Research of Properties and Preparation of Waterborne Polyurethane Adhesives for Shoes

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Abstract: In this paper, a waterborne polyurethane adhesive for shoes has been prepared by a composite method, and a series of tests such as peel strength, heat resistance, yellowing resistance, and hydrolysis resistance were performed on the sample. The results show that the performance of the water-based polyurethane adhesive prepared by this method has reached the level of similar products in the market. It has great promotion significance in shoe factories.

1. Introduction
Adhesives for shoes have undergone a development process from low-end to high-end, from non-environmental protection to environmental protection. The first generation is ordinary chloroprene adhesive, the second generation is graft-modified chloroprene and solvent-based polyurethane adhesive, and the third generation is methacrylic-modified “triphenyl-free” chloroprene adhesive, graft-modified Neoprene adhesive and polyurethane (PU) adhesive [1]. Although the third generation has solved the problem of benzene pollution, it still cannot solve the problem of organic matter volatility (VOC). In the 1990s, the fourth generation of environmentally-friendly adhesives appeared, the main representative of which is water-based adhesives, and the outstanding performance and outstanding performance of water-based polyurethane adhesives are particularly noticeable [2-5].

Water-based polyurethane is a binary colloid system with water as the dispersion medium. The adhesive products made from it are highly adhesive, non-toxic, odorless, do not generate static electricity, and have good flame retardancy. It is suitable for metals, fabrics, leather, The bonding of rubber, EVA and other shoe materials can basically replace solvent-based polyurethane adhesives.

At present, except for a small number of Taiwan-funded enterprises in China-and only limited to high-end travel shoes such as NIKE, ADIDAS, REEBUK, and special requirements from European and American importing countries-most of them still use solvent-based polyurethane adhesives except water-based polyurethane adhesives.

This situation is caused by various reasons. First, in some aspects, the performance of water-based polyurethane is worse than that of solvent-based polyurethane adhesives [6]; second, domestic environmental protection legislation is incomplete or enforcement is not good enough; third, although there has been some domestic industrialization of water-based polyurethane in recent years The degree of progress has been improved, but the gap is still relatively large compared with foreign countries. Fourth, the matching adhesive additives are basically in the initial stage.

According to the author's research, the water-based polyurethane adhesive products currently used in shoe factories are mainly from Taiwan Dadong, South Korea Dongcheng, Taiwan Nanbao and other companies.

In this article, the author has prepared a waterborne polyurethane adhesive for shoes by a compound
method. The test results show that it can basically meet the on-site bonding requirements of shoe factories.

2. Experimental part

2.1. raw material
Dispercoll U 54, Bayer Material Technology Trading (Shanghai) Co., Ltd.; MYT 6996A, Bayer Material Technology Trading (Shanghai) Co., Ltd.; L75N, Borchers; BYK 024, Germany's Becker.; BYK 375, Germany's Becker.

2.2. Preparation of water-based polyurethane adhesive
Add the appropriate amount of U 54 emulsion and 6996A emulsion to a suitable stainless steel container. Turn on the stirring; add the leveling agent BYK 375 and antifoaming agent BYK 024 in this order. After stirring for 5 minutes, L75N was slowly added dropwise. After adjusting to the target viscosity, stirring was continued for 30 minutes and then stopped. Then use a 60-mesh filter to filter the prepared glue solution, and the filtered glue solution is the target sample.

2.3. Performance test

2.3.1. Appearance
Visually check its glue state.

2.3.2. Viscosity
The target sample was placed in a constant temperature biochemical incubator at 25 °C for 24H. After stabilization, the viscosity was measured with a rotor viscometer (BROOKFILDE, LVDVE230).

2.3.3. Solid content
Weigh 2 to 5 g (W2) of the sample in a clean and dry watch glass, and place it in a 120 °C constant temperature blast drying oven (Shanghai Jinghong, DHG-9246A) for about 2 hours. Cool down to room temperature and weigh. (W1), then the solid content = (W1 / W2) × 100%.

Note: In the three tests of 1.3.1-1.3.3, the target sample is directly taken for testing, and from 1.3.4-1.3.8, 3 to 5% of the curing agent is added to the target sample and stirred Test under mixing.

2.3.4. Determination of hydrolysis resistance
The test piece uses canvas with a length × width = 60 mm × 25 mm specification. Both test pieces are coated with glue and placed in a drying box at 55 ~ 60 °C. After drying for 3 ~ 4 minutes, the two bonding surfaces are bonded to each other. Then press it under the pressure of 3-4 KG for 10s, and leave it at room temperature for a period of time, store it in a hydrolysis-resistant machine at 70 °C × 95% humidity, and then take it out every 7 days to test its peel strength.

2.3.5. Determination of peel strength
The test piece uses a PVC sheet with a length × width × thickness = 120 mm × 25 mm × 3 mm. The surface of the test piece is cleaned with methyl ethyl ketone. Both test pieces are glued and placed in a drying box at 55 ~ 60 °C for 3 ~ After 4 min, the two bonding surfaces were bonded to each other, and the pressure was applied with a press (Wenling Tingwei Vacuum Equipment, TW-1A type) at a pressure of 3 to 4 KG for 10 s, and it was left at room temperature for 5 min. High-speed rail inspection instrument, AI-7000S). During the test, clamp one end of it in the upper and lower clamps symmetrically, and the clamping part cannot slide. Start the tensile tester. The upper and lower clamps were separated at a rate of (100 ± 10) mm / min, and the mean value of the peeling force was read on a digital display to obtain the initial peeling strength. The peel length of the specimen is (50 ± 10) mm. The unpeeled part was left at room temperature for 24 h. The peeling test was performed in the same procedure, and the average peeling force was read to obtain the later peeling strength, and the form of failure was recorded.
2.3.6. Determination of heat resistance
The test piece uses a PVC sheet with a length × width × thickness of 60 mm × 25 mm × 3 mm. The surface is cleaned with methyl ethyl ketone. Both test pieces are glued and placed in a drying box at 55 ~ 60 ℃ and dried for 3 ~ 4 minutes. After 4 minutes, the adhesive surfaces of the test pieces were put on each other, and then pressed with a press at a pressure of 3 to 4 KG for 10 seconds. The test pieces were placed for 5 minutes after gluing, then placed in a constant-temperature drying oven at a temperature of (70 ± 1) ℃, and then taken out after holding for 10 minutes, and the length of the cracked surface was measured to determine the heat resistance value.

2.3.7. Determination of viscosity retention time
Take a rubber strip with a length × width = 60 mm × 25 mm specification, roughen it, and then brush and dry it. Immediately after drying, take it out of the oven and place it in a 25 °C constant temperature room, and then start counting from this time. At an interval of 1min, apply 5mm from the end of the rubber to each other. When applying the next time, you must cut off the last bonding part with scissors., Until it can not be posted, this time is recorded as the sticky maintenance time.

2.3.8. Pot life determination
Pot life is the normal usage time after the glue and curing agent are prepared. This is because the water-based polyurethane begins to react and crystallize after the hardener is added. If the crystal is dried and activated after the crystallization is complete, the formed adhesive film will no longer be sticky. This phenomenon is called "dead glue". Dead glue is irreversible. Therefore, the prepared glue must be used up in the pot life of the glue.

2.3.9. Determination of yellowness
Take a white EVA cube with length × width × thickness = 10 mm × 10 mm × 10 mm. After cleaning the surface, apply the glue. When applying the glue, make it as thin and uniform as possible to avoid the build-up and lack of glue. Then place it at 55~ 60. Dry in a drying box at ℃. After drying, place it in a yellowing machine (Chinese high-speed rail detection instrument, GT-7035UB) and irradiate it with 2H, take it out and compare it with a standard color chart, and read the level of yellowing.

3. Results and discussion
The U 54 water-based polyurethane emulsion produced by Bayer has 50% high solid content, no yellowing, low activation temperature, high initial peel strength, and stable performance. It has been in the domestic and foreign markets since its introduction to the market, leading position. However, the disadvantage of this product is its poor heat resistance, which greatly limits the promotion and application of the emulsion in the shoe adhesive industry. Bayer is also aware of this, and in 2008 developed another water-based polyurethane emulsion MYT 6996A. The emulsion has a large molecular weight and is particularly outstanding in heat resistance, but it has the disadvantage of poor initial viscosity, especially compared with U54.

Therefore, U54 and 6996A are highly complementary. Through the method of orthogonal experiments, the author found an optimal ratio of the two. At this ratio, supplemented with auxiliary additives, a shoe adhesive product with excellent performance and comparable to market rivals was formulated.

The prepared adhesive sample has a milky appearance, a viscosity of about 5000 CPS / 25 °C, and a thixotropic coefficient of 1.8 to 2.0. It is very suitable for brushing the surface of rubber, MD EVA, leather, canvas and other shoe materials.

The solid content of the gel sample reaches 50%, and the moisture can be dried by drying at 55-60 °C for 2 to 5 minutes. The glued surface has high bonding strength, and the year-on-year performance has reached the level of solvent-based polyurethane adhesive. For rubber and PVC materials, the initial peel strength can be more than 6.0 N / mm, and the later peel strength can be more than 10.0 N / mm or the material is damaged.
For shoe adhesives, in addition to being easy to apply and having good initial tack, other properties are also indispensable, such as heat resistance, yellowing resistance, and hydrolysis resistance. In the heat resistance test of this rubber sample, the heat resistance value can reach 25 mm, and under the environmental condition of 70 °C × 10min, it does not pop open at all. In the yellowing test, the yellowing resistance value can reach 4.8, which is basically not yellowing. This can be used for the bonding of white or light-colored shoe materials, and there is no need to worry about the yellowing of the manufactured shoes to affect the appearance. In the hydrolysis resistance test, after five weeks of hydrolysis resistance test, it was found that the bonding surface can still maintain more than 70% strength in the first 3 weeks.

4. Conclusion
Bayer water-based polyurethane emulsions U54 and 6996A were used as the main raw materials, followed by adhesive samples prepared by the corresponding functional assistants. The samples were tested for peel strength, heat resistance, and hydrolysis resistance. The test results show that the glue sample has high peel strength, good heat resistance, excellent hydrolysis resistance, etc., and its comprehensive performance has reached the level of waterborne polyurethane adhesives in the market for similar shoes.

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