

Article

The FA Polymerization Disruption by Protic Polar Solvent

Guillaume Falco, Nathanaël Guigo*, Luc Vincent, Nicolas Sbirrazzuoli*

¹ Université Côte d'Azur, Université Nice-Sophia Antipolis, Institut de Chimie de Nice, UMR CNRS 7272, 06108 Nice Cedex 02, France

* Correspondence: Nathanael.Guigo@unice.fr, Nicolas.Sbirrazzuoli@unice.fr

Abstract: Furfuryl alcohol (FA) is a biobased monomer derived from lignocellulosic biomass. The present work describes its polymerization in presence of protic polar solvents, i.e. water or isopropyl alcohol (IPA), using maleic anhydride (MA) as acidic initiator. The polymerization was followed from the liquid to the rubbery state by combining DSC and DMA data. In the liquid state, IPA disrupts the expected reactions during all the FA polymerization due to a stabilization of the furfuryl carbenium center. This causes the initiation of the polymerization at higher temperature, which is also reflected by higher activation energy. In water system, the MA opening allows to start the reaction at lower temperature. A higher pre-exponential factor value is obtained in that case. The DMA study of final branching reaction occurring in the rubbery state has highlighted continuous increase of elastic modulus until 290 °C. This increasing tendency of modulus was exploited to obtain activation energy dependences (E_a) of FA polymerization in the rubbery state.

Keywords: Renewable resources, Lignocellulosic Biomass, Polymerization, Reaction Mechanisms, Furfuryl Alcohol.

1. Introduction

Lignocellulosic biomass appears as an important renewable source for fabrication of organic polymeric materials [1] [2] [3]. In this line, furan derivatives [4] such as 5-hydroxymethylfurfural [5] or furfural [6] are respectively obtained from C₆ or C₅ sugar dehydrations [7] in the bio-refinery processes. These two compounds are among the most interesting biobased building blocks to design a sustainable chemistry [8] and they can further be transformed [9] in, for instance, 2,5-furandicarboxylic acid and furfuryl alcohol (FA) respectively. These latter compounds are indeed the two top of the class of biobased precursors used for their polymerization ability.

FA is an attractive biobased compounds which has the particularity to homopolymerize in poly(furfuryl alcohol) (PFA) under acid catalyzed condition, leading to a strong reticulated network with high thermomechanical properties [10]. These advantages make the PFA an excellent biobased alternative in industrial process such as foundry mold [11] or wood reinforcement [12]. Other studies have opened several applications ways of this eco-friendly polymer as the fabrication of carbon nanospheres [13], hybrid materials with silica [14] [15], fully biobased composites with several natural fibers [16] [17], or copolymers with the combination of vegetable oils [18] [19].

The FA polymerization mechanism [10] [20] [21] is complex and can be divided in two steps. The first polymerization step occurs in liquid phase with the influence of the acid initiator. This step consists in the formation of FA oligomers by polycondensation from an active furfuryl carbenium center. The second step leads to three-dimensional branched polymer through Diels-Alder cycloaddition between the formed oligomers. Furthermore, side reactions can also occur. First, an electrophilic addition [22] of the active furfuryl carbenium center on the conjugate form of the

oligomer can occur increasing the heterogeneity of the final 3D network. Another reaction that was reported in the literature is the FA furan ring opening [20], which preferably starts via C-O bond breaking [23]. Although spectroscopic [10] [24] and theoretical [25] studies have highlighted the low percentage of furan ring-opening during the FA polymerization. These side reactions may have a significant impact on the final polymer structure. Indeed, opening furan rings during the FA polymerization, leads to a lower final crosslinking density by decreasing Diels-Alder reaction, resulting on direct impact on the mechanical properties of the final polymer [26]. Furthermore, obtaining these opened furan structures is amplified by the addition of protic polar solvents suggesting disruption mechanisms of FA polymerization.

This paper aims to study the disruption effect of protic polar solvents during the polymerization of FA. Both water and isopropyl alcohol (IPA) were added as protic polar solvents in FA formulations with maleic anhydride (MA) as acidic initiator. The polymerization evolution was followed from the liquid state by Differential Scanning Calorimetry (DSC) and additionally from the rubbery state by Dynamic Mechanical Analysis (DMA). The study provides for the first time an advanced isoconversional analysis of FA polymerization kinetics over a wide temperature range and including two stages of polymerization, i.e. early liquid state and final rubbery state. The obtained variations of effective activation energy, E_{α} , are interpreted as a function of the extent of conversion, α , and of the temperature. Important changes in the polymerization mechanism are discussed.

2. Materials and Methods

2.1 Materials

Furfuryl alcohol (FA) ($M_w = 98.10 \text{ g.mol}^{-1}$, b.p. = 170 °C, purity 99%), isopropyl alcohol (IPA) ($M_w = 60.10 \text{ g.mol}^{-1}$, b.p. = 82 °C, purity >99.7%) and maleic anhydride (MA) ($M_w = 98.06 \text{ g mol}^{-1}$, m.p. = 51–56 °C, purity >99%), were obtained from Aldrich Chemical Co.

2.2 Preparation of liquid FA/solvent mixtures

Three different liquid formulations containing FA, maleic anhydride (MA) and protic polar solvents were prepared for DSC investigation namely: FA/MA (100/2); FA/MA/water and FA/MA/IPA (50/50/1). MA was used as acidic initiator of FA homopolymerization and added with 2% w/w compared to FA. For mixtures containing solvents, IPA or ultra-pure water (conductivity 2 $\mu\text{S.cm}^{-1}$) was added to equivalent quantity of FA (50/50 w/w) with 1% of MA to keep same initiator ratio as FA/MA.

2.3 Preparation of cured PFA materials

Three different reticulated resins were prepared from liquid formulations used in DSC study, i.e. FA/MA (100/2); FA/MA/water and FA/MA/IPA (50/50/1). Pre-polymers were prepared in a PTFE round-bottom flask by heating approximatively 15 grams of liquid formulations. The mixtures were vigorously stirred during the overall process to lead to homogenous final polymers. The synthesis of each furanic resin was realized in two steps. The first pre-polymerization step was the same for the three resins. Blends were heated at around 85 °C during 1 hour in a round bottom flask. A condenser was used to avoid evaporation of solvent or FA and to induce sufficient interactions between FA (or FA homopolymers) and the protic polar solvent. For the second step, the condenser was removed

and the resulting mixtures were placed at 100 °C. Temperature was increased by 10 °C every 30 minutes to obtain a highly viscous resin ($\sim 10^3$ Pa.s⁻¹). To reach the desired viscosity, FA/MA and FA/MA/water were heated to 120 °C while FA/MA/IPA was heated to 140 °C.

Then, the obtaining pre-polymers were introduced in a silicon mold and were cured for 2 hours under pressure (~ 10 bars) respectively at 160 °C for FA/MA and FA/MA/water and at 180 °C for FA/MA/IPA. This step was conducted to obtain rigid materials. The second curing step under pressure was essential to avoid formation of holes in the PFA material (due to water evaporation by polycondensation of FA), which can modify the mechanical or the thermal performances of the final materials.

2.4 Analytical techniques

Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC-1 equipped with a FRS5 sensor (with 56 thermocouples Au-Au/Pd) and STAR[®] software for data analysis. Temperature and enthalpy calibrations were performed by using indium and zinc standards. Samples of about 10 mg were placed into sealed 30 μ L high-pressure crucible. The DSC measurements of FA polymerization were conducted at the heating rates of 1, 2, 4 and 6 °C.min⁻¹.

Dynamic mechanical properties were carried out on a Mettler-Toledo DMA 1 in tensile mode equipped with STAR[®] software for curves analysis. The samples dimensions were 15.00 (length), 4.50 mm (width) and 1.50 mm (thickness) (± 0.01 mm). The experiments were performed from 25 to 350 °C, at a frequency of 1 Hz and with a heating of 1, 2 and 4 °C.min⁻¹.

The DSC and DMA data were treated with an advanced isoconversional method to realize a kinetic study and especially to compute the activation energy dependency (E_a) of FA polymerization. These computations were realized with an internal software [27] [28].

2.5 Theoretical approaches

Isoconversional methods are amongst the more reliable kinetic methods for the treatment of thermoanalytical data, see for example [29] [30] [31] [32]. The ICTAC Kinetics Committee has recommended the use of multiple temperature programs for evaluation of reliable kinetic parameters [30]. The main advantages of isoconversional methods are that they afford evaluation of the activation energy, E_a without assuming any particular form of the reaction model, $f(\alpha)$ or $g(\alpha)$ and that a change in the E_a variation, called E_a -dependency, can generally be associated to a change in the reaction mechanism or in the rate-limiting step of the overall reaction rate as measured with thermoanalytical techniques.

Polymerizations are frequently accompanied by a significant amount of heat released, thus cure kinetics can be easily monitored by DSC. It is generally assumed that the heat flow measured by calorimetry is proportional to the process rate [33]. Thus, the extent of conversion at time t , α_t is computed according to eq.(1)

$$\alpha_t = \frac{\int_{t_i}^t (dQ/dt) dt}{\int_{t_i}^{t_f} (dQ/dt) dt} \quad (1)$$

where dQ/dt is the heat flow, t_i the time at which the process initiates (i.e., the respective heat flow become detectable), and t_f the time at which the process finishes (i.e., the heat flow falls below the detection limit). The denominator represents the total transformation heat released during cure (Q).

In a more general sense, the extent of conversion can be determined as a change of any physical property associated to the reaction progress. For this, the physical property has to be normalized to rely between 0 and 1. If the shear modulus changes with the reaction progress, an extent of conversion can be defined as follow:

$$\alpha_t = \frac{G'_t - G'_{t_i}}{G'_{t_f} - G'_{t_i}} \quad (2)$$

where G' is the shear modulus measured by DMA (or dynamic rheometric) experiments at time t , and where t_i and t_f have the same meaning as in eq.(1).

The general form of the basic rate equation is usually written as[33],[34]:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (3)$$

T is the temperature, $f(\alpha)$ is the differential form of the reaction model that represents the reaction mechanism, E is the activation energy and A is the pre-exponential factor (in s^{-1}).

The advanced isoconversional method[27],[33],[35],[36] used in this study is presented in eq.(4) and eq.(5) and have been derived from eq.(3)

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (4)$$

$$J[E_\alpha, T(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT(t)}\right] dt \quad (5)$$

where E_α is the effective activation energy. The E_α value is determined as the value that minimizes the function $\Phi(E_\alpha)$. This method is applicable to any arbitrary temperature programs $T_i(t)$ and uses a numerical integration of the integral with respect to the time. E_α is computed for each value of α generally in the range 0.02 - 0.98 with a step of 0.02. For each i -th temperature program, the time $t_{\alpha,i}$ and temperature $T_{\alpha,i}$ related to selected values of α are determined by an accurate interpolation[27] [28]. The software developed can treat any kind of isothermal or non-isothermal data from DSC, calorimetry (C80), TGA, DMA or rheometry[27] [28] [37] [38].

3. Results and discussion

3.1. FA polymerization evolution from the liquid state

3.1.1 Non-isothermal DSC investigation

The **Figure 1** shows non-isothermal DSC data obtained during FA polymerization and in presence of protic polar solvent as water and IPA. The data of polymerization without solvent are presented in insert of **Figure 1** for comparisons (reference system). The reference system shows a single asymmetric thermal event, while the addition of solvents significantly modify the heat flow curves shapes with appearance of a shoulder or a second peak. This observation leads to the hypothesis of a change in the polymerization pathways. In FA/MA/water mix, the first peak is predominant. It is followed by a broad thermal event that could correspond to secondary reaction or residual cross-links between FA oligomer. For FA/MA/IPA mix, the polymerization pathway seems

different from the other two systems due to a second and predominant thermal event. Moreover, the FA polymerization reactions are shifted to higher temperature. The protic character of IPA due to its high dipolar moment ($\mu_{\text{IPA}} = 1.70$ D) can explain this. The first step of FA polymerization starts with the formation of an active furfuryl carbenium center [10]. Thus, in this system, IPA slow down the formation rate of the carbenium center by forming hydrogen bonds and a solvation sphere with the hydroxyl group of FA [39]. These effects could also occur in presence of water which also present a high dipolar moment ($\mu_{\text{water}} = 1.85$ D). However, the fact that MA is opened in maleic acid in presence of water should be also taken into account. The $\text{pK}_{\text{a}1}$ of maleic acid is very low (~ 1.8) and decreases the pH of the mix. The FA polymerization being initiated in acid catalyzed condition, the MA opening releases protons that allow starting the condensations at lower temperature. Contrary to IPA, the slowdown effect due to solvation is counterbalanced by the formation of H^+ due to the MA hydrolysis, which results in earlier initiation of FA polymerization with water.

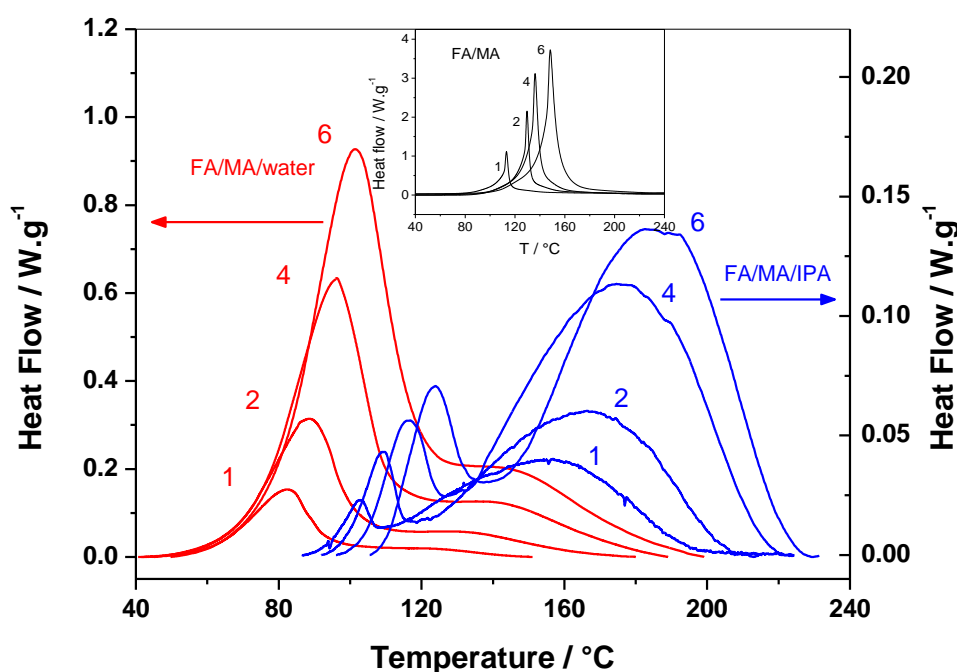


Figure 1: Non-isothermal DSC curves for the curing of FA/MA/water (red lines) and FA/MA/IPA (blue lines). Insert: FA/MA cure without solvent. The heating rates in $^{\circ}\text{C}\cdot\text{min}^{-1}$ are indicated by the curves.

These curves have been used to estimate the reaction heat released during the reaction (Q) by integration of DSC peaks. The reaction heat values obtained for FA/MA/water and FA/MA/IPA systems are summarized and compared to the FA reference system [40] (**Table 1**). In order to compare values obtained between each formulation, the data were reported to the mass of FA. FA/MA/IPA systems show decreasing reaction heat values with increasing heating rate. The values of the reaction heat are 2.4 to 3.5 times smaller than the reference values. Moreover, the reaction heat (Q) depends on the amplitude of the first thermal event which is rather associated to initiations reactions. Indeed, increasing the heating rate allow less time for initiation reactions to take place and leads to a decrease of the reaction heat. These decreasing values, combined with the particular thermal events of this mix (two distinct peaks), suggests possible interaction between FA and IPA.

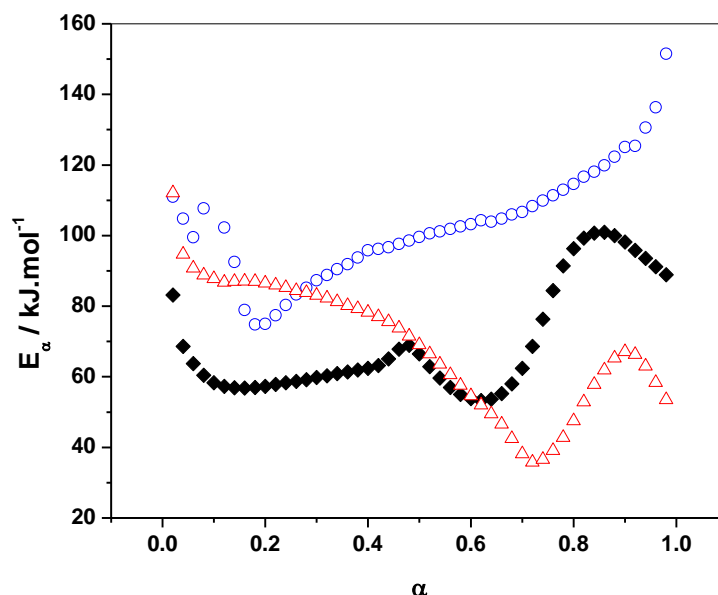
Table 1: Reaction heat (Q) reported to the mass of FA for the three different systems: FA/MA/water, FA/MA/IPA and FA/MA

	FA/MA/water	FA/MA/IPA	FA/MA (reference)
$\beta / ^\circ\text{C}\cdot\text{min}^{-1}$		$Q / \text{J}\cdot\text{g}^{-1}$ of FA	
1	490 ± 20	300 ± 30	709 ± 30
2	632 ± 30	230 ± 20	685 ± 30
4	678 ± 30	216 ± 20	620 ± 30
6	712 ± 30	168 ± 20	593 ± 30

In the case of FA/MA/water system, the opposite tendency occurs. The reaction heat increases with the heating rate. On the other hand, the highest reaction heat value of FA/MA/water mix ($712 \text{ g}\cdot\text{mol}^{-1}$) obtained for the fastest rate is almost the same as the reaction heat value of FA/MA reference mix at the slower rate ($709 \text{ g}\cdot\text{mol}^{-1}$). Thus, the heating rate considerably affects the reaction mechanism, which confirms the assumption of a complex multi-step polymerization mechanism. This also indicates that the final properties of the materials will be completely different according to the temperature domain used for curing the system.

3.1.2 E_a vs. α -dependence

Model-free advanced isoconversional analysis was employed to highlight new insights on the complex polymerization mechanism and kinetics in presence of solvents. **Figure 2** represents the E_a dependencies with extent of conversion (α). Analysis of the E_a -dependencies clearly indicates a complex mechanism that involves several chemical steps, each of them having its own activation energy. As a result, each increasing and decreasing parts of the effective activation energy (E_a) can be associated with changes in the rate-limiting steps of the overall polymerization.

**Figure 2:** Dependence of the effective activation energy (E_a) on extent of conversion of FA/MA/water (open red triangles), FA/MA/IPA (open blue circles) and FA/MA (solid black lozenges).

The three systems exhibit decreasing E_a values at the initial stages of the reaction (for α values until to 0.10 for reference and water systems, 0.20 for IPA system) that can be attributed to an autocatalytic step [41]. This initial step corresponds to the formation of an active furfuryl carbenium

center that will induce the polymerization. The longer decay of FA/MA/IPA E_a values to higher extent of conversion (0.20) confirms the hypothesis of interactions between FA and IPA by hydrogen bonds or solvation spheres, which slow down the autocatalytic step.

The FA disruption polymerization by IPA is also confirmed by the completely different activation energy dependency obtained compared to the two other systems. Indeed, while alternating decreasing and increasing values are obtained for FA/MA and FA/MA/water, the FA/MA/IPA system reveals a continuous activation energy increase for α values from 0.20 to 1. This progressive increase observed might correspond to competitive or consecutive reactions (i.e. condensation, Diels-Alder and possibly side reactions) during the polymerization [27]. On the other hand, E_a -dependencies of FA/MA/water and reference systems show several similarities. The polycondensation of FA occurs for $\alpha \sim 0.10$ to $\alpha \sim 0.40$ for the two systems. A slight E_a decrease for FA/MA/water and a slight increase for the reference system characterize this step. The presence of water decreases the viscosity, which facilitates the polymerization of FA.

For $\alpha \sim 0.48$, E_a values of both systems are very close and a slight increase in the activation energy is observed for the reference system. It has been demonstrated that this increasing tendency for the reference system is correlated with the high viscosity increase due to the formation of crosslinks [40]. This phenomenon is not visible for FA/MA/water due to the presence of water, which still induces a lower viscosity at same extent of conversion.

For $\alpha > 0.48$, the decreasing tendency for the two curves is still the same, with a slight shift to higher extent of conversion for the FA/MA/water system. At this stage of the reaction, the molecular mobility strongly decreases which induces a decrease of the reaction rate. Thus, the overall polymerization becomes controlled by the diffusion of short linear chains. This is mainly due to an increase of the viscosity of the system, which reduces the chemical reactions rates and leads to a decrease of E_a [41]. This decrease is observed for both systems and is characteristic of a transition from kinetic to diffusion regime [40]. Diffusion control generally become rate limiting when the characteristic relaxation time of the reaction medium exceeds markedly the characteristic time of the reaction itself [29]. This decrease to low E_a values is less marked but is also present for FA/MA system (E_a decreasing from 69 to 53 kJ.mol⁻¹ for α from 0.48 to 0.63) than FA/MA/water (E_a decreasing from 71 to 36 kJ.mol⁻¹ for α from 0.48 to 0.73). This indicates that diffusion control is more important in the presence of water. This will be explained by analysis of the dependence of the effective activation energy (E_a) on temperature (T).

Following this decrease, an increasing E_a -dependency is observed for both FA/MA (until $\alpha \sim 0.90$) and FA/MA/water (until $\alpha \sim 0.85$) systems and corresponds to an increase in molecular mobility due to temperature increase. This mobility increase permits to the chemical reaction to be reactivated and corresponds to the formation of chemical bonds in the gelled state by Diels-Alder cycloadditions. Finally, the last decrease is attributed to the diffusion of unreacted FA monomers [40].

According to **Figure 2**, E_a for FA/MA/water is always higher than E_a for FA/MA for $0 < \alpha < 0.60$ while the reaction in presence of water is shifted to lower temperatures (**Figure 1**). Generally, a higher activation energy shift the reaction to higher temperature. Thus, in this case it seems that the opposite effect is obtained. Because E and A have opposite effects regarding the shift of a reaction to lower or higher temperature, this observation could be explained by a higher value of the pre-exponential factor for FA/MA/water system. In order to verify this, pre-exponential factors were computed for FA/MA and FA/MA/water systems using the model-free method explained in detail in ref. [27]. The

method uses the so-called false compensation effect that allow to establish a relationship between E_α and $\ln A_\alpha$ in the form: $\ln A_\alpha = a E_\alpha + b$ and is based on the practical observation that for complex (multi-step) processes, the same experimental curve can be described by several reaction models. Once this relation has been established it is possible to compute $\ln A_\alpha$ in a model-free way using the value of E_α obtained for each α value with an advanced isoconversional method. The computations were realized for a heating rate of $2^\circ\text{C}\cdot\text{min}^{-1}$ and an extent of conversion $0.05 < \alpha < 0.15$. This range was selected in order to compute the pre-exponential factors for the very beginning of the reaction. The models that lead to the best fit ($r^2 > 0.9995$) were the models number 4,5,6,10,11,12,13 of ref. [27]. The parameters found for FA/MA are $a=0.29475 \text{ mol}\cdot\text{kJ}^{-1}$ and $b=-6.47597$ ($r^2=0.9984$) and for FA/MA/water $a=0.32955 \text{ mol}\cdot\text{kJ}^{-1}$ and $b=-6.23381$ ($r^2=0.9987$). These values confirm our hypothesis that much higher values for the pre-exponential factor are obtained in presence of water. As an example, the pre-exponential factors obtained for FA/MA and FA/MA/water for $\alpha = 0.10$ are $4.48 \cdot 10^4 \text{ s}^{-1}$ and $7.23 \cdot 10^9 \text{ s}^{-1}$ respectively. These values confirm our hypothesis that much higher values for the pre-exponential factor are obtained in presence of water.

3.1.3 Additional kinetic computation of FA/MA/IPA

To better understand the complex reactivity of FA/MA/IPA, additional computations were performed on each thermal events of this system (see **Figure 1**). Thus, the E_α calculated from the first thermal event (before $120/140^\circ\text{C}$) is shown in **Figure 3a** while **Figure 3b** shows the E_α calculated from the second thermal event (after $120/140^\circ\text{C}$). It can be seen that the activation energy of **Figure 3a** has the same tendency as the curve of **Figure 2** from $\alpha = 0$ to $\alpha = 0.20$ with a continuous E_α decrease. Therefore, the first thermal event of FA/MA/IPA thermograms of **Figure 1** is the result of the autocatalytic step. The second thermal event could be related to competitive reactions during the polymerization. These competitive reactions are displayed in **Figure 3b** where a continuous increase of E_α for α from 0.20 to 1 is observed.

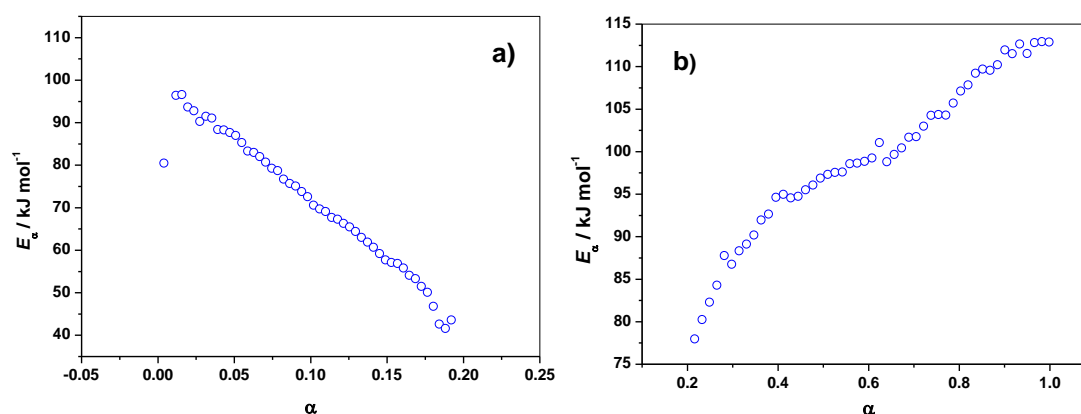


Figure 3 : Partial dependence of the effective activation energy (E_α) calculated from the non-isothermal DSC curves of FA/MA/IPA mix of **Figure 1**. a) from the first thermal event (before $120/140^\circ\text{C}$) and b) from the second thermal event (after $120/140^\circ\text{C}$)

3.1.4 E_α vs. T -dependence

The apparent activation energy can be also computed as a function of temperature (E_α - T dependency), by taking an average temperature associated with each value of the extent of

conversion. **Figure 4** represents the E_a -dependencies with temperature. Analysis of E_a - T values shows that the various rate-limiting steps are extended over a higher temperature range for the solvent systems and each of these steps takes place at different temperatures depending on the polymerization environment of FA. More precisely, **Figure 4** highlights that the reaction of FA/MA/water system is shifted to lower temperatures and the reaction of FA/MA/IPA to higher temperatures compared to the reference.

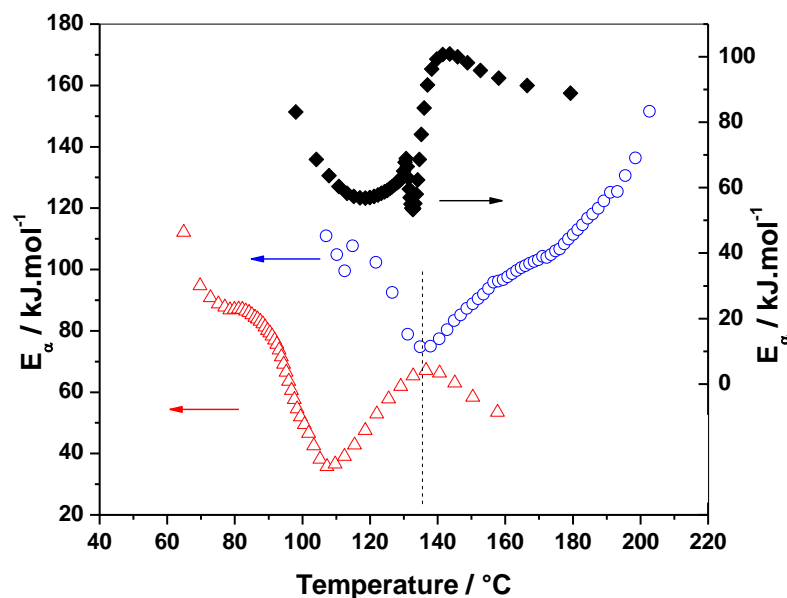


Figure 4: Dependence of the effective activation energy (E_a) on temperature (T) for non-isothermal cure of FA/MA/water (open red triangles), FA/MA (solid black lozenges) and FA/MA/IPA (open blue circles) systems.

Indeed, the first E_a decrease associated to the autocatalytic step occurs between 100-115°C for FA/MA, 60-75°C for FA/MA/water and between 120-140°C for FA/MA/IPA system. The shift to lower temperatures observed for the water mix system is explained by the easier MA opening into maleic acid due to the presence of water and correlate with the higher pre-exponential factor values previously reported. For FA/MA/IPA, analysis of the E_a - T dependency confirms the higher activation energy barrier for the initial stages of the polymerization of FA in presence of IPA instead of water. Furthermore, the polymerization reactions (i.e. condensation and Diels-Alder reactions) of this mix begins at 135 °C, i.e. when the polymerization is finished or almost finished for the two other formulations. This confirms our previous hypothesis that the solvation sphere formed between FA and IPA is very stable and hinder the reactions.

Another significant difference highlighted by the analysis of the E_a - T dependency is the secondary E_a decreasing values due to the diffusion regime. This stage is observed in a very short temperature range for FA/MA (131-133°C) while this step takes place over a wider temperature range for FA/MA/water (90-105 °C). For FA/MA/IPA system, this stage is absent and E_a values exhibit same tendency as in **Figure 2** where the major part of the FA/MA/IPA dependency demonstrates increasing E_a values. This E_a decrease characteristic of the diffusion control of small molecules is more pronounced for the FA/MA/water system (86 to 36 kJ.mol⁻¹) than for the FA/MA system (69 to 54 kJ.mol⁻¹), in agreement with the results of **Figure 2**. This could seem to be, a priori, contradictory. Nevertheless, analysis of the E_a - T dependency shows that this decrease occurs at much lower

temperature for the FA/MA/water system. This explains that diffusion control is more pronounced in the presence of water due to the inferior molecular mobility at lower temperature.

After the second decreasing step observed for FA/MA and FA/MA/water, the E_a values re-increase significantly in a very sharp temperature interval (133-141 °C) for the reference system. This is attributed to reactivation of chemical reactions and diffusion of long segments of the polymer chains. A similar increase is observed for the water system, but at lower temperature and in a wider temperature interval (107-136 °C). This final re-increase was attributed to the cross-links formation in the gelled state due to Diels-Alder cycloadditions [40]. Thus, addition of water, allows for the re-activation of chemical reactions at lower temperature, probably because of the higher mobility of the system.

3.2. Residual cross-linking reactions in rubbery state

3.2.1 Non-isothermal DMA investigation

Once polymerized, the mechanical properties of the three PFA were evaluated by DMA. Elastic moduli of the three materials are shown in **Figure 5**. This figure highlights decreasing moduli of about two decades between 30 and 130 °C for all the systems. This decreasing tendency is unambiguously attributed to the cooperative α -relaxation process of PFA chains commonly associated to the glass transition. Above 170 °C, i.e. from temperature range corresponding to the post-curing treatment, the elastic modulus increases for the three samples. This increase may correspond to residual cross-links occurring in solid PFA resins. As shown in **Figure 5**, the increase is more important when the PFA has been cured in presence of protic polar solvents (e.g. water or IPA). In particular, it can be deduced that polymerization via IPA is less complete since the re-increase is about one decade and accordingly the amount of residual cross-links is more important compared to the other systems.

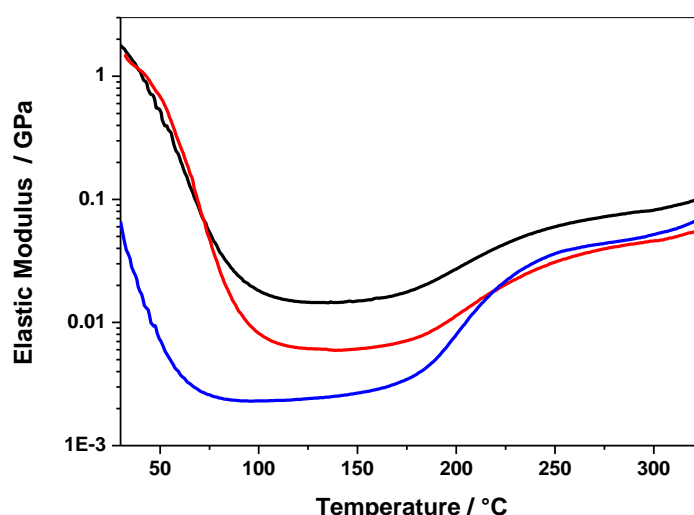


Figure 5: Elastic modulus vs temperature obtained during the first heating at 2 °C.min⁻¹ of reference PFA (black line), PFA/water (red line) and PFA/IPA (blue line)

Additional dynamic mechanical measurements were carried out at 1 and 4 °C.min⁻¹ on each polymers from 25 to 350 °C (**Figure 6**) in order to confirm the hypothesis of residual cross-links occurring in solid PFA resins. These DMA measurements performed at various heating rate were

conducted to show that this increase is not due to volatilization of either protic polar solvent added in formulations or water from FA polycondensations, which could remain trapped within polymer chains. These curves show that the moduli increase depends on the heating rate. Therefore, it can be deduced that it should be a kinetic phenomenon and not a thermodynamic phenomenon such as a solvent evaporation. Indeed, first-order thermodynamic transitions such as vaporization should be independent of the heating rate. It is interesting to note that the modulus increase is observed from 170 °C to 290 °C for the three systems in DMA, while no thermal event was recorded at a temperature higher than 220 °C on the first DSC heating curves. This clearly highlights the interest of using DMA measurements to identify residual crosslinks occurring in the rubbery state after intensive post-curing.

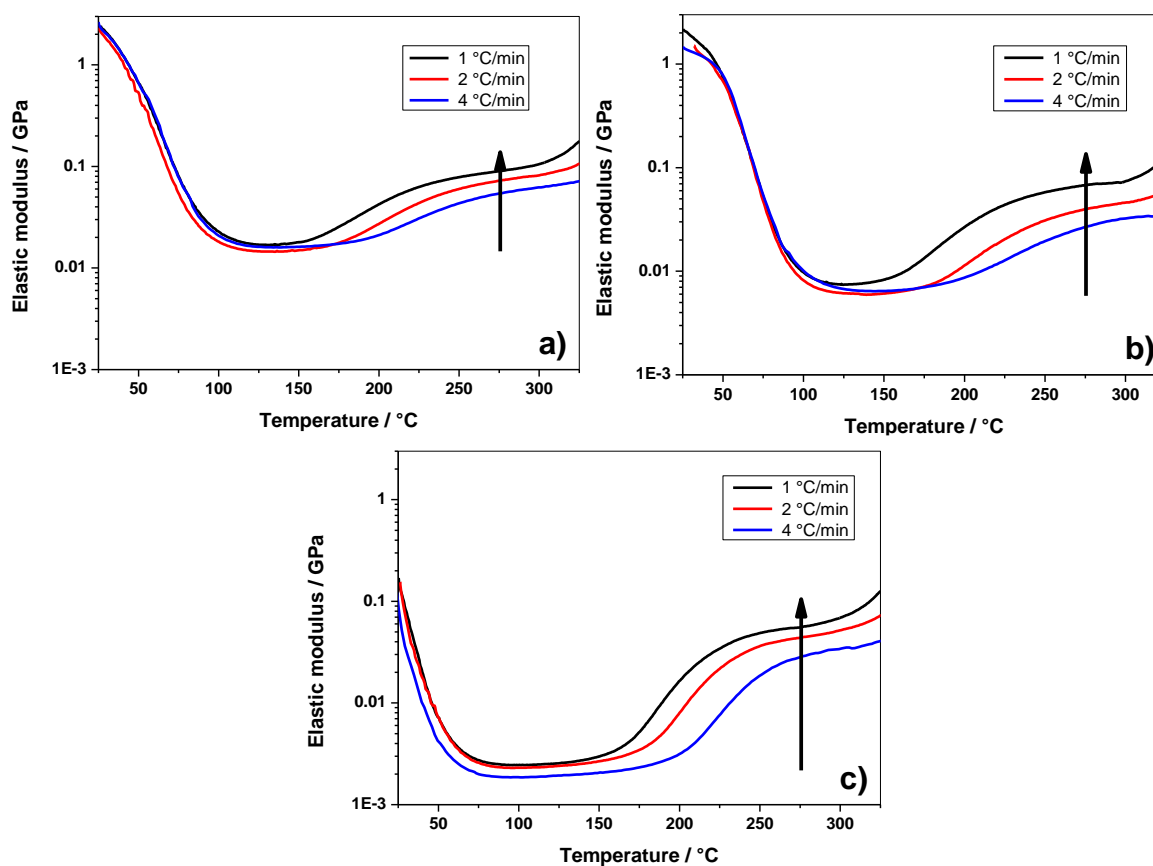


Figure 6: (a) Elastic modulus (E') of three PFA samples obtained by DMA at 1, 2 and 4 °C. a) FA/MA, b) FA/MA/water and c) FA/MA/IPA.

Then, the modulus increase above 150 °C clearly indicates that chemical reactions still occur in the rubbery state in the different PFA samples. The modulus increase is more important when the samples have been cured in presence of protic polar solvents (e.g. water or IPA). More precisely, the polymerization in presence of IPA is less complete since the re-increase and accordingly the amount of residual cross-links is more important compared to the other systems.

3.2.1 E_α vs. T -dependence

The kinetic of formation of these residual cross-links in the rubbery state was evaluated from the treatment of the DMA curves of **Figure 6**. For that purpose, the elastic modulus was normalized between 0 and 1 according to equation (2), in order to get an extent of conversion, α , for the cross-

links in the rubbery state. These data obtained on the three PFA samples were computed with an advanced isoconversional method (Equations (5) and (6)).

Figure 7a shows the E_a dependencies computed as a function of temperature. The three samples demonstrate increasing E_a values, which could correspond to a kinetic control by the diffusion of long polymeric chains. As the PFA material progressively cross-link in the solid state, the molecular mobility becomes more restricted which leads to an increase in the activation energy (E_a). The PFA cured w/o solvent (i.e. PFA/MA, black lozenges) has the highest E_a values, which indicates that the long chains are more constrained in comparison with the PFA samples cured in presence of solvents.

The E_a -dependencies of reference system obtained for polymerization from the liquid state (DSC measurements) and for additional cross-link occurring in the rubbery state (DMA measurements) were plotted in **Figure 7b**. As can be seen, there is a perfect continuity between the two dependencies, the final values of the reaction starting from the liquid state being in good agreement with the first values of the reaction starting from the rubbery state. Thus, combination of DSC and DMA data allows to study the polymerization kinetics and to get mechanistic information over a wide temperature range starting from the liquid state to end in the solid state

The modification of FA polymerization by the protic polar solvents (see **Figure 7**) give lower E_a values for reactions continuing in the rubbery state. The occurrence of ring opening reactions reduces the cross-link density and thus, molecular mobility in the rubbery state is promoted. This result is in agreement with the lower values of the elastic modulus (E') in the rubbery state for the PFA samples prepared with solvents (**Figure 5**). Absolute E_a values of FA/MA/water and FA/MA/IPA cannot be directly compared because these two samples were subjected to different post-curing treatment in order to obtain a sufficiently cohesive material for permitting DMA measurements. Nevertheless, the values are in the same order of magnitude.

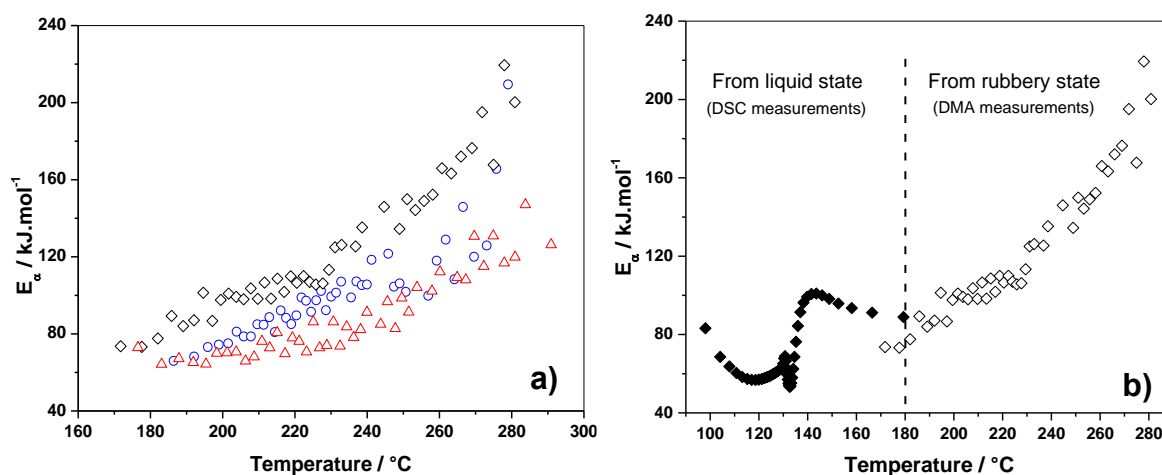


Figure 7 : (a) Effective activation energy dependency (E_a) as a function of temperature obtained from DMA measurements of **Figure 6** (black open lozenges: PFA/MA, red open triangles: PFA/MA/water, blue open circles: PFA/MA/IPA). (b) Continuous E_a from liquid state (DSC measurements) to solid state (DMA measurements) for FA/MA system.

4. Conclusions

The presence of solvent significantly disturbs the polymerization kinetics of FA. The autocatalytic stage is modified likely due to a stabilization of the furfuryl carbenium center by either water or IPA. In presence of water, the autocatalytic stage is less marked as the initiator, maleic anhydride, is

rapidly hydrolyzed into maleic acid, which induces the onset of polymerization reactions at lower temperatures. In this mix, we note that FA polymerization rate-limiting steps are similar to the reference system with only few variations of E_a values and temperatures of reaction. However, the presence of IPA shifts the beginning of the polymerization to higher temperature. Furthermore, E_a values of FA/MA/IPA clearly indicate that main reactions and other side reactions seems to occur in parallel and throughout the whole polymerization. The only similarity between E_a dependency of FA/MA/IPA and the two other systems is the autocatalytic step, which is characterized by a separately thermal event.

The DMA study has highlighted continuous increase of the elastic modulus attributed to further cross-links in the rubbery state until 290 °C. These additional reactions occurring in the rubbery plateau cannot be highlighted by DSC since the potential exothermic variation is too small for being detected. The E' variations obtained for different heating rates permitted to obtain E_a -dependency in the rubbery state. It was shown that the modification of FA polymerization by protic polar solvents slightly decreases E_a values in the rubbery state due to the increase of molecular mobility. For reference PFA, the E_a -dependencies obtained from the liquid state and from the rubbery state are in perfect continuity, which prove the validity of the new approach proposed to get mechanistic information over a very wide temperature range for complex polymerization.

Acknowledgments: The authors wish to thank Mettler-Toledo Inc. for fruitful collaboration and scientific exchanges. The Research Council of Norway (RCN) and the society Kebony (Norway) are also gratefully acknowledged for the European Project POLYWOOD, « *Wood-polymer composites for use in marine environments* ». The authors also gratefully acknowledged Région PACA (France) for financial support of the project ECOMOBIL.

References

1. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411-2502, 10.1021/cr050989d.
2. Isikgor, F.H.; Becer, C.R. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* **2015**, *6*, 4497-4559, 10.1039/c5py00263j.
3. Kamm, B.; Kamm, M.; Schmidt, M.; Hirth, T.; Schulze, M. Lignocellulose-based chemical products and product family trees. In *Biorefineries – industrial processes and products*, Kamm, B.; Gruber, P.R.; Kamm, M., Eds. WILEY-VCH Verlag GmbH & Co.: Weinheim, Germany, 2006; pp 97-149, 10.1002/9783527619849.ch20
4. Chheda, J.N.; Román-Leshkov, Y.; Dumesic, J.A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.* **2007**, *9*, 342-350, 10.1039/b611568c.
5. Rosatella, A.A.; Simeonov, S.P.; Frade, R.F.M.; Afonso, C.A.M. 5-hydroxymethylfurfural (hmf) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* **2011**, *13*, 754, 10.1039/c0gc00401d.
6. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sadaba, I.; Lopez Granados, M. Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energ. Environ. Sci.* **2016**, *9*, 1144-1189, 10.1039/C5EE02666K.
7. Gandini, A. The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **2011**, *13*, 1061, 10.1039/c0gc00789g.

8. Bozell, J.J.; Petersen, G.R. Technology development for the production of biobased products from biorefinery carbohydrates—the us department of energy’s “top 10” revisited. *Green Chem.* **2010**, *12*, 539, 10.1039/b922014c.
9. Gandini, A.; Lacerda, T.M.; Carvalho, A.J.F.; Trovatti, E. Progress of polymers from renewable resources: Furans, vegetable oils, and polysaccharides. *Chem. Rev.* **2016**, *116*, 1637-1669, 10.1021/acs.chemrev.5b00264.
10. Choura, M.; Belgacem, N.M.; Gandini, A. Acid-catalyzed polycondensation of furfuryl alcohol: Mechanisms of chromophore formation and cross-linking. *Macromolecules* **1996**, *29*, 3839-3850, 10.1021/ma951522f.
11. Oliva-Teles, M.T.; Delerue-Matos, C.; Alvim-Ferraz, M.C.M. Determination of free furfuryl alcohol in foundry resins by chromatographic techniques. *Anal. Chim. Acta* **2005**, *537*, 47-51, 10.1016/j.aca.2005.01.001.
12. Lande, S.; Westin, M.; Schneider, M.H. Eco-efficient wood protection: Furfurylated wood as alternative to traditional wood preservation. *Manage. Environ. Qual.: Int. J.* **2004**, *15*, 529-540, 10.1108/14777830410553979.
13. Ju, M.; Zeng, C.; Wang, C.; Zhang, L. Preparation of ultrafine carbon spheres by controlled polymerization of furfuryl alcohol in microdroplets. *Ind. Eng. Chem. Res.* **2014**, *53*, 3084-3090, 10.1021/ie4029939.
14. Spange, S.; Grund, S. Nanostructured organic-inorganic composite materials by twin polymerization of hybrid monomers. *Adv. Mater.* **2009**, *21*, 2111-2116, 10.1002/adma.200802797.
15. Bosq, N.; Guigo, N.; Falco, G.; Persello, J.; Sbirrazzuoli, N. Impact of silica nanoclusters on furfuryl alcohol polymerization and molecular mobility. *J. Phys. Chem. C* **2017**, *121*, 7485-7494, 10.1021/acs.jpcc.6b12882.
16. Deka, H.; Misra, M.; Mohanty, A. Renewable resource based “all green composites” from kenaf biofiber and poly(furfuryl alcohol) bioresin. *Ind. Crops. Prod.* **2013**, *41*, 94-101, 10.1016/j.indcrop.2012.03.037.
17. Guigo, N.; Mija, A.; Vincent, L.; Sbirrazzuoli, N. Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets. *Eur. Pol. J.* **2010**, *46*, 1016-1023, 10.1016/j.eurpolymj.2010.02.010.
18. Roudsari, G.M.; Misra, M.; Mohanty, A.K. A study of mechanical properties of biobased epoxy network: Effect of addition of epoxidized soybean oil and poly(furfuryl alcohol). *J. Appl. Polym. Sci.* **2017**, *134*, 44352, 10.1002/app.44352.
19. Pin, J.M.; Guigo, N.; Vincent, L.; Sbirrazzuoli, N.; Mija, A. Copolymerization as a strategy to combine epoxidized linseed oil and furfuryl alcohol: The design of a fully bio-based thermoset. *ChemSusChem* **2015**, *8*, 4149-4161, 10.1002/cssc.201501259.
20. Conley, T.; Metil, I. An investigation of the structure of furfuryl alcohol polycondensate with infrared spectroscopy. *J. Appl. Polym. Sci.* **1963**, *7*, 37-52, 10.1002/app.1963.070070104.
21. Dunlop, A.; Peters, F. *The furans*. Reinhold Publishing Corporation: New York, USA, , 1953; p 447.
22. Montero, A.L.; Montero, L.A.; Martínez, R.; Spange, S. Ab initio modelling of crosslinking in polymers. A case of chains with furan rings. *J. Mol. Struct.-Theochem* **2006**, *770*, 99-106, 10.1016/j.theochem.2006.05.027.

23. Wang, S.; Vorotnikov, V.; Vlachos, D.G. A dft study of furan hydrogenation and ring opening on pd(111). *Green Chem.* **2014**, *16*, 736-747, 10.1039/c3gc41183d.
24. Kim, T.; Jeong, J.; Rahman, M.; Zhu, E.; Mahajan, D. Characterizations of furfuryl alcohol oligomer/polymerization catalyzed by homogeneous and heterogeneous acid catalysts. *Korean J. Che. Eng.* **2014**, *31*, 2124-2129, 10.1007/s11814-014-0322-x.
25. Kim, T.; Assary, R.S.; Marshall, C.L.; Gosztola, D.J.; Curtiss, L.A.; Stair, P.C. Acid-catalyzed furfuryl alcohol polymerization: Characterizations of molecular structure and thermodynamic properties. *ChemCatChem* **2011**, *3*, 1451-1458, 10.1002/cctc.201100098.
26. Falco G.; Guigo, N.; Vincent, L.; Sbirrazzuoli N. Opening furan for tailoring properties of biobased poly(furfuryl alcohol) thermoset. *ChemSusChem*, (under review).
27. Sbirrazzuoli, N. Determination of pre-exponential factors and of the mathematical functions $f(\alpha)$ or $g(\alpha)$ that describe the reaction mechanism in a model-free way. *Thermochim. Acta* **2013**, *564*, 59-69, 10.1016/j.tca.2013.04.015.
28. Sbirrazzuoli, N. Is the friedman method applicable to transformations with temperature dependent reaction heat? *Macromol. Chem. Phys.* **2007**, *208*, 1592-1597, 10.1002/macp.200700100.
29. Vyazovkin, S. *Isoconversional kinetics of thermally stimulated processes*. Springer: Berlin, Germany, : 2015, 978-3-319-14175-6.
30. Vyazovkin, S.; Burnham, A.K.; Criado, J.M.; Pérez-Maqueda, L.A.; Popescu, C.; Sbirrazzuoli, N. Ictac kinetics committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **2011**, *520*, 1-19, 10.1016/j.tca.2011.03.034.
31. Vyazovkin, S.; Sbirrazzuoli, N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromol. Rapid Comm.* **2006**, *27*, 1515-1532, 10.1002/marc.200600404.
32. Papageorgiou, G.Z.; Achilias, D.S.; Karayannidis, G.P. Estimation of thermal transitions in poly(ethylene naphthalate): Experiments and modeling using isoconversional methods. *Polymer* **2010**, *51*, 2565-2575, 10.1016/j.polymer.2010.04.031.
33. Sbirrazzuoli, N.; Vincent, L.; Vyazovkin, S. Comparison of several computational procedures for evaluating the kinetics of thermally stimulated condensed phase reactions. *Chemometr. Intell. Lab.* **2000**, *54*, 53-60, 10.1016/S0169-7439(00)00103-9.
34. Atkins, P.; Paula, J.D. *Physical chemistry*. 9th ed., W.H Freeman: New York, USA: 2010, 978-1429218122.
35. Vyazovkin, S. Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature. *J. Comput. Chem.* **1997**, *18*, 393-402, 10.1002/(SICI)1096-987X(199702)18:3<393::AID-JCC9>3.0.CO;2-P.
36. Vyazovkin, S. Modification of the integral isoconversional method to account for variation in the activation energy. *J. Comput. Chem.* **2001**, *22*, 178-183, 10.1002/1096-987X(20010130)22:2<178::AID-JCC5>3.0.CO;2-#
37. Sbirrazzuoli, N.; Brunel, D.; Elegant, L. Different kinetic equations analysis. *J. Therm. Anal.* **1992**, *38*, 1509-1524, 10.1007/BF01975082.
38. Sbirrazzuoli, N.; Girault, Y.; Elegant, L. Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 3 - peak maximum evolution methods and isoconversional methods. *Thermochim. Acta* **1997**, *293*, 25-37, 10.1016/S0040-6031(97)00023-3.

39. Kim, T.; Assary, R.S.; Kim, H.; Marshall, C.L.; Gosztola, D.J.; Curtiss, L.A.; Stair, P.C. Effects of solvent on the furfuryl alcohol polymerization reaction: Uv raman spectroscopy study. *Catal. Today* **2013**, *205*, 60-66, 10.1016/j.cattod.2012.09.033.
40. Guigo, N.; Mija, A.; Vincent, L.; Sbirrazzuoli, N. Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5359-5366, 10.1039/b707950h.
41. Vyazovkin, S.; Sbirrazzuoli, N. Mechanism and kinetics of epoxy-amine cure studied by differential scanning calorimetry. *Macromolecules* **1996**, *29*, 1867-1873, 10.1021/ma951162w.