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# Thermogravimetric evaluation of polyester/sisal flame retarded composite

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**Abstract**

An unsaturated polyester/sisal composite was formulated to achieve UL 94 V-0 performance using decabromine diphenyl oxide associated with antimony trioxide as additives. Flame retarded (FR) samples exhibited a self-extinguishment time less than 1 s. The model-free kinetic approach was applied to data for thermal oxidative decomposition of normal and FR composite samples. The activation energy ($E$) was calculated as function of $\alpha$ (conversion) and $T$ (temperature), by using the Vyazovkin model-free kinetic method, allowing us to estimate conversion time for different temperature values.

Important differences were observed in the shape of the activation energy curves for normal and FR polyester/sisal composites.


*Keywords:* Flame-retardant; Polyester/sisal composites; Model-free kinetics

## 1. Introduction

Polymeric materials have an extremely important place in modern industry. Unsaturated polyesters are among the most commonly used matrices with a world consumption of approximately 1 million tonnes per year [1]. In order to reduce the flammability of these polymeric materials, chemicals are added in order to delay or even extinguish the burning process. The compositions that are most effective in fire retardancy are those containing phosphorous, bromine, chlorine, antimony, boron and nitrogen [2], with brominated flame-retardants the most commonly used [3].

Several flammability tests have been created for the consumer's protection [4], to evaluate the performance of the polymer exposed to fire. On a small scale these include: gram samples of the material are burned (UL 94 tests) [5], Brandschaucht and Epiradiateur [6], and limiting oxygen index (LOI). On a larger scale, pieces of furniture and even whole rooms are set on fire using either the cone calorimeter and full-scale fire test [7], respectively.

Thermal analysis (TA) has assumed an important role in the study of flame-retardants in polymers. TA supplies important information for the evaluation and the development of flame retarded (FR) polymers via the profile of their thermal decomposition [8–11].

In this work, the thermal degradation of thermoset polyester, containing decabromine diphenyl oxide and antimony trioxide, was studied. The polyester was evaluated by comparing thermogravimetry (TG) and conventional flammability UL 94 vertical burning test.

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## 2. Experimental

### 2.1. The polyester resins

Polyester samples were prepared by well-established procedures using commercial orthophthalic resin, Hoescht Apolite 8322. It contained styrene as a cross-linking agent and 10% (w/w) sisal fiber. The additives were supplied by manufactures as follows: antimony oxide from Cromex SA and decabromine diphenyl oxide from Princeton do Brasil. The additives were incorporated into the polymer using a high shear mixer prior to the addition of the curing catalyst and accelerator. The bromine concentration in the polyester was held at 7.5% (w/w). The molar ratio between Br:Sb was adjusted to 3:1 in each sample.

### 2.2. Thermogravimetry

To study the thermo-oxidation of these samples, a Mettler 851 thermobalance was calibrated over all heating rates, using a gas purge (the same conditions as those of the analysis). Polymer samples, of about 10 mg in a platinum crucible, were submitted to a pretreatment under a dry air atmosphere at 30 °C. They were then heated in the temperature range of 30–900 °C using heating rates of 5, 10 and 20 °C $min^{-1}$, with a controlled dry airflow of 120 $cm^3$ $min^{-1}$.

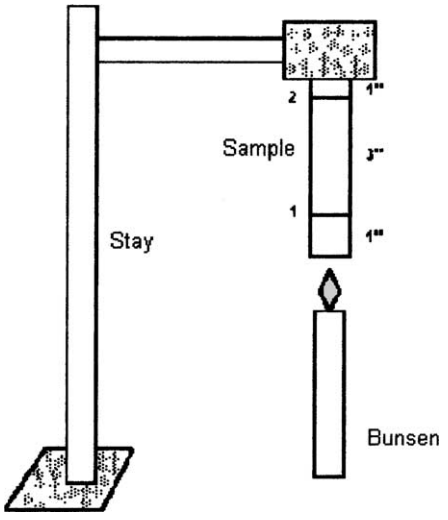


Fig. 1. Schematic of UL 94 V flammability test.

### 2.3. Flammability testing

The evaluation of the samples flammability was measured with the UL 94 burning test [5]. This test consists of holding vertically one of the ends of the sample and maintaining the other extremity in contact with the flame of a Bunsen burner for 10 s (Fig. 1). After the exposed period, the Bunsen burner is removed and the self-extinguish time is measured.

## 3. Results and discussion

### 3.1. Thermal analysis results

The amount of char residue formed in the thermal degradation of a polymer is a measure of its flame resistance [12]. The amount of final residue provides quantitative information about the flame-retardants activity as a catalyst for the formation of coke [13], which protects the polymer surface during combustion. The TG results indicate that more char (residue) is indicative of an effective flame-retardant action (compare Figs. 2 and 3).

The Br/Sb flame-retardant system used in this work promotes char formation, in comparison to the non-flame-retardant composite. The size of the second weight loss step and the final residues of TG curves, Figs. 2 and 3 indicate the latter difference, respectively. The char formation is also confirmed visually during the UL 94 burning test. For the polymeric samples studied, it appears that the bromine flame-retardant acts more effectively possibly in the gaseous phase. This observation is based on the formation of $SbBr_3$ [8] during combustion as a high density gas, suffocating polymer burning and limiting the oxygen access.

### 3.2. Kinetic study

Activation energies were calculated for the polymer degradation, with and without flame-retardant, using dynamic integral TG curves at various heating rates (Figs. 2 and 3), as proposed by Vyazovkin [14–16]. The theory is based on that $\partial\alpha/\partial T = k\,e^{-E/RT}\,F(\alpha)$ and that the activation energy $E(\alpha)$ is constant for a certain conversion (isoconvertional method).

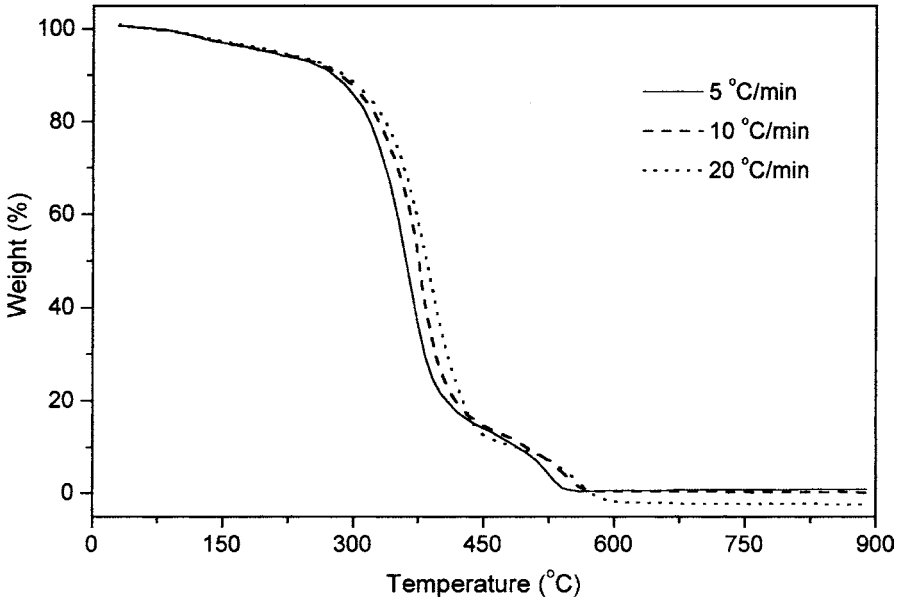


Fig. 2. TG curves for polyester/sisal composite: 5, 10 and 20 °C $min^{-1}$; air = 120 $cm^3$ $min^{-1}$.

A chemical reaction is measured at least at three different heating rates ($\beta$) and the respective conversion curves are calculated out of the TG measured curves.

For each conversion $\alpha$, $\ln \beta/T_\alpha^2$ is plotted versus $1/T_\alpha$, giving a straight line with the slope $-E_\alpha/R$, therefore the activation energy is obtained as a function of conversion.

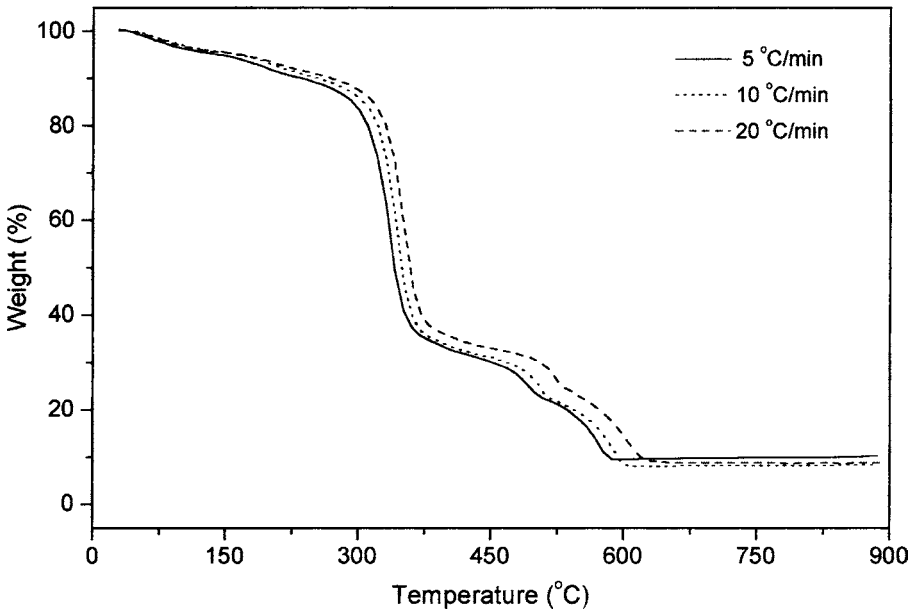


Fig. 3. TG curves for FR polyester/sisal composite: 5, 10 and 20 °C $min^{-1}$; air = 120 $cm^3$ $min^{-1}$.

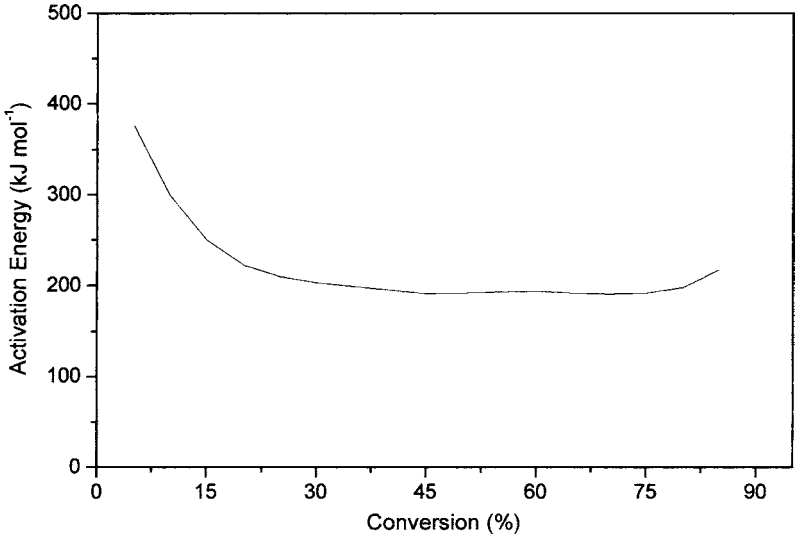


Fig. 4. Activation energy vs. conversion for polyester/sisal composite thermal degradation in air.

Taking the reaction rate equation, presented as $f(\alpha)$, and dividing by the heating rate $\beta = \mathrm{d}T/\mathrm{d}t$

$$\frac{\partial\alpha}{\partial t} = kf(\alpha) \rightarrow \frac{\partial\alpha}{\partial T} = \frac{k}{\beta}f(\alpha) \tag{1}$$

where $\partial\alpha/\partial t$ is the reaction rate ($s^{-1}$), $k$ the velocity constant ($s^{-1}$), $\alpha$ the conversion and $\beta$ is the heating rate ($K\,s^{-1}$).

Substituting $k$ by the Arrhenius expression $k = k_0\,e^{-E/RT}$ and rearranging gives

$$\frac{1}{f(\alpha)}\partial\alpha = \frac{k_0}{\beta}\,e^{-E/RT}\partial T \tag{2}$$

Integrating up to conversion, $\alpha$ (at the temperature $T$) gives

$$\int_0^{\alpha}\frac{1}{f(\alpha)}\partial\alpha = g(\alpha) = \frac{k_0}{\beta}\int_{T_0}^{T} e^{-E/RT}\partial T \tag{3}$$

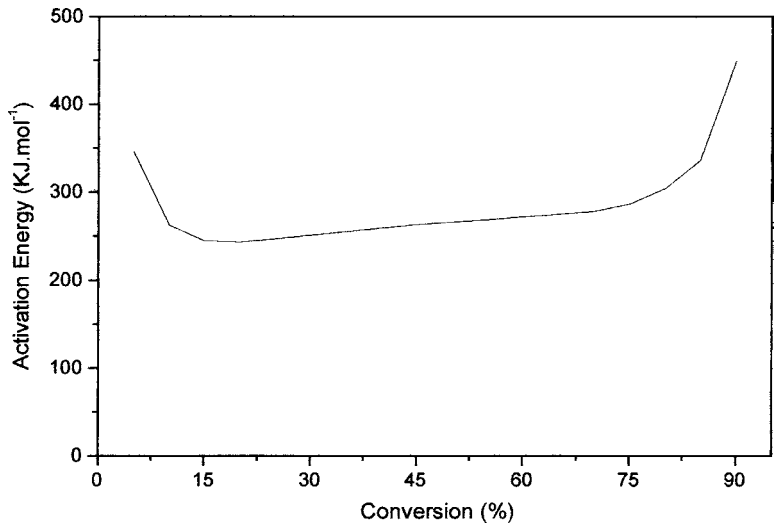


Fig. 5. Activation energy vs. conversion for FR polyester/sisal composite thermal degradation in air.

Table 1
Temperature for polyester/sisal degradation as a function of time, for different conversions

| Time (h) | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | 10% | 25% | 50% | 75% | 90% | 95% |
| 2 | 261 | 276 | 291 | 303 | 332 | 363 |
| 4 | 255 | 269 | 284 | 296 | 327 | 360 |
| 6 | 251 | 265 | 280 | 292 | 324 | 358 |
| 8 | – | 263 | 277 | 290 | 322 | 357 |
| 10 | – | 260 | 275 | 288 | 321 | 356 |
| 12 | – | 259 | 273 | 286 | 320 | 355 |
| 14 | – | 257 | 272 | 285 | 319 | 354 |
| 16 | – | 256 | 271 | 283 | 318 | 354 |
| 18 | – | 255 | 270 | 282 | 317 | 353 |
| 20 | – | 254 | 269 | 281 | 316 | 353 |
| 22 | – | 253 | 268 | 281 | 316 | 352 |
| 24 | – | – | – | – | – | – |

Table 2
Temperature for flame retarded polyester/sisal degradation as a function of time, for different conversions

| Time (h) | Temperature (K) | | | | | |
|---|---|---|---|---|---|---|
| | 10% | 25% | 50% | 75% | 90% | 95% |
| 2 | 265 | 287 | 302 | 321 | 375 | 410 |
| 4 | 260 | 279 | 292 | 311 | 369 | 403 |
| 6 | 256 | 274 | 287 | 305 | 365 | 398 |
| 8 | 254 | 270 | 283 | 300 | 362 | 396 |
| 10 | 253 | 267 | 280 | 298 | 361 | 395 |
| 12 | 251 | 265 | 278 | 295 | 359 | 392 |
| 14 | 250 | 263 | 276 | 293 | 358 | 391 |
| 16 | 249 | 262 | 274 | 291 | 357 | 389 |
| 18 | 248 | 261 | 272 | 289 | 355 | 388 |
| 20 | 247 | 259 | 271 | 288 | 354 | 387 |
| 22 | 246 | 258 | 269 | 286 | 353 | 385 |
| 24 | – | – | – | – | – | – |

Since $E/2T \gg 1$, the temperature integral can be approximated by

$$\int_{T_0}^{T} e^{-E/RT}\partial T \approx \frac{R}{E}T^2 e^{-E/RT} \quad (4)$$

Substituting the temperature integral, rearranging and logarithming, gives

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{Rk_0}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \quad (5)$$

This is defined as a dynamic equation, which is used for the determination of the activation energy for all conversion values (α) (see Figs. 4 and 5). It was observed that the normal composite and the FR composite exhibit different activation energy ($E$) curve profiles. Fig. 4 shows that $E$ starts decreasing in the beginning of normal composite degradation process and can be related to the evolution of combustible fragments from primary polymer cracking, stabilizing at about 200 kJ mol$^{-1}$. The $E$ curve for the FR com-

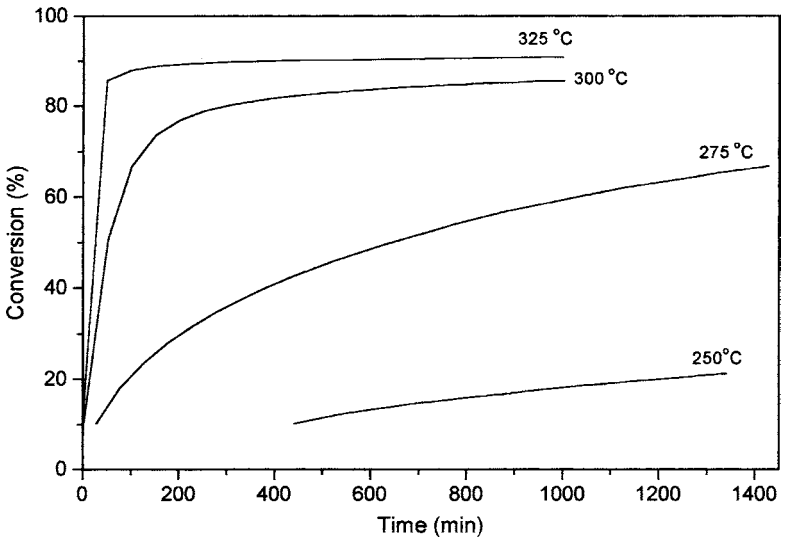


Fig. 6. Conversion vs. time for polyester/sisal composite.

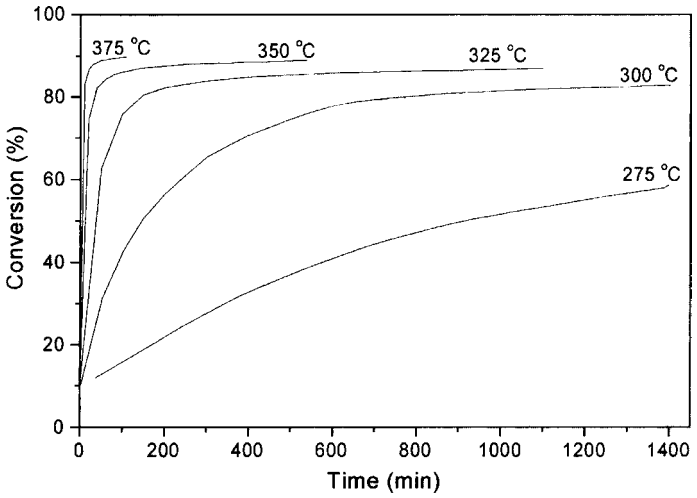


Fig. 7. Conversion vs. time for FR polyester/sisal composite.

posite is presented in Fig. 5. The presence of flame-retardant explains the higher $E$ values observed at 250–300. It is postulated that Br/Sb acts in the gas phase, deactivating free radicals responsible for the combustion process. In the last portion of composites thermal-oxidative degradation, >90% conversion, it is postulated that the rapid activation energy increase is due to the relative high polyunsaturated content in the samples, seen mainly in the FR composite sample.

The percentage degradation or conversion, as a function of time, for different temperatures, was calculated for both composites (Tables 1 and 2). The conversion time decreases considerably as a function of temperature (see Figs. 6 and 7).

### 3.3. Flammability

The polyester/sisal composite that was submitted to the UL 94 V test burned completely white. The FR samples achieved self-extinguishment in 0.72 s, which results in a V-0 classification, a very high security standard for polymer systems. The efficiency of a flame-retardant is inversely proportional to the sample self-extinguishment time.

## 4. Conclusion

TA measurements provide an important link between the degradation temperatures and thermal profiles of the materials, which can be used with international fire tests and standards for a full investigation of flammability.

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