Effect of DMPA Content on Properties of Waterborne Polyurethane

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Abstract

Waterborne polyurethane is dispersible in water medium, which has not only the excellent properties of solvent-borne polyurethane with good resistance, great adhesion, as well as outstanding toughness combined with good flexibility, but also advantages of incombustibility, low-odor and environmental friendliness. The environmental regulation and the increasing concern of people' s environmental protection are leading to the replacement of solvent-borne polyurethane, and nowadays it is widely used in industries such as films or adhesives. Now, many concentrations of raw materials that uses of research of local waterborne polyurethane are in the type aliphatic diisocyanate; to the waterborne polyurethane of the type aliphatic diisocyanate research less. Along with the living level of people of continuously increase, demand environmental protection, health and high performance product increasing and urgently, the green chemicals gradually become the future development' s main current. A series of soft segment waterborne polyurethane (WPU) were prepared from polyester polyol, isophorone diisocyanate and 2, 2-dimethyloipionic acid (DMPA) by prepolymerization. The properties of WPU dispersions and films were characterized by FT-IR, particle size analyzer, contact angle measuring instrument, and X-ray diffraction (XRD).The results of experiment showed that stability, viscosity of WPU emulsions improved with the DMPA content increasing, but the particle size of WPU decreased. Similarly the tensile strength increased in a certain contentration range of DMPA, and the waterproofness, the crystallinity of soft segment, contact angle and elongation at break of film decreased.

Key words DMPA waterborne polyurethane emulsion membrane

1. Introduction

The waterborne polyurethane is the base resin of the waterborne polyurethane adhesives, coatings and other applications forms. At present polyurethane coatings, adhesives, synthetic leather resin based on solvent-based, but solvent-based polyurethane contains high VOC so that the use is more and more restricted[1]. The waterborne polyurethane is a type of polyurethane ionomer, the biggest difference is that the ionic polymer can be dispersed in water when a sufficient amount of ionic groups embedded in the molecular chain compared with conventional solvent-based polyurethane[2-4].As we all know, there are different minimum amounts of the dispersion for the different types of hydrophilic monomers can be stable[5].

Meanwhile the interaction between ions and counter-ions also affect the performance of the water polyurethane. Waterborne polyurethane with different soft-segment structures were synthesized by hydrophilic group of DMPA, polyester polyol and IPDI in this experiment. The content of DMPA made effect on the particle size, viscosity, water resistance , mechanical properties and crystallization of waterborne polyurethane were studied.

2. Materials and Methods

2.1 Materials

Isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), poly (hexanediol adipate) glycol (PHA), Yantai Huada Chemical Co. , Ltd. ; triethylamine, AR, Tianjin Tianli Chemical Reagent Co., Ltd. ; DBTL, AR, Chengdu Kelong Chemical Reagent Factory; acetone, AR, Tianjin Fuyu fine Chemical Co. , Ltd.

2.2 Methods

2.2.1 Preparation of waterborne polyurethane emulsion

PHA was vacuum dried 0.5h at 105℃, and then mixing with IPDI added to four-necked flask that equipped with a stirrer, thermometer, condenser, N_2, and dropped in a small amount of DBTL, after reacted for 2h at 80℃, DMPA was added slowly until the -NCO content reached to the theoretical value. When the reaction cooled to 50℃, an appropriate amount of acetone was added to reduce the viscosity, followed by neutralization of pendant COOH with triethylamine to obtain the polyurethane prepolymer. The prepolymer was dispersed in deionized water with the high-speed stirring, agitated continuously to complete reaction until to obtain the waterborne polyurethane emulsion.

2.2.2 Preparation of polymer films

WPU dispersions were poured on glass at ambient condition. Most of water was evaporated for a long time after pouring, and residual moisture was further removed by vacuum pumping at 60℃ until no further weight changed.

2.3 Characterizations

2.3.1 Stability by centrifugation

The storage stability of the emulsion was measured by TDL-40B type low-speed centrifuge of Shanghai Anting Scientific Instrument Plant under the conditions of the rotational speed of centrifugal was 3000r/min and 15min at room temperature (corresponded to the storage stability of six months).

2.3.2Viscosity

The viscosity of the emulsion were measured by NDJ-8S digital viscometer at room temperature according to GB/T2797-1995, speed was 50r/min, 3 independent measurements were carried out and took the average results.

2.3.3 Dispersion size

The particle size of waterborne polyurethane emulsion was measured by Mastersizer 2000 laser particle size analyzer.

2.3.4 Infrared spectroscopy

FTIR spectra were collected using a VECTOR-22 system Fourier transform infrared spectrometer of Germany BRUKER company at a resolution of 1 cm^{-1}, and a minimum of 36 scans were signal-averaged at room temperature. And the test range was 4000-500cm^{-1}.

2.3.5 Mechanical properties

The WPU film tensile strength and elongation at break were tested by Chengde Jinjian universal testing machine and the tensile speed was 50mm/min.The specimen width was 6mm, subscript line spacing was 25mm, 3 independent measurements were carried out and took the average results.

2.3.6 Water absorption

The swelling was measured by immersing the films in water at room temperature. The percentage of swelling for a particular film was determined by measuring its weight increase as a function of time,

$$\text{Swell } (\%) = (W_2 - W_1)/W_1 \times 100$$

Where W_1 is the weight of the dried film and is W_2 its weight after water absorption.

2.3.7 Contact angle measurement

Contact angles were determined by Germany Dataphysics company contact meter employing distilled, deionized water as the reference liquid. About 3 independent measurements were carried out on different parts of the film dried at room temperatoptical contact angle measuring instrument. The tests were performed at room temperature, and the average contact angle was reported.

2.3.8 Crystallinity

The crystallinity was measured by Japan Rigalcu D/Max-3c Automatic X - ray diffraction, the experimental conditions were: Cu target, 40 kV, 30 mA, step width = 0.02°, starting θ = 5°, terminate θ = 40°.

3. Results and discussion

3.1 IR spectra of WPU

The synthesized WPU film was subjected to infrared spectroscopy, and shown in Figure 1.

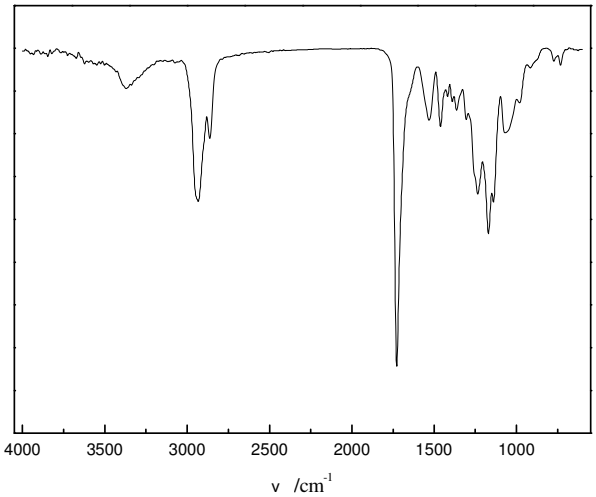

Fig.1 IR spectra of WPU with different structures of polyester polyol

Figure 1 showed that, the characteristic absorption peaks of the -NH were observed at 3371, 1532cm^{-1}, peaks of the -C=O were observed at 1727cm^{-1}, absorption peaks of -OH at 3530 cm^{-1} and absorption peaks of -NCO at 2280cm^{-1} ~ 2240cm^{-1} had basically disappeared, indicating that the -NCO and -OH completely generated a carbamate group through reaction; peaks of the -CH_2, -CH stretching band is observed at 2933cm^{-1}; peaks of the –CH_2 deformation vibration bands were observed at 1460cm^{-1}, 1434cm^{-1}; the benzene ring C=C skeleton stretching vibration had not appeared at 1620cm^{-1} ~ 1600cm^{-1}. Peaks of the C-O of polyester were observed at 1179cm^{-1}, 1170cm^{-1}. FT-IR analysis showed that the sufficient reaction between PHA and IPDI leaded to generate waterborne polyurethane.

3.2 The affection of DMPA content on waterborne polyurethane emulsion stability

During the preparation of the WPU, DMPA embedded in the molecular skeleton of the polyurethane by the reaction of OH with NCO. Due to the steric effect, the carboxyl group of DMPA molecules did not substantial participate in the polymerization reaction, until the reaction completed by neutralizing into a salt. Therefore, the synthesis of polyurethane had hydrophilic nature. The affection of DMPA content on particle size and viscosity of WPU emulsion as shown below.

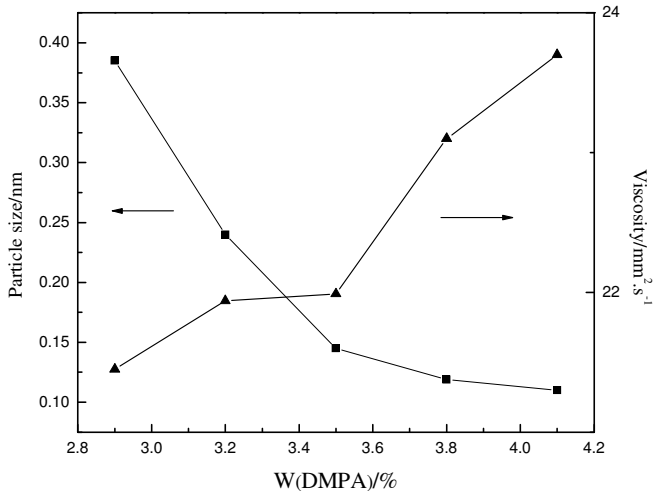

Fig.2 Effect of DMPA content on diameter and viscocity of WPU emulsion

Figure 2 shows that , in the case of constant content of other substances , as the DMPA content increases , WPU particle diameter decreased from 0.385μm to 0.11μm , when DMPA content was 4.1% , obtained the thicker particle, while after the DMPA content exceeded 3.5% , the emulsion particle diameter changed slowly and tended to a certain value. On the contrary, with the increase of DMPA content, viscosity of the emulsion increased from 21.45 mPa•s to 23.7 mPa•s. This was due to the increase of carboxyl content, then ions and counter-ions in the polyurethane molecule chain increased, the electric stagnate effect strengthened, role of ion hydration enhanced, hydrated membrane thicken, the effective volume of ions were larger than the true volume of the original particle, hydrated film thickness and the particle hydrodynamic volume increased resulted in the particle would produce resistance of the particles, so that the emulsion viscosity increased. In addition, the average particle size decreased, the number of particles increased, the average distance between the ions decreased, which mean that the chance of any two particles entered into the mutual attraction area increased rapidly, displacement became difficult and the viscosity increased[6].

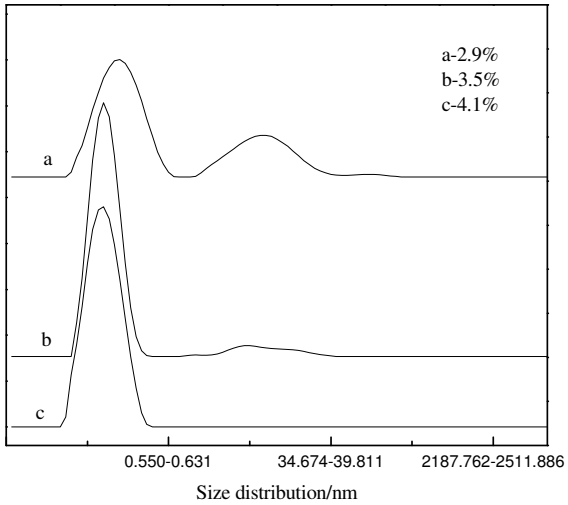

Fig.3 Effects of DMPA content on particle size distribution of WPU emulsion

According to the figure 3, the particle size distribution was broad as DMPA content was low. With the elevated of DMPA content, particle size distribution became narrower. It was because WPU hydrophilic enhanced made molecular chain more easily entered into the aqueous phase from the oil phase (acetone), each molecular chain entered into the aqueous phase in a short time, the more uniform particle size of the latex particles formed.

The affection of DMPA content on stability of waterborne polyurethane emulsion, we could use O. Lorentz electric double layer theory described the stabilize mechanism of Ionic waterborne polyurethane.

Table 1 Effects of DMPA content on appearance and stability by centrifugation of WPU emulsion

W(DMPA) %	Appearance	Stability by centrifugation
2.9	Milky-white emulsion	A little coagulation
3.2	White emulsion	No coagulation
3.5	White emulsion	No coagulation
3.8	White emulsion	No coagulation
4.1	Bluish	No coagulation

The above table showed that WPU emulsion within a certain contentration range of DMPA remained stable. When the DMPA content was low, the emulsion was milky white. With the increase of DMPA content, the emulsion became transparent with bluish. Mainly because the change number of micro particles per unit surface area increased, the formation of an electric double layer thickened, the electrostatic repulsion of the ionic bond increased, ion aggregation became harder.

3.3 The effects of DMPA content on the mechanical properties of waterborne polyurethane film

The polyurethane material is a multiblock copolymer which made of soft segment (mainly constituted by polyol oligomer) and rigid segment (mainly constituted by urethane bond). The thermodynamic incompatibility between the soft segments and hard segmensts result to microphase separation, and the degree of micro-phase separation directly determine its mechanical properties[7].

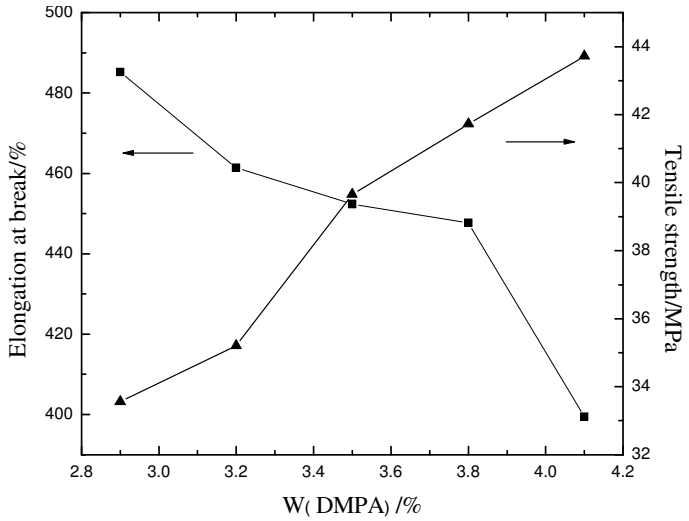

Fig.2 Effects of DMPA content on tensile strength and elongation at break of WPU membrane

As we can see from the above diagram, the tensile strength of the film reflected an upward trend with the increase of DMPA content, but the elongation at break a downward trend. This was mainly due to the less DMPA dosage, the system with low hard segment content, the intermolecular forces were small, resulting in the tensile strength of the product was lowed . However, because of the relatively high the soft segment content, the elongation at break was improved. An increasing of hard segment content would increase after added the concentration of the hydroxyl group, urethane bond and urea bond, as well as cohesive energy density. With DMPA content increasing, intermolecular coulomb force and hydrogen bonding were improved, resulted in an increasing of tensile strength.

3.4 The effects of DMPA content on water resistance of WPU membrane

In this experiment, polyester polyol, IPDI and DMPA were the main raw materials without cross linker, and selected in appropriate ratio. To study their effects on water absorbent of polyurethane film by changing the DMPA content.

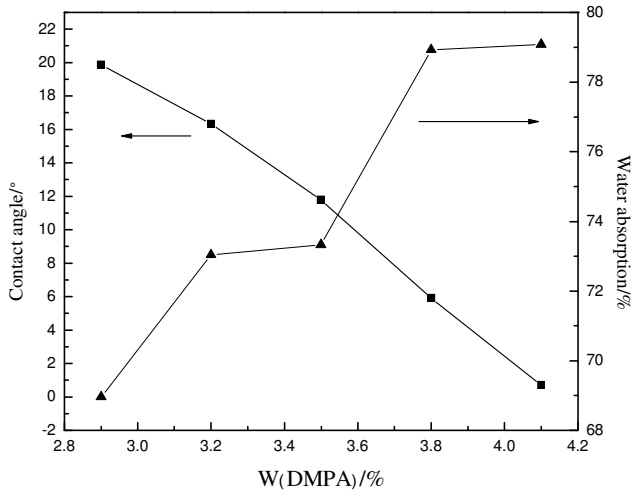

Fig.5 Effects of DMPA content on water absorbility and contact angle of WPU membrane

The effects of DMPA content on water absorption of WPU membrane were shown in Figure 5, the water absorption of the film increased with the increase of DMPA content. The maximal influence factor on film absorbent was the hydrophilic group content (i.e. COOH content). On one hand, the carboxyl group content affected the stability of the emulsion; on the other hand, it also affected the water absorption of the film. When the COOH content of the molecular chain was increased within a certain range, the stability of the polyurethane emulsion increased as well as the water absorption. The water resistance of the film was indicated by contact angle. With the decrease of DMPA content, the contact angle of the film increased, which was mainly because the COO^- content on the surface of WPU particles increased, so that the concentration of the ionic groups of the film surface improved, the droplets easier spread on the film surface, thereby the contact angle decreased, the water resistance was degraded.

3.5 The effects of DMPA content on the crystallization properties of WPU membrane

WPU has a special microphase separation structure and the soft and hard segments form respective crystallinity micro area. The figure below showed the XRD of the different DMPA dosage.

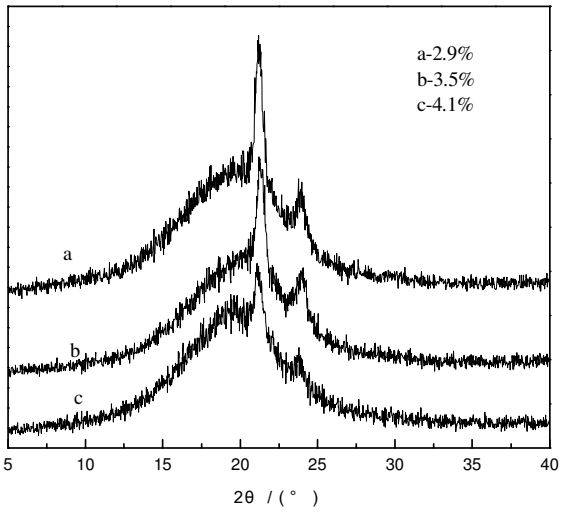

Fig.6 XRD spectra of WPU membranes with different content of DMPA

In the figure, there were strong diffraction peaks of soft segment at 21.3°and 24°.It explained that WPU had good crystalline structure and crystallization performance when the DMPA content was low. The diffraction peaks weaken with DMPA content increased at 21.3°and 24°. The molecular structure of DMPA contained a methyl side, which destroyed the regularity of hard segment, so the introduction of DMPA made crystallinity of WPU weaken. However, the compatibility between the soft and hard segments could not completely suppress the crystallization behavior of the soft segment, the diffraction curve soft segment mainly displayed. The product still had a considerable degree of micro-phase separation, only the peak intensity was weak. The position of the diffraction peak corresponded to a certain crystalline forms, but the arrangement and the degree of ordering of the molecular structure were very complex[8].

4. Conclusions

A series of soft segment crystallinity waterborne polyurethane were prepared through a prepolymer process using DMPA as hydrophilic group. Based on the performances of the emulsion and film were characterized and the experimental results showed that:

(1)The particle size of the emulsion was reduced, but the viscosity increased with the increasing of the DMPA content.

(2)The particle distribution of the emulsion was narrowed down with the increasing of the DMPA content.

(3)With the increasing of DMPA content, the contact angle and elongation at break of the film were reduced; the tensile strength increased with the increase of the DMPA content; the crystallization properties of the soft segment micro-area and water resistance decreased with the increase of the DMPA content.

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