

Synthesis and Characterization of Self-matting Waterborne Polyurethane Emulsion Modified by Silane Coupling Agent

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Abstract. Silane coupling agent has low surface energy, and its side chain contains organic groups that are easy to participate in the reaction. In the process of film formation, Si is easy to aggregate to the surface, which has the advantages of water and oil resistance, good permeability, low glass transition temperature and good thermal stability. Therefore, in this paper, four silane coupling agents such as KH540, KH550, KH560 and AEAPTMS were used to hydrophobically modify waterborne polyurethane (WPU). A series of self-matting waterborne polyurethane solutions were prepared with HTPB and PTMG as soft segments and IPDI as hard segment. The siloxane introduced in the WPU structure was hydrolyzed to form a Si-O-Si hydrophobic structure, which increased the crosslinking degree of the system and improved the water resistance of the system. It was also beneficial to increase the particle size and improved the extinction performance of WPU. Through comprehensive analysis, we found that the most suitable silane coupling agent for modifying self-matting WPU was AEAPTMS. After modification, the gloss of WPU leather coating can be reduced to 0.4 GU, and the surface energy can be reduced to 19.72 mJ/m². It greatly improved the extinction performance and water and solvent resistance of WPU, and has a wide application prospect in the field of WPU leather finishing agent.

Keywords: Silane coupling agent; self-matting; waterborne polyurethane.

1. Introduction

With the change of people's aesthetic concept, low gloss coatings are becoming more and more popular in surface decoration and architectural design. Compared with high-gloss coatings, low-gloss coatings are suitable for hiding slight scratches and defects, reducing dust and fingerprint aggregation[1-4], and reducing visual dispersion. They are widely used in wood and furniture, leather jewelry, automotive parts, and the outer surfaces of school and hospital walls.[5,6] The principle of extinction is that when a parallel beam of light is projected on the surface of the same material at a certain incident angle, if the surface is smooth, the reflected light will be reflected in parallel at the same angle. The specular reflection will occur, giving the feeling of high gloss. If the surface roughness is large, the light will be reflected in different directions at different angles. At this time, diffuse reflection occurs, and the feeling is low gloss. The principle of extinction is shown in Figure 1.[7]

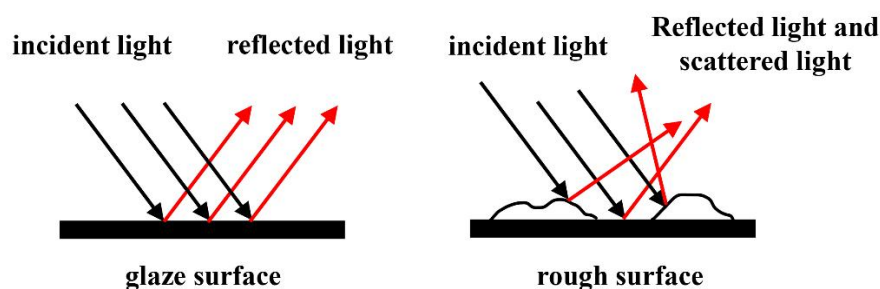


Fig. 1 Extinction principle diagram

The traditional method of preparing matting waterborne polyurethane is to physically blend the matting agent with waterborne polyurethane.[8] However, the matting agent particles are not fixed firmly and are easy to be detached from the surface, resulting in the disappearance of the rough

structure over time. The extinction effect and the stability of the emulsion decreases, and it's unfavorable to the bending resistance of the coating.[9,10] The self-matting WPU does not contain any additional matting agent, and only emulsion particles with similar effects to the matting agent are generated during the synthesis process. When the film is formed, they accumulate each other to form a microscopically rough surface to achieve the matting effect. It eliminates the defects caused by the use of matting agent and has good emulsion stability. Self-matting WPU is environmentally friendly and inexpensive, and can also improve the overall performance of waterborne polyurethane.[11]

After a long period of research and improvement, WPU leather finishing agents have achieved certain results, but there are still some shortcomings to be overcome. For example, WPU needs to be introduced some hydrophilic groups during the synthesis process,[10] so as to ensure that WPU emulsion particles can be stably dispersed and preserved in water. It will inevitably lead to a decrease in the water resistance of WPU. However, in practical applications, the water resistance of the coating is an extremely important indicator. Therefore, it is urgent to study the improvement of water resistance of self-matting WPU.

Silane coupling agent contains Si-O structure, and its bond energy ($460 \text{ kJ}\cdot\text{mol}^{-1}$) is much larger than that of C-C bond ($332 \text{ kJ}\cdot\text{mol}^{-1}$). It has good oxidation stability. At the same time, its side chain contains organic groups that are easy to participate in the reaction. The surface energy of silane coupling agent is low, and it is easy to aggregate to the surface during the film forming process. It has the advantages of water and oil resistance, good permeability, low glass transition temperature and good thermal stability, so it is often used as a modifier. Zhang et al.[12] successfully used divinyl terminated polysiloxane to modify acrylate and used it as pigment printing binder by cationic ring-opening polymerization. The results showed that the modified adhesive had better wet rubbing fastness and soft handle than the unmodified adhesive. Li et al.[13] synthesized silicone-modified WPU coatings using poly(adipate-1,4-butanediol)(PCL2000), TDI and Polydimethylsiloxane(PDMS) as the main raw materials, and explored their antifouling properties. The study found that the introduction of PDMS increased the thermal stability of the coating, and the surface free energy was reduced to $13.87 \text{ mJ}/\text{m}^2$.

In order to improve the extinction performance and water resistance of the current self-matting waterborne polyurethane leather finishing agent, the hydroxyl-polyether system with excellent extinction performance was selected on the basis of previous research.[14] The synthesis and properties of self-matting waterborne polyurethane with excellent comprehensive properties were studied by using silane coupling agent to extend the chain of WPU, which laid a foundation for the application of low gloss waterborne polyurethane leather finishing agent.

2. Materials and methods

2.1 Materials

The raw materials used in this study include hydroxyl terminated polybutadiene (HTPB; $\overline{M}_n=2000 \text{ g}\cdot\text{mol}^{-1}$); hydroxyl group content $0.71\sim 0.80 \text{ mmol}\cdot\text{g}^{-1}$), poly(tetra-methylene glycol) (PTMG; $\overline{M}_n=2000 \text{ g}\cdot\text{mol}^{-1}$), isophorone diisocyanate (IPDI, used as received), neopentyl glycol (NPG), 2,2-bis(hydroxymethyl)propionic acid (DMPA), 3-Aminopropyltrimethoxysilane(KH540), 3-Aminopropyltriethoxysilane(KH550), Glycidoxypropyltrimethoxysilane(KH550), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane(AEAPTMS), sodium 2-[(2-aminoethyl)amino] ethanesulfonate (AAS salt), N-methyl-pyrrolidone (NMP), ethylenediamine (EDA), trimethylamine(TEA), neodecanoic acid bismuth($3+$) salt. All these raw materials were analytical reagents and purchased from MacklinChemical Reagent Co. Ltd. (Shanghai, China).

Table 1. Three Scheme comparing

sample	ω (HTPB)*	ω (DMPA)	ω (AAS)	R值	silane coupling agents	ω (silane coupling agents)
WPU-none	20%	0.5%	0.50%	1.3	----	----
WPU-KH540					KH540	0.5%
WPU-KH550					KH550	
WPU-KH560					KH560	
WPU-AEAPT MS					AEAPTMS	

* ω (HTPB) is the percentage of HTPB in the total mass of HTPB and PTMG.

2.3 Characterization

2.3.1 FTIR-ATR

The infrared absorption of waterborne polyurethane was tested by the 8700 Fourier transform infrared spectrometer (ATR-FTIR, Nicolet, USA). The sample was scanned 48 times at a resolution of 4 cm^{-1} over the frequency range of $4000\sim 400\text{ cm}^{-1}$.

2.3.2 Particle size analysis

The emulsion was diluted with deionized water to a mass fraction of 0.01 % and tested using a Zetasizer Nano ZS90 laser particle size tester. The test temperature was room temperature, the stability time was 2 min, and the average value was measured three times.

2.3.3 Gloss test of self-matting WPU leather coatings.

10 g WPU emulsion and 0.1 g wetting agent (BYK381) were mixed for 10 min, coated on the PVC leather using a 40 mm wire rod, and subsequently placed in an oven at $120\text{ }^{\circ}\text{C}$. After drying for 2 min, the leather samples were taken out for gloss test. According to GB/T9754-2007 “paints and varnishes—determination of 20° , 60° and 85° specular gloss of paint films without metallic pigments”, the 60° gloss was determined using the Ref 101N photometer from Sheen. The average value of three tests was used as the final result.

2.3.4 SEM

A SU8020 scanning electron microscope (TESCAN MIRALMS) was used to observe the surface morphology of the polyurethane coating film on the leather. The operating voltage was 3 kV, and gold was sprayed before the sample test to improve the conductivity.

2.3.5 Water absorption test of film

The dried film was cut out of a $2\text{ cm}\times 2\text{ cm}$ sample and weighed as m_0 . It was completely immersed in deionized water and taken out after soaking for 24 h. The water on the surface of the sample was quickly dried and weighed as m_1 . Calculate the water absorption of the film according to the following formula:

$$\text{water absorption} = \frac{m_1 - m_0}{m_0} \times 100\%$$

2.3.6 Contact angle of self-matting WPU leather coatings.

The static contact angle of leather coatings was measured at $25\text{ }^{\circ}\text{C}$ with OCA20 contact angle tester (Dataphysics, Germany). The surface energy of WPU coating was calculated by measuring the contact angles of five different solvents (Distilled water, diiodomethane, formamide, ethylene glycol and glycerol).

3. Results and discussion

3.1 Structural characterization of silane coupling agent modified self-matting WPU

From Figure 3, it can be seen that the peak at 2264 cm^{-1} of IPDI was the characteristic absorption peak of-NCO group. In WPU, there was no absorption peak at 2264 cm^{-1} , indicating that IPDI had been fully involved in the reaction. The peak at 1078 cm^{-1} in the infrared spectrum of KH550 was the characteristic absorption peak of Si-O-CH₂CH₃ group, and the peaks at 802 cm^{-1} and 1095 cm^{-1} in WPU-KH550 were the stretching vibration peaks of Si-O-Si, indicating that KH550 was successfully introduced into WPU and hydrolyzed to obtain Si-O-Si crosslinked structure. The absorption peak at 3328 cm^{-1} was the characteristic peak of-NH, and the peak intensity of WPU-KH550 was greater than that of WPU-none. After the WPU was modified by silane coupling agent, the-NH₂ of KH550 reacted with-NCO to form a urea group, thereby increasing the -NH content, which also indicated that KH550 successfully participated in the reaction. In the WPU spectrum, 1716 cm^{-1} was the characteristic absorption peak of carbamate bond, and $2854\sim 2941\text{ cm}^{-1}$ was the C-H stretching vibration absorption peak of-CH₃ and-CH₂. These are typical characteristic peaks of polyurethane, indicating that the reaction has been successfully completed.

In the infrared spectra of WPU modified by different silane coupling agents, the vibration absorption peaks of Si-O-Si appeared at 1095 cm^{-1} and 802 cm^{-1} , and the characteristic absorption peaks of -NH at 3328 cm^{-1} were strengthened, indicating that the four silane coupling agents were successfully involved in the reaction.

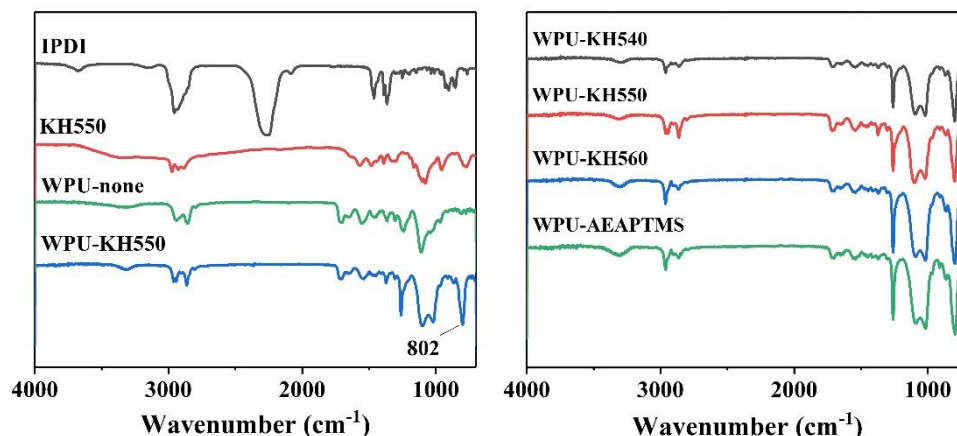


Fig. 3 Infrared spectra of raw materials and WPU

3.2 Effect of silane coupling agent on particle size of WPU

The particle size of self-matting WPU modified by different silane coupling agents is shown in Fig.4. It can be seen that the particle size of the unmodified WPU emulsion is 2630 nm, and the particle size increased after the modification of the silane coupling agent. The maximum particle size of WPU-AEAPTMS was 3139 nm. The Si-O-CH₃ or Si-O-CH₂CH₃ groups in the molecular structure of silane coupling agent were introduced into the WPU molecular chain. When water was added to disperse and emulsify, the alkoxy group was hydrolyzed to form a cross-linked network of Si-O-Si, which was more difficult to be sheared and dispersed during emulsification. Therefore, the particle size of WPU modified by silane coupling agent increased.

Among the four silane coupling agents, AEAPTMS has the most obvious effect on the particle size of WPU. AEAPTMS contains two amino groups. When it reacts with the -NCO group of WPU prepolymer, its reactivity and the degree of crosslinking is greater. In addition, there is only one amino group in KH550, and it plays a capping role in the WPU molecular chain, which have limited effect on the growth of WPU molecular chain and the increase of crosslinking degree. AEAPTMS can connect multiple pre-polymerized WPU molecular chains, significantly increasing the molecular weight and crosslinking degree of WPU. Therefore, when the silane coupling agent with the same amino content is added, AEAPTMS has a greater influence on the particle size of WPU.

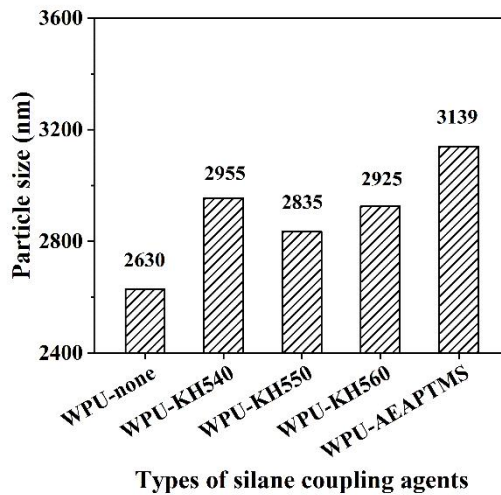


Fig. 4 Particle size of WPU modified by different silane coupling agents

3.3 Effect of silane coupling agent on the gloss of WPU

The leather finishing diagram of WPU modified by different silane coupling agents and its 60 ° gloss data are shown in Fig.5 and Fig.6. The gloss of WPU leather coating modified by four silane coupling agents is 0.3 GU or 0.4 GU, which can achieve excellent extinction effect. Among them, WPU modified by KH550 and AEAPTMS can better retain the original effect of leather when finishing. The Si-O-Si cross-linked structure formed by hydrolysis after the introduction of silane coupling agent makes it more difficult to be sheared and dispersed, and the particle size increases. It can form a microscopic rough surface. Large-sized microspheres larger than the visible light wavelength make the incident light strongly curved and diffusely reflected. This strong light scattering ability conforms to the principle of film extinction.

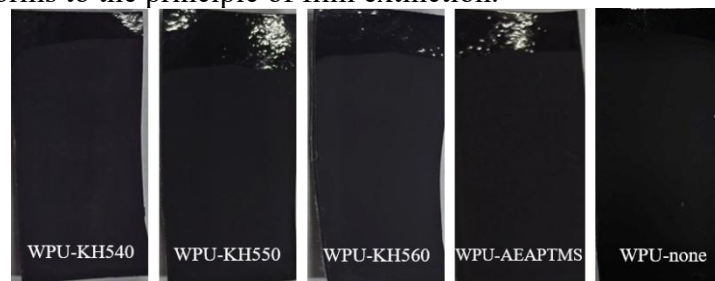


Fig. 5 Leather finishing photos of WPU modified by different silane coupling agents

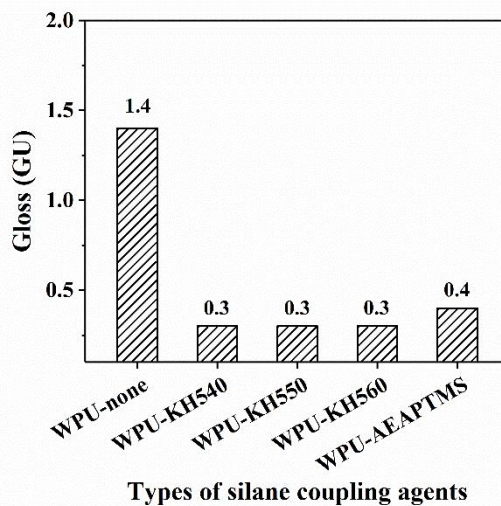


Fig. 6 Particle size of WPU modified by different silane coupling agents

Figure 7 is the SEM image of WPU leather finishing surface modified by different silane coupling agents. Compared with the unmodified WPU leather coating in Figure 7(f), the surface roughness of Figure 7(a)~(d) modified by silane coupling agent increased significantly, and the microscopic rough protrusions formed by the close accumulation of spherical particles were more clearly visible. Among them, the WPU modified by AEAPTMS has a suitable particle size gap, which makes the micro-surface of the matting coating present a uniform distribution of micro-protrusions. There are two reasons why AEAPTMS modification can form a suitable microscopic rough surface and excellent extinction effect. On the one hand, when the same amount of Si was introduced, AEAPTMS introduced more amino groups, and the degree of crosslinking increased to increase the WPU molecular chain. At the same time, it can also cross-link the WPU chain with smaller molecular weight. So that a series of emulsions of different sizes in WPU increased at the same time, resulting in a uniform increase in the final microscopic roughness. On the other hand, the introduction of more amino groups increased the degree of crosslinking, which increased the rigidity of the emulsion particles. When the emulsion film is formed, the deformation of the particles squeezing each other was smaller, and the fusion with the surrounding particles was less, which can better maintain the original state of the particles. Therefore, its uneven microscopic surface was more obvious under the scanning electron microscope.

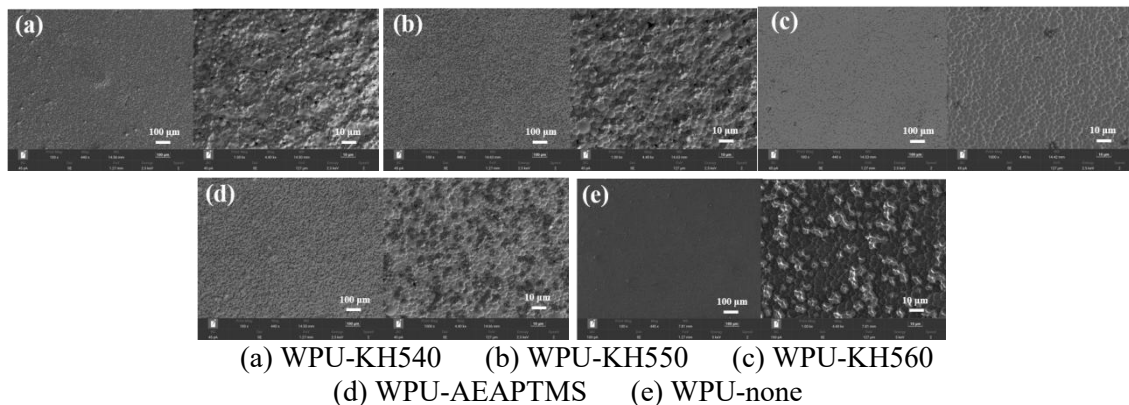


Fig. 7 The SEM image of WPU leather finishing surface modified by silane coupling agents

3.4 Effect of silane coupling agent on the water absorption of WPU

The water absorption of WPU film modified by different silane coupling agents is shown in figure 8. The water absorption of unmodified WPU-none was 5.89 %. After the introduction of silane coupling agent, the water absorption decreased, and the lowest water absorption of WPU-AEAPTMS was 1.40 %. The Si-O bond contained in the silane coupling agent is hydrolyzed to form a Si-O-Si hydrophobic structure. When the WPU modified by the silane coupling agent is formed, the Si-O-Si group is gathered on the surface of the film, thereby reducing the water resistance of the WPU film. At the same time, crosslinking occurs after the introduction of silane coupling agent, which reduces the voids inside the molecular chain and reduces the water absorption.

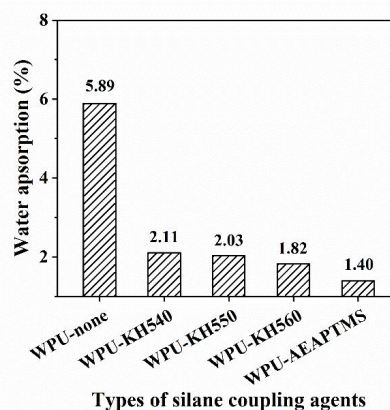


Fig. 8 The water absorption of WPU film modified by silane coupling agents

3.5 Effect of silane coupling agent on the contact angle and surface energy of WPU

The surface energy of WPU was calculated by LW-AB method proposed by Van Oss et al.[15,16]. For solids or liquids, the surface energy can be expressed as :

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-} \tag{1-1}$$

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} = \gamma_L^{LW} + 2\sqrt{\gamma_L^+ \gamma_L^-} \tag{1-2}$$

Here, γ^{LW} is the Lifshitz-van der Waals component; γ^{AB} is the Lewis acid-base component; γ^+ is the Lewis acid component; γ^- is the Lewis base component. Therefore, we can obtain a new relationship between interfacial tension and solid and liquid surface energy, as shown in Eq. (1-3).

$$\gamma_{SL} = \left(\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_L^+ \gamma_s^-} - \sqrt{\gamma_s^+ \gamma_L^-} - \sqrt{\gamma_s^- \gamma_L^+} \right) \tag{1-3}$$

It can be concluded from Eq.(1-3) that the solid surface energy component can be calculated as long as the contact angles of three liquids with known surface tension components on the solid surface are measured. Suppose that the contact angles of liquid L_1 、 L_2 and L_3 with three kinds of surface tension on a solid surface are θ_1 、 θ_2 、 θ_3 respectively. Substituting them into Formula (1-3), and the surface energy can be calculated according to the contact angle.

In this paper, distilled water, glycerol, formamide, diiodomethane and ethylene glycol are selected as detection liquids. The surface energy parameters of each liquid are shown in Table 2.

Table 2. Surface energy parameters of liquids for testing (mJ/m²)

Liquid	molecular formula	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
distilled water	H2O	72.8	21.8	25.5	25.5
glycerol	C3H8O3	64	34	3.92	57.4
formamide	CH3NO	58	39	2.28	39.6
diiodomethane	CH2I2	50.8	50.8	0	0
glycol	C2H6O2	48	29	1.92	47

Table 3 shows the equilibrium contact angles of liquid distilled water, glycerol, formamide, diiodomethane and ethylene glycol on the surface of WPU leather coating.

Table 3. Contact angle of WPU leather coating surface (°)

Sample	distilled water	glycerol	formamide	diiodomethane	glycol
WPU-none	96.3	90.4	81.5	31.6	58.3
WPU-KH540	105.5	96.1	93.7	36.1	63.5
WPU-KH550	105.2	99.8	99.6	33.8	61.5
WPU-KH560	104.2	101.5	100.3	32.9	62.9
WPU-AEAPT MS	110.9	108.3	106.4	44.3	66.2

Studies[17] have shown that LW-AB method for the detection of liquid commonly used combination scheme is: a liquid is Lewis acid-base neutral distilled water, the second liquid is non-polar diiodomethane, the third liquid can be glycerol, formamide, ethylene glycol and other polar liquids in any one. Therefore, in this paper, the combination of distilled water-glycerol-diiodomethane (WGD), distilled water-formamide-diiodomethane (WFD) and

distilled water-glycol-diiodomethane (WED) was selected to calculate the surface energy parameters of polymers. The results are shown in Tables 4.

Table 4. The surface energy values of WPU detected by LW-AB method (mJ/m²)

Sample	WGD	WFD	WED	Average surface energy
WPU-none	30.78	29.69	27.28	29.25
WPU-KH540	27.98	23.95	25.96	25.96
WPU-KH550	27.61	19.61	27.71	24.98
WPU-KH560	26.65	18.22	27.53	24.14
WPU-AEAPTMS	21.10	15.11	22.95	19.72

The modification of WPU by silane coupling agent can greatly improve the contact angle and surface energy of WPU leather coating, and the modification effect of AEAPTMS is the best. Taking the water contact angle as an example, compared with the WPU-none contact angle of 96.3 °, the water contact angle of WPU-AEAPTMS was greatly increased to 110.9 °, and the formamide contact angle was increased by 24.9°. The surface energy data calculated by the formula are shown in Table 4. The surface energy of unmodified WPU was 29.25 mJ/m², and the surface energy of WPU-AEAPTMS was reduced to 19.72 mJ/m², which greatly improved the water resistance and solvent resistance of WPU applied to leather coatings. This was due to the Si-O-Si hydrophobic structure obtained after crosslinking of the silane coupling agent with WPU. The hydrophobic structure migrated to the surface when the film was formed, thus helping to reduce the surface energy of WPU.

4. Conclusion

In this paper, four kinds of self-matting waterborne polyurethane emulsions modified by different silane coupling agents were successfully synthesized. After modified by silane coupling agent, the gloss and water resistance of the WPU were greatly improved. After comprehensive analysis, it is found that the most suitable silane coupling agent for WPU is AEAPTMS. When the same content of Si is introduced, it can bring more amino groups, which makes the performance improvement of WPU more significant. The gloss of WPU-AEAPTMS was reduced to 0.4 GU. The water absorption was reduced to 1.4%, and the surface energy was as low as 19.72 mJ/m². WPU-AEAPTMS has excellent extinction effect and water resistance, and has potential applications in the field of self-dull waterborne polyurethane.

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