Synthesis and Properties of Sulphonic Acid Type Polyurethane†

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In this paper, we reported a low cost and easy method for the preparation of sulphonic acid type polyurethane, which choose polyether polyol alcohol (PPG-1000), isophorone diisocyanate as the main raw material. By aliphatic diamine sulphonate, sulphonic acid groups was introduced to polyurethane chain, at the same time, polyurethane main chain was extended. Then the sulfonate type polyurethane emulsion was synthesized and solid content was 30 %. The products were characterized by means of FTIR and TG. Polyurethane emulsion had good storage stability and its film had good mechanical properties.

Keywords: Waterborne polyurethane, Aliphatic diamine sulphonate, Sulphonic acid type polyurethane.

INTRODUCTION

As an environmental friendly polymer materials, waterborne polyurethane had excellent mechanical properties, cold resistance, non-toxic, having widespread application in the field of adhesives, paint, etc. With the requirement for environmental protection, the research and development of waterborne polyurethane were very active^{1,2}. At present, waterborne polyurethane was mainly carboxylic acid type, its property was poor than solvent-based polyurethane. The main reason was that the hydrophilic chain extender was the key to determine its property^{3,4}. This paper adopted aliphatic diamine sulphonate as hydrophilic chain extender, which not only contained strong hydrophilic group but also had secondary amino group and primary amino group. Secondary amino group and primary amino group can react with isocyanate groups (-NCO), thus waterborne polyurethane has excellent properties.

EXPERIMENTAL

Isophorone diisocyanate (IPDI) (Shanghai Chemical Reagent Co., Ltd.) was purified by distilling under reduced pressure at 120 °C. Poly(propyl eneglycol) (PPG-1000) (Basf Co., Ltd.) was dried under the pressure of 10 mmHg at 110 °C for 12 h. Aliphatic diamine sulfonate (AAS) (Aldrich Co., Ltd). Acetone was distilled and kept with 4 Å molecular sieve before use. Other reagents were of analytical grade and used as received.

Synthesis of sulfonic acid type polyurethane (SPU):

The SPU was prepared according to the procedure shown in **Scheme-I**. The calculated amount of PPG-1000 was added into a round bottomed flask equipped with mechanical stirrer and thermometer and kept dehydration for 4 h at 120 °C. The calculated amount of isophorone diisocyanate and stannous octanoate were added and the mixture was stirred at 90 °C for 4 h under nitrogen atmosphere. Then the mixture was cooled down to 40 °C, the calculated amount of aliphatic diamine sulfonate and acetone were charged to the mixture and kept stirring at 40 °C for 2 h. The calculated amount of deionized water were added and the mixture was emulsified at 3000 rpm. Further processes evaporated acetone by vacuum distillation. Sulphonate type waterborne polyurethane emulsion was obtained⁵ and the solid content was 30 %.

Preparation of sample: The obtained SPU emulsion was cast onto Teflon plates, air-dried at room temperature for 2 days, then heated from 60-120 °C at the rate of 5 °C/h and kept at 120 °C for 2.5 h. The obtained films, signified as films 1-9, as shown in Table-2, were sampled for water uptake (W_R), FTIR and thermogravimetry analysis (TGA).

Characterization: Water uptake (W_R) was measured as follows: The dried films A-I were weighed and immersed in distilled water at 25 °C for one and a half days. Surfaces of the wet films were then carefully dried and the films weighed. Water uptake was calculated as the relative weight gain per gram of the dry film sample⁶.

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Scheme-I: Preparation process of SPU

FTIR spectra of the SPU were recorded using FTIR spectrometer (Vector 22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of $4000\text{--}400\text{ cm}^{-1}$.

The thermal behaviour of SPU was analyzed with a Shimadzu TGA-50H analyzer under air flow and with a heating rate of $10\text{ }^\circ\text{C/min}$.

RESULTS AND DISCUSSION

PPG-1000/IPAI/AAS ratio effect on the stability, Ts and Eb of SPU: The orthogonal experiment design was adopted to optimize the design parameters because this approach can minimize the testing time and the experimental costs. The optimum experimental parameters can easily be determined using the orthogonal array. This paper considers three controllable factors (PPG-1000, IPDI, AAS) and each factor has three level. An $\text{L9}(3^3)$ orthogonal array is chosen, so the factors and levels are given in Table-1.

TABLE-1 FACTORS AND LEVELS OF ORTHOGONAL EXPERIMENT				
Factors	Description	Level 1 (mol)	Level 2 (mol)	Level 3 (mol)
A	PPG-1000	0.02	0.025	0.033
B	IPDI	0.05	0.1	0.15
C	AAS	0.03	0.04	0.05

Nine experimental trials were designed according to the $\text{L9}(3^3)$ orthogonal array and the corresponding Ts, Eb were obtained and listed in Table-2.

KTs and kEbi are the average output of response Ts and Eb for certain factor at level i, respectively. R_{Ts} and R_{Eb} are the related range. The results of intuitive analysis displays that the effect of B factor (IPDI) is greater than others, Moreover, the effect of A factor (PPG-1000) on Ts is obvious and C factor

TABLE-2 L9 (3 ³) MATRIX AND ORTHOGONAL EXPERIMENTAL RESULTS					
Sample No.	Factors			Indexes	
	A	B	C	Eb (%)	Ts (Mp)
1	0.02	0.05	0.03	462	6.7
2	0.02	0.1	0.04	426	7.8
3	0.02	0.15	0.05	383	9.7
4	0.025	0.05	0.04	593	5.8
5	0.025	0.1	0.05	447	7.6
6	0.025	0.15	0.03	395	9.5
7	0.033	0.05	0.05	635	4.7
8	0.033	0.1	0.03	475	6.3
9	0.033	0.15	0.04	408	9.3
KTs1	8	5.7	7.5	—	—
KTs2	7.6	7.2	7.6	—	—
KTs3	6.8	9.5	7.3	—	—
RTS1	1.3	3.8	0.3	—	—
kEb1	424	563	444	—	—
kEb2	478	449	475	—	—
kEb3	506	395	488	—	—
REb2	82	168	44	—	—

has a relative impact on Eb, so those are negligible. Therefore, the optimum combination is $\text{A}_3\text{B}_3\text{C}_2$ and then the corresponding formula is isophorone diisocyanate (0.033 mol), PPG-1000 (0.15 mol) and aliphatic diamine sulfonate (0.04 mol).

Structure analysis of SPU by FTIR: The chain structure of SPU was confirmed by FTIR spectroscopy. FTIR spectra of SPU is shown in Fig. 1. The FTIR spectrum of SPU showed the typical absorption peaks of polyurethane at 3300 cm^{-1} [$\nu(\text{NH})$], $2870\text{--}2972\text{ cm}^{-1}$ [$\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$], 1703 cm^{-1} [$\nu(\text{C=O})$], 1538 cm^{-1} [$\delta(\text{N-H})$] and 1068 cm^{-1} [$\nu(\text{SO}_3\text{Na})$], 620 cm^{-1} , 530 cm^{-1} [$\delta(\text{SO}_3\text{Na})$]. The NCO absorption peak at 2270 cm^{-1} disappeared in the spectrum, showing that NCO group has completely reacted during the reaction between aliphatic diamine sulfonate and prepolymer I.

Fig. 1. FTIR spectra of SPU

Thermal stability (TGA analysis): TGA was applied to evaluate the thermal stability of SPU. Thermo-gravimetric (TG) and differential thermo-gravimetric (DTG) curves of cured SPU latex film were shown in Fig. 2. TG curve showed two stages of degradation process at $190\text{--}265$ and $350\text{--}375\text{ }^\circ\text{C}$ and DTG curve displayed that the two temperatures corresponding to the maximum mass loss rate were 261 and $353\text{ }^\circ\text{C}$, respectively. Thermal stability parameters, including the initial decomposition temperature (IDT) and thermal degradation temperature (Td); the initial decomposition temperature of SPU

Fig. 2. TGA and DTG of SPU

was 191 °C and the thermal degradation temperature of SPU was 220-245 °C. Obviously, the initial decomposition temperature of SPU was higher than 180 °C and the thermal degradation temperature value was higher than 220 °C, indicating that the SPU can endure relatively high temperature in air.

Water uptake (W_R): Water uptake (W_R) values of the films were shown in Table-2. It can be seen that for all the SPU films, the W_R values were relatively high. This was due to the high hydrophilicity of the sulphonate groups in the SPU chains. From Table-3, it can be seen that the W_R generally increases as sulphonate content increases. Such trend was mainly due to increasing the high hydrophobicity of sulphonate groups.

TABLE-3
WATER UPTAKE (W_R) OF SPU FILMS 1-9

Film	1	2	3	4	5	6	7	8	9
W_R (%)	54.0	62.7	99.7	86.1	220.9	67.2	123.3	65.4	87.3

Conclusion

A sulphonic acid type polyurethane (SPU) was prepared by adopting aliphatic diamine sulphonate as extender. When the molar ratio of IPDI, PPG-1000, AAS was 0.033/0.15/0.04, the mechanical properties of SPU was best. T_s is 9.3 MPa and E_b was 408 %. The chain structure of SPU was confirmed by FTIR. The characterizations showed that the SPU present relatively high thermal stability with thermal degradation temperatures in the range of 220-245 °C. At the same time, the stability of SPU emulsion was good. Further work on the improvement of water resistance of SPU was under way.

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