

Influence of Aromatic Amine Hardeners in the Cure Kinetics of an Epoxy Resin Used in Advanced Composites

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Composite structures for aerospace applications are mainly made by the well-known prepreg technology. In order to achieve adequate prepreg processing schedules, and consequently maximum fiber strength utilization, one has to know in deep the cure kinetics of matrix, which held the fibers together. This work describes a procedure to study the cure kinetic and has as example how aromatic amine hardeners influence the cure kinetics of an epoxy resin used in advanced composites. The investigation was carried out by using the DSC technique and it was found that depending on the system used the cure kinetics of the formulation obeys order n or autocatalytic order.

Keywords: epoxy resin, cure kinetic, DSC, advanced composites

1. Introduction

Structural composites are engineering materials made of oriented reinforcing fibers dispersed in a metallic, ceramic or polymer matrix¹. The use of composites moved forward in components of aircrafts and space structures due mainly to project flexibility, easy processing, lower density ($\sim 2 \text{ g.cm}^{-3}$), as well as high mechanical strength and modulus. That matcher the requirements of the structures during service^{2,3}. This turns the composites particularly attractive as substitutes of the metallic alloys for high demanding aeronautical and space applications.

This work focuses on polymer composites, which are materials made of reinforcing fibers in an embedded polymer matrix. However, the properties of composites depend on other factors, such as the moulding techniques and cure cycles⁴. As a consequence, it is very important that the values of the properties used during the design phase of a certain component consider the process variables, in order to obtain products of high quality and required mechanical strength.

Thus, it is fundamental to know all the parameters involved in the cure cycle. For that, one of the most used techniques in the study of the kinetics of polymerization is the differential scanning calorimetry (DSC). The understanding of the cure kinetics that will delineate the cure cycle to be used in the processing of prepregs is of fundamental importance for good quality advanced composites⁴. The cure kinetics can be followed by using two DSC methods: dynamic and isothermal⁵.

The isothermal method can identify two types of reaction: n order or autocatalytic order^{6,7}. If the maximum peak of the isotherm is close to $t = 0$, the system obeys kinetics of n order and it can be studied either by dynamic or isothermal methods^{5,7-9}. In the case when the maximum peak is formed in between 30 and 40% of the total time of the analysis, the cure is autocatalytic and it should be studied exclusively by isothermal method^{5,7-9}.

The n order model assumes that the reaction obeys the Equation 1:

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

where v is the velocity of reaction, α is the reaction rate or conversion rate in a given time t . By a linear plotting Equation 1, it is possible to know the values of n and k .

Conversely, the autocatalytic model considers independent reaction orders: m and n , as shown in Equation 2:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \quad (2)$$

The parameters $d\alpha/dt$ and α are obtained from DSC isotherms. The reaction rate is obtained by the reaction heat ratio (dH/dT), at a temperature T , from the total enthalpy ΔH_o (equation 3).

$$\frac{d\alpha}{dt} = (dH/dt) / \Delta H_o \quad (3)$$

where ΔH_o is the experimental enthalpy corresponding to the total area up to the reaction peak or from the theoretical enthalpy found in the literature.

The value of α is determined by measuring the partial reaction heat at a time t , ΔH_p , divided by the total reaction heat is taken from the isothermal reaction, ΔH_{iso} , (Equation 4)

$$\alpha = \frac{\Delta H_p}{\Delta H_{iso}} \quad (4)$$

Finally, with a minimum of three isotherms, one can obtain the kinetic parameters E (activation energy) and A (pre-exponential factor) from Arrhenius plots.

Excellent reviews concerning mechanisms and kinetics of thermoset cure are presented in literature^{4,8,10-13}. Despite the considerable current research effort in the field of epoxy resin cure, numerous issues have yet to be addressed. There is a number of partially conflicting explanations proposed in recent years for the reaction mechanisms of epoxy system cure^{4,10,13-18}. This work describes a procedure to study the cure kinetic of polymeric systems and has as example how aromatic amine hardeners influence the cure kinetics of an epoxy resin used in advanced composites.

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2. Experimental

2.1. Materials

2.1.1. Polymer resin base

An epoxy resin of the type diglycidyl ether of bisphenol-A (DGEBA), having commercial name D.E.R. 331 - Dow Chemical Products Ltda, was used as received. This resin is liquid at room temperature, it is bifunctional and have an average molecular mass of 378 g.mol⁻¹; an epoxy equivalent weight of 189 and 23% of epoxy groups. Epoxy resin cures mainly by opening the pendant epoxy group either at room temperature or high temperature, depending on the curing agent used¹⁰.

2.1.2. Curing agent

The curing agents used were the diphenyl diaminosulfone (DDS), commercial name HT 976, supplied by Hustman and the 4,4'-diamine-diphenylmethane (DDM), code D.E.H.50, supplied by Dow Chemical Products.

DDS is a powdered curing agent, pink color, and have to be melted for use. DDM is provided as brown flakes, and also have to be melted for use. Both curing agents are aromatic amines. Table 1 lists physical properties of DDS and DDM curing agents.

2.1.3. Preparation of the formulations

The formulations are prepared by mixing the DGEBA resin in appropriate stoichiometric proportions of 30 pph DDS and 27 pph DDM. Then they are heated up to the hardener melting temperature, for approximately 10 min, being soon cooled down in the same interval of time.

2.1.4. Characterization

DSC scannings were carried out in a Perkin-Elmer-7 Thermal Analysis System, previously calibrated with indium, under constant flow of nitrogen (100 mL.min⁻¹) and heating rate of 10 °C.min⁻¹. The weight of the samples varies from 10 to 15 mg. Sealed aluminum pans were used.

For each formulation a scanning was accomplished (Table 2), in which total heat of reaction (ΔH_p) and isothermal temperatures for kinetic studies were obtained. The isothermal scanning gives the value of the partial heat of reaction (ΔH_p). Table 2 shows the experimental conditions for obtaining the isotherms for the two formulations under study.

The computer program Isothermal Kinetics, in the central module of the Perkin Elmer equipment, allows the determination of variables related with the cure kinetics of each formulation. This computer software also provides the reaction order that better fits to the resin system under study²⁰.

3. Results and Discussion

Table 3 presents the results of the dynamic runs obtained by DSC of the epoxy systems DGEBA/DDS and DGEBA/DDM. The onset, peak and final temperature taken from the dynamic run have lower values for the DGEBA/DDM system than the DGEBA/DDS system. On the other hand, the total heat of DGEBA/DDM system is higher than DGEBA/DDS system.

For the DGEBA/DDM system the reaction temperatures are lower than for the DGEBA/DDS system. This happens, probably, due to the fact that DDM has a lower melting point in relation to DDS (Table 1), which in turn needs a lower energy to melt and then proceeds the cure reaction. Besides that, there is a different between the relative

Table 1. Properties of the diphenyl diamine sulfone and of the 4,4'-diamine-diphenylmethane¹⁹.

Curing agent	DDS	DDM
Melting point peak (°C)	175	94.0
Weight of active hydrogen (g.mol ⁻¹)	57	49.5
Molecular weight (g.mol ⁻¹)	248	226

Table 2. Parameters used for obtain of the curves of DSC.

DSC Curves	DGEBA/DDM	DGEBA/DDS
Dynamic run	T _{initial} = 50 °C T _{end} = 250 °C	T _{initial} = 75 °C T _{end} = 330 °C
Isothermal run 1	100 °C	160 °C
Isothermal run 2	110 °C	170 °C
Isothermal run 3	120 °C	190 °C
Isothermal run 4	130 °C	200 °C

Table 3. Comparison among the dynamic scanning of the formulations DGEBA/DDS and DGEBA/DDM.

Dynamic run	DGEBA/DDM	DGEBA/DDS
Onset temperature (°C)	86	123
Peak temperature (°C)	157	226
Final Temperature (°C)	224	298
ΔH_0 (J.mol ⁻¹)	- 374	- 271

reactivity of the DDS and DDM due to the electron density of two molecules. DDS should be less reactive since the sulfone moiety will pull electron density away from the amine groups, whereas the methane moiety in DDM will not.

It is noticed that the reaction between epoxy resin and DDM has a higher amount of heat released than the one with DDS. This suggests that in the case of prepreg processing the DGEBA/DDM formulation would be more sensitive to the effects of accelerated cure than the DGEBA/DDS formulation. Therefore, in the determination of cure cycles for composite processing, the control of the processing conditions must be much more controlled when using the DDM hardener.

Being known the dynamic run of the DGEBA/DDS and DGEBA/DDM formulations three specific temperatures were chosen for the isothermal runs. The isothermal temperatures were chosen between the beginning of the reaction (X_p) and peak temperature, because main kinetic events of the reaction occur in that area. Another isothermal run was obtained at a temperature of one fourth distance from the initial temperature and the peak temperature, which gives information on the kinetic order of the studied formulation system^{5,7,8}.

Figure 1 shows a DSC curve where maximum evolution of heat, or the maximum reaction rate (da/dt), occurs at the beginning of the reaction, i.e., at a conversion $\alpha \sim 0$. Therefore, the DGEBA/DDS system obeys n order cure kinetics. The n order kinetics implies that the formulation obeys Equation 1. The order n reaction also describes the shape of the isothermal run (exponential function), as observed in the Figure 1, and gives the necessary data to the study of the reaction mechanism. Thus, the value of n influences the rate of reaction of the formulation, which in turn allows the determination of appropriate cure cycles for composite processing.

Figure 2 exhibits the isothermal run that characterizes the reac-

tion order from the DGEBA/DDM formulation. It is observed that the maximum heat evolution (the maximum reaction rate $d\alpha/dt$) occurs in between 30 and 40% of the total reaction time, i.e., at a conversion $\alpha \neq 0^{6,21}$. Therefore, the DGEBA/DDM system obeys the autocatalytic cure kinetics.

Autocatalytic cure kinetics implies that the formulation obeys Equation 2. The constant m is related to the autocatalytic concentration of the reaction, i.e., the concentration of hydroxyls groups that are being generated as cure proceeds and the constant n is related to the consumption of epoxy groups. Besides, m influences the initial rate of reaction and controls the symmetry of the curve²¹ and the constant n defines the reaction type, i.e., by the shape of the curve. Thus, the total reaction order ($m + n$) is obviously higher than order n reaction kinetics. This means that formulations having reaction kinetics of order n and order ($m + n$) must be treated differently when cure cycles for optimum composite processing schedules are required.

4. Order n cure kinetics

Data from Table 3 and results taken from the isotherms of the formulation DGEBA/DDS system allows calculation of the kinetic parameters that are presented in Table 4. These kinetic parameters were obtained by using the "Isothermal kinetics" software²⁰.

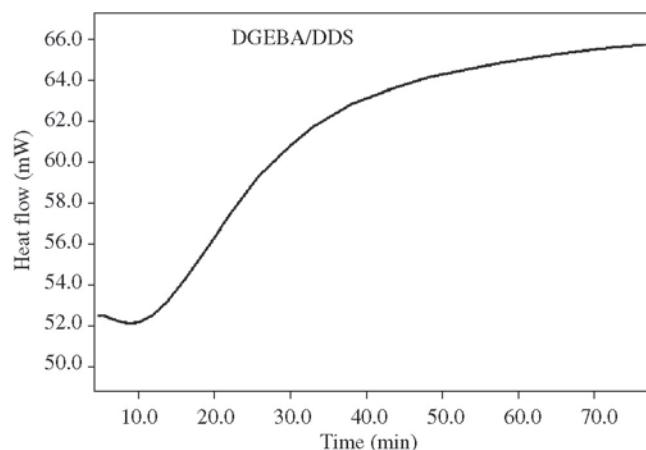


Figure 1. Typical cure isotherms at 170 °C showing n order reaction mechanism for the system DGEBA/DDS.

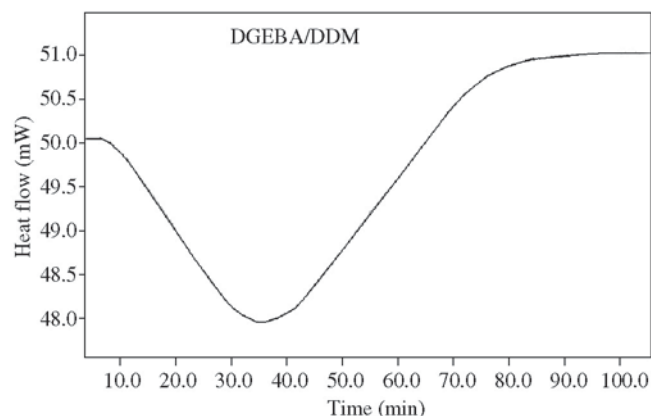


Figure 2. Typical isotherm curve showing autocatalytic mechanism of reaction for the formulation DGEBA/DDM.

It is observed from the results of Table 4 that the value of isothermal ΔH increases (in module) as isothermal cure temperature goes higher. The increase on isothermal reaction temperature for exothermic reactions generates heat in a higher proportion than the heat generated on the reaction itself.

It is also verified that the Arrhenius constant rate (k) and the reaction order n increases as reaction temperature goes higher. The increase in reaction temperature causes a distinct distribution of molecule speeds (and energies) followed by an increase in the average value of energy from reactant molecules. As a consequence, a larger number of molecules have enough energy, through collision, to surpass the activation barrier and, consequently, the reaction rate may increase^{6,22,23}.

The results from isothermal runs allow obtaining the values of the reaction rates and the conversion. Figure 3 shows the reaction rate from each isotherm reaction temperature that was obtained as function of the reaction time for DGEBA/DDS system. There is a maximum of reaction rate for each isotherm reaction temperature. Figure 4 presents the reaction rate ($d\alpha/dt$) as a function of conversion (α) where it is clear a maximum at $\sim 20\%$ conversion for all isothermal reaction temperatures. This maximum conversion for the isotherms is related to the mechanisms for both reaction order n and for the autocatalytic reaction order²¹. Therefore, for DGEBA/DDS system, the plots from Figures 3 and 4 confirm the reaction order n previously found.

Plots from Figures 3 and 4, show also that, in general, the $d\alpha/dt$ value reaches a maximum at a definite time and/or definite conversion. In the plot of Figure 3 it is verified that temperature has a pronounced influence on the reaction rate. At lower temperatures (~ 160 °C) the curve has a smaller slope than at higher temperatures and the reac-

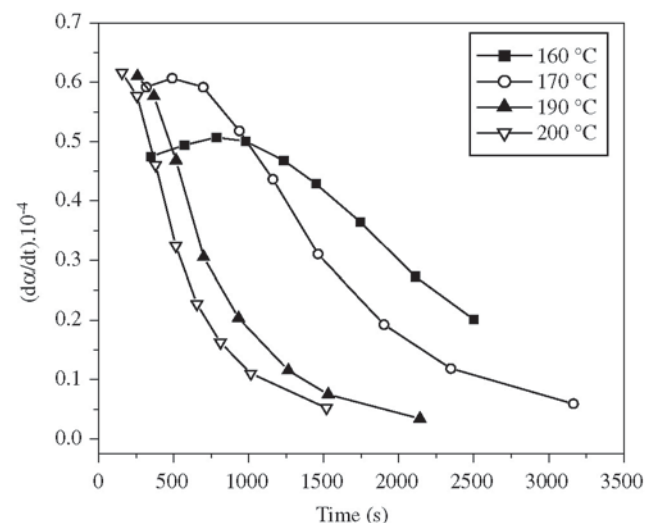


Figure 3. Isothermal reaction rate as a function of reaction time at 160 °C, 170 °C, 190 °C and 200 °C for the system DGEBA/DDS.

Table 4. Results for isothermal enthalpies (ΔH_{iso}) and kinetic parameters (k and n) from the formulation system DGEBA/DDS.

T (C)	ΔH_{iso} (J.g ⁻¹)	k (T)	n
160	-194	$4.50 \cdot 10^{-4}$	0.38
170	-224	$8.99 \cdot 10^{-4}$	0.58
190	-260	$1.43 \cdot 10^{-3}$	0.78
200	-280	$2.01 \cdot 10^{-3}$	0.96

tion takes more time to reach the maximum conversion rate ($d\alpha/dt$). At higher temperatures ($\sim 190 - 200$ °C) the curve becomes steeper in the beginning of the reaction and reaches the maximum reaction rate. Therefore, at the beginning of composite processing, smaller temperatures are desirable once they help an adequate prepreg handling, moulding and cure control. This avoids undesirable fast-uncontrolled reactions, which can compromise quality and properties of the product.

Figure 4 confirms the observations taken from Figure 3. The DGEBA/DDS system has maximum conversion around 15%. According to Equation (1), when conversion (α) is equal to zero, the k (reaction rate constant) value can be found from plots of $d\alpha/dt$ as a function of time or as function of conversion, i.e.:

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha)^n, \text{ [if } \alpha = 0 \text{ thus } d\alpha/dt = k].$$

However, from chemistry point of view such consideration is not valid since there is no reaction at a zero conversion, and, therefore, there is no reaction rate constant. Comparing these data with the k values from Table 4 it is verified that both are of the same order of magnitude.

Figure 5 shows the Arrhenius plot ($\ln k$ vs $1/T$) for DGEBA/DDS formulation. The curve represents the activation energy and the value found is $46.4 \text{ kJ}\cdot\text{mol}^{-1}$. According to the literature, chemical reactions have activation energies in between 30 and $100 \text{ kJ}\cdot\text{mol}^{-1}$. The activation energy of very viscous systems is smaller, $10\text{-}20 \text{ kJ}\cdot\text{mol}^{-1}$ ²³. Therefore, the value of activation energy for DGEBA/DDS system agreed with the values found in literature²⁴⁻²⁹.

5. Mechanism of Autocatalytic Cure

Table 5 shows results for DGEBA/DDM formulation obtained by isothermal reaction runs. The data were calculated by the "Isothermal kinetics" software.

It is observed that, as for the DGEBA/DDM system, the isothermal ΔH , the rate constant and the kinetic exponent n increase proportionally as a function of temperature. Then, a higher number of molecules acquires enough energy for collision, reaching the reaction activation barrier and, consequently, increasing the reaction rate^{6,22,23}. On the other hand, the kinetic exponent m decreases as temperature increase due to the effect of the thermal catalysis, superseding the

autocatalytic effect of m ²¹. Figure 6 illustrates the variation of m and n with the temperature.

It can be verified in Figure 6 that at 78 °C the kinetic exponents m and n have the same value ($m = n = 1.34$). This means that at the early beginning of the polymerization reaction, the autocatalytic effect is the same as the thermal effect. On the other hand, the value of m decreases as cure temperature increases, approaching zero when the temperature reaches nearly 226 °C. It should be noted that, a value nearly constant for the total reaction order ($m + n = 3$) is obtained throughout the polymerization reaction, with n corresponding to nearly 75% and m to 25% of the total reaction order.

The isothermal reaction rate as function of time obtained for the DGEBA/DDM autocatalytic system is shown in Figures 7 and 8. The conversion α is also shown. Each cure isotherm has a maximum at the $d\alpha/dt$ parameter, which is typical for an autocatalytic mechanism of n order²⁰. In this case, the curves are more defined than the ones shown in Figures 3 and 4, according to previous results presented by Seferis²¹.

Figures 7 and 8 also show the influence of the temperature on the reaction rate. The curve obtained at the lowest temperature (100 °C) presents the lowest slope, and the reaction takes longer to reach the maximum conversion rate ($d\alpha/dt$). As temperature increases ($\sim 110\text{-}130$ °C) the curves become steeper, reaching the maximum reaction rate in a short time. Therefore, in order to get a tight control of the polymerization reaction during composite processing, it is advisable to use lower temperatures in the beginning of the cure cycle. This prevents uncontrolled reactions, which could lead to a composite having poor mechanical properties.

The maximum reaction rate occurs at nearly 45% of conversion (Figure 8), suggesting that, when the cure reaction reaches its

Table 5. Results of enthalpy of the isotherms (ΔH_{iso}) and kinetic parameters (k , n and m) of the DGEBA/DDM system.

T (°C)	ΔH_{iso} (J.g ⁻¹)	k(T)	n	m
100	- 347	$3.79 \cdot 10^{-3}$	1.64	1.17
110	- 372	$5.21 \cdot 10^{-3}$	1.76	0.97
120	- 375	$7.67 \cdot 10^{-3}$	1.89	0.96
130	- 380	$10.2 \cdot 10^{-3}$	2.02	0.88

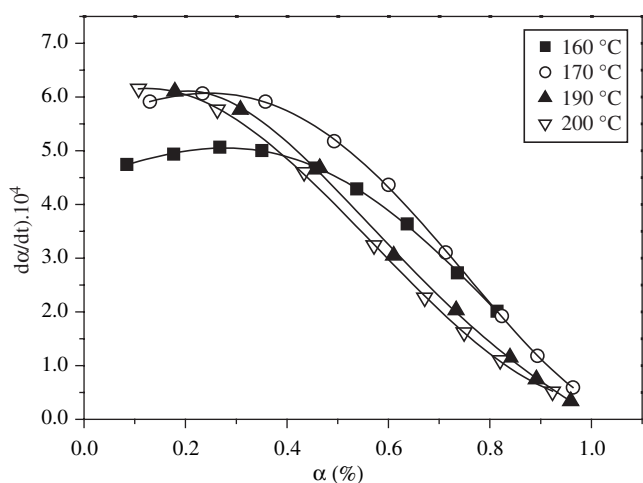


Figure 4. Isothermal reaction rate as a function of the conversion at 160 °C, 170 °C, 190 °C and 200 °C for the system DGEBA/DDS.

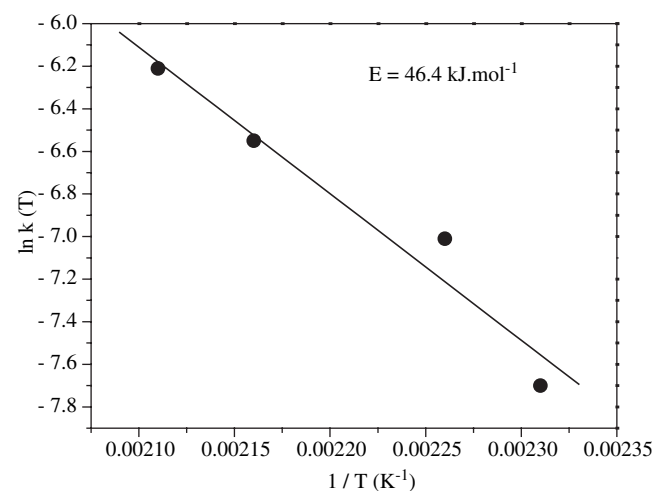


Figure 5. Arrhenius plot of the isothermal reaction rate constants for the DGEBA/DDS systems.

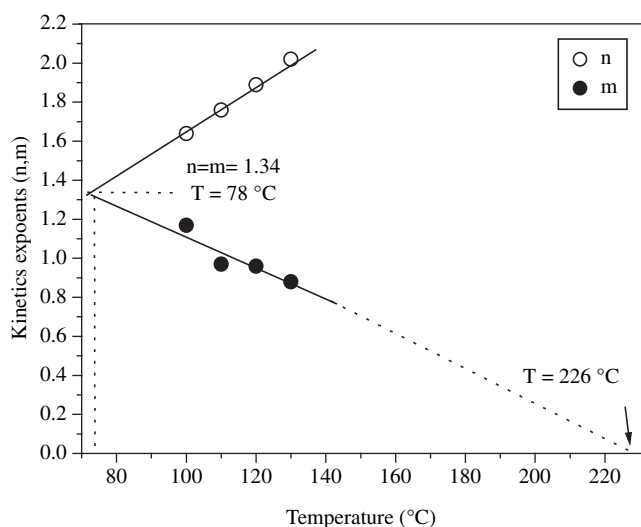


Figure 6. Effect of the temperature on the kinetic exponents m and n of the DGEBA/DDM system.

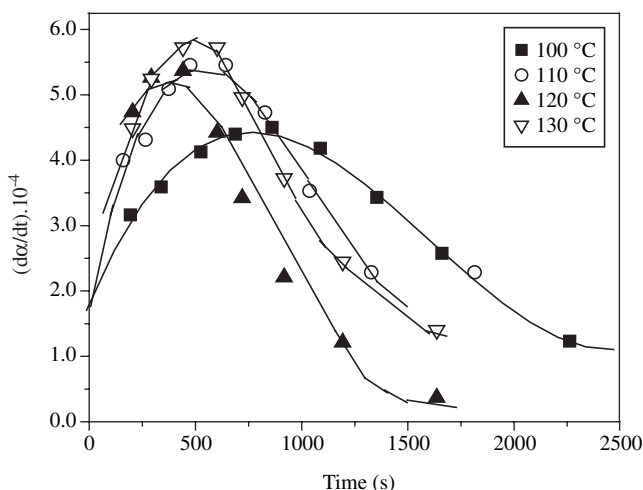


Figure 7. Isothermal reaction rate vs. time for the DGEBA/DDM system.

highest conversion rate, 45% of the total epoxy groups have already been consumed.

Figure 9 shows the activation energy obtained from the slope of the Arrhenius plot of $\ln k$ as a function of inverse absolute temperature ($1/T$). The value of $47.2 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained for the activation energy, which is within the range of $30\text{--}100 \text{ kJ}\cdot\text{mol}^{-1}$ usually found in the literature^{23, 24-27}.

6. Conclusion

The polymerization temperature for the DGEBA/DDM mixture is lower than for the DGEBA/DDS system. The DDM curing agent has a lower melting point than DDS, and consequently, less energy is required to melt and start the polymerization reaction. Besides that, the relative reactivities of the DDS and DDM curing agent are different due to the differences electron density of two molecules. DDS should be less reactive since the sulfone moiety will pull electron density away from the amine groups, whereas the methane moiety in DDM will not.

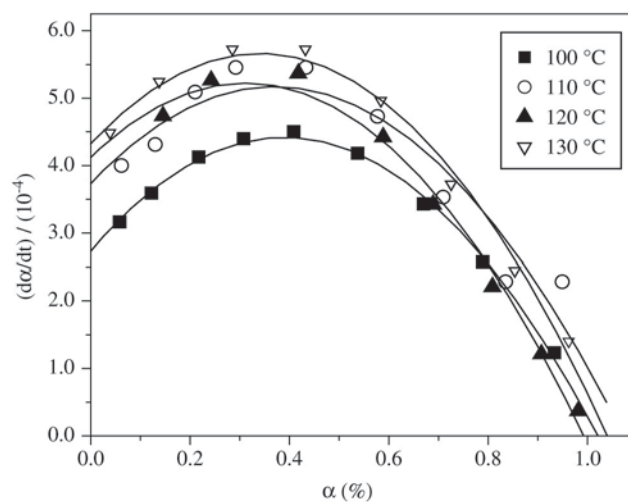


Figure 8. Isothermal reaction rate vs. conversion α for the DGEBA/DDS system

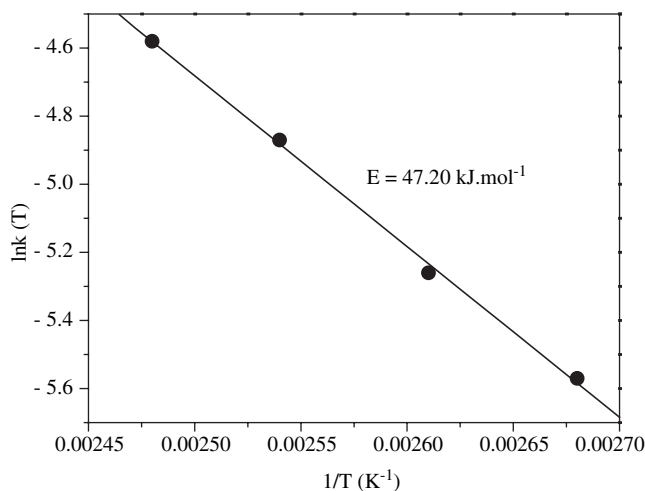


Figure 9. Arrhenius plot for the DGEBA/DDM system.

The DGEBA/DDM formulation has a reaction order ($m + n$) higher than the DGEBA/DDS formulation and, as a consequence, a higher reaction rate. This means that during the prepreg preparation with DDM is necessary to carry out a very tight control of the cure cycle.

The isotherm shapes are related to the reaction order for each formulation. The well-defined isotherms obtained with the DGEBA/DDM formulations are characteristics of an autocatalytic reaction. On the other hand, with the DGEBA/DDS formulations the isotherms are formed nearly the zero time, without definition, indicating reaction of order n .

The activation energy of both, DGEBA/DDM and DGEBA/DDS reactions, are very close to each other and within the range found in the literature.

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