Application of Isothermal and Model-Free Isoconversional Modes in DSC Measurement for the Curing Process of the PU System

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ABSTRACT: The dynamic, isothermal, and model-free isoconversional modes of differential scanning calorimetry measurement were used to monitor the curing process of the polyurethane system. Conversions obtained from these three methods were in good agreement with one another, indicating that isothermal and model-free isoconversional modes can successfully be used for monitoring the curing process. For the isothermal mode, the highest reaction rate occurred at time zero, and autoacceleration was not observed for this system. From the model-free isoconversional mode, it was possible to calculate the activation energy changes during the curing process. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1474–1480, 2001

Key words: isoconversional method; activation energy; differential scanning calorimetry (DSC); cure kinetics; polyurethane (PU)

INTRODUCTION

The relationship between the reaction rate and conversion α is different for each process and must be determined experimentally. A traditional dynamic mode of differential scanning calorimetry (DSC) measurement is often used for monitoring the curing process of thermosets. The glass-transition temperature (T_g) and the residual curing enthalpy changes (ΔH_r) can be obtained, and the conversion of the curing process can be calculated from the curing enthalpy changes. A one-to-one relationship has been found to exist between T_g and ΔH_r.[1–6] In industry, curing reactions are normally carried out under isothermal conditions. Thus, the isothermal mode of DSC measurements corresponds well to the practice. In general, isothermal methods are better at distinguishing dif-

ferent reaction mechanisms, and they give a more accurate and reliable description of the curing process. Isothermal curing has previously been applied for establishing an accurate kinetic model for the epoxy systems.[7]

The curing of thermoset resins is a complicated process because of the kinetics of the curing and the changes in the physical properties of the system. In the curing process, the liquid resin slowly becomes solid as the reaction proceeds. Thus, it is obvious that the mechanisms are also changing. Mathematics based on the chemical reaction may describe the start of the reaction, but at the end, when it is controlled by diffusion, this approach fails.[3,5,8,9] For this kind of process, the function of α is complicated and generally unknown. In such cases, an nth-order algorithm leads to unreasonable kinetic data.[10–12] A few other kinetic models, such as those of Kissinger and Flynn, Wall, and Ozawa, and an autocatalytic model developed by Kamal have been applied to analyze the kinetics of epoxy systems, and reasonable results have

been obtained.[13] However, these models still cannot describe the actual experiments accurately. In 1992, Vyazovkin and Lesnikovich proposed a novel model-free isoconversional approach.[14] This isoconversional approach is very flexible because the data are not forced to fit into any particular form. It offers a reliable mathematical description of the chemical reality and makes it possible to accurately predict the path of even the most complicated reactions. Applications of the isoconversional method in the curing process of the epoxy system have been reported.[15–18]

In this study, the traditional dynamic and the isothermal modes of DSC measurements were used to monitor the curing process of a polyurethane (PU) system. We also applied the model-free isoconversional mode to predict the activation energies (E_a's) and conversions at different curing temperatures.

EXPERIMENTAL

The two components of PU provided from Gairesa Ltd. (La Coruna, Spain) were employed throughout the work. The tetrafunctional polyol (number-average molecular weight = 400) was a polyether/polyester containing 0.117 wt % of an accelerator, dibutyl tin dilaurate, on polyol. The other component was a pure aliphatic isocyanate based on hexamethylene diisocyanate. The stoichiometric ratio (w/w) of polyol/isocyanate was 1.42/1.

All experimental data reported in this work were obtained with an ME-DSC-821 differential scanning calorimeter (Mettler-Toledo, Sweden) installed with STAR^e software (version 6.01). Because of the wide range of temperatures (-120 to $350°C$), the temperature and heat flow were calibrated with four standard materials (heptane, bidistilled water, indium, and zinc).

After the PU components were mixed, the mixtures (5–9 mg or 18–20 mg for the isothermal mode) were sealed in standard 40-μL aluminum pans. The sealed samples were measured with three different methods. In the first method, the traditional dynamic mode, the uncured samples were placed inside the oven for prespecified times at five different temperatures: 25, 40, 50, 65, and 80°C. After curing times from 5 min to 12 h, the samples were allowed to cool to room temperature and were then scanned from -120 to $250°C$ at the rate of 10°C/min under a continuous nitrogen flow to determine ΔH_r. The total heat of the reaction (ΔH_{tot}) was determined by the scan of an uncured

sample. The basic assumption of the use of DSC data to calculate the molar conversion α is that the heat evolved during the curing reaction is proportional to the extent of the reaction. The fractional conversion α_{DSC} was calculated as follows:[19,20]

$$\alpha_{\mathrm{DSC}} = 1 - \frac{\Delta H_r}{\Delta H_{\mathrm{tot}}} \qquad (1)$$

In the second method, the isothermal mode of the DSC measurement, the extent of the reaction at a constant temperature was measured as a function of time. The measurements were performed at five different temperatures between 25 and 80°C. The scan of an empty pan at each temperature was used as a background measure and was subtracted from the sample measurements.

In the third method, the fast-curing dynamic mode, the uncured samples were scanned from -30 to 300°C at different heating rates (0.5, 1, 2, 5, and 10°C/min). The results were analyzed by the model-free isoconversional method with STAR^e software to obtain E_a versus the conversion and the conversion versus the curing time at different temperatures.

RESULTS AND DISCUSSION
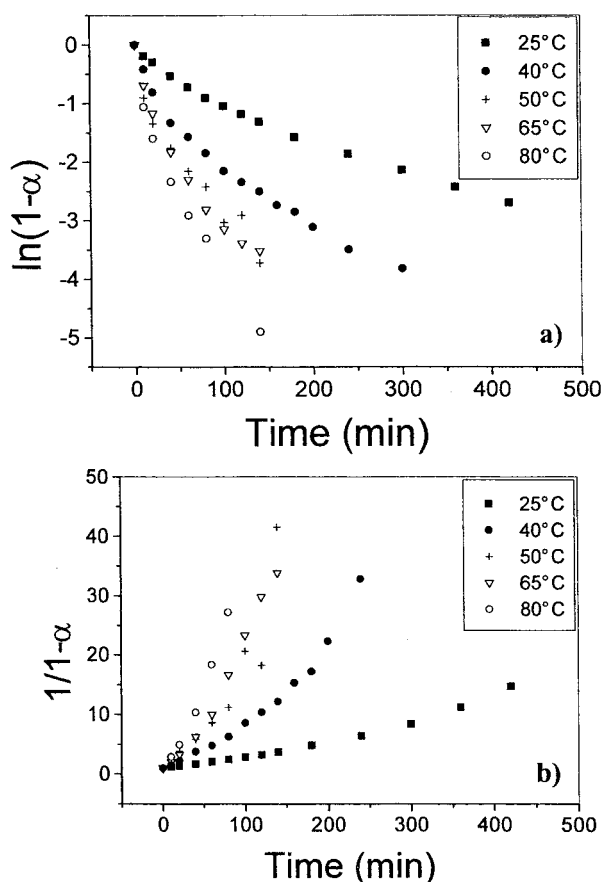
Traditional Dynamic Mode of DSC Measurement

DSC scans obtained of samples cured at 25°C for 5 and 365 min are shown in Figure 1. The obtained ΔH_r was used directly to calculate the extent of the reaction according to eq. (1). If the curing reactions under different temperatures follow nth-order kinetics[20] (i.e., first-order or second-order reaction kinetics), plotting either $\ln(1 - \alpha_{\mathrm{DSC}})$ or $1/(1 - \alpha_{\mathrm{DSC}})$ versus time should yield a linear dependence. The plots obtained for this system at different temperatures are shown in Figure 2. As discussed before,[21] only part of the curing reaction supported the nth-order reaction kinetics, indicating that nth-order reaction kinetics did not describe the process accurately. For complicated reactions such as polymerization, because of the constantly changing reactants as the chain grows, developing a new kinetic model is necessary.

Isothermal Mode of DSC Measurement

DSC curves from the isothermal mode at different temperatures are shown in Figure 3. The area
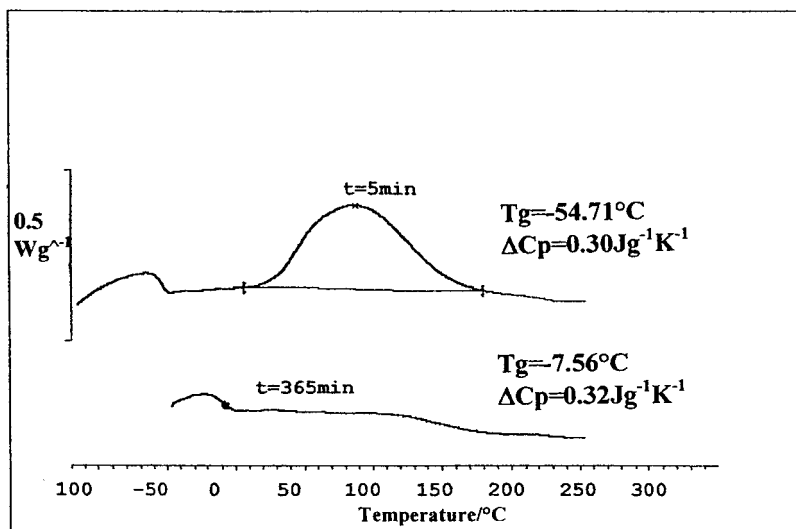
Figure 1 Typical DSC scans obtained by the traditional dynamic mode for samples cured at 25°C for 5 and 365 min.

Figure 2 (a) $\ln(1 - \alpha_{\mathrm{DSC}})$ and (b) $1/(1 - \alpha_{\mathrm{DSC}})$ as a function of time obtained from traditional dynamic mode of DSC measurements at different temperatures.

under the isothermal curve up to any time t represents the heat of the reaction at time t, ΔH_t. The obtained relationship of enthalpy changes versus the curing time is shown in Figure 4. The maximum reaction rate clearly occurred at time zero, and autoacceleration did not take place.[22,23] The conversion α_{ISO} at time t and temperature T was calculated by the following equation:[20]

$$\alpha_{\mathrm{ISO}} = \Delta H_t/\Delta H_{\mathrm{tot}} \qquad (2)$$

where the total heat, ΔH_{tot}, of the isothermal reaction at temperature T was determined from the traditional dynamic mode. These results are compared with those obtained from the traditional dynamic mode in Figure 5. The conversions at a certain temperature and time were very close to each other, although some differences could be observed at conversions higher than 0.6. For the traditional dynamic method, at each curing time a new sample had to be measured, whereas for the isothermal method one sample could be used through the whole curing process at a certain temperature. This led to smoother curves and more reliable results. Hence, with this very simple method, the isothermal mode of DSC measurement, conversion versus curing time at different temperatures could be accurately calculated.

Theory and Application of the Model-Free Isoconversional Mode of DSC Measurement

The model-free isoconversional mode of DSC measurement is based on the theory proposed by Vyazovkin.[14,24–27] The theory assumes that E_a is con-
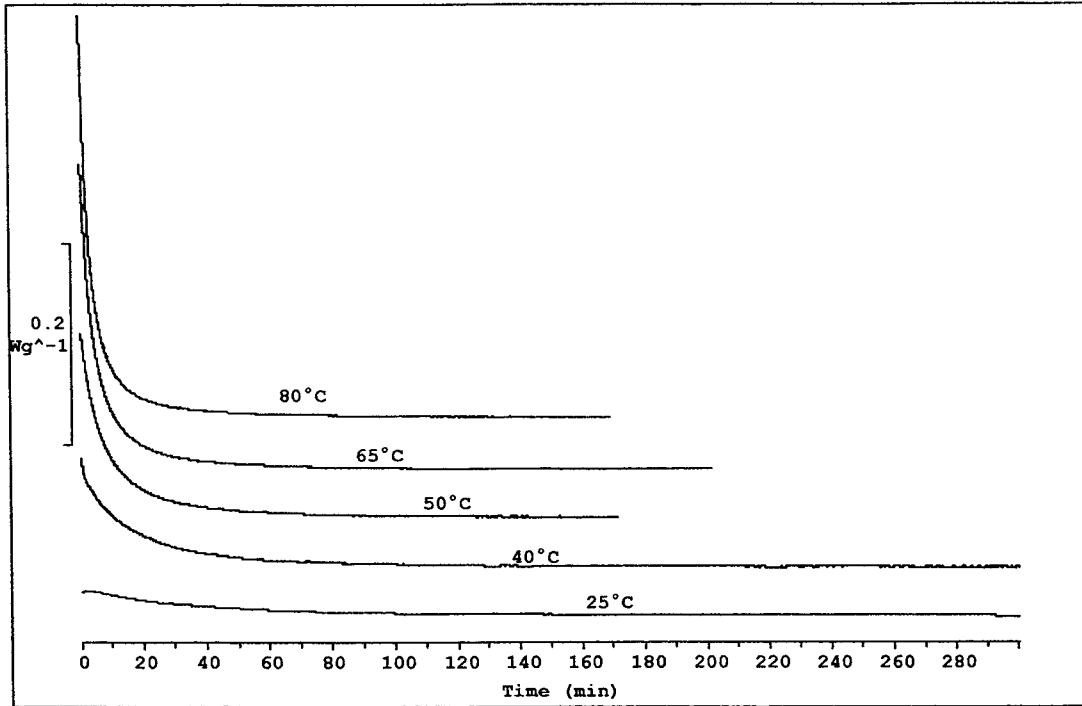
Figure 3 DSC curves from the isothermal mode at different temperatures.

stant for a certain conversion α and is described by the basic kinetic equation

$$\frac{d\alpha}{dt} = k_0 e^{-E_a/RT} f(\alpha) \qquad (3)$$

where k_0 (preexponential factor) and E_a are Arrhenius parameters, α is the extent of conversion, $f(\alpha)$ is the reaction model, t is time, T is the temperature, and R is the gas constant. In practice, it is more convenient to use the integral
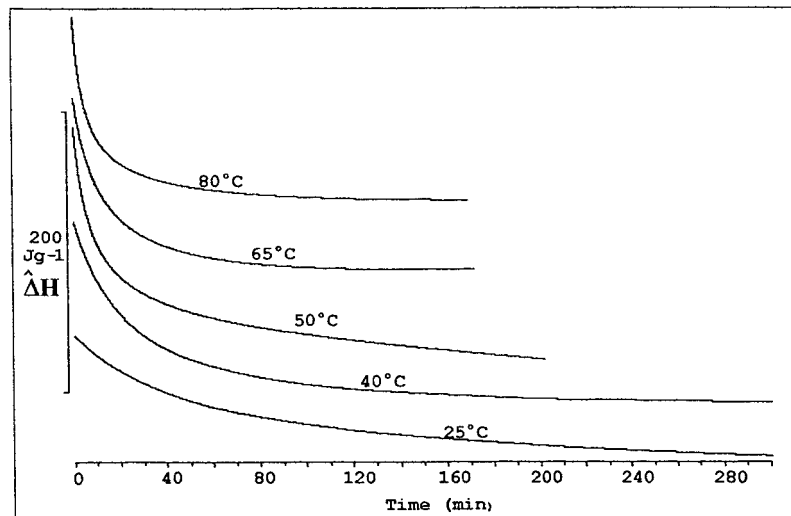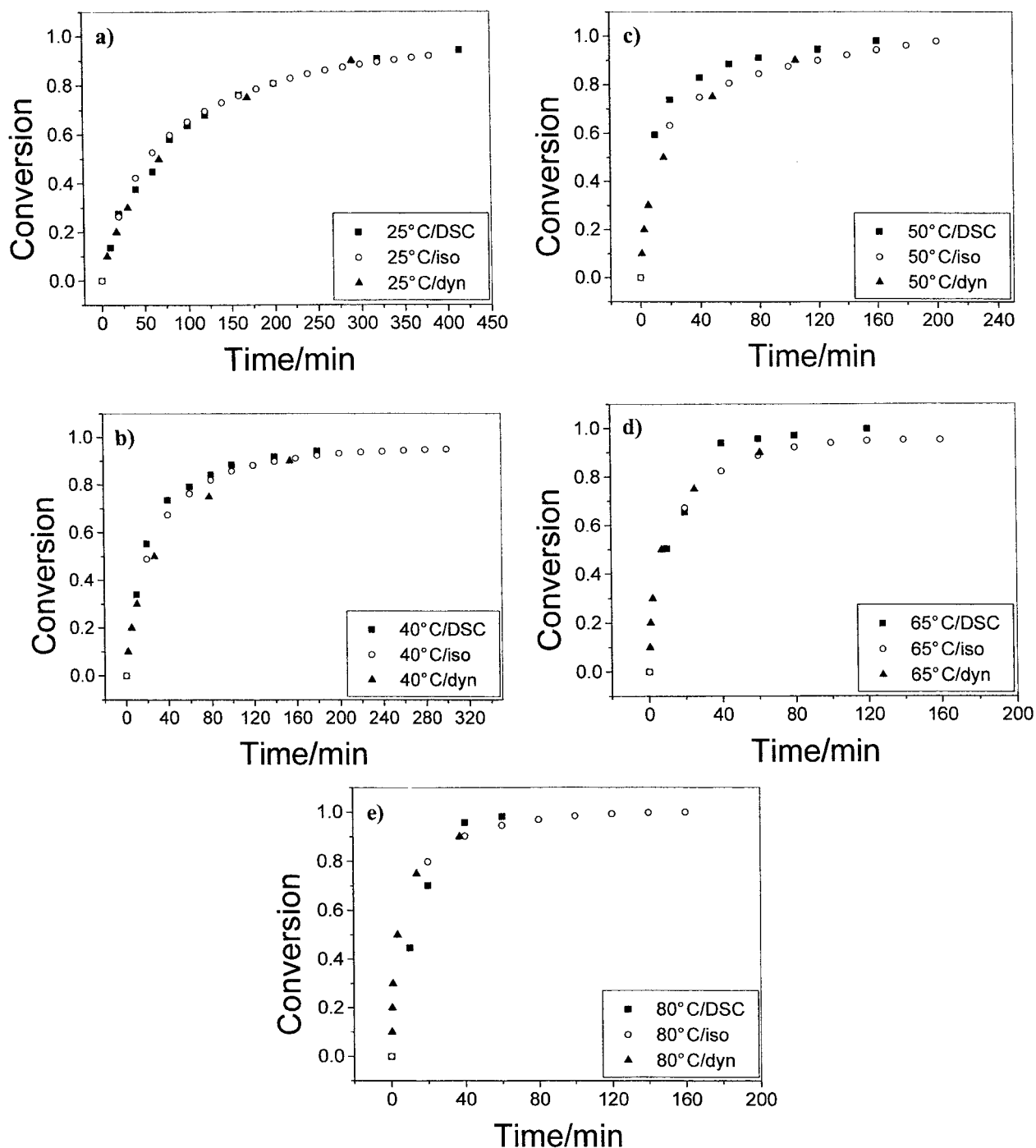

Figure 4 Enthalpy changes versus curing time obtained from the isothermal mode of DSC measurement at different temperatures.

Figure 5 Conversion versus curing time at (a) 25, (b) 40, (c) 50, (d) 65, and (e) 80°C from three different methods: the traditional dynamic (DSC) and the isothermal (ISO) modes of DSC measurements and the application of the model-free isoconversional method to analyze the data from the fast-curing dynamic mode.

forms of eq. (3). In this study, E_a was obtained from the following equation:

$$\ln \frac{\beta}{T_\alpha^2} = \ln\left[\frac{Rk_0}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \qquad (4)$$

where $\beta = dT/dt$ is the heating rate and $g(\alpha) = \int f(\alpha)d\alpha$.

DSC scans from the fast-curing dynamic mode at different heating rates are shown in Figure 6. The conversion α was determined from fractional
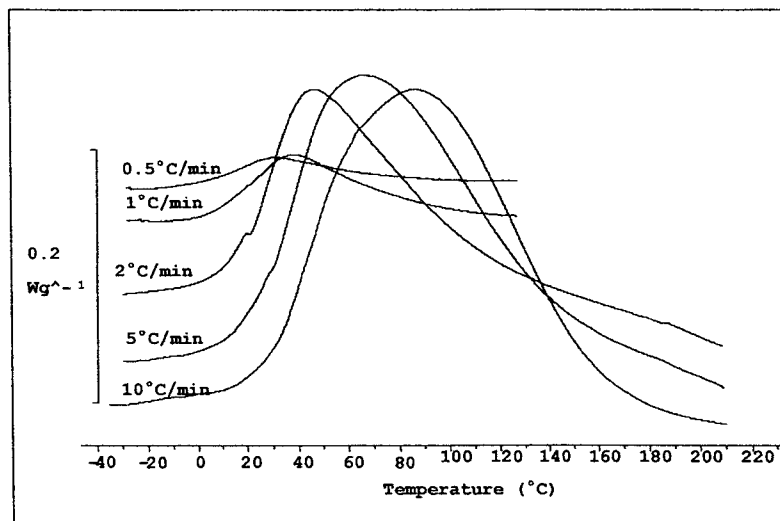
Figure 6 DSC scans from the fast-curing dynamic mode at different heating rates.

areas of DSC peaks, and the E_a's for each conversion α were calculated from eq. (4). The resulting dependence of E_a on α is presented in Figure 7. E_a decreased during the curing process from 125 to 28 kJ/mol. Half of the decrease took place at conversions $\alpha < 10\%$. In a previous study,[28] we determined the apparent E_a of 40 ± 3 kJ mol^{-1} for the curing process of the same PU by applying three different methods. In these methods, the E_a's were estimated in terms of single-step kinetics, that is, under the assumption of constant E_a throughout the curing process. Therefore, the obtained values were averages that were rather in-

sensitive to the changes in the mechanism and kinetics during the curing process. Thus, direct comparison with these results of changing E_a cannot be made, although it seems that the previous values represent the average value of E_a in the conversions from 20 to 100%.

The integration of eq. (3) leads to the basic equation of the isoconversional method. The time to a certain conversion α is[14,24]

$$t_\alpha = [\beta e^{-E_\alpha/RT_0}]^{-1} \int_{T_0}^{T_\alpha} e^{-E_\alpha/RT} \, dT \qquad (5)$$
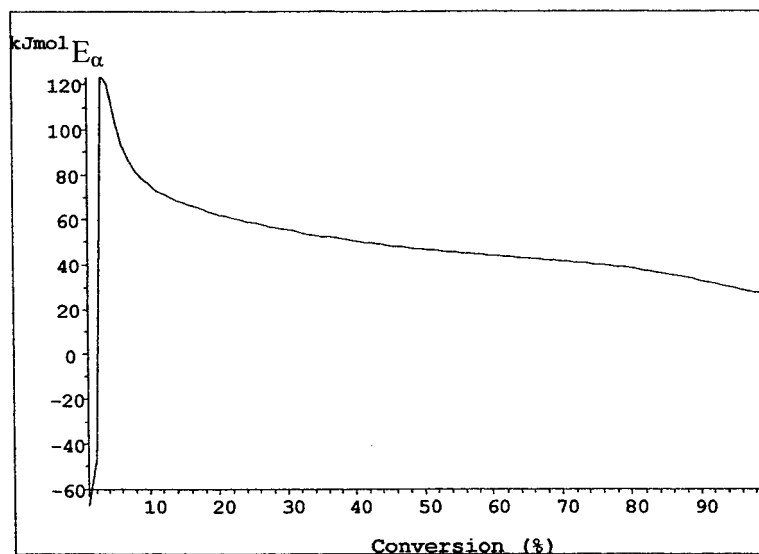

Figure 7 E_a versus the conversion calculated by the isoconversional method.

The conversion versus the curing time obtained from the traditional dynamic mode, the isothermal mode, and predicted by the model-free isoconversional method of DSC measurement is shown in Figure 5 for five different temperatures: 25, 40, 50, 65, and 80°C. The predicted conversions α_{MFK} with the isoconversional mode were in good agreement with the other two methods. Thus, the obtained dependence of E_a on α seems to be reliable, and the assumption of constant E_a for a certain conversion is reasonable. Equation (5) suggests the dependence of E_a on α is the only information necessary to satisfactorily predict the cure at different temperatures. This is primarily because the entire dependence of E_a on α substituted into eq. (5) implicitly takes into account the actual complexity of the cure.

CONCLUSIONS

The results obtained from the isothermal and model-free isoconversional modes of the DSC measurements are in very good agreement with those obtained from the traditional dynamic mode. Thus, both of these methods can be used for monitoring the curing process of the PU system. The isothermal method gives a more accurate and reliable description of the curing process than the traditional dynamic method. Also, the isothermal measurements are easier to perform. The model-free isoconversional method is very flexible because the data are not forced to fit into any particular form, and it offers a reliable mathematical description of the process. The basic idea in this method is that the reaction rate at a constant conversion depends only on the temperature. For a single-step process, E_a would be independent of α and could have the meaning of the intrinsic E_a. For a multistep process, the isoconversional method reveals the dependence of E_a on α. This helps not only to disclose the complexity of a process but also to identify its kinetic scheme. However, neither the explicit model nor its parameters are necessary to predict the curing progress at a given temperature; only the dependence of E_a on α is needed.

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