EVALUATION OF THERMAL BEHAVIOR AND CURE KINETICS OF A CURAUÁ FIBER PREPREG BY THE NON-ISOTHERMAL METHOD

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Abstract:

Curauá fibers have low-cost, low density, biodegradability and offer a relative high tensile strength level when applied in composites materials. The prepreg is a composite material constituted by fibers impregnated with a measured amount of resin matrix. Learning more about how the thermal properties of the matrix can be affected by curauá fibers, this work evaluated the thermal behavior and cure kinetics of a curauá fibers/ epoxy prepreg through Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The *in natura* or alkali treated (KOH or NaOH) curauá fibers blankets impregnated with epoxy resin were prepared using a manual rolling process. The prepreg samples containing 20 wt.% of fibers were analyzed when the matrix in the composite presented a semisolid tacky (B-stage). The prepreg cure kinetics was investigated by a non-isothermal isoconversional method, and the T_g was evaluate using the DSC data. The variables related to the curing kinetics were obtained on dynamic conditions with heating rates of 2.5, 5.0 and 10 °C/min. The prepreg activation energy was calculated at a given function of the extent of conversion. According to the dynamic runs, the prepreg T_g was higher for treated fibers than *in natura*. The 2.5 °C/min rate provided a curing cycle with a lower and controlled temperature when compared to the others heating rates and the humidity weight loss of prepreg amounted was ~2.8%. The KOH prepreg presents the highest activation energy and the *in natura* prepreg the lowest one. The kinetic conditions established will be used in further experiments to obtain natural fibers composites from prepregs.

Keywords: cure kinetics; prepreg; curauá fibers; epoxy; thermal analysis.

1. INTRODUCTION

The application of plant fibers in composites materials has increased because they have good mechanical properties regarding strength per weight, as well their renewability and relative low cost [1]. One of the greatest promising vegetable fibers is the curauá (*Ananas erectifolius*) planted in the Amazon Region in the north region of Brazil [2]. This natural fiber presents a comparable cost to other fibers in Brazil, however, its strength is higher than sisal, coir or jute, and approximately accomplish the physical properties of high-cost flax or even glass fibers.[3].

Prepreg materials are becoming progressively common in the composites industry due to their ease of application, stable properties and high-quality surface completion [4]. The prepreg is a significant product in which fibers are impregnated with a measured amount of resin. The continuous fibers are responsible for the highest strength and modulus and discontinuous are cheaper and easy to process [5].

In prepregs, the resin used is staged or advanced (B-staged) to the point where the thermoset matrix in the composite is a tacky semisolid, which consents the layers to be layed up to procedure a laminate that can be cured. The thermal analysis is one of the experimental techniques that it has been used to monitor the curing reactions of thermosetting systems. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) permit to find the performance of polymer composites, as well as the glass transition temperature (T_g), the degree of cure and kinetics parameters of polymeric matrices [6]. The heat unconfined in the curing reaction is directly related to the conversion degree measured at a specific stage of the curing process [7]. The simplest way to quantify the cure degree of a partially reacted sample includes DSC measurement of a residual exotherm, comparing that to the heat of reaction measured on a completely unreacted sample. The conversion or extent of reaction α_{cure} can be calculated according to the Equation (1):

$$\alpha_{cure} = 1 - \frac{\Delta H_{res}}{\Delta H_{dyn}} \tag{1}$$

where ΔH_{res} is the residual heat of reaction measured from the sample, and ΔH_{dyn} is the heat of reaction measured by a dynamic scan of a "fresh" unreacted sample of the same prepreg [8]. The kinetic studies are essentially determined by the fundamental equation that governs the rate of reaction and can be expressed as a function of the temperature (T) and the extent of conversion (α) as following Equation (2):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where $k(T)$ is the rate constant, t is the time, and $f(\alpha)$ is the reaction model. For epoxy cures, $f(\alpha)$ is usually taken in the form of $(1 - \alpha)^n$ for nth order or of $\alpha^m(1 - \alpha)^n$ for autocatalytic reaction; where: α is the degree of conversion, n and m are the orders of the reaction [9-12]. The temperature dependence on the rate constant is presented by replacing $k(T)$ to the Arrhenius Equation (3):

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

where A is the pre-exponential factor, E_a the activation energy, and R is the ideal gas constant. When a constant rate is used to heat the sample, the temporal dependency showed in Equation (2) is excluded through the simple transformation, resulting in the Equation (4):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{4}$$

where $\beta = dT/dt$ is the heating rate. Used for both isothermal and non-isothermal conditions, the extent of conversion (α) is usually obtained by dividing the partial heat ΔH_p evolved at temperature T by the total heat ΔH_0 produced during the entire reaction, which gives the Equation (5):

$$\alpha = \frac{\Delta H_p}{\Delta H_0} \tag{5}$$

The kinetic parameters estimated from the non-isothermal DSC data are commonly different from those evaluated from isothermal DSC investigations [13]. A non-isothermal method is a more accurate measure to calculate the prepreg curing kinetics. In this method, the kinetic data can be obtained in a relatively short-period of time, which can make it very attractive. However, an isothermal method can lead to experimental errors because generally renders the destabilization of the DSC heat flow at the origin of the cure measurement [11].

The kinetic parameters A and E_a estimated experimentally are functions of the fundamental kinetic parameters of an individual step. For epoxy-based systems, thus, it is correct to call them the effective kinetic parameters. Since the influence of each step varies with the extent of conversion and temperature, the real activation energy will also vary intensely with these factors. In contrast, on the isoconversional method, the activation energy is calculated at a given function of conversion [10]. Furthermore, this method can be applied to evaluate both simple and complex chemical reactions [14,15]. Consequently, the rewards of using these monitoring techniques support the knowledge of the polymeric behavior of these materials, helping parameter processing control, which affects the mechanical properties and the morphological characteristics [16].

In the present work, we investigate the influence of fibers treatment on the thermal behavior and kinetics parameters of a curauá fiber prepreg. The curing kinetics and the curing cycle were based on an isoconversional method, which uses a non-isothermal and DSC data to determine these parameters.

2. EXPERIMENTAL

2.1 Materials

The curauá fibers used in this study were provided by the Center for Support to Community Action Projects (CEAPAC) from Santarém - PA. The fibers were available *in natura* with 80 cm length. Also, the polymer used as a matrix was a DGEBA epoxy resin based on Diglycidyl ether of bisphenol-A (DGEBA) with an amine-based curing agent.

2.2 Fibers treatment

The *in natura* fibers were chopped into small pieces of 4-6 cm and dried at 80 °C for 3 h. To improve the adhesion between matrix and reinforcement two different procedures for surface modification were applied to the curauá fibers: (1) The *in natura* fibers were soaked in distilled water at a ratio of 10:1 (water/fibers) for 1 h. The fibers were mercerized in 10% (w/v) potassium hydroxide solution (KOH), and the material was stirred at 150 rpm for 3 h at room temperature. Later, the fibers were washed in distilled water until pH neutralized and dried at room temperature for 48 h and at 80 °C for 3 h. (2) The *in natura* fibers were washed in distilled water at 80 °C for 2 h and dried at room temperature for 48 h. The fibers were mercerized in 5% (w/v) sodium hydroxide solution (NaOH) at 50 °C for 2 h with manual stirring. After the reaction time, the fibers were washed in distilled water until pH neutralized and dried at room temperature for 48 hours and at 80 °C for 3 h.

2.3 Prepregs Obtainment

Initially, curauá fibers blanket from each treatment was produced by discontinuous fibers. The matrix solution was prepared at room temperature by mixing proper quantities of DGEBA epoxy monomer and a specific hardener. The ratio used to produce the samples were 12 phr (parts per hundred) and corresponds to the stoichiometric composition. The fibers blanket (20 wt%) was impregnated with the matrix solution using a manual rolling process. The prepregs remained for 38 h curing at room temperature to a certain extent where the matrix in the composite presented a semisolid tacky (B-stage). To slow down the resin curing process, the prepregs were kept -18 °C for further analysis. The prepregs received a terminology according to the fibers treatment: *in natura*, KOH and NaOH prepregs.

2.4 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) analysis were performed on a Q600 SDT equipment (TA Instruments, USA) under an inert atmosphere of nitrogen with a flow rate of 50 mL/min. The samples with 10 ± 0.5 mg were deposited in a sealed alumina pan. Two analysis configurations with different parameters and objectives were proposed: (1) In the dynamic study the analyses carry out under a heating rate of 5 °C/min from room temperature up to 600 °C; (2) In the cure kinetics study the analyses were performed under heating rates of 2.5, 5 and 10 °C/min from room temperature up to 300 °C.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analyses

The thermal stability and degradation of prepregs were determined by the thermogravimetric and its derivative thermogravimetric curves (TG – DTG). This characterization permitted not only to study the influence of fibers chemical modification but also to determine the limit of temperature application for this material.

The composites presented two-steps of degradation as we can see in Figure 1. Table 1 shows the data of humidity, degradation temperature and residue in the end of analysis. The first stage of prepregs weight loss occurs between 40 and 150 °C, and is related to the vaporization of the water present in the samples [17].

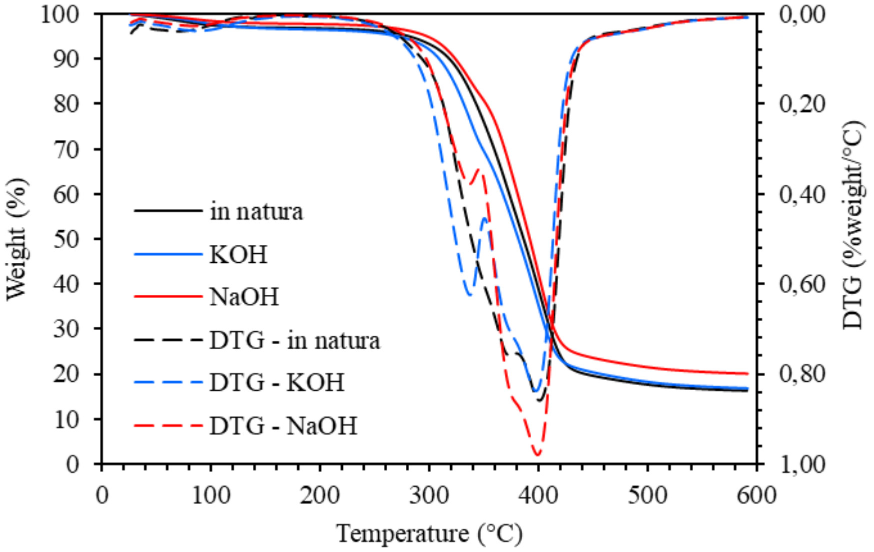

Figure 1: TG and DTG curves for curauá/ epoxy prepregs as a function of fiber treatment at the heating rate of 5 °C/min.

According to data, the NaOH prepreg present lower water vaporization (2.13%) and consequently better thermal stability at 150 °C. Although lignocellulosic fibers contain a significant level of water, the presence of the matrix influenced the vaporization and prevented the water from being released.

Table 1: TGA data for curauá fiber/ epoxy prepreg according to the fibers treatments.

Prepreg	Humidity (%)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	The residue at 600 ºC

					(%)
in natura	3.03	325.2	401.0	423.5	16.3
KOH	3.31	322.6	397.7	418.9	16.8
NaOH	2.13	341.5	399.4	421.2	20.1

According to Table 1, the T_{onset} of decomposition for the prepregs occurred between 322.6 and 341.5 °C, that is a higher temperature than the typical processing range (100–120 °C for curing). In the case of "thermal runaway", if a sufficient high temperature is reached during the curing process, the resin will begin to decompose, decreasing mechanical properties [18]. The second stage of weight loss showed thermal degradation peaks around 400 ºC. According Table 1, the NaOH prepreg exhibited the higher thermal stability at the beginning of the degradation (T_{onset}). In contrast, the *in natura* and KOH prepregs presented a decrease in T_{onset} degradation stage of 16.3 and 18.9 °C, respectively. All prepregs presented a residual weight between 16.3 and 20.06% at 600 ºC.

3.2 Differential Scanning Calorimetry Analyses

Figure 2 shows the DSC curves obtained from the non-isothermal runs for the uncured and cured prepregs. The thermal properties such as glass transition temperature (T_g), cure peak temperature ($T_{cure\ peak}$), enthalpy involved on the process (ΔH) and degree of cure (α_{cure}) are summarized in Table 2.

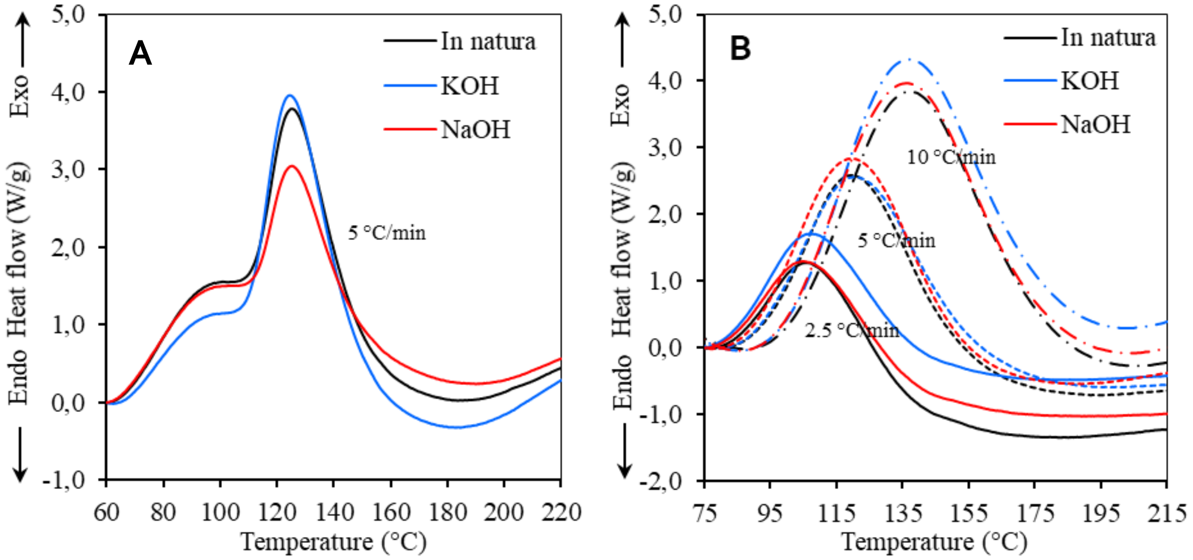

Figure 2: DSC curves of curauá fiber/ epoxy prepregs according to the different curing time: 0 hours (just prepared) (a) and 38 hours (semisolid tacky) (b).

The values of *ΔH* were obtained from DSC curves as exposed in Table 2 and corresponding to the heating rate of 5 °C/min. The glass transition temperature (T_g) for NaOH (59.9 °C) was higher than *in natura* and KOH prepreg (55.8 and 56.7 °C, respectively). The cured prepregs also present a higher T_g than the uncured samples (~6 °C). This growth in T_g can be explained by the fact that while the degree of crosslinking growths, the T_g of the epoxy resin also increases [16]. The curing peak for cured prepregs was found to be ~120 °C.

Table 2: DSC data of curauá fibers/ epoxy prepregs according to the different curing time.

Curing time	Sample	T_g (°C)	$T_{cure\ peak}$ (°C)	ΔH (J/g)	α_{cure} (%)
0 hours	neat resin	42.1	121.9	477.4	0
	in natura	49.9	125.1	184.3	0
	KOH	49.0	124.5	174.1	0
	NaOH	48.2	125.0	156.5	0
38 hours	neat resin	55.8	117.6	203.9	57.29
	in natura	55.8	119.7	142.9	22.46
	KOH	56.7	120.8	133.1	23.55
	NaOH	59.9	119.9	119.1	23.90

The average degree of curing (α_{cure}) was evaluated 57.29% for the neat resin. In prepregs, the α_{cure} was estimated ~23.3%, which is 34% lower concerning the neat epoxy. The reduction on the degree of curing can be associated to the addition of fiber on the matrix. A minor exothermic peak was also detected between 180 and 280 °C, which may be attributed to crosswise reactions, like homopolymerization and etherification of epoxide groups that usually take place at high temperatures [19].

3.4 Cure Kinetics

Non-isothermal DSC curves obtained at three different heating rates, 2.5, 5 and 10 °C/min for the curauá fibers/ epoxy prepregs was shown in Figure 2b, and it can be observed that all profiles have a single shape with a single exothermic peak at ~120 °C.

The total enthalpy involved in the curing process of the prepregs was obtained from the integration of the area under these DSC curves. The extent of conversion α was calculated by Equation 5 and is shown in Figure 3a.

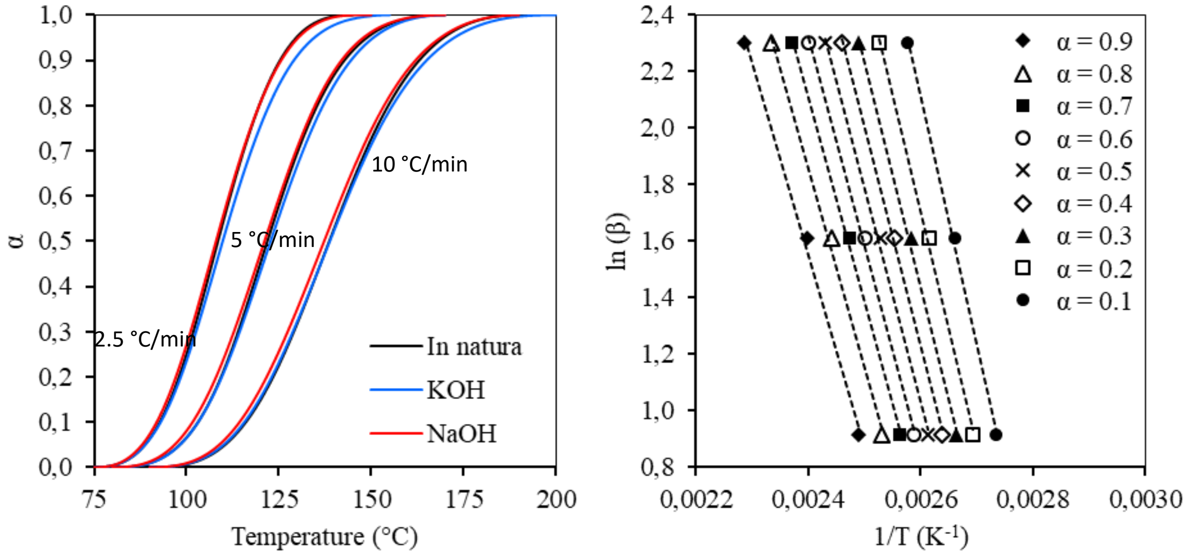

Figure 3: Reaction conversion profiles of the curauá fiber/ epoxy prepregs at different heating rates (a); Plots of ln (β) x 1/T (K^{-1}) for the *in natura* prepreg at different fractional conversions (b).

The application of the non-isothermal method was used to generate the conversion extension plot according to the different heating rates. From these curves, it was possible to extract the data relating the essential temperatures in different heating ratios (β) to reach the specific degree of conversion [10]. The plots of ln (β) against 1/T (K^{-1}) was generated from the conversion profiles and are present on the Figure 3b.

The activation energy (E_a) was calculated for each degree of conversion applying linear regression (Figure 4). The information about the E_a is presented in Table 3.

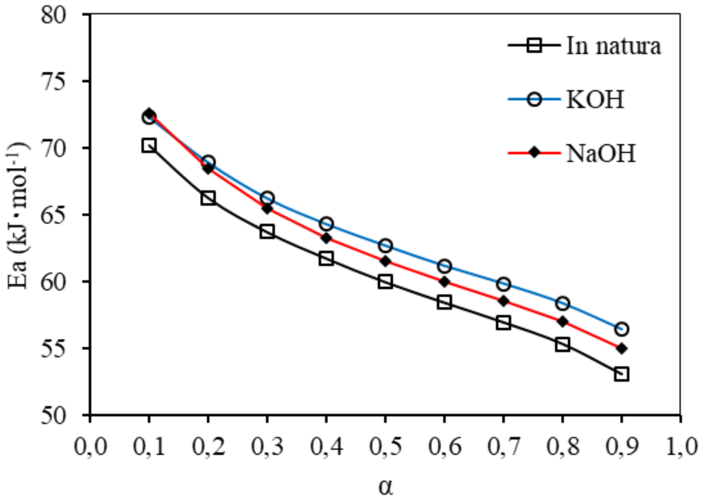

Figure 4: Activation energy of the curauá fiber/ epoxy prepregs as a function of the extent of conversion.

Table 3: Kinetics parameters obtained by the non-isothermal isoconversional method of the curauá fiber/ epoxy prepregs at α=0.5 extent of curing.

Prepreg	R^2	ln A (s^{-1})	Ea ($kJ \cdot mol^{-1}$)
in natura	0.9982	19.83	59.95
KOH	0.9985	20.64	62.69
NaOH	0.9985	20.38	61.57

The activation energy decreased with the progress of the curing extension for all samples, ranging from 72.63 to 53.05 $kJ \cdot mol^{-1}$. The KOH prepreg present the highest average activation energy (63.35 $kJ \cdot mol^{-1}$) and the *in natura* prepreg the lowest one (61.40 $kJ \cdot mol^{-1}$).

4 CONCLUSIONS

The fibers treatment influences on the thermal stability of the prepregs. The TG and DTG curves suggested the NaOH is the highest thermal stable prepreg between all samples and the T_{onset} was recorded at 341.5 °C. The decomposition of all composites mainly happened at ~400 °C and the residue at 600 °C was found between 16.28 and 20.06%. The NaOH treated fibers resulted in T_g higher than *in natura* and KOH prepregs, and the average degree of curing of prepregs was evaluated ~23.3%. An isoconversional method using the Arrhenius equation was developed and applied to analyze the curing kinetics, and the activation energy was calculated at a given function of the extent of conversion. The KOH prepreg presents the highest activation energy and the *in natura* prepreg the lowest one. The characterization of these prepregs was necessary to define the final processing conditions and to evaluate the cure cycle used to manufacture polymeric composite components.

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