



An aqueous PU finishing agent modified by hydroxyl silicone

Keyong Tang, Fang Wang, Xuejing Zheng, Bing Zhu, Guoli Dai

College of Materials Science & Engineering, Zhengzhou University, Zhengzhou, China, phone:

0086-371-67763216, email: keyongtangzzu@yahoo.com

Abstract: Aqueous polyurethane is widely used in leather making as a finishing agent, because it is environmentally friendly. However, the properties of presently exploited aqueous polyurethanes cannot reach the level of solvent-based polyurethanes. Such disadvantages as small elongation (extensibility), bad adhesion, easily yellowing, and brittle do exist in aqueous polyurethane finishing agent. The permeability of leathers is usually remarkably affected by the finishing with polyurethane finishing agent. Many attempts have been made in recent years to modify the aqueous polyurethanes (PU) in order to get finishing agent with excellent properties. On the other hand, organosilicone has been deeply studied and used in many field with excellent achievements. In the present paper, a kind of aqueous polyurethane (PU) finishing agent was synthesized with IPDI, PTMG, DMPA, and n-butylamine, in which hydroxyl-terminated polydimethylsiloxane (OH-terminated PDMS) was added in three different ways, i.e., one-step-added method, two-step-added method and added as a chain-extended agent. Its properties were studied using infrared elongation, spectroscopy, DSC and were compared with the water- resistance and dry and wet erase-resistance properties of the films. It indicated that the chain segments from reacting by OH-terminated PDMS and IPDI worked as hard segments and that the elongation and water- resistance of PU with OH-terminated PDMS added in as chain-extend agents were better than those with OH-terminated PDMS added in one-step or two-step method. The elongation could reach 1300% and the ratio of water absorption was just 1/4 of the latter PU films', when the same amount of OH-terminated PDMS was added in the system. As result of finishing process, it was better when OH-terminated PDMS was added in the top layer than added in the middle layer. It also showed that the dry erase-resistance could reach grade 5 and that wet erase-resistance could reach grade 4.5.

Keywords: aqueous polyurethane, finishing agent, hydroxyl-terminated polydimethylsiloxane (Hydroxyl silicone)

1. Introduction

The present aqueous polyurethane can not reach the level in the properties of solvent-based polyurethane^{[1][2]}. However, only by changing the monomer ratio to improve the properties of polyurethane can usually can not meet the needs for excellent polyurethane. So attempts have been done to modify the polyurethane molecule.

The internal rotation of the C-O-C bonds in silicone oil is very easy. So the materials with



silicone are good in some physical properties and silicone oil has found a wide application in many fields. The use of organic silicone oil in the modification of polyurethanes should be a good way to prepare finishing agent for leather making. In the preparation of water-based polyurethane modified with amino silicone, Chen et al ^[3] found that with increasing the silicone oil content in the polyurethane film, the Young's modulus decreases, while the tensile strength and elongation at break increase gradually. Similar results had been obtained by Zhu et al ^[4] in their studies on the modification of polyurethane with hydroxyl silicone. In the study on the modification of polyurethane with amino silicone by Chen et al ^[5], however, a different conclusion was obtained. They found that with increasing the amino silicone content, the elongation at break increased in the first period of stretching followed by a decrease. The maximum elongation at break appeared at the silicone amount of 10%, an increase of 52%, compared with that of the unmodified polyurethane. At the same time, many studies have shown that the surface properties of polyurethane were changed by the addition of silicone. Chen et al ^[3] found that the polarity of the polyurethane surface was changed when the silicone was added in the synthetic process of polyurethane. Zhu^[4] et al found that the surface tension of polyurethane decreased gradually with the increase of the amount silicone used. Silicone has a low surface tension and a high surface activity. With the increase of the silicone amount, the polysiloxane block content in the polyurethane molecular chain will increase, the polar intensity of the molecular chain will decrease, the aggregation capacity of the molecules will be weakened. So the surface tension of the polyurethane emulsion was decreased. In short, the addition of silicone is an effective way to increase the elongation at break of polyurethane, while to a certain extent, the water resistance of water-based polyurethane may be improved. However, from viewpoint of the lower the surface tension of polyurethane, silicone modification is not good. The surface polarity is decreased and the adhesive force between polyurethane and the basis materials is weakened.

With hydroxyl silicone as modifying agent, the polyurethane was modified by hydroxyl silicone to improve the flexibility and water resistance of polyurethane finishing agent. Three different methods were tried, i.e., one-step method, two-step method, and hydroxyl silicone chain-extension method. The elongation, IR, DSC, water absorption and other properties of the polyurethane finishing agent were studied. The final product was used in the finishing of leathers and the finishing results were compared. It was indicated that the chain-extension method is the best in the three ways.



2. Experimental

2.1 Main materials and apparatus

Isophorone diisocyanate (IPDI, 95%), dimethylol propionic acid (DMPA), and poly tetrahydrofuran (PTMG, Mn=2000 are from Yantai Wanhua Polyurethane Co., Ltd. Hydroxyl silicone and n-butylamine were from Tianjin Chemical Reagent Factory. The dibutyltin dilaurate (AR) was from Chengdu Silicone Research Center , Ministry of Chemical Industry, China. Both triethylamine and acetone were analytical agent are purchased from Tianjin Chemical Reagent Factory. NETZSCH thermal analyzer was made by the NETZSCH company, Germany. The FT-IR-8700-type variable temperature Fourier transform infrared spectrometer was made by Shimadzu Corporation. The CMT6000 Universal electronic testing machine was from the New Sans Co. Ltd., Shenzhen, China. The MCJ-01A friction testing machine was from the Labthink technology development center, Jinan, China.

2.2 Synthesis of the water-based polyurethane finishing agentt

One-step: IPDI and PTMG were weighed with the -NCO/-OH ratio of 1.1:1. The DMPA was 8% in weight of the reaction mixture and the dibutyltin dilaurate was 3 ‰ in weight of the reaction mixture. The hydroxyl groups of the silicone were controlled at 5%, 10%, 15% and 20% of the total hydroxyl content in the polymerization. The DMPA, PTMG, and hydroxyl silicone were by added to a four-necked bottle, with dibutyltin dilaurate as catalyst, the mixture was allowed to react at 80 °C for 3h to yield the prepolymer. In the prepolymerization process, some acetone was added to dissolve the pre-polymer. triethylamine some triethylamine was added for neutralization according to amount of DMPA, and the mixture was rapidly cooled to 25 °C. The n-butylamine, 10% of the amount of isocyanate groups in weight, was added for chain-extension at 80 °C. The reaction time was 5min. After being stirred for water dispersion at the speed of 500r/min, light blue translucent polyurethane emulsion was obtained.

Two-step: The procedure and the amount of all reagents were the same as that of the one-step except that the hydroxyl silicone was added when the pre-polymerization lasted for 2h.

Chain Extension: IPDI and PTMG were weighed with the -NCO/-OH ratio of 1.1:1. The DMPA was 8% in weight of the reaction mixture and the dibutyltin dilaurate was 3‰ in weight of the reaction mixture. The DMPA and PTMG were added to a four-necked bottle, with dibutyltin dilaurate as catalyst, the mixture was allowed to react at 80 °C for 3h to yield the pre-polymer. In the pre-polymerization process, some acetone was added to dissolve the pre-polymer. According to amount of DMPA added, some triethylamine was added for neutralization, and the mixture was rapidly cooled to 25 °C. The n-butylamine, 10% of the amount of isocyanate groups in weight, was added for chain-extension at 80 °C. The reaction time was 5min. After being stirred for water dispersion at the speed of 500r/min, light blue translucent polyurethane emulsion was obtained.

2.3 Film forming of the polyurethane

The water-based polyurethane emulsion was poured in a PP film mold we made ourselves.



After being dried at 50 °C for 72h, the films were then dried at room temperature for another 48h to yield the polyurethane film for subsequent study.

2.4 Characterization of the properties

Mechanical properties: The mechanical properties of the polyurethane films were obtained according to GB/T 508-1998, with the thickness of 1mm (± 0.4 mm) of standard, dumbbell-shaped samples. The minimum force was 0.01N and the stretching speed was 500mm/min.

FT-IR analysis: The FT-IR spectra of the polyurethane films were obtained on a Fourier transforming infrared spectroscopy from Shimadzu Corporation, Japan.

Thermal Analysis: The glass transition temperature (T_g) of the PU films were determined by DSC. The work was done at the 10 °C/min of heating and cooling speed from -100 °C to 200 °C temperature range. The samples were cooled from room temperature to -100 °C, and then heated to 200 °C to obtain the glass transition temperature of the polyurethane films

Water absorption of the PU films: The Prepared polyurethane films were placed in a vacuum oven with the vacuum degree of 0.91MPa at 70 °C to constant weight, about 5h was needed. The polyurethane films were weighed, noted as m_1 . The films were then immersed into distilled water for a certain period and weighed again, noted as mass m_2 . The water absorption was calculated as:

$$\square \text{Water } \square \text{absorption} = \frac{m_2 - m_1}{m_1} \times 100 \%$$

The water absorption was plotted against water soaking time to yield the relationship between water absorption and soaking time.

Finishing: In this study, three layers named bottom, middle, and top were conducted with the pigment paste only in the middle layer. In the middle finishing, the ratio of pigment paste to polyurethane emulsion was 1:2. After the finishing mixture was carefully and evenly brushed on the surface of leathers, the samples were removed in the constant temperature drying oven to be dried at 70 °C.

Wet and dry rub resistance ^[6]: The rubbing head was wrapped with white lining, and used to rub the samples with determined pressure, back and forth on the surface of the samples. In the rubbing process, a portion of the surface color of the samples was transferred on the lining on the rubbing head. Grey card was used to compare the color of the white lining to determine color level.

The technical indicators are as follows: pressure load: 80g.cm⁻²; rubbing speed: 43 cycles/min; rubbing length: 60mm; dry rubbing: 25 back and forth; wet rubbing: 20 back and forth; the water content of white lining was 70%-75%. The white lining was the National Standard (GB/T406) and the Gray Card was the National Standard (GB250-1995)

3. Results and discussion

3.1 Influence of hydroxyl modification on the mechanical properties of polyurethane films

In this study, three different ways of adding hydroxyl silicone to modify polyurethane was



employed: one-step, two-step, and chain-extension way. In both ways of one-step and two-step, the amount of hydroxyl silicone was calculated as the hydroxyl groups accounted for the total hydroxyl content in percentage. Figure 1 shows the curves of the elongation at break of polyurethane films vs. hydroxyl silicone content. From Figure 1, we knew that the elongation at break of the polyurethane films decreases with increasing the amount of hydroxyl silicone, no matter whether the one-step way or two-step way was used. This phenomenon is different from those by Zhu and Chen^{[4][5]}. In their work, they found that the elongation at break of polyurethane films increased gradually with increasing the amount of silicone to reach an maximum.. This may be related to the length of the silicone chain. The molecular chain of the hydroxy silicone is small to increase the hard segment content in the synthesis process of polyurethane, resulting in an increased interaction between hard segments. The same as the performance of pure PU, the hydrogen bonds or crystallization of polyurethane lead to the decrease in the elongation at break.

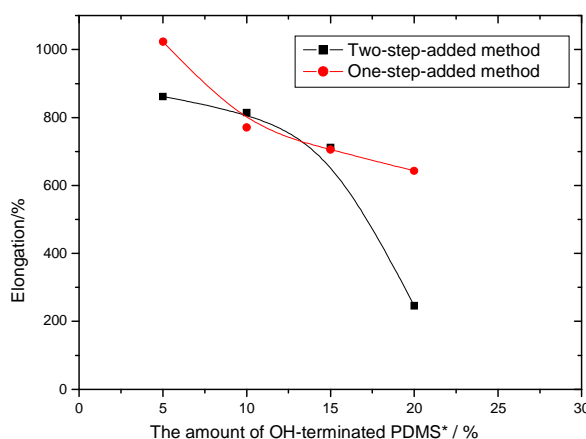


Fig. 1 Relationship between the elongation at break and the hydroxyl silicone
* the hydroxyl ratio of OH-terminated PDMS and all –OH in the system

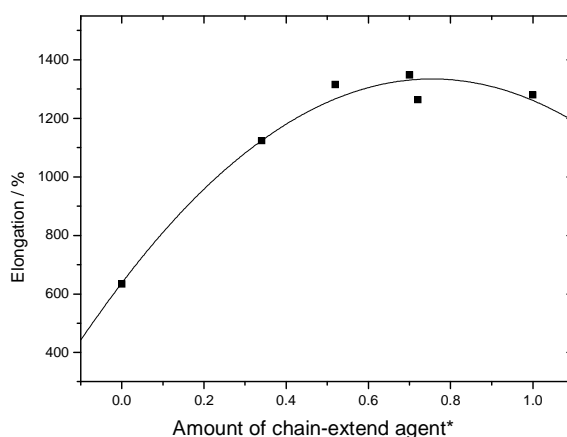


Fig. 2 The elongation at break vs. amount of chain-extend agents
*the mol ratio of chain-extend agent and dissociative –NCO



Fig. 2 shows the relationship of the elongation at break and the amount of chain-extension agent when the hydroxyl silicone was applied as chain-extension agent. When the amount of chain-extension agent accounts for 60% of the fully extended amount, a maximum was reached in elongation at break. Further more hydroxyl silicone leads to a decrease in elongation at break again. The maximum elongation at break is 1 300%. Compared to those by one-step and two-step, the way of chain-extension is the best to improve the elongation at break.

3.2 FT-IR spectra of hydroxyl silicone modified water-based polyurethane

Figure 3-7 were the FT-IR spectra of hydroxyl silicone modified polyurethane films at different IR wave number ranges. The samples in Figure 3 were obtained with different silicone content by two-step way. The peak at 802cm⁻¹ increases with increasing the content of hydroxyl silicone to form an obvious peak gradually. The absorption peak represents the swing vibration of Si-CH₃, indicating the reaction between hydroxyl silicone and the polyurethane molecule. The peak at 1240cm⁻¹ of the water-based polyurethane film in Figure 4 was the absorption the C-O-C. Although the bending vibrations of Si-CH₃ are also in the region, because of the amount of hydroxyl silicone is too small compared to that of the polyurethane, the peak should be the strong absorption of C-O-C in the polyurethane. Figure 5 indicated the changes in absorption of the single bond of N-H in the modified polyurethane. [7]The absorption of N-H single bond appears in the range from 3447 to 3600 cm⁻¹ without hydrogen bonds. When hydrogen bonds are formed, the absorption peak moves to lower wave number, in the range of 3300 to 3380 cm⁻¹. Hydrogen bonds may be formed between the H in N-H and the O in C-O-C or C=O. So a shoulder peak appeared in 1047cm⁻¹ in Figure 6. The emergence of the shoulder peak was because of the absorption peak of the Si-O-Si was covered for the little amount of hydroxyl silicone in the system. The changes of C=O in the water-based polyurethane were shown in Figure 7. The absorption of C=O of polyurethane without hydrogen bonds usually occurs in the range of 1730 to 1745cm⁻¹ and that with hydrogen bonds moves to lower wave number. [8] The absorption of C=O appeared in 1712cm⁻¹ and no obvious shoulder peak was found at a higher wave number. Therefore, most of the C=O groups took part in the formation of hydrogen bonds. Besides, the blunt and broad peak at 1654cm⁻¹ indicated the formation of urea. In short, there are Si-O-Si bonds and hydrogen bonds between the hard segments in the hydroxyl silicone modified polyurethane. By comparing Figure 6 and Figure 1, the area of the shoulder peak of the hydrogen bonded C-O-C increases with increasing the hydroxyl silicone content, indicating the increased level of bonding of C-O-C. The higher the hydrogen bonding degree between the soft segment and the hard segment is, the more difficult for the soft segment molecular in the polyurethane to move, which will decrease the elongation of polyurethane. The decrease of the elongation at break with increasing the hydroxyl silicone content in the polyurethane (Figure 1) was consistent to the changes in the absorption area of hydrogen bonded C-O-C in polyurethane, indicating that the elongation at break of polyurethane is related to the hydrogen bonds and the movements of the soft segment.

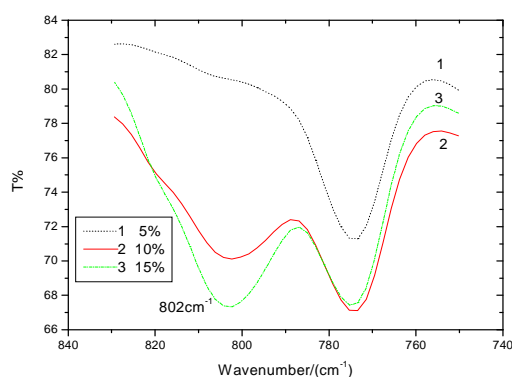


Fig 3 Infrared spectra of the hydroxyl silicone modified PU film by two-step way (840-740cm⁻¹)

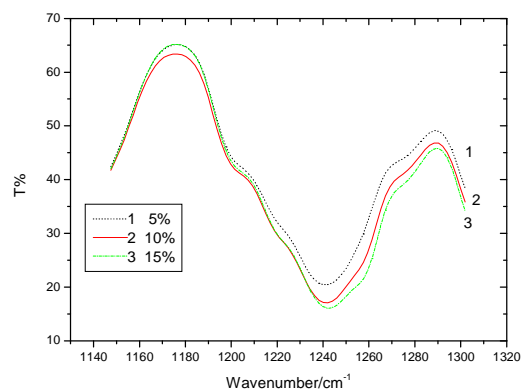


Fig 4 Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1140-1320cm⁻¹)

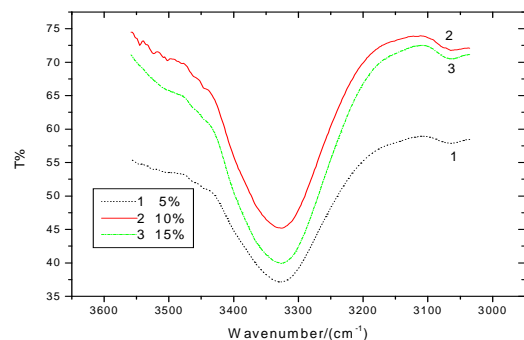


Fig 5 Infrared spectra of the hydroxyl silicone modified PU film by two-step way (3600-3000cm⁻¹)

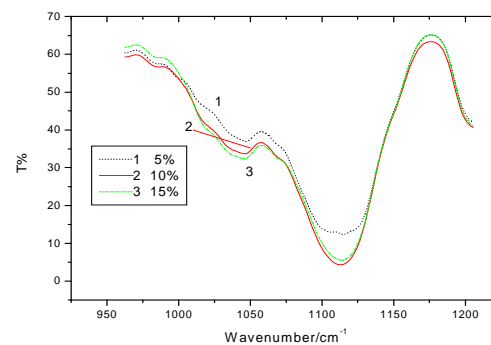


Fig 6 Infrared spectra of the hydroxyl silicone modified PU film by two-step way (950-1200cm⁻¹)

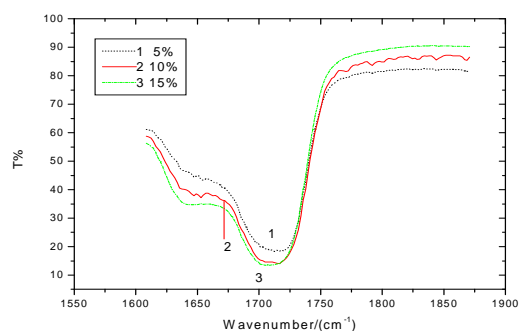


Fig 7 Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1550-1900cm⁻¹)

3.3 DSC analysis of the hydroxyl silicone modified polyurethane^[9, 10, 11]

The DSC curves of the hydroxyl silicone modified polyurethane by two-step way were shown in Figure 8 and Figure 9. Step endothermic was found both at low temperature range and high



temperature range, suggesting the glass transition in the polyurethane sample. The temperature range in Figure 8 was from -100 °C to -30 °C. When the amount of hydroxyl silicone is 5%, no obvious glass transition was found. When it was 10%, the T_g was -79 °C with the endothermic of 0.0706J/mg. At the amount of 15%, the T_g was -81 °C and the endothermic was 0.1246J/mg. The results for the 20% sample were similar to the 15% one. The movement of the soft segment for the samples with 15% and 20% of hydroxyl silicone is easy than that with 10% hydroxyl silicone, which may be good to increase the elongation. The DSC curves of the hydroxyl silicone modified polyurethane in the temperature range from -50 °C to 200 °C were shown in Figure 9. At the amount of hydroxyl silicone of 5%, T_g was 19 °C with the endothermic of 1.079J/mg. When the amount of hydroxyl silicone was 10%, the T_g was 31 °C and the endothermic was 0.3964J/mg. For the 15% sample, the T_g was 6 °C and the endothermic was 0.3023J/mg. The T_g was -14 °C and the endothermic was 0.2886J/mg for the sample with the hydroxyl silicone of 20%. It was indicated that the the maximum interaction between hard segments appears at the the amount of hydroxy silicone of 10%. The interaction between the hard segments decreases with increasing the hydroxyl silicone amount above 10%.

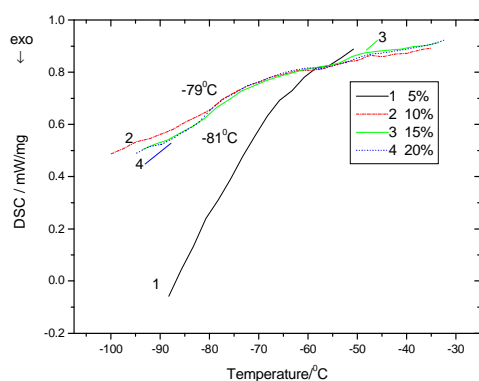


Fig 8 DSC curves of the hydroxyl silicone modified PU films by two-step way (-100 ~ -30 °C)

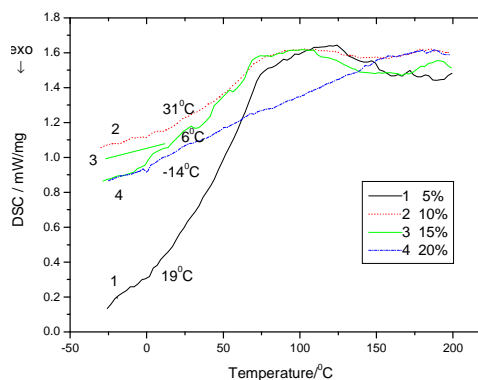


Fig 9 DSC curves of the hydroxyl silicone modified PU films by two-step way (-100 ~ -30 °C)

The DSC curves of the modified polyurethane films with hydroxyl silicone as chain-extension agent were shown in Figure 10-11. The same results as Figure 8-9 was found: step endothermic was found both at low temperature range and high temperature range, suggesting the glass transition in the polyurethane sample. The temperature range in Figure 10 was from -100 °C to -20 °C. When the amount of hydroxyl silicone was 52%, the T_g of the polyurethane was -82 °C with the endothermic of 0.2913J/mg. 67% of hydroxyl silicone gave a polyurethane with the T_g of -81 °C and endothermic of 0.1934J/mg. At the amount of 75%, the polyurethane presents a T_g of -81 °C and an endothermic of 0.244J/mg. At the hydroxyl silicone amount of less than 75%, the endothermic decreases with increasing the hydroxyl silicone amount, but in 75%, the endothermic increases. When compared with 2, we found



that a change in the elongation at break appeared at the hydroxyl silicone amount of 75%. The DSC curves of the hydroxyl silicone chain-extended polyurethane in the temperature range from -70 °C to 125 °C were shown in Figure 11. At the hydroxyl silicone amount of 52%, the Tg of the polyurethane was 5 °C with the endothermic of 0.4054J/mg. The 67% of hydroxyl silicone yielded a Tg of -1 °C and an endothermic of 0.3388J/mg. When the hydroxyl silicone was 75%, the Tg was 1 °C with the endothermic was 0.3757J/mg. With increasing the amount of hydroxyl silicone as chain-extension agent, the endothermic decreases gradually for the hard segments to move. The elongation at break of the hydroxyl silicone chain-extended polyurethane films increases with increases the amount of hydroxyl silicone, suggesting that the elongation at break of the polyurethane is related to the intermolecular interactions in it.

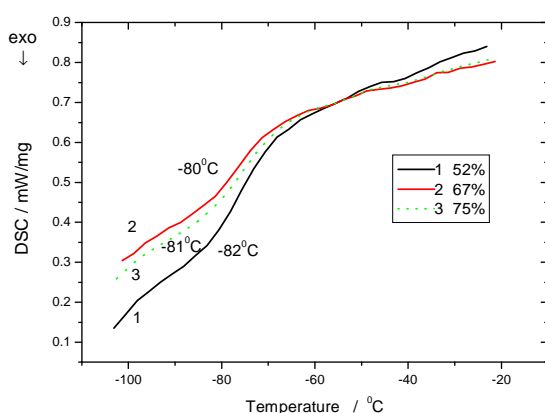


Fig 10 DSC curves of PU film
chain-extended by hydroxyl silicone (-100 ~
-20 °C)

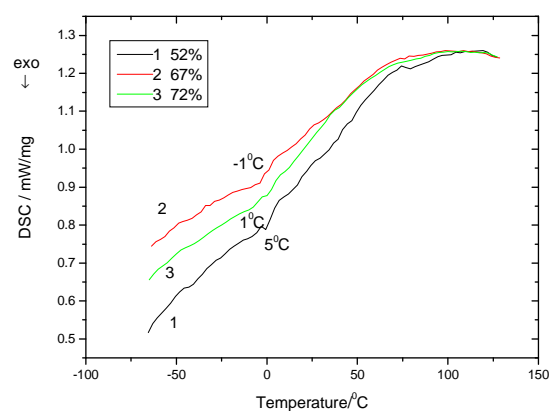


Fig 11 DSC curves of PU film
chain-extended by hydroxyl silicone (-70 ~
150 °C)

In summary, for the polyurethane chain-extended by hydroxyl silicone, there appeared both the glass transition of the soft segment (at -80 °C or so) and glass transition of the hard segments (around 0 °C), indicating the phase separation between the hard segments and the soft segments. It was also indicated that the reaction between the hydroxyl silicone and the isocyanate took place in the hard segments. This may be the reason why, for the one-step way and the two-step way, the elongation at break of the polyurethane films decreases with increasing the amount of hydroxyl silicone.

3.4 The water absorption of rge hydroxyl silicone modified polyurethane

The water-base polyurethane without hydroxyl silicone modification will be dissolved when being soaked in water for a few hours. For example, the weight of water-based polyurethane chain-extended by ethylene diamine wills decrease when being soaked in water for 6h, indicating the hydrolysis of the product. In the present study, for the polyurethane chain-extended by hydroxyl silicone, no weight loss was found even after being soaked in water for 24 hours. The water absorption curves of the polyurethane films by the ways of one-step, two-step, and chain-extension were shown in Figure 12. For the samples by the ways of one-step and two-step, when being soaked in water for 24 hours, the water absorption



decreases with increasing the amount of hydroxyl silicone. At a small amount of hydroxyl silicone, the water absorption of the two-step sample decreases faster than that of the one-step one. For the chain-extended sample, the water absorption increases and then decreases with increasing the amount of hydroxyl silicone. The water absorption of the chain-extended sample is much less, compared with the samples by the other two ways. At the same amount of hydroxyl silicone, the polyurethane of the chain-extended one shows the smallest, only 1/4 of those by the other two ways, indicating that the way of chain extension with hydroxyl silicone is a more efficient way to modify polyurethane..

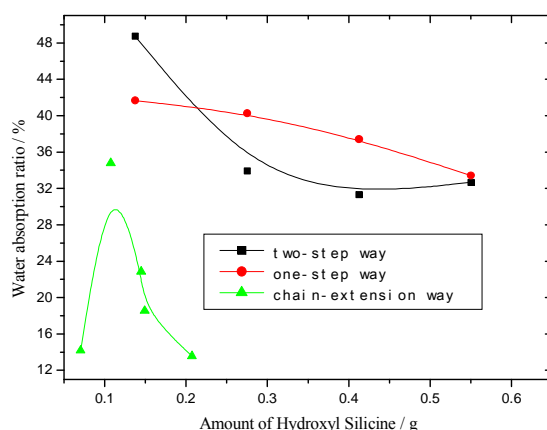


Fig. 12 Water absorption of PU modified by hydroxyl silicone in different ways

3.5 Dry/wet rubbing resistance

The finishing agents were applied in the finishing of leathers. The bottom finishing was the traditional finishing agent, while the hydroxyl silicone was used in the middle finishing and top finishing. The dry/wet rubbing resistance of the samples was studied as listed in Table 1.

Table 1 Dry/wet rubbing resistance of the finished samples

Samples	Amount of the hydroxyl silicone in finishing coat (g)	Wet rubbing resistance grade	Dry rubbing resistance grade
1 (Top finishing)	0.02	3.5	5
2 (Top finishing)	0.05	4	5
3 (Top finishing)	0.08	4.5	5
4(Middle finishing)	0.05	2.5	5
5 (Middle finishing)	0.08	2	5

From Table 1, it should be noted that synthesized water-based polyurethane finishing agent is good at dry rubbing resistance and the wet rubbing resistance is related to the amount of hydroxyl silicone used in the finishing. When the hydroxyl silicone modified polyurethane is used in top finishing, the wet rubbing resistance of the leathers increases gradually with



increasing the amount of hydroxyl silicone in it. No obvious improvement in wet rubbing resistance was found when the hydroxyl silicone modified polyurethane was used in middle finishing. So top finishing is a good choice for hydroxyl silicone modified polyurethane to improve the dry/dry rubbing resistance of coatings.

4. Conclusions

The reaction between hydroxyl silicone and isocyanate took place in the hard segments in polyurethane. The elongation at break of hydroxyl silicone modified polyurethane films is related to the location of hydrogen bonding. The polyurethane chain-extended with hydroxyl silicone shows a better elongation at break and water resistance, compared with those by ways of one-step and two-step. When being used in top finishing, hydroxyl silicone modified polyurethane may provide the dry rubbing resistance of 5 and the wet rubbing resistance of 4.5.

Acknowledgements

The financial supports from the National Natural Science Foundation of China (Grant No. 50973097, 21076199) and Program for Science & Technology Innovation Talents in Universities of Henan Province (No. 2009HASTIT015) are gratefully acknowledged.

References

- [1] Martin Melchior, Michael Sonntag, Claus Kobusch, Eberhard Jürgens. Recent developments in aqueous two-component polyurethane (2K-PUR) coatings. *Progress in Organic Coatings* . 2000,40 :99-109
- [2] F.M.B.Coutinho&M.C.Delpech. Some Properties of Films Cast Polyurethane Aqueous Dispersions of Polyether-Based Anionomer Extended with Hydrazine. *Polymer Testing* .1996, 15:103-113
- [3] Hong Chen, Quli Fan, Xuehai Yu. Studies of Waterborne Polyurethane Modified with Amino Silicone, 1999, 12(3): 297-300
- [4] Chunfeng Zhu, Gangjin Chen. Synthesis and Characterization of Polyurethane Cationic Emulsion Modified with Hydroxyl Terminated Poly(dimethylsiloxane), *Fine Chemicals*, 2004, 21(8): 608-611
- [5] Jinghua Chen, Weiqu Liu, Yining Xuan. Modification of Polyether Polyurethane with Amino Siloxane, *Chinese Journal of Applied Chemistry*. 2004, 21(6): 629
- [6] Weiqi Jiang. *Physicochemical Analysis of Leathers*. Beijing: China Light Industry Press. 1999.105-108
- [7] P. N. Lan, S. Corneille, E. Schacht. Synthesis and characterization of segmented polyurethanes based on amphiphilic polyether diols. *Biomaterial*.1996,(17): 2273-2280



- [8] Stefan Oprea, Stelian Vlad, Aurelian Stanciu. Poly(urethane)s. Synthesis and characterization. *Polymer*. 2001, (42): 7257-7266
- [9] L.F.Wang, Q. Ji, T. E. Glass, T. C. Ward. Synthesis and characterization of organosiloxane modified segmented polyether polyurethane. *Polymer*. 2000 (41): 5083-5093
- [10] H. M. Jeong, B. K. Kim, Y. J. Choi. Synthesis and properties of thermotropic liquid crystalline polyurethane elastomers. *Polymer*. 2000(41):1849-1855
- [11] Tzong-Liu Wang, Tar-Hwa Hsieh. Effect of polyol structure and molecular weight on the thermal stability of segmented poly(urethane)s. *Polymer Degradation and Stability*. 1997(55):95-102