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Preparation and properties of waterborne epoxy coatings modified by TiO_2 transparent emulsion

Li Huo*, Pengfei Zhang, Li Wan

Department of Biochemistry, Baoding University, Baoding, 071000 (P.R.CHINA)

E-mail : huolichenchen@sina.com

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 TiO2 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(TiO2)/W(waterborne epoxy coatings) = 2 %), the properties of the films are still unchangsd, which it may be actual applied.

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KEYWORDS

Waterborne epoxy coatings;
TiO_2 Transparent emulsion;
Modify;
Photocatalysis.

INTRODUCTION

The waterborne epoxy coatings has excellent anti-corrosion properties, low VOC (volatile organic composite), smaller odor and can be washed, they it can be used for floor in airports, hospitaal, factory and others; household coating; the coating of metal cans as well as electrical appliances, medical equipment and other fields[1-8]. TiO_2 as a photocatalyst is non-toxic, tasteless, and good at thermal stability and heat resistance, no burning, low cost, and has Self-cleaning properties and decomposing bacteria and pollutants to benefit the natural ecological environment, so TiO_2 has been one of the hot spots, and The photocatalytic of TiO_2 transparent emulsion is better than that of TiO_2 white emulsionon[9, 10].

In this paper, TiO_2 transparent emulsion was Prepared by hydrolysis under the room temperature and added to 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. It will Provide the theory basis on high functional waterborne epoxy coatings with cleaning, sterilization, environmental protection.

EXPERIMENTAL

Materials

Tetrabutyl titanate ($Ti(OBu)_4$), Rhodamine B, Acetic Acid (CH_3COOH), ethanol (CH_3CH_2OH), 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

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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[9-10]

(A) $Ti(OBu)_4$ is slowly dropped into anhydrous etha nol stirring on the isothermal magnetic stirrer ($V(Ti(OBu)_4)$/V(ethanol)=1: 8).

(B) Deionized water and acetic acid (HAC) are added to the anhydrous ethanol [(V(water): (V(HAC): V (ethanol)=2:1:4), 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[7]

TETA (n(TETA) : n (Phenyl Glycidyl Ether) = 3:1) is added to the reaction vessel with condensation and stirring device, slowly adding Phenyl Glycidyl Etherusing a funnel under 60 ! and react for 2h, and slowly adding epoxy resin (n(epoxy resin E-51) : n (Phenyl Glycidyl Ether) = 1:1) under 40 !, heated to 90 ! and reacted for 1h; dropping slowly proper amount of acetic acid and react ing for 1h. adding slowly proper amount of water in 90 !, 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) [W(E-51)/W(the mixture) = 1:1] 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 ×50 mm ×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 degradating 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:

degradation rate% = $(A_0 - A)/A_0 \times 100\%$

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 1 : The coating performance of waterborne epoxy coatings modified by TiO_2 Transparent Emulsion

Contents of TiO_2	Appearance	Pencil hardness	Adhesion	Flexibility /mm	Impact resistance/ N·cm^{-1}
0%	Transparent,glossy	4H	1	0.5	50
2%	Transparent,glossy	5H	1	0.5	50
4%	Transparent,glossy	5H	1	1	45
6%	Transparent,glossy	5H	2	1.5	40
8%	Transparent,glossy	5H	2	3.0	30

will be self congregation and appeare 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 incresed 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 beacause It is suggested that agglomerated particles reduced the photocatalytic activity[10]. The mechanism of film expect to be investigated.

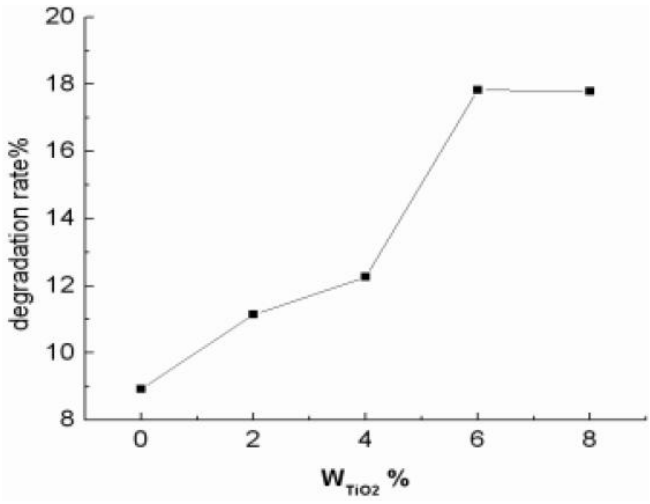

Figure 1 : Degradation rate of Rhodamine B solution containing different concentration TiO_2 transparent emulsion

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 optinum 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 to11%. 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 diperse evenly in waterborne epoxy curing agent, and presented good photocatalytic properties in a certain of content. It may be actually applied.

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