

# Synthesis of Ionic and Non-Ionic Modified Waterborne Polyurethane Curing Agent

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**Abstract:** By using HDI and TMP as the main raw materials, polyethylene glycol 400 (PEG400) is used as a non-ionic hydrophilic modifier, and sodium hydroxyethyl sulfonate is used as an ionic hydrophilic modifier to synthesize a dual hydrophilic modified polyurethane curing agent. Research revealed that introducing PEG400 for hydrophilic chain segments and sodium hydroxyethyl sulfonate for hydrophilic ionic groups in the polyurethane curing agent component leads to a uniform distribution of hydrophilic components, significantly enhancing compatibility with the aqueous polyol component, and results in excellent film performance. The synthesis process and film were characterized using Fourier transform infrared spectroscopy and high-resolution scanning electron microscopy in the study.

**Keyword:** Coating; Water polyurethane; Curing agent; Two-package; Double modification

**Online publication:** January 23, 2024

## 1. Introduction

Waterborne polyurethane with two components is not only environmentally friendly but also exhibits a low film-forming temperature, high film gloss, good wear resistance, water resistance, and solvent resistance. It currently stands as a research hotspot in waterborne coatings<sup>[1]</sup>. The two-component waterborne polyurethane consists of a polyisocyanate curing agent component and a water-based polyol component, which are uniformly mixed before coating. During film formation, the NCO in the curing agent reacts with the -OH in the polyol to form a cross-linked film.

In the realm of two-component waterborne polyurethane, hydrophilic-modified polyisocyanate finds widespread use, with two main categories: non-ionic modification and ionic modification. Non-ionic hydrophilic modification primarily employs polyether modification, introducing hydrophilic non-ionic ether segments into the molecular structure of polyisocyanate by reacting polyisocyanate with polyethylene glycol monomethyl ether. While this imparts hydrophilicity, it also introduces challenges related to water resistance and crystallinity tendencies<sup>[2-6]</sup>. Ionic modification includes cationic modification and anionic modification. Cationic modification introduces tertiary amine groups on the polyisocyanate molecule, obtained through acid

neutralization to form salts. However, cations have a promoting effect on the reactivity of NCO groups with active hydrogen, accelerating the reaction rate with water, leading to decreased system stability, multiple steps, and high cost [7,8]. Anionic modification introduces carboxyl or sulfonic acid groups on the polyisocyanate molecule, obtained through neutralization with a base, resulting in a curing agent with a pH of less than 7, which slows down the reaction rate of NCO with water, but additional neutralization steps are still required, adding complexity [9-11].

This study uses polyethylene glycol 400 (PEG400) and sodium hydroxyethyl sulfonate to perform non-ionic and ionic composite hydrophilic modification on hexamethylene diisocyanate-trimethylol propane (HDI-TMP) prepolymers. This approach combines the advantages of both hydrophilic modification methods, compensating for their respective shortcomings, and does not necessitate neutralization agents, thereby simplifying the process. The synthesized curing agent, studied in this research, exhibits a high NCO content, easy dispersal in water, and excellent compatibility with the water-based polyol component, resulting in outstanding coating performance.

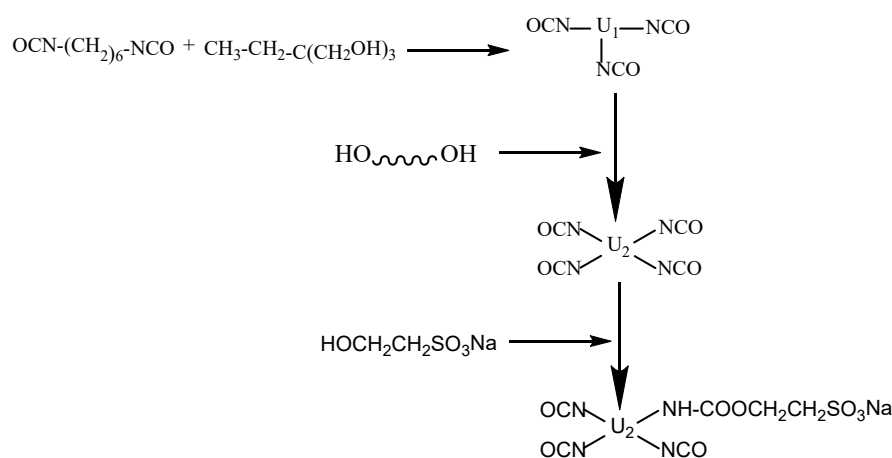
## 2. Experiment

### 2.1. Materials

Hexamethylene diisocyanate (HDI) was purchased from Wanhua Chemical Group Co., Ltd. (China). Polyethylene glycol 400 (PEG400) was obtained from Sinopharm Medicine Holding Group Co, Ltd. (China). Trimethylolpropane (TMP) was purchased from LookChem Chemical Group Co., Ltd. (China). Sodium 2-hydroxyethyl sulfonate (SHS; purity > 98%) was provided by Shanghai Jingchun Co., Ltd. (China). Polyurethane polyol components (hydroxyl value = 26.63 mgKOH/g) were self-made.

### 2.2. Synthesis of curing agent

The appropriate amount of HDI was added into a four-neck flask, with a condensing tube, thermometer, and stirring paddle. The TMP solution was then dripped into the flask within 1 h at 40°C under stirring. After that, the mixture was kept at 80°C for 4.5 h, during this process, PEG400 was added to the mixture, followed by keeping the mixture at 73°C for 1.5 h with the addition of sodium hydroxyethyl sulfonate. Finally, the double hydrophilic modified polyurethane curing agent was obtained. The reaction scheme is illustrated in **Figure 1**.



**Figure 1.** The synthesis process of curing agent.

### 2.3. Preparation of the film

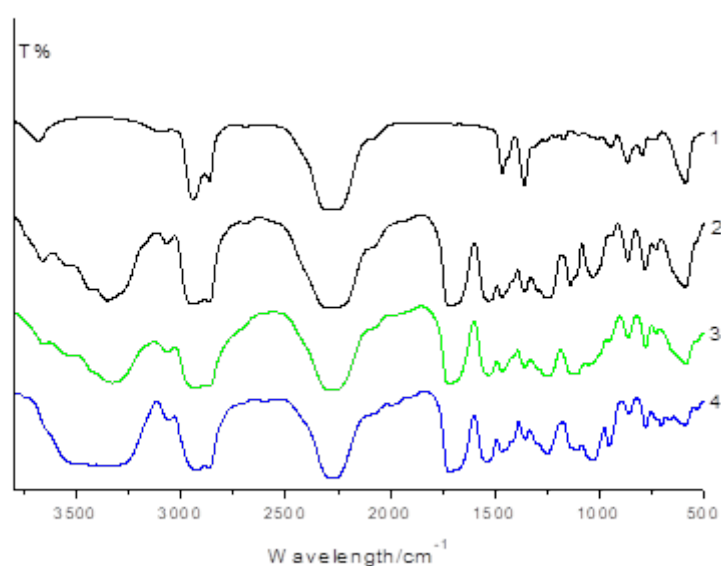
The curing agent and polyurethane polyol components were mixed well with the ratio of , and then the emulsion was coated on the steel substrate. The film was stored at room temperature for 2 h and then dried at 50°C for 24 h.

### 2.4. Characterization

The molecular structure and chemical composition of the curing agent were characterized using the Fourier transform infrared spectrometer (WQF-410). The hardness of the films was measured using a pencil hardness tester, the average value of three times was taken as the final pencil hardness. Gloss measurement was performed with a QZX-60A gloss meter (Tianjin material test factory). Ethanol resistance was tested using the drop method. Drops of 50% (volume fraction) ethanol solution were dropped on the paint film and covered with a glass surface dish or a plastic cover to prevent the liquid from evaporating too quickly. The paint was cleaned with water or a clean cloth after being placed at room temperature for 1 h, and the degree of coloring of the liquid on the paint was observed. Water absorption was evaluated in terms of the difference between the wet mass ( $W_1$ ) and dry mass ( $W_2$ ) of the coating, and was calculated using the following equation:

## 3. Result and discussion

### 3.1. Fourier transform infrared spectroscopy (FTIR) analysis

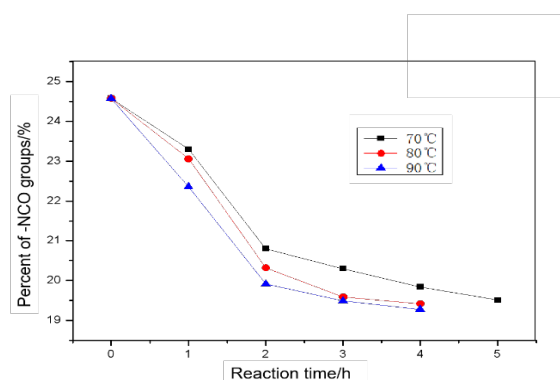


**Figure 2.** FTIR spectra of the progress of the polyurethane curing agent synthesis. (1) The material of HDI; (2) The product with TMP reaction for 3 hours; (3) The polymer after reacting with PEG400 for 1.5 h; (4) The curing agent

**Figure 2** shows the synthesis progress of the polyurethane curing agent. From the infrared absorption spectrum of HDI, the peak at  $2,304\text{ cm}^{-1}$  is ascribed to the  $\text{-NCO}$  group. After the reaction between HDI and TMP, the  $\text{N-H}$  stretching vibration peak is observed at about  $3,331\text{ cm}^{-1}$ , which indicates that the TMP has successfully reacted with HDI. During the synthesis progress, the peak of the  $\text{N-H}$  group widens gradually, which indicates that TMP and PEG400 have been introduced into the macromolecules of the curing agent. Besides, the peaks at  $1,203\text{ cm}^{-1}$  and  $1,052\text{ cm}^{-1}$  represent the  $\text{S=O}$  asymmetric and symmetrical stretching vibration, which indicates that the sodium hydroxyethyl sulfonate has reacted with the precursor.

### 3.2. The effect of reaction time and reaction temperature of HDI and TMP

According to the reaction equation between HDI and TMP, as the reaction progresses, the proportion of –NCO groups gradually decreases. The percent of –NCO groups decrease is displayed in **Figure 3**, which is detected by the toluene-di-n-butylamine method. From **Figure 3**, in the case of the same ratio of HDI and TMP, the percent of –NCO groups in the structure decreases with the extension of reaction time. When the reaction was conducted at 80°C for 3 h, the NCO content was close to the theoretical content and then remained unchanged. When the reaction is under 70°C, the theoretical content can be reached at 70°C after a 5-hour reaction. At 90°C, the NCO content was close to the theoretical content for the initial 3 h but subsequently decreased. This reduction is mainly attributed to the elevated temperature causing carbamate group generation, leading to a side reaction with the NCO group and consequently consuming the NCO group. It is evident from this experiment that the optimal reaction conditions are set at 80°C for 3 h.



**Figure 3.** The relationship of NCO content with temperature and reaction time

### 3.3. The ratio of HDI and TMP analysis

The theoretical molar ratio of the synthesized HDI-TMP prepolymer is 3:1 (). However, due to the occurrence of side reactions, it was necessary to control in practical application. The effects of ratios on the coating properties were studied as shown in **Table 1**. It indicated that both gloss and hardness were enhanced with the increasing of . This is because the increasing of made the TMP reaction completely and HDI-TMP prepolymer molecular structure tended to idealize. However, too high ratio led to too much free NCO groups, which were directly modified by polyethylene glycol and sulfonate, resulting in not only decreased cross-linking density, water resistance, and alcohol resistance but also increased water absorption. Therefore, the appropriate for this experiment was about 3.0.

**Table 1.** The effect of ratio on the film properties

	2.1	2.5	3.0	3.5	4.0
Gloss (60°)	103.8	105.2	112.7	115.4	120.9
Hardness	2H	3H	3H	3H	3H
Flexibility (mm)	1	1	1	1	1
Adhesion	0	0	0	0	0
Impact resistance (kg/cm)	45	45	45	45	45
Water absorption (%)	6.8	9.3	14.8	20.1	25.9
Resistance to ethanol	No change	Micro-whitened	Micro-whitened	Whitened	Whitened
Mixed state with polyol dispersion	Good	Good	Good	Good	Good

### 3.4. PEG400 content analysis

**Table 2** shows the properties of the film with the additions of PEG400 in the curing agent under the condition that and sodium hydroxyethyl sulfonate dosage remains unchanged. It was easily found that the gloss, water absorption of film, and compatibility with polyurethane polyol dispersion were further enhanced according to the molecular weight and hydrophilicity of the PEG400. In addition, the introduction of polyethylene glycol into the molecular structure of the curing agent as a soft segment had a great impact on the flexibility of the coating film. All things considered, the optimal dosage of PEG400 in this experiment is 15.8%.

**Table 2.** The effect of PEG400 content on the curing agent and film properties

PEG content (w%)	12.1	14.2	15.8	17.0	18.0
Outside	Pale yellow & translucent	Pale yellow & translucent	Pale yellow & translucent	Pale yellow & translucent	Pale yellow & translucent
Viscosity of the curing agent(s)	52	56	59	64	67
Gloss (60°)	107.8	110.7	117.3	120.8	126.6
Hardness	3H	3H	3H	3H	3H
Flexibility (mm)	2	1	1	1	1
Adhesion	0	0	0	0	0
Impact resistance (kg/cm)	50	50	50	50	50
Water absorption (%)	6.7	9.8	13.1	19.8	22.4
Mixed state with polyol dispersion	Floccule	Floccule	Good	Good	Good

### 3.5. SHS content analysis

SHS was introduced into the curing agent as the anionic hydrophilic modifier because of the strong hydrophilicity of sulfonate groups which led to an increase in water absorption of the coating films as shown in **Table 3**. Additionally, the surface of the films was smooth and compact due to the good compatibility of the curing agent and polyethylene glycol, which could be responsible for the improvement of the gloss of the film with the increase of sodium hydroxyethyl sulfonate content. In order not only to ensure good compatibility with polyol components but also to make the water absorption relatively low, the appropriate amount of SHS is about 3.17%.

**Table 3.** The effect of sodium hydroxyethyl sulfonate content on the film properties

Content (%)	3.06	3.17	3.40	3.60	3.78
Gloss (60°)	106.3	110.5	114.2	126.1	128.9
Hardness	3H	3H	3H	3H	3H
Flexibility (mm)	1	1	1	1	1
Adhesion	0	0	0	0	0
Impact resistance (kg/cm)	50	50	50	50	50
Water absorption (%)	5.4	9.6	14.4	16.8	19.3
Mixed state with polyol dispersion	Floccule	Good	Good	Good	Good

### 3.6. The effect of

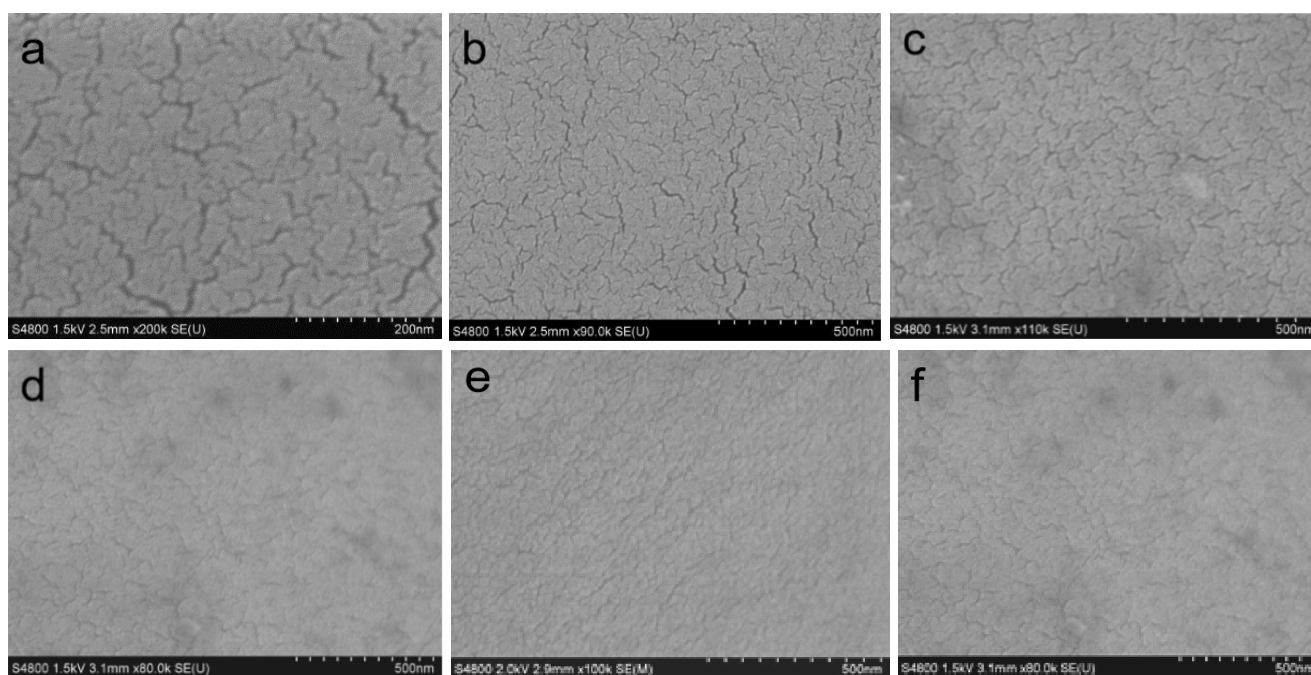
The influence of polyurethane curing agents and self-made polyurethane polyol components on film

properties was studied by changing different ratios, and the results are shown in **Table 4**. With the increase of the ratio, the hardness of the film increases, the water resistance and solvent resistance improve, and the gloss increases initially and then decreases. The main reason was that with the increase of the curing agent dosage, the content of the carbamate group and urea group generated by the reaction of the curing agent and polyol component changed, which led to the increase in film hardness. Simultaneously, the amount of curing agent is directly proportional to the crosslinking density of the film, thereby the film becomes smoother and brighter. Nevertheless, more urea groups and CO<sub>2</sub> are generated, and as the compatibility of the urea group and carbamate group is poor, this leads to reduced gloss.

**Table 4.** The effect of ratio on the film properties

	1.2	1.4	1.6	1.8	2.0
Surface drying time (min)	32	37	41	47	50
Gloss (60°)	107.8	109.5	114.3	118.3	110.4
Hardness	3H	3H	3H	4H	4H
Flexibility (mm)	1	1	1	1	1
Adhesion	0	0	0	0	0
Impact resistance (kg/cm)	50	50	50	50	50
Water absorption (%)	74.6	67.1	23.5	16.4	9.2
Resistance to ethanol	Serious whitened	Whitened	Whitened	Micro-whitened	Micro-whitened

**Figure 4** shows the scanning electron microscopy of uncured polyurethane polyols and coating films with different proportions. It can be seen that the surface of the uncured polyol coating is not smooth and has large cracks. With the increase of the ratio, the surface of the coating becomes more regular and smooth, the cracks become smaller, and the densification becomes better, which is also consistent with the changes in hardness, water resistance, and other properties tested in **Table 4**.



**Figure 4.** The SEM image of films. (a) polyurethane polyols; (b) ; (c) ; (d) ; (e) ; (f)

## 4. Conclusion

A series of double hydrophilic modified waterborne polyurethane curing agents were prepared with HDI/TMP/PEG400/SHS, which had better compatibility with polyol components. The WPU films had good flexibility, gloss, and low water absorption when the ratio of HDI/TMP was 3.0, with an optimal dosage of PEG400 and SHS of 15.8% and 3.17%, respectively.

## Disclosure statement

The authors declare no conflict of interest.

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