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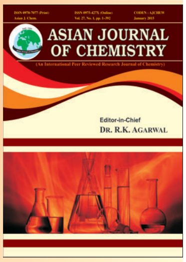

Preparation and Pyrolysis Kinetics of Polyester-Based Waterborne Polyurethanes with High Solid Content

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The waterborne polyurethane emulsion with a solid content 51.43 wt % was prepared by using main raw materials comprising polyester polyol, isophorone diisocyanate and 2,2-dimethylol propionic acid. The relationship between the particle size distribution and the maximal volume fraction of dispersed phase of the waterborne polyurethanes was simulated through a mathematical model of close packing of sphere particles. The emulsion structure and properties of the resulting emulsion films were characterized by a Fourier transform infrared spectroscopy, a laser particle size analyzer, a universal testing machine, a contact angle meter. The thermal decomposition process of the waterborne polyurethanes was analyzed by a thermal gravimetric analyzer. According to using simulations of Kissinger's, Ozawa's and Crane's methods, the activation energy, the reaction order and the frequency factor of the thermal decomposition process of waterborne polyurethanes were calculated as 116.097 kJ/mol, 0.911, 1.963 × 10^7 s^{-1}, respectively. Besides, the high-solid-content waterborne polyurethane with a viscosity of 316 mPa·s was found to exhibit a wide particle size distribution, a good water resistance and excellent mechanical properties.

Keywords: High solid content, Waterborne polyurethane, Particle size, Pyrolysis kinetics.

INTRODUCTION

Compared to the solvent-based polyurethane, waterborne polyurethane (WPU) is a binary colloidal system, in which water is the dispersion medium, which has advantages including non-toxic, non-flammable and environmental friendly, which has been widely applied in the leather finishing agents, papermaking additives, coating and glue agents, *etc*., which is limited for their further industrial application due to longer drying time and higher energy consumption in the same solid content. Based on this background, the improvement of the sold content in waterborne polyurethanes is one of the most effective ways to solve the problem[1], which can be achieved *via* three following methods *i.e.*, controlling the particle size distribution, increasing the particle diameter and deforming emulsion particle shapes under a certain viscosity[2]. Furthermore, the thermal performance is an important factor for increasing solid content of the waterborne polyurethanes. However, pyrolysis process is rather complicated, which is studied to analyze pyrolysis mechanisms of the materials and realize their properties[3-5].

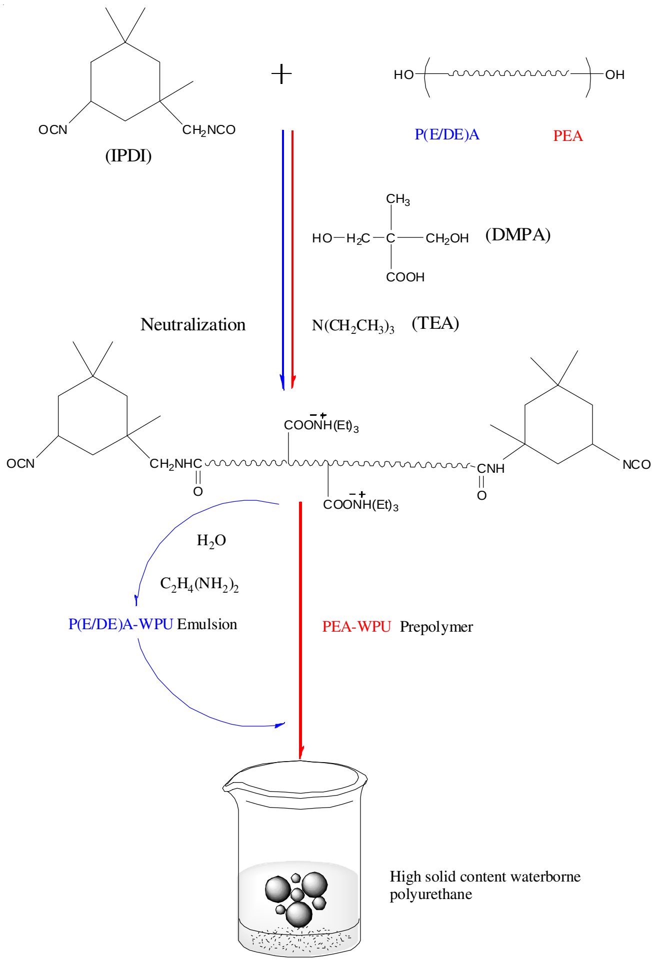
In this study, the waterborne polyurethane emulsion with high solid content was synthesized by using poly(ethylene-glycol-adipate) diols (PEA), poly(ethylene-glycol/diethylene-glycol-adipate) diols [P(E/DE)A], isophorone diisocyanate (IPDI), 2,2-dimethylol propionic acid (DMPA) as the main raw materials through a mathematical model of close packing of sphere particles. Main properties of the emulsion and its films were investigated[6]. And its pyrolysis kinetics was explored by TG[7,8]. The key pyrolysis parameters, including the activation energy (E), pre-exponential factor (A) and reaction order (n), were obtained *via* different simulation methods, which can be used to further understand the thermal performance and related mechanisms of waterborne polyurethanes with high solid content, as well as to provide a theoretical basis and guidance for their future development and industrial applications.

EXPERIMENTAL

Isophorone diisocyanate (IPDI), 2,2-dimethylol propionic acid (DMPA), poly(ethylene-glycol-adipate)diol (PEA), poly(ethylene-glycol/diethylene-glycol-adipate)diols [P(E/DE)A] were provided by Yantai Huada Chemical Co., Ltd. (Mn = 2000); triethylamine, AR, was supplied by Tianjin Tianli Chemical Reagent Co., Ltd; dibutyltin dilaurate, AR, was offered by Chengdu Kelong Chemical Reagent Factory; acetone, AR, was afforded by Tianjin Fuyu Fine Chemical Co., Ltd.

A TDL-40B low-speed centrifuge was provided by Shanghai Anting Scientific Instrument Factory; NDJ-8S digital viscometer was supplied by Shanghai Nirun Intelligent Technology Co., Ltd.; XWW-20-type universal testing machine was offered by Chengde Jinjian instrumentation Co., Ltd.

Preparation of waterborne polyurethane emulsion:



P(E/DE)A and IPDI (mP(E/DE)A:mIPDI = 2.5:1) were added to a four-necked flask with a stirrer, thermometer, condenser and nitrogen in/outlet, then a small amount of DBTL was dropped into the mixture, after reacted for 2 h at 80 °C, DMPA (mDMPA:mP(E/DE)A =1:17) was added into mixture slowly and reacted for 2 h, the prepolymer was cooled and neutralized to pH 7.0 ± 0.5. The prepolymer was dispersed in deionized water to obtain the waterborne polyurethane emulsion [P(E/DE)A-WPU]. P(E/DE)A was replaced by PEA to obtain waterborne polyurethane prepolymer PEA-WPU according to the above method, waterborne polyurethane prepolymer PEA-WPU was emulsified in the above P (E/DE) A-WPU emulsion to obtain a high solid content of waterborne polyurethane emulsion.

Preparation of waterborne polyurethane film: The waterborne polyurethane films were prepared on a cleaned glass plate directly and allowed to dry at a gradient temperature (60/90 °C) in oven. The thickness of the films was 0.25 mm.

Methods of pyrolysis: Basic equation of thermal analysis kinetics is as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion percentage, dα/dt is the reaction rate, k(T) is the relation between the rate constant and temperature, f(α) is a function of the reaction mechanism. There is a close relation between the rate constants and the temperature of the kinetic equation. The relation of rate constant and temperature is the most common below.

$$k = Ae^{-\frac{E}{RT}} \tag{2}$$

where A is pre-exponential factor, E is the activation energy, R is the universal gas constant and T is the absolute temperature. The common kinetic equation of heterogeneous system was obtained by the formula (2) put into equation (1).

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \tag{3}$$

According to the difference of reaction mechanism functions, the dynamic model can be divided into n order model, the autocatalytic model and Kamal model, respectively. The n order model of the following formula (4) was utilized to study the pyrolysis kinetics of waterborne polyurethane with high solid content in this paper.

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n \tag{4}$$

Dynamic calculation is carried out according to the Kissinger method[9] by using the relationship between the peak temperature and heating rate values of derivative curve. The method doesn't involve the selection of mechanism function, which is relatively simple and reliable. Ozawa method[9] is suitable for multi-carbon polymer, which avoid the errors resulted from reaction mechanism selection because it does not involve the selection of reaction mechanism. Kissinger and Ozawa methods were selected for the calculation of the activation energy E (average value) in this paper. The average value was put into formula (4) for pre-exponential factor A and then the reaction order n was solved by Crane equation. As shown in equation (5)-(7):

Kissinger equation:

$$\ln\frac{\beta}{T_m^{\ 2}} = \ln\frac{AR}{E} - \frac{E}{RT_m} \tag{5}$$

Ozawa equation:

$$\frac{d\ln\beta}{dT_m^{-1}} = -1.052\frac{E}{R} \tag{6}$$

Crane equation:

$$\frac{d\ln\beta}{dT_m^{-1}} = -\frac{E}{nR} - 2T_m \tag{7}$$

β is the heating rate and T_m is the TGA peak in the equation.

According to the deformation of equation (5), we have:

$$\frac{d\ln\left(\beta/T_m^2\right)}{dT_m^{-1}} = -\frac{E}{R} \tag{8}$$

When E/nR T_m^2, the formula (7) can be simplified into the formula (9):

$$\frac{d\ln\beta}{dT_m^{-1}} = -\frac{E}{nR} \tag{9}$$

Performance test of high solid content waterborne polyurethane: The measured method of -NCO content of the prepolymer, emulsion storage stability and viscosity were shown in the references[10-12]. The test method of mechanical properties and water absorption of the films were shown in the literature[13,14].

Determination of solid content: About 1 g (m) of the sample was placed in a clean watch glass, dried to constant weight at 120 °C and weighed (m_0), the solid content = (m_0/m) × 100 %.

Particle size: The particle size was measured by Mastersizer 2000 laser particle size analyzer from British Malvern Instruments Co., Ltd.

Infrared spectra: Fourier transform infrared (FTIR) spectra were conducted on a VECTOR-22 type FTIR from Germany BRUKER company in the range from 4000 to 500 cm^{-1}.

Contact angle measurement: Contact angles were determined by Dataphysics optical contact angle measurement of Germany Dataphysics Company.

Pyrolysis analysis: The TG curves of waterborne polyurethane with high solid content were got under nitrogen atmosphere at flow rate of 40 m^3/min by Q1000DSC + LN CS + FACS Q600SDT type thermal analysis system of American TA company The samples were heated from room temperature to 773.15 K at a heating rate of 5, 10, 15, 20 K/min, respectively. Generally, 5-10 mg samples were used for the pyrolysis analysis.

RESULTS AND DISCUSSION

IR analysis of waterborne polyurethane with high solid content: Fig. 1 showed the FTIR of waterborne polyurethane with high solid content. The absorption peaks at 3390 and 1542 cm^{-1} attributed to NH. The absorption peak at 3529 cm^{-1} is assigned to the stretching peak of C=O. The NCO absorption peak at 2280-2240 cm^{-1} disappeared, as illustrated that NCO reacting with OH completely generated carbamate. The stretching vibrational peak at 2950 cm^{-1} is attributed to the stretching of methyl and methylene group. In-plane flexural vibrational absorptions at 1460, 1380 and 1465 cm^{-1} are assigned to the flexural of methyl and methylene group. The absorption peaks at 1200 and 1139 cm^{-1} is attributed to characteristic peak of the C-O bond existing in the polyester. The results indicated that waterborne polyurethane was synthesized completely.

Properties analysis of waterborne polyurethane with high solid content

Curing process of waterborne polyurethane emulsion: The process of film cured from waterborne polyurethane emulsion was given in Fig. 2, which was divided into three stages: First, hydrosolvent volatilized. Second, after free water volatilization was over, the emulsion particles closed each other resulting in extrusion deformation. Water penetrated into the surface and then volatilized through the capillary channel and film inward. Third, polymer molecules mutually entangled and gradually fused together, the residual moisture could only

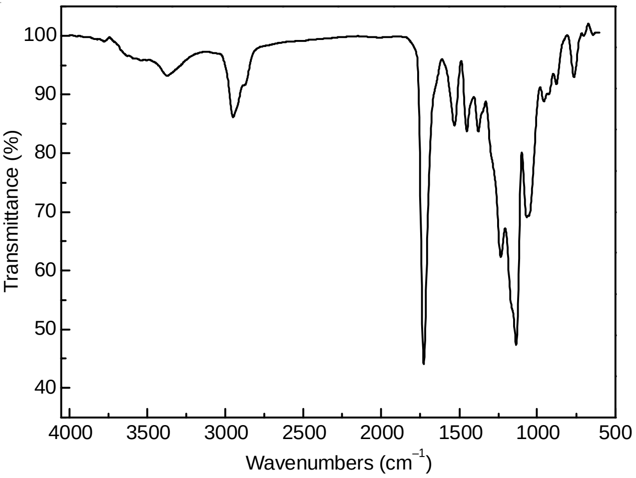


Fig. 1. FTIR spectra of waterborne polyurethane with high solid content

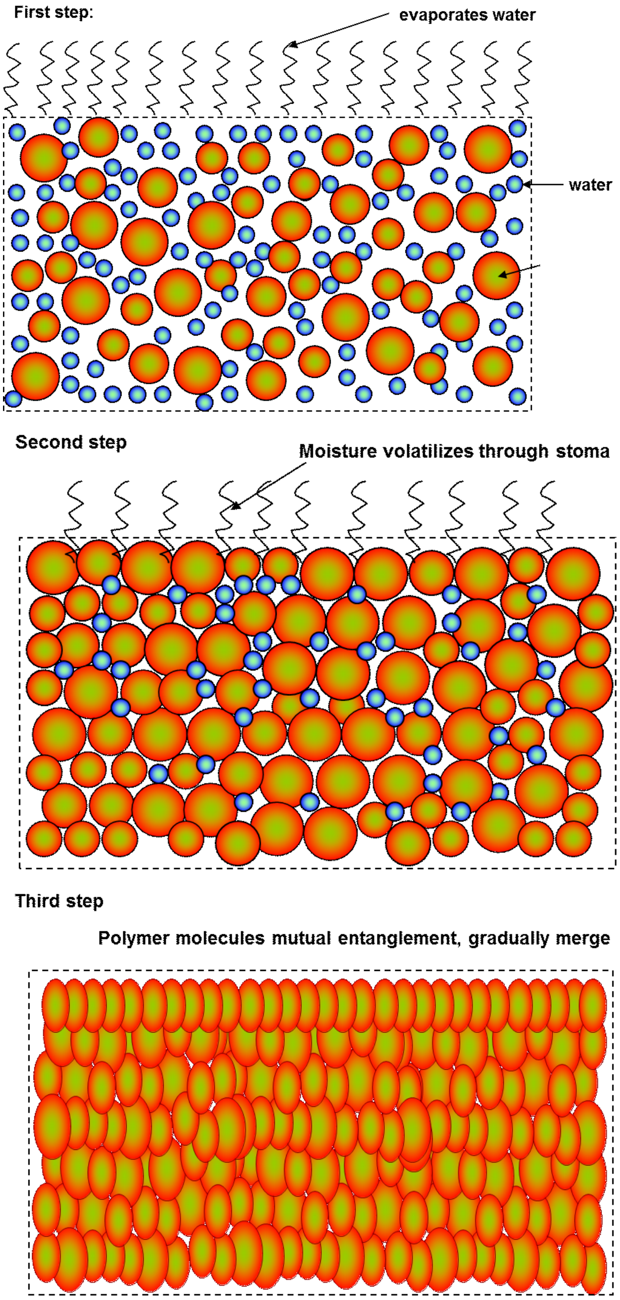


Fig. 2. Film forming process of waterborne polyurethane emulsion

infiltrate outwards, as was also the slowest stage in the process of curing stage. Obviously, with the improvement of solid content of waterborne polyurethane emulsion, the moisture decreased in the system, the speed of forming film accelerating and the drying time shortening.

Relationship between the partical size, viscosity and solid content of waterborne polyurethane: The improvement of solid content is often accompanied by the increase of viscosity in the process of waterborne polyurethane preparation. However, high viscosity is not good for production and improvement of solid content of waterborne polyurethane. The viscosity, solid content and storage stability of the emulsion are important performance indexes of waterborne polyurethane products. The physical indexes of synthetic products were shown in Table-1.

TABLE-1
PERFORMANCE OF WPU WITH HIGH SOLID CONTENT

Physical properties	Solid content (%)	Storage stability	Average particle size (nm)	Viscosity (mPa·s)
Measurement	51.43	No precipitation	424.835	316

As presented in Table-1, the resulting waterborne polyurethane emulsion with high solid content had good stability, high solid content and suitable viscosity. The reasons were as follows: On the one hand, the particles with big diameter arranged and dispersed mutually relatively well-ordered in the water. The water-soluble macromolecules existed in spherical crimped state with resistence less, however, the water-soluble micromolecule occured in the freely extensile low-energy state. Because of the prevention of macromolecule, micromolecule in the free state could not mutually wind, associate and bond, which led to a light increase of the emulsion viscosity. On the other hand, hydrogen bond formed by reacting soft segment of polyester urethanes containing ester group and urethane bond of hard segment, which promoted the mixture of soft segment and hard segment. The degree of microphase separation was relatively low. Meanwhile hydrophilicity of polyester urethanes was fairly strong so that phase separation was more conducive to occur at the time of emulsion, which improved the solid content and lowered the emulsion viscosity to some extent. Therefore, controlling suitable particles of emulsion was favorable to maintain stability of the emulsion in the preparation of waterborne polyurethane emulsion with high solid content.

From Fig. 3 the prepared waterborne polyurethane with high solid content presented the trend of ternary particle size distribution, in which larger size particles made up the smaller proportion. It was proved that diversification particle size distribution improved emulsion solid content while not making the viscosity improved too much. It can be deduced that proportion of larger size particle should be increased to get higher solid content (more than 60 %) of emulsion and the ratio between large and small particle size must be bigger than a certain value. Only in this way could small particles preferably fill in the space of large particles in the best packing state, which was also in accord with mathematical model of close packing of sphere particles. With an increase of solid content, the particle size and particle size distribution increased simultaneously. Because solid content improved, the relative amount of micelle in the polymer increased, larger particles forming at the same time. Furthermore, with the increase of solid content, probability of particle collision and coalescence increased. Probably there existed more coalescence particles in this system, making particle size and distribution increased.

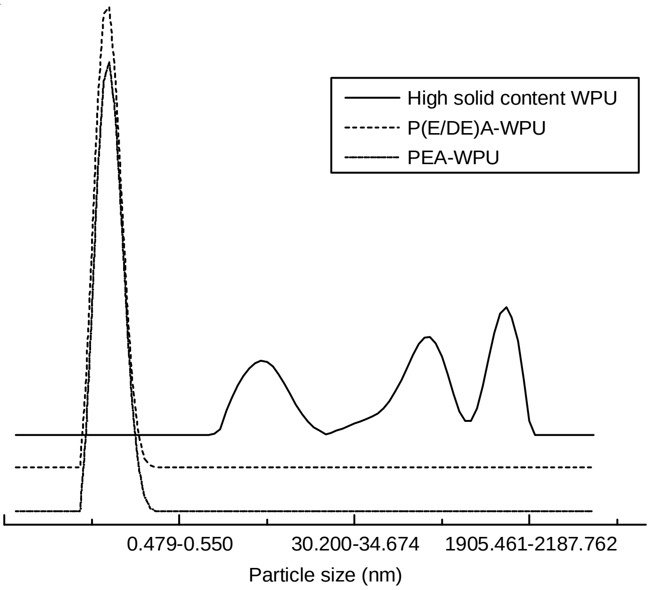


Fig. 3. Particle size distribution of waterborne polyurethane

Performance contrast of waterborne polyurethane films with different solid content: As shown in Table-2, high solid waterborne polyurethane owned good water resistence compared with waterborne polyurethanes prepared with two kinds of raw materials, whose water absorption ratio was 6.72 % and contact angle was 101.1°. So the particle size of waterborne polyurethane had a great influence on film water resistence. This was because tight arrangement of waterborne polyurethane molecule with high solid content made hydrone difficult to get into the film inward so that the water resistence was improved. The improvement of solid content of waterborne polyurethane had not obvious effects on mechanical properties. The tensile strength was 29.21 MPa. The elongation at break was 653.25 %. This property was somewhere in between those of the waterborne polyurethanes synthesized by two kinds of raw materials.

Thermal decomposition analysis of waterborne polyurethane with high solid content: Under nitrogen atmosphere, the TG and DTG curves of high solid waterborne polyurethane were achieved from room temperature to 773.15 K with heating rate of 5, 10, 15 and 20 K/min (Fig. 4).

TG-DTG analysis of different heating rates: Taking the heating rate of 10 K/min as an example, the thermal decomposition of waterborne polyurethane was mainly divided into three stages. The initial weight loss temperature was about 240 °C. The temperature range of the first stage was from 240 to 345 °C. The temperature range of the second phase was from 345 to 400 °C. The temperature of the third stage began from 400 °C and ended until 480 °C. Due to rupture of C-O bond of urethane group in the polyurethane hard segment part,

TABLE-2
PERFORMANCE OF WATERBORNE POLYURETHANE WITH HIGH SOLID CONTENT

Waterborne polyurethane	Solid content (%)	Average particle size (nm)	Mechanical properties		Water resistance	
			Tensile strength (MPa)	Elongation at break (%)	Water absorption (%)	Contact angle (°)
PEA-WPU	26.15	0.104	31.24	619.00	11.68	89.9
P(E/DE)A-WPU	27.17	0.101	27.65	677.75	16.83	85.9
High solid content WPU	51.43	424.835	29.21	653.25	6.72	101.1

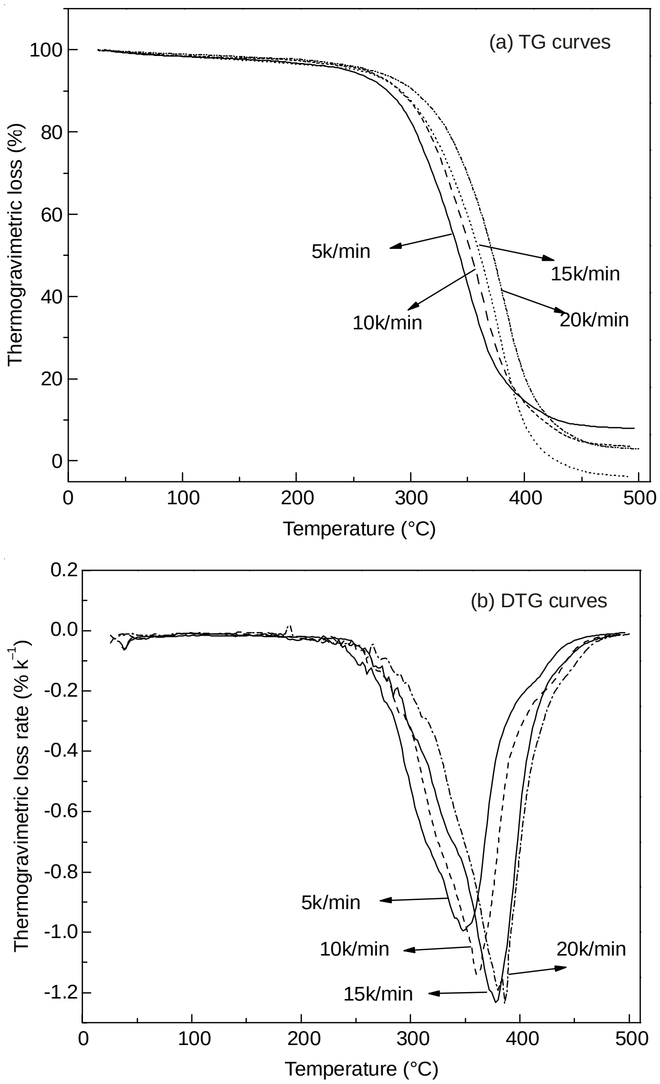


Fig. 4. TG curves for the thermal decomposition of waterborne polyurethane with high solid content at different heating rates

isocyanate and polyol were generated, which were further decomposed into amine, olefins and CO_2. Diimide formed by part of isocyanae product reacting each other in the process of thermal degradation. The decomposition finished mostly till 400 °C. When temperature increased further, the diimide was decomposed again and formed isocyanate. From Fig. 4(b), heating rate had less effects on the thermal weight loss rate below 300 °C. When temperature was more than 300 °C, the temperatures of weight loss peak corresponding to heating rate of 5, 10, 15 and 20 K/min in TG curves were 348, 363, 377 and 384 °C, respectively. With the increase of heating rate, decomposition behaviour of waterborne polyurethane with high solid content presented a hysteresis phenomenon.

Thermal decomposition analysis of high solid waterborne polyurethane: E and A of thermal decomposition reaction were calculated on the basis of Kissinger equation, Ozawa equation and TG-DTG curves. The necessary parameters of equation were shown in Table-3.

Fig. 5 illustrated $1/T_m$ (as ordinates) linear fittings of ln β or ln (β/T_m^2) (as abscissas), respectively. As shown in Fig. 5, the correlation coefficients of the fitting curves were 0.99611 and 0.99611, respectively. This indicated that there were good linear relationships among ln β[ln (β/T_m2)]and $1/T_m$. Activation energy of waterborne polyurethane with high solid content was calculated as E_1 (= 121.144 kJ/mol) and E_2 (= 111.050 kJ/mol) by slopes of fitting curve guided into equation (6) and (8). The average value of E_1 and E_2 was E = 116.097 kJ/mol. Pre-exponential factor A was 1.963×10^7 s^{-1} got by E guided into equation (5).

The pyrolytic reaction order n of waterborne polyurethane with high solid content was 0.911 by slope of fitting curve led into equation (9), which was a non-integer. It was shown that the pyrolysis of waterborne polyurethane with high solid content was a complex process. The pyrolysis reaction parameters A, E and n were put in equation (4) so that the pyrolysis kinetics equation of waterborne polyurethane with high solid content was obtained below:

$$\frac{d\alpha}{dt}=1.963\times10^{7}e^{-\frac{13964.0366}{T}}\left(1-\alpha\right)^{0.9}$$

The equation can quantitatively describe the thermal stability of materials, which will have great significance for the preparation and application of waterborne polyurethane with high solids content.

TABLE-3
KINETICS PARAMETERS OF THERMAL DECOMPOSITION OF WATERBORNE POLYURETHANE WITH HIGH SOLID CONTENT AT DIFFERENT HEATING RATES

β (K min^{-1})	ln β (K s^{-1})	T_m (K)	T_m^{-1} (× 10^{-3} K^{-1})	ln (β/T_m^2) (s K^{-1})
5	-2.4849	621.15	1.609917089	-15.34805185
10	-1.7918	636.15	1.5719563	-14.70262824
15	-1.3863	650.15	1.538106591	-14.34070057
20	-1.0986	657.15	1.52172259	-14.07443689

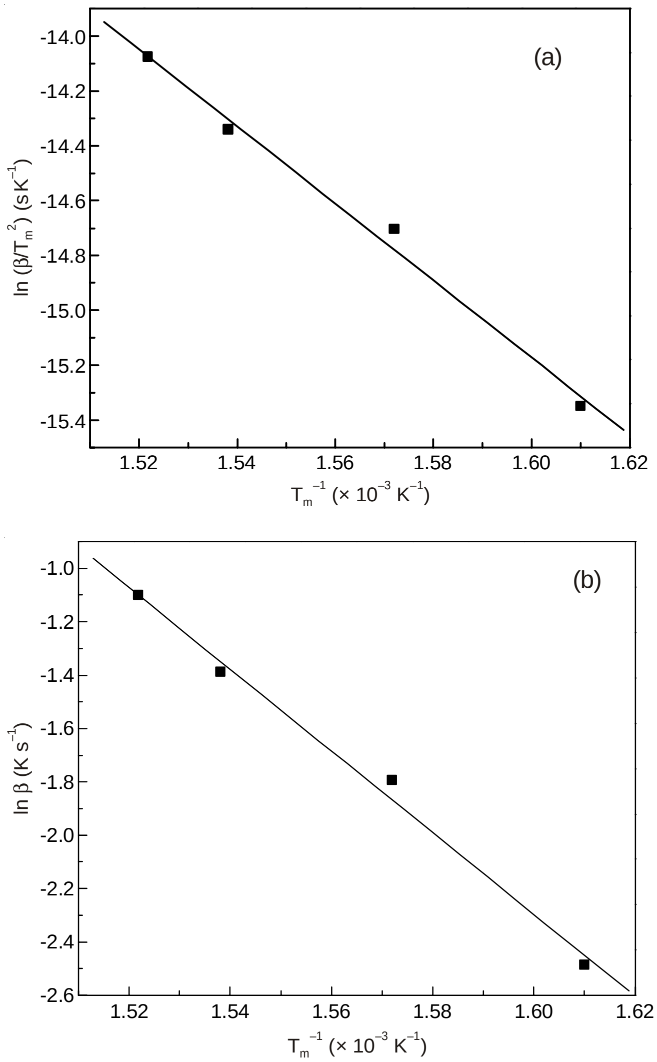


Fig. 5. ln β-1/T_m and ln (β/T_m^2)-1/T_m curves for waterborne polyurethane with high solid content; (a) ln β-1/T_m curves (b) ln (β/T_m^2)-1/T_m curves

Conclusions

- The particle size of waterborne polyurethane with high solid content presented the trend of ternary distribution, whose properties were as follows: The average particle size was 424.835 nm. The viscosity was 316 mPa·s. Emulsion stability was good. Water resistance improved. Mechanical properties had little change.

- The pyrolysis process of waterborne polyurethane with high solid content was divided into three stages. As the heating rate rose, the corresponding temperature of weight loss peak increased in turn so that delay decomposition phenomenon of waterborne polyurethane with high solid content occurred. The kinetics of waterborne polyurethane pyrolysis reaction was a complex reaction similar to 1. The activation energy E was 116.097 kJ/mol. Pre-exponential factor was 1.963×10^7 s^{-1}. Reaction order n was 0.9. The kinetic equation of waterborne polyurethane pyrolysis reaction was:

$$\frac{d\alpha}{dt} = 1.963\times10^7 e^{-\frac{13964.0366}{T}}\left(1-\alpha\right)^{0.9}$$

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