Cure Kinetic of Castor Oil-Based Polyurethane

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ABSTRACT: This research presents the kinetic studies on the cure reactions of a new material, castor oil-based polyurethane resin. Thermal analysis by isothermal differential scanning calorimetry was used, as a variety of factors affect its cure, including formulation and polymerization process. The kinetic reaction of this catalyzed system is described by nth order equation. Castor oil, a vegetable triglyceride, was reacted with methylene diphenyl 4,4'-diisocyanate to produce an elastomeric matrix. The objective of this research is thermal characterization of new polyurethane that is less aggressive to humans and environment; therefore, castor oil used on the synthesis is derived from a natural and renewable resource. The activation energy measured for the castor oil-based polyurethane resin studied in this work was about 56 kJ/mol. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3168–3171, 2011

Key words: activation energy; curing of polymers; polyurethane; differential scanning calorimetry; kinetics

INTRODUCTION

Castor oil is a vegetable triglyceride, not used for feeding. The molecule is, characteristically, formed by hydroxyl groups and applied as a polyol in the synthesis of crosslinked polyurethane.[1] Figure 1 shows the representative composition of the oil. Viscous liquid castor oil is obtained from expressing or extracting with solvent from *Ricinus communis* plant seeds, which belong to the *Eurphorbiacae* family.[2,3]

Castor plant grows in countries with tropical and subtropical climates that present averages temperatures about 20–26°C and low air humidity. Main producers are India, China, and Brazil, which were responsible for 92% of the worldwide production in 2001.[4] The yearly worldwide production of seeds is about 1 million tons; consequently, the oil production remains around 500,000 tons.[2,5]

There are different varieties of castor seeds, but on average, it is possible to obtain 46 to 55 wt % of oil.[2] This oil is a natural resource, which is considered to be closer to a pure compound, where 87–90% of the fatty acid presents in their constitution is the ricino-leic acid. About 10–13% are nonhydroxylated fatty acids, which include linoleic and oleic acids.[1,6] The average composition of the castor oil is indicated in Table I.

The vegetable castor oil has been widely applied in the chemical industry as a raw material for paints, coatings, inks, and lubricants. It is also used as biomaterial in implants and therapeutics agents, even applied in optics and electronic devices. For application in isocyanate reactions to produce polyurethanes elastomers, millable, castables, adhesives, coatings and foam, it is considered to be appropriate. Some semirigid foams used as thermal insulation are produced through castor oil/polyether mixture and toluene diisocyanate reaction.[2,7]

Normally, polyurethanes result from a reaction through a diol, characterized by the hydroxyl group —OH and a poliisocyanate, which presents the functional group —NCO.[8]

The main purpose of this study is to calculate the activation energy of a new polyurethane that is less aggressive to humans and environment; therefore, castor oil used on the synthesis is derived from a natural and renewable resource.

Kinetic study

Thermal analysis by differential scanning calorimetry (DSC) is one of the experimental methods mostly used in the literature for cure kinetics reactions, considering the rate of heat generation is proportional to the rate of the reaction cure.[9,10] Both isothermal and
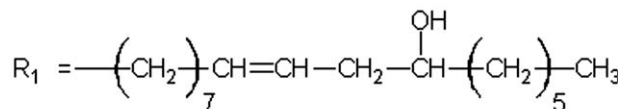
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where:

$R_1 = -\left(CH_2\right)_7 CH=CH-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-\left(CH_2\right)_5 CH_3$
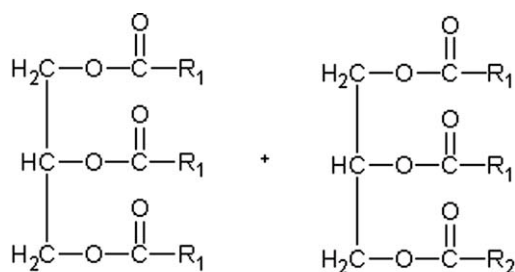
R_2 = other fatty acid derivates

Figure 1 Castor oil triglyceride.[2]

dynamic modes are used. It is possible to identify two types of reaction by isothermal analyses; one is the nth order and the other is the autocatalytic. The nth order reaction occurs when the maximum peak of the reaction rate takes place near to the zero time ($t = 0$), and it can be studied by isothermal and dynamic modes. In the case where the maximum peak is formed between 30% and 40% of the analysis total time, the reaction is autocatalytic, and it must be studied by dynamic mode, exclusively.[11,12]

The nth order model is expressed by eq. (1)[9,13,14]:

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

where k is the reaction rate constant (1/s), α is the cumulative conversion at a given time t, n is the reaction exponent, and $d\alpha/dt$ is the conversion rate (1/s).

The reaction rate constant obeys an Arrhenius temperature dependency, as indicated in eq. (2)[9,13,14]:

$$k = A \cdot e^{(-E_a/RT)} \qquad (2)$$

where A is the frequency factor (1/s), E_a is the activation energy of the cure reaction (kJ/mol), R is the

TABLE I
Average Composition of Castor Oil[2]

Components	Concentration (%)
Ricinoleic acid	89.0
Linoleic acid	4.2
Oleic acid	3.0
Stearic acid	1.0
Palmitic acid	1.0
Dihydroxystearic acid	0.7
Linolenic acid	0.3
Eicosanoic acid	0.3

universal gas constant (8.32 J/mol K), and T is the temperature (K).

The Arrhenius equation relates the frequency of the collisions between molecules and the probabilities by which those collisions are conducted in a favorable way. The increase in the activation energy decreases the velocity of the reaction.[13]

Performing the logarithm of eq. (2), eq. (3) is obtained:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (3)$$

The graphic $\ln k$ versus $1/T$ shows a straight line where the activation energy and the frequency factor are obtained by angular and linear coefficient of the straight line, respectively. A minimum of three isothermal experiments in different temperatures are necessary to obtain these parameters.[11,12,15]

DSC has been used to study the cure reaction from the mixture castor oil and isophorone diisocianate, based on a nonisothermal method, to produce polyurethane according to Rodrigues et al.[7] Results indicate $E_a/R = 9.5 \times 10^3$ K, when related to $\alpha = 0.5$. The calculated activation energy for Ref. 7 was $E_a = 79$ kJ/mol.

Ajithkumar et al.[16] analyzed kinetics of castor oil-based polyol and toluene diisicianate reactions. The polymerization kinetic was studied under isothermal conditions using dibutyl tin dilaurate as a catalyst. The activation energies were obtained in the range 21.4 to 30.1 kJ/mol and depending on the catalyst concentration in the system.

The evaluation of activation energy in reactive systems can be used to predict the kinetic mechanisms involved in the cure reactions as well the reactivity of different monomers and cure temperature.

EXPERIMENTAL PROCEDURE

Materials

The polyurethane based on castor oil is cured at room temperature. It is a bicomponent formed by a polyol and a prepolymer commercially designated as D405 and IC201, respectively.[17] Kehl Industry from Brazil provides these reagents and has its patent.

The polyol D045 is liquid at room temperature, presents yellow color and density in the range 1.0 to 1.2 g/cm^3, according to the manufacturer. It is soluble in water and produces biodegradable residue.[17]
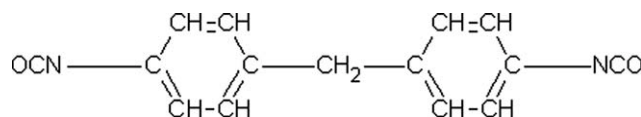

Figure 2 Methylene diphenyl 4,4'-diisocyanate.

TABLE II
Results of DSC Dynamic Scanning

T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔH_{dyn} (J/g)
35.0	82.3	140.0	−89.8

The prepolymer IC201 is composed by methylene diphenyl 4,4′-diisocyanate, which structure is displayed in Figure 2. It is liquid at room temperature, with dark brown color and a density about 1.24 g/cm^3, as informed by the manufacturer. This reagent is insoluble in water; however, it reacts producing CO_2 and an inert and not biodegradable residue.[17]

Methods

Reagents were mixed according to the stoichiometric quantity of 2 : 1 in mass of polyol and isocyanate, respectively. The components were mixed about 3 to 5 min, followed by deposition of a small amount on sample container.

The kinetic parameters of activation energy, preexponential factor, and reaction order were determinate according ASTM E2070[18] using a series of isothermal experiments at four temperatures.

The sample was cured in dynamic scanning to obtain the isothermal temperatures for the kinetic studies using the following four temperatures: 45, 50, 55, and 60°C.

DSC dynamic scanning was carried out in a Perkin Elmer Thermal Analysis System, model Pyris 1, under constant flow of 20 mL/min of nitrogen and heating rate of 10°C/min. Sealed aluminum pan was used.

DSC isothermal measurements were performed in a SII Nano Technology INC, series EXSTAR 6000, model DSC 6220, under constant flow of 20 mL/min of nitrogen. Sealed aluminum pans were used.
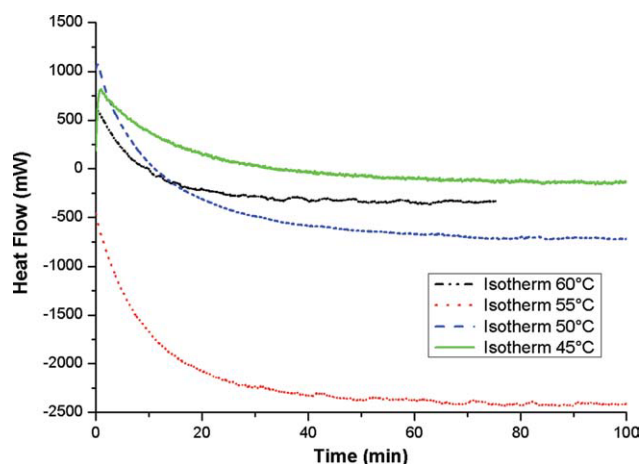
TABLE III
Results of Isothermal Enthalpies (ΔH_{iso}) and Kinetic Parameters (k and n)

T (°C)	$\Delta H_{iso} \times 10^{-2}$ (J/g)	$k \times 10^{-2}$ (T)	n
45	96.86	3.897	1.687
50	74.03	5.735	1.547
55	52.83	7.594	1.407
60	22.73	10.31	0.895

RESULTS AND DISCUSSION

Table II presents dynamic scanning results from the mixture. It is possible to observe that polymerization initial and peak cure temperatures are 35.0 and 82.3°C, respectively. The negative value of ΔH_{dyn} shows an exothermic cure reaction with release of heat.

From initial and peak cure temperatures, isothermal temperatures for kinetic studies at 45, 50, 55, and 60°C were chosen. Four isothermal scanning are used to determine the nth order of the resin. Figure 3 presents isothermal curves obtained by DSC scanning.

Analysis from Figure 3 indicates that the maximum heat evolution occurs at the start of the reaction time; therefore, the system obeys the nth order cure kinetics, in accordance to eq. (1).

Data from Table II and Figure 3 were used to calculate kinetics results exhibit in Table III. Table III shows decrease in ΔH_{iso} values with increase in the isothermal cure temperature. It is also possible to observe a relationship between the reaction exponent (n) and the rate constant (k). Increasing temperature provides an increase of molecules velocity followed by an increase in the average energy value. Consequently, a large number of molecules acquire
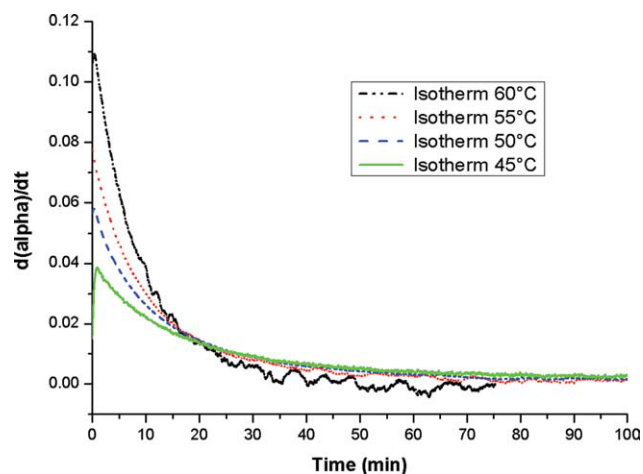

Figure 3 Cure isotherms measured by DSC at 45, 50, 55, and 60°C showing the typical nth order reaction mechanism curve shape. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 Isothermal reaction rate as a function of time at 45, 50, 55, and 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
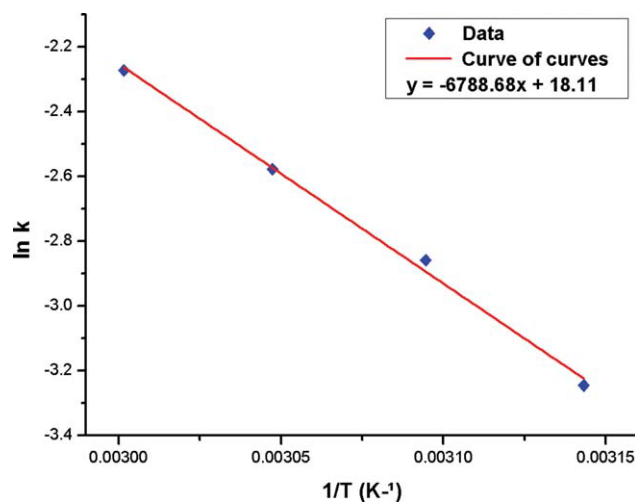
Figure 5 Arrhenius plot of the isothermal reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant energy to exceed the reaction activation barrier through collisions.[11]

For the four isothermal curves, the conversion rate and cumulative conversion (α) as a function of time were calculated through results obtained in Figure 3. The isothermal reaction rate as a function of time at 45, 50, 55, and 60°C is represented in Figure 4.

According to Figure 4, the conversion rate is significantly influenced by the cure temperature used. For lower temperatures, as presented by the isotherm run at 45°C, the curve is smoother and, consequently, takes more time to obtain the maximum conversion rate. Therefore, lower temperatures of polymerization allow higher control of the cure.

Results from Table III are necessary to plot Figure 5, which shows the Arrhenius approach used to determine the activation energy. This angular coefficient represents the activation energy of the castor oil-based polyurethane.

Generally, chemical reactions present activation energy from 30 to 100 kJ/mol; in the case of viscous system, this value stays in the interval from 10 and 20 kJ/mol.[11] The lower the activation energy, the faster the reaction rate.[13]

The activation energy of the castor oil-based polyurethane is 56.4 kJ/mol and indicates a relatively high reactivity system.

CONCLUSIONS

The DSC technique is confirmed to be adequate to the kinetic cure study of polyurethane system.

The formulation studied presented an nth order polymerization reaction, as values of the reaction order increases progressively with the temperature.

The activation energy measured the studied system is 56.4 kJ/mol.

References

1. Trân, N. B.; Vialee, J.; Phan, Q. T. Polymer 1997, 38, 2467.
2. Ogunniyi, D. S. Bioresour Technol 2006, 97, 1086.
3. Vilar, W. Chemistry and Technology of Polyurethanes. Available at: <http://www.poliuretanos.com.br>. Accessed on March 3, 2006.
4. Biodiesel. World production from castor beans. Available at: <http://www.biodieselbr.com/plantas/mamona/producao-mundial-mamona.htm>. Accessed on May 10, 2006.
5. Santos, R. F.; Barros, M. A. L. Cultivation of castor bean. Available: <http://sistemasdeproducao.cnptia.embrapa.br/fonteshtml/mamona/cultivodamamona/importancia.htm>. Accessed on May 10, 2006.
6. Silvestre Filho, G. D. MD dissertation, University of São Paulo; 2001. Available at: <http://www.teses.usp.br/>. Accessed on March 10, 2005.
7. Rodrigues, J. M. E.; Pereira, M. R.; Souza, A. G.; Carvalho, M. L.; Dantas Neto, A. A.; Dantas, T. N. C.; Fonseca, J. L. C. Thermochim Acta 2005, 427, 31.
8. Solomons, G.; Fryhle, C. Organic Chemistry; LTC: Rio de Janeiro, 2002.
9. Yousefi, A.; Lafleur, P. G.; Gauvin, R. Polym Compos 1997, 18, 157.
10. Turi, E. Thermal Characterization of Polymeric Materials; Academic Press: San Diego, 1997.
11. Costa, M. L.; Rezende, M. C.; Pardini, L. C. Química Nova 2000, 23, 320.
12. Costa, M. L.; Rezende, M. C.; Pardini, L. C. Influence of aromatic amine hardeners in the cure kinetics of an epoxy resin used in advanced composites. Mater Res 2005, 8, 65.
13. Brown, T. L.; Lemay, H. E., Jr.; Bursten, B. E.; Burdge, J. R. Chemistry, The Science Central; Pearson Prentice Hall: São Paulo, 2005.
14. ASTM E2070 – Standard Test Method for Kinetic Parameters by Differential Scanning Calorimetry using Isothermal Methods, 2008.
15. Mothé, C. G.; Azevedo, A. D. de. Thermal Analysis of Materials; iEditora: São Paulo, 2002.
16. Ajjithkumar, S.; Kansara, S. S.; Patel, N. K. Eur Polym J 1998, 34, 1273.
17. Kehl. Available at: <http://www.kehl.ind.br/>. Accessible at: March 15, 2006.
18. ASTM E2070: Standard Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods. United States of America, 2008.