Polymer Testing 69 (2018) 259–265

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Analysis Method

Two-component waterborne polyurethane: Curing process study using dynamic in situ IR spectroscopy

Chunpeng Chai*, Jinghui Hou, Xuanhe Yang, Zheng Ge, Muhua Huang, Guoping Li

School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

A R T I C L E I N F O

Keywords:
Two-component waterborne polyurethane
Curing
IR spectroscopy
In-situ reaction study

A B S T R A C T

The cure reaction of hydroxyl-terminated waterborne polyurethane(HWPU) dispersion and the hydrophilic-modified polyisocyanate to a two component waterborne polyurethane(2K-WPU) in the presence of water environment was monitored by dynamic in situ Fourier transform infrared spectroscopy. With the progress of the reaction, the peak of -NCO group at 2271 cm^{-1} intensity decreases as a function of reaction time and totally disappears when the reaction is completed, and the hydrogen bond urethane gradually disappears. At different temperatures the reaction rate is different, but there is a great linear fit of the integrated form of the Jander equation versus time. The curing mechanism correspond to Jander equation basically. According to the change of particle size between the HWPU dispersions with 2K-WPU dispersions and the curing mechanism, the curing model was got. The chain of HWPU wrapped hexamethylene diiso-cyanate(HDI) trimer, the product appeared in three-dimensional diffusion and spherically symmetric.

1. Introduction

As increasing demand for reducing volatile organic compounds (VOCs) and hazardous air pollutants emissions, two-component waterborne polyurethane (2K-WPU) coatings are attractive choices due to excellent mechanical properties, chemical resistance, room temperature cure characteristics and low VOCs [1]. It has been widely used in automotive, industrial products, wood, plastic, leather and other coating [2]. Two-component waterborne polyurethane (2K-WPU) was synthesized by the reaction between hydroxyl-terminated waterborne polyurethane(HWPU) dispersion and the hydrophilic-modified polyisocyanate [1]. The polyol and isocyanate react with each other forming the polyurethane network (Fig. 1). The forming process of polyurethane networks is one of the key factors for properties of 2K-WPU. Therefore, it is very important to understand the curing kinetics mechanisms of the different polyurethane reactions to obtain the optimal curing conditions. However, the 2K-WPU system is quite complicated, because of the presence of water. The water can react with isocyanate to prevent the formation of polyurethane cross-linked network (Fig. 1). The generation of CO_2 has an effect on the film. The formation of three-dimensional cross-linked network structure is one of the important factors for adjusting the curing parameters and the final product properties.

To regulate the curing conditions of 2K-WPU system, it would be necessary to understand the kinetic mechanism. Several reports have already studied the kinetics of polyurethane formation reaction [3–10], however, the kinetic reaction of polyurethane polyol with polyisocyanate in the presence of water environment is still unknown to researchers. In general, the kinetics of polyurethane formation reactions were studied based on the infrared (IR) spectroscopy studies, isothermal differential scanning calorimetry (DSC) analysis or high-field nuclear magnetic resonance spectroscopy. Siddiqui et al. [4] used the DSC to monitor the multi-step complex reactions occurring during cure that quartz/cyanate-ester prepreg was performed based on polymer cure. However, DSC monitor the progress of reaction by measuring the change of heat during the reaction. In aqueous systems, the water evaporation has an effect on the heat change during the reaction. Hailu K et al. [5] used low field nuclear magnetic resonance relaxometry and near infrared spectroscopy to study the progress of the cure reaction of polyurethane with respect to time. But the NMR relaxation rate reflects the molecular dynamics of the polymer chains, which is determined by the geometrical restrictions in the resin and follows, therefore, approximately the product concentration. Among them, FTIR spectroscopy is known as a very rapid and robust method for polymer characterization and for monitoring the reaction kinetics of polymerization. Li Y et al. [3] used the dynamic in situ FTIR to monitor reactions of hydroxyl-terminated glycidylazide polymer (GAP) or poly (ethylene oxide-*co*-tetrahydrofuran) (PET) polymers. The influence of catalytic systems on the cure kinetics of polyurethane reaction was investigated clearly. Both urethane monomers and polymers have distinctive absorption peaks in the FTIR spectrum, even in the complex polymer

---

* Corresponding author.
E-mail address: chaicp@bit.edu.cn (C. Chai).

https://doi.org/10.1016/j.polymertesting.2018.05.021
Received 18 April 2018; Accepted 16 May 2018

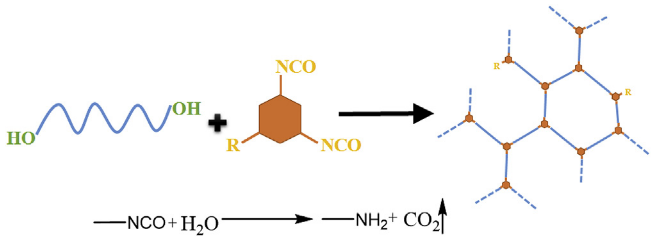

Fig. 1. The reactions of 2K-WPU system.

reactions [11]. Moreover, the accuracy of FTIR in monitoring reaction kinetics is comparable to that of thermal analysis techniques [12]. Thus, this work used dynamic in situ IR spectroscopy to monitor the reaction process so as to work out kinetic mechanism functions, rate constant, and related kinetic parameters.

In this work, hydroxyl functional polyurethane aqueous dispersion was synthesized.2K-WPU system is consisted of HWPU and HDI trimer. The difference between the HWPU dispersions and 2K-WPU dispersions were measured by particle size. The curing kinetics of polyurethane polyol with poly-isocyanate were monitored by dynamic in situ IR spectroscopy. The linear regression and correlation coefficient were obtained for polyurethane reactions using least square method. In addition, the kinetic parameters were calculated by Arrhenius law and Eyring equation. The kinetic parameters would be helpful to adjust the curing conditions including curing time and temperature, which could improve the properties for the 2K-WPU film.

2. Experimental section

2.1. Material

All the chemical reagents used in this work were of analytically grade, and were obtained from commercial sources in China. Isophorone diisocyanate (IPDI), Junsei Chemical Co. Ltd. dimethylol propionic acid (DMPA), Trimethylolpropane(TMP), triethylamine(TEA) and acetone (AC) were purchased from China Medicine, Shanghai Chemical Reagent Corporation; polypropylene glycol (PPG),Mn = 1000, Daicel Chemical Industries, Ltd.; the hydrophilic-modified polyisocyanate was Bayhydur® XP 2547 prepared by polyethylene glycol monomethylether and hexamethylene diiso-cyanate (HDI) trimer, tetramer and other polymer (Bayer)– NCO content, 22.5 ± 0.5%. The structure of polyisocyanate was shown in Fig. 2. DMPA, and PPG were vacuum desiccated and IPDI was vacuum distilled before using. About 0.5% T12 solution in diethyl phthalate was used and 0.5% TPB solution in dioctyl sebacate taken from Beijing Chemical Plant. All the materials above mentioned were used without further purification unless otherwise specified.

2.2. Synthesis of hydroxyl functional polyurethane aqueous dispersion (HWPU)

IPDI, PPG and DMPA were first introduced into a three-necked flask reactor equipped with a mechanical stirrer, a thermocouple and a reflux condenser and reacted for 4 h at 90 °C under a nitrogen atmosphere. The temperature was adjusted to 70 °C, TMP was added the system and reacted for 2 h. In addition, TEA (same molar content as DMPA) was added and stirred for 30 min to neutralize the system. Deionized water was then added to the reaction system and the solution was emulsified using high speed shear (3000 rpm). The ratio of NCO to OH in the reactants was 0.8 for all reactions. Then deionized water was added into the reaction system and high speed shearing (2500–3000 rpm) was used to emulsify the solution. Finally, HMPU with a solid content of 30 wt% was obtained. Fig. 3 shows a schematic diagram for the synthesis of HWPU.

2.3. Synthesis of two-component waterborne polyurethane(2K-WPU)

The hydroxyl-functional polyurethane aqueous dispersion weighted was added into a beaker, and Bayhydur®XP2547 with the calculated amount was also added to the beaker and stirred with high speed (3000 rpm) for 10 min.

2.4. Characterizations

A Nano-ZS90 Zeta-sizer (Malvern Instrument, UK) was used to study the particle size of resultant HWPU and 2K-WPU emulsions at 25 °C ± 0.1 °C. The samples were prepared by diluting the emulsions with deionized water to adjust the solid content to 0.01 wt%.

2.5. FTIR spectroscopy measurement

The in situ FTIR spectroscopy was carried out using a Nicolet 8700 type infrared spectrometer (Thermo Electron Corporation, USA), with spectral resolution of 4 cm^{-1}, and the scanning range was from 4000 to 1000 cm^{-1}. Dry air was continuously flowed into the instrument until the absorbance of all impurities was constant and the background spectrum was recorded to eliminate the influence of the air. Then, a stoichiometric amount of polyurethane polyol(HWPU) with Bayhydur®XP2547 poly-isocyanate in an equimolar (–NCO/–OH = 1.5) was uniformly mixed and 0.3% catalyst was added further. The mixture was spread on the surface of CaF_2 tablets placed in a thermos controlled chamber, which was preheated at the desired temperature in the FTIR spectrometer. The relationship between the –NCO absorbance (A) and time (t) was acquired using the IR spectra of working software OMNIC quantitative calculation of the peak width was determined. The catalyst concentration of each measured samples was maintained at 0.3%.

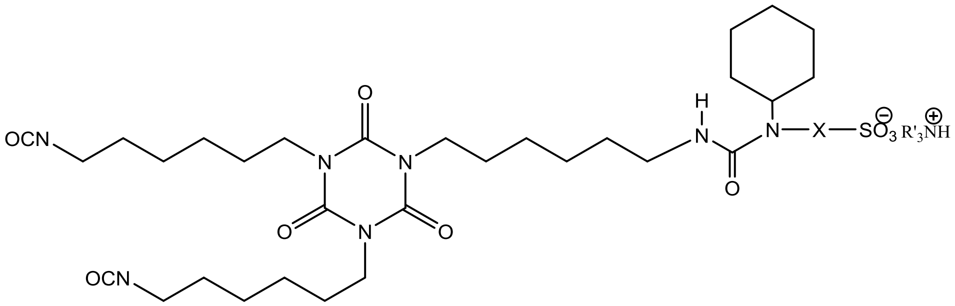

Fig. 2. The chemical structure of Bayhydur® XP 2547.