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ANISOTHERM STUDY OF THE INFLUENCE OF FLAX FIBERS ON CURING KINETICS OF BIOBASED EPOXY RESIN

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ABSTRACT

Composites materials made of biobased matrices reinforced with natural fibers are a solution considered to meet the environmental constraints of industry. Interactions between a partially biobased epoxy resin and flax fibers were investigated using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis type trials (DMA). DSC analysis revealed that the catalyst effect of water increases the variation of entropy and lead to higher $E\alpha$ values. DMA measurements highlight that composite with wet fibers has a higher T_g value after manufacturing and it is a consequence of the higher reactivity induced by water. By contrast, composite reinforced by dried flax fiber showed a lower curing reactivity and by consequence lower $E\alpha$ values and T_g value after manufacturing. Both composites were stored under relative humidity conditions after manufacturing and evidenced an increase of T_g due to water absorption. A post-curing helped the composite with dried fiber to reach maximum T_g while it wasn't the case for composite with wet fibers due to chaotic network geometry caused by the entropic effect. Water contained by the flax fibers can act as a plasticizer after the post-curing as the T_g decrease with the absorbed water. This work gives a better understanding to the role of water naturally contained by flax fibers and point out the fact that monitoring the moisture of flax fibers is a key parameter to manufacture biobased composites.

1 INTRODUCTION

Interest for composite materials made of biobased matrices and reinforced with natural fibers is constantly growing. Besides their low environmental impact these materials exhibits good mechanical properties and low densities for mass reduction that are valuable for many industrial sectors [1]–[4]. Among numerous natural fibers, flax fibers are the most widely used. This popularity is due to their versatility as they exhibit interesting properties like high tensile strength [5], good vibration absorption [6], for a well-mastered harvesting method [7]. With a better Life Cycle Assessment than many petroleum-based matrices reinforced by synthetic fibers [8]–[10], bio-composites should already have overwhelmed the market of composite. But actually, the use of these eco-friendly materials remains limited due to technological locks such as the variability of fiber dimensions and the sensitivity to climatic changes. In addition to these physical issues, the presence of a natural fibers itself in a thermoset resin can modify its curing kinetics leading to lower performances [11].

The aim of this work is to study the influence of flax fibers on the crosslinking of a partially biobased epoxy resin during and after its curing. Crosslinking reaction of epoxy-amine systems consists in the epoxy ring opening from a primary amine by nucleophile attack. It is generally suggested that the curing mechanism is guided by two reaction paths [12]: (1) reaction initiated by compound containing nitrogen - hydrogen bond known as non-catalytic reactions, (2) reaction catalysed by compounds containing oxygen - hydrogen bond known as catalytic reactions. On the one hand, some researchers showed that proton donor groups such as H_2O and ROH tend to accelerate the reaction [13], [14]. On the other hand, Canavy et al. recently showed that cellulosic compound of the fibers can interact with amine functions from the hardeners and lead to a lower network quality [15].

In this paper we investigate the role of the flax fibers and water that they contained on the curing kinetics of an epoxy-amine and their influence on network formation. For this purpose, samples of pure epoxy, epoxy with glass fibers, epoxy with wet or dried flax fibers were studied during curing of the resin and after composite manufacturing. First, Differential Scanning Calorimetry (DSC) was used to quantify the influence of wet / dried fibers on curing kinetics. Then, glass transition temperatures were studied using Dynamic Mechanical Analysis (DMA) to evaluate the influence on the network formation. From DSC results, an isoconversional method was used to obtain the activation energy and to have a better understanding of the phenomenon involved during crosslinking.

2 MATERIALS AND METHODS

2.1 Materials

Partially bio-based epoxy resin (56 %) GreenPoxy SR56 and hardener SD7561 were purchased from SICOMIN®.

Flax fabrics used was a unidirectional untreated flax fabric with an areal weight of 210 g/m² and were kindly supplied by TERRE DE LIN®. Mat of glass with an areal weight of 300 g/m² were used as non-organic reference reinforcement.

2.2 Sample preparation

Flax fabrics were dried using an oven at 103°C for 24 hours to reach a theoretical water content of 0 % wt [16].

Then a part of the plies was impregnated with the epoxy resin to give samples GP/FF0% (Figure 1). The rest of the plies were stored in a controlled temperature and relative humidity chamber at 20 °C and 75 % RH until saturation to reach 10 %wt of absorbed water. When the water weight reached 10 %, plies were impregnated with epoxy resin to obtain samples GP/FF10% (Figure 1). Glass fiber composite were directly manufactured from the glass fabrics to obtain samples GP/GF. All composite samples were manufactured using hand lay-up process. The volume fiber fraction was 30 % for each composite manufactured.

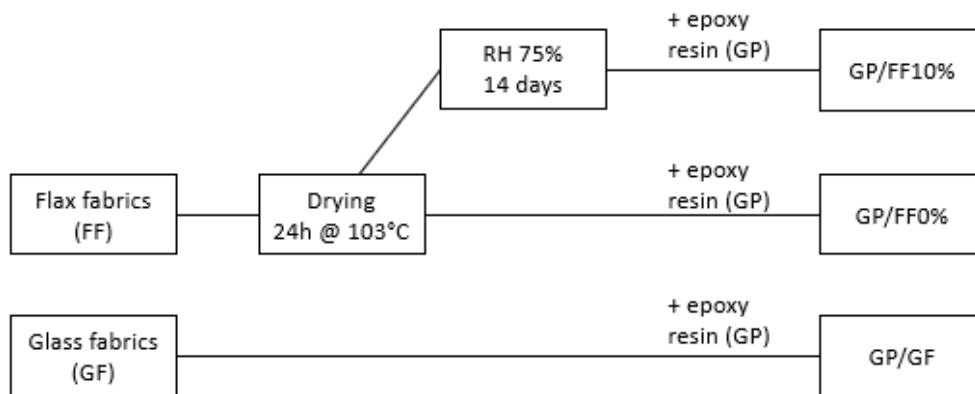


Figure 1: Sample preparation protocol

DMA samples were stored in various conditions (table 1) to follow the evolution of glass transition temperature (T_g).

Storage name	24h@20°C	240h@20°C	20h@60°C
S1	X	-	-
S2	-	X	-
S3	X	-	X

Table 1: Storage conditions of composite samples after preparation

Storage condition S1, made by keeping the samples at a temperature of 20°C and a relative humidity of 65 % for 24 hours, was chosen to allow the stabilization of the sample. Storage condition S2, 10 days (240 hours) at 20°C, allows samples to regain a sufficient amount of water to observe the effect of aging. Last storage condition S3, a post - curing at 60°C for 20 hours, gives fully cured composites.

2.3 Differential Scanning Calorimetry (DSC)

A fresh mixture of resin and hardener was made before each thermal analysis. Non-isothermal DSC runs were performed using a DSC Q10 from *TA instruments* to evaluate the behavior of pure epoxy, glass / epoxy composites and flax / epoxy ones with different water contents. Samples were sealed in aluminum pans and then heated from 25°C to 250°C at different heating rates β : 4 °C.min⁻¹, 6 °C.min⁻¹, 8 °C.min⁻¹, 10 °C.min⁻¹ and under a constant nitrogen atmosphere of 50 mL.min⁻¹.

An integral isoconversional method was used in this study to analyze the curing kinetics of pure epoxy and its composites. This method relies on the isoconversional principle that is: Reaction rate only depends on temperature for a given degree of conversion [17]. Therefore, the heat flow is directly proportional to the reaction rate, and so the degree of conversion can be determined following equation (2):

$$\alpha = \frac{H_t}{H_T}$$

where α is the degree of conversion, H_t is the enthalpy at fixed time and temperature and H_T is the total enthalpy of the reaction. It is generally accepted that the reaction rate can be expressed by the Arrhenius equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

with the rate constant k associated to temperature defined as:

$$k(T) = A \exp\left(\frac{-E_\alpha}{RT}\right)$$

With A the pre-exponential factor that is the frequency of collision between molecules (entropy), R the gas constant, E_α the activation energy and T the temperature.

If the sample is cured at heating $\beta = dT/dt$ we obtain:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha)$$

Kinetic evaluation was done using the Kissinger - Akahira - Sunose (KAS) method [18] as recommended by ICTAC committee [19]

The basis of the KAS method is the integral form of equation 4 that leads to an approximated form of the temperature integral:

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT \equiv \frac{AE_\alpha}{\beta R} p\left(\frac{E_\alpha}{RT}\right)$$

This equation is integrated into a logarithmic form as:

$$\ln(g(\alpha)) = \ln\left(\frac{AE_\alpha}{R}\right) - \ln \beta + \ln\left[p\left(\frac{E_\alpha}{RT_\alpha}\right)\right]$$

With the approximation:

$$p\left(\frac{E_\alpha}{RT_\alpha}\right) \cong \frac{\exp\left(-\frac{E_\alpha}{RT_\alpha}\right)}{\frac{E_\alpha}{RT_\alpha}}$$

and equation 5 can be rewritten:

$$\ln \frac{\beta}{T_\alpha^2} = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_\alpha}$$

Thus, the plot of $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ versus $\frac{1}{T_\alpha}$ following different heating rates β should give slopes equal to $-\frac{E_\alpha}{R}$ and intercepts equal to $\ln \frac{A_\alpha}{g(\alpha)}$ [20], [21].

After the kinetic analysis a second run was performed to obtain the glass transition temperature T_{gDSC} of each sample (heating rate 10 °C/min from 25°C to 250°C). Glass transition temperature T_g values was estimated using tangent method with the software *Universal Analysis*.

2.4 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) type tests were performed on a Kinetech® apparatus to study the mechanical relaxation associated to the glass transition of composite samples and to estimate the mechanical glass transition temperature T_{gDMA} . Principle of the test is to alternatively apply a positive and a negative torsion angle to the sample. At the beginning of a torsion step, the required torque to apply on the sample to obtain the torsion angle is measured and is called the instant torque C_i . The torsion is maintained for 2 seconds to measure the relaxed torque C_r . A relaxation curve is obtained by the difference of C_i and C_r and the analysis of this curve allows one to determine the region of glass transition. When the glass transition temperature of the material is reached, the relaxation curve shows a maximum that correspond to the T_{gDMA} (Figure 2).

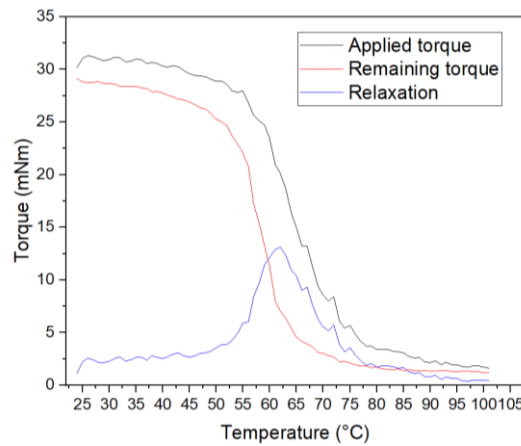


Figure 2: Glass transition temperature estimation via Kinetech®

3 RESULTS

3.1 DSC curing monitoring

The curing of pure epoxy resin (GP), epoxy reinforced by glass fibers (GP/GF), epoxy reinforced by wet flax fibers (GP/FF10%) and epoxy reinforced by dried flax fibers (GP/FF0%) was investigated by non-isothermal DSC runs. Thermograms of each batch are shown in Figure 3. Three samples for each heating rate have been analyzed. Since repeatability was good, results below only show one representative curve for each heating rate.

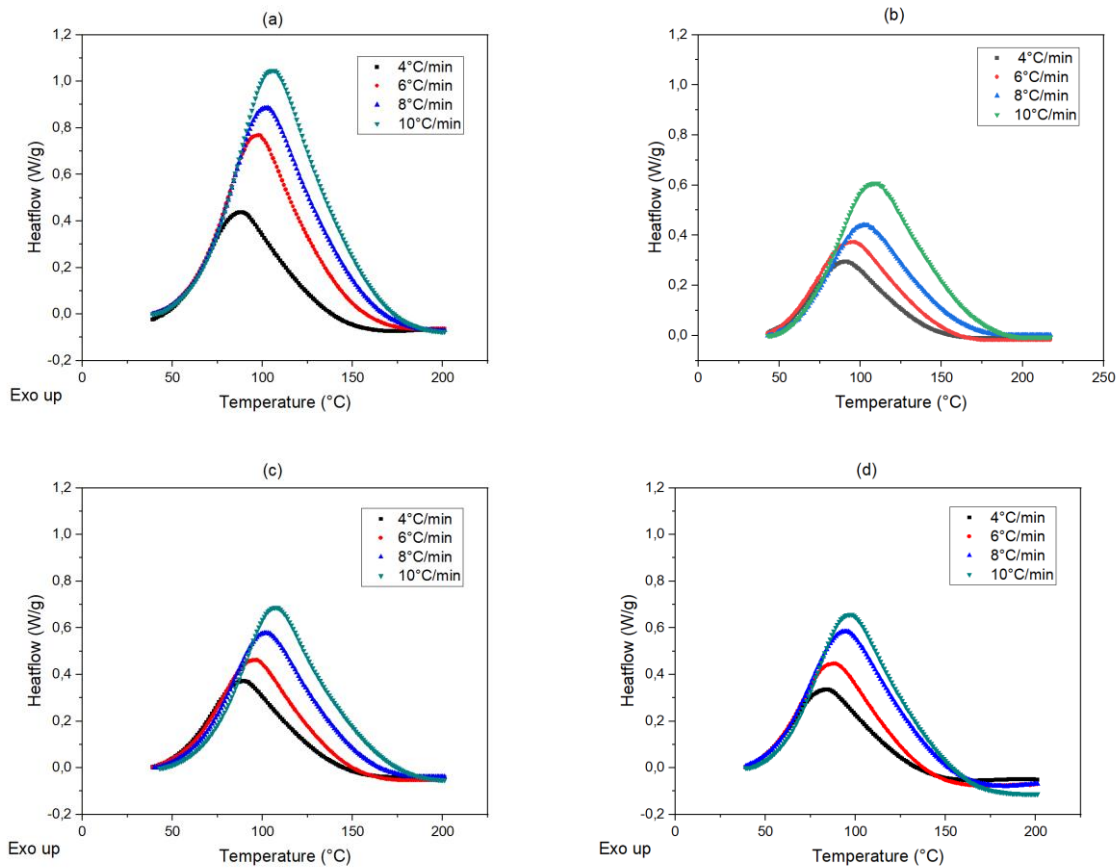


Figure 3: DSC thermograms of GP (a), GP/GF (b), GP/FF0% (c) and GP/FF10% (d)

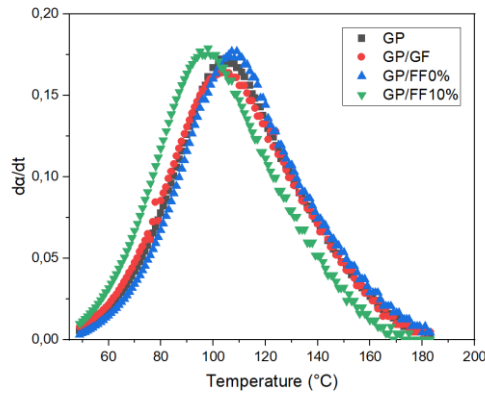
Values of onset temperature (T_{onset}), temperature of exothermic peak (T_{peak}) and enthalpy are reported in Table 2. T_{peak} and T_{onset} shift to higher temperatures as the heating rates increases for each sample. This is due to the fact that low heating rates allow the distribution of temperature to be more homogeneous, thus the curing starts earlier. Also at higher heating rates, high temperatures are quickly reached. This behavior is well known for epoxy curing [22], [23].

It can also be observed that T_{peak} and T_{onset} values of GP, GP/GF and GP/FF0% are very similar (Table 3). When fibers are wet, exothermic peaks shift for each rate to lower temperatures. A decrease in the enthalpy can be noticed for the composites with fibers in comparison with pure epoxy resin. This behavior indicates that fibers absorb a certain amount of heat during the reaction.

Sample	T_{onset} (°C)	T_{peak} (°C)	Enthalpy (J.g ⁻¹)
$\beta = 4^{\circ}\text{C}.\text{min}^{-1}$			
GP	54 ± 3	90 ± 3	404 ± 16
GP/GF	53 ± 2	89 ± 3	234 ± 9
GP/FF0%	53 ± 1	90 ± 1	303 ± 17
GP/FF10%	46 ± 2	83 ± 1	224 ± 55
$\beta = 6^{\circ}\text{C}.\text{min}^{-1}$			
GP	59 ± 1	98 ± 1	408 ± 11
GP/GF	57 ± 1	95 ± 1	215 ± 17
GP/FF0%	57 ± 1	96 ± 1	280 ± 15
GP/FF10%	50 ± 1	89 ± 1	256 ± 11
$\beta = 8^{\circ}\text{C}.\text{min}^{-1}$			
GP	64 ± 2	104 ± 1	412 ± 19
GP/GF	60 ± 2	100 ± 2	224 ± 37
GP/FF0%	62 ± 1	103 ± 1	245 ± 4
GP/FF10%	54 ± 3	96 ± 1	282 ± 75
$\beta = 10^{\circ}\text{C}.\text{min}^{-1}$			
GP	66 ± 1	107 ± 1	405 ± 25
GP/GF	63 ± 1	105 ± 2	252 ± 54
GP/FF0%	67 ± 1	109 ± 1	241 ± 28
GP/FF10%	58 ± 1	98 ± 1	228 ± 24

Table 2: DSC data from pure epoxy analysis and its composites

Reaction heat flow obtained from kinetic analysis (Figure 3) was used in equation 1 to calculate the conversion α and the curing rate $\frac{d\alpha}{dt}$ of each sample. The catalyst effect of water presence in flax fiber was highlighted by the plot of the curing rate versus the temperature at $\beta = 10^{\circ}\text{C}.\text{min}^{-1}$ (Figure 4) showing that the curing rate of composite with wet flax fibers increases earlier comparing to other samples.


 Figure 4: Comparison of the curing rate at $\beta = 10^{\circ}\text{C}.\text{min}^{-1}$ as a function of the temperature for each material

From DSC data, the activation energy E_a has been evaluated using the isoconversional KAS method (eq. 4). Results are plotted in Figure 5.

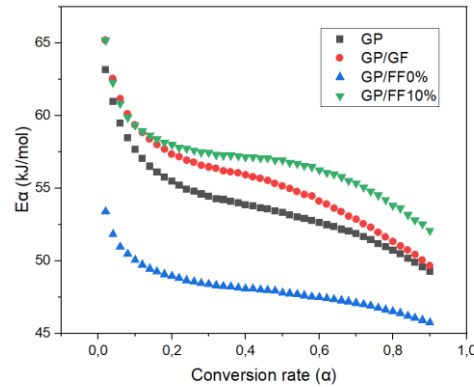


Figure 5: Activation energy E_{α} dependence to conversion rate from anisotherm data

Activation energy E_{α} varies differently with degree of conversion for pure epoxy and its composites. For every sample, the activation energy is higher in the first stage of the curing and decreases over time. Values from epoxy reinforced by dried flax fibers showed lower trend indicating that it has an influence on the curing reaction. By contrast, composite reinforced by wet flax fibers showed the highest E_{α} at every conversion rate. Values of E_{α} found here are consistent with the literature on biobased epoxy resins ($45 - 80 \text{ kJ.mol}^{-1}$) [24]–[26].

A second run has been performed for each sample to determine the glass transition temperature of materials (Table 3).

Sample	T_{gDSC} ($^{\circ}\text{C}$)
GP	92 ± 1
GP/GF	89 ± 1
GP/FF0%	92 ± 1
GP/FF10%	87 ± 1

Table 3: Average glass transition temperature for pure epoxy and its composites

Despite a slower curing start from composite with dried fibers, we obtain the same T_{gDSC} as pure epoxy sample indicating that there is no modification on the final geometry of the epoxy network. By contrast, T_{gDSC} value of composite with wet fibers show a slight decrease that seem to be due to the fast and chaotic epoxy network formation [11], [27].

3.2 T_{gDMA} measurements

DMA measurement were performed to observe the evolution of the glass transition temperature over time in function of different type of treatments after manufacturing (Table 1).

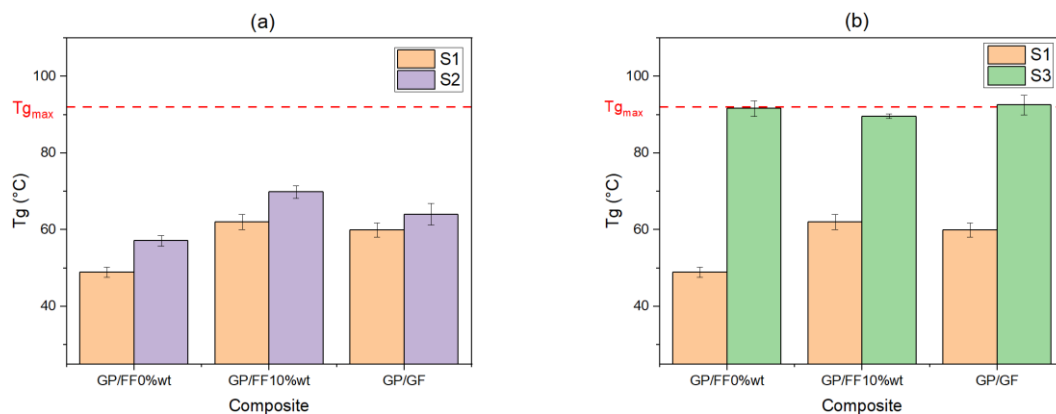


Figure 6: T_{gDMA} comparison for S1 / S2 storage (a) T_{gDMA} comparison for S1 / S3 storage (b)

For samples stored following S1 conditions (Table 1), measured values are below $T_{g_{max}}$ indicating a partial crosslinking (Figure 6a). GP/FF10% showed higher value than GP/GF confirming the faster network formation assumed in curing monitoring. GP/FF0% showed a lower value than GP/GF confirming latent crosslinking. After 10 days at 20 °C and 60 %RH (S2) $T_{g_{DMA}}$ values of every sample increased (Figure 6b). We can observe that the average increase of $T_{g_{DMA}}$ values for composites with natural fibers is more important (around 8 °C) than composite with glass fibers (around 4 °C). To complete $T_{g_{DMA}}$ measurements under S2 conditions, comparing samples were stored under 75 %RH and 97 %RH to observe the evolution of water uptake for each composite. Results are shown in Table 4:

RH	GP/GF	GP/FF0%	GP/FF10%
60%	0.6	3.5	2.3
75%	0.6	4.8	3.7
97%	2.1	12.5	11.1

Table 4: Average moisture absorption of composite materials after a storage in various humidity chambers

Water uptake increases with higher relative humidity percentage and is more important for composites reinforced by natural fibers. For post-cured samples (S3) it can be observed that all samples have nearly reached the maximum T_g (92 °C). These results are in good accordance with glass transition temperatures values measured on the DSC second run (Table 3).

4 DISCUSSION

As shown by our results, water absorbed by flax fibers has a huge effect on curing kinetics of epoxy - amine system. Exothermic peak temperatures measured by DSC (Table 2) showed that water contained in flax fibers accelerates the crosslinking reaction of the epoxy - amine system. It is confirmed by the plot of the curing rate ($\frac{d\alpha}{dt}$) versus the conversion rate (α) (Figure 4) as the crosslinking reaction of the composite with wet flax fibers starts earlier comparing to other samples. This effect was first shown by Chen et al. [28]. Moreover Choi et al. pointed out that only a small amount of water has a strong catalyst effect on the curing of the mixture (< 2 % wt) [13]. For higher amounts Sharp et al. [27] showed the creation of water molecules clusters preventing the crosslinking resulting in lower $T_{g_{DMA}}$ values. As our fibers contained about 10 % of water, it could be expected that some water molecules clusters are formed in our samples. The addition of flax fibers in epoxy - amine system was studied by Boutin et al. [11]. They also observed the curing acceleration induced by water contained in flax fibers.

From a kinetic point of view, it corresponds to an increase of the variation of entropy. Variation of entropy describes how much a system is irreversible and is proportional to the pre-exponential factor A of the Arrhenius equation presented in eq. 4 [29]. Increasing variation of entropy leads to higher E_a values [30]. In our study activation energy E_a calculated using KAS method showed "s" shape curves (Figure 5) similar to results found by Sbirrazuoli [31], Roudsari et al. [32] and Perrin et al. [20]. At low conversion rates (<0.2) the decrease of E_a is linked to a change in the curing mechanisms [26], switching from non-catalyzed reaction to auto-catalyzed reaction due to increasing number of hydroxyl groups generated by amines reacting with epoxides. At higher conversion rates (>0.7) the second decrease of E_a is due to the diffusion-controlled reaction kinetics effect [25]. This dependency of activation energy on the increasing extent of curing is known as the kinetic compensation effect (KCE) [30]. As the crosslinking starts earlier for composite with wet fibers (Figure 3), an irreversible state is quickly reached, increasing the entropy variation and so the pre-exponential factor A leading to higher values for E_a than for pure epoxy and epoxy with glass fibers (Figure 5). On the contrary, E_a values of composites with dried fibers are lower, highlighting the decreased reactivity observed on DSC with higher peak temperatures values for GP/FF0% (Table 2). It is strengthened by the recent study of Canavy et al. [15] showing that cellulose from flax fibers can interact with amine-based hardeners. The creation of hydrogen bonds between amine groups and hydroxyl groups from the fiber cellulose inhibits amino-

epoxy interactions. However, those interactions are not irreversible since T_{gDSC} (Table 2) and T_{gDMA} (Figure 6b) of GP/FF0% are equal to pure epoxy T_g values after a post-curing.

From DMA experiment, samples stored under S1 condition (i.e. 24 hours after manufacturing) showed that samples with dried fibers have the lowest T_{gDMA} values showing that the lesser reactivity (Table 2), the lower crosslinking density. This is in good agreement with Kuo et al. [33] that showed that glass transition temperature of thermoset polymers is dependent of the reactivity of the reaction and the crosslinking density. In the same way, composite with wet fibers has the highest T_{gDMA} value (Figure 6a) as a consequence of higher reactivity induced by catalyst effect of water. Furthermore, T_{gDMA} from S2 samples showed a global increase compare to S1 samples due to natural crosslinking (Figure 6b). It can be linked to the amount of water regained by samples (Table 4) allowing them to reach higher crosslinking density. This effect is more important for natural fiber reinforced composites as glass fiber are less sensitive to water ageing (Table 4). Lower crosslinking densities observed for GP/GF and GP/FF0% don't have consequences on the final shape of the network. A post-curing at 60 °C for 20 hours (S3) or a DSC second run can bring sufficient amount of energy to allow them to reach max glass transition temperature as shown by T_{gDMA} value in Figure 6b and T_{gDSC} values in Table 3. By comparison T_{gDMA} and T_{gDSC} values for composite with wet fibers did not reach the maximum value. It could be caused by water clusters as suggested by Sharp. et al. [27]. But we assume that this could also be linked to a formation of a more chaotic network. As water catalyzes the crosslinking reaction, a less perfect network is formed preventing GP/FF10% samples to reach maximum T_g .

Another effect of water contained by natural fibers is that water molecules that are still trapped in composite networks or regained after post-curing bring a plasticizing effect on sample. The presence of H₂O molecules increases the mobility of macromolecular chains and leads to a decrease in the T_g value [34]. Many studies showed that moisture absorption of epoxies leads to degradation in mechanical properties and have effect on glass transition temperature [13], [34]–[36].

A weighing method was done on GP/FF0%, GP/FF10% and GP/GF samples and evidenced this plasticizing effect. Successive DMA type trials gave the evolution of T_{gDMA} in function of water content (Figure 7). Initial T_g of post-cured samples was 92 °C. We observed that after the storage T_{gDMA} drastically decreased to 55 °C for GP/FF10%, 67 °C for GP/FF0% sample and to 72 °C for GP/GF. However, the temperature applied to the sample during DMA procedure brought enough energy to the epoxy-amine system to allow water evaporation. As the water evaporates during DMA procedure, T_{gDMA} increases. Figure 7 show that water quickly exits the glass fibers sample and the T_{gDMA} reached its maximum after the third consecutive procedure. Composite with dried fibers needed five DMA procedures to recover the maximum T_{gDMA} highlighting that water is absorbed deeper due to presence of flax fibers as they are a greater diffusion channel for water. Concerning the wet fibers composite, T_{gDMA} did not reach maximum value confirming the assumption of an incomplete, chaotic resin network formation induced by water presence during curing.

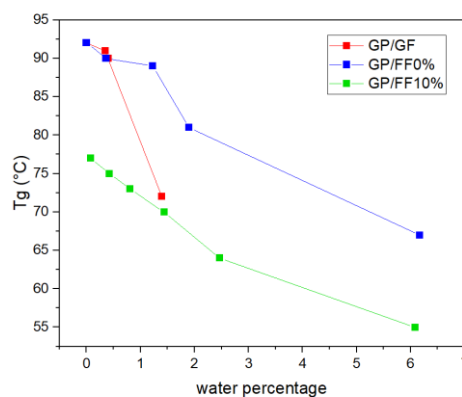


Figure 7: T_{gDMA} values of GP/GF, GP/FF0% and GP/FF10% for different water content

5 CONCLUSION

The influence of flax fibers on curing kinetics of a bio-based epoxy resin has been studied here. Results showed that water contained by flax fibers has a huge influence on curing kinetics as it accelerates the crosslinking. This effect leads to a faster irreversible state that increases the activation energy by a compensation effect. On the contrary, a decrease in the reactivity of dried flax fiber composites is observed and can be induced by amine-cellulose interaction. The consequence is a lower glass transition temperature after manufacturing comparing composite with wet fibers. From this state, water absorbed by both composites participated to the natural crosslinking as the T_g increased. After a post-curing both composites with dried fiber and reference with glass fibers reached maximum T_g value. The lower value observed for composite with wet fibers after post-curing has been attributed to formation of a more chaotic network geometry induced by entropic effect preventing a complete crosslinking. Amount of water still present after post-curing or regained after post-curing tends to decrease the glass transition temperature by a plasticization effect. This effect is greater with natural fibers as they are more sensitive to water absorption. Nonetheless, for glass fibers and dried flax fibers composites, a simple heating program can raise the glass transition temperature to its initial value by water evaporation. But, for composite with wet fibers water evaporation did not achieve to reach maximum T_{gDMA} because of incomplete, chaotic network formation due to water presence.

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