

A STUDY OF CROSS-LINKING KINETICS OF CYANATE ESTER RESIN

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ABSTRACT

Thermostable resins, such as cyanate esters (CEs), exhibit thermal stability at high temperature. However, CEs are highly exothermic during the curing process. Thus, a thorough understanding of the polymerization during the RTM process (Resin Transfer Molding) is important in order to achieve a full conversion and then good mechanical characteristics for the final product, while preventing any degradation of the matrix. This article deals with cure kinetics of Primaset PT30[®] resin studied by DSC scans which falls under two methods, dynamic and isothermal. The enthalpy of reaction H_T is evaluated by using the dynamic method and the isothermal method evaluates both the reaction rate $\frac{d\alpha}{dt}$ and the curing degree α . In addition, the model expression proposed in this study is Kamal-Sourour model in order to predict the matrix curing.

1 INTRODUCTION

Cyanate ester resins (CEs), typically Phenolic Triazine (PTs), belong to the class of high-performance thermosetting polymers. CEs are widely used in the aerospace industry due to their high glass transition temperature ($T_g > 300^\circ\text{C}$), good thermal stability, low water uptake and epoxy-like processability [1]. However, the cross-linking reaction of PTs exhibits highly exothermic process, resulting in non-linear increase in internal temperature, which may cause a temperature overshoot. Hence, a lot of care should be taken while curing relatively thick composites and kinetics study must be carried out in order to understand the cure process of this matrix.

PT cross-linked network is synthesized from prepolymers with functionality $f > 2$ [2], which undergo the cyclotrimerization process reacting three functional $-\text{OCN}$ groups (fig. 1a) and form afterward triazine rings (fig. 1b). Continued reacting of triazine rings leads to the formation of the cross-linked thermoset, also known as polycyanurates (fig. 1b).

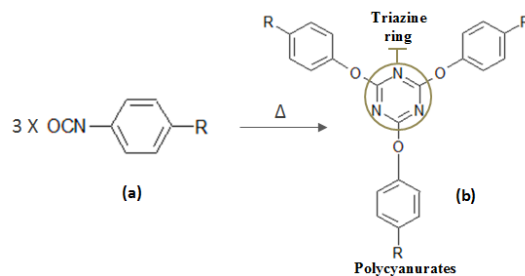


Figure 1: Cyclotrimerization (a), cross-linked thermoset (b)

However, residuals often remain after the synthesis of CE monomers. Studies have shown that these impurities contain hydroxyl groups –OH (such as phenols), which act as the polymerization initiator. No reaction takes place if completely purified CE monomers are heated and thus, a small amount of phenolic impurities are needed to start the reaction [4]. Figure 2 shows the reaction mechanism scheme initiated by a phenyl group proposed by Grigat [5] and then by Bauer et al. [6-7].

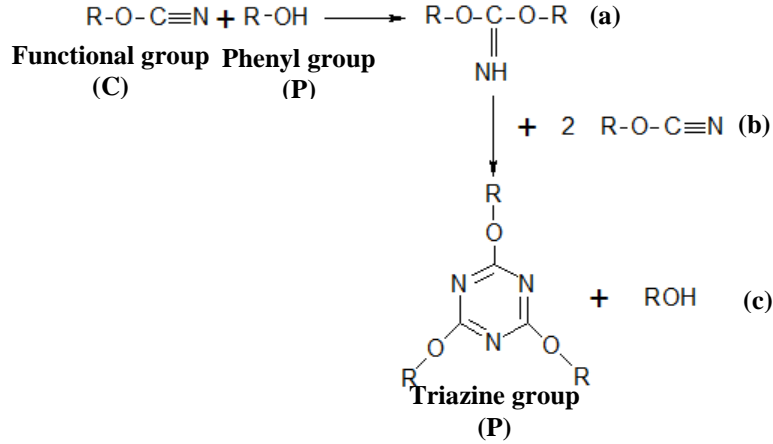


Figure 2: Reaction with phenols

In fact, the phenyl group reacts with a first –OCN functional group to form imidocarbonate (a). The imidocarbonate reacts with two other functional groups (b) to produce a triazine ring and the phenyl group is restituted (c). Equation 1 shows the cyclotrimerization reaction:



Where C: –OCN group; P: phenyl group; T: triazine ring

The cyclotrimerization process shows an autocatalytic behavior generated by the reaction of triazine rings into the system[4]. Although the cyclotrimerization reaction is the major phenomenon, it has been noted that metallic catalysts (with a very small amount) may be added to the monomer in order to reduce the final composite price by accelerating (catalyzing) the reaction rate as well as decreasing the curing time [8-9].

To better control cure kinetics, researchers have been interested in modelling kinetics of cyanate esters, typically dicyanate esters [10], taking into account changes in concentrations of different reactive species occurring during the cyclotrimerization process. Given the presence of both autocatalytic and catalytic mechanisms, it was agreed to choose the phenomenological model of Kamal-Sourour (KS) in the framework of this study (Eq.2).

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{max} - \alpha)^n \quad (2)$$

α_{max} is the maximal degree of conversion for each isothermal measurement. The kinetic parameters of the model are the reaction orders m and n, as well as the thermo-dependent reaction constants k_1 linked to the catalytic mechanism (Eq.3) and k_2 linked to the autocatalytic mechanism (Eq.4).

$$k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) \quad (3)$$

$$k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \quad (4)$$

Where: A_1 and A_2 : constants, E_1 and E_2 : activation energies ($\text{J}\cdot\text{mol}^{-1}$) and R : gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). DSC measurements are carried out in order to determine KS parameters.

2 EXPERIMENTAL AND METHODS

The resin used in this study is Primaset PT30[®] from Lonza[®]. Figure 3 shows the prepolymer PT30[®] with a molar mass of $320\text{-}420 \text{ g}\cdot\text{mol}^{-1}$ and a density of $1.25 \text{ g}\cdot\text{cm}^{-3}$.

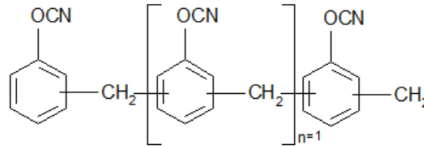


Figure 3: Primaset PT30[®] prepolymer

In order to achieve an optimal degree of cure, it is recommended to cure the resin in two steps: at low temperature (about $200 \text{ }^\circ\text{C}$) and then post-curing at higher temperature (between $260 \text{ }^\circ\text{C}$ and $290 \text{ }^\circ\text{C}$). Thus, studying the behaviour of the resin at high and low temperatures would be interesting to evaluate kinetics cure evolution during the polymerization process. To do this, the kinetic study of the PT30[®] is carried out by differential scanning calorimetry using a NETZSCH 200 F3 DSC under nitrogen ($50 \text{ mL}\cdot\text{min}^{-1}$). Samples are prepared in sealed aluminium pans of mass $5.0 \text{ mg} \pm 0.2$. Prior to any test, the resin has high viscosity at ambient temperature. Thereafter, it is heated to $80 \text{ }^\circ\text{C}$ to be softened. Once heated, the resin is poured into a pan. Finally, the pan is sealed and then placed on the DSC sample holder for following measurements. Two kinds of DSC tests are carried out according to the standard NF EN ISO 11357-5 [11]:

- Dynamic DSC method: according to the standard, it is mandatory to apply a heating ramp and to measure the heat flow as a function of temperature (or time). The purpose of this measurement is to determine the total heat of reaction H_{tot} of the PT30 resin. For this purpose, three heating rates are chosen for this study ($2, 5$ and $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$).
- Isothermal DSC method: actually, the resin needs to be cured at isothermal temperature. According to PT30 curing data sheet [12], it's highly recommended to cure, firstly at a low temperature (200°C) and then to post-cure at higher temperatures (260°C - 290°C). According to the standard NF EN ISO 11357-5, figure 4 represents an example of an isothermal cycle containing two DSC steps applied to each sample. Firstly, a fast heating ramp is applied at $100 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ followed by a first isothermal dwell (T_{stab}) at $150 \text{ }^\circ\text{C}$ for 5 minutes to stabilize the signal and eliminate the thermal history of the matrix. Thereafter, the heating ramp of $100 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ is applied followed by an isothermal dwell (T_{iso}), with $T_{\text{iso}} = \{260 \text{ }^\circ\text{C}, 270 \text{ }^\circ\text{C}, 280 \text{ }^\circ\text{C} \text{ and } 290 \text{ }^\circ\text{C}\}$ to determine the isothermal heat reaction H_{iso} . Finally, the second step consists of carrying out a dynamic DSC at $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to evaluate the residual enthalpy H_{res} generated by unreacted functional groups (Fig. 4).

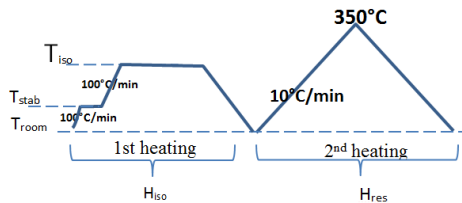


Figure 4: DSC isothermal heating steps

3 RESULTS AND DISCUSSION

In order to determine the total heat of reaction, the DSC tests are carried out up to 350 °C (below the degradation temperature of matrix [14]). Figure 5 represents the heat flow as a function of temperature. When the heating rate increases, reaction rate shifts from low to higher temperatures, as well as the maximum peak is more important.

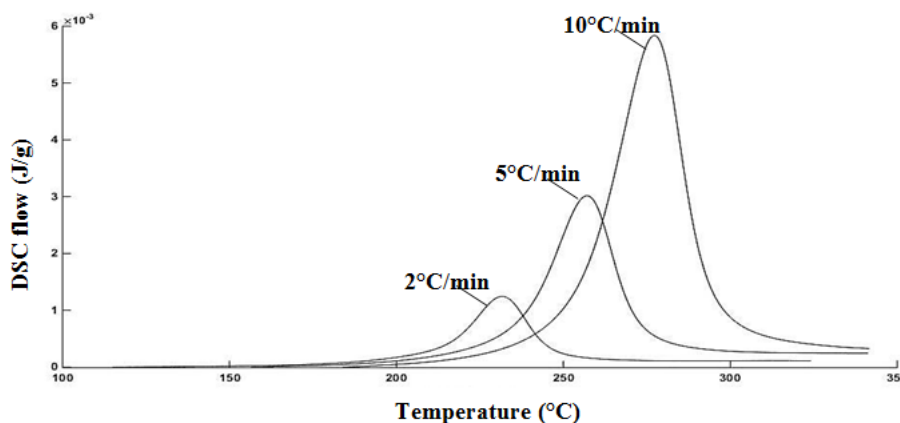


Figure 5: DSC flow rate vs. temperature (exo. up)

Table 1 presents the average of the total heat reaction (J/g) calculated from the tests performed at the corresponding heating ramp. According to the standard NF EN ISO 11357-5 [11], 3 tests were carried out at both 10 and 5 °C/ min and 5 tests were carried at 2 °C/min.

Heating rate (°C/min)	Total heat of reaction (average J/g)	Standard deviation (%)
2	742,3	3,9
5	790,3	5,3
10	783,9	4,2

Table 1: Mean total heat reaction H_{Tot} at 2, 5 and 10 °C/min

For the same sample mass (5 mg), the total heat of reaction decreases at a low heating rate (2 °C.min⁻¹) due to decreased molecular mobility and intramolecular diffusion [15]. Furthermore, other factors which can influence the polymerization reaction (cyclotrimerization) and the reaction rate are typically the presence phenyl groups (impurities), as well as moisture. On the one hand, phenols are organic compounds possessing hydroxy (-OH) as a functional group. These hydroxy groups release mobile hydrogens that may react with the functional CE groups -OCN in the case of acids, Lewis acids or bases are present initially [4]. Depending on the acidity of phenols, they could be incorporated into the network, which modifies the chemical structure and thus, the thermal and mechanical characteristics of the matrix. On the other hand, the presence of moisture has a real effect on chemical structure since the carbamates, products from the reaction of water with cyanates, induce not only the formation of linear chains that react with unreacted -OCNs not contributing to the cross-linked system, but also carbamates start decomposing at around 150 °C- 200 °C to release one again other hydroxyl groups (-OH) which may makes the explanation of the results sometimes complex.

The total heat of reaction determined by the DSC dynamic study is $H_{tot}=772 \pm$ J/g, which corresponds to the average value of dynamic tests at 2, 5 and 10 °C/ min. After evaluating the kinetic reaction by the dynamic method, an isothermal study is carried out taking into account the cure and the post-cure at different temperatures T_{iso} = [200 °C, 220°C, 230°C, 240°C, 250°C, 260°C]. Fig. 6 shows the evolution of the heat flow as a function of time at different isotherms. It is noted that when the temperature of the isotherm decreases, the intensity of the signal decreases too and the width of the peak becomes greater.

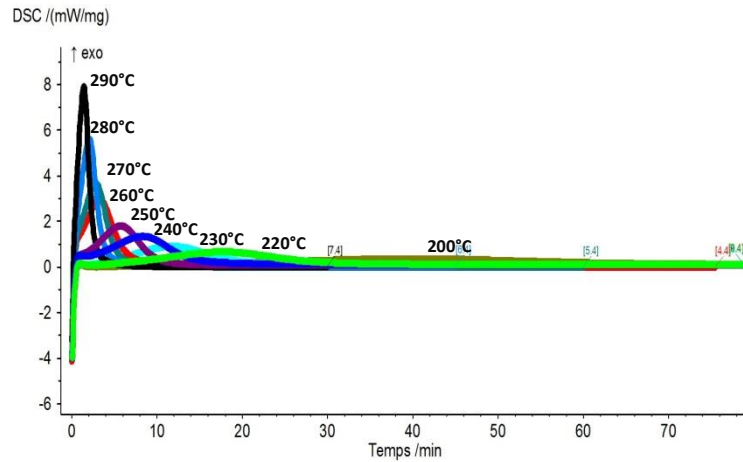


Figure 6: DSC flow versus time

The maximal degree of conversion α_{\max} was assumed to be calculated as the ratio of H_{tot} minus H_{res} reported to H_{tot} (Eq.5) to better predict the evolution of the degree of conversion during the curing cycle.

$$\alpha_{\max} = \frac{H_{\text{tot}} - H_{\text{res}}}{H_{\text{tot}}} \quad (5)$$

Cure kinetics modelling based on Kamal-Sourour (KS) model is carried out to better optimize the curing cycle during the RTM process. KS model was included in a Matlab[®] program based on least-square Levenberg-Marquardt non-linear regression algorithm in order to calculate the unknown kinetic parameters of the model. To do this, experimental data was used to calculate the reaction rate $\frac{d\alpha}{dt}$ (Eq.6) and the degree of conversion α (Eq.7)

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{tot}}} \dot{H}(t) dt \quad (6)$$

$$\alpha = \frac{1}{H_{\text{tot}}} \int_{t_i}^{t_{iso}} \dot{H}(t) dt \quad (6)$$

Fig.7 shows the evolution of the reaction rate (a) and the degree of conversion (b) as a function of time compared to KS model curves at high and low isothermal temperatures. Thus, kinetic parameters are calculated for each isothermal scan. It should be noted that the degree of conversion versus time curves have a sigmoid shape, characteristic of the autocatalytic mechanism [13]. Due to confidentiality, numerical values of KS parameters are removed. However, it has been noticed that the reaction order, n and m are not sensitive to the temperature variation (Fig.8a-b). Moreover, the rate constants k_1 and k_2 (Fig7.c) are thermodependant.

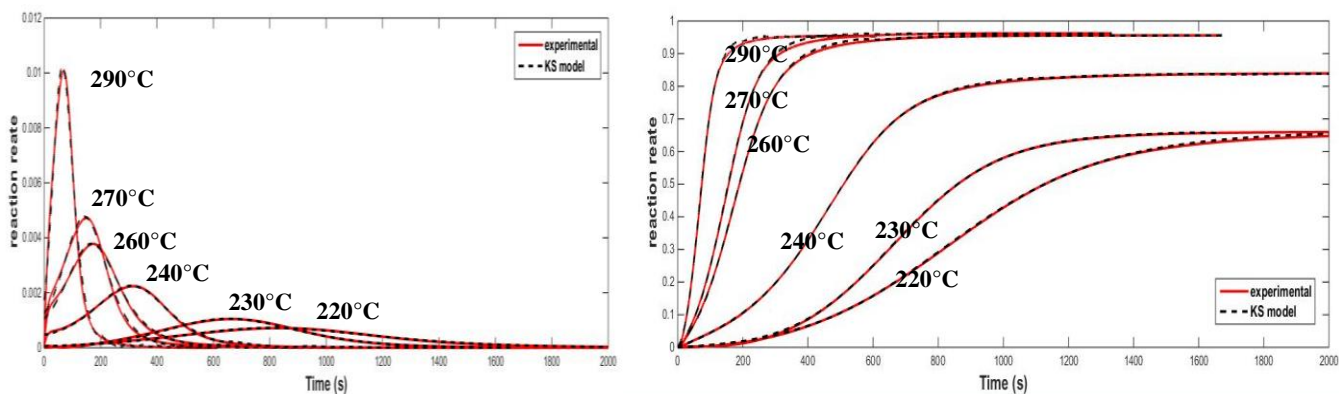


Figure 7: Example of KS modelling: Reaction rate vs. time (a); Degree of conversion vs. time (b)

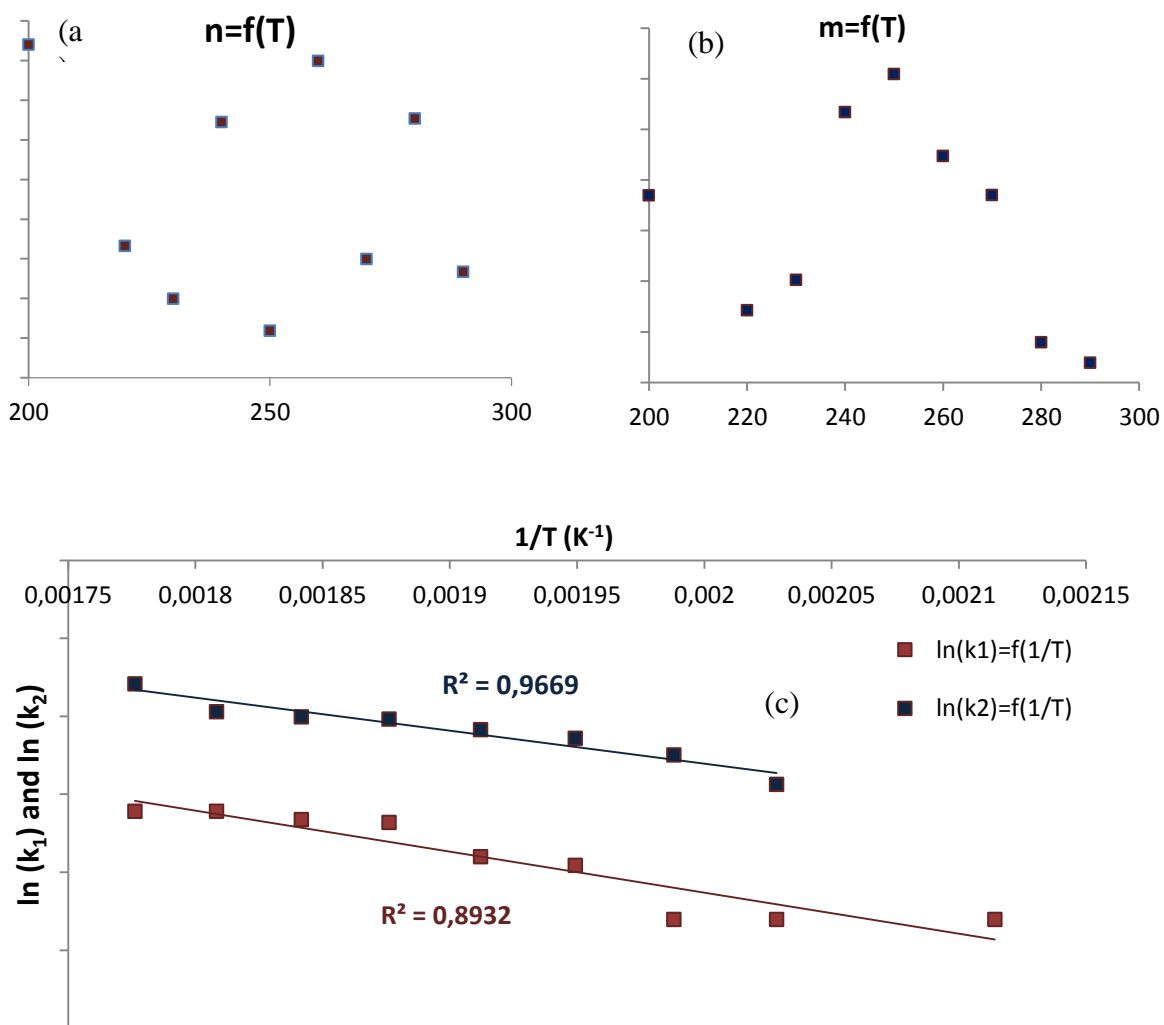


Figure 8: KS parameters.: (a): $n=f(T)$; (b) $m=f(T)$; (c) $\ln(k_1)=f(1/T)$; (c) $\ln(k_2)=1/T$

3 CONCLUSION AND PERSPECTIVES

The characterization of the kinetics of the PT30 resin is complex, as the chemical constitution of the matrix remains confidential. A first kinetic approach was made using the Kamal-Sourour phenomenological model, taking into account both the reaction of the triazine rings responsible for the autocatalytic mechanism and the catalytic mechanism generated by the presence of impurities in the resin.

KS parameters are obtained using kinetic modeling at high and lower temperatures (200 °C-290 °C). Results have shown that $k_2 > k_1$ and thus, activation energy E_1 linked to the autocatalytic mechanism is lower than E_2 associated to the catalytic mechanism, which is in good agreement with the used resin (cyclotrimerization is the main reaction process and no catalysts are added on purpose).

Once the KS parameters are determined, numerical simulations will be performed based on solving the heat conduction equation including internal heat generation produced by curing reactions to better predict the cure cycle during RTM process.

4 REFERENCES

ACKNOWLEDGEMENTS

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