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Thermochimica Acta 427 (2005) 31–36
thermochimica acta
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DSC monitoring of the cure kinetics of a castor oil-based polyurethane

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Received 20 May 2004; received in revised form 10 August 2004; accepted 12 August 2004
Available online 25 September 2004

Abstract

Differential scanning calorimetry (DSC) has been used to monitor the reaction between castor oil and isophorone diisocyanate (IPDI), using a non-isothermal method, at different heating rates. The NCO/OH ratio in these systems was 1, so that the concentration of NCO and OH groups could be considered equivalent during all the experiments. Despite the complexity of the system, in which different order kinetics are possible, as well as physically controlled diffusion processes, data were fitted to a simple kinetic model, of apparent order n, apparent activation energy E_A, and apparent frequency factor A_0. The dependency of these parameters on heating rate was used to analyze kinetics of polymerization of these systems.

Keywords: Polyurethane; Kinetics; Bulk polymerization; Differential scanning calorimetry (DSC)

1. Introduction

Since, in the late 1930s, Otto Bayer and co-workers discovered and patented the chemistry of polyurethanes, these materials have found an increasingly outstanding position among the most important organic polymers for intensive technological applications [1]. This class of polymer has, as the characteristic chemical group present in their chains, the urethane group (resultant from the reaction of a hydroxyl and an isocyanate group). It has been used in radically different applications: one can find them used as biomaterials in implants and therapeutic agents [2,3], as materials for engineering applications [4], applied in electronic [5] and non-linear optical devices [6], and in the coating industry [7]. This broad spectrum of applications is closely linked to the plethora of physical forms that these materials can assume: one can find them, for instance, in the form of elastomers [8,9], rigid and flexible foams [10,11], adherent films [12], and powders [13]. In the field of biodegradable polymers, polyurethanes based on castor oil and different diisocyanates have been suggested as potentially interesting materials [14].

The physical properties of these materials are closely related to the occurrence of virtual crosslinking between the macromolecules [15,16]. This virtual crosslinking is the result of hydrogen bonding between the N–H and carbonyl groups from the urethane-rich phase [17]. However, depending on their thermal history, these materials may undergo changes in critical physical properties (such as Young's modulus, e.g.), due to change from metastable forms (in which there is a higher occurrence of interactions between hard and soft phases) to the more segregated and stable morphology, in long periods of time [18,19].

Thermal history is related to changes in temperature that a given polyurethane sample is submitted; however, in the case of bulk polymerization, it is also bound to heat flow within the sample, resultant from the kinetics of polymerization. It has been shown that, when working with reactive injection molding (RIM), there is the development of a temperature profile through the obtained specimen, which results

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0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.08.010

in specimens with more complex and unstable morphologies [20]. As a consequence, a proper control and understanding of the bulk polymerization process is critical for applications which demand reproducibility, not to mention the cure control, by itself.

Many studies on the kinetics of solution polymerization of these systems have been carried out: Epharim et al. have characterized the influence of nature of the solvent on the rate of the reaction and found that the effect on the rate was correlated with the dielectric constant of the solvent, while deviations from the second-order kinetics were attributed to hydrogen bonding between alcohol and solvent molecules [21]. Orberth et al. have characterized the occurrence of catalysis via urethane group and showed that the order of the reaction, depending on the conditions, may vary from two to three (occurrence of autocatalytic effect) [22]. As a matter of fact, a second-order kinetics is the usual behavior found, when analyzing the reaction of isocyanate and, in the case of asymmetric diisocyanates, two specific velocities have been found (one related to each isocyanate group) [23–25]. This approach, in the case of bulk polymerization (depending on the temperature and degree of crosslinking), is limited by the occurrence of diffusion-controlled processes (in this case, not only chemistry governs the cure kinetics: as conversion increases, purely viscoelastic processes become more and more important) [26]. Therefore, a kinetics which is also a function of diffusion-controlled processes rules the time-conversion dependence, as has been widely reported for other stepwise polymerization mechanisms, such as in the case of epoxide resins [27,28].

The objective of this work is to describe the kinetics of the bulk reaction between castor oil and isophorone diisocyanate (IPDI) using a simple kinetic expression of apparent order, energy of activation, and frequency factor, in non-isothermal conditions. Since exact reaction kinetics is much more complex than this expression, different values of apparent activation energies, reaction order, and frequency factor will be obtained for different heating rates/degrees of conversion. The mechanism of bulk polymerization will be discussed in terms of the dependence between these factors and temperature.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, 99%, purchased from Aldrich) and dibutyltindilaurate (DBTDL, PA, purchased from Aldrich) were used without further purification. Castor oil (hydroxyl number 188, functionality 2.75, kindly supplied by Proquinor, Brazil) was dried at vacuum at 100 °C for 4 h before using in the experiments.

2.2. Polymerization monitoring by DSC

The system castor oil-IPDI was monitored via DSC using a SHIMADZU DSC-50H equipment. The measurements were carried out, using a sample weight of 26–27 mg with an empty cell as the reference. Two systems were analyzed: (1) mixtures of castor oil and IPDI with NCO/OH ratio of 1 and (2) mixtures of castor oil and IPDI with NCO/OH ratio of 1 and the addition of 0.01 wt.% of DBTDL as catalyst. The samples were placed in a liquid cell of aluminum and heated from room temperature to 250 °C with heating rates of 5.0, 7.5, 10.0, 12.5 and 15.0 °C/min, with an accuracy of 0.1 °C. In the case of the system without catalyst, it was not possible to run the experiments at 12.5 and 15.0 °C/min, due to liquid cell instability. A nitrogen supply was used to purge gas, at a flow rate of 50 mL/min. The instrument was calibrated using indium (purity): 99.99%, melting point 156.4 °C, ΔH = 6.80 mcal/mg.

3. Results and discussion

As discussed in Section 1, in bulk polymerization systems, kinetic processes are rather complex, so that, for a first approach, the process of polyurethane preparation, at a given heating rate, was represented as a simple and generic kinetic expression, assumed to be of nth order (or, more exactly, it will have an *apparent reaction order* of n): ath order in relation to OH and bth order in relation of NCO). Since all the systems used in the experiments had an NCO/OH ratio of 1, it resulted in [NCO] = [OH] at any time, during the process of polymerization. As a consequence, the kinetic expression, associated to a specific velocity k_n, can be written as

$$-\frac{\mathrm{d[NCO]}}{\mathrm{d}t} = -\frac{\mathrm{d[OH]}}{\mathrm{d}t} = k_n[\mathrm{NCO}]^a[\mathrm{OH}]^b = k_n[\mathrm{NCO}]^n, \quad (1)$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_n(1-\alpha)^n, \quad (2)$$

where

$$\alpha = \frac{[\mathrm{NCO}]_0 - [\mathrm{NCO}]}{[\mathrm{NCO}]_0} \quad (3)$$

is the degree of conversion, $K_n = k_n[\mathrm{NCO}]_0^{n-1}$, $[\mathrm{NCO}]_0$ being the initial concentration of NCO groups at time $t = 0$.

If the complete reaction between all NCO groups and all OH groups had an enthalpy of ΔH_0, then $\alpha = H(t)/\Delta H_0$ (where $H(t)$ is the accumulated energy liberated at a time t during the reaction), and Eq. (2) could be rewritten as

$$\frac{1}{\Delta H_0}\frac{\mathrm{d}H}{\mathrm{d}t} = K_n\left(1 - \frac{H(t)}{\Delta H_0}\right)^n \quad (4)$$

The specific velocity k_n can be related to the temperature T through an Arrhenius dependence relationship:

$$k_n = A_0 \mathrm{e}^{-E_\mathrm{A}/RT} \quad (5)$$

where R is the universal gas constant, A_0 is an *apparent frequency factor*, and E_A an *apparent energy of activation*. Substitution of (5) in (4) finally yields:

$$\frac{dH}{dt} = \frac{A_0}{(\Delta H_0)^{n-1}} e^{-E_A/RT} [\Delta H_0 - H(t)]^n, \qquad (6)$$

Time and temperature are related by the heating rate:

$$T = T_0 + \beta t \Rightarrow dT = \beta dt, \qquad (7)$$

where T_0 is the initial temperature and β is the heating rate. Substitution of (7) in (4) would result in

$$\frac{dH}{dt} = \frac{\beta A_0}{(\Delta H_0)^{n-1}} e^{-E_A/RT} [\Delta H_0 - H(T)]^n, \qquad (8)$$

Eq. (8) should now be numerically solved, so that the resulting curves $H(T) \times T$ would be adjusted to the data through nonlinear regression on the parameters E_A, ΔH_0, and A_0: the values of $H(T)$ can be easily obtained through numerical integration of dH/dt data from the equipment. However, the data should be fitted via a nonlinear regression coupled to the Runge-Kutta method for the solution of (8) [29]. Another way to determine the parameters could be through Eq. (4): dH/dt, T, and $H(t)$ can be obtained from the equipment: the data should then be adjusted via multivariate nonlinear regression. In this work, a hybrid procedure was used to obtain the parameters. For each heating rate, the integrated H data, was expressed as a function of temperature, using a power series:

$$H(T) = \sum_{i=1}^{9} a_i (T - T_R)^i \qquad (9)$$

where the a_is are the parameters of the power series and T_R is a reference temperature, which was chosen to be the temperature at which exothermic processes were first recorded by the DSC equipment. The perfect fit between data and the series can be visualized in Fig. 1. Eq. (9) was then substituted in (6), resulting in:

$$\frac{dH}{dt} = \frac{A_0}{(\Delta H_0)^{n-1}} e^{-E_A/RT} \left[\Delta H_0 - \sum_{i=1}^{9} a_i (T - T_R)^i\right]^n \qquad (10)$$

Eq. (10) may now be used to correlate dH/dt to T, via univariate nonlinear regression, so that the parameters ΔH_0, A_0, E_A, and n can be determined. However, Vyazovkin and Sbirrazuoli have found this approach (i.e., via reaction order model and single heating curve) rather problematic, when working with epoxyanhydride cure [30], in accordance with the procedure recommended by the ICTAC Kinetics Project [31–35]. As a consequence, in a first step, we analyzed the dependence of the apparent activation energy with the conversion, using the isoconversional method [33]. According to this method, the reaction kinetics is described as a “model free” one, in the form of

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha), \qquad (11)$$

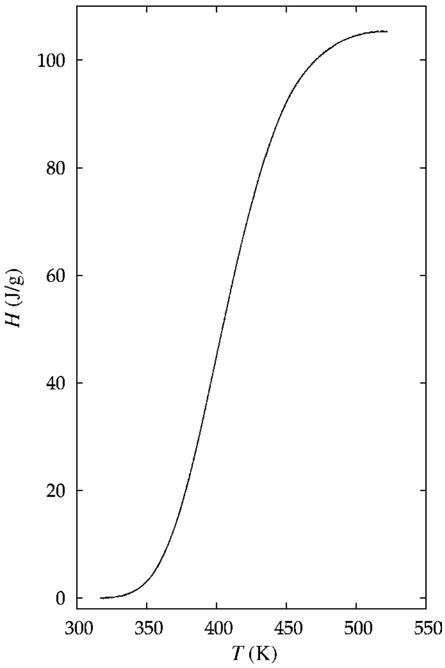

Fig. 1. H as a function of temperature for the reaction of castor oil and IPDI at a heating rate, $\beta = 5\ \mathrm{K\ min^{-1}}$. Solid lines: experimental data; dotted lines: data described by Eq. (4).

where $f(\alpha)$ does not have a definite form. According to this method, the apparent activation energy may be regarded as dependent of the conversion, as follows:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT}. \qquad (12)$$

As a consequence, from plots of $\ln(d\alpha/dt)$ (at constant α) versus reciprocal temperature, one can determine E_α from the slope of the resultant plot. The values of E_α were calculated for our experiments and the resultant data are displayed in Fig. 2. From the referred figure, one can observe that:

- E_α for the catalyzed system is lower than its value for the system without catalyst (for any value of α).
- One can see that in the case of the system with catalyst, E_α continuously rises with conversion. It is consistent with an increase in viscosity of the system, making the diffusion of reactive species more difficult (diffusion controlled reactions).
- For lower degrees of conversion, E_α decreases for the system without catalyst. As already related in the literature [22], urethane groups formed in the polymerization may catalyze the reaction, decreasing the apparent activation energy, as a consequence.
- This sort of decrease was not detected in the case of the system with catalyst and may have three reasons: (i) the decrease in activation energy due to catalysis is relatively more important than the decrease in activation energy due to autocatalysis; (ii) for systems with catalyst, higher conversions are reached at lower temperatures resulting in diffusion controlled processes at lower degrees of conversion;

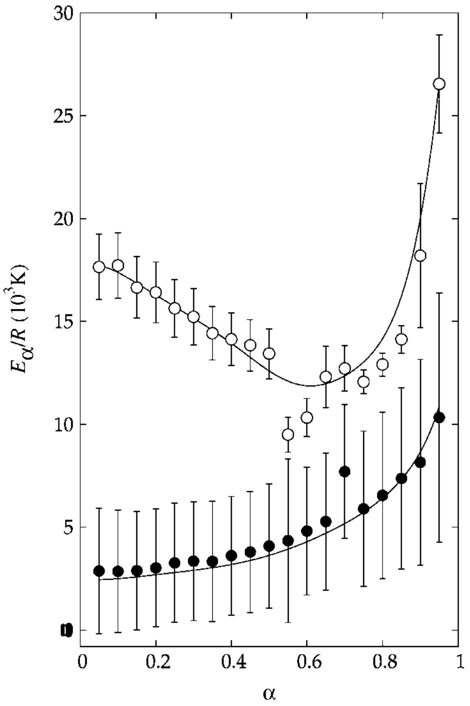

Fig. 2. Apparent energy of activation (obtained via isoconversional method), E_α as a function of conversion. Open circles: without catalyst; filled circles: with catalyst.

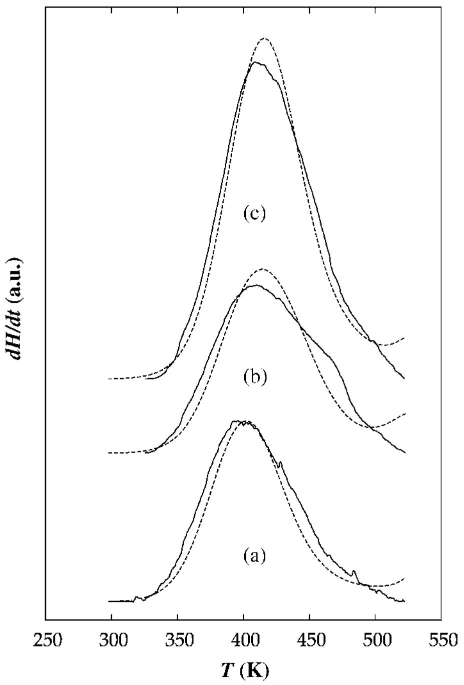

Fig. 3. DSC thermograms for the reaction of castor oil and IPDI, without catalyst. The solid lines represent experimental results; dotted lines represent Eq. (10). Heating rates: (a) β = 5 K min^{-1}, (b) β = 7.5 K min^{-1}, (c) β = 10 K min^{-1}.

(iii) experimental errors involved in the determination of E_α.

For data fitting with Eq. (10), however, one needs a definite value of E_A/R. Data were well fitted for $E_A/R = 9.5 \times 10^3\ K$ (reaction without catalyst) and $9.5 \times 10^3\ K$ for the catalyzed system (which are related to values of E_α at $\alpha \approx 0.5$). Figs. 3 and 4 show the thermograms for the systems without and with catalyst, respectively. One can see that data fit reasonably to Eq. (10), the slight discrepancy being due to the complex phenomena involved in polymerization, which were not taken into account for the sake of simplicity of analysis. Nevertheless, it can be observed in both experimental and theoretical curves, that the exothermic peak is shifted to higher values of temperature, as heating rate is increased. This behavior has already been observed for polymeric systems and is a direct consequence of the kinetics of the reaction: as heating rate increases, a higher amount of unreacted groups will be present at higher temperatures, regardless of the reaction order, resulting in DSC peak shifting [36].

Fig. 5 shows the dependence of the preexponential factor, A_0, in relation to the heating rate, β. One can see that the non-catalyzed reaction has a much higher apparent frequency factor than the catalyzed one. As the medium viscosity decreases (higher conversions will occur at higher temperatures, in the case of the system without catalyst), the frequency of collisions between reactant groups will increase: that could be the reason for a higher value of A_0 for the non-catalyzed reaction.

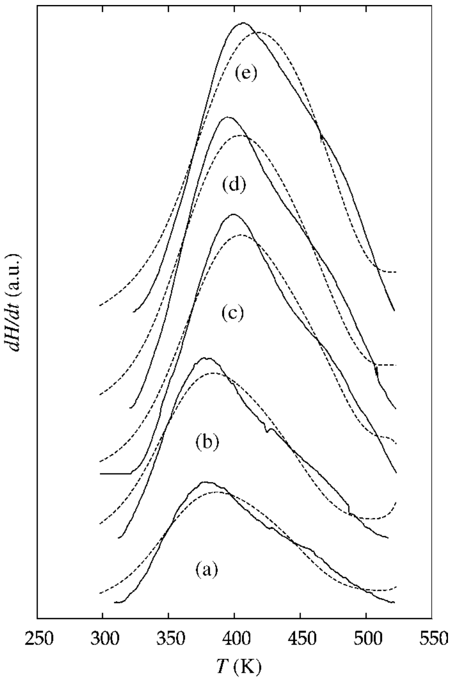

Fig. 4. DSC thermograms for the reaction of castor oil and IPDI, with 0.01 wt.% of catalyst. The solid lines represent experimental results; dotted lines represent Eq. (10). Heating rates: (a) β = 5 K min^{-1}, (b) β = 7.5 K min^{-1}, (c) β = 10 K min^{-1}, (d) β = 12.5 K min^{-1}, (e) β = 15 K min.

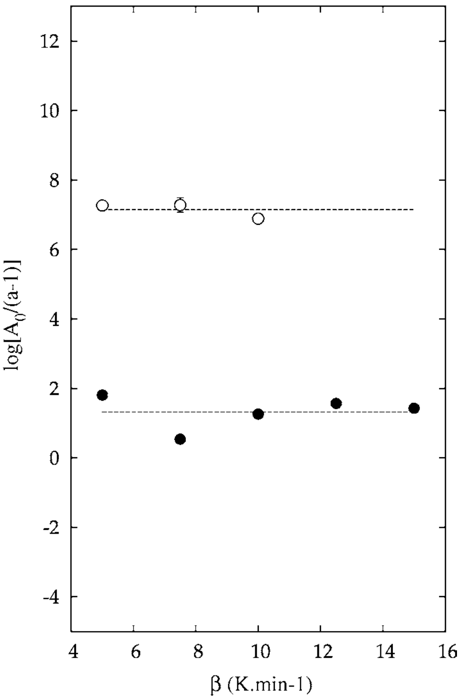

Fig. 5. Apparent frequency factor, A_0, as a function of heating rate, β. Open circles: without catalyst; filled circles: with catalyst.

Fig. 6 displays the dependence of the apparent reaction order, n, and the heating rate, β. A reaction order of ca. 3, in the case of the system without catalyst is consistent with the results from dependent apparent energy of activation: autocatalysis is more important in the case of the system without catalyst [37]. In the case of the system with catalyst the reaction order tends to be around 2 (autocatalysis is not detected, or is not important) due to the reasons already mentioned when analyzing E_α results.

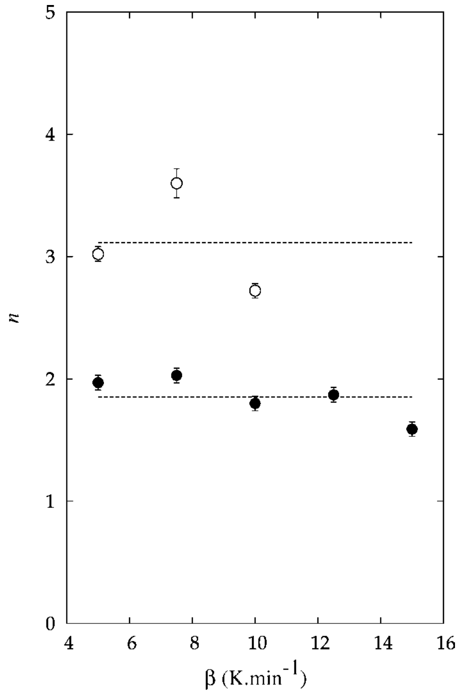

Fig. 6. Apparent reaction order, n, as a function of heating rate, β. Open circles: without catalyst; filled circles: with catalyst.

4. Conclusion

Polyurethane formation may be monitored using DSC experiments and a simple kinetic model of a reaction of apparent order n, apparent activation energy E_A, and apparent frequency factor A_0. The isoconversional method as well as the values of apparent reaction order show that autocatalysis is more important in the case of the system without catalyst. The dependence of activation energy with degree of conversion also shows the role of diffusion controlled processes in the polymerization of these systems.

Acknowledgments

The authors wish to thank PROPESQ-UFRN, CNPq, CAPES, and MCT for financial support during the course of this work.

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