Preparation of Aqueous Anti-yellowing Polyurethane Dispersion Used as Surface Layer for Transfer-film Leather

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Abstract: The Aqueous anti-yellowing polyurethane dispersions used as surface layer for transfer-film leather were successfully synthesized based on interior emulsification method. In this paper, effects of three kinds of catalysts and a kind of crosslinker on PU dispersions synthesis and mechanical properties of dry-film were studied. The results show: the surface layer based on the aqueous anti-yellowing polyurethane dispersion has good mechanical properties, anti-yellowing, and its application properties are close to those of solvent born products.
Keywords: aqueous polyurethane dispersions; surface layer; anti-yellowing

1 Introduction

Up to now, in the domestic production of synthetic leather, solvent PU resin is widely used as surface coating and adhesive material, which is polymerized with butanone (MEK), ethyl acetate and dimethylfomamide (DMF). These solvents are toxic. Meanwhile, the organic catalysts used during polymerization will do serious harm to the ecological environment. Therefore, it's an evitable trend in the technical development of transfer-film leather production to replace solvent PU resin with non-organotin aqueous PU resin.

The aqueous resin prepared in this paper is a kind of anion PU water dispersion synthesized by interior emulsification method, with special polyester diol, disocyanate, non-organotin organic metal coordination catalysts as raw materials. This kind of PUD is characterized as good stability, physical property and it application properties close to that of solventborne PU products.

2 Experiments

2.1 Materials

The raw materials employed in this study are listed in Table 1 .All materials were used without further fortification.

Tab. 1 Raw materials

Raw materials	Company
Polyester polyol	Guangdong Tyen Chemicals CO.,LTD
DMPA	Perstorp Group
Butanediol	YongDa Chemical Development Center
Acetone	YongDa Chemical Development Center
IPDI	Rhodia
DBTDL	YongDa Chemical Development Center
TEA	YongDa Chemical Development Center
EDA	YongDa Chemical Development Center

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2.2 Synthesis of PUD

The PUD were synthesized by the prepolymer mixing process. Firstly, polyester polyol, DMPA, butanediol and acetone were placed in a four necked separable flask(equipped with thermometer ,a stirrer, a condenser and a heat jacket)and heated at 50℃ for 30 min. Then ,IPDI was poured into mixture which was heated to 60℃ under moderate stirring (150-180rpm). After that, a drop of catalyst was added at this temperature. The reaction mixture was allowed to react at 60-65℃ until the theoretical NCO content was reached. The change in the NCO value during the relation was determined with the standard dibutylamine back titration method (ASTM D 1638).The mixture was cooled to 50℃ Then , acetone was added to decrease the viscosity of solution. TEA was added to neutralize the carboxyl group of urethane prepolymer. After 30min of neutralization ,distilled water was added to the reaction mixture with vigorous stirring(2000-2300rpm).The dispersion was chain-extended by the dropping of EDA/H2O at 40℃ for 1h. Finally, PUD was obtained after evaporation of acetone.

2.3 Main technical index of PUD and its film

2.3.1 Properties of PUD

Appearance: milk-white and slight blue liquid

PH Value: 6.5~9.5

Solid content %: 30±3

Viscosity (25℃)/mPa • S: not more than 100

Liquid stability (50℃)/a:≥15 days

Liquid anti-yellowing (natural light)/a: ≥4.5

2.3.2 Film formation:

Modulus: 40~60

Tensile strength/Mpa: ≥300

Elongation at break%: ≥400

2.3.3 Preparation of film

Pour the liquid on a plastic cap, then put it under a lamp house. Remove the film after two days of film formation, keep the film dry and place it in a desiccators for afterwards use.

2.4 Preparation and main technical properties

2.4.1 Preparation of PUD paste

Weight PUD, additives, distilled water and color paste into a tin, then put the tin under a high-speed disperser, stirring the mixture at speed of 700~800rpm, adding anti-bubbling agent and crosslinking agent when stirring. Next, input thickener and increase speed to 1500 rpm, filter the mixture after stirring for 10 minutes. Static defoam the mixture for one night.

2.4.2 Main technical properties

Solid content %: 30±3

Appearance: white viscous liquid

Viscosity: 2500±1000CP

Modulus: 40~60

Anti-yellowing rate:≥4.5

Twisting durability: ≥80000 times

Processability: good levelling property on release paper, with no sinkhole and roll marks.

3 Results and discussion

3.1 Effect of sort of catalysts on kinetic

DBTDL was popularly used in polyurethane preparation. However, it was limited nowadays for environmental reason. In this study, two kinds of catalysts (cat1, cat2) without any organtin were employed to prepare PUD. It can be seen from Fig1 that NCO content of prepolymer with DBTDL and CAT1 decreased at first 4hrs, then kept stable. But for cat2, its NCO content decrease continually till gelation. This is because the CAT2 can not only play role in reaction of –NCO and –OH group, but also in tri-polymerzition of NCO group.

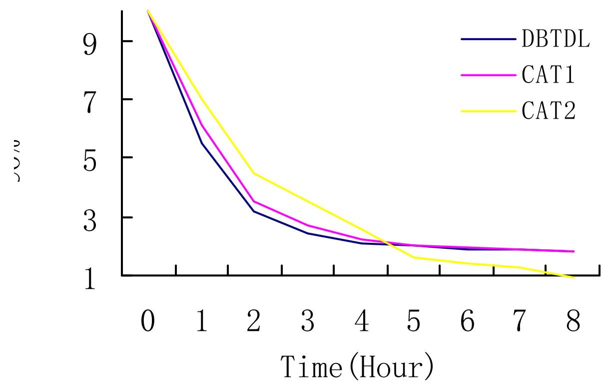

Fig.1 Effect of sort of catalystes on kinetic

3.2 Effect of sort of catalysts on prepolymer viscosity

The Fig2 shows prepolymer viscosity versus reaction time. For prepolymer with CAT2, its viscosity increased gradually till gelation which also proved that CAT2 can catalyze tri-polymerization .

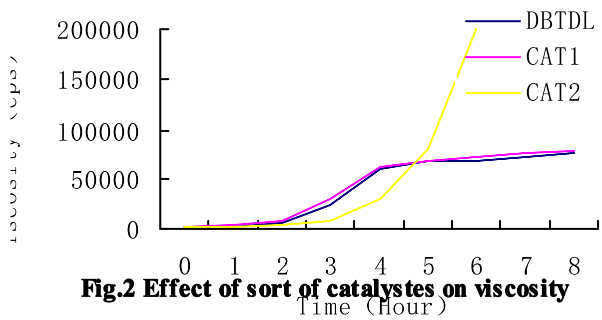

Fig.2 Effect of sort of catalystes on viscosity

3.3 Effect of sort of catalysts on prepolymer twist durability

Twist durability is one of the most important properties of aqueous PU resin for transfer-film leather surface coating, for the reason that the leather used for shoes, garments and sofa should stand up to twisting for a period of time.

The above figure shows that twist durability of the film increased after reaction of prepolymer employed with organotin and CAT1 for 3-4 hours, and the twist durability tend to be stable after 4 hours of reaction. The reason is that the molecular weight grows larger as the reaction gradually completes. By contrast, prophase reaction is slow with CAT2, and the twist durability is not good. Though during the metaphase of reaction, the molecular weight increase, twist durability degrades due to over-density after catalysts crosslinking. During the reaction anaphases, too large Viscosity results in gelling.

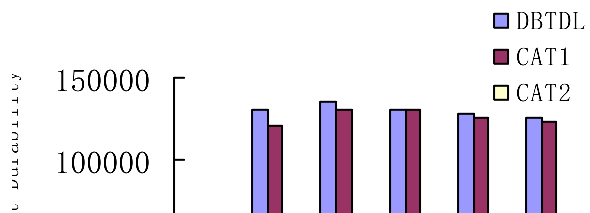

Fig.3 Effect of sort of catalysts on prepolymer twist durability

3.4 Effect of crosslinker on aqueous resin hydrolysis durability

The stated aqueous resin is synthesized on self-emulsifying system. The resin film will asorb some amount of water after drying, for there are hydrophilic groups in the molecular chain. For PAUR polyurethane, hydrolysis durability of ester bonds is not good, so the molecular chain will break and molecular weight will come down in long-term exposure to moisture.

Place aqueous resin on grained release paper, bake to get a dry resin film. Test with a hydrolysis machine, adjust temperature to 80℃ and humidity to 95%,watch line retentivity of the dry film. As stated in the figure, for resin without crosslinker, line of the dry film disappeared after two days, the surface became sticky and hydrolysized. When 2% of crosslinker is employed, hydrolysis durability increased immensely. The dry film can stand up to 14 days of high temperature and high humidity, keeping good lining and dry smooth touch.

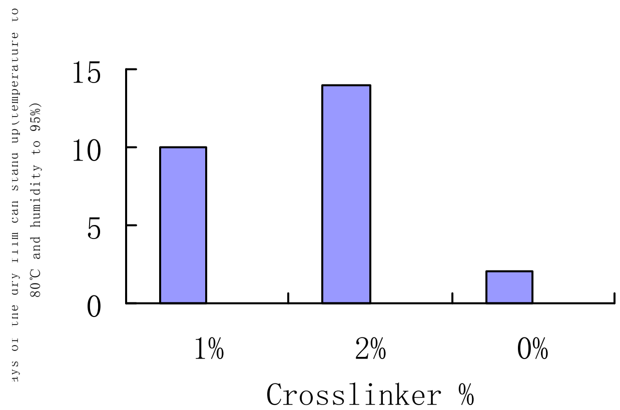

Fig.4 Effect of crosslinker on aqueous resin hydrolysis durability

4 Conclusion

a. Aqueous polyurethane used as surface-coat layer for transfer-film leather has become industrialized in Guangdong Tyen Chemicals Co., Ltd., whose aqueous PU resin bears analogous properties and performance to those of solvent products and the equal products from overseas countries.

b. The stated aqueous resin required little adjustment of process for synthetic leather. It reduces production cost with its economical price performance ratio.

c. With the success of its research and development, the aqueous PU resin is going to be an overall substitute for solvent PU resin. This will radically settle problems, such as public health and environment pollution, leading synthetic leather production to a virtuous cycle to keep advantage in international competition.

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