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# Thermogravimetric analysis and kinetic study of pine wood pyrolysis

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***ABSTRACT*** The thermal stability of lignocellulosic materials is an important parameter for application of these natural materials as reinforcements in thermoplastic composites. In this study, the thermogravimetric analysis was used to evaluate the thermal decomposition, activation energy and mechanisms of degradation of two pine wood species. The results indicate higher extractive content in wood may lead to lower thermal stability. *Pinus elliottii* showed higher thermal stability and higher activation energy than *Pinus taeda*. Diffusion process controlled the thermal degradation mechanisms for both wood species. The results showed for both species studied *Pinus elliottii* is recommend the development of composites based on its higher thermal stability. The methods used in this study were helpful to obtain valuable information about the thermal stability of wood and to determine the best conditions for preparation of wood composites.

**Keywords:** wood; pyrolysis; thermal degradation; activation energy; solid state reaction.

## Introduction

Nowadays, significant attention has been dedicated to the utilization of wood and others natural fibers as reinforcements for composites (GEORGE et al., 2013; POLETTO et al., 2014; MATTOS et al., 2015). This scenario is driven by environmental concerns and by the unique combination of high performance, great versatility, biodegradability and processing advantages at low cost presented by lignocellulosic materials. However, some drawbacks, such as high level of moisture absorption, relatively low degradation temperatures and filler agglomeration bonds need to be overcome because of the tendency of wood to form hydrogen (SLIWA et al., 2012; POLETTO et al., 2012a)

The thermal stability of wood is an important parameter when wood is used for development of thermoplastic composites. During the processing stages, wood and polymer are submitted at temperatures above 200°C, which is the temperature that starts the wood degradation (SHEBANI et al., 2008; BIANCHI et al., 2010). Thus, thermal degradation of wood can lead to undesirable for the properties of composites, such as odor, discoloration and loss of mechanical strength (SHEBANI et al., 2008).

Therefore, determining the thermal stability of wood may be an interesting option to avoid wood degradation during the preparation of the thermoplastic composites. Thermogravimetric analysis (TGA) is useful to study the thermal stability and thermal degradation kinetic parameters of wood and others lignocellulosic materials (WONGSIRIAMNUAY, TIPPAYAWONG, 2010; BIANCHI et al., 2010; SANCHEZ-SILVA et al., 2012).

A considerable amount of works haves been reported on the study of wood thermal degradation (YANG et al., 2006; YAO et al., 2008; SHEBANI et al., 2008; BIANCHI et al., 2010; SANCHEZ-SILVA et al., 2012). However, the literature has a lack about the influence of wood components on the thermal stability and degradation kinetics of wood and its correlation with the development of composite materials. In this context, the aim of this work was to investigate the thermal degradation and kinetic parameters of two pine wood species obtained from wastes of Brazilian lumber industry, that are

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commonly used for the development of thermoplastic composites. The thermal stability and solid state reaction kinetics of woods from both *Pinus taeda* (PIT) and *Pinus elliottii* (PIE) species were evaluated by means of thermogravimetric analysis.

## Theoretical background

The rate of solid state decomposition reaction can be stated as follow: (BIANCHI et al., 2010):

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \qquad \text{Equation 1}$$

Where: $k$ is the rate constant and $f(\alpha)$ is the reaction model, a function dependent on the reaction mechanism. Equation 1 expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the rate constant and the reduction in the reactant concentration. In this study, the conversion rate $\alpha$ is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \qquad \text{Equation 2}$$

Where: $m_0$ is the initial weight of the sample, $m_f$ is the final weight and $m_t$ is the sample's weight at time ($t$). The rate constant $k$ is generally given by the Arrhenius equation:

$$k(T) = Ae^{\frac{-Ea}{RT}} \qquad \text{Equation 3}$$

where $E_a$ is the apparent activation energy (kJ.mol$^{-1}$), $R$ is the gas constant (8.314 kJ.mol$^{-1}$), $A$ is the pre-exponential factor (min$^{-1}$) and, $T$ is the absolute temperature (K). The combination of Equations 1 and 3 gives the following relationship:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} f(\alpha) \qquad \text{Equation 4}$$

For a dynamic TGA in a non-isothermal experiment, introducing the heating rate $\beta = dT/dt$ into Equation 4, Equation 5 is obtained as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) e^{-E_a/RT} f(\alpha) \qquad \text{Equation 5}$$

Equations 4 and 5 are the fundamental expressions of analytical methods used to calculate kinetic parameters on the basis of the TGA data (SANCHEZ-SILVA et al., 2012; POLETTO et al., 2014). Several methods were used to estimate the activation energy values for thermal degradation processes (BIANCHI et al., 2010; SANCHEZ-SILVA et al., 2012; POLETTO et al., 2014). The Equation 5 is normally solved using differential or integral methods (BIANCHI et al., 2010; POLETTO et al., 2014). The method proposed by Flynn-Wall-Ozawa is generally used to evaluate the thermal degradation kinetics of wood and polymeric materials (YAO et al., 2008; BIANCHI et al., 2010; POLETTO et al., 2014)

### *Flynn-Wall-Ozawa method*

The activation energy values for the degradation process can be determined by the isoconversional method proposed by Flynn-Wall-Ozawa (FWO). This method can be used for determination of the $E_a$ values without any knowledge of the reaction mechanisms. This is defined by Equation 6 (FLYNN; WALL, 1966; OZAWA, 1965):

$$\log\beta = \log\left[\frac{AE_a}{g(\alpha)R}\right] - 2.315 - 0.4567\frac{E_a}{RT} \qquad \text{Equation 6}$$

Where: $\beta$ is the heating rate, $A$ is the pre-exponential factor, $g(\alpha)$ is a function of the conversion, $E_a$ is the activation energy and R is the gas constant. Therefore, for different heating rates ($\beta$) and a given degree of conversion ($\alpha$), a linear relationship is observed by plotting log $\beta$ vs. $1/T$, and the $E_a$ is obtained from the slope of the straight line (FLYNN; WALL, 1966; OZAWA, 1965).

### *Criado method*

The thermal degradation mechanism for solid state reactions can be determined using the Criado method (CRIADO et al., 1989), which can accurately determine the reaction mechanism in a solid reaction process. This is defined by a $Z(\alpha)$ type function:

$$Z(\alpha)=\frac{\left(d\alpha/dt\right)}{\beta}\pi(x)T \qquad \text{Equation 7}$$

Where $x = E_a/RT$ and $\pi(x)$ is an approximation of the temperature integral that cannot be expressed in a simple analytical form. In this study, the fourth rational expression of Senum and Yang (PÉREZ-MAQUEDA; CRIADO, 2000) were used, which gives errors of lower than than $10^{-5}$ % when x >20. The master curves as a function of the conversion degree corresponding to the different models listed in Table 1 (BIANCHI et al., 2011) were obtained according to Equation 8:

$$Z(\alpha)= f(\alpha)g(\alpha) \qquad \text{Equation 8}$$

From Equations 5 and 8, the following relationship can be derived:

$$Z(\alpha)=\frac{d\alpha}{dT}\frac{E_a}{R}e^{\frac{E_a}{RT}}P(x) \qquad \text{Equation 9}$$

Equation 9 is used to represent the experimental curve. By comparing these two curves, the type of mechanism involved in the thermal degradation can be identified.

## Materials and methods

### *Materials*

Wood flour samples used in this study were obtained from wastes of a Brazilian lumber industry. The species investigated were *Pinus taeda* (PIT) and *Pinus elliottii* (PIE). Table 2 shows the chemical composition of the woods from previous studies (POLETTO et al., 2010; POLETTO et al., 2012b). Wood samples with particle size of 200-300 μm were vacuum oven-dried at 105°C for 24 h before the thermogravimetric analysis.

### *Thermogravimetric analysis*

The thermogravimetric analysis was carried out in a TGA50 – Shimadzu equipment under $N_2$ atmosphere with a purge gas flow of 50 $cm^3.min^{-1}$ from 25 to 600°C. Approximately 10 mg of each wood sample were used. The analysis was carried out at four different heating rates (5, 10, 20 and 40° $C.min^{-1}$). The systematic error for temperature was 3°C. The results obtained were used to calculate the kinetics parameters.

## Results and Discussion

Figure 1 shows the results of the thermogravimetric analysis performed in the woodsstudied. The water loss was observed below 100°C, and further the degradation took place as a three-step process. In the first step, the main hemicelluloses degradation occurred around 300°C. Around 350°C occurred the main process of cellulose degradation process, and finally the lower lignin degradation was around 380°C. According to Kim et al. (2006), the glycosidic linkage of cellulose

**Table 1.** Algebraic expressions for *g(α)* and *f(α)* for the most frequently used mechanisms of solid state reaction processes (CRIADO et al., 1989).
**Tabela 1.** Expressões algébricas para *g(α)* e *f(α)* para os mecanismos mais frequentemente utilizados nos processos de reação no estado sólido (CRIADO et al., 1989).

| **Mechanism – Solid state process** | **g(α)** | **f(α)** |
|---|---|---|
| A2 - Nucleation and growth (Avrami eq.1) | $[-\ln(1-\alpha)]^{1/2}$ | $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ |
| A3 - Nucleation and growth (Avrami eq.2) | $[-\ln(1-\alpha)]^{1/3}$ | $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ |
| A4 - Nucleation and growth (Avrami eq.3) | $[-\ln(1-\alpha)]^{1/4}$ | $4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$ |
| R1 - Phase boundary controlled reaction (one-dimensional movement) | $\alpha$ | $1$ |
| R2 - Phase boundary controlled reaction (contracting area) | $[1-(1-\alpha)^{1/2}]$ | $2(1-\alpha)^{1/2}$ |
| R3 - Phase boundary controlled reaction (contracting volume) | $[1-(1-\alpha)^{1/3}]$ | $3(1-\alpha)^{2/3}$ |
| D1 - One-dimensional diffusion | $\alpha^{2}$ | $(1/2)\alpha$ |
| D2 - Two-dimensional diffusion (Valensi equation) | $(1-\alpha)\ln(1-\alpha)+\alpha$ | $-[\ln(1-\alpha)]^{-1}$ |
| D3 - Three-dimensional diffusion (Jander equation) | $[1-(1-\alpha)^{1/3}]^{2}$ | $(3/2)[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$ |
| D4 - Three-dimensional diffusion (Ginstling-Brounshtein equation) | $[1-(2/3)\alpha]-(1-\alpha)^{2/3}$ | $(3/2)[1-(1-\alpha)^{1/3}]^{-1}$ |
| F1 - Random nucleation with one nucleus on the individual particle | $-\ln(1-\alpha)$ | $1-\alpha$ |
| F2 - Random nucleation with two nuclei on the individual particle | $1/(1-\alpha)$ | $(1-\alpha)^{2}$ |
| F3 - Random nucleation with three nuclei on the individual particle | $1/(1-\alpha)^{2}$ | $(1/2)(1-\alpha)^{3}$ |

**Table 2.** Chemical composition of the wood investigated (POLETTO et al., 2010; POLETTO et al., 2012b).
**Tabela 2.** Composição química das espécies de madeira investigadas (POLETTO et al., 2010; POLETTO et al., 2012b).

| Wood species | Holocellulose (%) | Lignin (%) | Extractives (%) | Ash (%) |
|---|---|---|---|---|
| *Pinus taeda* (PIT) | 61.2 ± 0.2 | 25.6 ± 0.1 | 9.3 ± 0.7 | 3.9 ± 0.3 |
| *Pinus elliottii* (PIE) | 61.2 ± 1.1 | 33.8 ± 1.0 | 4.5 ± 0.1 | 0.8 ± 0.1 |

between 255 and 350°C and the degradation of lignin between 250 and 500 °C.

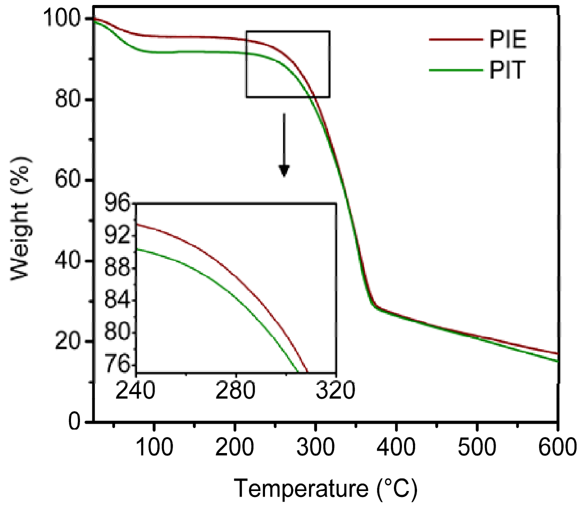

**Figure 1.** Thermogravimetric curves of woods studied.
**Figura 1.** Curvas termogravimétricas das madeiras estudadas.

As can be seen in detail in Figure 1, PIE wood presented higher thermal stability than PIT wood. In temperatures below to 100 °C, the weight loss in PIT is higher than in PIE. This behavior might be associated with higher quantities of water present in the wood structure of PIT and with its highest extractive content. As presented in Table 2, the extractive content in PIT is two times higher than in PIE. Extractives are compounds with lower molecular mass, which can promote wood ignition at relative lower temperatures as a result of their higher volatility and, as a consequence, may accelerate the wood thermal degradation (YANG et al. 2006; SHEBANI et al., 2008; JOHN; THOMAS, 2008).

Wood is commonly used in thermoplastic composites processed at temperatures above 200°C (SHEBANI et al., 2008). Thus, PIT wood may initiate a more pronounced thermal degradation during the composite processing and can leads to undesirable properties, such as browning and loss of c mechanical properties of the composites. On the other hand, PIE wood is more suitable to apply as reinforcement in composites due their higher thermal stability.

The initial weight loss temperature ($T_i$) is considered as the temperature which the wood samples lose 3% of its weight (Table 3). PIT wood presented the lowest $T_i$ value, which may be associated with the higher quantities of absorbed water and volatility of lower molecular mass compounds, such as lipids, terpenoids, fatty acids, resin acids and waxes, all of them present in the extractives (SHEBANI et al., 2008). Furthermore, the main degradation temperature of cellulose is associated with the derivative thermogravimetric (DTG) peak. PIE wood presented higher cellulose stability than PIT wood, probably because the lower extractives content associated with higher lignin content, as discussed before. On the other hand, PIT wood had higher quantity of residue at 600 °C than PIE wood, probably due to higher inorganic contents in this wood, which corroborates with the results of ash content presented in Table 2.

**Table 3.** Thermal degradation temperatures and residue at 600°C of woods studied.

**Tabela 3.** Temperaturas de degradação térmica e teor de resíduo a 600°C para as madeiras estudadas.

| **Wood species** | $T_i$ (°C) 3 wt% loss | DTG peak (°C) | Residue at 600°C (%) |
|---|---|---|---|
| *Pinus taeda* (PIT) | 47 | 352 | 16.9 |
| *Pinus elliottii* (PIE) | 63 | 355 | 15.1 |

## *Apparent activation energy (Ea)*

The activation energy calculated according to FWO method through TGA analysis is called apparent activation energy, since represents the sum of the activation energy from chemical reactions and physical processes that occurs simultaneously during thermal degradation (YAO et al., 2008). Because the kinetic behavior is similar for both woods studied, only PIE wood was chosen as a representative model for the presentation of the Ea results. Therefore, Figure 2 shows the results of the application of the FWO method with conversion values from 0.2 to 0.8. The linear fits obtained from the plots of log β versus 1/T are also shown in Figure 2. The Ea values were calculated from the slope obtained from the straight line fit. The correlation coefficients values ranged between 0.975 and 0.999, for both species studied.

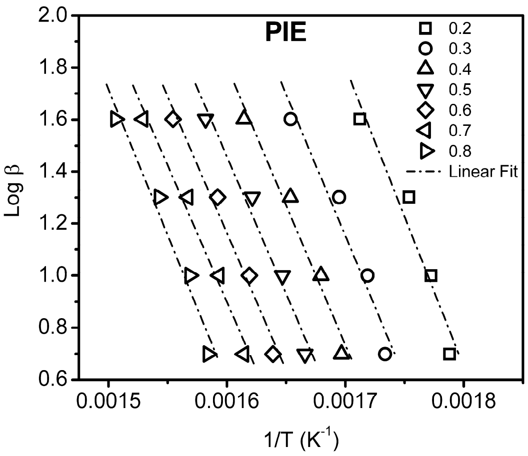

**Figure 2.** FWO method applied to PIE wood showing the linear fits obtained.

**Figura 2.** Aplicação do método de FWO para a madeira PIE mostrando os ajustes lineares obtidos.

The activation energy values varied between 150-171 kJ.mol$^{-1}$ for PIT wood and ranged between 164-197 kJ.mol$^{-1}$ for PIE wood (Figure 3). The higher activation energy for PIE wood confirms the higher thermal stability of this wood when compared with PIT wood. On the other hand, PIT wood presented lower activation energy when the conversion values ranged between 0.2-0.3. For PIE wood, the activation energy was 197 kJ.mol$^{-1}$ and 181 kJ.mol$^{-1}$ when conversion values are 0.2 and 0.3, respectively, while for PIT wood the activation energy were only 169 kJ.mol$^{-1}$ and 166 kJ.mol$^{-1}$, for the same conversion values. This result confirms that extractives promote the thermal degradation of wood at lower temperatures, and, consequently, reducing the activation energy values. When the main cellulose degradation occurs, between 0.4-0.6, both woods presented almost the same activation energy values. However, when the main lignin degradation process occurs between 0.7-0.8, PIE wood presented higher activation energy values than PIT wood, which had a direct relation with the higher content of lignin in PIE wood.

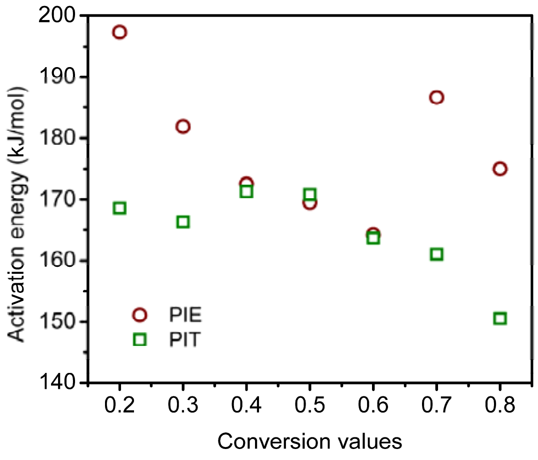

**Figure 3.** Activation energy variation according to conversion for the woods. investigated

**Figura 3.** Variação da energia de ativação de acordo com a conversão para as espécies de madeira estudadas.

## *Degradation mechanisms*

The Ea values obtained by FWO method were used to determine the thermal degradation mechanisms proposed by Criado et al. (1989). This method uses reference theoretical curves obtained from Equation 8 that are derivatives of the f(α) and g(α) functions represented in Table 1. These curves are called master curves and are compared to experimental data to determine the mechanisms of the solid-state degradation process (CRIADO et al., 1989). As presented in Table 1, the algebraic expressions that represent the theoretical mechanisms are separated into four groups: $A_n$, $R_n$, $D_n$ and $F_n$. Respectively, these mechanisms describe: nuclei formation processes for the propagation of thermal degradation; diffusion processes that are related to heat transfer capacity along the material structure; reaction mechanisms controlled by the surface of the sample; and the random degradation of nuclei.

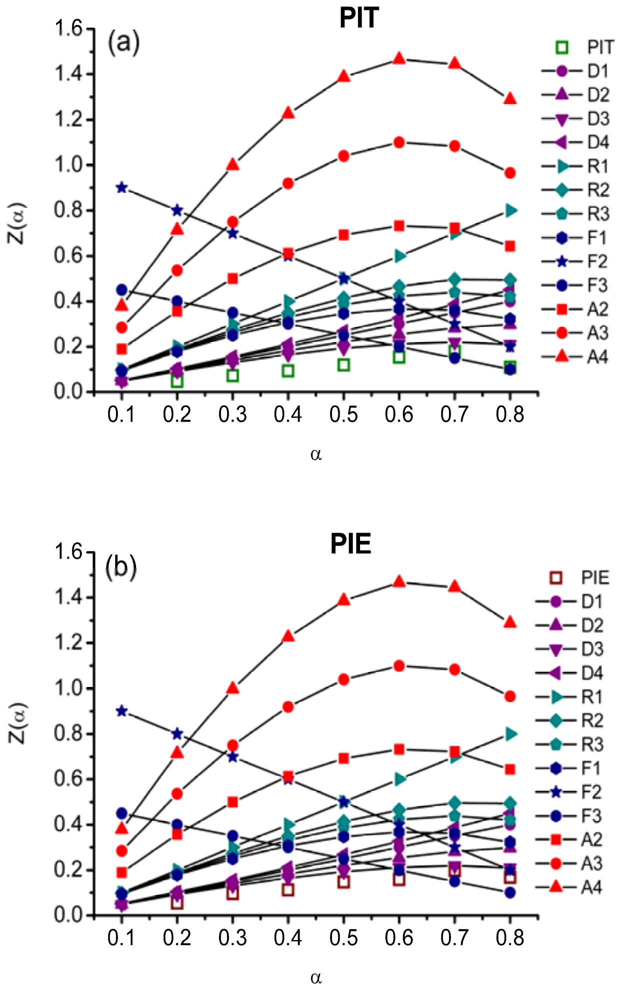

**Figure 4.** Master curves and experimental data obtained through the Criado method for PIT wood (a) and PIE wood (b).

**Figura 4.** Curvas mestre e dados experimentais obtidos utilizando o método de Criado para PIT (a) e PIE (b).

The determination of experimental Z(α) values for each wood was carried out with heating rate of 10 °C.min$^{-1}$ using the Equation 9. Figure 4 shows the master curves and the results of experimental data obtained for both woods studied.

The experimental data (Figure 4) shows that for both woods in the range of 0.2-0.3 the degradation mechanism overlap the $D_1$, $D_2$, $D_3$ theoretical mechanisms. According to Criado et al. (1989), these degradation mechanisms refers to the diffusion process in one, two and three dimensions, respectively (). Based on this result, at lower conversion values, the degradation occurs by heating transfer throughout the wood structure. When the conversion values are higher than 0.3, the experimental Z values for both woods overlap the $D_3$ mechanism, associated with the diffusion process in three dimensions. Similar results were described by Wu; Dollimore (1998) and Bianchi et al. (2010). The degradation process probably initiates in the extractives and, then, initiates the degradation of hemicelluloses, cellulose and lignin of wood by means of a diffusion process in three dimensions.

## Conclusions

The thermal degradation of pine wood was influenced by its chemical composition. Higher extractive contents may accelerate the degradation process and, consequently, reduce the thermal stability of wood. The results also showed that PIE wood had both higher thermal stability and higher activation energy than PIT wood. The degradation mechanism for both woods is governed by diffusion process, mainly by diffusion process in three dimensions, a $D_3$ mechanism. Understanding the thermal stability and degradation mechanisms of different woods can provide valuable parameters to determine the best processing conditions to avoid wood degradation in the preparation of wood polymer composites.

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