Study on the Synthesis of Water-dispersible Acrylic Resin Containing Hydroxyl Group`

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Abstract: Hydroxy acrylic resin is a long-chain polymer material formed by cleavage and recombination of double bonds of various acrylates and methacrylates under the action of initiators. Among them, MMA and BA provide the rigidity of the molecular chain and For flexibility, HEMA provides the hydroxyl groups required for cross-linking and curing, and MAA gives the resin water solubility. By rationally designing different monomer dosages, resin products with high gloss and high hardness are prepared, and through paint making experiments, the paint film Performance is tested.

Keywords: Water-borne resin; Acrylic; Hydroxy resin

1. Introduction

With the rapid development of economy and society, the problem of environmental pollution has become a problem that must be solved in the process of economic development[1-2]. Eco-friendly coatings have attracted the attention of researchers because of their use of water or eco-friendly solvents as a dispersive medium, which greatly reduces the use of volatile organic solvents (VOCs) in their products[3]. The film-forming substances used in coating products can be divided into: resin, emulsion, dispersion and so on. Because the vast majority of emulsion products in the high-speed mixing process is prone to the phenomenon of milk breaking, resulting in product failure. Although the dispersion has the advantages of emulsion and resin, its high[4].

Acrylic resin has high hardness, high gloss characteristics, is widely used in vehicle protection, equipment protection, infrastructure construction and other fields[5-6]. However, acrylic resin in poor water resistance, low solid content, high viscosity and other deficiencies, in order to reduce the viscosity of the resin and improve the solid content, the introduction of the silicon carbonate shrinkgies (E10-p) to modify the resin research, E10-p as a reactive solvent[7-8], can reduce the VOC content of the resin, and because E10-p has epoxy group, At high temperature[9], the hydronization of the key forms a hydroxyl, and the esterification reaction with organic acids, forming an ester base with a large spatial bit resistance effect, which can effectively reduce the viscosity of the resin[10-11].

2. Experiment

2.1 Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), hydroxyethyl methacrylate (HEMA),glycidyl tert-carbonate (E10-p) ,propylene glycol butyl ether (PnB), N, N-dimethylethanolamine (DMEA), tert-butyl peroxybenzoate (TBPB) , 2,4-diphenyl-4-methyl-1-pentene (AMSD) are all industrial grade. Deionized water is homemade in the laboratory.

2.2 Instruments

BT100-1F peristaltic pump, ZNHW intelligent constant temperature electric heating jacket, 78-1 magnetic heating stirrer, RW20 stirrer, FS-1 experimental disperser, DZF vacuum drying box, NETZSCH DSC-214 differential scanning calorimeter, QFZ-II adhesion tester.

2.3 Synthesis of water-dispersible hydroxy acrylic resin

Add a certain amount of PnB, 50% of E10-pto a four-necked flask equipped with a stirring device, a thermometer, and a condenser. Warm to 140℃ and hold the reaction for 30 minutes. The remaining monomer and 90% TBPB and AMSD Mix evenly, slowly add to the flask within 3h, hold for 1h, add 5% of TBPB and AMSD to react for 1h, add the remaining TBPB and AMSD to warm to 150 ℃ for 1h, cool to 80 ℃, add a certain amount of DMEA adjusts the pH, quickly stirs for 30 minutes,

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adds a certain amount of deionized water under high-speed stirring, and mixes for 30 minutes at high speed to obtain a water-dispersible hydroxy acrylic resin. The water-dispersible hydroxy acrylic resin formulation is shown in Table 1.

Table 1 Water-dispersed hydroxyl acrylic resin formula

name	Dosage /%	effect
MMA	52-60	Provide hardness
HEMA	14-18	Provides hydroxyl
BA	2-7	Provides flexibility
MAA	4-6	Provide water solubility
E10-p	4-6	Reduce viscosity
TBPB	3-5	Initiator
AMSD	1-2	Chain transfer agent

2.4 Preparation of coatings

Take a certain amount of resin, add water-based defoamer, substrate wetting agent, film-forming aid, deionized water under high-speed stirring, and mix evenly at high speed to obtain an aqueous hydroxy-containing acrylic varnish. The curing agent is DNW-5500 isocyanate curing agent. The acrylic varnish formulation is shown in Table 2.

Table 2 Acrylic varnish formulations

name	Dosage /%
Resin	60.0
Defoamer	0.1
Substrate wetting agent	0.1
Film-forming aid	0.4
water	39.4

2.5 Test

2.5.1 Calculation of theoretical hydroxyl content

In the resin synthesis process, the calculation formula of the theoretical hydroxyl content is shown in Formula 1. The theoretical hydroxyl content of the resin can be calculated by the molecular weight and mass fraction of hydroxyethyl methacrylate, and the theoretical hydroxyl value = theoretical hydroxyl content×33. However, since -OH reacts with -COOH during the reaction, it is necessary to perform a titration measurement on the actual acid value and subtract the difference between the theoretical acid value and the actual acid value to obtain an approximate actual hydroxyl value. The calculation formula of the theoretical acid value is shown in Equation 2.

$$\text{Hydroxyl content} = \frac{m_{(OH)}}{M_{(OH)}} \times m \times 17$$

m（OH）：Mass fraction of hydroxyethyl methacrylate
M（OH）：Molecular weight of hydroxyethyl methacrylate
m：Amount of synthetic resin

Formula 1 Calculation formula of theoretical hydroxyl content

$$\text{Theoretical acid number} = \frac{m_{(COOH)} \times 56100}{86.1}$$

m（COOH）：Methacrylic acid mass fraction

Formula 2 Calculation formula of theoretical acid value

2.5.2 Acid value determination

Take about 1g of neutralized resin, accurate to 0.001g, take 50g of 1: 1 mixed hydrogenated toluene and ethanol solution to completely dissolve the resin, add 3-4 drops of phenolphthalein indicator, use 0.1mol/L potassium hydroxide The standard solution was titrated, and the end point was that the solution was initially reddish and did not change color within 30s. Measure the amount of potassium hydroxide standard solution and calculate the actual acid value of the resin.

2.5.3 DSC analysis

The dried resin was measured for the glass transition temperature (Tg) using a differential scanning calorimeter. The test was performed under the conditions that the protective gas was nitrogen, the temperature range was -10-100℃, and the heating rate was 10K / min.

2.5.4 Solid content test

Take a certain amount of resin, weigh the resin (accurate to 0.01), and dry it at 140℃ for 2h. After taking out and cooling sufficiently, measure the remaining weight. Solid content = weight after drying / weight before drying × 100%.

2.5.5 Varnish performance test

According to n (-NCO): n (-OH) = 1.5: 1, mix the curing agent and acrylic resin uniformly, add appropriate amount of substrate wetting agent and defoaming agent, dilute to the construction viscosity, spray on the iron plate after grinding After the surface is dried, it is dried in an oven at 80℃. for 30 minutes, and cured at room temperature for 7 days to test the performance of the paint film.

Adhesion test: Spray the paint on the surface of the iron plate with a thickness of 25-35 μm, bake it at 80℃ for 30 minutes, and maintain it at room temperature for 7 days, then use an adhesion tester to test it.

Impact resistance test: The coating was sprayed on the surface of the iron plate with a thickness of 50±5 μm, dried at 80℃. for 30 minutes, and maintained at room temperature for 7 days, and then tested using an impact tester.

Gloss Test:The colored paint was applied to the surface of the iron plate with a thickness of 50±5 μm, dried at 80℃. for 30 minutes, and maintained at room temperature for 7 days, and then measured using a 60 ° angle gloss meter.

Thermal Reserve Performance Test: Take a certain amount of paint and store it in an oven at 50±2℃, and observe the change of paint state.

Freeze-thaw performance test: Take a certain amount of paint and place it in the environment of -18±2 ℃ for 16h, take it out and place it in the environment of 23±2 ℃ for 8h, repeat it several times, and observe the change of paint state.

3. Results and discussion

3.1 Acid value and water solubility

By changing the amount of MAA introduced, the resin was prepared with a neutralization degree of 100%. The water dispersibility of the prepared resin was studied. The relationship between the acid value and water solubility of the resin is shown in Table 3.

Table 3 Relationship between acid value and water solubility

MAA introduction	Theoretical acid value / mgKOH / g	Actual acid value / mgKOH / g	Water soluble	Resin state
2.0%	13.72	7.24	Insoluble / 3h stratification	Milky opaque
2.5%	17.15	9.55	Insoluble / 3h stratification	Milky opaque
3.0%	20.58	10.88	Soluble / 48h stratification	Milky transluc ent
3.5%	24.01	13.96	Soluble / 72h stratified	transluc ent
4.0%	27.43	17.39	Soluble / 30d without delamination	transluc ent
4.5%	30.86	21.08	Soluble / 30d without delamination	Transpa rent
5.0%	34.29	23.86	Soluble / 30d without delamination	Transpa rent

There is an antagonistic relationship between the water solubility and water resistance of the resin. In order to ensure that the resin has good water solubility and stability and also has good water resistance, the amount of MAA introduced should be controlled between 4.5% and 5%. The acid value is between 30.86-34.29 mgKOH / g, and the actual acid value is between 21.08-23.86 mgKOH / g.

3.2 Paint film performance test

By adjusting the ratio of soft and hard monomers and functional monomers, acrylic resin dispersions with different glass transition temperatures and hydroxyl content were prepared. Samples of different resins were prepared and the properties of the samples were tested. Table 4 shows.

Table 4 Paint film performance test table

project	CY-1	CY-2	CY-3	CY-4	CY-5	CY-6
Tg / ℃	20	30	30	35	40	40
Hydroxyl content /%	2.5	2.5	3.3	3.3	3.5	4.0
Solid content /%	42.4	43.1	42.8	42.7	42.5	42.8
Surface drying time / min	60	45	30	25	20	15
Adhesion / level	1	1	1	1	2	2
Impact resistance / level	1	1	1	1	2	2
Gloss (60 °)	86	87	88	89	88	86
Thermal storage stability ≧	30d	30d	30d	30d	30d	30d
Freeze-thaw stability ≧	5 times	5 times	5 times	5 times	5 times	5 times

According to the testing of paint film properties, when the glass transition temperature is below 30℃, the paint film has a low hardness and a long surface drying time, and the phenomenon of re-adhesion has occurred in a long-term wet state. When the glass transition temperature is above 40 ℃, the hardness of the paint film is high, but the adhesion and impact resistance are poor. It was finally determined that under this scheme, the optimal theoretical glass transition temperature should be controlled between 30-35℃.

The increase of hydroxyl content is beneficial to the crosslinking of the paint film, and at the same time can improve the water solubility of resin and the hardness of the paint film, but the increase of hydroxyl content will lead to increased resin viscosity, the scheme will control the theoretical hydroxyl content at 3.3%, the theoretical hydroxyl value in 108.95 mgKOH /g.

3.3 Actual parameters

By theoretical calculation of the resin, the theoretical hydroxyl content of the resin was determined to be 3.30%, the theoretical hydroxyl value was 108.95 mgKOH /g, and the theoretical acid value was 34.29 mgKOH/g. Due to some side reactions in the reaction process, the actual values of the parameters of each part need to be measured. After titration testing of the resin, it was finally determined that the actual acid value was about 21.5-24 mgKOH/g, the actual hydroxyl content was 2.95-3.05%, and the actual hydroxyl value was 97.35-100.65 mgKOH/g. The resin parameters are shown in Table 5.

Table 5 Determination of resin parameters

parameter	Theoretical value	Actual value
Acid value	30.86-34.29 mgKOH /g	21.0-24.0 mgKOH /g
Hydroxyl content	3.30%	2.95-3.05%
Hydroxyl value	108.95 mgKOH /g	97.35-100.65 mgKOH /g

3.4 DSC analysis

The DSC-214 differential scanning calorimeter was used to detect the samples. The test temperature range is -10-100 ℃, the heating rate is 10 K/min, and the sample mass is 5-10 mg. The weight loss curve is recorded, and its thermal stability and phase transition temperature are analyzed by the curve. It can be seen from Figure 1 that the glass transition temperature of this resin is 29.72 ℃, the specific heat change is 1.158 J/(g*K), and there is no exothermic peak of crystal melting, so it can be inferred that the synthesized product did not Crystallization. The design glass transition temperature of this product is 30 ℃, and the actual test glass transition temperature is 29.72 ℃, which is basically consistent with the design value.

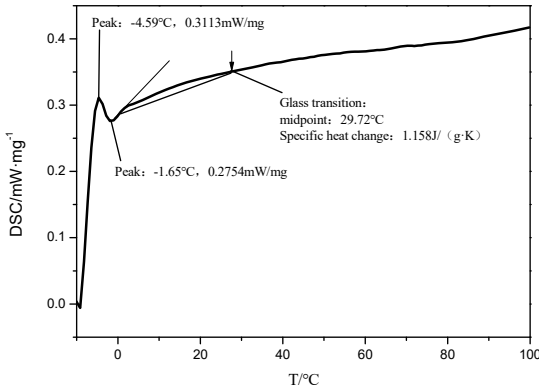

Figure 1 Resin DSC

4. Conclusions

By synthesizing the water-dispersed hydroxy acrylic base resin to determine the synthesis parameters of the base resin, it is finally determined that the amount of MAA introduced in the base resin should be controlled between 4.5%-5%, and the theoretical acid value is 30.86-34.29 mgKOH/g , The actual acid value determined by titration is between 21.08-23.86 mgKOH/g; the theoretical hydroxyl content is 3.30%, the theoretical hydroxyl value is 108.95 mgKOH/g, the actual hydroxyl value is 97.35-100.65mgKOH/g; Tg should be controlled at 30℃ about. The prepared base resin has good properties in terms of adhesion, flexibility, hardness, gloss, storage properties, etc. The 60° gloss test result is around 90°.

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