GEL TIME MEASUREMENTS ON CARBON FIBER/EPOXY RESIN PREPREGS

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Abstract

The curing process of a modified epoxy resin/carbon fibre prepreg, Hercules 8552/AS4, has been analyzed by means of differential scanning calorimetry (DSC) and Rheometrics Dynamic Spectrometer (RDS). Isothermal and non−isothermal experiences have been carried out and similar studies have been perfomed on the neat resin Hercules 8552. DSC and RDS data have been compared with the main goal of stablishing a correlation between the gel time determined by both means, together with the ones measured in a Fisher−Johns apparatus.

A simple criterion for obtaining the gel point by DSC measurements has been found. Comparison between the three type of test showed a very good agreement for the calculated gel times. The activation energies of the gelification process have been calculated and similar values have been obtained for the three data series.

1 INTRODUCTION

In the last few years, the modelling of processing of composites has generated considerable interest among engineers and scientists. This type of modelling studies have the ultimate goal of reducing production times, optimizing cure cycles and tailor-making composites with the desired properties.

However, the use of models implies that the chemical and rheological properties of the material need to be known. The term chemorheology was coined to describe a simultaneous change of chemical and rheological properties of thermosets during cure. Unfortunately, a complete chemorheological characterization of the material during cure is a formidable task. Both, the reaction kinetics and resin viscosity are function of time and temperature. A fundamental study will be directed, then, towards the mathematical description of these relationships, in order to be able to predict the degree of cure and viscosity for any cure cycle.

The curing of a thermoset is a very complex process in which several steps are present. Even in the simplest case of the curing of an epoxy resin with an amine, the kinetics of the reaction involves a primary and a secondary epoxy/amine addition reaction, as well as processes of homopolimerization.

In general terms, the chemistry of the cure begins with a linear growing of the chain, followed by branching and finally crosslinking. As the reaction proceeds, the molecular weight increases rapidly and eventually several chains become linked together into networks of infinite molecular weight. This sudden and irreversible transformation from a viscous liquid to an elastic gel is called the gel point, and it marks the onset of the infinite network. Gelation is then, a characteristic of great significance for thermosets.

From a processing viewpoint, gelation is very critical since the polymer does not flow and is no longer processable beyond this point. On the other hand, gelation occurs at a well-defined stage in the course of the chemical reaction, being an important feature to be taken into account for the quality control of aerospace structural materials.

Another phenomenon, distinct from gelation, that may occur at any stage during cure, is vitrification of the growing chains or network. This transformation from a viscous liquid or elastic gel to a glass, occurs when the glass transition temperature of these growing chains or network becomes coincidental with the cure temperature . Vitrification brings an abrupt halt to curing as this is affected by viscosity and molecular mobility. Vitrification is a reversible transition; cure can be brought back by heating as this produces the devitrification of partially cured thermosets.

The entire polimerization process can be divided in two parts separated by the point of gelation. Depending on the temperature and degree of cure, four physical stages can be observed: liquid, ungelled glass, rubber, and gelled glass[1,2]

To characterize the curing phenomena of thermosetting resins, several complementary techniques can be used, and information on a macroscopic as well as on a molecular level can be obtained. These methods include chromatography, infrared spectroscopy, nuclear magnetic resonance, Raman spectroscopy, chemical fractionation and changes in physical properties such as refractive index, density, electrical resistivity and viscosity. In addition, the exothermic curing reaction of thermosetting has been widely studied by means of dynamic mechanical measurements and calorimetry.

There are several reasons for this type of studies to be carried out on prepregs samples:

- Neat resin is not always available for the manufacturer of composite parts and also, the state of advancement of this neat resin may differ from that found in a particular prepreg batch used for the production of composite parts.

- Obtaining the resin from the prepreg is not a solution either, as some other problems can arise, i.e., how to remove the resin from the prepreg without modifying the resin itself. If solvent techniques are used for this purpose, the removal of the last residual solvent is extremely difficult. Residual solvent plasticizes the resin and thereby changes its characteristics. On the other hand, extracting the resin from the prepreg by using heat and mechanical manipulation can stage, and also contaminate, the resin.

- The presence of fiber may affect both the chemical and rheological behaviour of the resin during the cure.

This work focusses on the characterization of the chemistry and rheology of the curing process of a modified epoxy-amine cured/carbon fiber reinforced composite material (Hercules 8552/AS4).

DSC and viscosity data has been obtained and subsequently compared with the main goal of establishing a correlation between the gel time determined by both means. Several isothermal and dynamic conditions have been applied for the curing of prepreg and also, neat resin samples, and results are compared.

2 EXPERIMENTAL PART

The composite material selected for this study was Hercules 8552/AS4 prepreg tape with a 33% resin content. This prepreg represents a current generation 180^0C curing prepreg system. The epoxy matrix is essentially based on a modified epoxy resin with a thermoplastic material added. Both, neat resin and prepreg were supplied from the same production batch by Hercules (H.A.E.S.A.) in β-stage. In this stage, several molecules of the epoxy system have already reacted with the curing agent. Nevertheless, the extent of reaction in this β-stage has been considered negligible for all the calculations carried out in this study

2.1 Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Perkin-Elmer differential scanning calorimeter DSC-7, and sample weights ranging from 10 to 15 mg were used.

- Isothermal studies were performed at 150,158 and 177^0C. Residual heat (ΔH_{res}) was determined by a subsequent run from 50 to 300^0C at a heating rate of $20^0C/min$. The corresponding T_g cured were also obtained from these runs.

- Dynamic measurements were carried out in a temperature range form 50 to 300^0C and heating rates of 5, 10 and $20^0C/min$ were used. Glass transition temperature of the cured samples were determined by a second run in the same temperature range at a heating rate of $20^0C/min$.

2.2 Rheological studies

Rheological measurements were carried out using a Rheometrics RDS-7700 equipment, in a parallel-plate geometry.

Plates of $25mm$ radius were used, and a gap size of $0.6 \pm 0.1mm$ was fixed. Measurements were performed at 10% strain and different angular frequencies ranging from 10 to 100 rad/s were used.

Isothermal and dynamic runs under analogous conditions to the ones previously described in paragraph 2.1 were carried out.

Measurements of the gelification time by using a Fisher-Johns apparatus where carried out at 150, 158 and 177^0C for neat resin and prepreg samples . The gel point was taken as the time at wich no resin movement was observed when moderate pressure was applied.

3 RESULTS AND DISCUSSION

The processing and therefore ultimate properties of thermosets, depend on their composition as well as on the network structure generated before reaching the gel point. Accurate predictions of the material properties imply the knowledgement of the polymerization kinetics and related viscosity changes.

In this work, calorimetric data, viscosity profiles and mechanodinamical properties of Hercules 8552/AS4 have been used to analyze its chemorheological behaviour.

Differential scanning calorimetry constitues a phenomenological approach for studying the kinetics of the curing of thermosets. This type of approach provides a monitorization of some of the changes that take place during the curing without any particular insight into the type of reaction itself. Figure 1 shows, as an example, the DSC obtained for the curing of the neat resin 8552 under isothermal conditions at 150^oC. In this figure a shoulder beyond the minimum of the curing curve can be noticed. Similar results were found for all the experiments performed under other isothermal conditions using either neat resin or prepreg samples.
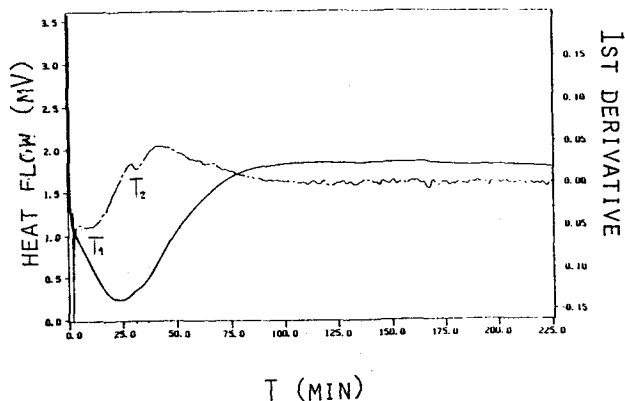

Figure 1: DSC curve obtaiened for the isothermal cure of neat resin Hercules 8552 at 150^oC (−), and its first derivative (−·−).

The calculation of the isothermal heat of reaction (ΔH_{iso}) from the DSC experiments was performed by trapezoidal integration of the heat flow/time data. The baseline was obtained by horizontal extrapolation of the heat flow once a constant value was reached.

The residual heat (ΔH_{res}) was determined by a subsequent dynamic run. Figure 2 shows the DSC obtained for the neat resin after isothermal curing at 150^oC during 240 minutes. This dynamic experiments shows an increase of the heat capacity in the region of 175^oC.
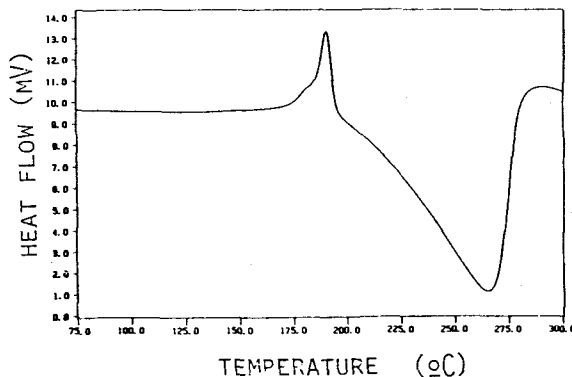

Figure 2: DSC curve obtained at a heating rate of $20^oC/min$, for a sample of neat resin Hercules 8552 previously cured at 150^oC

Beyond T_g, devitrification occurs and the completion of the cure reaction takes place. The integration of the obtained exothermic curve is so called residual heat (ΔH_{res}). Average values for ΔH_{iso}, ΔH_{res} and ΔH_T $(= \Delta H_{iso} + \Delta H_{res})$ are collected in table 1, for both neat resin and prepreg samples.

Table 1: DSC results of isotherm il scans

	T_c (°C)	t_{peak} (min)	ΔH_{iso} (J/g_r)	α	$T_{g_{iso}}$ (°C)	ΔH_{res} (J/g_r)	ΔH_T (J/g_r)	T_g (°C)
RESIN	150	23.8	-375.5	0.55	174.12	-142.7	-518.2	206.1
	158	16.6	-413.7	0.60	177.46	-114.2	-527.9	199.2
	177	7.4	-489.1	0.71	195.32	-61.3	-559.4	205.2
PREPREG	150	26.8	-320.4	0.51	167.55	-192.0	-512.4	206.8
	158	18.6	-343.8	0.55	177.3	-135.3	-479.1	208.4
	177	8.4	-427.5	0.68	189.4	-73.8	-501.3	201.6

An increase of ΔH_{iso} with the cure temperature can be noticed. Nevertheless, the total heat of reaction (ΔH_T) remains almost constant, being 532 J/g and 497 J/g the average values determined for neat resin and prepreg samples, respectively.

The variation of ΔH_{iso} with the cure temperature can be explained as a consequence of structural changes due to the polymerization process. As the glass transition temperature approaches the isothermal cure temperature, the molecular mobility is strongly reduced and the reaction becomes diffusion controlled. The reaction stops when the T_g reaches the cure temperature. Due to this vitrification process higher values for the extent of the reaction are found For the higher cure temperature.this feature is easily illustrated by the obtained T_g in the subsequent dynamic run, $T_{g_{iso}}$ (see table 1). This values obtained at a heating rate of $20°C/min$ are a bit higher than the theoretical ones . Smaller quantities have obtained at $2°C/min$. Non isothermal measurements were analyzed in a similar way than isothermal ones. Figure 3 shows the thermogram obtained at a heating rate of $10°C/min$ for a prepreg sample. The trapezoidal integration ot the cure curve gives the ultimate heat of reaction (ΔH_{ult}). The ΔH_{ult} values obtained under different dynamic conditions are collected in table 2. The results show no variation of the ultimate heat of reaction with the heating rate.
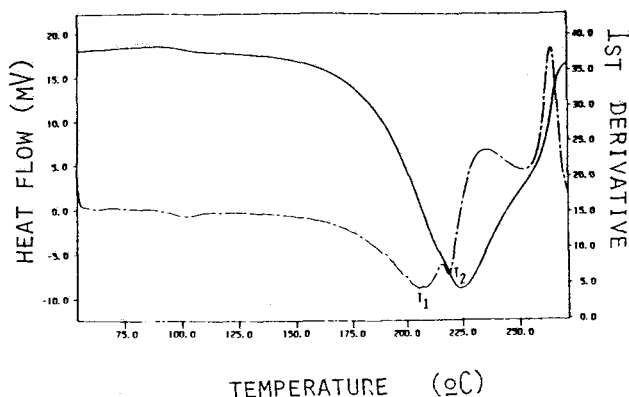

TEMPERATURE (°C)

Figure 3: DSC curve obtained at a heating rate of $10°C/min$ for a sample of Hercules 8552/AS4 (—) and its first derivative (- -).

Table 2: DSC results of dynamical scans

	ϕ (°C/min)	T_{INF1} (°C)	T_{INF2} (°C)	T_p (°C)	ΔH_{ult} (J/g_r)	T_g (°C)
RESIN	2	164.6	175.5	179.2	-626	203.1
	2	164.7	175.9	179.2	-668	206.3
	2	164.7	174.7	179.0	-701	202.0
	5	188.2	199.8	204.4	-574	-
	10	204.3	216.5	222.5	-604	195.8
	10	203.3	216.8	223.6	-570	202.1
	10	207.0	218.2	224.1	-553	211.0
PREPREG	2	166.7	179.1	183.2	-627	205.2
	2	166.5	178.8	183.8	-673	207.0
	2	165.9	178.7	183.5	-666	-
	5	189.4	200.6	206.8	-667	210.2
	10	207.3	220.0	226.9	-647	196.7
	10	206.3	219.8	227.2	-651	183.1

The average ΔH_{ult} shows a higher value than the previously calculated ΔH_T. However, this fact has no physicochemical significance, and can be easily explained due to the difficulty of monitoring the isothermal cure reaction from the very beginning. Dynamic experiments provide a better information of the total heat involved in the curing process. Therefore, the average value of ΔH_{ult} can be considered as the corresponding to the 100% cured system. The determined ΔH_{ult} values were 684 J/g and 626 J/g for neat resin and prepreg samples, respectivily.

For the analysis of the kinetics of the cure reaction, it has been assumed that the extent of the reaction (α) is proportional to the involved heat. The ratio between the heat of reaction at a given time (or temperature) and the ultimate heat of reaction, gives, then, the extent of the reaction. The apparent extent of the reaction (β) was determined from the ratio between the heat of reaction at a given time and the complete heat of reaction of a given experiment.

The reaction and apparent reaction rates can be formulated as:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{ult}} \left(\frac{dQ}{dt} \right) \qquad (1)$$

$$\frac{d\beta}{dt} = \frac{1}{\Delta H_{iso}} \left(\frac{dQ}{dt} \right) \qquad (2)$$

It follows:

$$\frac{d\alpha}{dt} = \frac{\Delta H_{iso}}{\Delta H_{ult}} \frac{d\beta}{dt} \qquad (3)$$

The figure 4 shows the variation of the apparent extent of the reaction β with time for isothermal and dynamic conditions. As it can be seen, similar results for neat resin and prepreg samples were obtained.

The complexity of the cure reactions of comercial thermoset resins used as matrices in composite materials, makes difficult the development of a kinetics model and the application of fundamental theories. Since the cure reaction of an epoxy resin has been found to be autocatalitic[3] , a simple n^{th} order kinetics expression is viable to provide an accurate quantitative decription of the complete curing process. In this sense, several authors[4-8] have applied empirical expressions describ-
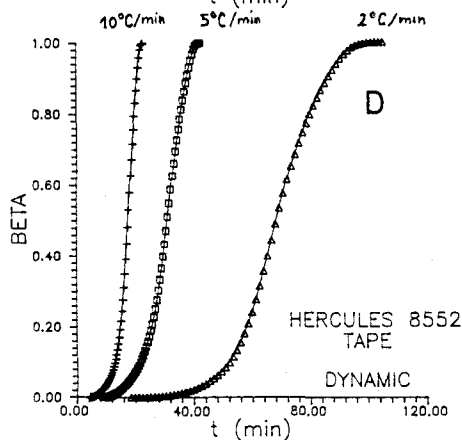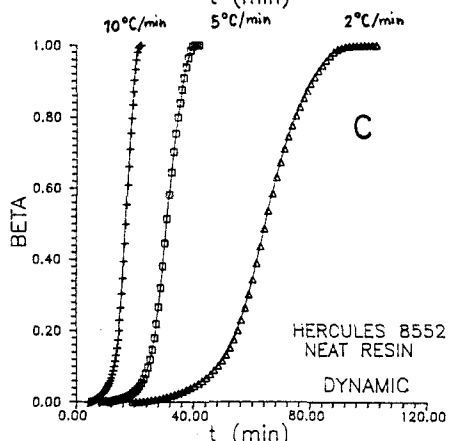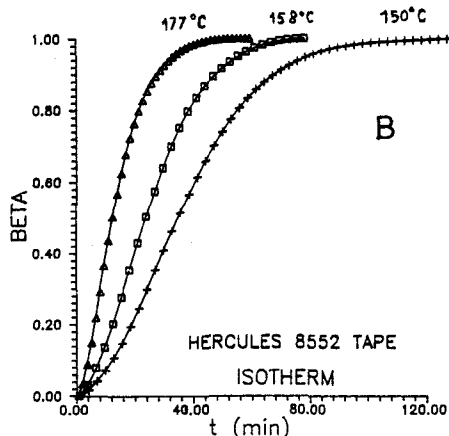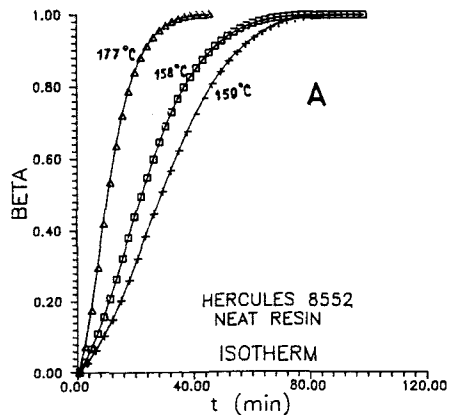
Figure 4: Plots of the apparent extent of reaction (β) versus time (t), for neat resin and prepreg (tape) under isothermal and dynamic conditions.

ing the autocatalytic kinetics of an amine-cured epoxy resin as follow:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (4)$$

where $(m + n)$ represents the overall reaction order.

The rate constants K_1 and K_2, are temperature dependent and follow Arrhenius law:

$$K_1 = K_{10}exp(-E_{a1}/RT) \qquad (5)$$

$$K_2 = K_{20}exp(-E_{a2}/RT) \qquad (6)$$

As it has been already mentioned, a shoulder appears on the obtained DSC curves similar behaviour has been repeated for other thermoset systems and the kinetics of the cure reaction has been found to be dependent on the reaction degree[9-11].

In this study , kinetic parameters have been also calculated assuming that the rate of reaction is given by:

$$\frac{d\alpha}{dt} = K_3(1 - \alpha)^n \qquad (7)$$

where

$$K_3 = K_{30}exp(-E_{a3}/RT) \qquad (8)$$

The kinetics parameters shown in exressions 4 to 8, have been calculated from the isothermal DSC data obtained for the neat resin, by applying a non linear regression analysis (these values ara shown in table 3.)

Table 3: Kinetic properties for the Hercules 8552 resin

$T(^{\circ}C)$	$K_1(s^{-1})$	$K_2(s^{-1})$	m	n	$K_3(s^{-1})$	n
150	0.000155	0.00194	0.90	1.05	0.000504	0.66
158	0.000248	0.00263	0.90	1.12	0.000675	0.75
177	0.000537	0.00443	0.89	1.25	0.00155	0.82

The calculated m values show no dependence with temperature, while n has been found to be temperature dependant. The variation of the kinetic constants with temperature is shown in figure 5
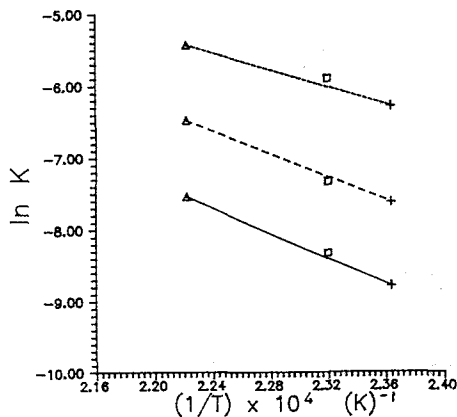

Figure 5: Variation of the kinetic constants with temperature: $K_1(-)$, $K_2(\cdots)$ and $K_3(- - -)$.

The calculated activation energies were found to be:

$$E_{a1} = 7.16\ 10^4\ J/mol$$
$$E_{a2} = 4.77\ 10^4\ J/mol$$
$$E_{a3} = 5.02\ 10^4\ J/mol$$

Similar values have been reported for other epoxy systems[8,9,12].

A change in the mechanism of the reaction has been found at α values ranging from 0.32 to 0.36. Experimental data and model predictions show an excellent agreement over the analyzed temperature range (figure 6). A special mention has to be made regarding the theoretical prediction of the shoulder found experimentally.

Another important feature to be pointed out is the nonzero value calculated for the apparent rate of reaction at $\beta = 0$. This behaviour has been found to be general in the cure of epoxy-amine systems, although not clear explanation has been given[13,14].
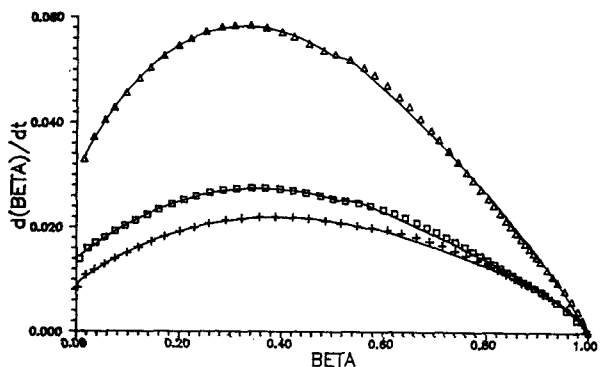
Figure 7: Variation of the viscosity with time for isothermal experiments carried out with neat resin ($\triangle$) and prepreg samples ($\blacktriangle$)

Figure 6: Comparison between model predictions (−) and experimental results obtained at 150(+),158($\square$) and 177$^\circ C$($\triangle$)

Figure 8: Variation of the viscosity with the extent of the reaction for the experiments carried out on neat resin at 150(+),158($\square$) and 177$^\circ C$($\triangle$)

Concerning the rheology of a reacting system, two main effects can be considered to be governing its behaviour. The first one is related with the variation of segmental mobility and the second one is associated with molecular structural changes induced by the cure reactions.

In this study, curves of the viscosity profile versus time and temperature have been obtained for neat resin and prepreg samples under isothermal and dynamic cure conditions (figure 7). The results show small differences in the viscosity behaviour of the reinforced and unreinforced resin.

The variation of viscosity with temperature, prior to gel point, follows an experimental function[15-17], the correlation between viscosity (η)and α values constitues a very useful information for β−staying debulking and degassing procedures. A plot of $log\eta$ versus α is given in figure 8 for the three isothermal experiments performed on neat resin.
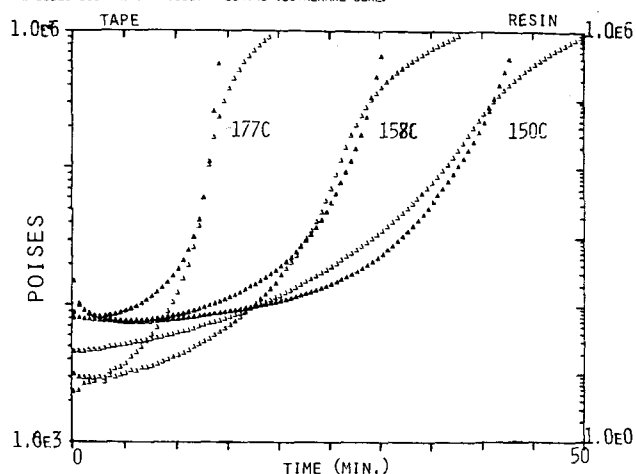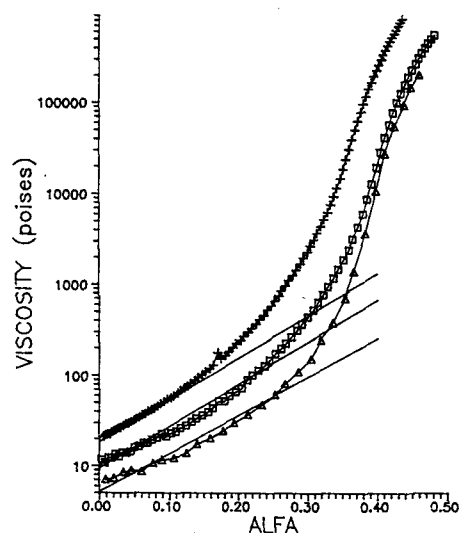
Empirical equations to correlat rheological and calorimetric data, have been proposed in the literature, such as[9,18,19]:

$$\eta = \eta_\infty exp(E_a/RT + K\alpha) \qquad (9)$$

where:

$$\eta_{\infty,K} = \text{constant}$$
$$E_a = \text{Activation energy}$$
$$R = \text{Universal gas constant}$$
$$T = \text{temperature}$$

Altought it is well known[20,21], this empirical equation does not derive from fundamental principles such as the branching theory or the free volume concept, but it constitues an useful tool for the analysis of the data.

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Equation 9 can be rewritten in the form:

$$ln(\eta) = A + K\alpha \qquad (10)$$

where

$$A = ln(\eta_\infty) + \frac{E_a}{RT} \qquad (11)$$

K and A values were calculated from expression 10 by linear regression, giving $K = 10.7$. The determined A value was used for the calculation of η_∞ and E_a, wich were found to be $3.5 \ 10^{-8}$ poises and $7.0 \ 10^4 J/mol$ respectivily. The viscosity data calculated from expression 10 have also been plot in figure 8. A reasonable agreement between experimental and calculated data can be observed for low degrees of cure. At degrees of cure higher than about 0.2 the resin begins to gelify and a high viscosity increase is observed.

Loss (G') and storage (G'') moduli versus time for the isothermal experiments are plot in figure 9 for the prepreg sample. Initially, the dynamic moduli increase sharply and then gradually level off.
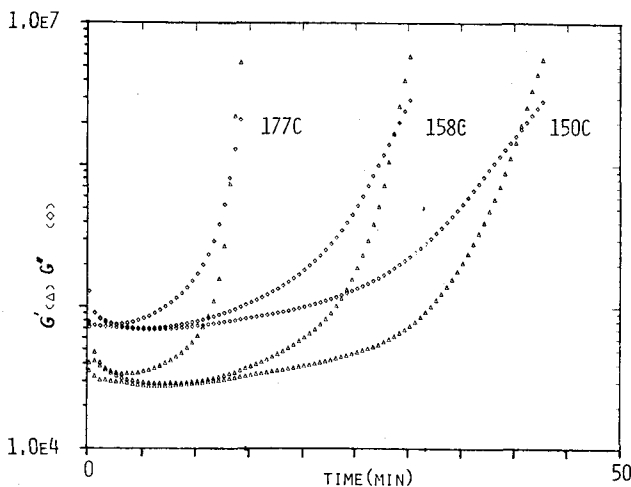
Figure 9: Variation of the dynamic moduli with time for Hercules 8552/AS4 under isothermal conditions

It has been reported[22] that the gel time can be determined as the point where G' equals G'', i.e., where the transformation from viscous liquid to elastic rubber takes place. At this point, a rapid increase of the viscosity is found (figure 7).

The activation energy for the gelation process has been calculated from the variation of the moduli crossover with temperature and values of values $6.22 \ 10^{-4}$ and $6.84 \ 10^4$ J/mol for the neat resin and prepreg samples, respectivily have been found.

Experimental curves obtained for dynamic measurements carried out on neat resin are shown in figure 10.An increase of the gelification temperature with the heating rate can be observed. Moreover, yhe minimun values for the loss and storage moduli, decrease also as the heating rates increases.

The activation energy of the gelification process was also calculated and values of $7.58 \ 10^4$ and $7.74 \ 10^4$ J/mol for the neat resin and prepreg samples, respectivily were found.

Similar values of the activation energies have been found for both, neat resin and prepreg.
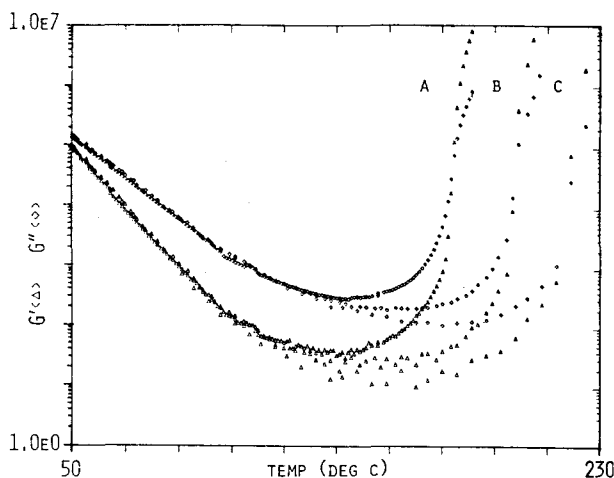
Figure 10: Plot of the dynamic moduli versus temperature for the experiments carried out on neat resin at 2(A), 5(B) and $10^\circ C/min$(C).

Gelation, has been defined as an isoviscous event[23]. The criterion of fixing a viscosity value at which gelation is considered to occur, has been applied for the determination of the gel time.

In this study, values of $\eta_{gel} = (\eta_{minimun} + 10^3)$ poises and $\eta_{gel} = (\eta_{minimun} + 10^5)$ poises for neat resin and prepreg samples respectivily have been chosen.

The gelification times calculated following the criterion of $G' = G''$ $(T_{gel}G' = G'')$ and this last criterion $(T_{gel}\eta)$ are shown in table 4. An excellent agreement of the T_{gel} calculated by both methods has been found.

Table 4: Results of the gelation studies under dynamic conditions

| ϕ | | RDS | | DSC | |
($^\circ C/min$)	ν (rad/s)	$T_{gel} \ G' = G''$ ($^\circ C$)	$T_{gel} \ \eta$ ($^\circ C$)	T_{INF2} ($^\circ C$)	α_{gel}
2	10	179.9	177.4	175.4	0.50
2	50	180.5	179.0	-	0.52
2	100	180.5	178.7	-	0.52
5	10	200.5	198.8	199.8	0.43
10	10	217.1	217.5	217.2	0.45
2	10	183.0	181.6	178.9	0.44
2	50	181.5	182.3	-	0.42
2	100	181.0	183.0	-	0.41
5	10	200.9	201.8	220.0	0.44
10	10	220.0	222.5	219.9	0.43

For some epoxy resin systems, a temperature/frequency dependence has been described in the literature[22]. Therefore, the influence of the frequency of the upper plate oscillatory motion on the obtained T_{gel} values has also been analyzed in this work. Experimental frequencies in the range from 10 to 100 rad/s have been used, and no change in the obtained T_{gel} values have been found.

As it was previously mentioned, one of the main goals of this study is the comparison of the results obtained by different experimental techniques. In order to correlate rheological and calorimetric data, values of the extent of the reaction at the gel point (α_{gel}) were calculated from the DSC measurements. For each experimental condition the time/temperature at which G'

equals G'' was selected and used to calculate the values of the extent of the reaction from the analogous DSC experiment.

The calculated α_{gel} values for both dynamic and isothermal conditions are shown in tables 4 and 5 . According to Flory's theories[24], gelation occurs at a fixed extent of the reaction, as long as the mechanism of the reaction is not temperature dependent. In our case, the slight differences found in the 2-termined α_{gel} values could be explained in terms of a change in the kinetics as it was previously mentioned.

Table 5: Results ot the gelation studies under isothermal conditions

T ($^\circ C$)	RDS		DSC	Fisher$-$Johns	α_{gel}
	t_{gel} $G' = G''$ (min)		t_{INF2} (min)	$t_{gel_{FJ}}$ (min)	
150	37.7		40.9	43.0	0.37
158	28.7		31.8	32.5	0.39
177	13.1		14.2	15.5	0.45
150	40.6		41.1	42.8	0.30
158	28.7		33.2	29.0	0.34
177	13.2		16.1	16.0	0.37

The analysis of the first derivative of the DSC data (figures 1 and 3) showed the existence of two minima corresponding to inflection points in the cure curve. A comparison between Rheometric, Fisher-Johns and DSC data (table 5) showed a very good agreement for the calculated gel times (t_{gel}) being the t_{INF2} the corresponding to the second inflection point of the DSC curve. For dynamic experiments, this second inflection point is located just before the minimun of the cure curve.

For the measurements carried out under isothermal conditions, this point appears beyond the minimun, being this different behaviour due to the different extents of reaction found under both type of experimental conditions. From this gel time values obtained by DSC (t_{INF2}), the activation energy of the gelification process was determined, and the following values were obtained:

Isothermal: Neat resin $E_a = 6.46 \ 10^4$ J/mol

Prepreg $E_a = 6.64 \ 10^4$ J/mol

Dynamic: Neat resin $E_a = 6.68 \ 10^4$ J/mol

Prepreg $E_a = 6.92 \ 10^4$ J/mol

Table 6 shows the calculated activation energies of the gelification process under isothermal conditions, and comparison of the values, show a good agreement for the three type of experiments. For other epoxy systems, it has been defined the gel time as the time at which the first inflection point ($INF1$) in the DSC curves appears[25].

However, inour case it has been clearly demostrated that gelation doesn't occur at this point, what shows the need for the gelification studies to be carries out in the case$-$to$-$case framework.

Table 6: Activation energy for the gelification process under isothermal conditions

	E_a (J/mol) 10^{-4}		
	DSC	Rheometer	Fisher$-$Johns
RESIN	6.46	6.22	6.10
PREPREG	6.64	6.84	5.65

4 CONCLUSIONS

The most remarkable features resulting from this investigations can be summarized as follows:

- Kinetic studies carried out on the Hercules 8552 epoxy system, have shown the c curing process to be autocatalytic and diffusion controlled as it has been reported for other resin systems.

- Theoretical equations have been applied for the analysis of the curing process, and an excellent agreement between model predictions and DSC data has been found.

- The kinetic parameters corresponding to the curing of the Hercules 8552 epoxy resin, have been shown a dependence with the degree of cure and temperature.

- The rheological behaviour of the epoxy system under study, has been found to be no affected by the presence of the fibers.

- Rheological and DSC experiments have shown that, under dynamic conditions a better reproducibility of results is obtained.

- The comparison of the gel times obtained by different techniques (DSC, rheometer, Fisher$-$Johns apparatus) has shown an excellent agreement.

- The study of the gelification process of Hercules 8552 by different techniques, has prved the validity of the criterion applied for the determination of the gel time from DSC data.

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