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Kinetic evaluation of decabromodiphenil oxide as a flame retardant for unsaturated polyester

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Abstract

The bromine performance of decabromodiphenyl oxide as a flame retardant element was evaluated alone and associated with antimony oxide in unsaturated polyester and its composite with sisal (agave sisalana) fibers using thermal analytical techniques and the UL-94 V flammability test.

The flame retardancy impact was studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), through determination of parameters as percent final residue in inert atmosphere, heat of combustion and the thermal oxidative decomposition kinetics, following the Flynn and Wall model. It was observed that bromine increased the activation energy of polyester decomposition by 87%, when used in conjunction with antimony trioxide. The flame retarded samples exhibited self-extinguishment times of less than 1 s.

Keywords: Flame retardant; Polyester/sisal composite; Thermal analysis

1. Introduction

A great part of the combustible materials found nowadays has a polymeric base. Among the thermoset resins, the unsaturated polyesters the are most commonly used, with a world consumption of approximately 1×10^6 t per year [1].

With the objective of reducing the flammability of those polymeric materials, some substances are added in order to delay or even extinguish the burning process. The compositions that have been shown to be the most effective in fire retardancy are those containing phosphorus, bromine, chlorine, antimony, boron and nitrogen [2], where brominated flame retardants are the most widely used [3].

Flammability tests, internationally recognized for the consumer's protection [4], were created to evaluate the performance of a polymer exposed to fire on a small scale, these include tests in which grams of the material are burned (UL-94 tests) [5], Brandschaucht and Epiradiateur [6] and limiting oxygen index (LOI). On large scale, tests in which pieces of furniture are set on fire and even whole rooms, the ''cone calorimeter'' and ''full scale fire test'', may be used [7], respectively.

Thermoanalytical techniques assume an important role in the study of flame retardants in polymers. These methods supply important information for the evaluation and the development of flame retarded polymeric systems. Parameters examined may include a profile of their thermal decomposition, the size of the

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final solid residue (thermogravimetric analysis; TGA) and the heat of combustion of the system differential scanning calorimetry (DSC) [8–12].

In this work, the thermal degradation of a thermoset polyester, containing decabromodiphenyl oxide and antimony trioxide, was studied by a conventional flammability UL-94 vertical burn test and by thermal analysis.

2. Experimental

2.1. The polyester resins

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

2.2. TGA

To study samples thermoxidation, a DuPont 951 thermobalance was calibrated over all heating rates, using a gas purge, in the same conditions as those of the analysis. Polymer samples, of about 10 mg in a platinum crucible, were submitted to a pre-treatment under a dry air atmosphere at 30 °C. They were then heated in the temperature range 30–1000 °C using heating rates of 2.5, 5.0, 10 and 20 °C min^{-1}, with a controlled dry air flow of 120 cm^3 min^{-1}. Decomposition was also studied in a dynamic nitrogen atmosphere, at 10 °C min^{-1}.

2.3. DSC

Samples, of approximately 10 mg weighed in aluminum crucibles, were analyzed using a TA Instruments DSC 2010. DSC curves were obtained in dry air atmosphere in a flow of 60 cm^3 min^{-1} and heating rate of 10 °C min^{-1}.

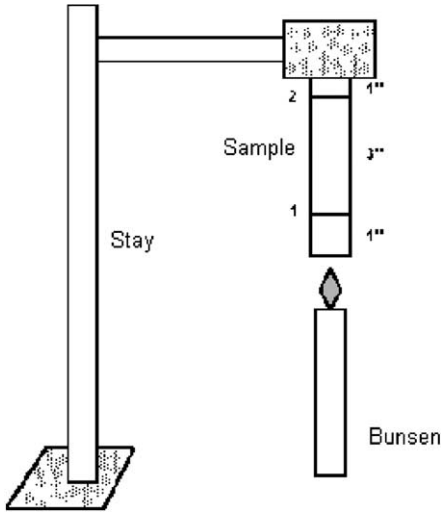

Fig. 1. Schematic of UL-94 V flammability test.

2.4. Flammability testing

The evaluation of sample flammability was made using the UL-94 vertical burn test [5]. For this test the sample, of specified dimensions, is held vertically. The unclamped end is contacted with the flame of a bunsen burner for 10 s (Fig. 1). At the end of period, the flame is removed and time for self-extinguishment is measured.

3. Results and discussion

3.1. Thermal analysis results

The amount of char residue formed on the thermal degradation of a polymer in a inert atmosphere is a measure of its flame resistance [10,13]. The final residue provides quantitative information regarding the flame retardant activity as a catalyst for the formation of coke [14], which protects the polymer surface during the combustion.

The dacabromodiphenyl oxide/antimony oxide flame retardant system used in this work did not increase char formation. Char formation for the composite containing additive (0.5%) is nearly identical to the non-flame retarded composite (0.0%) (Figs. 2 and 3, respectively). This is as would be expected. It is known that brominated flame retardants are gas-phase active producing bromine atoms or hydrogen bromide

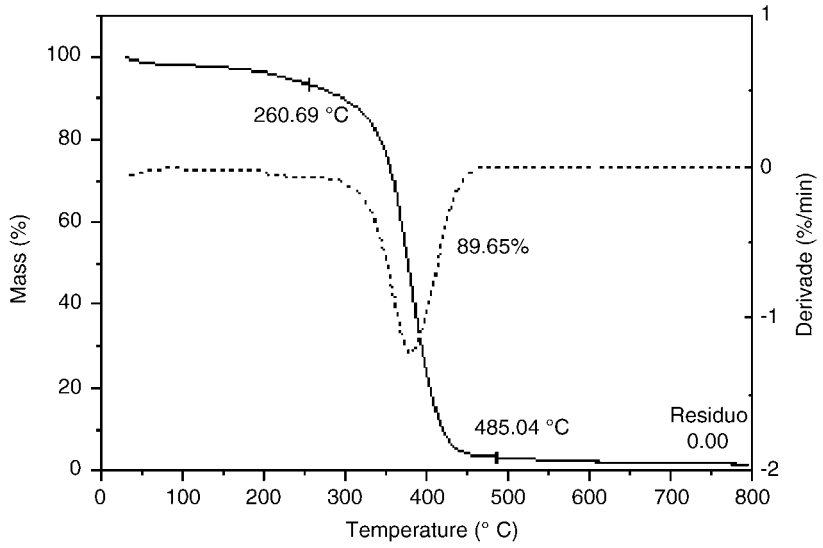

Fig. 2. Thermogram for the decomposition of a polyester/sisal composite: 10 °C min^{-1}; nitrogen = 120 cm^3 min^{-1}.

that interrupt the flame propagation reactions. The synergist, antimony oxide, facilitates this process via the formation of volatile antimony bromide. The antimony oxide is not sufficiently acidic as to promote cross-linking.

DSC curves indicated that the heat of combustion for flame retarded composite was smaller than that for the untreated composite, 1347 J g^{-1} versus 1009 J g^{-1}. This suggests that the additives were effective in limiting combustion for this system.

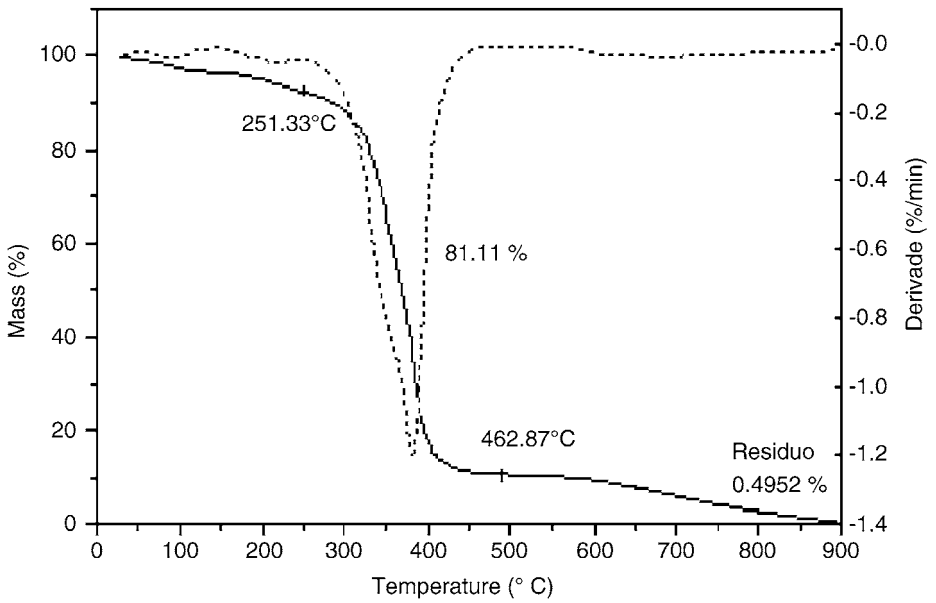

Fig. 3. Thermogram for the decomposition of a polyester/sisal composite containing decabromodiphenyl oxide 1.5% (w/w) and antimony trioxide 2.15% (w/w): 10 °C min^{-1}; nitrogen = 120 cm^3 min^{-1}.

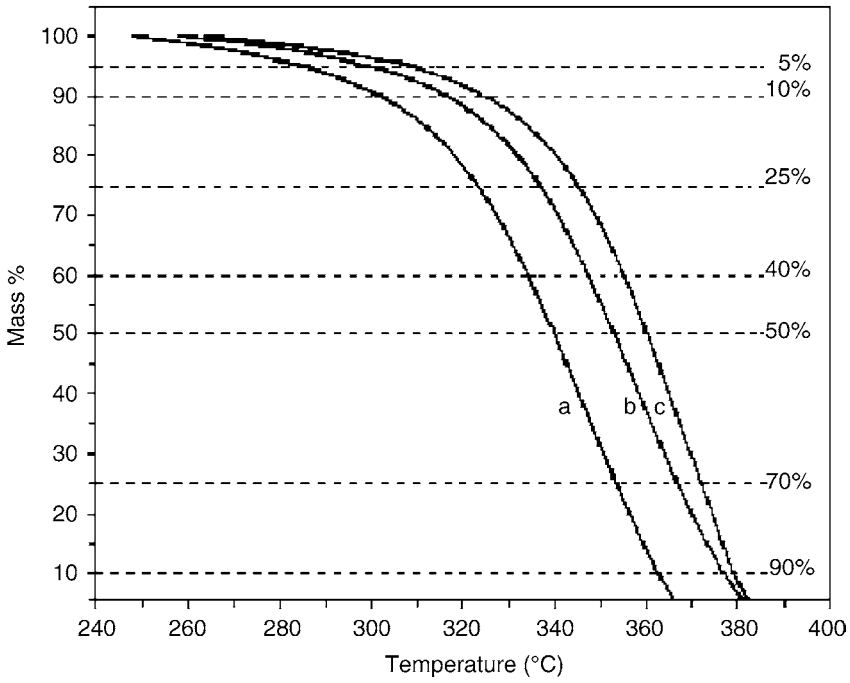

Fig. 4. Thermal degradation of a polyester/sisal composite at different heating rates: a = 5 °C min^{-1}; b = 10 °C min^{-1}; c = 20 °C min^{-1}; air = 120 cm^3 min^{-1}.

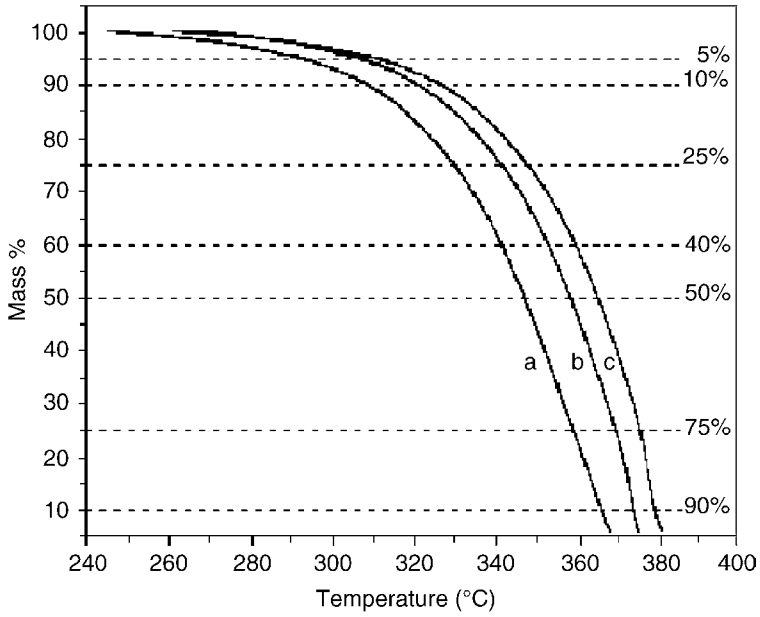

Fig. 5. Thermal degradation of a flame retarded (decabromodiphenyl oxide/antimony oxide) polyester/sisal composite at different heating rates: a = 5 °C min^{-1}; b = 10 °C min^{-1}; c = 20 °C min^{-1}.

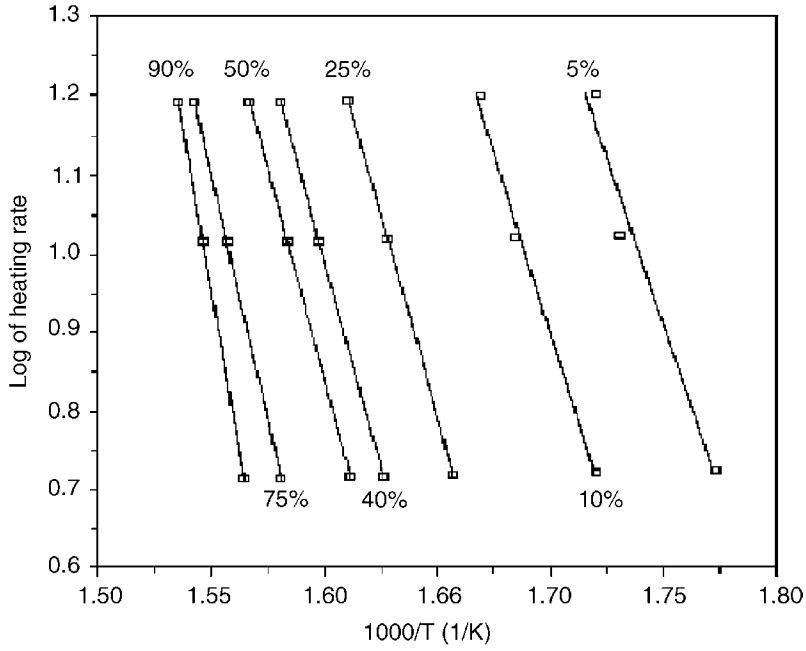

Fig. 6. Logarithm of heating rate vs. the reciprocal temperature for polyester/sisal composite (in percentage). Activation energy is determined by differentiating these curves.

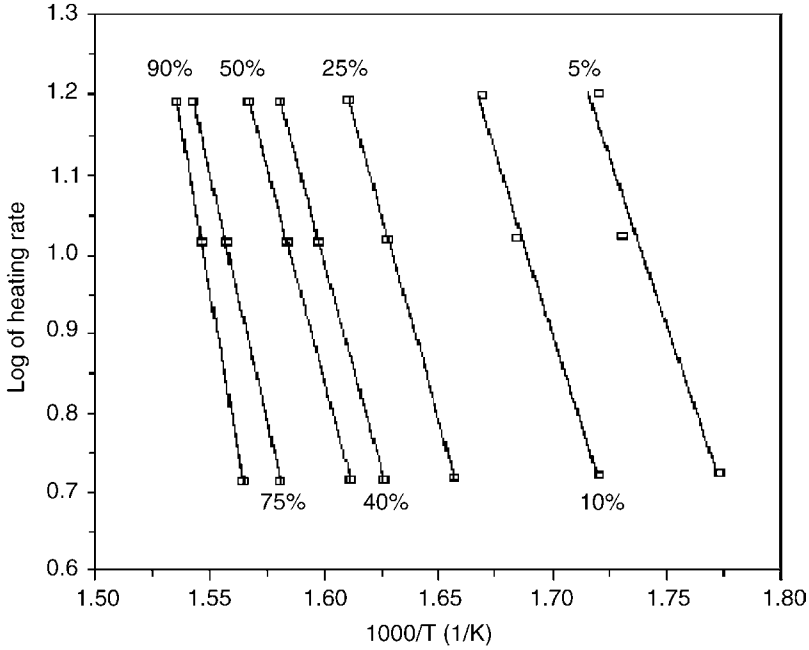

Fig. 7. Logarithm of heating rate vs. the reciprocal temperature for flame retarded polyester/sisal composite (in percentage).

3.2. Kinetic study

Activation energies for polymer degradation, with and without flame retardant, were determined using dynamic integral TGA at different heating rates, Figs. 4 and 5, as proposed by Flynn and Wall [15]. The apparent activation energy (E) was obtained employing the expression:

$$E \cong -4.35 \frac{\partial \log \beta}{\partial 1/T} \quad (1)$$

where β is the heating rate and T the absolute temperature (Figs. 6 and 7).

The activation energy for degradation of the polyester/sisal composite containing the flame retardant additive was much larger than that for the untreated composite. The activation energy for decomposition increased 87% upon addition of the flame retardant.

Degradation showed to increase 87% when formulated with Br/Sb flame retardant system.

3.3. Flammability test

In the UL-94 test the polyester/sisal composite burned completely. A comparable sample containing the flame retardant achieved self-extinguishment in just 0.48 s, permitting it to be classified as V-0, a very high security standard for polymeric systems. The efficiency of a flame retardant is inversely proportional to the sample self-extiguishment time.

4. Conclusions

Thermal analysis can be utilized in an assessment of the effectiveness of the flame retardant additives for polymeric materials. Thermal profiles for the decomposition and temperatures of initial degradation are both useful in this assessment. It has been demonstrated that decabromodiphenyl oxide/antimony oxide is an effective flame retardant for a polyester/sisal composite.

Acknowledgements

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