical properties. When TiO$_2$ transparent emulsion was 2% w/w, the degradation rate by degradating 7mg/L Rhodamine B was to 11%. At the same time, their physical properties were little change. It shows that the method of adding TiO$_2$ transparent emulsion urged TiO$_2$ to disperse evenly in waterborne epoxy curing agent, and presented good photocatalytic properties in a certain of content. It may be actually applied.