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Synthesis And Application Of Aliphatic Polyurethane Resin Modified By Silicone For Synthetic Leather

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Abstract: Silicone modified aliphatic polyurethane resin was synthesized from polyester polyol, isophorone diisocyanate (IPDI) and polyether modified polysiloxane (PO-PDMS). The effects of different organosilicon content on polymer state, mechanical properties, water resistance and yellowing resistance, and the application of organosilicon modified aliphatic polyurethane resin on synthetic leather were investigated. The results show that compared with physical blending, the copolymerization of PO-PDMS with polyurethane can effectively improve the compatibility of silicone and polyurethane resin. After the modification of silicone, the modulus of polyurethane resin film is reduced, the tensile strength is maintained at about 48 MPa, the water resistance is significantly improved, and the yellow resistance is not affected. When the mass fraction of PO-PDMS is 2% to 4%, the heat resistance and feel of synthetic leather can be effectively improved.

Keyword: Ynthetic leather; fatty polyurethane; silicone-polyurethane; yellow stain;hand feel

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With the improvement of people's living standards and aesthetic taste, synthetic leather products not only need to be strong and durable, but also have good appearance and touch, which puts higher requirements on the production of polyurethane resin for synthetic leather he biggest feature of fatty polyurethane resin is its excellent yellowing resistance, which is often used in light-colored high-grade synthetic leather products.

In the production of synthetic leather and the treatment of synthetic leather after the stage,

in order to improve the surface touch of synthetic leather, increase the water resistance and heat resistance of synthetic leather, a small amount of silicone additives will be added to synthetic leather. Because the compatibility of silicone additives and polyurethane resin is not good, adding a small amount of silicone will affect the existing researchers through the method of copolymerization of silicone and polyurethane resin, improve the compatibility of silicone and polyurethane, to avoid the side effects caused by incompatibility.

Finally, the luster of synthetic leather, the amount of organic silicon will precipitate, resulting in the surface of synthetic leather.

In this experiment, polyester polyol, isophorone diisocyanate (IP-DI) and polyether modified polysiloxane (PO-PDMS) were used as the main raw materials, and polysiloxane was copolymerized in polyurethane chain segment to synthesize silicone modified aliphatic polyurethane resin. The effect of silicone content on the appearance of polyurethane resin and the application property of synthetic leather was analyzed.

1. EXPERIMENTAL PART

1.1 MAIN RAW MATERIALS AND EQUIPMENT

Polybutylene adipate (PBA,M=2000);Industrial grade, Qingdao Xinyutian Chemical Co, LTD; Isophorone diisocyanate (IPDI), Isophorone diamine (IPDA), Industrial grade, Evoni-kDegussa Company; Polyether modified polysiloxane (PO-PDMS), Industrial grade, Maitu High-tech Materials Group; 1, 4-butanediol (BDO),CP,Shanghai Chemical Reagent Co., LTD. Wulian Chemical Plant; Dibutyltin dilaurate, toluene, ethyl acetate, AR, Shanghai Chemical Reagent Co., LTD. N, N-dimethylformamide, butanone, AR, Hangzhou Shuanglin Chemical Reagent Factory; Common aliphatic polyurethane resin, homemade. EUROSTAR 2000 Mixer, IKA Group, Germany; GT-AI-3000 type electronic tension machine, GT-7035-UB type yellowing resistance test box, high-speed Rail Testing Instrument (Dongguan) Co, LTD. DHG-9123A thermostatic air drying oven, Shanghai Yiheng Scientific Instrument Co, LTD. X-rite 8200 color difference meter, Aiseli Corporation, USA; PICO-GLOSS 560mc gloss meter, ERICHSEN GMBH.

1.2 SYNTHESIS PROCEDURE

1.2.1 Preparation Of Silicone Modified Aliphatic Polyurethane Resin

Accurately weighed PBA2000 and PO-PDMS were added into a 1000mL four-port glass reactor, which was heated to 100℃, dehydrated under vacuum for 1h, then IPDI and some toluene were added, and the reaction was conducted at 80℃ for 3h.

Samples were taken, and the NCO content of the prepolymers was determined by di-n-butylamine method. When the NCO mass fraction of the prepolymer reaches the theoretical value of 7.16%, BDO is added to extend the chain, the reaction continues for 3h at 80℃, and the NCO content is measured by sampling. When the NCO mass fraction reaches the theoretical value of 4.23%, the reaction is cooled and stopped.

Add the remaining toluene, butanone and ethyl acetate into the above materials, stir well, then drip IPDA into the reactor to control the reaction temperature to keep below 40℃. When the viscosity of the resin reaches the set value, the drip of IPDA is stopped, and the solid mass fraction of silicone modified aliphatic polyurethane resin is about 25%.

1.2.2 Preparation Of Blended Modified Polyurethane Resin

A certain amount of PO-PDMS was added to the common aliphatic polyurethane resin and stirred for 30 min to obtain the silicone blend modified polyurethane resin as a comparative experiment.

1.2.3 Preparation Of Modified Polyurethane Resin Film

The defoamed polyurethane resin was poured on a 150mm× 150mm polyteflon plate, placed in a low temperature oven at 40℃ for 24h, and then placed in a high temperature oven at 130℃ for 15 min to make a polyurethane resin film with a film thickness of about 0.1mm.

1.2.4 Preparation Of Polyurethane Finishing Agent And Synthetic Leather Paste

The modified polyurethane resin and solvent were mixed according to the ratio in Table 1 and then stirred evenly to prepare polyurethane finishing agent and synthetic leather paste.

Formulation of polyurethane finishing agent and synthetic leather paste (mass part)

Components	Finishing agent	Synthetic leather slurry
Modified polyurethane resin	50	70
N,N-Dimethylformamide		20
Toluene		10
Ethyl acetate	50	-

When the NCO mass fraction of the prepolymer reaches the theoretical value of 7.16%, BDO is added to extend the chain, the reaction continues for 3h at 80℃, and the NCO content is measured by sampling. When the NCO mass fraction reaches the theoretical value of 4.23%, the reaction is cooled and stopped. Add the remaining toluene, butanone and ethyl acetate into the above materials, stir well, then drip IPDA into the reactor to control the reaction temperature to keep below 40℃.

1.3 ANALYSIS AND TESTING

1.3.1 Mechanical properties test

Test according to the method specified in GB/T 1040.3-2006 "Determination of tensile properties of plastics".

1.3.2 Water absorption test

The modified polyurethane resin film was prepared into a 50mm × 50mm sample, and its mass was called m.Put in the removal sub-water at 50 ° C for 24 h, then take out, quickly wipe the surface moisture said its mass is m, water absorption rate $w=(m_1-m_0)\times100\%/m$.

1.3.3 yellowing resistance test

The modified polyurethane resin film made in 1.2.3 was irradiated by ultraviolet light in a yellowing resistance test chamber with a UV power of 30W×2.

Shine for 4h, and then test the color difference △E before and after ultraviolet irradiation with a color difference meter, and then determine the yellowing resistance level according to GB/T 250-2008 "Gray sample card for evaluating color change".

1.3.4 Brightness test

The polyurethane finishing agent prepared by the method of 1.2.4 was rolled on the surface of the dry synthetic leather, and then the surface gloss of the dry synthetic leather was tested by a gloss meter.

1.3.5 Heat resistance adhesion test

The synthetic leather sample was prepared by using the synthetic leather paste prepared

in 1.2.4 as the dry surface layer, and then the heat resistance adhesion was tested according to the method specified in GB/ T8949-1995 "Polyurethane dry artificial leather".

2 .RESULTS AND DISCUSSION

2.1 INFLUENCE OF SILICONE CONTENT ON THE APPEARANCE OF MODIFIED POLYURETHANE RESIN

Two methods of block copolymerization and physical blending were used to investigate the influence of silicone content on the appearance of polyurethane resin solution and its film, and the results are shown in Table 2.

Effect of organosilicon content on the appearance of copolymerized and blended polyurethane resin and its film

Mass Fraction (%)	Polyurethane Resin Solution Block Copolymer	Polyurethane Resin Solution Physical Blend	Polyurethane Resin Film Block Copolymer/Physical Blend
0	Colorless and transparent	Colorless and transparent	Colorless and transparent
2	Colorless and transparent	Turbid	Colorless and transparent, Semi-transparent
4	Colorless, extremely slightly turbid	Turbid	Colorless and transparent, Semi-transparent

Mass Fraction (%)	Polyurethane Resin Solution Block Copolymer	Polyurethane Resin Solution Physical Blend	Polyurethane Resin Film Block Copolymer/Physical Blend
6	Colorless, slightly turbid	Turbid	Colorless and transparent, Semi-transparent
10	Slightly turbid, slightly yellowish	Severely turbid	Colorless and transparent, Semi-transparent
15	Slightly turbid, slightly yellowish, more turbid	Severely turbid, separated after overnight storage	Colorless and transparent, Semi-transparent

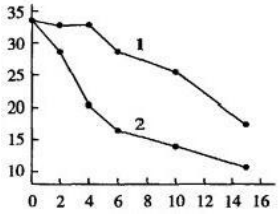
As can be seen from Table 2, the unmodified common aliphatic polyurethane resin is colorless and transparent. When the mass fraction of silicone in the modified aliphatic polyurethane obtained by the block copolymerization method (relative to the solid portion of polyurethane resin, the same below) is between 2% and 6%, the modified polyurethane resin has a good appearance and is colorless transparent or slightly cloudy liquid.When the mass fraction of silicone exceeded 10%, the modified polyurethane resin began to turn yellow and cloudy, which was mainly caused by the incompatibility of silicone and polyurethane resin.

Although through copolymerization, silicone and polyurethane resin reached the molecular level of mixing, with the increase of silicone content, silicone aggregation and phase separation occurred in the polyurethane chain segment. This results in a cloudy polymer. This phase separation is still at the microscopic level, and no stratification occurs from the outside of the polyurethane resin, and the state of the resin is still good, while the aliphatic polyurethane resin modified by physical blending with the same silicone content has serious turbidity and stratification.

The film is colorless and transparent, and the film is translucent after blending PO-PDMS with common aliphatic polyurethane resin. The results showed that the compatibility of silicone and aliphatic polyurethane resin was improved by block copolymerization.

2.2 INFLUENCE OF SILICONE CONTENT ON GLOSS OF POLYURETHANE FINISHING AGENT

The gloss of polyurethane resin coating can also reflect the compatibility of polyurethane resin and silicone resin.In this experiment, polyurethane finishing agent was prepared by block copolymer and physical blending modified aliphatic polyurethane resin, and then rolled on the surface of synthetic leather. The influence of silicone content on the gloss of copolymer and blending modified aliphatic polyurethane finishing agent was investigated. The results are shown in Figure 1



1 - block copolymerization; 2 - Physical blending

Effect of organosilicon content on gloss of polyurethane finishing agent

As can be seen from Figure 1, when the mass fraction of organosilicon is less than 4%, the gloss of the organosilicon modified fatty polyurethane obtained by block copolymerization method has little change, and when the mass fraction of organosilicon is more than 4%, the gloss of the coating decreases significantly.

For the aliphatic polyurethane resin modified by physical blending, the luster decreased obviously after adding polyether modified silicone. At the same silicone content, the gloss of the aliphatic polyurethane film modified by block copolymerization is obviously better than that of the aliphatic polyurethane modified by physical blending.

This is because the distribution of silicone in the aliphatic polyurethane resin modified by block copolymerization is more uniform and the effect on finish gloss is less.

2.3 INFLUENCE OF SILICONE CONTENT ON THE PROPERTIES OF POLYURETHANE RESIN FILM

The mechanical properties, water resistance and viscosity resistance of polyurethane resin are affected by the introduction of silicone chain segments. In the experiment, the effect of silicone content on the properties of silicone modified aliphatic polyurethane resin film under block copolymerization method was investigated, and the results were shown in Table 3.

Effect of silicone content on the properties of silicone modified aliphatic polyurethane resin film

Mass Fraction (%)	0	2	4	6	10	15
100% Modulus/MPa	9.7	8.6	8.4	7.3	6.9	6.3
300% Modulus/MPa	30.8	23.5	22.6	21.5	18.1	16.3
Tensile Strength/MPa	57	46	49	50	48	40
Elongation at Break/%	430	420	420	440	460	470
Water Absorption/%	2.05	1.80	1.25	1.07	0.84	0.38
Yellowing Resistance/Grade	5	5	5	5	5	5

As can be seen from Table 3, due to the introduction of relatively soft polysiloxane and polyether chain segments into the polyurethane during the modification process, the

modulus of the silicone modified aliphatic polyurethane resin film gradually decreases and the elongation at break increases with the increase of silicone content. When the mass fraction of organosilicon is less than 10%, the tensile strength of the film is slightly lower than that of the non-added organosilicon sample, and is kept close to 48 MPa. When its mass fraction is 15%, the tensile strength is reduced to 40 MPa, but still maintains a high mechanical strength.

The results in Table 3 also show that with the increase of silicone content in polyurethane resin, the water absorption rate of polyurethane resin film gradually decreases, and the water resistance increases. With the increase of silicone content organic,the degree of aggregation of silicon chain segments on the surface increases gradually, and the density of the arrangement increases gradually, resulting in the water absorption of polyurethane materials decreases with the increase of organic silicon content.

However, the yellowing resistance of polyurethane resin film reached grade 5 after modification of different contents of silicone, and the yellowing resistance of polyurethane resin was not affected by silicone modification.

2.4 APPLICATION OF SILICONE MODIFIED POLYURETHANE RESIN ON SYNTHETIC LEATHER

Because polyurethane resin is a thermoplastic resin, the synthetic leather made under high temperature and high pressure often occurs adhesion, which affects the use. After modification by silicone, the polysiloxane chain segments are aggregated on the surface of synthetic leather to form a protective layer and prevent the adhesion of synthetic leather surface. In this experiment, silicone modified polyurethane resin was applied to synthetic leather, and the changes of silicone content on thermal adhesion and finish feel of synthetic leather were investigated. The results are shown in Table 4.

Effect of organosilicon content on application performance of organosilicon modified polyurethane resin on synthetic leather

Mass Fraction (%)	0	2	4	6	10	15

Mass Fraction (%)	0	2	4	6	10	15
Heat Resistance Adhesion/Grade	3	5	5	5	5	5
Coating Feel	Slight roughness	Smooth sensation	Oily sensation	Strong oily sensation	Intense oily feeling	Intense oily feeling

As can be seen from Table 4, when the mass fraction of silicone is 2%, the anti-adhesion performance of synthetic leather has been significantly improved; When the organic silicon mass fraction is 2%~4%, the feel of synthetic leather is more comfortable smooth or oily. As the amount of silicone continues to increase, there is a feeling of oil on the surface, but it makes the feel worse.

Therefore, in order to improve the feel, it is more appropriate to maintain the mass fraction of silicone at 2% to 4%. This is because the pure polyurethane resin feels dry, silicone modified polyurethane resin in the coating drying process, silicone will move to the surface of the polyurethane resin with a soft greasy feeling, the higher the content of silicone, the more enriched the surface, the stronger the oil feeling.

3. CONCLUSION

(1) The silicone modified aliphatic polyurethane resin solution obtained by PO-PDMS block copolymerization has good transparency, stability, and better transparency after film formation, and higher film gloss, indicating that block copolymerization has greatly improved the compatibility of silicone and polyurethane resin.

(2) With the increase of PO-PDMS content in aliphatic polyurethane resin, the modulus of copolymerized polyurethane resin film decreased gradually. When the mass fraction of silicone reached 6%, the tensile strength reached a maximum of 50 MPa; The water resistance of polyurethane resin can be improved by silicone modification, and the

yellowing resistance has no effect.

(3) Silicone modified aliphatic polyurethane resin applied to synthetic leather, when the mass fraction of silicone is 2% to 4%, it can significantly improve the heat resistance adhesion and feel of the synthesized leather.

TAKE PART IN THE ESSAY

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