

The preparation method of nonionic waterborne polyurethane

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ABSTRACT

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In this paper we simulate the preparation of non-ionic waterborne polyurethane which was prepared by the use of toluene diisocyanate, polyethylene glycol and polypropylene glycol as the main raw materials, which were then dispersed and emulsified in deionized water. In the synthesis stage, we studied the synthesis process, and explore the effects of hydrophilic monomer, polyethylene glycol molecular weight and dosage, NCO/OH, chain extender and solid content on the viscosity and stability of polyurethane aqueous dispersions. Comparing with ionic waterborne polyurethane. The water-based polyurethane has a wide tolerance, which is not affected by acid, alkali or electrolyte, and can be compatible with other ionic compounds, so has certain advantages in textile finishing.

1. INTRODUCTION

Waterborne polyurethane is a new type of polyurethane which uses water as medium instead of organic solvent, containing very little or no organic solvent system of, invented in 1943, the inventor of the polycaprolactam, West Germans, Schlock, in the presence of emulsifier or protective colloid, put the diisocyanate emulsion in water, and add diamine under intense agitation, successfully synthesized cationic polyurethane. However, due to its high price and poor storage stability, it has not been applied seriously. In 1953, the United States Du Pont company Wyandott, in organic solvents, using difunctional degrees of polyols and excess diisocyanate, synthesized a kind of pre-polymers with NCO sealing side, then added the appropriate emulsifier the chain extender demine into the pre-polymers and some water, dispersed the mixture with the strong shear force, finally, polyurethane emulsion was synthesized. However, due to the large amount of emulsifiers, the long reaction time and the coarse particles of the emulsion, the poor storage stability and the poor mechanical properties of the rubber layer, the polyurethane emulsion did not realize industrialization. For the first time, the polyurethane emulsion achieved industrialization in 1967 and Input market in the United States, in 1972, Bayer company took the lead in using polyurethane water emulsion as leather finishing agent and began to produce in large quantities. Waterborne polyurethane became an important commodity. In the 70-80 age, Some waterborne polyurethane products in the United States, Germany, Japan and other countries have been developed from trial production to practical production and application. Some companies have a wide range of waterborne polyurethane products. Such as Germany Bayer company's sulfonic acid type anionic polyurethane emulsion, Impranil and Dispercoll KA series, the United States Wyandotte chemical company's X and E series, the Japanese

big Japan ink company's Hydran, HW and AP series, and so on. Since then, the development of waterborne polyurethane is very rapid, it is reported that between 1992 and 1997, the average annual growth rate of water-borne polyurethane is 8%.

Domestic research began in 1972. It was originally developed for waterborne electrophoresis' paints. The project was undertaken by the 54 Research Institute of the fifth Ministry of machinery industry and Shenyang municipal paint factory. Subsequently, waterborne polyurethane has been widely used in adhesives, fabric finishing agents, leather finishing agents and so on, and the water resistance and storage stability of waterborne polyurethane are basically solved in "75" scientific and technological research [1].

Although some properties of waterborne polyurethane still differ from those of solvent based polyurethane, they are non-toxic, nonflammable, environmentally free, energy saving, safe, and good in film permeability, Moreover, due to the high price of solvents and the strict restriction on the use of organic solvents and waste emissions by environmental protection departments, it has become an important development direction for waterborne polyurethane to replace solvent based polyurethane. In the twenty-first Century, waterborne polyurethane was developing towards environmental protection, coating, economy and low toxicity.

Because of the superior properties of waterborne polyurethane, waterborne polyurethane has been widely used in textile, leather, adhesives, printing and dyeing industries [2]. However, most of the research and development are anionic cationic waterborne polyurethane, and the research data of nonionic waterborne polyurethane is very little. Because of the absence of hydrophilic anions and cations, nonionic aqueous PU is not ionized in aqueous solutions and is unaffected by acids, bases, and salt, compatible with other ionic compounds. The stability of the matrix is better due to the poor adhesion to the matrix without ionization, non-toxic

and will not lose polyurethane finishing Properties. The fabric with good stability after finishing with non ionic water PU. In this paper, the synthesis and preparation of a nonionic waterborne polyurethane were studied.

2. PREPARATION PRINCIPLE AND SYNTHESIS METHOD

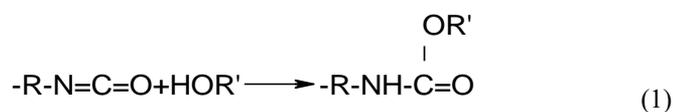
2.1 Preparation principle

With polyisocyanate and polyether or polyester polyol as raw material, using the reaction between -OH base of polyol and -NCO based of polyisocyanate to get polyurethane prepolymer, then dispersed in water, prepolymer and water appears extender chain reaction, form larger molecules, hydrophobic part of large molecules is curling together to form particles center. hydrophilic part is distributed on the particle surface to form hydration layer, then a stable water dispersible polyurethane emulsion is finished [3].

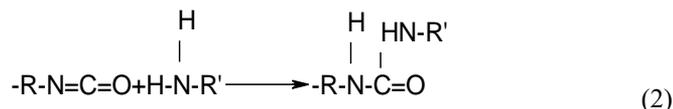
Because isocyanate is a highly unsaturated group, it has a high reaction activity with active hydrogen compounds. The main chemical reactions are as follows:

(1) Reaction of isocyanates and alcohols

This reaction is the most common reaction in polyurethane synthesis and is one of the most basic reactions in polyurethane synthesis.

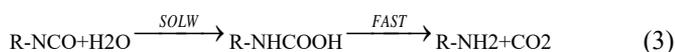


(2) The isocyanate and amine react to form urea



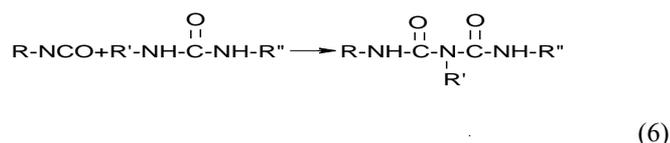
(3) Isocyanates and water reaction

Wurtz A. thinks [4] that isocyanates and water reactions first produce unstable amino acid, which is then decomposed into carbon dioxide and amine. If excess isocyanates are present, the generated amine reacts with isocyanates to form urea, the Chemistry reaction equations are:

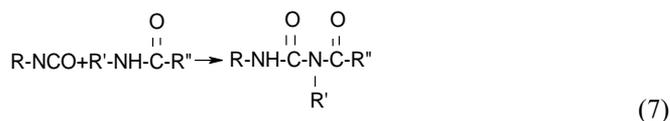


From the above reaction equation, it can be seen that in the process of synthesizing waterborne polyurethane, in order to avoid the formation of bubbles, the content of moisture in the raw materials should be reduced as far as possible.

(4) Isocyanides and urea reaction



(5) Isocyanate and carbamate reaction to produce allyl formate



2.2 Synthesis and preparation of non-ionic water-based polyurethane

Polyurethane is very hydrophobic and can neither be directly dissolved in water nor dispersed in water. Therefore, polyurethane cannot be obtained by synthesizing polyurethane in the traditional process and then dispersing it into water. Because of the rapid reaction of isocyanate to water, it is difficult to prepare in water, so new method must be adopted to synthesize waterborne polyurethane. At present, there are many reports about the emulsification mechanism of ionic waterborne polyurethane. O. Lorenz use the theory of electric double layer [5-6] to give a very good description on the stability mechanism of ion type waterborne polyurethane prepolymer dispersion: When the prepolymer is dispersed, the hydrophobic molecular chain curls into the nucleus of the particle, and the hydrophilic group with the ion is located on the surface of the particle, and the hydrophilic group faces the water. As particles continue to do Brown motion and positive and negative ions together, the result is a double electron layer on the particle - water interface, where particles and particles constantly act as irregular Brown motion. As a result, the movement velocity of outer ion lower than velocity of the electric double layer behind the inner ions (inner ions and large molecular chains together). Therefore, the surface charge of the particle is not neutral, and the electromotive force is generated. This electromotive force prevents particles from approaching each other and condenses and acts as an emulsifier. The higher the potential, the greater the repulsive force between the particles, the less likely the particles are to aggregate and the more stable the emulsions are.

And of ionic polyurethane is studied in this paper, its dispersion particle stability mechanism is different from the ionic polyurethane, in non-ionic dispersions, the hydrophilic polyethylene oxide chain distribution on the surface of particles, and the stretch in the water, when the particles are in close proximity, the chain segment in the water phase of freedom of movement, cause the system entropy decreases, so the exclusion between particles is spontaneous.

Method is introduced in this paper: dehydrated accurate weighing has to PEG, join PPG mixture is equipped with a thermometer, mixer, reflux condenser pipe 500 ml flask, four bubbled into nitrogen and add measurement good toluene diisocyanate reaction about 1.5 h at 90°C, with n-butyl amine titration to determine the reaction end point, until the NCO % is consistent with the theoretical value; The temperature dropped to 60-70°C, according to the needs, to join the measurement good chain extender reaction about 2.5 h; The reaction endpoint was determined by the dibutylamine titration method, until the NCO% was consistent with the theoretical value. Cool to 40°C, add a small amount of acetone solvent, stirring evenly, make its can be completely dissolved in solvent; Finally, the synthesis of polymers of ice water injection to ions slowly, high-speed shear dispersion 10 min, the emulsion gets bubble pour into big plastic, foam

pour into a 250 ml glass bottles, stored in the shade, observe the emulsion stability.

3. RESEARCH ON EXPERIMENTAL PROCESS

3.1 Determination and effect evaluation of reaction temperature and reaction time

The prepolymerization reaction is to polymerize with diisocyanate and polyether diol and hydrophilic monomer and generate a prepolymer with a certain molecular weight with -NCO. Pre - NCO content in polymers, determines the subsequent reaction formula and technological conditions, and affect the physical and chemical properties of the final product, so the accurate temperature control and Pre - the content of NCO group in the polymer becomes the key to the whole process of synthesis.

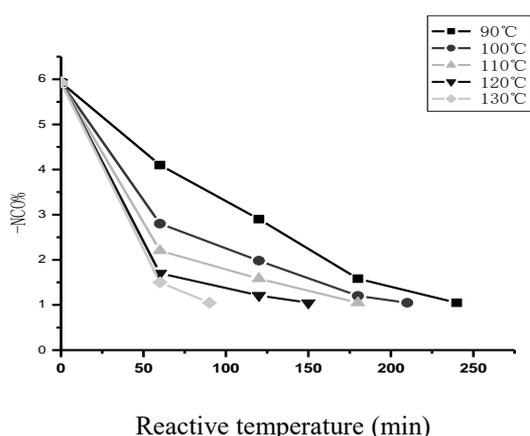


Figure 1. The relationship of -NCO group content with reactive temperature

The changes of NCO content in the prepolymer reaction were determined by di-n-butylamine method. From Fig.1 analysis, it can be seen that the content of NCO decreases linearly with time as the reaction progresses. When the performed reaction to certain time tends to a constant value, and - NCO content is slightly lower than the theoretical value, and this contains trace amounts of raw materials can be associated with the impurities of - NCO group reaction, and the impurities can be not to remove the moisture in polyether.

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As shown in Fig.1, the higher the reaction temperature, the higher the reaction rate. At the beginning of the reaction, NCO content decreased faster, because of the high active PEG and TDI reaction in the system. Found that when the temperature is too high (above 120°C), - NCO content quickly reached the theoretical value, and at the same time a large number of heat makes the performed reaction is difficult to control and easy gel. Above 100°C, isocyanate group and carbamate or urea key reaction, producing crosslinked bond, and above 130°C temperature, carbamate, urea generated by formate or biuret very unstable, may break down. When the reaction temperature is too low, the reaction speed is slower. So that the release of heat and heat is easy to control, but the cycle is too long and inefficient. Polyethylene reaction temperature of 90-100°C is more appropriate, moderate reaction time and easy to control the performed reaction.

3.2 Influence of prepolymer and water

The emulsifying process of prepolymer is competitive process water and prepolymer mixing process with water and prepolymer reaction process, combined the analysis of realistic experimental conditions from the microscopic process mixed. Experiments show that the improved water speed can get better emulsion with water velocity increases, dilution water can to reduce the viscosity of the system, so as to shorten the mixing time, reduce the occurrence of side effects. When using different strategies for water, emulsifying process is different, the following is explained through experiment [7-8].

After the prepolymer is synthesized, it is necessary to disperse it to the water to obtain the emulsion. At this time, there are two ways to choose: A: to add the prepolymer to the ionized water; B: deionized water will be added to the prepolymer to disperse. After a large number of experiments, the results showed that the different emulsification results were significantly different, and the following results were shown in several groups. See following table 1:

Table 1. The effect of feeding mode of prepolymer and water

Formula	Join the way	viscosity (map.s)	Appearance
NCO/OH=1.2, PEG/PPG=40/60	A: Prepolymer is added to the ionized water.	2100	Yellow, slightly transparent.
	B: The deionized water will be added to the prepolymer.	300	Yellow, opaque
NCO/OH=1.2, PEG/PPG=50/50	A: the prepolymer is added to the ionized water	620	Yellow, translucent
	B: will go to the ionic water to join the prepolymer	700	Yellow, whitish, opaque
NCO/OH=1.2, PEG/PPG=70/30	A; the prepolymer is added to the ionized water	465	Yellow, almost transparent
	B: will go to the ionic water to join the prepolymer	485	Yellow, whitish, slightly transparent

Polyurethane emulsion is a kind of substance (pre polymers, oil phase) in another substance (water) in the process of dispersion, exists because of the addition of chain extender and itself a lot of water to oil phase precipitation produce gel reaction and high speed stirring dispersion process of competition, and the stability of the dispersed particles after and then gathered in the process of competition, dispersing process can be an advantage is a key to the success or failure of the emulsion.

It can be seen from the experimental results that the viscosity ratio measured by method A is smaller than that of the method B, and the transparency is better. This is because method A, deionized water by high speed stirring, pre polymers join quickly dispersed particles of micron order of magnitude, can effectively avoid the dispersed particles after gathered themselves together, and made the emulsion performance is good. Methods A and B, because the prepolymer viscosity is large and dispersed slowly, the particles are dispersed and the particles are gathered together, making it easy to produce gels. So the viscosity is slightly larger.

At the same time, in order to avoid the pre polymers in the - NCO causing viscosity increases, after reaction with water to maintain the low temperature system, the general of 0 to 4°C deionized water temperature.

3.3 Influence of mixing speed

The emulsification process of prepolymer is the competition process of water and prepolymer mixing process and reaction process of water and prepolymer. The process of mixing is analyzed, combined with the actual process conditions, the experiment is carried out. It was found that a better emulsion can be obtained by increasing the water rate. With the increase of water rate, the dilution of water can reduce the viscosity of the emulsion, thus shortening the mixing time and reducing the occurrence of side effects. Similarly, when water is emulsified with a lower temperature, low temperature water can remove more heat from the system and reduce the reaction rate between the prepolymer and water, so as to gain time for dispersion.

Water-based polyurethane prepolymer is a transition process from "oily water" to "water pack oil". The reverse process of PU hydroemulsification is in fact the process of the partial accumulation of hydrophobic segments in the molecular chain segment [8], which is to overcome the strong coulomb force in this process. Therefore, the powerful and rapid mechanical agitation is one of the factors that make the prepolymer dispersed in the water phase and make it a stable emulsion.

At the same time, we compared the mixing speed, as in table 2

Table 2. The influence of the stirring speed to stability

Stirring speed ($r \cdot \min^{-1}$)	Emulsion stability
≥ 500 , faster	Light yellow water solution, stable system White latex, layer after a period
< 500 , The slower	

3.4 Influence of k and NA ion content in polyethylene glycol

From the system, it can be catalyzed the foregoing side reaction, the reaction rate increases with the increase of alkali content of impurities, until the product appear gel.

Sample (molecular weight) K(ug/g) Na(ug/g)
prepolymerization

Table 3. The influence of the K^+ , Na^+ content in Polyethylene glycol (PEG) on emulsion polymerization

Sample (molecular weight)	K(ug/g)	Na(ug/g)	Prepolymer condition
PEG (1000)	128.66	79.86	Gel after added and react for 1h
PEG (1500)	5.98	83.78	The normal reaction
PEG(2000)new	109.89	51.89	Gel immediately after adding TDI
PEG(2000)old	17.13	84.11	The normal reaction

As can be seen from table 3, excessive K content can lead to prepolymer reaction gel. This is because of in acidic conditions, isocyanate mainly reacts with hydroxyl reaction to produce polyurethane prepolymer. In alkaline conditions, it also reacts with urea and polyurethane, which is easy to gel. In order to ensure the smooth reaction of the reaction and inhibit adverse reactions, the reaction medium should always be kept under acidic conditions, and the pH value is usually below 5.

In order to make the performed acidic reaction system, can choose organic acid or inorganic acid as acid inhibitor, through cost considerations, we chose the phosphoric acid and benzoyl chloride experimental comparison, and ensure the PH value is around 5.

Table 4. The effect of two different acids

Type of acid resistance polymerization	Prepolymer appearance
Phosphoric acid	Brown with a flocculation Brown, transparent
Benzoyl chloride	

3.5 Stability of non-ionic water-based polyurethane emulsion acid, alkali resistance and electrolyte resistance

Because of the non-ionic water-based PU, the hydrophilic anion and cationic group are not introduced. Therefore, the acid resistance, alkali resistance and electrolyte stability of the emulsion should be stronger than the anionic water-based PU emulsion and the cationic water-based PU emulsion.

The pH value of the non-ionic polyurethane emulsions measured in this experiment was 5-6, with 5 % hydrochloric acid, 5 % sodium hydroxide and 10% sodium chloride solution, to observe the stability of the emulsion. The results are shown in table 5:

Table 5. The stability of nonionic polyurethane emulsion

Projects	The PH value	Emulsion stability
Acid stable	3	stable
Alkali resistance	12	stable
Resistance of the electrolyte	Add a small amount of sodium chloride solution	stable

And compared with the anionic waterborne PU and cationic water based PU, alkali resistance (5% sodium

hydroxide solution) PH=12 resistance electrolyte (10% sodium chloride solution)

Table 6. The compare of stability for bearing acid, alkali and electrolyte

Type	Acid resistance (5% hydrochloric acid solution) PH=3	Alkali resistance (5% sodium hydroxide solution) PH=12	Resistance electrolyte (10% sodium chloride solution)
Non-ionic waterborne PU	stable	stable	stable
Anionic waterborne PU	breaking of emulsion	stable	breaking of emulsion
Anionic waterborne PU	stable	breaking of emulsion	breaking of emulsion

It can be seen from table 6 that the anionic water-dispersible polyurethane has good alkali resistance and is unstable in the presence of acid and electrolyte. The dispersible polyurethane of cationic water is stable under acidic conditions and unstable in alkaline and electrolyte. For non-ionic water dispersible polyurethane, whether under acidic conditions or in alkaline and electrolyte presence, it is stable. These are obviously related to the properties of the hydrophilic monomer in the polyurethane chain. The results are similar to surfactant properties.

It can be seen that non-ionic waterborne PU has a wide PH tolerance, which is not affected by acid, alkali and electrolyte, and can be compatible with other ionic compounds, which has certain advantages in textile finishing.

3.6 Film and water resistance study

To take a certain amount of synthesis of water-based PU

Table 7. The recipe and basic properties of dispersions

NCO/OH	PEG/PPG	Percentage of PEG in prepolymer (%)	Membrane water absorption (%) 2H	Film shape after soaking 24h
1.2	40/60	33.9	12.1	Become pale
1.2	50/50	42.6	33.6	Dissolution
1.2	70/30	60.4	61.7	Dissolution
1.2	100/0	87.7	Dehydrated	Dissolution

Hydrophilic monomer content is higher, the greater the bibulous rate of membrane structurally, polyurethane molecular chain containing ester base, key, methylene ether, ethylene oxide and carboxyl anions, etc., including ethylene oxide and carboxyl anion and water affinity of the strongest, most water adsorption ability. So the more hydrophilic groups, the more water the membrane adsorbs, the less water resistant.

Absorbing mechanism of polyurethane: first is the penetration of water molecules and spread, because the polar groups easily with water and the association, under the effect of water molecules, the weakened resin molecular interactions that increases the distance between the molecules, cause swelling of resin, and even dissolve. Therefore, when polyurethane absorbs water, it quickly reaches a peak and

on the PP board salivate film-forming, let stand under normal temperature for a week, and then put into oven, baking 90 minutes under 130°C. The experiment shows that the synthetic emulsion is difficult to film, because PEG hygroscopicity is serious, the intensity is low and difficult to solidify, which is consistent with the reference to the related books [9].

The hydrophilicity of the aqueous polyurethane synthesized by us is achieved by adding polyethylene glycol hydrophilic monomer. Therefore, the amount of polyethylene glycol will affect the water resistance of the emulsion.

We design the polyethylene glycol (PEG) and poly(propylene glycol as the oligomer glycol, control the NCO/OH ratio and under the condition of invariable in solids, change the PEG in the pre polymers component, a set of the emulsion was prepared, and the emulsion and film properties are analyzed. Table 7:

then dissolves or dissolves. By, if improve the water resistance of polyurethane, must introduce crosslinking groups, the polyurethane molecular couplet net, smaller gap between molecules, make water is difficult to penetrate also enhanced intermolecular forces at the same time, makes the water resistance of the polyurethane film greatly improve [10].

3.7 Infrared spectroscopy analysis

Infrared spectrum analysis is an important physicochemical analysis method. Using infrared spectrum, we analyzed the synthesized aqueous polyurethane.

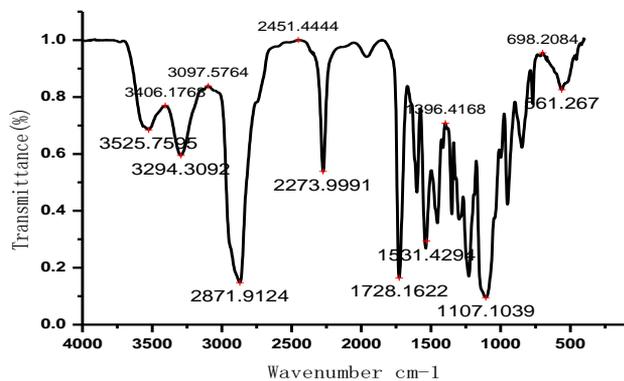


Figure 2. The IR spectrum of Prepolymer

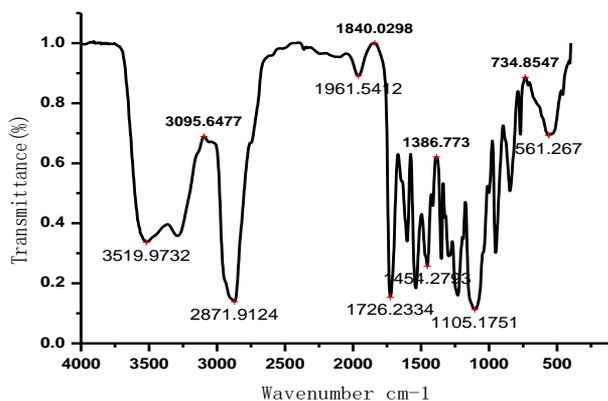


Figure 3. The IR spectrum of dispersion

Observe IR spectra 2 and 3, and analyze the following:

1728.16 cm^{-1} for urea bond $\text{C}=\text{O}$ stretching vibration peak, to 1531.43 cm^{-1} ammonia acyl II NH deformation vibration peak, 3294.31 cm^{-1} for NH stretching vibration peak. The above three peaks are the characteristic vibration peaks of polyurethane. 1107.10 cm^{-1} for polyurethane polyether $\text{C}-\text{O}-\text{C}$ stretching vibration peak, 1602 cm^{-1} for benzene ring skeleton stretching vibration peak, 2891.92 cm^{-1} for CH symmetric stretching vibration peak, both figures have several peaks, the visible is the synthesis of our products to use aromatic isocyanate and polyether polyols polyurethane reaction. 1454.28 cm^{-1} is a telescopic peak of urea carboxylate $\text{C}=\text{O}$, indicating that urethane is produced in polyurethane. The difference of figure 2 and 3 is that: In figure 3, the distinction between 2274 cm^{-1} peak disappear, this is because when polymer dispersed in water, $-\text{NCO}$ group chain extension reaction with water and affections generated the formic acid ester, so 3294.31 cm^{-1} peak increased. The infrared spectrogram of waterborne polyurethane synthesized by this experiment is very consistent with the spectrogram presented in the relevant literature [11-13].

4. CONCLUSION

In this paper we have following conclusion:

(1) By studying effect of the content of NCO group on reaction time and reaction temperature, we concluded that the

performed reaction temperature control in 90-100 $^{\circ}\text{C}$, abd reaction time control in 3.5 hours is reasonable;

(2) When emulsification, method A (dispersing the prepolymer into the ionized water) is less viscous than method B (dispersing the deionized water into the prepolymer), and the performance is better. At the same time, in order to avoid the $-\text{NCO}$ in the prepolymers to react with water (the reation will cause viscosity increases) must general keeps 0-4 $^{\circ}\text{C}$ deionized water temperature;

(3) When dispersing, the mixing speed should be greater than 500 \cdot min.

(4) The concentration of alkali impurities in prepolymer can lead to prepolymer reaction gel. By means of cost and effect, it was added that the organic acid benzoyl chloride was added prior to pre-polymerization, and the appropriate amount of added value was 0.2% ~ 0.4% of TDI. The PH value of the system is 5 ~ 6, and the reaction is stable.

(5) To study the content of NCO/OH , PEG, PEG molecular weight, chain extension agent and the influence of solid content on the viscosity and stability, and we concluded that: as with the increase of the NCO/OH ratio, PEG molecular weight, chain extender and with the increase of solid content, viscosity of emulsion is increasing. With the increase of PEG content, the viscosity first increases and then decreases, and the emulsion appearance changes from opaque to transparent, gradually change into colloidal solution.

(6) Compared with the anion and cation waterborne PU, it is concluded that the non-ionic water-based PU has good acid resistance, alkali resistance and electrolyte resistance.

(7) The synthetic emulsion is applied into film formation difficultly, because of serious PEG hygroscopicity, the film solidify difficultly, has low strength and poor water resistance. Above property is consistent with relevant books mentioned. So in next step, we will focus on improving performance.

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