Research progress on hydrolytic stability of polyester polyurethane dispersions

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Abstract: This review summarizes the progress made by polyester polyurethane dispersions at home and abroad, focusing on improving their storage stability and coating film resistance to hydrolysis in the past ten years, and proposes suggestions for their research directions.

1. Preface
Aqueous polyurethane refers to a binary colloidal system formed by dissolving or dispersing polyurethane in water, so it is also called water-based polyurethane or water-based polyurethane [1]. Water-based polyurethane is widely used in adhesives, coatings, finishing agents and fabric coatings, fiber surface treatment agents and paper surface treatment agents due to its advantages of adjustable softness and hardness, high bonding strength, good flexibility, and low temperature resistance [2].

Waterborne polyurethanes are classified into polyether polyurethanes and polyester polyurethanes according to the types of polyols used during synthesis. Polyester polyurethane refers to an emulsion formed by using polyester polyol oligomers, chain extenders, and diisocyanates as raw materials and dispersing polyurethane prepared by ordinary methods in water. Since polyester type has higher strength and hardness than polyether type, polyester is usually used as the soft segment of polyurethane. However, the presence of ester groups is very easy to hydrolyze, so polyester polyurethane dispersions are poor in hydrolysis resistance.

The effect of water on polyurethane has two aspects. One is that water enters between the molecules and acts like a plasticizer. It generates hydrogen bonds with the polar urethane in the molecules, which greatly weakens the hydrogen bonds between the main polymer chains, resulting in polyurethane Physical performance is reduced. This water absorption is reversible and belongs to a physical change. After drying and dehydration, the original performance can still be restored. The second is the chemical change of hydrolysis, which is irreversible. Among various polyurethane hydrolysis, the polyester type is the most obvious. The ester group of the main chain is hydrolyzed to produce two shorter chains, one of which is a hydroxyl group at the end of the short chain and the other is a carboxyl group. The acidic carboxyl group accelerates the further hydrolysis of other ester chains, which is an autocatalytic chain reaction [3].

The hydrolysis mechanism of polyester polyurethane [4] is shown in Figure 1:
In order to improve its poor water resistance, scholars and scientific research institutions at home and abroad have conducted a lot of research and exploration, and achieved important results. By consulting the literature in this field, the author found that the ways to improve the water resistance of polyester polyurethane can be mainly divided into the following four categories: (1) Adding additives; (2) Improving monomers and processes; (3) Crosslinking modification; (4) Compound modification. Among them, compound modification mainly includes: silicone modification, epoxy resin modification and acrylic acid modification.

2. Additional additives
When the polyester polyurethane dispersion is in contact with water for a long time, the polyester segment will undergo a hydrolysis reaction and break to form carboxyl groups. At this time, an auxiliary agent similar to carbodiimide can be added to the system to react the carboxyl group in the system to form a stable ureide to inhibit the continuation of hydrolysis, thereby improving the hydrolysis resistance of polyester polyurethane. The mechanism is as follows:

\[ RNCNR \stackrel{\text{carbodiimide anti-hydrolysis mechanism}}{\longrightarrow} RCOOH \]

The research results show that [5], adding carbodiimide to polyester polyurethane, when the mass fraction of addition is 0.1 to 5%, the hydrolysis resistance of the material is greatly improved.

At present, Germany's LANXESS company Rhein Chemie produces various specifications of hydrolysis resistant products such as Stabaxol-1, Stabaxol-P, Stabaxol-P100, and Stabaxol-P200.

3. Improve monomer and process
The selection of polyester polyol monomer is very important to improve the hydrolysis resistance of waterborne polyurethane. Ertel [6] found that the hydrolysis resistance of polyester polyurethane increases with the increase of the hydrophobic group in the molecule and the decrease of the ester group content, and its hydrolysis resistance increases. In addition, Turpin's six-atom empirical rule [7] also shows that the degree of hydrolysis of polyester-based waterborne polyurethane dispersions is related to the composition of polyester diols. The greater the steric hindrance factor of polyester diols, the smaller the degree of hydrolysis. Therefore, long-chain dibasic acids and diols can be used as raw materials (such as sebacic acid, 1,6-adipic acid, 1,6-hexanediol, etc.) to prepare hydrolysis-resistant polyester polyurethane. Someone in China has studied the influence of alcohol chain extenders on the performance of waterborne polyurethane [8], and found that the use of trifunctional alcohols as chain extenders can improve the water resistance of the film.

Polycarbonate or polyether backbone-based polyurethane dispersions exhibit excellent hydrolysis resistance. Therefore, when preparing polyester polyurethane dispersions, you can consider using an appropriate amount of polyether polyol or polycarbonate polyol to To make up for the lack of hydrolysis resistance of polyester polyurethane dispersions. Yang CH et al. [9] and Yen MS [10] respectively reported the synthesis of water-dispersed polyurethane with ternary polyglycol, and
proposed the use of composite polyglycol to complement each other's advantages and complement each other to synthesize a water-dispersed polyurethane with excellent performance. This provides a good idea for the modification of water-dispersed polyurethane, and composite modification will also become an inevitable development trend.

The choice of hydrophilic chain extender also affects the hydrolysis resistance of the entire system. With the increase of the hydrophilic chain extender, the stability of the polyurethane dispersion will be increased, but the water resistance of the film will also decrease. Therefore, if considering the water resistance of the film, add as little hydrophilic monomer as possible. If the same macromolecular chain contains ionic and non-ionic hydrophilic groups, due to their synergetic effect, a small amount of internal emulsifiers (ie ionic hydrophilic groups) can meet the stability requirements. In order to have the advantages of both ionic and non-ionic waterborne polyurethane dispersions, ionic and non-ionic hydrophilic groups can be introduced at the same time. Bayer and Mobay emphasize that it is necessary to introduce ionic and non-ionic hydrophilic groups into the same polyurethane molecular chain, so that it can have good resistance to multiple electrolytes and low sensitivity to other additives, and the thermal stability of the film is also better. The combination of the two has a synergetic effect, which can reduce the required content of hydrophilic groups in the structure and improve the water resistance of the material after film formation. In addition, compared with carboxylate polyurethane, sulfonate polyurethane contains little or no amine compounds, and has high solid content, high ionic strength, low viscosity, excellent acid and alkali resistance stability, and good appearance reproducibility. At the same time, the formed latex film has high crystallinity, large initial adhesion, high bonding strength and good water and heat resistance[11]. Bayer's Desmodur® U series sulfonate polyurethane dispersion has been widely used in coatings, adhesives and fabric finishing agents, and its performance has reached the solvent-based similar products.

The Shanxi Institute of Applied Chemistry adopts the method of combining process and formula design, introduces special segments into the molecule, and uses ordinary polyester polyols to prepare water-based polyurethane adhesives with excellent water resistance. The bonded test pieces are in water. Natural soaking for 3 months and 6 months has no change in strength, and the effect is better than adding carbodiimide substances, and it avoids the disadvantage of storage stability reduction caused by the addition of such substances.

4. Crosslinking modification
Crosslinking modification is to connect linear polyurethane macromolecules through chemical bonds to form a polyurethane resin with a network structure. It is a very effective way to convert thermoplastic polyurethane resin into thermosetting resin. The crosslinked waterborne polyurethane coating film can exhibit excellent water resistance, solvent resistance and mechanical properties. It is one of the most effective ways to improve the performance of waterborne polyurethane resins. Part of the waterborne polyurethane prepared by mature crosslinking modification technology, such as two-component Water-separable polyurethane has reached or even exceeded the performance of solvent-based polyurethane resins.

Cross-linking is usually divided into internal cross-linking method and foreign-linking method. The internal cross-linking method is convenient to use, but it is easy to produce high-viscosity prepolymer during production, which leads to difficult emulsification and easy to produce gel; the external cross-linking method usually adds a cross-linking agent before use, and forms cross-links by heating or other methods. Structure, thereby improving the water resistance and other comprehensive properties of the coating film, so it is not very convenient to use, but this method is very effective and has been paid more and more attention.

Bayer's Desmodur® D series product is a cross-linking agent. The product is added to the aqueous polyurethane dispersion at a ratio of 3% to 5% before use, which can effectively improve the water resistance of the coating film. At present, supporting the use of Desmodur® U series waterborne polyurethane emulsions and Desmodur® D series cross-linking agents in adhesives, coatings and other fields occupy a dominant market position.
5. **Compound modification**

5.1 **Silicone modification**
Polyorganosiloxane is a type of polymer with repeated Si-O bonds as the main chain and directly connected to the organic group on the silicon atom. It is customary to refer to silane monomers and polysiloxanes as organosilicon. Due to the special structure and composition of silicone, it has the advantages of good low temperature flexibility, low surface tension, good biocompatibility, flame resistance, good weather resistance, and good thermal stability. The use of silicone to modify waterborne polyurethane can combine the excellent properties of the two and make up for their respective defects, so that the modified waterborne polyurethane exhibits good hydrophobicity, surface enrichment, low temperature flexibility and other properties.

Qing Ning et al. used polyester polyol, silicone oligomer, polyisocyanate, chain extender and hydrophilic chain extender as the main raw materials to prepare anionic silicone copolymer modified polyurethane emulsion. The results show that the silicone-modified polyurethane emulsion has good stability, and the siloxane segments can be enriched on the surface of the emulsion film, which has a significant surface modification effect on the polyurethane material, which improves the water resistance, while the mechanical properties of the body are not changed.

Li Wei et al. used polyester polyol, isophorone diisocyanate, methyl methacrylate, etc. as raw materials to synthesize a water-based polyurethane acrylic emulsion, and then added organosiloxane containing pendant amino groups and unsaturated double bonds after chain extension modification, a series of silicone modified polyurethane emulsions were obtained. The study found that after the modification of silicone, the water resistance of the system was significantly improved, and in terms of water resistance, the diamino silicone was better than the mono amino silicone. It was also found that the organic silicon with reactive groups on the branch Silicon performs better in terms of water resistance.

5.2 **Modification of epoxy resin**
Epoxy resin has the advantages of good chemical and thermal stability, high strength, strong adhesion and good processing performance, but it also has shortcomings such as brittleness after curing, poor impact resistance, easy cracking, insufficient flexibility and poor wear resistance. The epoxy resin is a polyhydroxy compound, and the epoxy resin is grafted into the polyurethane backbone to obtain waterborne polyurethane with better performance. Changshu Institute of Technology based on the waterborne epoxy resin synthesized in advance, using TDI, polyester polyol, trimethylolpropane and epoxy resin AG-80 as the main raw materials, successfully under the action of various additives Developed a blue-blue epoxy resin modified waterborne polyurethane emulsion. The product's anti-chemical corrosion performance has been significantly improved. After immersing in water for 48 hours (or immersing in acetone for 24 hours), the coating film is complete and does not turn white. Good comprehensive performance (such as tensile strength of 35 MPa, film hardness of 0.92 and elongation at break of 490%, etc.) This project solves the problems of traditional waterborne polyurethane emulsions such as difficulty in emulsification, poor storage stability and frequent gelling, and its practical value Higher.

Li Likun uses isophorone diisocyanate and polyester polyol as the main raw materials, and dimethylolpropionic acid as the hydrophilic chain extender. It is modified by adding different types and different contents of epoxy resin E12 and E51. Performance, synthesized epoxy resin modified waterborne polyurethane emulsion. The results show that the E12 modified waterborne polyurethane dispersion has larger particle size, lower viscosity and excellent storage stability than the E51 modified waterborne polyurethane dispersion. Because of the cross-linked structure formed in the E12 modified waterborne polyurethane system, it has better mechanical properties and lower water absorption.

Lai Xiaojuan et al. used polyester diol as the soft segment, isophorone diisocyanate and hexamethylene diisocyanate as the hard segment, and epoxy resin E244 as the macromolecular crosslinking agent. A series of epoxy resin modified anionic waterborne polyurethane self-emulsifying
emulsions, and a cured film of modified waterborne polyurethane was prepared. Through the contact
angle test, it was found that as the content of E244 increases, the contact angle tends to increase,
which means that Epoxy resin has a greater impact on the water resistance of polyurethane. As its
content increases, the water resistance of polyurethane is increasing.

Jiang Shouxia et al. [19] found that when the amount of epoxy resin E-20 gradually increased, the
water resistance gradually increased, but the viscosity of the system gradually increased, and the
hardness gradually increased. The industrial production system is unfavorable. Therefore, when the
amount of epoxy resin added is 6.0-8.0%, the comprehensive effect of the modified aqueous
polyurethane dispersion is best.

5.3 Acrylic modification
Among the various modification methods, the most eye-catching is the research of
polyurethane/polyacrylic acid modified composite emulsion, which is called "the third generation of
waterborne polyurethane". Acrylic resin has the advantages of high mechanical strength, aging
resistance, light resistance and yellowing resistance, and good water resistance. Modification of
waterborne polyurethane with acrylic monomers can make up for the shortcomings of waterborne
polyurethane and organically combine the properties of polyurethane and acrylic. It shows the
advantages of high hardness, good abrasion resistance, chemical resistance, and no environmental
pollution.

The copolymerization modification of acrylate compounds to waterborne polyurethane is to add
acrylate into the polyurethane emulsion, and then through the initiator for free radical polymerization
to prepare a composite emulsion [20]. The preparation methods are mainly as follows [21]: (1) Blending
of polyurethane emulsion and acrylate emulsion, and copolymerizing with a crosslinking agent to form
a polyurethane and acrylate composite emulsion; (2) First synthesize a polyurethane polymer emulsion,
which is The seed emulsion is then subjected to acrylate emulsion polymerization to form a
polyurethane and acrylate composite emulsion with a core/shell structure; (3) The two emulsions
penetrate each other with molecular lines, and then react to form a polymer interpenetrating network
of polyurethane and acrylic Ester composite emulsion; (4) Synthesis of unsaturated urethane monomer
with C=C double bond, and then emulsion copolymerization of macromonomer and acrylate monomer
to obtain polyurethane and acrylate copolymer emulsion.

Xiang Shanglin et al. [22] used a self-emulsification method to prepare a polyester water
borne polyurethane emulsion, and then modified it with acrylate to prepare a waterborne polyurethane and
acrylate copolymer emulsion, and combined the polyacrylate emulsion with the polyurethane emulsion
in different proportions. mix. The results show that acrylate can improve the water resistance of
waterborne polyurethane adhesives, and the copolymerized polyurethane/acrylate composite emulsion
is better than the blended type.

Du Ying et al. [23] used toluene diisocyanate, polyester, dimethylolpropionic acid as raw materials,
hydroxyethyl acrylate as grafting agent, and butyl acrylate as modifier, to prepare acrylate-modified
waterborne polyurethane for wood processing Lotion. The results show that the self-made emulsion
has high bonding strength, good water resistance, no stringent requirements on the water content of the
raw materials, low hot pressing temperature, and excellent comprehensive performance.

Liu Jingsong et al. [24] used isophorone diisocyanate, dimethylolpropionic acid, polyester diol,
trimethylolpropane, 1,4-butanediol and hydroxyethyl acrylate as the main raw materials to prepare
Acrylate modified waterborne polyurethane adhesive emulsion was prepared by adding acrylate
monomer to the waterborne polyurethane emulsion terminated by hydroxyethyl acrylate for free
radical polymerization. The results show that when w(-COOH) is 1.48% to 1.50%, w(PA) is 30%, and
m(MA):m(BA) is 4:2, the water resistance of the modified waterborne polyurethane adhesive,
Excellent heat resistance and flexibility, bonding strength up to 5.9 N/mm.

6. Conclusion
With the advancement of technology, there are more and more modification methods and methods.
These new modification methods provide people with new ideas for preparing polyester waterborne polyurethane dispersions with excellent hydrolysis resistance. At present, the focus of waterborne polyurethane research at home and abroad is high performance and high functionality. The development of high performance and multi-purpose products that meet market needs is the future development direction of waterborne polyurethane. Further technical innovation of polyester waterborne polyurethane dispersion resistance to hydrolysis should include the following:

(1) Research on the synthesis of new types of polyester diols or polyether diols and the strengthening of composite (binary or ternary) polyglycols to synthesize water-dispersed polyurethanes.

(2) Develop and apply high-efficiency hydrophilic chain extenders and special crosslinking agents to improve the stability of water-dispersed polyurethane emulsions and the water and solvent resistance of the coating film. Strengthen the research on the effect of chain extender type and dosage on performance.

(3) Strengthen the research of compound modified water-dispersed polyurethane (especially acrylic modification, silicone modification, epoxy resin modification) to improve the comprehensive performance of water-dispersed polyurethane.

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