

Crosslinking Kinetics of the Formation of Lignin-Aminated Polyol-Based Polyurethane Foam

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ABSTRACT: FTIR-ATR (Fourier Transform Infrared-Attenuated Total Reflectance) spectroscopic analysis was used to study the kinetics of the formation of the polyurethane foam, which was prepared by reacting a mixture of lignin-aminated polyol (LAP) and glycol (PEG) with diphenylmethane diisocyanates (MDI-50) in the presence of water as blowing agent. The crosslinking reactions were followed by monitoring the change of the absorbance of the NCO group at 2270 cm^{-1} in

FTIR-ATR spectra. The apparent activation energy (E_a) calculated according to n -th order reaction model was 16.44 kJ/mol , and the frequency factor (A') was 2.69 min^{-1} . Furthermore, the crosslinking reaction is approximated to be a first-order reaction. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 152–157, 2012

Key words: crosslinking; polyurethanes; kinetics; FTIR

INTRODUCTION

With numerous advantages, such as light weight, good heat insulation, excellent strength and corrosion resistance, electrical insulating properties, sound absorbing properties and low density, the consumption of polyurethane foams (PUFs) has grown rapidly, and the PUFs become indispensable part in our daily life.¹

The foams have been developed into many types and classes of products, such as insulation materials for apartment houses, cold stores, pipelines. PUFs are prepared by the polymerization of isocyanates with polyols (oligomers with 2–6 hydroxyl groups in a molecule), in which the reacting mixture are foamed using one or more blowing agents. The foam formation process consists of various steps: mixing of the monomers and bubble nucleation, rise of the liquid foam, phase separation, which leads to rapid modulus rise and cell opening, and formation of a foamed elastomer.^{2,3}

Knowledge of kinetic parameters of the foam foaming is essential on the design and processing of polymerization reaction and composite technologies. Kinetic prediction of the cure pattern over a wide temperature range is also of interest. Although a few

studies on the dynamics of foaming of polyurethane foams have been previously carried out,^{4,5} the dynamics of polyurethane foam formation with two polyols as model has not been studied. Fourier transform infrared (FTIR) spectroscopic analysis is one of the most versatile spectroscopic techniques and is widely used in monitoring crosslinking reactions of nonsolvent systems to study the mechanism on molecular level in details. This technique allows detecting the variation of functional groups at different periods, which is based on the change of the absorbance of the functional groups in FTIR spectra in the reaction process. For instance, Hocker⁶ reported that the carbonyl group present in soluble urea (1715 cm^{-1}) interacts sooner with urethane carbonyls (1730 cm^{-1}) than that of soluble D-urea (1697 cm^{-1}). Michael⁷ has study the reaction kinetics and development of structure during foam formation in model flexible polyurethane foam systems with FTIR spectroscopy. Elwell⁸ conducted to investigate the reaction kinetics and structure development in model flexible polyurethane foam systems, the decay of isocyanate has been correlated to the polymerization kinetics and evolution of hydrogen bonded urea, the knowledge of which has provided determination of exotherm for the foam formation. More recently, Friebe⁹ studied the synthesis reaction of diphenyl urethane from phenol and phenyl isocyanate catalyzed by AlCl_3 in chloroform solution with FTIR-ATR probe, and the activation energy was obtained.

In this article, the lignin-based polyurethane foams blown at different temperature were prepared. The crosslinking kinetics of foaming was discussed in

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detail by FTIR-ATR spectroscopic analysis, and the kinetic datum including conversion rate, apparent rate constant, apparent activation energy, and kinetic equation were obtained. The basic chemistry reactions that take place during foam formation were showed in Figure 1.

EXPERIMENTAL

Materials

Diphenylmethane diisocyanate (MDI-50) with 50% 4,4' and 50% 2,4-isomers was supplied by Yantai Wanhua Co., Shandong, China. Lignin-aminated polyol was prepared in our laboratory. Stannous octoate, the catalyst used in polyurethane foam manufacturing, was obtained from Sinopharm Chemical Reagent Co., Shanghai, China. AK-8801, a silicone surfactant used to stabilize the foam, was a commercial product from Dymatic shichuang Chemical Co., Nanjing, China. Distilled water was used as blowing agent. Glycol (PEG) with average M_n 600 and the other chemicals used in the experiment were obtained commercially.

Preparation of lignin-aminated polyol

Lignin-aminated polyol was prepared from lignin, diethanolamine, and formaldehyde by the Mannich reaction as the previous report.¹⁰

Preparation of lignin-aminated polyol-based PUF

In a plastic cup, 100 parts of PEG, 25 parts of lignin-aminated polyol, one part of water, one part of catalyst, and two parts of silicone were added and pre-mixed thoroughly at ambient temperature. Then, MDI-50 (isocyanate index 1.5) was added into the cup and mixed with a high speed mixer (3000 rpm) for 10 s. The mixture was poured immediately into a cubic paper container and heated to the respective reaction temperature (40, 50, 60, and 70°C) to produce free-rise foam. Each sample was tested on three times by FTIR-ATR spectrometer for different times, which was removed from the middle of the foam.

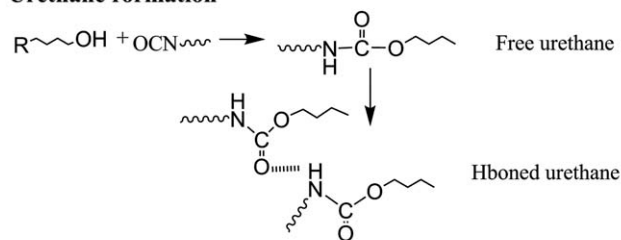
FTIR-ATR spectroscopy

FTIR-ATR spectra were recorded in Nicolet iS10 (Nicolet Instrument Co.) spectrometer with a diamond crystal. Spectra of the samples were obtained averaging 32 scans between 4000 cm^{-1} and 650 cm^{-1} with a resolution of 2 cm^{-1} .

Estimation of conversion rate

The crosslinking kinetics reaction was taken as a measure of the reduction in concentration of the absorbing substance. To relate conversion with

Urethane formation



Urea formation(The blowing reaction)

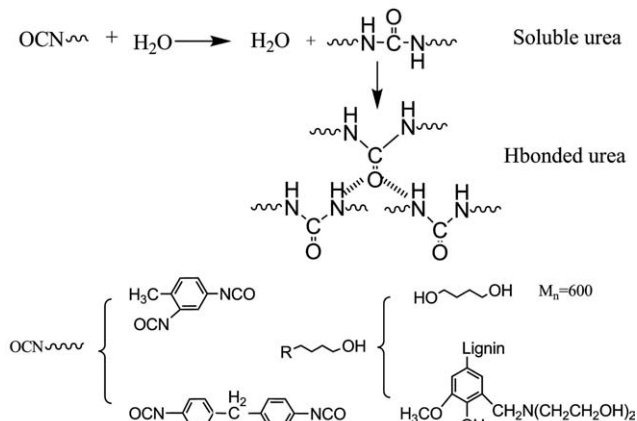


Figure 1 Schematic representation of the chemistry reaction taking place during PUF formation.

absorbance changes the peak of isocyanate group, -NCO stretching band appearing at 2270 cm^{-1} was measured at different times. Quantification of this was based on the Lambert-Beer law [eq. (1)].

$$A_0 = \varepsilon cl \quad (1)$$

According to Beer-Lambert Law, the conversion rate α of isocyanate can be calculated by the following equation:

$$\alpha = \frac{A_0/\varepsilon l_0 - A_t/\varepsilon l_t}{A_0/\varepsilon l_0} \quad (2)$$

The bulk concentration of -NCO changed greatly during the polymerization, and an internal reference must be taken to compensate the large change in density. For normalization of the decay in the isocyanate absorbance, the peak of the benzene absorbance at 1600 cm^{-1} was used as the reference, which does not change in concentration during the reaction.^{7,11} Therefore, the isocyanate conversion rate is calculated as follows:

$$\alpha = \frac{\frac{A_0/\varepsilon l_0}{A_0^r/\varepsilon^r l_0} - \frac{A_t/\varepsilon l_t}{A_t^r/\varepsilon^r l_t}}{\frac{A_0/\varepsilon l_0}{A_0^r/\varepsilon^r l_0}} = \frac{A_0 - A_t}{A_0^r - A_t^r} = 1 - \frac{A_t A_0^r}{A_t^r A_0} \quad (3)$$

where A_0 and A_t are the absorbance of NCO group at time zero and t . A_0^r and A_t^r are the absorbance of

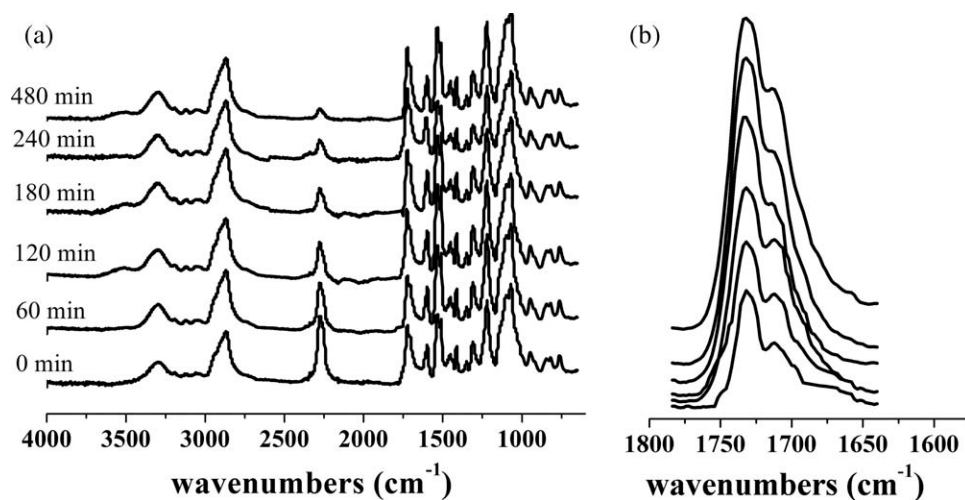


Figure 2 FTIR spectra of PUF at different times at 60°C.

benzene ring (1600 cm^{-1}) at time zero and t . Absorbance can be expressed as peak value.

RESULTS AND DISCUSSION

FTIR-ATR spectroscopic analysis

In the formation process of polyurethane foam, the diisocyanates reacted with polyols, to give a urethane linkage, and, the blowing agent (water) reacted with diisocyanates to produce carbon dioxide and urea at the same time (Fig. 1). The FTIR-ATR spectra during foam formation at different crosslinking reaction times at 60°C were shown in Figure 2. The vibrancy peak of NCO at 2270 cm^{-1} weakened gradually in the reaction progress, which was characteristic absorption band of diisocyanates. The typical adsorption of carbonyl group at $1780\text{--}1640\text{ cm}^{-1}$ increased gradually with the prolonging reaction times, which was associated with urethane, soluble urea, hydrogen-bonded (H-bonded) urethane, and hydrogen-bonded urea. Both urethane and soluble urea were taken place simultaneously, not sequentially in the crosslinking reaction.^{7,12} The type of interaction, the frequency range at which the particular absorbance occurs and a reference to the assignment were showed in Table I.

TABLE I
Infra-Red Band Assignments Observed in the Polyurethane Foam

Frequency (cm^{-1})	Band assignment	Reference
1730	Free urethane	12,13
1715–1710	Soluble urea	13
1697–1695	Free urea	6
1710–1700	H-bonded urethane	14
1645–1640	H-bonded urea	15

Kinetic parameters

The conversion rates were calculated from quantitative analysis of FTIR-ATR by eq. (3). The plots of conversion rates versus time at different crosslinking temperatures were shown in Figure 3. It was shown that conversion rate increased with time and temperature until it reached the maximum of conversion.

A number of equations have been suggested to describe the kinetics of the catalyzed isocyanate and alcohol reaction. It is generally accepted that these reactions follow pseudo-second-order kinetics,^{16,17} but this kinetic model generally holds true only up to a medium-to-low degree of conversion. Because several physical phenomena (e.g., an increase in viscosity), autocatalytic effects of the newly formed urea or urethane groups may occur subsequently. In this article, two main kinds of reactions occurred simultaneously in the foaming. In polymerization

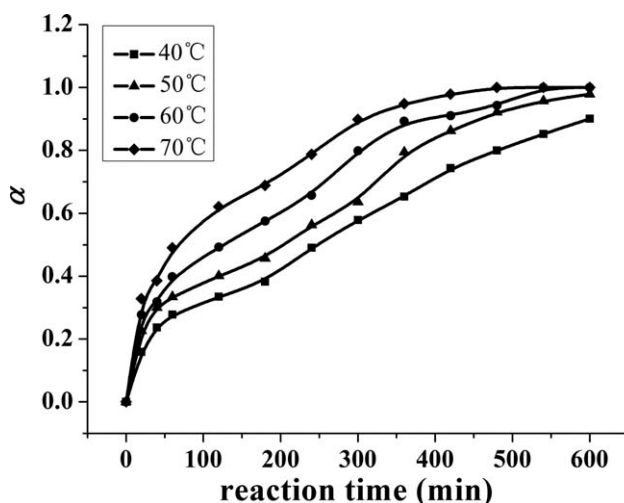


Figure 3 Plots of α versus time at respective reaction temperature.

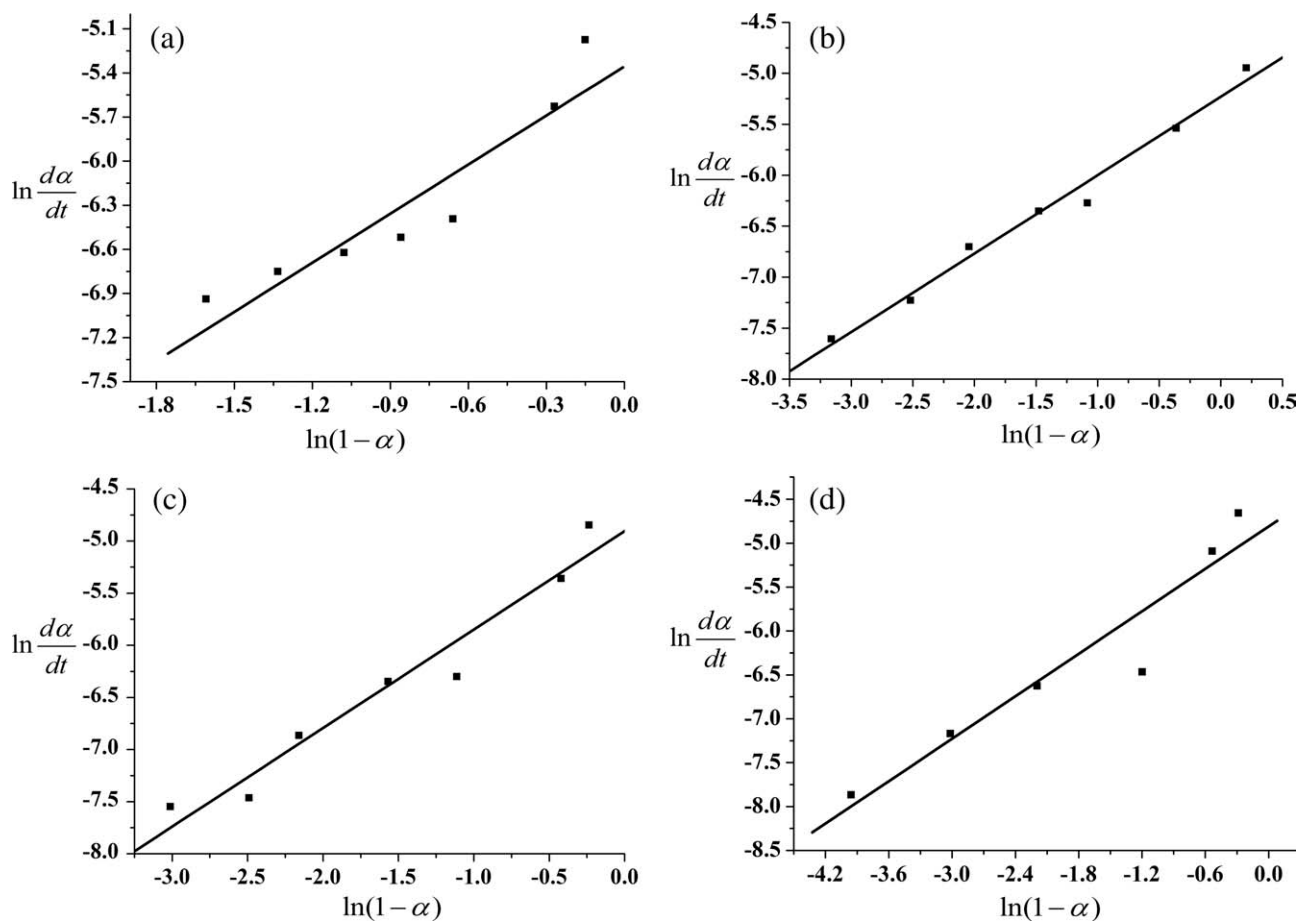


Figure 4 Plots of $\ln \frac{d\alpha}{dt}$ versus $\ln(1 - \alpha)$ at respective reaction temperature: a 40°C, b 50°C, c 60°C, and d 70°C.

reaction, the diisocyanates reacted with PEG and LAP, giving the urethane linkage. In blowing reaction, the chemical blowing agent (water) reacted with diisocyanates to produce carbon dioxide and urea. Although the process of the foaming was simple in concept, the formation of foam from liquid materials involved a complex combination of chemical and physical factors.^{18,19} Furthermore, it was difficult to isolate an individual reaction and measure its rate occurring during the foaming. Nevertheless, it was possible to measure the concentration of formation as a function of time, and the amount of diisocyanates reacted may be modeled using

TABLE II
General Parameters of the n -th Order Reaction Kinetic Model

T (°C)	n		$k \times 10^{-3}$ (min^{-1})	$E_a \times 10^{-3}$ (J/mol)	A' (min^{-1})
	Measured Value	Average Value			
40	1.11	0.92	4.72	16.44	2.69
50	0.82		6.07		
60	0.95		7.42		
70	0.81		8.16		

apparent rate constant which could provide a better understanding of overall reaction process. Thus the experimental data were inspected according to n -th order reaction kinetic model. According to the reaction theory, the kinetic equation can usually expressed as follows²⁰:

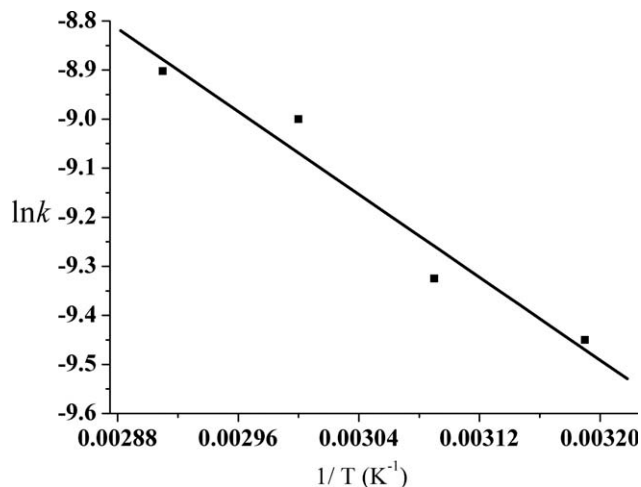


Figure 5 Curves $\ln k$ with T^{-1} for apparent activation energy.

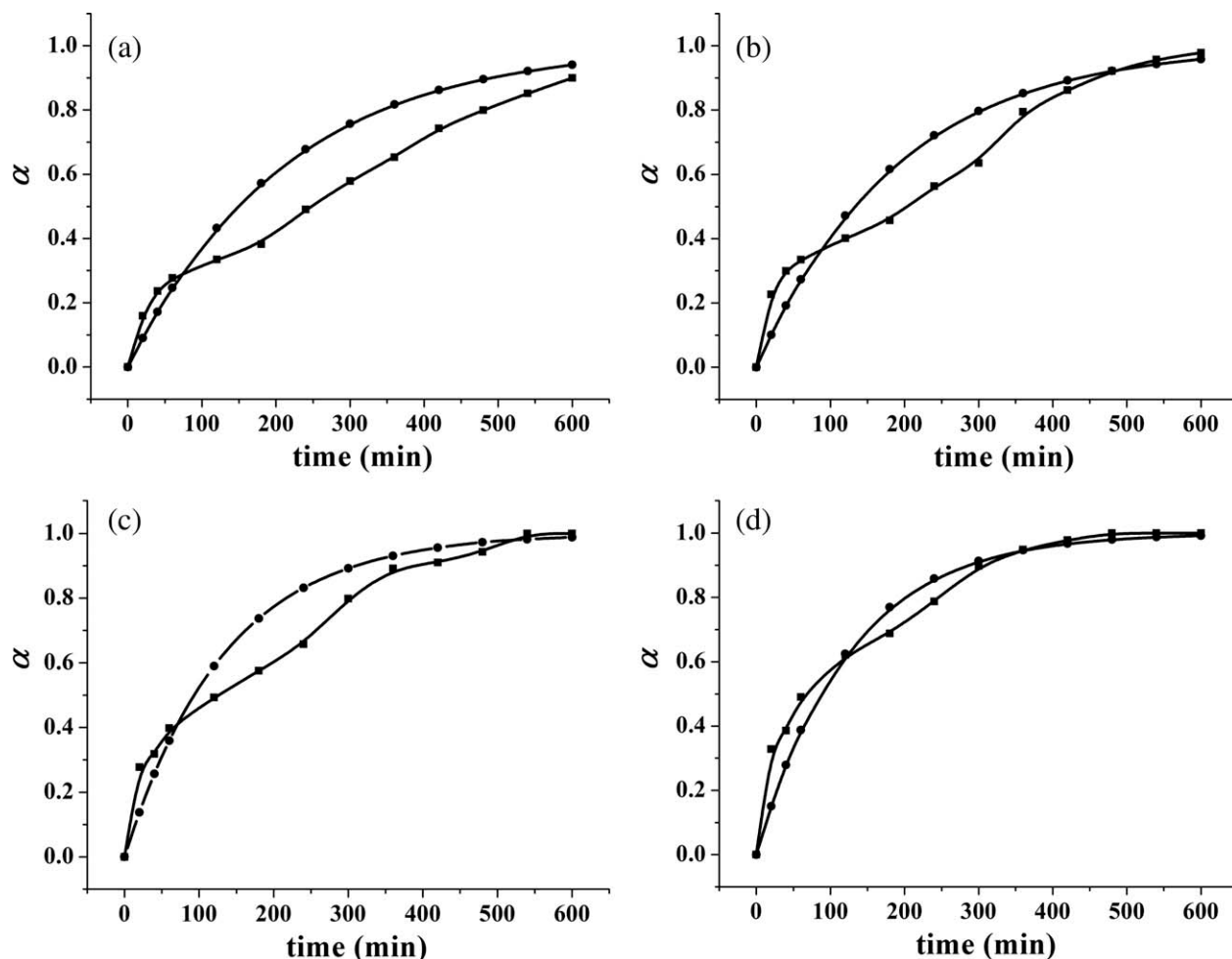


Figure 6 Comparison of experimental curves and calculating curves by first-order reaction kinetic model: a 40°C, b 50°C, c 60°C, d 70°C; ■- experimental data, ● - calculated from the kinetic equation.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (4)$$

where $k = A' \exp(-\frac{E_a}{RT})$, which is apparent rate constant, α is conversion rate, and n is the apparent reaction order.

Taking logarithms of eq. (4), the following equation can be obtained:

$$\ln \frac{d\alpha}{dt} = \ln k + n \ln(1 - \alpha) \quad (5)$$

From this equation, it is easy to determine the reaction order and reaction rate constant by plotting $\ln[\frac{d\alpha}{dt}]$ against $1/T$ (Fig. 4). The slope of line equaled to n and intercept equaled to $\ln k$. The kinetic parameters were summarized in Table II. The reaction conditions such as temperature, catalyst, and reactant concentration had no effect on the reaction order which only related to the performance groups. k was a constant depending only on temperature. It was indicated from the results that the rate constant increased with increasing reaction temperature and

the crosslinking reaction was approximated to be a first-order reaction.

According to Arrhenius equation, the relation between reaction rate constants and reaction temperatures was listed as the following equation:

$$\ln k = \ln A' - \frac{E}{RT} \quad (6)$$

The data of apparent activation energy (E_a) and apparent frequency factor (A') were shown in Table II, which was determined from the slope and intercept of the Arrhenius plot of $\ln k$ versus $1/T$ (Fig. 5). Assuming an Arrhenius temperature dependence of the rate constant and first order kinetics of this system, the rate of crosslinking reaction was expressed as $\frac{d\alpha}{dt} = 2.69 \exp(-1.644 \times 10^4/RT)(1 - \alpha)$.

Crosslinking process simulation

The reaction rate constant of the first order reaction kinetic equation is theoretically calculated using the integral expression of eq. (4) when n equals to 1.

$$\ln \frac{1}{1-\alpha} = kt \quad (7)$$

The dynamics simulation on the rate constant of PUF formation process by eq. (7) was shown in Figure 6. It was indicated from the results that there were little difference between the response and calculating curves. So the first-order reaction kinetic model can be used to characterize the crosslinking reaction of the formation of polyurethane foam based on lignin-aminated polyol.

CONCLUSIONS

Crosslinking reaction of polyurethane foam based on lignin-aminated polyol was studied by FTIR-ATR spectroscopic analysis. The n -th order treatment proved systematically the most adequate way of representing the kinetic features of this system. It was shown from the results that the crosslinking reaction was approximated to be a first-order reaction. According to Arrhenius equation, the apparent activation energy (E_a) was obtained to be 16.44 kJ/mol, and the apparent frequency factor (A') was 2.69 min⁻¹. Conversion rates of the crosslinking reaction calculated from kinetic equation were found to be close to those obtained from experimental data.

References

1. Daniel, K.; Vahid, S. *Handbook of Polymeric Foams and Foam Technology*; Oxford University Press: New York, 1991.
2. Neff, R. A.; Macosko, C. W. *Rheol Acta* 1996, 35, 656.
3. Yasunaga, K.; Neff, R. A.; Zhang, X. D.; Macosko, C. W. *J Cell Plast* 1996, 32, 427.
4. Baser, S. A.; Khakhar, D. V. *Polym Eng Sci* 1994, 34, 632.
5. Tesser, R.; Serio, D.; Sclafani, A.; Santasescaria, E. *J Appl Polym Sci* 2004, 92, 1875.
6. Hocker, J. *J Appl Polym Sci* 1980, 25, 2897.
7. Michael, J. E.; Anthony, J. R.; Henri, J. M. G.; Henry, C. V. L. *Polymer* 1996, 37, 1353.
8. Elwell, M.; Ryan, A. J.; Grünbauer, H. J. M.; Van, L. H. C. *Polymer* 1996, 8, 1353.
9. Friebe, A.; Siesler, H. W. *Vibr Spectr* 2007, 43, 217.
10. Huo, S. P.; Kong, Z. W.; Chen, J.; Wu, G. M.; Nie, M. C. *Chem Ind Forest Prod* 2010, 30, 93.
11. Mu, S. L.; Gou, A. C. *J Polym Reas* 1996, 3, 173.
12. Bailey, F. E.; Critchfield, F. E. *J Cell Plast* 1981, 17, 333.
13. Camargo, R. E.; Macosko, C. W.; Tirrell, M.; Wellinghoff, S. T. *Polym Commun* 1983, 24, 314.
14. Burkhart, G.; Kollmeier, H. J.; Schloens, H. H. *J Cell Plast* 1984, 20, 37.
15. Priester, R. D.; O'Neill, R. E.; Turner, R. B.; Harthcock, M. A.; Davis, B. L. *J Cell Plast* 1990, 26, 346.
16. Aneja, A.; Wikes, G. L.; Yurtsever, E.; Yilgor, I. *Polymer* 2003, 44, 757.
17. Iskender, Y.; Brian, D. M.; Serkan, U.; Emel, Y.; Timothy, E. L. *Polymer* 2004, 45, 5829.
18. Menges, K.; Schwesig, H.; Hahn, G. *Org Coat Plast Chem* 1981, 44, 229.
19. Artavia, L. D.; Macosko, C. W. *J Cell Plast* 1990, 26, 490.
20. Fu, X. C.; Shen, W. X.; Yao, T. Y. *Physical Chemistry*; Higher Education Press: Beijing, 1990.