SUPPORTING INFORMATION

1 Theoretical

1.1 Kinetics analysis

The isoconversional methodology was used for the determination of the apparent activation energy during the curing process.[1] The basis for this methodology is the assumption that the reaction rate can be expressed as separate functions of conversion *x* and temperature *T* as:

$$\frac{dx}{dt} = k(T) \cdot f(x) \qquad \textbf{(1)}$$

Where $k(T) = A \cdot exp(-E/RT)$ is the kinetic constant, A is the preexponential factor, E is the activation energy, R is the gas constant and $f(x)$ is the model representing the reaction mechanism governing the curing process. In other words, it is assumed that the reaction mechanism is not affected by the temperature schedule of the curing process. Therefore, the apparent activation energy at a given degree of conversion E_x can be calculated as follows:

$$\frac{dln(dx/dt)}{dT^{-1}} = \frac{dln(f(x))}{dT^{-1}} + \frac{dln(k(T))}{dT^{-1}} \equiv -\frac{E_x}{R} \qquad \textbf{(2)}$$

This is the basis for the differential or Friedman method. Linear regression of $ln(dx/dt)$ against the inverse of temperature for different experiments at a given degree of conversion, yields the slope $-E_x/R$ and the intercept at the origin $ln(A_x \cdot f(x))$.

The method was applied at regular conversion intervals of 0.01 (relative). The isoconversional curing kinetics analysis was performed using the sample temperature instead of the reference temperature in order to account for the deviations from the program temperature occurring when the sample is releasing or absorbing heat.[1]

Simulation of experimental curing processes was made by numerical integration of the expression below making use of the isoconversional data, using the Simpson method. The isoconversional information at conversion 0 was extrapolated from the initial values, and interpolation within the conversion range was performed whenever necessary.

$$\frac{dx}{dt} = \exp\left[ln(A_x \cdot f(x)) - \frac{E_x}{R \cdot T}\right] \qquad \textbf{(3)}$$

The analysis was carried out using epoxy group conversion x_{epoxy} instead of calorimetric conversion x. For the transformation of x into x_{epoxy} in the first curing stage, the following expressions were used:

$$x_{epoxy} = r \cdot \frac{\Delta h_1}{\Delta h_{total,1}} \quad \textbf{(4)}$$

$$\frac{dx_{epoxy}}{dt} = r \cdot \frac{dh/dt}{\Delta h_{total,1}} \quad \textbf{(5)}$$

Where r is the thiol:epoxy equivalent ratio, Δh_1 is the reaction heat evolved in the first curing stage up to a time/temperature, dh/dt is the heat flow and $\Delta h_{total,1}$ is the total heat evolved during the first stage of the curing process.

In the case of the second curing stage, the analysis was carried out on pre-cured samples (after completion of the first curing stage) and the expressions used are the following:

$$x_{epoxy} = r + (1-r) \cdot \frac{\Delta h_2}{\Delta h_{total,2}} \quad \textbf{(6)}$$

$$\frac{dx_{epoxy}}{dt} = (1-r) \cdot \frac{dh/dt}{\Delta h_{total,1}} \quad \textbf{(7)}$$

Where r is the thiol:epoxy equivalent ratio, Δh_2 is the reaction heat evolved in the second curing stage up to a time/temperature, dh/dt is the heat flow and $\Delta h_{total,2}$ is the total heat evolved during the second stage of the curing process.

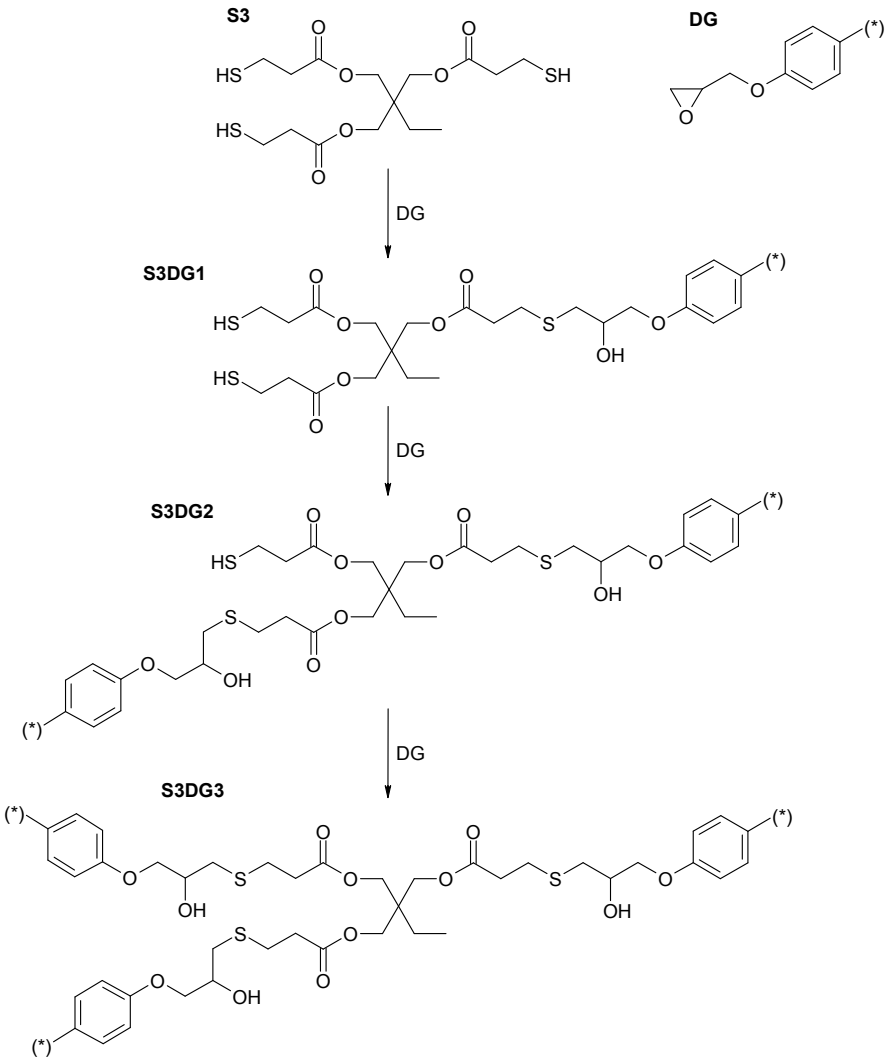
The conversion of epoxy groups during the second during stage of samples inmersed in a silicone oil bath at 25 ºC was calculated from the residual heat corresponding to the second during stage $\Delta h_{res,2}$ as:

$$x_{epoxy} = r + (1-r) \cdot \left(1 - \frac{\Delta h_{res,2}}{\Delta h_{total,2}}\right) \quad \textbf{(6)}$$

1.2 Network build-up model

The thiol-epoxy reaction is an ideal step-wise reaction from the network build-up point of view and can be modelled using well-established methods.[2-4] In this case, a method based on the random combination of structural fragments[2] has been used The following schemes identify the fragments that are present during the polycondensation process between DGEBA and the 3-

functional thiol crosslinker used in this work. Note that it has been assumed independent reactivity of the epoxy groups in the DGEBA monomer [2] so that the DGEBA monomer can be split into two fragments with a (*) virtual bond. The reaction between the thiol and DGEBA leads to fragments with an increasing number of (*) virtual bonds depending on the degree of reaction. Assuming independent reactivity, all fragments containing (*) bonds can be randomly combined with other fragments containing (*) bonds.



Scheme 1: Structural fragments appearing during the thiol-epoxy reaction.

In this case of ideal polycondensation, the normalized concentration of all the structural fragments can be easily calculated as shown in Table 1. Note that the concentration of the different fragments is expressed using the same code but in lowercase. The initial concentration of epoxy fragments is dg_0 and the initial concentration of thiol crosslinker fragment is $s3_0$. The equivalent ratio between thiol and epoxy groups is defined as:

$$r = \frac{3 \cdot s3_0}{dg_0} \quad \textbf{(8)}$$

The conversion of thiol groups is related to the conversion of epoxy groups x_{epoxy} as:

$$x_{thiol} = \frac{x_{epoxy}}{r} \quad (9)$$

For thiol-epoxy formulations with $r < 1$, the maximum epoxy group conversion will be r.

Table 1: Expression of the normalized concentration of the reactive species during curing of thiol-epoxy formulations (see Scheme 1), assuming ideal polycondensation behaviour.

Fragment	Normalized concentration
DG	$dg0 = dg_0 \cdot (1 - x_{epoxy})$
S3	$s3 = s3_0 \cdot (1 - x_{thiol})^3$
S3DG1	$s3dg1 = s3_0 \cdot 3 \cdot (1 - x_{thiol})^2 \cdot x_{thiol}$
S3DG2	$s3dg2 = s3_0 \cdot 3 \cdot (1 - x_{thiol}) \cdot x_{thiol}^2$
S3DG3	$s3dg3 = s3_0 \cdot x_{thiol}^3$

The following mass balances during the epoxy-thiol curing process are satisfied:

$$dg + s3dg1 + 2 \cdot s3dg2 + 3 \cdot s3dg3 = dg_0 \quad (10)$$

$$s3 + s3dg1 + s3dg2 + s3dg3 = s3_0 \quad (11)$$

The total mass of the system must also remain constant. Taking into account the mass of each fragment (see Table 2 and Scheme 1):

$$\begin{aligned} M_{total} &= \sum m_i = dg \cdot M_{dg} + s3 \cdot M_{s3} + s3dg1 \cdot (M_{s3} + M_{dg}) + s3 \\ &= dg_0 \cdot M_{dg} + s3_0 \cdot M_{s3} \end{aligned} \quad (12)$$

Table 2: Capture probabilities and masses associated to each structural fragment.

Fragment	$P_{i,*}$	M_i	m_i	M_{wi}
DG0	$\frac{dg}{n_{total,*}}$	M_{dg}	$dg \cdot M_{dg}$	$M_{dg} + W$
S3	0	M_{s3}	$s3 \cdot M_{s3}$	M_{s3}
S3DG1	$\frac{s3dg1}{n_{total,*}}$	$M_{s3} + M_{dg}$	$s3dg1 \cdot (M_{s3} + M_{dg})$	$M_{s3} + M_{dg} + W$
S3DG2	$\frac{2 \cdot s3dg2}{n_{total,*}}$	$M_{s3} + 2 \cdot M_{dg}$	$s3dg2 \cdot (M_{s3} + 2 \cdot M_{dg})$	$M_{s3} + 2 \cdot (M_{dg} + W)$
S3DG3	$\frac{3 \cdot s3dg3}{n_{total,*}}$	$M_{s3} + 3 \cdot M_{dg}$	$s3dg3 \cdot (M_{s3} + 3 \cdot M_{dg})$	$M_{s3} + 3 \cdot (M_{dg} + W)$

In order to determine the relevant average statistics before and after the gel point, one first has to define the capture probabilities of the different fragments taking into account that, assuming the fragments issue a (–) bond ($P_{i,-}$) or a (+) bond ($P_{i,+}$):

$$P_{i,*} = \frac{i_*}{n_{total,*}} = \frac{i \cdot n_{i,*}}{n_{total,*}} \quad \textbf{(13)}$$

Where i is the normalized concentration of each fragment, and $n_{i,*}$ are the number of (*) bonds issued by each fragment, respectively. $n_{total,*}$ is the total number of (*) bonds present in the system, which can be calculated as:

$$n_{total,*} = \sum i \cdot n_{i,*} = dg + s3dg1 + 2 \cdot s3dg2 + 3 \cdot s3dg3 = dg_0 \quad \textbf{(14)}$$

The calculated capture probabilities of each fragment are shown in Table 2.

1.2.1 Pre-gel statistics

One can define the expected average weight pending from the (*) bonds, W, from the probability of capturing a fragments with a (*) bond, the mass of the fragment M_i and the expected average weight pending from the other (*) bonds:

$$W = P_{dg} \cdot M_{dg} + P_{s3dg1} \cdot (M_{s3} + M_{dg}) + P_{s3dg2} \cdot (M_{s3} + M_{dg} + W) + P_{s3dg3} \cdot (M_{s3} + M_{dg} + 2 \cdot W) \quad \textbf{(15)}$$

After some reorganization:

$$W = \frac{P_{dg} \cdot M_{dg} + P_{s3dg1} \cdot (M_{s3} + M_{dg}) + P_{s3dg2} \cdot (M_{s3} + M_{dg}) + P_{s3dg3} \cdot (M_{s3} + M_{dg})}{1 - P_{s3dg2} - 2 \cdot P_{s3dg3}} \quad \textbf{(16)}$$

The gel condition is that the expected molecular weight attached to the (*) bonds, W, becomes infinite. This is equivalent to:

$$1 - P_{s3dg2} - 2 \cdot P_{s3dg3} = 0 \Rightarrow P_{s3dg2} + 2 \cdot P_{s3dg3} = 1 \quad \textbf{(17)}$$

It can be easily shown that this gel point condition is equivalent to that of the well-known following expressions for the gel point conversion of epoxy groups $x_{epoxy,gel}$ and the critical equivalent ratio between thiol and epoxy groups, r_c.

$$x_{epoxy,gel} = \sqrt{\frac{r}{(f-1) \cdot (g-1)}} \quad \textbf{(18)}$$

$$r_c = \frac{1}{(f-1)\cdot(g-1)} \quad \textbf{(19)}$$

The mass-average molecular weight M_w can be calculated taking into account the mass fraction of each of the fragments and their total expected mass (M_{wi}), taking into account the expected average pending masses (see Table 2):

$$M_W = \sum w_i \cdot M_{wi} = \frac{1}{M_{total}} \cdot \sum m_i \cdot M_{wi} \quad \textbf{(20)}$$

1.2.2 Post-gel statistics

In order to study the network properties in the postgel state, one has to define the extinction probabiliy Z of the (*) virtual bond, which is calculated in a recursive manner from the capture probability of each fragment and their probability of finite continuation, taking into account the other virtual bonds (*) issued by the fragment:

$$Z = P_{dg} + P_{s3dg1} + P_{s3dg2} \cdot Z + P_{s3dg3} \cdot Z^2 \quad \textbf{(21)}$$

Before the gel point, the only possible solution is $Z = 1$, because all the fragments must have a finite continuation. After the gel point, a trivial solution equal to 1 is found but another non-trivial solution (decreasing with increasing conversion down to a value of 0 for a fully crosslinked network) is found, which can be used to determine relevant network parameters during the crosslinking process.

Taking into account that the probability of finding an infinite continuation from a bond is equal to the complementary extinction probability $1 - Z$, the concentration of crosslinks (fragments issuing 3 branches with infinite continuation) is:

$$n_{cross} = s3dg3 \cdot (1 - Z)^3 \quad \textbf{(22)}$$

The effective network strand density[2, 4-6] is calculated taking into account the functionality of the crosslinks as:

$$n_{strand} = \sum_{i \geq 3} \left[n_{cross,i} \cdot \frac{i-2}{2} \right] = n_{cross} \cdot \frac{1}{2} \quad \textbf{(23)}$$

The sol fraction w_{sol} is determined from the fragments having only finite continuation:

$$w_{sol} = \frac{1}{M_{total}} \cdot \left[m_{dg} \cdot Z + m_{s3} + m_{s3dg1} \cdot Z + m_{s3dg2} \cdot Z^2 + m_{s3dg3} \cdot Z^3 \right] \quad \textbf{(24)}$$

The gel fraction is calculated as $w_{gel} = 1 - w_{sol}$. See Table 2 for the mass contribution of each fragment. The mass-average molecular weight of the soluble fraction can be simply calculated from the application of the pre-gel statistics expressions assuming a concentration of the fragments equal to that in the soluble fraction.

Analogous expressions for the different statistical averages can be found in the literature.[2, 7]

2 Results

2.1 Kinetics analysis

Figure 1 shows the isothermal curing of DG174S3-X formulations at 50 ºC and comparison with a formulation containing a higher molecular weight DGEBA (with higher hydroxyl group content).

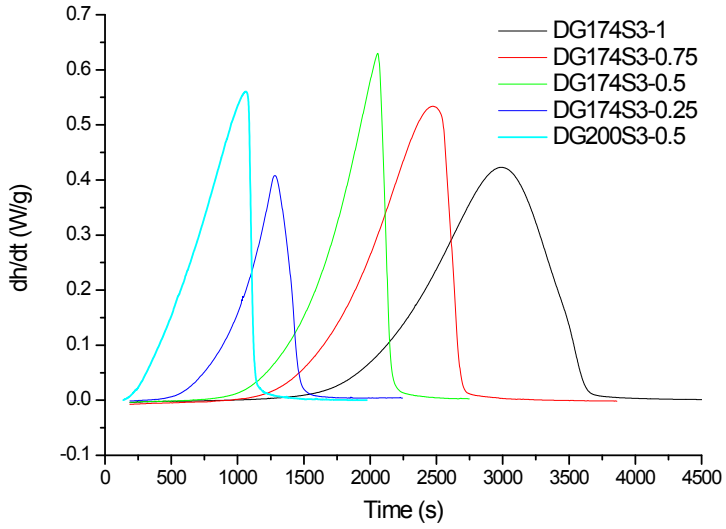


Figure 1: Heat flow during curing of DG174S3-X formulations at 50ºC and of formulation DG200S3-0.5 (using DGEBA with 200 g/eq) plotted with respect to the curing time.

Figure 2 shows the isothermal and dynamic curing of DG174S3-0.5 formulations used for the kinetics analysis of the first curing stage.

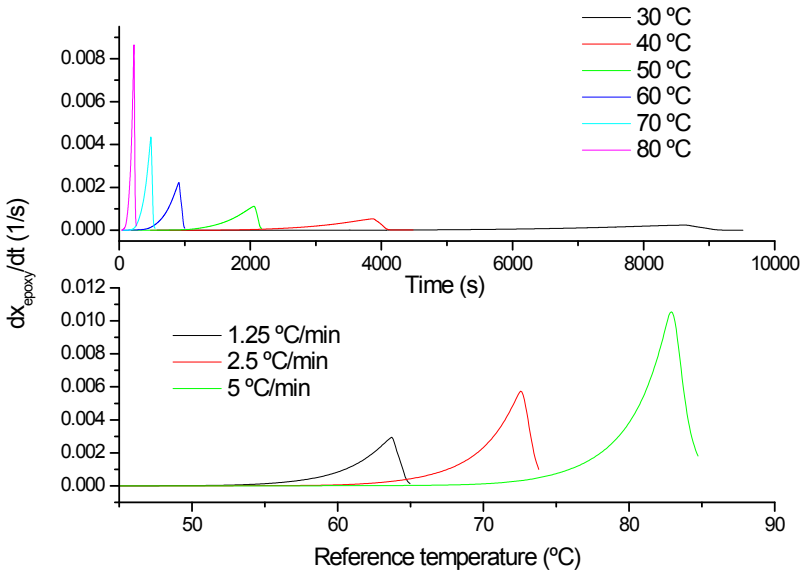


Figure 2: Plots of reaction rate with respect to time and temperature corresponding to the first stage of the curing of formulation DG174S3-0.5, under isothermal and dynamic conditions.

Figure 3 shows the isothermal and dynamic curing of DG174S3-0.5 formulations used for the kinetics analysis of the second curing stage, after pre-curing the samples in the DSC.

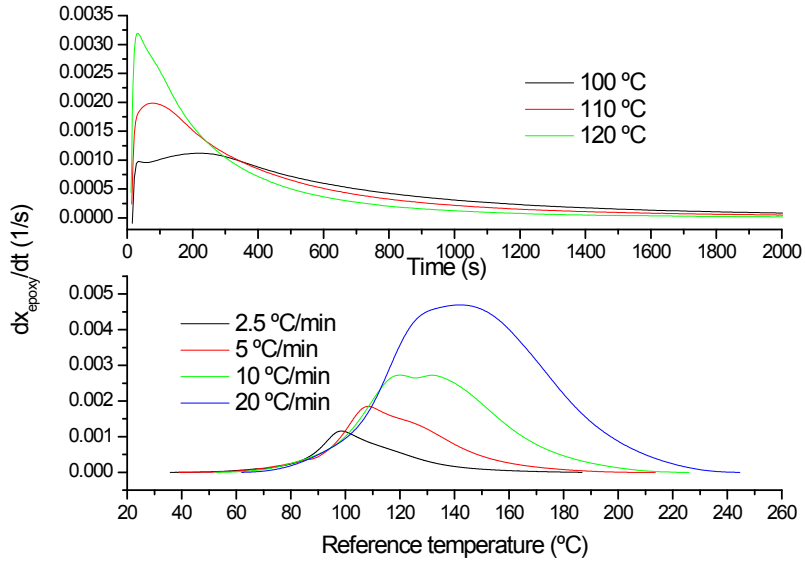


Figure 3: Plots of reaction rate with respect to time and temperature corresponding to the second stage of the curing of formulation DG174S3-0.5, under isothermal and dynamic conditions.

2.2 Thermal-mechanical properties and network structure

The following figure illustrates the evolution of the main structural parameters during the first curing stage of DG174S3-0.75 formulation.

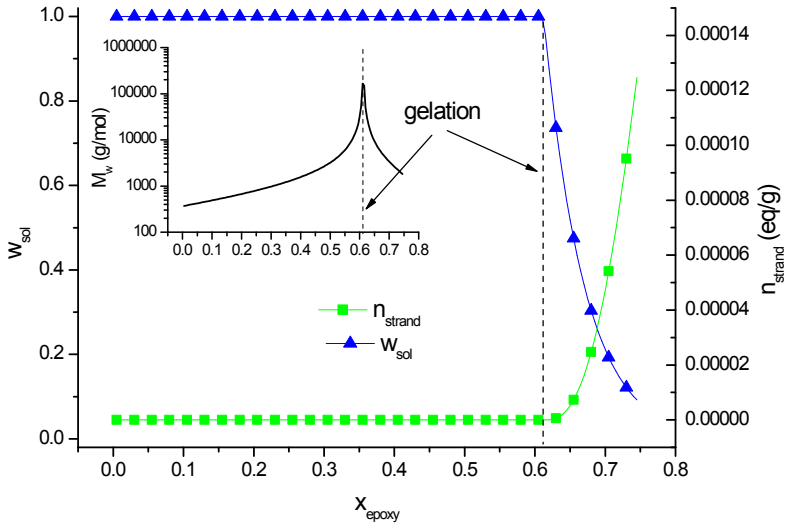


Figure 4: Statistical averages obtained for the network build-up process during the first stage of the curing of DG174S3-0.75 formulation.

3 References

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