THERMAL DEGRADATION AND DECOMPOSITION OF JUTE/VINYLESTER COMPOSITES

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Thermal analysis of jute fibre reinforced vinylester resin with 30 vol% of fibre were performed by TG/DTG under dynamic conditions. The fibres were treated with alkaline solution at different temperatures and the final composition (cellulose, hemicellulose and lignin) of the fibre was determined by chemical analysis. Apparent activation energies were determined using a variety of conventional thermogravimetric methods. Two peaks were found in the composite differential curves: the first peak close to 327 and the second peak at 408ºC. The apparent activation energy values for the second peak decreased when fibre were treated. The addition of the jute fibres produced a slightly decrease in the thermal stability of the composites.

Introduction

There exist several fibre treatments or process of purification for cellulosic fibres. Alkaline treatment is a purifying treatment that removes impurities such as waxes, pectins, hemi-celluloses and mineral salts. It produces changes of the super-molecular structure and morphology of cellulosic fibres. On the alkaline treatment of jute fibres reports the removal of lignin and hemicelluloses [1–5], and as consequence the treatment not only modified the surface of the fibre, but also change the morphology of the fibre [6]. Alkaline treatment drives to interlocking between fibres and matrix and as results composites with better mechanical properties can be obtained [7].

Natural fibres are a complex mix of organic materials and, as a result of that, thermal treatment produces a variety of chemical and physical changes. Fibres thermal stability can be studied using thermogravimetric analysis (TG). Thermal degradation of this kind of materials involves loss of moisture, dehydration (180–280ºC), glycosan formation and depolymerization, volatilisation and char formation. In thermogravimetric curves two decomposition steps can be distinct: the first peak at 300ºC corresponds to hemicellulose decomposition and depolimerisation of the glucosidic unions of cellulose. The second one appears at around 360ºC and it is due to the thermal decomposition of α-cellulose. The third important component: lignin presents a wider peak that appears between 200 and 500ºC, with a maximum at 350ºC, is superposed to the other two peaks [8–10].

Pyrolysis reaction between cellulose and lignin produces gases and follow a first order kinetic. Lignin is more thermally stable than cellulose and hemicellulose [11–13]. The thermal decomposition of jute fibres at 200ºC and higher temperatures produces volatiles and the obtained composites exhibit low density and poor mechanical properties [11].

The determination of kinetic parameters for thermal degradation from TG data has been widely used in different kind of composites [14, 15].

The literature on thermal degradation and the application of kinetics models are still limited for this materials in spite that them are growing up in the use in automotive applications. The aim of this work was to study the effect of fibre chemical modification on the thermal degradation of jute/vinylester composites at temperatures around the processing temperatures because the thermal degradation of the fibres at low temperatures can produce the detriment of the final mechanical properties. Final mechanical properties will be determined in a future work.

Theoretical approach

When a reaction is study by a differential thermal analysis (DTA); the sample mass decreases at low rate as pyrolysis begins; then falls precipitously over a narrow range of temperatures and finally shift to zero slopes as the reactant is consumed. The shape of the curve is determined by the kinetic parameters such as: reaction order, rate constants and activation energy [16–18]. Generally, kinetic studies are based on the equation:

$$d\alpha/dt = kf(\alpha) \tag{1}$$

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where α is the degree of conversion or fractional mass loss, k is the rate constant and t is the time. This equation gives the relationship between the rate of conversion, $d\alpha/dt$, the reactant concentration loss and the rate constant at a fixed temperature.

If it is assumed that the rate of conversion is proportional to the reactant material concentration, the conversion function $f(\alpha)$ can be expressed as:

$$f(\alpha)=(1-\alpha)^n \qquad (2)$$

On the other hand, the rate constant, k, is correctly approximated by an Arrhenius type equation, and by combining all equations and introducing the heating rate, β, the final equation is:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right)dT \qquad (3)$$

where E_a is the apparent activation energy, A is the preexponential factor, n is the apparent order of reaction, R is the universal gas constant and T is the absolute temperature. The last one is the general equation utilized for all analytical methods to obtain kinetic parameters on the basis of TG data. Although, there are several methods, the most useful are that in that the reaction order is not assumed. The methods used in this work are described on Table 1.

In order to fit the experimental results, a function of $f(\alpha)$ for the Eq. (1) with two exponents: n and m were also used.

$$\frac{d\alpha}{dt} = k'(1-\alpha)^n \alpha^m \qquad (4)$$

By comparing with Eq. (1), in this kinetic expression the kinetic decomposition constant k depends on the conversion by the expression: $k'\alpha^m$. Each experimental curve was deconvoluted into two peaks (Lagrangian integral) and they were fitted by a non-linear curve fitting mode. Marquard methods were applied for finding the fitting parameters: m, n and k. Then, if α_1 and α_2 are the conversions of the first and

the second peak respectively, the complete decomposition kinetics expression is defined on two intervals:

$$\frac{d\alpha}{dt} = \begin{cases} d\alpha_1/dt \text{ for } 0<\alpha<0.416 \\ d\alpha_2/dt \text{ for } 0.416<\alpha<1 \end{cases} \qquad (5)$$

Then, considering each peak conversion from 0 to 1, the global conversion can be determined by using the following expression:

$$\int_0^1 \frac{d\alpha}{dt}dt = 0.4\int_0^1 \frac{d\alpha_1}{dt}dt + 0.6\int_0^1 \frac{d\alpha_2}{dt}dt \qquad (6)$$

Experimental

Materials

Vinylester Derakane 411-350 resin from Dow was used, Poliresinas San Luis, Buenos Aires, Argentina, kindly supplied it. Jute supplied by Casthanal, Brazil, was used as reinforcement. The resin was reinforced with 30 vol% of untreated and alkaline treated jute fibre mat. The fibre mat was cut to short fibre of approximately 1 mm. This powder was manual mixed with the liquid resin and specimens of 10 mm of diameter and 1 mm of thickness were prepared in order to obtain a homogeneous specimen. All plaques were post cured in an oven at 140°C for 120 min.

Alkaline treatment

The fibres were treated with Na(OH) aqueous solution (5 mass%) for 24 h at two different temperatures: 25 and 60ºC. Then they were washed with distilled water until all the sodium hydroxide was eliminated, that is until the pH was neutral. Subsequently, fibres were dried at 60ºC until constant mass was found.

Methods

Dynamic thermogravimetric measurements were performed by using a Shimadzu TG-DTG instrument.

Table 1 Degradation methods used in this work

Method	Utilized equation	References
Friedman	$\ln\left(\dfrac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) - \dfrac{E_a}{RT}$	[18]
Flynn and Wall	$\dfrac{-d\log\beta}{d\left(\dfrac{1}{T}\right)} = 0.457\dfrac{E_a}{R}$	[19]
Ozawa	$\log F(\alpha) = \log\left(\dfrac{AE_a}{R}\right) - \log\beta - 2.315 - 0.4567\dfrac{E_a}{RT}$	[18, 20]
Van Krevelen	$\left[\ln\left(\dfrac{1}{1-\alpha}\right) - 1\right] = \ln\left[\dfrac{A}{\beta}\left(\dfrac{0.368}{T_m}\right)^{E_a/RT}\dfrac{1}{\dfrac{E_a}{RT_m}+1}\right] + \left(\dfrac{E_a}{RT_m}+1\right)\ln T$	[18, 20]

Temperature programs for dynamic tests were run from 25 to 1000ºC at heating rates in the range of 5 to 15ºC min^{-1}. TG/DTG tests were carried out under nitrogen atmosphere (20 mL min^{-1}) in order to prevent any thermoxidative degradation and specimens with more than 16 mg were used for the measurements. Samples with higher heating rates than 15ºC min^{-1} could not be considered because at high heating rate voids were produced in the specimens and it was not possible to obtain the same behaviour than for the other heating rates.

Determination of fibres composition

The major fibre constituents (α-cellulose, hemicellulose and lignin) of untreated and alkaline-treated jute fibre samples were determined by chemical analysis following standard procedures. The holocellulose content of the jute fibre was determined by the gradual removal of lignin, which was achieved by treating dewaxed jute fibres with 0.7% sodium chlorite at pH 4 at the boil for 2 h using a fibre to liquor ratio of 1:50. It was then treated with sodium bisulphite solution, followed by filtering, washing and drying at 100ºC till constant mass was reached. α-cellulose content was determined by treating holocellulose with 17.5% NaOH solution. Hemicellulose content was estimated from the difference between the holocellulose and α-cellulose contents of the fibre. Solubilizing all constituents other than lignin by the action of 72% sulphuric acid did lignin determination. Powdered jute sample was treated with 72% sulphuric acid solution at 2ºC for 48 h, followed by dilution to 3% acid concentration and boiled for 2 h under reflux. The insoluble residue was filtered, washed and dried in an oven at 100ºC until constant mass was achieved.

Results and discussion

TG and DTG curves obtained for untreated and alkaline treated jute fibres at 10ºC min^{-1} are presented in Fig. 1. Untreated jute fibres present two decomposition steps: first at 300ºC corresponding to hemicellulose and glucosidic unions de-polymerisation and second one at 365ºC corresponding to the thermal destruction of the α-cellulose what shows considerable mass loss at this temperature. Lignin presents a broad peak in all the range [5]. When fibres are alkaline treated the first peak disappear and the second one is shifted to lower temperatures. The absence of the first decomposition peak may be due to the partial extraction of hemicellulose and lignin. The decomposition of lignin and hemicellulose goes to higher temperature and their peaks are inside the second one. Table 2 shows the fibres constituent determination after fibre treatment.

TG and DTG curves obtained for different studied materials at 10ºC min^{-1} are presented in Fig. 2. Vinylester presents one decomposition peak with maximum at 436ºC. Vinylester/jute fibres composite shows two different steps: one at 368ºC and the other one at around 434ºC. The first peak can be assigned to the decomposition of fibres and the second one is related to the decomposition of the vinylester matrix. Table 3 shows the values of heating rate and temperature at the maximum decomposition rate, obtained for the matrix, untreated and treated jute fibres and composites. The shape of the mass loss curves is similar for all heating rates analysed but the maximum degradation rate is slightly shifted to higher values as the heating rate increases. This effect can be attributed to heat transfer problems between the temperature of the specimen and the temperature measured for the instrument.

In all cases, is it possible to see that the thermal stability of vinylester decreases by the presence of
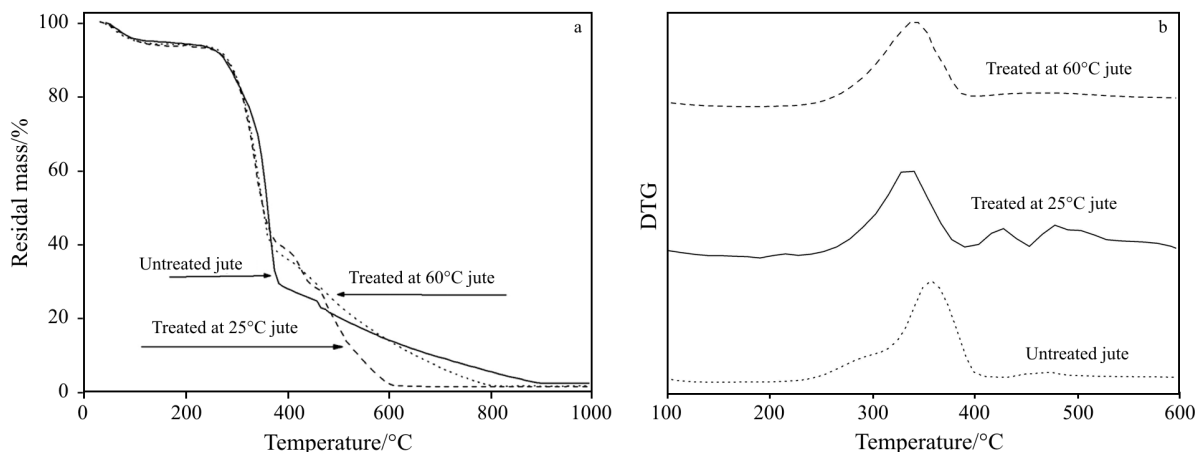

Fig. 1 a – TG and b – DTG curves obtained for untreated and alkaline treated jute fibres at 10ºC min^{-1}; — – untreated, --- – alkaline treated at 25ºC, ··· – alkaline treated at 60ºC

Table 2 Untreated and alkaline treated jute fibres composition

Fibres	α-cellulose/%	Hemicellulose/%	Lignin/%	Other components (ash, moisture, pectins)/%
Untreated	71.1	15.9	11.8	1.2
Treated 25ºC	80.3	9.6	7.6	2.5
Treated 60ºC	84.6	7.1	5.8	2.5

Table 3 Temperatures at the maximum decomposition rate for different fibre fractions obtained at different heating rates.

Peak	Corresponding to	Heating rate/ºC min^{-1}		
		5	10	15
first/ºC	untreated* fibre	350	356	357
	alkaline treated fibre (25ºC)	327	340	353
	alkaline treated fibre (60ºC)	328	344	358
	untreated fibre in composite	327	352	355
	alkaline treated fibre (25ºC) in composite	327	350	353
	alkaline treated fibre (60ºC) in composite	329	349	358
second/ºC	VE matrix	428	436	456
	VE matrix in composite with untreated fibre	406	425	437
	VE matrix in composite with treated fibre (25ºC)	409	434	443
	VE matrix in composite with treated fibre (60ºC)	411	433	440

*Untreated jute presented another peak at around 300ºC due to hemicellulose and lignin compounds
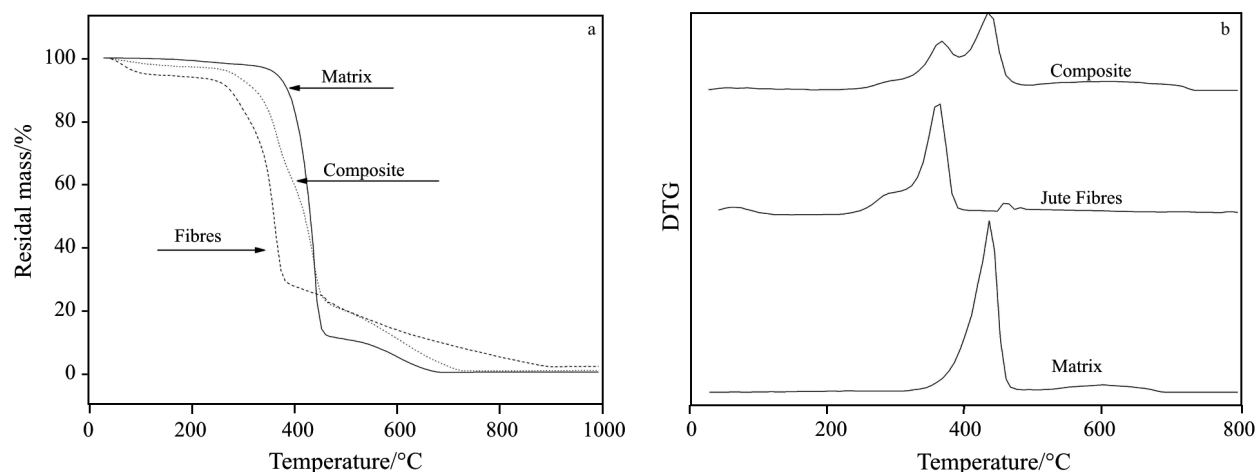
Fig. 2 a – TG and b – DTG curves obtained for raw material at 10ºC min^{-1}; — – matrix, --- – untreated fibres, ··· – composites

jute fibre. The residual mass curves of composite materials are intermediate between that of the matrix and fibres alone. Although the treatment of the fibres conducted to a lower degradation temperature peak, the first peak, at temperatures around 300ºC, disappear due to the decrease in the hemicellulose content. On the other hand, the temperature of second peak slightly increases with the fibre treatment.

Figure 3 shows that alkaline treated jute fibres at room temperature exhibited the higher residual mass, this result is very important for structural applications.

Kinetic parameters were predicted from the dynamic TG/DTG data. In this work, a general model can be used for a general kinetic approach taking into account each separate peak. These peaks were deconvoluted using a Lorentzian multi-peak curve, as shown on Fig. 4 for vinylester/untreated jute fibres at a heating rate of 10ºC min^{-1}.

The differential method of Friedman allow us to obtain the kinetic parameters as a function of conversion from TG curves measured at different heating rates. This is a very important method since it does not make any assumptions about the reaction order. As can be seen in Figs 5 and 6 in the first peak the activation energy is almost constant with the conversion for the treated fibres composites but increases with the conversion for untreated fibres composite. This result indicates that, in the last case, the degradation mechanism
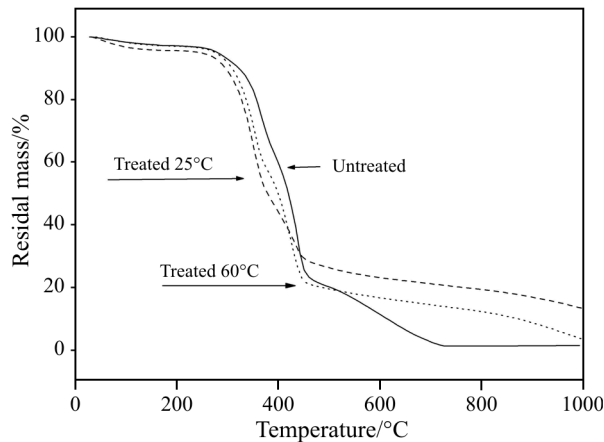
Fig. 3 TG curves obtained for composites with untreated and alkaline treated jute fibres at 10ºC min⁻¹; —— – untreated, --- – alkaline treated at 25ºC, ··· – alkaline treated at 60ºC
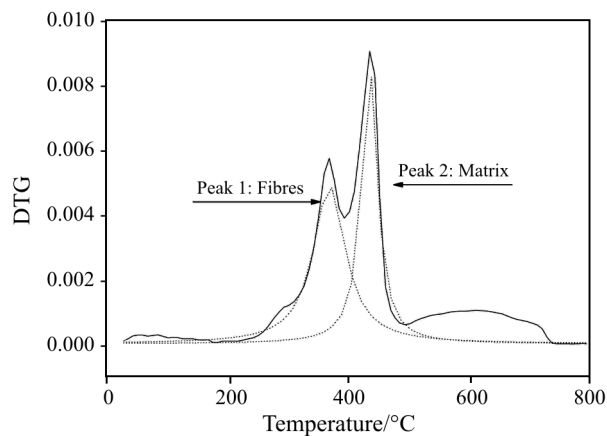

Fig. 4 Deconvolution using a Lorentzian multi-peak curve for jute/vinylester composites at a heating rate of 10ºC min⁻¹; —— – experimental curve, ··· – Lorentzian multipeak fit

changes throughout the whole process and the higher activation energy could be put down to the presence of the lignin in the untreated fibres. Ferdous *et al*. [21] showed that for lignin the activation energy increases with increase in temperature. When fibres are treated, lignin is partially removed and this behaviour was not observed. Also Kumar *et al*. [22] found that the aromatic rings of the lignin improve the thermal resistance of jute fibres. In the second peak the activation energy changed with conversion, but the changes are around an average value without tendency.

Ozawa and Flynn and Wall are essentially the same method. Both are simple methods to determine activation energies from TG curves. Iso-conversional plots for different materials and activation energies are shown in the Fig. 6. The tendencies observed analysing the data with Friedman method are also observed in the case of Ozawa's method.

Average values of activation energies of both peaks obtained from Friedman and Ozawa methods are shown on Table 4. In spite that the activation energy changed with the conversion, especially for the untreated composites, the average values indicates the comparative changes between the fibres decomposition (first peak), and the vinylester matrix decomposition (second peak).

Van Krevelen method was also applied to the different resin and untreated – treated jute fibres composites. The activation energies obtained by this method for both peaks are resumed in the Table 5. Average energy values are in the same range than those obtained by Friedman and Ozawa methods.

In order to obtain a more accurate model that could fit the whole DTG curve, the expression (4) with three fitting parameters and the Marquard method was used. The peaks were fitted as indicate Eqs (5) and (6). Figure 7 shows the result for DTG curve of one of the composites and Table 6 summarises all the k', m and n values. This fitting method is important especially for

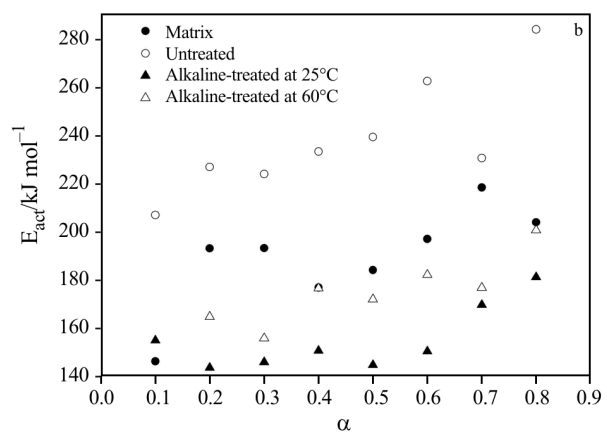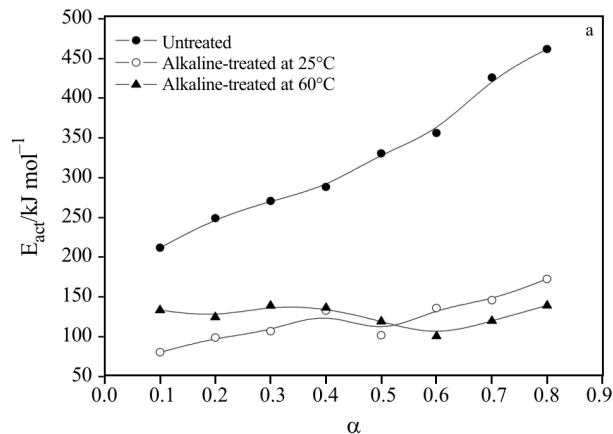**Fig. 5** Activation energy for different conversions obtained by Friedman's method for jute/vinylester composites: a – first peak, b – second peak

Table 4 Average values of the apparent activation energy obtained from Friedman and Ozawa methods for the decomposition process for both peaks: fibres and matrix

Material	Peak	Friedman average E_{act}/kJ mol^{-1}	Ozawa average E_{act}/kJ mol^{-1}
matrix	second	189±21	155±36
untreated fibres composite	first	323±87	296±87
	second	238±24	229±20
alkaline treated 25ºC composite	first	121±30	106±26
	second	155±13	153±10
alkaline treated 60ºC composite	first	126±13	133±17
	second	171±19	16±7

Table 5 Apparent activation energy values as a function of heating rate obtained from Van Krevelen method for the decomposition process for the second peak

Material	Apparent activation energy E_a/kJ mol^{-1}			Average E_{act}/kJ mol^{-1}
	5ºC min^{-1}	10ºC min^{-1}	15ºC min^{-1}	
matrix	139	137	147	141±24
untreated fibres composite	221	221	219	220±1
alkaline treated 25ºC composite	153	152	151	152±1
alkaline treated 60ºC composite	169	171	172	171±2

Table 6 Decomposition kinetic parameters obtained by the Marquard fitting method

Heat rate/°C min^{-1}	Material	First peak			Second peak		
		k	m	n	k	m	n
5	matrix	–	–	–	7.99	3.13	3.09
	untreated fibre composite	0.62	1.80	1.89	0.90	1.78	1.82
	25ºC treated fibre composite						
	60ºC treated fibre composite	0.651	1.89	1.92	0.85	1.82	1.76
10	matrix	–	–	–	5.14	2.43	2.31
	untreated fibre composite	1.20	1.80	1.88	1.84	1.78	1.80
	25ºC treated fibre composite	1.12	1.97	2.06	1.76	1.80	1.84
	60ºC treated fibre composite	1.32	1.74	1.82	1.56	1.70	1.73
15	matrix	–	–	–	4.80	2.02	1.81
	untreated fibre composite	1.94	1.81	1.89	2.66	1.79	1.82
	25ºC treated fibre composite	2.0	1.80	1.89	2.70	1.80	1.82
	60ºC treated fibre composite	1.92	1.80	1.89	2.44	1.83	1.86
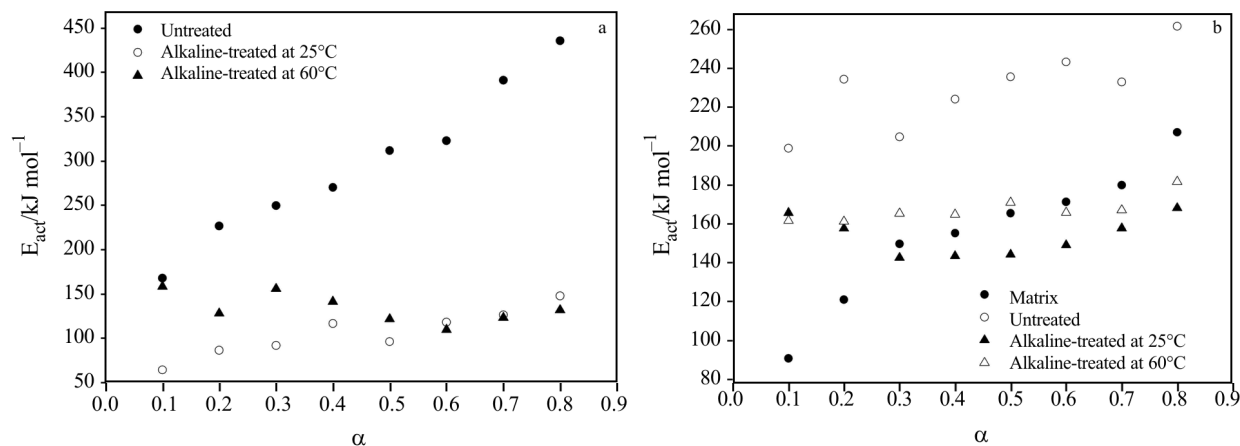
Fig. 6 Activation energy for different conversions obtained by Friedman's method for jute/vinylester composites: a – first peak, b – second peak
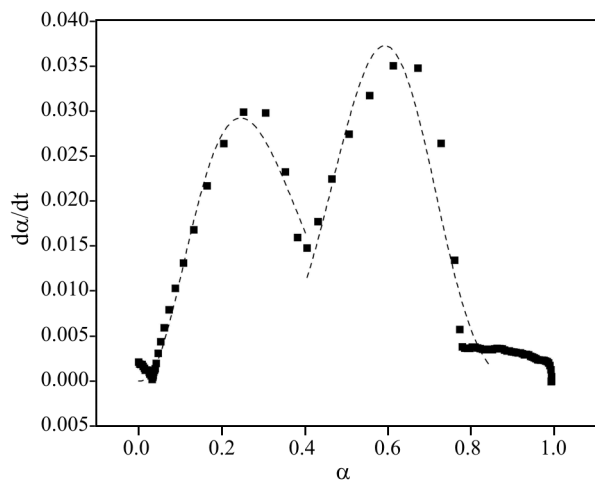
Fig. 7 Marquard fitting of the DTG curve (5ºC min^{-1}) for the 60ºC treated fibre composite. ■ – experimental data; --- – fitting curve

the untreated sample where the apparent activation energy depends on the conversion.

Conclusions

The composition of the jute fibres after alkaline treatments was quantified. The alkaline treatment on the jute fibres produced the extraction of hemicellulose and lignin compound.

Two different peaks were detected by the thermal gravimetric analysis for the jute fibres. The second and main peak at higher temperature (~350°C) was attributed to cellulose and some lignin compound. The first peak at low temperature (~300°C) decreased as the hemicellulose and lignin were extracted and the second peak shifted to lower temperature.

Two main different peaks were obtained in the thermal decomposition of composites based on jute and vinylester cured resin. The first peak (~327°C) was attributed to the jute fibres and the second peak to the vinylester matrix (~408°C). As a consequence, the kinetic parameters of the decomposition process in non-isothermal measurements could be determined. By using different models to fit the differential decomposition curves, it was possible to find that the activation energy depends on the conversion for untreated fibre based composites, and therefore the mechanism of decomposition depends on the degradation temperature. The activation energy of the decomposition of the matrix in the composite was higher when the jute fibres were untreated. The reaction was faster in the second stage, corresponding to vinylester matrix.

The first peak of the composite decomposition shifted to low temperatures, and as a consequence, the thermal stability of vinylester decreased by the presence of jute fibre. However, the alkaline treatment of the jute fibre produced a slight decrease in the thermal stability of the composite due to lignin extraction.

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