



Correlation of Raw Materials and Waterborne Polyurethane Properties by Sequence Similarity Analysis



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Anionomer-type waterborne polyurethane dispersions (PUDs) were obtained from poly (propylene glycol) (PPG), isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA) through a modified prepolymer isocyanate process. Two series of polyurethanes were prepared (Groups A and B) and a new prediction model based on grey relational analysis is introduced to predict the impact order of raw materials on several properties, such as solids content, viscosity, acid number and electrolytic stability of polyurethanes. It is found that the model can successfully predict the impact of raw materials on the properties through the designed demonstration experiments. Furthermore, the results of the prediction model show that DMPA plays a key role in viscosity, partial acid values and electrolytic stability.

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1. Introduction

Waterborne polyurethane dispersions (PUDs) represent extraordinarily versatile polymeric materials that are used as coatings for various fibres, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes and textile dyes^[1]. For wide application, a low-cost synthesis of polyurethanes with good performances is significant in polyurethanes industry. To obtain polyurethanes with good performances, the effects of structure and raw materials on performances have been widely discussed.

The main research about the structure's influence on performance focuses on the soft- and hard-segments, phase separation and crystallinity^[2–5], etc. The relations between the bulk structure and performances of polyurethane have been widely and deeply discussed. Seefried et al.^[6] reported that the degree of phase separation or domain formation was strongly influenced by the bulkiness and symmetry of the diisocyanate. Wang and Cooper^[7] studied the impact of phase separation, domain structure on the physical properties

of polyurethane by utilizing differential scanning calorimetry, dynamic mechanical and infrared dichroism experiments. They concluded that the application properties, such as mechanical properties, depended primarily on the content and phase separation of hard- and soft-segments. Meanwhile, Jo et al.^[8] prepared polyurethane with various polyols, consisting of soft segment. Hard- and soft-segments ratio was regarded as the key factor for the variation of micromorphology and mechanical property. Pielichowska et al.^[9] reported the influence of chain extender on properties of polyurethane, indicating that the thermal stability increased without chain extender. According to previous researches, the bulk structure of polyurethane determines properties, especially the applied performance of polyurethane. Traditionally, the recognized research approach is "raw materials → structure → properties". However, the direct correlation of bulk structure and properties is not suitable for industrial production, for major consideration herein is the ratio of raw materials rather than the structure design in industry^[10]. Moreover, one kind of materials may have multiple influences on a structure, for instance, diisocyanate dictates the phase separation, crystallinity, hard- and soft-segments ratio, etc. And the multiple influences definitely have cross-impact on the properties of polyurethane, which is rather complex and may confuse researchers and producers. Actually, the bulk structure is directly determined by the dosage molar ratio of raw materials, including different kinds of diisocyanate,

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oligomer polyols, chain extender^[11–15], and the dimethylolpropionic acid (DMPA)^[14,16,17]. Thus, we propose a new design route of ‘raw materials → properties’ to exclude the multiple influences of structure on the properties of polyurethane.

Little attention has been paid to the influence sequence of all raw materials on one of the applied properties, such as the solids content, viscosity, acid number (AN), etc. These properties are vital for the application of polyurethane, for example, the AN is one of the most important performances of binder in printing ink industry. A large acid number will lead to an enhancement of the viscosity of ink, even a retrogradation, while a small value may bring a poor wettability to pigment of the binder, a poor flow property and glossiness of the printing ink^[16]. Thus, the predication and control of the application properties are necessary in the preparation and use of polyurethane. Actually, PUD is mainly synthesized by five kinds of raw materials at least, all of which may have direct or indirect influences on the properties of the polyurethane dispersions. Additionally, the synergistic effect gives birth to manifold influences of all raw materials on one property. In the design of the recipe, emphasis of one property of PUD makes it difficult to achieve the synergistic effect. Therefore, it is extremely necessary to find out how the raw materials contribute to one of the properties of PUD. A mathematical model called grey correlation model is considered to predict the relations between raw materials and properties of PUD. The grey correlation model is based on geometric similarity sequence analysis and correlation measure among grey sequences to quantify the correlation of multiple sequences of different levels relative to a certain level. In mathematical theory, it is a geometric analysis that reflects the proximity of the space of the discrete series, and the fundamental idea of grey correlation model is to determine and order the correlations between designed factors. Through this model, the proximity of multiple sequences of the grey system can be analysed to identify the relations between different levels relative to a certain level. The proximity is named as grey correlation degree, and the higher the degree, the closer the relationship between sample sequences and compare sequences. In this research, properties of PUD are considered sample sequences, while the amount of raw materials are the compare sequences.

2. Experimental

2.1. Materials

The diisocyanate used was isophorone diisocyanate (IPDI, 98 wt% purity, purchased from Jingchun Chemical, Shanghai, China), which is liquid at room temperature. Poly (propylene glycol) (PPG, molecular weight (M_w) = 2000, acid value \leq 0.08 mg of KOH/G, hydroxyl value = 54–58 mg of KOH/G, dried under vacuum, at 120 °C) and dimethylolpropionic acid (DMPA) (both purchased from Jingchun Chemical, Shanghai, China) were used as oligomer glycol and hydrophilic chain extender. 1,4-Butanediol (BDO, 99.5 wt% purity), triethylamine (TEA, 99 wt% purity), and 1-methyl-2-pyrrolidone (NMP, 99 wt% purity) were purchased from Fuchen Chemical, Tianjin, China. Dibutyltin dilaurate (DBTDL) was purchased from Qingxi chemical, Shanghai, China. Acetone, about 15–20 mL, was used throughout the process and deionized water was used as dispersing phase at last.

2.2. Synthesis of waterborne polyurethane dispersions

The general recipe used for the preparation of polyurethane dispersions (PUD) is listed in Table 1. Two groups of experiments (group A: A1, A2, A3 and group B: B1, B2, B3, B4, B5, B6) were designed and carried out in this research. For group A, three aqueous PUDs with different molar ratios of isocyanate groups to oligomer hy-

Table 1
Recipe for the preparation of polyurethane for prediction (g)

Sample	Ingredient					
	IPDI	PPG-2000	DMPA	NMP	BDO	TEA
A1	16.664	49.626	3.570	5.984	0.990	2.912
A2	22.285	50.285	3.966	6.637	2.679	2.974
A3	27.769	50.043	4.325	7.166	4.328	3.26
B1	22.229	50.280	5.632	6.539	2.593	2.974
B2	29.122	50.278	3.938	6.539	2.593	2.974
B3	22.228	50.281	3.938	6.539	4.254	2.974
B4	22.229	50.276	3.938	6.539	2.593	4.708
B5	22.229	60.288	3.938	6.539	2.593	2.974
B6	22.229	50.291	3.938	6.539	2.593	2.974

droxyl groups (hard-/soft-segment molar ratio of 3, 4, and 5, respectively) were synthesized to explore the impact of hard-/soft-segment proportion on polyurethane dispersions properties, while PUDs in group B experiments were synthesized on the basis of optimal hard-/soft-segment molar ratio through the result of group A experiments to study the impact of each raw material on properties of the dispersions. The DMPA content was set to be 5 wt% (with respect to the prepolymer weight) in group A experiments^[18]. PPG and IPDI were added to a four-necked flask (500 mL) equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic water bath. The reaction was carried out at 80 °C for 2.5 h, then DBTDL was added when the first reaction had occurred for 2 h, followed by the addition of DMPA dispersed in NMP at 60 °C. The reaction continued at 80 °C for another 2 h. Subsequently, the resulting prepolymer was cooled to about 35 °C, and then BDO with a small amount of acetone and TEA in 120 g of deionized water were poured into the flask. In the whole process, a moderate amount of acetone was used to reduce the viscosity. After the reaction, the residual acetone was removed in a vacuum drying oven at 50 °C and 0.05 MPa for 1 h. In this research, DBTDL (catalyst) and acetone (co-solvent removed after the reaction) were not taken into account due to their ineffectiveness^[19].

2.3. Characterization and property measurements

Fourier transform infrared spectroscopy (FTIR) measurement was used to identify the structure of PUDs, the infrared spectra of the dried polyurethane films were obtained with a Fourier Transform IR spectrophotometer (SHIMADU FTIR-8400S (CE)) and recorded in the transmission mode at room temperature by averaging 20 scans at a resolution of 16.0 cm^{-1} . The spectra were analysed in the frequency range of 4000–400 cm^{-1} . Proton nuclear magnetic resonance spectroscopy (^1H NMR) spectra were obtained on a Bruker-400 MHz spectrometer, using sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard, with D_2O (0.5 mL) as solvent.

Solids content measurement was carried out according to ISO 124:1997 standard. About 1.5 g of PUDs was placed in a glass garden with a diameter of 60 mm. The solids content of every sample was calculated as the average of three measurements of weight before and after water evaporation. Brookfield viscosities of the PUDs were obtained using Brookfield viscometer DV-II+ (Brookfield Engineering Laboratories, Stoughton, MA, USA). About 250 mL sample was placed in a beaker at room temperature of 25 °C and using spindle No. 61 with a stirring speed of 100 r/min. The Brookfield viscosity of every sample was calculated as the average of three experimental determinations. ANs of PUDs were measured according to ISO 2114:2000 standard. The indicator titration in part A was carried out in the measurement. Phenolphthalein indicator dissolved in ethyl alcohol as the standard described was prepared. For each determination, the AN values can be calculated, in milligrams of KOH per gram, from Eq. (1):

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