

MODIFICATION OF WATERBORNE PU FINISHING AGENT WITH HYDROXYL SILICONE

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ABSTRACT. In the present paper, a waterborne polyurethane (PU) finishing agent was synthesized with isophorone diisocyanate (IPDI), polytetrahydrofuran (PTMG), dimethylol propionic acid (DMPA) and n-butylamine, in which hydroxyl-terminated polydimethylsiloxane (OH-terminated PDMS) was added in three different ways, i.e., one-step, two-step and as a chain-extension agent. The PU was characterized using FT-IR and DSC and the water resistance and dry/wet rubbing resistance of the PU films were studied and compared. It was found that the chain segments by the reaction with OH-terminated PDMS and IPDI act as hard segments, and the elongation at break and water resistance of PU with OH-terminated PDMS as chain-extension agents are better than those with OH-terminated PDMS in both ways of one-step and two-step. The elongation at break could reach 1300% with the water absorption of only 1/4 of the latter PU films, when the same amount of OH-terminated PDMS is added in the system. It is better that OH-terminated PDMS is added in the top layer than added in the middle layer. The dry rubbing resistance could reach grade 5 with the wet rubbing resistance of grade 4.5.

KEY WORDS: waterborne polyurethane, polyurethane (PU), finishing agent, hydroxyl-terminated polydimethylsiloxane (Hydroxyl silicone)

MODIFICAREA UNUI AGENT DE FINISARE POLIURETANIC PE BAZĂ DE APĂ CU SILICON HIDROXIL

REZUMAT. În lucrarea de față, s-a sintetizat un agent de finisare poliuretanic (PU) pe bază de apă, cu diizocianat de izoforonă (IPDI), politetrahidrofuran (PTMG), acid dimetilol propionic (DMPA) și n-butilamină, în care s-a adăugat polidimetilsiloxan cu hidroxil terminal (PDMS cu OH terminal) în trei moduri diferite, adică, într-o singură etapă, în două etape și ca agent de extensie a catenei. PU a fost caracterizat prin analiza FT-IR și DSC și s-au studiat și comparat rezistența la apă și la abraziunea uscată/umedă a peliculelor PU. Prin reacția cu PDMS cu OH terminal și IPDI, s-a constatat că segmentele de lanț acționează ca segmente dure, iar alungirea la rupere și rezistența la apă a PU cu PDMS cu OH terminal ca agenți de extensie a catenei sunt mai bune decât valorile PU cu PDMS cu OH terminal într-o singură etapă și în două etape. Alungirea la rupere poate ajunge la 1300% cu absorbția de apă a numai 1/4 din peliculele PU în varianta de sinteză în două etape, atunci când se adaugă aceeași cantitate de PDMS cu OH terminal. Este mai bine să se adauge PDMS cu OH terminal în stratul superior decât în stratul de mijloc. Rezistența la abraziune uscată poate atinge gradul 5, iar rezistența la abraziune umedă, gradul 4.5.

CUVINTE CHEIE: agent poliuretanic pe bază de apă, poliuretan (PU), agent de finisare, polidimetilsiloxan cu hidroxil terminal (silicon hidroxil)

MODIFICATION D'UN AGENT DE FINITION PU À BASE D'EAU AVEC DU SILICONE HYDROXYLÉ

RÉSUMÉ. Dans cet article, on a synthétisé un agent de finition polyuréthane (PU) à base d'eau avec du diisocyanate d'isophorone (IPDI), du polytétrahydrofurane (PTMG), de l'acide diméthylol propionique (DMPA) et de la n-butylamine, dans lesquels on a ajouté le polydiméthylsiloxane à terminaison hydroxyle (PDMS à terminaison OH) de trois manières différentes, c'est-à-dire en une étape, en deux étapes et comme agent d'extension de chaîne. Le PU a été caractérisé en utilisant l'analyse FT-IR et DSC et la résistance à l'eau et la résistance au frottement sec / humide des films PU ont été étudiées et comparées. On a constaté que, par la réaction avec PDMS à terminaison OH et IPDI, les segments de chaîne agissent comme des segments durs, et l'allongement à la rupture et la résistance à l'eau de PU avec PDMS à terminaison OH comme agents d'extension de chaîne sont meilleurs que ceux avec PDMS à terminaison OH ajouté en une seule étape et en deux étapes, également. L'allongement à la rupture peut atteindre 1300% avec l'absorption d'eau de seulement 1/4 de ces derniers films PU, lorsque la même quantité de PDMS à terminaison OH est ajoutée dans le système. Il est préférable que le PDMS à terminaison OH soit ajouté dans la couche supérieure plutôt que dans la couche intermédiaire. La résistance au frottement à sec peut atteindre le grade 5 et la résistance au frottement humide, le grade 4,5.

MOTS-CLÉS : agent polyuréthane à base d'eau, polyuréthane (PU), agent de finition, polydiméthylsiloxane à terminaison hydroxyle (silicone hydroxylé)

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INTRODUCTION

The present waterborne polyurethane cannot 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 usually cannot meet the needs for excellent properties of polyurethane. So attempts have been done to modify the polyurethane in molecular level.

The internal rotation of the -Si-O-Si-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 waterborne 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 of the polyurethane decreased, while the tensile strength and elongation at break increased 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 had 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 *et al.* [4] 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, and the aggregation capacity of the molecules will be weakened. So the surface tension of the polyurethane emulsion

was decreased. In short, the use of silicone is an effective way to increase the elongation at break of polyurethane, and the water resistance of waterborne polyurethane may be improved to a certain extent. However, from viewpoint of the low surface tension of polyurethane, silicone modification is not a very good choice, because the surface polarity is decreased and the adhesive force between polyurethane and the basis materials is weakened.

In the present work, 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 ways were tried, i.e., one-step way, two-step way, and hydroxyl silicone chain-extension way. The elongation at break, FT-IR, DSC, water absorption and other properties of the polyurethane finishing agent were applied in the study. The final product was used in the finishing of leathers with the finishing results compared. It was indicated that the chain-extension way is the best in the three ways, indicating a potential application in the modification of PU finishing agent in leather making.

EXPERIMENTAL

Main Materials and Apparatus

Isophorone diisocyanate (IPDI, 95%), dimethylol propionic acid (DMPA), and poly tetrahydrofuran (PTMG, Mn=2000) were from Yantai Wanhua Polyurethane Co., Ltd, China. Hydroxyl silicone and n-butylamine were from Tianjin Chemical Reagent Factory, China. The dibutyltin dilaurate (AR) was from Chengdu Silicone Research Center, Ministry of Chemical Industry, China. Both triethylamine and acetone were analytical agent and purchased from Tianjin Chemical Reagent Factory, China. Thermal analyzer was made by the NETZSCH company, Germany. The FT-IR-8700-type variable temperature Fourier transform infrared spectrometer was made by Shimadzu, Japan. 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.

Synthesis of the Waterborne Polyurethane Finishing Agent

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 added to a four-necked bottle, and with dibutyltin dilaurate as catalyst, the mixture was allowed to react at 80°C for 3 hours to yield the prepolymer. In the prepolymerization process, some acetone was added to dissolve the prepolymer. Some triethylamine was added for neutralization according to the 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 5 min. 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 2 hours.

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, and 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 the 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 5 min. After being stirred

for water dispersion at the speed of 500r/min, light blue translucent polyurethane emulsion was obtained.

Film Forming of the Polyurethane

The waterborne polyurethane emulsion was poured in a PP film mold. After being dried at 50°C for 72 hours, the films were then dried at room temperature for another 48h to yield the polyurethane film for subsequent study.

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 polyurethane films were placed in a vacuum oven with the vacuum degree of 0.91MPa at 70°C to constant weight, about 5 h 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 according to equation (1).

$$\text{Water absorption} = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

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.

Dry/Wet Rubbing 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, the color on the surface of the samples was transferred on the lining of 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 grey card was the national standard (GB250-1995) one.

RESULTS AND DISCUSSION

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. In both ways of one-step and two-step, the amount of hydroxyl silicone was calculated as the ratio of hydroxyl groups to total hydroxyl content in percentage. Figure 1 shows the curves of the elongation at break of polyurethane films vs. hydroxyl silicone content. In Figure 1, 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 a maximum. This may be related to the length of the silicone chain. The molecular chain of the hydroxyl silicone is small, which might increase the hard segment content in the synthesis process of polyurethane, resulting in an increased interaction between hard segments. Similar to the performance of pure PU, the hydrogen bonds or crystallization of polyurethane should account for the decrease in the elongation at break.

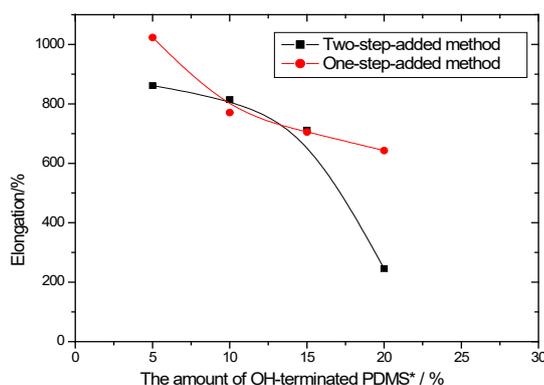


Figure 1. Relationship between the elongation at break and the hydroxyl silicone
*the hydroxyl ratio of OH-terminated PDMS to total -OH in the system

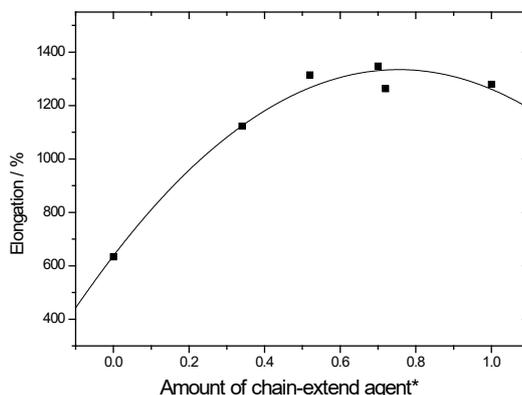


Figure 2. The elongation at break vs. amount of chain-extension agents
*the molecular ratio of chain-extension agent and dissociative –NCO

Figure 2 shows the relationship between 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 dissociative –NCO, a maximum was reached in elongation at break. Furthermore, hydroxyl silicone leads to a decrease in elongation at break again. The maximum elongation at break is 1300%. Compared to those by one-step and two-step, the way of chain-extension is the best to improve the elongation at break.

FT-IR Spectra of Hydroxyl Silicone Modified Waterborne Polyurethane

Figures 3-7 are the FT-IR spectra of hydroxyl silicone modified polyurethane films at different IR wave number ranges. The samples were obtained with different silicone contents by two-step way. In Figure 3, the peak at 802 cm^{-1} increases with increasing the content of hydroxyl silicone to form an obvious peak gradually. The absorption peak represents the oscillating vibration of Si-CH₃, indicating the reaction between hydroxyl silicone and the polyurethane molecule. The peak at 1240 cm^{-1} of the waterborne polyurethane film in Figure 4 was the absorption of the C-O-C. Although the bending vibrations of Si-CH₃ are also in the region, because 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 appeared 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 atom in N-H and the O atom in C-O-C or C=O. A shoulder peak appeared in 1047 cm^{-1} in Figure 6. The emergency of the shoulder peak might be because 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 waterborne polyurethane were shown in Figure 7. The absorption of C=O of polyurethane without hydrogen bonds usually occurs in the range from 1730 to 1745 cm^{-1} and that with hydrogen bonds moves to lower wave number [8]. The absorption of C=O appeared in 1712 cm^{-1} and no obvious shoulder peak was found at a higher wave number. Therefore, most of the C=O groups take part in the formation of hydrogen bonds. Besides, the obvious broad peak at 1654 cm^{-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.

In Figures 6 and 7, the area of the shoulder peak of the hydrogen bonded C-O-C increases with increasing the hydroxyl silicone content, indicating an increased bonding degree of C-O-C. The higher the hydrogen bonding degree between the soft segment and the hard segment, the more difficult for the soft segment molecules in the polyurethane to move, which will decrease the elongation of polyurethane. The decrease

in 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 segments.

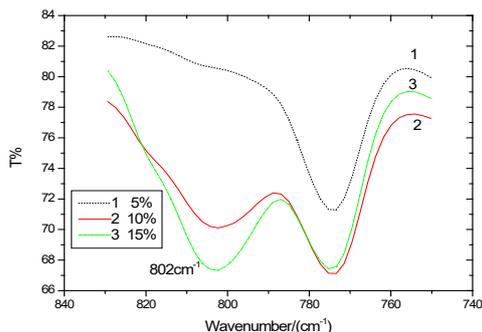


Figure 3. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (840-740 cm^{-1})

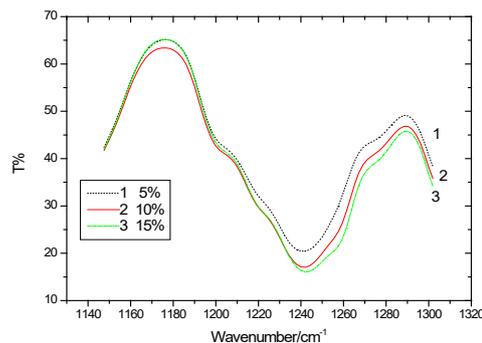


Figure 4. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1140-1320 cm^{-1})

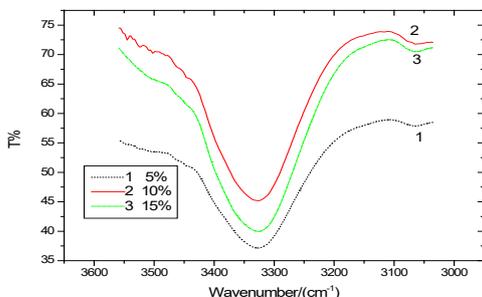


Figure 5. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (3600-3000 cm^{-1})

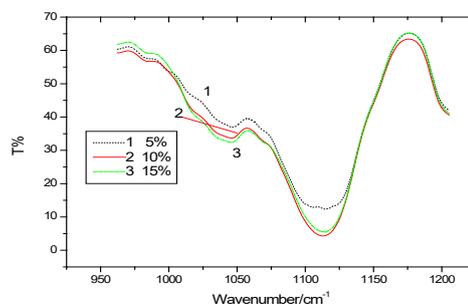


Figure 6. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (950-1200 cm^{-1})

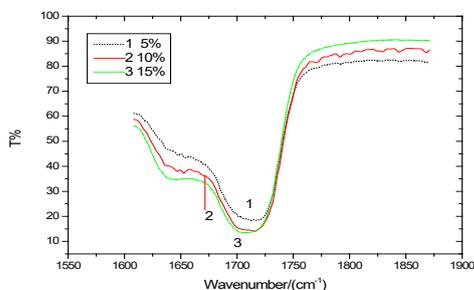


Figure 7. Infrared spectra of the hydroxyl silicone modified PU film by two-step way (1550-1900 cm^{-1})

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 at both 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. At the amount of 10%, the T_g was -79°C with the endothermic of 0.0706 J/mg . At the amount of 15%, the T_g was -81°C and the endothermic was 0.1246 J/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 easier than that with 10% hydroxyl silicone, which may be good to increase the elongation at break of the PU finishing agent. 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%, Tg was 19°C with the endothermic of 1.079 J/mg . When the amount of hydroxyl silicone was 10%, the

Tg was 31°C and the endothermic was 0.3964 J/mg . For the 15% sample, the Tg was 6°C and the endothermic was 0.3023 J/mg . The Tg was -14°C and the endothermic was 0.2886 J/mg for the sample with the hydroxyl silicone of 20%. It was indicated that the maximum interaction between hard segments appears at the amount of hydroxyl silicone of 10%. The interaction between the hard segments decreases with increasing the hydroxyl silicone amount above 10%.

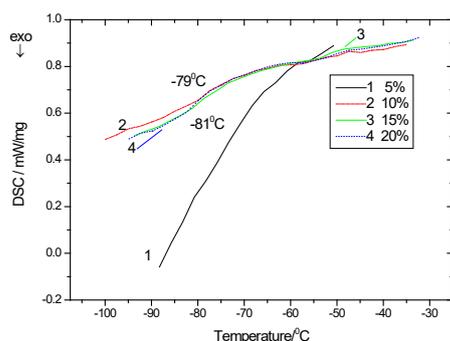


Figure 8. DSC curves of the hydroxyl silicone modified PU films by two-step way (-100°C ~ -30°C)

The DSC curves of the modified polyurethane films with hydroxyl silicone as chain-extension agent are shown in Figure 10-11. The same results as Figure 8-9 were obtained: 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 -30°C . When the amount of hydroxyl silicone is 52%, the Tg of the polyurethane is -82°C with the endothermic of 0.2913 J/mg . 67% of hydroxyl silicone gave a polyurethane with the Tg of -81°C and endothermic of 0.1934 J/mg . At the amount of 75%, the polyurethane presented a Tg of -81°C and an endothermic of 0.244 J/mg . At the hydroxyl silicone amount of less than 75%, the endothermic decreases with increasing the hydroxyl silicone amount, while in 75%, the endothermic increases. By comparing with the result Figure 2, 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

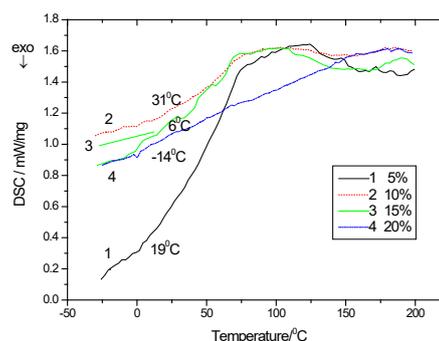


Figure 9. DSC curves of the hydroxyl silicone modified PU films by two-step way (-50°C ~ 200°C)

amount of 52%, the Tg of the polyurethane was 5°C with the endothermic of 0.4054 J/mg . The 67% of hydroxyl silicone yielded the PU with a Tg of -1°C and an endothermic of 0.3388 J/mg . When the hydroxyl silicone was 75%, the Tg was 1°C with the endothermic of 0.3757 J/mg . With increasing the amount of hydroxyl silicone as chain-extension agent, the endothermic decreases gradually, which does good for the hard segments to move. The elongation at break of the hydroxyl silicone chain-extended polyurethane films increases with increasing the amount of hydroxyl silicone, suggesting that the elongation at break of the polyurethane is related to the intermolecular interactions in it.

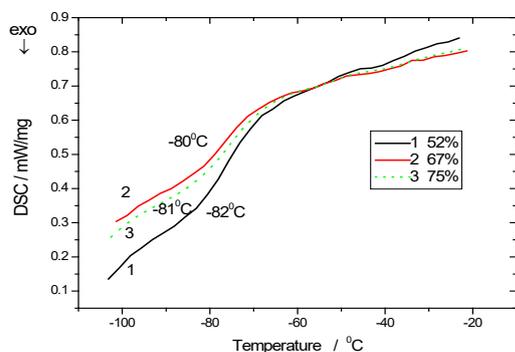


Figure 10. DSC curves of PU film chain-extended by hydroxyl silicone (-100~-20°C)

In summary, for the polyurethane chain-extended by hydroxyl silicone, there appeared both the glass transitions of the soft segment (at -80°C or so) and 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 takes 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.

Water Absorption of the Hydroxyl Silicone Modified Polyurethane

The waterborne polyurethane without hydroxyl silicone modification will be dissolved when being soaked in water for a long time. For example, the weight of waterborne polyurethane chain-extended by ethylene diamine decreases when being soaked in water for 6 hours, 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 both 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

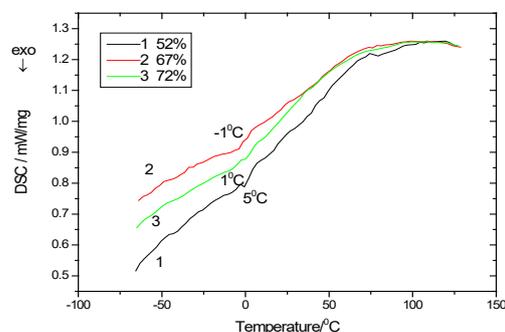


Figure 11. DSC curves of PU film chain-extended by hydroxyl silicone (-70~150°C)

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 those of 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.

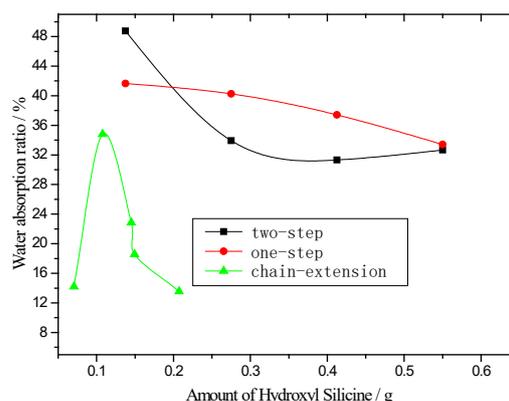


Figure 12. Water absorption of PU modified by hydroxyl silicone in different ways

Dry/Wet Rubbing Resistance

The PU finishing agents chain-extended with hydroxyl silicone were applied in the finishing of leathers. The bottom finishing was the traditional finishing agent, while the hydroxyl silicone was used only in the finishing of both layers of middle and top. The dry/wet rubbing resistance of the samples was studied with the results shown in Table 1.

Table 1: Dry/wet rubbing resistance of the finished samples

Samples	Amount of 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

In Table 1, the synthesized waterborne 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/wet rubbing resistance of coatings.

CONCLUSIONS

The reaction between hydroxyl silicone and isocyanate takes 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 showed 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.

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