

CURE KINETICS OF POLYURETHANE/SILICA SYSTEM TOPCOATS IN NAVAL APPLICATIONS

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ABSTRACT

The cure kinetics of polyurethane/silica system resins (used as topcoats in naval applications) are investigated by means of isothermal differential scanning calorimetry. The enthalpy isotherm generated during the sweep increases, while the residual enthalpy decreases. This is due to the increased mobility of the double bonds as the temperature rises, causing a reduction of the remaining and as yet unreacted double bonds, although the sum of $\Delta H_{iso} + \Delta H_{res}$ remains practically constant. By representing the Arrhenius equation in its logarithmic form, two slopes (E_a) are obtained for the same system which indicates that both mechanisms are involved in the curing reaction. The first mechanism may correspond to the crosslinking reaction of the urethane group, while the second may correspond to a secondary reaction due to the high temperatures at which the study is conducted.

Key words: cure kinetics, polyurethane resin, silica, DSC.

INTRODUCTION

This work focuses on curing polyurethane resins that are loaded for use as topcoats (two-component polyurethane) on the superstructures of light vessels, which pro-

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vide a high-gloss paint that is only able to maintain its brightness for a period of between two to four years.

During the curing of thermosetting materials a number of complex chemical and physical changes occur as the material turns from a viscous liquid to a highly crosslinked solid. All these changes, reflected in the cure kinetics and the chemical viscosity of each individual resin system, determine the optimum set of process parameters for the production of a material that will have the best morphological and structural properties for a given application. This is essential to prevent degradation of the coatings (R. García et al., 2010).

Several authors Díaz et al. (2008), Panagiotis et al. (2000) and Yousefi et al. (1997) have experimentally shown that the mechanism responsible for the curing process of a thermosetting resin may be studied through two methods:

Enthalpies residual method: samples are isothermally cured at T_c in a vacuum oven at different curing times, and then analyzed in the calorimeter. We obtain the dynamic DSC curve for each sample and determine the residual enthalpy of the sample.

Conventional isothermal method: by means of dynamic scans can obtain the temperature range at which the resin polymerizes, so we can determine the temperature at which we should perform isothermal sweeps. The next step is to study the kinetics of polymerization at a constant temperature.

Many researchers have proposed various methods to study the curing kinetics of polyurethane systems. Differential Scanning Calorimetry (DSC) is a useful method with which to study the exothermic curing reaction. Using DSC, kinetic analysis can be evaluated by isothermal and non-isothermal methods. By comparing the methods of kinetic analysis from isothermal and non-isothermal DSC measurements, it is evident that using the isothermal DSC experiment, the reaction rate as well as the curing process are simultaneously monitored throughout the course of the reaction. The kinetics parameters are calculated by applying a single method.

In the present study, the curing kinetics of polyurethane/silica were investigated by isothermal DSC. We have taken systems with a high proportion of silica load, cured at several temperatures. They are optimal temperatures for quick curing and for avoiding cracks and structural defects in the moulding production processes. This work will provide information that may be used to optimise the curing conditions of a high-silica loaded polyurethane system.

EXPERIMENTAL

Materials

The polyurethane resin used in this study results from a reaction of isocyanate and polyol. It was cured with a high loading of silica. The weight ratios of the isocyanate/ SiO_2 /polyol/ pentadyone mixture were 100/365/80/0.37.



All the products were supplied by Ciba Specialty Chemicals. The chemicals were mechanically well mixed for 10 minutes at 30 °C to obtain a homogeneous mixture. After mixing the mixture was immediately stored in a refrigerator maintained at –20 °C to prevent any further reaction.

Techniques

Differential scanning calorimetry (DSC TA Instruments Q200) was employed in this study. The initial mixture was taken out of a refrigerator in a vial and left for around 15 minutes at room temperature until the condensed moisture on the surface had completely evaporated. Approximately 10 mg of the mixture was put into a DSC hermetic aluminium pan and then sealed by crimping. The sealed pan with the sample was isothermally cured in the calorimeter for 70 minutes at different cure temperatures. A nitrogen purge gas was used to avoid any oxidation of the samples during the experiments. The cure temperatures in this study were 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 °C.

RESULTS AND DISCUSSION

Prior to the isothermal curing measurements, the sample was scanned from 0 to 200 °C at 5, 10, 15 °Cmin^{–1}. From these scans, we are able to determine the optimum range of curing, temperature of maximum effectiveness and global polymerization enthalpy:

- Optimum range of curing: 20–110 °C
- Temperature of maximum effectiveness: 106.24 °C
- Total polymerization enthalpy: 80.02 J/g

The results of the isothermal experiments are shown in figure 1 for different curing temperatures, T_c . It can be seen that the cure rate of the systems increases with the reaction temperature.

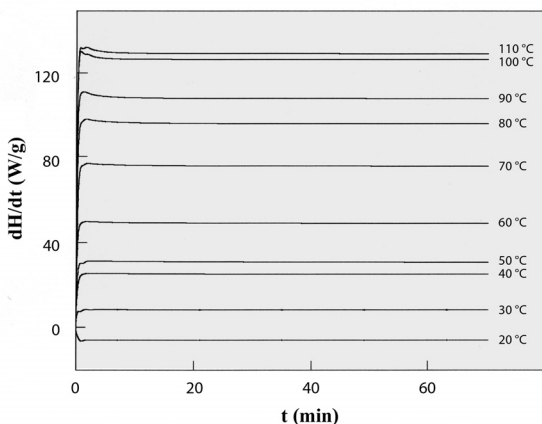


Figure 1. DSC curves from the polyurethane system cured for various temperatures.

All of the resin systems were subjected to dynamic runs at constant heating rates (10 °C/min) from –40 to 200 °C, in order to determine their conversion profiles and total reaction heat released during dynamic curing. From these scans, we are able to determine T_g and examine residual exothermic peaks by cure reactions to obtain the residual heat. In this study, T_g was taken as the inflection point of the step-transition. The values of the isothermal

heat of curing (ΔH_{iso}), and residual heat of curing (ΔH_{res}) are shown in Table I, where we see that the enthalpy isotherm generated during the sweep increases, while the residual enthalpy decreases. This is due to the increased mobility of the double bonds with increasing temperature, causing a reduction of the double bonds remaining unreacted, but the sum of $\Delta H_{\text{iso}} + \Delta H_{\text{res}}$ remains practically constant see Ivankovic et al.; 2003

T (°C)	H _{ISO} (J/g)	H _{RES} (J/g)	H _{ISO} +H _{RES} (J/g)
20°	34.20	43.25	77.45
30°	46.36	38.62	84.98
40°	62.93	20.09	83.02
50°	75.18	7.098	82.27
60°	74.35	4.50	78.85
70°	78.00	1.06	79.06
80°	81.00	0	81.00
90°	82.00	0	82.00
100°	80.00	0	80.00
110°	80.27	0	80.27

Table I. Kinetic parameters for the polyurethane system.

However, certain characteristic aspects of isothermal curing heats should be highlighted. Other authors such as Mahfuz et al.(2004) and Saha et al., (2009) have observed that the reaction takes places very rapidly at the highest curing temperatures, the curing heat during the time required for temperature equilibration is not fully recorded in the DSC curve, which results in a decrease in the values ΔH_{iso} . In our case ΔH_{iso} has not decreased, which is because the reaction speed is slower because of the high silica loading of our systems. Similar behaviour that has already been observed in systems studied previously with other resins (Díaz et al.; 2008). The maximum values are observed in the interval of 80-110 °C for these systems. In these temperature intervals, the values of ΔH_{iso} are very close to those measured non-isothermally at 10 °Cmin⁻¹: 80.02 J/g.

The following expression calculates the theoretical reaction rate, $(d\alpha/dt)$, from the heat flux as a function of the curing time, $(dH/dt)_t$:

$$\frac{d\alpha}{dt} = \frac{\left(\frac{dH}{dt}\right)_t}{\Delta H_{\text{din}}} \quad (1)$$

where, total generated enthalpy is that obtained from dynamic scanning, ΔH_{din} . In Figure 2, we can see the curves thus obtained at different temperatures. In this figure we see that the time required to reach maximum speed torque becomes smaller as



the temperature increases. This behavior is explained by the increased mobility of the double bonds with increasing temperature, as the residual enthalpy decreases.

From the enthalpy generated during the reaction, the evolution of the global conversion may also be calculated on the basis of the following theories:

- The density and heat capacity of the resin gradually changed in the liquid-solid transition phase within the temperature range in use.
- The reaction can be complete if the temperature is high enough for a sufficiently long period of time. The amount of heat generated during the curing reaction is directly proportional to the degree of cure of the sample at that time.

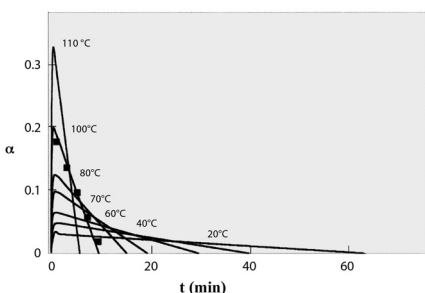


Figure 2. Times dependencies of the isothermal curing degree at 20, 40, 60, 70, 80, 100 and 110 °C.

ly long period of time. The amount of heat generated during the curing reaction is directly proportional to the degree of cure of the sample at that time.

The degree of cure, α , at any time t during the isothermal reaction can be obtained from:

$$\alpha = \frac{\Delta H_{din} - (\Delta H_{res})_t}{\Delta H_{din}} \quad (2)$$

Where $(\Delta H_{res})_t$ is the residual enthalpy at each instant t , which is obtained by integrating the dynamic curve to perform a dynamic scan on the same sample that has undergone an isothermal scan at every instant t .

Figure 3 represents the evolution of the reaction rate versus time for the different temperatures in use. Note that the reaction rates increases as the temperature rises, which in turn increases the mobility of double bonds, as already discussed above. However, total conversion was not reached at any of study temperatures, such that the double bonds remain “trapped” in the microgel structure, as observed by Catherine et al. (2000) and Um et al.(2002).

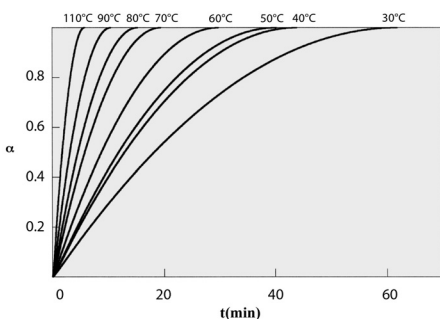


Figure 3. Time dependencies of the isothermal curing degree for polyurethane system.

Once we know the reaction rates and fractional conversions they can be represented as $d\alpha/dt$ vs α with the different temperatures in use (figure 4). It observed that the maximum speed is reached at times near the gel time, suggesting that the decline in the reaction rate is related to the sharp increase in viscosity that occurs during gelation.

On the other hand, differential scanning calorimetry has been used to determine the activation energy of the process. The rela-

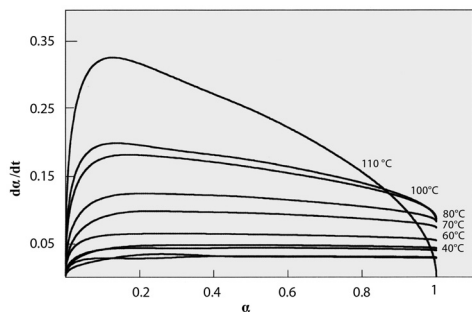


Figure 4. The isothermal reaction rate as a function of curing degree at 40, 60, 80, 90, 100 and 110 °C.

relationship between the activation energy, the heating rate and temperature which produces the maximum exothermic peak is based on the work of Malucelli et al.; 2005. It was observed that the extent of the reaction at the maximum exothermic peak is constant and independent of the heating rate. Based on this fact, the relationship between heating rate and the temperature at which the maximum, T_m , appears is given by the expression:

$$\frac{d(\ln v)}{d(1/T_m)} = -\frac{E_a}{R} - 2T_m \quad 3$$

As v represents a function of $1/T_m$ (Figure 5), we can obtain a straight line the slope of which may be used to calculate the activation energy, that has a value of 55.026 kJ/mol.

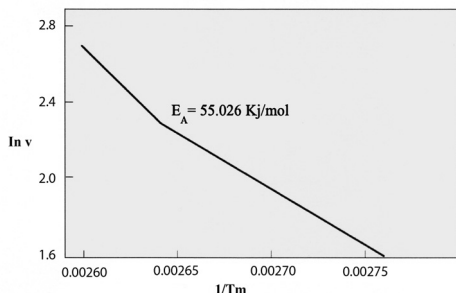


Figure 5. The $\ln v$ versus $1/T_m$ for polyurethane samples.

A study by DSC is very useful for the determination of the kinetics of curing of these resins. The data obtained by this technique can be used for the kinetic study of the isothermal curing reaction. Its simplest model corresponds to the expression of order n :

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

where, $d\alpha/dt$ is the reaction rate, α , is the degree of conversion (degree of cure), n is the reaction order and k is the rate constant, which depends on temperature and is given by the Arrhenius equation:

$$k = A \exp(-E_a / RT) \quad 5$$

where, E_a is the activation energy of the reaction, A is the pre-exponential factor, R the universal gas constant and T the absolute temperature isothermal. For an isother-



mal test, equation (2) predicts the maximum reaction rate at time 0, so if an isothermal process is characterized by a thermogram showing its maximum velocity at a point other than the initial one, the so-called autocatalytic model is used by Silva et al. (2010) and Malucelli et al. (2005) expressed in the following form:

$$\frac{d\alpha}{dt} = K \cdot \alpha^m \cdot (1 - \alpha)^n \quad 6$$

where, $d\alpha / dt$ = reaction rate, α = degree of conversion and k , m and n = kinetic parameters of the model.

Up until now, it had been considered that total conversion was reached at the end of the curing process, however a linear dependence must exist between the final degree of conversion and the study temperature (test Panagiotis et al.; 2000). This behavior leads to reconsider the kinetic equations, in such a way that the reaction rate is considered to be 0 when it reaches the maximum degree of cure. Thus, the expression for the autocatalytic model is given by the following expression:

$$\frac{d\alpha}{dt} = k \cdot \alpha^m \cdot (\alpha_m - \alpha)^n \quad 7$$

where, α_m is the degree of conversion reached at the maximum test temperature. The parameters k , m and n for each temperature are obtained by the linear regression multiple. For a first approximation of the value of n , the expression is written in logarithmic form in the autocatalytic model see Silva et al.; 2010:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k \cdot \alpha_m) + n \cdot \ln(\alpha_m - \alpha) \quad 8$$

A representation of $\ln(d\alpha / dt)$ versus $\ln(1 - \alpha)$ gives a straight line whose slope yields the value of n , as shown in Figure 6. Both m and k may be rearranged as follows to obtain the value of the above equation:

$$\ln\left(\frac{d\alpha/dt}{(\alpha_m - \alpha)^n}\right) = \ln k + m \cdot \ln \alpha \quad 9$$

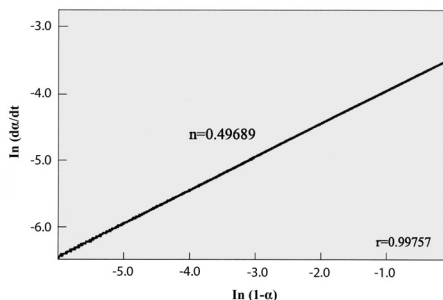


Figure 6. The $\ln (d\alpha / dt)$ vs $\ln (1-\alpha)$ for polyurethane samples.

Representation of the first term of the equation, using the value of n obtained above, as a function of $\ln \alpha$, which results in a straight line that is used to calculate the value of m of the slope and the value of k from the intercept of the origin (Figure 7).

Applying the above process gives a first approximation, and more precise values for an iterative procedure are then applied. The new value of n is obtained from the equation that is rearranged as follows:

$$\ln \left(\frac{d\alpha / dt}{k\alpha^m} \right) = n \cdot \ln (\alpha_m - \alpha) \quad 10$$

The first term of the equation is calculated from the m and k values obtained and plotted against $\ln (\alpha_m - \alpha)$, obtaining a straight line the slope of which is the new value of n . With this value of n , the new values of m , k , are obtained through the process described above. The values obtained in this way were very similar to those calculated in the first calculation (Xie et al., 1993).

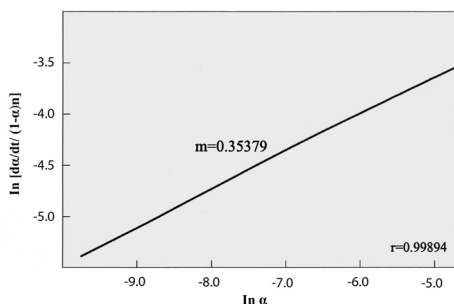


Figure 7. The $\ln (d\alpha / dt (1-\alpha)^n)$ versus $\ln \alpha$.

In Table II, we can see the kinetic parameters, where m and n are orders of reaction of the system and k is the reaction rate constant. In the range of polymerization from 20 to 110 °C, the reaction order to monomer undergoes a slight increase that can be attributed to a change in the reaction mechanism, but which is not considered a representative variation and is therefore not taken into

account. Thus, the average value has been assigned 1. Under analysis, the observed rate of polymerization increases with increasing temperature.

Given this dependence on temperature, the Arrhenius equation is satisfied, which expressed in its logarithmic form is:

$$\ln k = \ln A - E_a/RT \quad 11$$



T (°C)	n	m	n + m	K (min - 1)
20	0.49761	0.35377	0.85138	0.024
30	0.50134	0.31896	0.82030	0.050
40	0.49717	0.37823	0.87540	0.052
50	0.49889	0.35553	0.85442	0.049
60	0.50201	0.34512	0.84713	0.063
70	0.50309	0.35849	0.86158	0.093
80	0.50303	0.35894	0.86197	0.108
90	0.50652	0.35650	0.86302	0.144
100	0.50650	0.35037	0.85687	0.133
110	0.50700	0.35870	0.86570	0.271

Table II. Kinetic parameters for the autocatalytic model.

By representing $1/RT$ vs $\ln k$, we can determine the slope of the line to obtain the activation energy of the system. One can see from Figure 8 that this system has 2 pending, which indicates that two mechanisms are involved. The first mechanism may correspond to the crosslinking reaction of the urethane group, while the second may correspond to a secondary reaction due to high temperatures at which the study is conducted (Malucelli et al.; 2005).

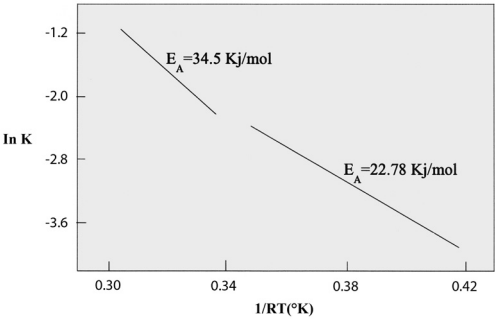


Figure 8. Representation of the Arrhenius law for polyurethane samples.

The values of activation energy obtained are:

$$\begin{aligned} E_{A1} &= 34.50 \text{ kJ/mol} \\ E_{A2} &= 22.78 \text{ kJ/mol} \\ E_{\text{Total}} &= 57.28 \text{ kJ/mol} \end{aligned}$$

This energy is very similar to that obtained experimentally in Figure 5 (55.026 kJ/mol), which suggests that the autocatalytic model is reliable.

CONCLUSIONS

In the present study, the curing kinetics of polyurethane/silica have been investigated by isothermal DSC. We have examined systems with a high proportion of silica load, cured at several temperatures. The conventional isothermal method allows us to obtain very similar values of the enthalpies of polymerization using both dynamic and isothermal sweeps. By representing the equation in its logarithmic form, the Arrhenius equation gives us two slopes (Ea) for the same system which points to the



presence of two curing reaction mechanisms. The first mechanism may correspond to the crosslinking reaction of the urethane group, while the second may correspond to a secondary reaction due to the high temperatures at which the study was conducted. Furthermore, the value of the activation energy is similar to that obtained by other methods which points to the reliability of the autocatalytic model.

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CINÉTICA DE CURADO DE PINTURAS DE ACABADO, PARA APLICACIONES NAVALES, COMPUESTAS POR POLIURETANO Y SÍLICE

RESUMEN

En este trabajo hemos estudiado, mediante calorimetría diferencial de barrido (DSC), la cinética de curado de resinas de poliuretano cargadas con sílice, utilizadas como pinturas de acabado en aplicaciones navales. Hemos observado que la entalpía generada en los barridos isotermos realizados aumenta mientras que la entalpía residual de la muestra disminuye. Este comportamiento se debe a la mayor movilidad de los dobles enlaces a medida que aumenta la temperatura, aunque la suma de $\Delta H_{\text{iso}} + \Delta H_{\text{res}}$ se mantiene prácticamente constante. Cuando representamos la ecuación de Arrhenius en su forma logarítmica, obtenemos dos rectas con pendientes diferentes lo cual indica la existencia de dos mecanismos en la reacción de curado en estas pinturas. El primer mecanismo puede corresponder a la reacción de reticulación del grupo uretano, mientras que el segundo sería el responsable de una reacción secundaria, consecuencia de las altas temperaturas a las que se lleva a cabo el estudio.

METODOLOGÍA

En el presente estudio hemos realizado un exhaustivo estudio de todos los parámetros implicados en el proceso de curado del sistema poliuretano/sílice, utilizado como pintura de acabado en aplicaciones navales.

Materiales

La resina utilizada en este estudio resulta de una reacción de polimerización entre el isocianato y el polioliol con una alta concentración de sílice. La composición de la mezcla fue de 100/365/80/0.37 para un sistema isocianato/sílice/polioliol/pentadiona.

Técnicas

La técnica experimental utilizada en este estudio ha sido la calorimetría diferencial de barrido (DSC TA Instruments Q200). Las muestras utilizadas no superaron los 10 mg de masa, una vez sellado el crisol, éste es introducido en el horno calorimétrico, donde se realizaron los correspondientes barridos isotermos y dinámicos. Las temperaturas de curado utilizadas fueron were 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 °C.



Método

Diversos autores han demostrado experimentalmente que el mecanismo seguido por las resinas termoestables en su proceso de curado se puede estudiar a través de dos métodos:

- *Método de las entalpías residuales*: aquí las muestras son curadas isotérmicamente a una T_c en una estufa de vacío a distintos tiempos de curado t_c , y posteriormente se analizan en el calorímetro. Para cada muestra se obtiene la curva DSC dinámica y se determina la entalpía residual de la muestra.
- *Método isotérmico convencional*: por medio de los barridos dinámicos podemos obtener el intervalo de temperatura a la que polimeriza la resina, de esta forma podemos determinar la temperatura a la que realizaremos los barridos isotérmicos. El siguiente paso consiste en estudiar la cinética de polimerización a temperatura constante.

En nuestro caso hemos empleado en primera instancia el método isotérmico convencional y luego una vez determinado los parámetros de intervalo de curado, temperatura óptima y entalpía de polimerización hemos empleado el método de las entalpías residuales. Este método nos ha permitido determinar el resto de los parámetros cinéticos del sistema como son: constante de velocidad, orden de reacción, grado de conversión, energía de activación, etc.

CONCLUSIONES

El método isotérmico convencional nos permite obtener valores muy similares de las entalpías de curado o polimerización obtenidas por los barridos dinámicos. Si representamos la ecuación de Arrhenius, en su forma logarítmica, obtenemos dos rectas con pendientes diferentes (E_a) correspondientes a los dos mecanismos de curado que presenta el sistema. Además el valor de la energía de activación así obtenido es similar al obtenido por otros autores y métodos lo cual nos indica la fiabilidad del modelo autocatalítico elegido en este estudio.