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# **Application Of Organosilicon Modified Solvent-Free Polyurethane Resin In Synthetic Leather**

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**Disclaimer:** The following silicone Leather industry standard was translated from Chinese Language standard version. Due to Language habits and the translator's personal English Level, there may be some inaccuracies.

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**Abstract:** A series of solvo-free polyurethane synthetic leather was prepared by a two-component pouring process. The mass fraction of isocyanate (B component), NCO, isocyanate index (r value), Effect of soft segment type and silicone modification on properties of synthetic leather. Fourier transform infrared spectroscopy (FTI 'IR) shows that the isocyanate is fully inverted with the polysilicon polyol (OF - OH-702E). Dynamic thermomechanical analysis (DMA) showed that the glass transition temperature (L) OF the two-component polyurethane modified by OF-OH-702E decreased from 26.4 °C to 26.4 °C - 40.35 ° C. The experimental data show that when the mass ratio OF soft polycarbonate diol (PCDL-2000) and OF - OH - 702E in B component is 90/10 and the mass fraction of one NCO is 16wt %, The reaction product with polytetrahydrofuran diol (PTMG-2000) type A component has the best comprehensive performance according to r value of 1.05, and the stripping strength of solvo-free synthetic leather prepared is 110N/cm<sup>3</sup>. Taber H a 22 10009 Wear-resistant 1620 RPM, a 20. C 87,000 times fastness to folding, 10 weeks of 70°C95RH % constant temperature and humidity test peel strength retention rate of 85.2%, meet the synthesis for sports shoes Leather standard.

**Key words:** solvent-free; Polyurethane; Organosilicon; Synthetic leather

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Polyurethane synthetic leather has excellent strength, wear resistance, folding resistance and feel and features similar to the appearance of natural leather, widely used in sofa furniture, Clothing, footwear, automotive and other fields. Traditional polyurethane synthetic leather is made from polyurethane resin with toluene, butanone and N, N dimethylformamide (DMF) as solvents, but these solvents have toxic side effects, poor ecological and environmental protection, and easy to cause fire accidents.

The technology of solvent-free two-component polyurethane synthetic leather is a new method to manufacture synthetic leather, which is developed by combining the low pressure pouring machine with synthetic leather production technology. The prepolymers of A and B components with low viscosity were prepared respectively, and then were coated on the release paper by pouring machine after stirring at a certain proportion at high speed. This process does not contain any organic solvent, and the reaction is exothermic, low energy consumption, the mechanical properties of the solvent-free polyurethane synthetic leather produced can be comparable to solvent-based polyurethane, but the deficiency is the low temperature performance deviation, need to be further improved.

Silicone resin has good water resistance, high temperature resistance, low surface energy and low glass transition temperature, and has been widely used in the modification of polyurethane resin. The polyurethane synthetic leather prepared by the reaction of hydroxy-terminated silicone and isocyanate into the polyurethane chain segment has the characteristics of good low temperature flexibility, hydrolysis resistance and soft feel. But up to now, there are few reports about silicone modified solvo-free two-component polyurethanes used in synthetic leather. In this paper, the environmental protection type of solveless polyurethane synthetic leather was prepared by silicone modified solvless two-component polyurethane. The effects of B component NCO content, r value, soft segment type and silicone modification on peel strength, wear resistance, cold resistance and hydrolysis resistance of synthetic leather were comprehensively evaluated.

## 1. EXPERIMENTAL PART

### 1.1 EXPERIMENTAL MATERIALS

MDI(Industrial grade, Wanhua Chemical Group Co., LTD.); Polycarbonate diols (PCDL, Mn=2000)(industrial grade, Asahi Kasei Co., LTD.); Polytetrahydrofuran diol (PTMG, Mn=2000)(industrial grade, Mitsubishi Chemical Co., LTD.); Polybutylene adipate diol (PBA, Mn=2000)(industrial grade, Hefei Amway Polyurethane New Materials Co., LTD.); OF - OH - 702E(hydroxyl =50mgKOH/g)(industrial grade, Maitu High-tech Materials Group Co., LTD.); 1,4 monobutanediol (1, 4-BG)(industrial grade, BASF, Germany); BiCAT 8108(Industrial grade, leading US chemical company); Chinox 1010(Industrial grade, Taiwan Double Bond Chemical Co., LTD.).

## **1.2 PREPARATION OF SOLVENT-FREE TWO-COMPONENT POLYURETHANE**

### (1) Preparation of component A

Will PTMG a 2000 at 90°C ~ 1000°C, Dehydrate at 0.08-0.1 MPa for 3 ~ 5h, then add 1, 4BG, Chinox 1010, BiCAT 8108 in sequence, and stir at 60°C ~ 80°C for 4 ~ 6h to obtain component A.

### (2) Preparation of component B

MDI and Chinox 1010 were put into the reactor and mixed evenly, and then the dehydrated PCDL-2000 and OF - OH - 702E were added, and the temperature was raised to 65°C to 90°C for stirring reaction until the detected value of an NCO group was  $\pm 0.2\%$  different from the theoretical value, and B component was obtained.

### (3) Preparation of solvent-free polyurethane synthetic leather

After adding pigment paste, component A and component B are placed in a low pressure pouring machine to set a certain mass ratio, and then fully mixed by the pouring machine and coated on the release paper. Put in the oven at 110°C to bake until the A and B components react to the wire drawing state, and then put in the oven at 130°C to fully mature for 5 ~ 8min. Solvent-free polyurethane synthetic leather was obtained by separating the release paper after cooling.

## **1.3 TESTING AND CHARACTERIZATION**

### (1) Measurement of viscosity

The BROOKFIELD RVDV - I Prime viscometer was used to determine the viscosity values of components A and B at 25°C, and the average value was measured for 5 times.

### (2) T - peel strength test

According to GB/T2791-1995 standard, GT-7010-AEP tensile testing machine of high-speed Railway Testing Instrument Co., Ltd. was used to test the tensile speed of 100mm/min for 5 times, and the average value was obtained.

### (3) Hydrolysis resistance test and peel strength retention rate calculation

According to ASTM D3690, the test was conducted for 10 weeks at a temperature of 70°C and relative humidity of 95%. The peel strength of the solvent-free polyurethane synthetic leather was tested again, and the peel strength retention rate was calculated according to the following formula to evaluate the hydrolysis resistance.

Peel strength retention rate = (initial peel strength - peel strength after constant temperature and humidity test) \* 100% / initial peel strength

#### (4) Taber wear resistance test

According to the QB/T 2726-2005 standard, the wear resistance of solvent-free polyurethane synthetic leather was determined by the GT-7012-T-TABer abrasion testing machine of high-speed Railway Testing Instrument Co., LTD., with the selection of H 22, 1000 grams.

#### (5) Folding fastness performance test

According to QB/T 2714-2005 standard, the folding fastness of solvent-free polyurethane synthetic leather was tested at a low temperature of 20°C.

#### (6) Fourier transform infrared spectrum

BRUKER Instruments TENSOR27 FT-IR spectrometer is used, the transmission resolution is  $2\text{m}^{-1}$ , the spectrum range is  $600 \sim 4000\text{cm}^{-1}$ .

#### (7) Dynamic thermomechanical analyzer

Use PerkinElmer Instrument company DMA8000 dynamic thermomechanical analyzer, sample size: (10×10×2 mm, method: fixed method, temperature range: 80°C ~ 15°C, heating rate: 5°C / min, frequency: 1Hz.

## 2. RESULTS AND DISCUSSION

### 2.1 EFFECTS OF NCO CONTENT AND R VALUE ON PROPERTIES OF SOLVENT-FREE SYNTHETIC LEATHER

Components A and B are transported to the mixing head by a low-pressure pouring machine. The viscosity of polyester diols and polycarbonate diols is greater than

7000mp.s, which is difficult to use in the equipment. Therefore, PTMG-2000 with appropriate viscosity is selected as the soft section of component A. The properties of synthetic leather prepared by using MDI and PTMG-2000 to synthesize B component with different NCO content and then reacting with A component according to different r values are shown in Table 1.

-NCO 含量 /%	r 值	粘度 /mp·s	耐磨 / 转	-20℃耐折牢度 / 万次	剥离强度 / (N·30mm <sup>-1</sup> )	剥离强度保留率 /%
16	0.95	2540	730	7.2	61	74.8
16	1	2540	770	7.8	68	79.3
16	1.05	2540	815	8.1	72	82.5
16	1.1	2540	825	7.3	70	78.7
12	1.05	3632	765	8.4	60	81.8
14	1.05	2965	790	8.3	67	82.4
18	1.05	1954	810	6.5	73	82.5
20	1.05	1329	820	5.8	75	81.5

As can be seen from Table 1, as the NCO content of component B increases from 12% to 20%, the polymerization degree of the prepolymer decreases, the average molecular weight decreases, and the free small molecule MDI increases, resulting in the viscosity decreasing from 3632mp·S to 1329mp·s. When r value is 1.05, with the increase of NCO content, the hard segment mass fraction of polyurethanes formed by the reaction increases, and more carbamate groups with higher cohesion are contained, which leads to the increase of peel strength and wear resistance. Due to the increase of NCO content, the average molecular weight of component B decreases, the intermolecular force increases, and the rotation capacity in the molecular chain decreases, so that the low temperature folding fastness decreases from 84,000 times to 58,000 times. It can be seen from Table 1 that the retention rate of peel strength after hydrolysis resistance is little affected by the content of one NCO, and the properties are better when the content of one NCO is 16%.

When the NCO content is 16%, the molecular weight of polyurethane gradually increases with the increase of r, and the mechanical properties such as wear resistance and peel strength increase. When r value is greater than 1, the excess isocyanate cross-links with the active hydrogen on the molecular chain to form a small network structure, which can increase the intermolecular force and further improve the wear resistance and peel strength. When r value increased from 1.05 to 1.1, due to the lack of adequate straight-chain growth reaction of polyurethane molecular chains, short molecular chains were generated during hydrolysis, resulting in a decrease in the retention rate of peel strength. The cross-linking reaction increases the cohesion and the surface wear resistance from 815 RPM to 825 RPM. Excessive crosslinking makes the film brittle, and

the peeling strength and low temperature folding fastness decrease.

## 2.2 INFLUENCE OF SOFT SEGMENT TYPE ON PROPERTIES OF SOLVENT-FREE SYNTHETIC LEATHER

The properties of synthetic leather prepared by MDI and different types of soft segment diols with 16% NCO component B and r value of 1.05 with component A are shown in Table 2.

软段类型	粘度 /mp·s	耐磨 / 转	-20℃耐折牢度 / 万次	剥离强度 / (N·30mm <sup>-1</sup> )	剥离强度保留率 /%
PTMG-2000	2540	815	8.1	72	82.5
PBA-2000	5353	1160	7.6	110	51.5
PCDL-2000	5588	1320	7.4	119	83.6

It can be seen from Table 2 that polycarbonate diols have higher cohesion than polyether diols and polyester diols, and the B component synthesized with them has higher viscosity. Three types of component B viscosity can meet the requirements of the equipment. Compared with polyester diol PBA-2000 and polycarbonate diol PCDL-2000, polyether diol PTMG-2000 has the advantages of free rotation of ether-oxygen bond and better flexibility of chain segment, and the prepared polyurethane has the lowest interforce between soft and hard segments, resulting in the maximum microphase separation degree of soft and hard segments, and has better low temperature breakfastness. Because the polarity of the ester group and the carbonate group is higher than that of the ether oxygen group, the oxygen atoms on these groups are easy to form hydrogen bonds with the hydrogen atoms in the hard segment, thus strengthening the intermolecular force, making PBA-2000, PCDL-2000 than PTMG-2000 polyurethane synthetic leather has better peeling strength, wear resistance and other mechanical properties. Because the formation of ester group and hydrolysis are reversible reactions, the peel strength retention rate of PBA-2000 solvo-free synthetic leather after hydrolysis resistance test is only 51.5%. The experimental data show that the synthetic properties of solvent-free polyurethane synthetic leather with PCDL-2000 as soft segment are better.

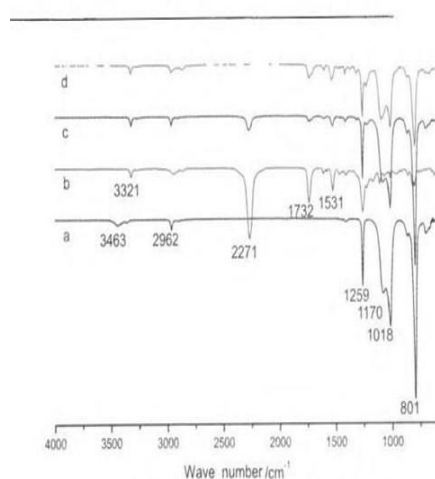


## 2.3 EFFECT OF ORGANOSILICON ON PROPERTIES OF SOLVENT-FREE SYNTHETIC LEATHER

Although the solventless polyurethane resin with the soft section of polycarbonate PCDL-2000 in 2.2 has better comprehensive physical properties, the data show that its low temperature folding fastness is still not ideal. In the experiment, hydroxyorganosilicon is introduced to improve the low temperature folding fastness.

### 2.3.1 Structure characterization of organosilicon modified solvent-free polyurethane

The infrared spectrum of organosilicon modified B component and reaction with A component to form a film is shown in Figure 1.



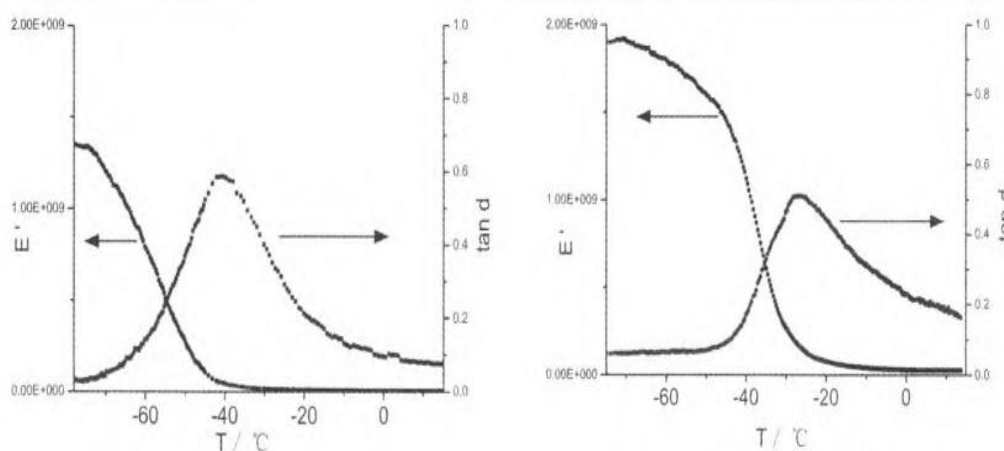
In FIG. 1, a is the spectral line OF -- OH -- 702E, the characteristic absorption peak of hydroxy-group at  $3463\text{cm}^{-1}$ , a  $-\text{CH}_3$  in  $\text{Si}-\text{CH}_3$  at  $2962\text{cm}^{-1}$ , and the stretching vibration peak, the bending vibration absorption peak of  $\text{Si}(\text{CH}_3)_2$  at  $1259\text{cm}^{-1}$ , and the vibration absorption peak of  $\text{Si}-\text{O}-\text{Si}$  at  $1018\text{cm}^{-1}$ . The swaying vibration peak of  $\text{Si}-\text{CH}_3$  is at  $796\text{cm}^{-1}$ . b is the spectrum line after the reaction of MDI and PCDL-2000. There is an  $\text{N}=\text{C}=\text{O}$  asymmetric stretching vibration absorption peak at  $2271\text{cm}^{-1}$ , the stretching vibration absorption peak at  $1732\text{cm}^{-1}$  of carbonyl group of carbonate bond, and the stretching vibration peak at  $3321\text{cm}^{-1}$  and  $1531\text{cm}^{-1}$  of carbamate group formed by the reaction. The results showed that the hydroxyl group in PCDL-2000 completely participated in the reaction and formed the isocyanate sealed prepolymer. c is the spectrum line after the reaction OF b with OF - OH - 702E. The hydroxyl peak disappears at  $3463\text{cm}^{-1}$ , and the absorption peak of NCO decreases at  $2271\text{cm}^{-1}$ , indicating that the

OF - OH - 702E reaction imparts into the polyurethane chain segment to form terminal isocyanate prepolymers. d is the spectrum line after the reaction of organosilicone-modified B component and A component to form A film. The hydroxyl group in A component is completely reacted, and an NCO absorption peak at  $2271\text{cm}^{-1}$  is also fully involved in the reaction.

### **2.3.2 Dynamic mechanical properties analysis of organosilicon modified solventless polyurethane**

MDI and PCDL-2000 reacted with MDI, PCDL-2000 (90wt %) and OF-OH-702E (10wt %) to generate prepolymers with NCO OF 16%, and reacted with component A with R-value of 1.05 to prepare the DMA curve of polyurethane coating, as shown in FIG. 2 and FIG. 3.

FIG. 2 and FIG. 3 show that the polyurethane coating before and after silicone modification has obvious internal friction absorption peaks, indicating that the polyurethane has a certain degree of microphase separation in the soft and hard segments. The carbamate group and the cross-linked structure formed by the reaction formed the hard segment microregion, and the low polarity polycarbonate, polyether and silicone formed the soft segment microregion. When stressed, the hard segment in the glassy state plays an anchoring role, while the soft segment can consume energy through molecular movement when it reaches a high elastic state from the glassy state, which causes the energy storage modulus ( $E'$ ) to drop sharply, and the loss factor ( $\tan \delta$ ) forms an absorption peak, showing the position of the soft segment  $T_g$ . The  $T_g$  before and after modification is  $26.4^\circ\text{C}$  and  $40.35^\circ\text{C}$  respectively, that is, the OF - OH - 702E significantly improves the low temperature performance of polyurethane. The right peak of the loss factor before modification is flatter than that after modification, which indicates that the polyurethane before modification contains more movable segments of different levels in the soft segment, that is, the silicone modified polyurethane has a higher degree of phase separation between the soft and hard segments.



### 2.3.3 Influence of organosilicon modified solventless polyurethane on the comprehensive properties of synthetic leather ring

The properties OF synthetic leather prepared by different mass ratios of PCDL-2000, OF-OH-702E and MDI with component B with NCO content of 16% and component A with R-value of 1.05 are shown in Table 3.

OF-OH-702E wt%/%	粘度 /mp·s	耐磨 / 转	-20℃耐折牢度 / 万次	剥离强度 /(N·30mm <sup>-1</sup> )	剥离强度保留率 /%
5	5475	1430	7.6	112	83.9
10	5328	1620	8.7	110	85.2
15	5164	1540	9.3	98	85.6
20	4897	1280	9.5	83	85.7

As can be seen from Table 3, the viscosity and peel strength OF component B decrease with the increase OF the content of OF-OH-702E, which is because the Si-O bond in the OF OH-702E of silicone polyols is easy to rotate internally and has low polarity, which destroys the crystallization of polyurethane and reduces the intermolecular force. It is also due to the "internal plasticizing" effect caused by silicone polyols that improves the low temperature folding fastness. The introduction of silicone reduces the surface energy of polyurethane, reduces the degree of dryness of the surface, and improves the wear resistance. However, when the percentage OF of - OH - 702E is greater than 10wt %, the wear resistance of polyurethane decreases when the silicone plays a major role in the

weakening of the intermolecular force. The polarity of silicone and polyurethane is very different. With low surface energy, silicone chain segments will slowly migrate and aggregate and stabilize on the surface of synthetic leather. An SI-OR group has hydrophobicity, which makes the wettability of water to polyurethane synthetic leather worse and the retention rate of peel strength improved.

When the content OF OF-OH-702E is 10wt %, the comprehensive performance is better, which can meet the comprehensive performance requirements of synthetic leather for sports shoes. At the same time, the introduction of silicone makes the synthetic leather feel comfortable, smooth and not dry.

### 3. CONCLUSIONS

- (1) MDI, PCDL-2000 was used to synthesize A B component with NCO content of 16%, and PTMG-2000 type A component was reacted to the drawing state according to  $r$  value of 1.05, and the synthetic leather was cured with cloth base. The comprehensive physical properties of synthetic leather were more balanced.
- (2) FT-IR analysis OF the B component prepolymer and coating showed that the OF - OH - 702E of silicone polyol could be completely embedded into the molecular chain of polyurethane. DMA analysis shows that the low temperature performance and the microphase separation degree OF soft and hard segments are improved after the introduction of OF-OH-702E,  $T_g$  which decreases from 1 26.4 °C to 1 40.35 °C.
- (3) The low temperature resistance of solvent-free synthetic leather can be significantly improved by introducing the solvent-free polyurethane modified by organosilicon. The overall properties OF solvo-free synthetic leather are better when the amount of OH-702E of silicone polyol is 10% of the soft section of B component. In addition, OF - OH - 702E can also improve the dry touch of synthetic leather surface.

### REFERENCE

- [1] Li Shaoxiong, Liu Yijun. Polyurethane resin and its application [M]. Beijing: Chemical Industry Press. 2002:16.
- [2] JIANG Yingying, Sun Ming, WU Liang. Analysis of process and environmental impact of polyurethane synthetic leather. Guangdong Chemical Industry, 2011,38 (7) : 252-253.
- [3] Ma Zhanfeng, Liao Zhengpin. Booming synthetic leather industry in China [J]. Science

and Technology Information Development and Economy, 2003,13 (3) : 123-125.

[4] Yang Shuilian, Zhou Beiyong. Clinical analysis of occupational acute dimethylformamide poisoning [J]. Chinese Journal of Industrial Medicine, 2000,13 (4) : 212-214.

[5] Ma Xingyuan, Wu Ze, Zhang Shufang, et al. Forming mechanism and key technology of solvent-free polyurethane synthetic leather [J]. China Leather, 2013,42 (17)

[6] Feng Jianyan, Gao Futang, Zhang Xiaolei, et al. Development, current situation and trend of artificial leather [J]. China Leather, 2006,35 (15) : 101:13.

[7] Zhao Yuhua, Jia Lincai, Kang Maoqing, et al. Study on dynamic properties of high-performance cast polyurethane elastomers [J]. China Plastics, 2003,17 (6) : 52-55.

[8] Wu Ze. Study on preparation technology and properties of solvent-free polyurethane synthetic leather [D]. Shaanxi University of Science and Technology, 2014.

[9] Cui Lujuan, Wu Xiaoqing, Zuo Haili. Research progress of silicone modified polyurethane. Chinese Adhesives, 2007,16 (1) : 53-56.

[10]Yilgor I, Yilgor E, Erenturk B. Effect of Structural Variations on the Synthesis and Structure Property Behavior of Segmented Silicone Urethane and Copolymers[J]. Polymer Synthesis, Polymer Preprints, 2004, 45(1): 561—562.

[11]Zhang C Y, Zhang X Y, Dai J B, et a1. Synthesis and Properties of PDMS Modified Waterborne Polyurethane—acrylic Hybrid Emulsion by Solvent-free Method 【J】. Progress in Organic Coatings, 2008, 63(2): 238—244.

[12]IRINA K, KONKUS DAVID M, IEY DAVID A. Low—temperature Heat-activated Adhesives with High Heat Resistance Properties[P]. US: 6515070. 2003—02—04. □