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EFFECT OF HALOGENATED FLAME-RETARDANT ADDITIVES IN THE PYROLYSIS AND THERMAL DEGRADATION OF POLYESTER/SISAL COMPOSITES

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An unsaturated polyester/sisal flame retardant composite was formulated using decabromine diphenyl oxide associated with antimony trioxide as additives. The development and use of natural or vegetable fiber reinforced composites is increasing worldwide, since natural fibers come from renewable sources and their use contributes to the so-called ‘green technology’. In the present study, the synergic effect of a bromine/antimony (3:1 molar ratio) based flame retardant system with 7.5% Br (mass/mass) added to composites investigated by TG, UL-94V and pyrolysis on a coupled Pyr-GC/MS device. The efficiency of the flame retardant system is confirmed by TG and UL-94V test where the composite containig flame retardant system obtained the highest classification (V-0).

Keywords: *composite, halogenated flame retardant, pyrolysis, sisal fiber, thermogravimetry*

Introduction

The development and use of natural or vegetable fiber reinforced composites is increasing worldwide. The main advantages of these composites are associated to factors such as their low mass, low raw material and processing costs and a good set of mechanical properties. Furthermore, natural fibers come from renewable sources and their use contributes to the so-called ‘green technology’. These composites, however, exhibit a few deficiencies, which limit their use and are mainly associated with their hygroscopic nature and low fiber/polymer matrix adhesion. Vegetable fibers are biodegradable and this characteristic can either be considered an advantage or a disadvantage. It will be a disadvantage for long lasting applications and will be considered an advantage for short-term applications as the discarded material will decompose and reduce pollution, as the amount of residues to be disposed of or to be recycled is diminished [1].

Thermoset polymer composites have been traditionally considered to be non-recyclable plastic materials. They are chemically crosslinked and therefore are not fusible or soluble, and consequently cannot be remolded into other shapes. The use of these materials as fillers in the manufacture of new composites leads to further difficulties, which are associated with compatibility and filler content. Pyrolysis can be considered an alternative and appropriate method for partial recycling thermoset composites. During pyrolysis (heating without oxygen) the organic portion of the material is decomposed into gases, which can be useful as fuels or chemical sources, while the inorganic components remain unmodified and therefore can be recycled, either as mixtures or as individual components which can be added as fillers into other composites or other plastic materials [2].

In order to reduce the flammability of polymeric materials, some substances are added in order to delay or even to prohibit the burning process, thus expanding their applications. The most effective flame retardant compounds are those containing phosphorus, bromine, chlorine, antimony, boron and nitrogen [3]. Cost and effectiveness have made brominated compounds to be the most commonly used flame retardant in the market today [4]. Thermal analysis has assumed an important role in the study and choice or of flame retardants to be used in polymers. Important information for the evaluation and development of these compounds can be obtained by their thermal decomposition profiles [5–11].

Pyrolysis device coupled to GC-MS is a technique that allows the identification of gaseous products derived from the decomposition of the materials being analyzed. Therefore, it may become a very promising technique for the tertiary recycling of thermoset composites, so far as it identifies and suggests the use of their gaseous degradation products as raw materials or precursors of synthetic routes to generate new products.

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In the present study, the effect of the incorporation of a flame retardant system containing 7.5% Br, based on a bromine/antimony 3:1 molar ratio, into unsaturated polyester/sisal composites was analyzed by TG, Flamabillity UL-94V test and by a Py-GC/MS system. In the investigated system the reinforcing fillers are natural fibers and the storage of large amounts of these composites might lead to fire hazards. Therefore the addition of flame retardant agents could reduce or minimize these hazards [8, 12, 14, 16] and the use of thermal analysis. Since recycling of thermoset plastics and composites is either difficult or expensive, it is suggested that the incineration of these products and the use of their pyrolysis subproducts may be not only economically viable, but also an interesting alternative.

Experimental

The composites

A commercial pre-accelerated orthophthalic polyester resin was used as the matrix. The resin (GAMA 301), provided by Embrapol S.A., was further diluted with 10% (*v*/*v*) styrene monomer. Curing took place at room temperature with the addition of 1% (*v*/*v*) MEK. Composites having 10% *v*/*v* sisal were prepared by hand lay-up process. Composites with even smooth surfaces were obtained by closing the mold with a glass plate. In order to produce flame resistant composites, flame retardant additives were incorporated into the matrix by means of a high shear mixer operating at 500 rpm for 5 min prior to the curing agent addition. The components of the flame retardant system employed were antimony trioxide and decabromine diphenyl oxide, supplied by Silaex. These agents were added to the polyester resin in such a way that the bromine concentration was kept at 7.5% Br (mass/mass) and the Br:Sb molar ratio was adjusted to 3:1. In every case, demolding took place 3 h after processing and, to allow total curing, the samples were stocked for at least 28 days before testing.

Thermogravimetry (TG)

The effect of flame retardant agents addition on the thermal decomposition of the composites was investigated by determining the amount of char residue formed during thermogravimetric analysis. Polymer samples, of about 10 mg were placed to an alumina crucible and were submitted to a pretreatment under nitrogen atmosphere at 30ºC, for 60 min. The samples, with and without flame retardant, were heated in a Mettler 851 thermobalance operating in a temperature range of 30–1000ºC at a heating rate of 10 K min^{-1}, and in a constant nitrogen flow of 120 mL min^{-1}.

Flammability testing

The evaluation of the samples flammability was made through UL-94 vertical burning test [5]. This test consists of holding vertically one of the end of the sample and maintaining the other extremity in contact with the flame of a Bunsen burner for 10 s. After that period, the Bunsen burner is removed and the self-extinguishment time is measured.

Pyrolysis

Pyrolysis was employed for the characterization of the degradation products. The analyses were carried out in a Pyrolysis-CG/MS coupled system, from Shimadzu, composed by a Pyr–4A, a GC 17A gas chromatograph and a QP 5000 mass detector.

1 mg of each sample was pyrolysed in a platinum crucible and the degradation products were subsequently analyzed using helium as the carrier gas, at a flow rate of 1.5 mL min^{-1}, with a Petrocol DH 50.2 25 m×0.2 mm×0.3 μm capillary column. The following temperature program was used: initial temperature of 40°C for 5 min, followed by heating at a rate of 7°C min^{-1} up to 280°C and holding isothermal for 15 min. The interface temperature was hold at 300°C.

Results and discussion

Thermogravimetry (TG)

The amount of char residue formed in the thermal degradation of a polymer is a measure of its flame resistance [13]. The final amount of residue provides quantitative information about the flame retardant activity as a catalyst for coke formation, which protects the polymer surface during the combustion [5, 14, 15].

Thermal decomposition profile of the individual components (antimony trioxide and decabromine diphenyl oxide) of the flame retardant system are presented in the Fig. 1.

Figure 1 shows that antimony trioxide it is stable up to 462°C and presented maximum rate of decomposition at 692°C, while the thermal decomposition of decabromine diphenyl oxide occurs in the temperature range of 252–542°C with a maximum at 442°C. The amount of the residue at 500°C was 5.5% for the antimony trioxide and 0% for the decabromine.

Figure 2 shows the thermal degradation of the flame retarded system containing 7.5% Br. It takes place in four steps. Step I, which occurred in the same temperature range is shown in Fig. 1, was associated with the

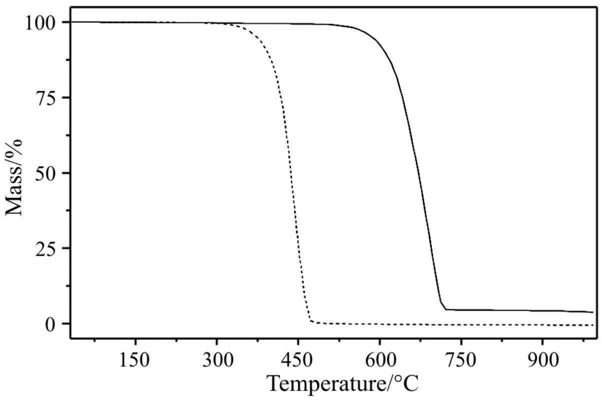

Fig. 1 TG curves of — – antimony trioxide and --- – decabromine diphenyl oxide

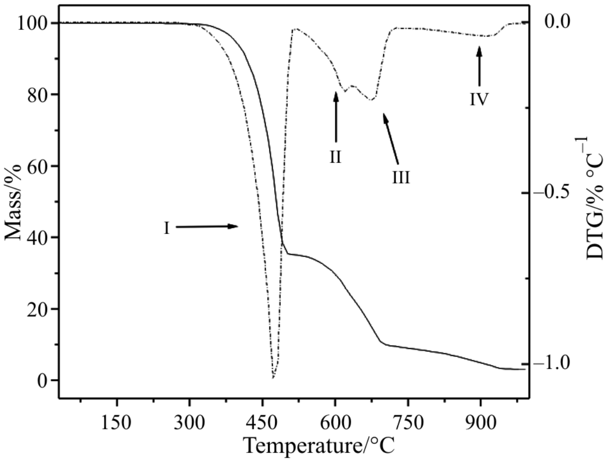

Fig. 2 TG and DTG curves of flame retardant system

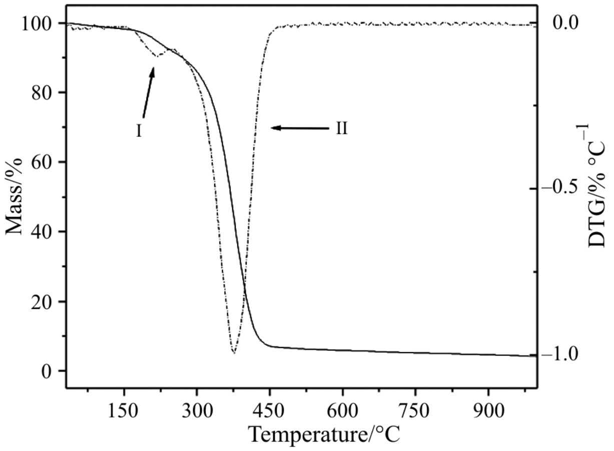

Fig. 3 TG and DTG curves of native composite

partial thermal decomposition of decabromine diphenyl oxide. Steps II and III are thought to indicate a synergistic behavior for the flame retardant system (decabromine diphenyl oxide and Sb_2O_3) which were associated to the formation of antimony halides ($SbBr_3$), which behavior is reported by Turi [5]. Step IV, which takes place in the 651–1000°C temperature range, was attributed to the decomposition of Br/Sb residues. The TG curves of the composites without and with the addition of the flame retardant system are displayed in Figs 3 and 4, respectively.

The results indicate the thermal decomposition of the normal composite (N) takes place in two main mass loss steps (Fig. 3). On the other hand, four steps are displayed in the thermal degradation of the flame retarded composite (FR). For both composites, Step II is associated to the decomposition of the polymer matrix and of the sisal fiber. For the SR composites (Fig. 4), the synergism of the Br/Sb system and the generation of $SbBr_3$, Steps III and IV, suggests that the action of the brominated flame retardant is more effective in the gaseous phase. The efficiency of flame retardant system used in this work can be predicted by at 500°C, indicating that the flame retardant system acted as a catalyst for coke formation, which protects the FR composite surface from heat and oxygen access, during combus-

Table 1 Temperature interval and value of mass loss steps of composites S and SR as a function of temperature

Steps	S		SR		Decabromine		Antimony		Flame retardant (7.5% Br)	
	T/ °C	T_{max}*/ °C	T/ °C	T_{max}*/ °C	T/ °C	T_{max}*/ °C	T/ °C	T_{max}*/ °C	T/ °C	T_{max}*/ °C
I	122–255	220	110–253	220	252–542	442	462–762	692	252–522	472
II	255–508	377	253–473	341					522–632	621
III			473–651	581					632–734	673
IV			651–100	851					734–982	920
Residue (500°C)/%	6.58		30.86							
Residue (1000°C)/%	0		6.89						3	

*T_{max} values are corresponding to DTG peak temperatures.

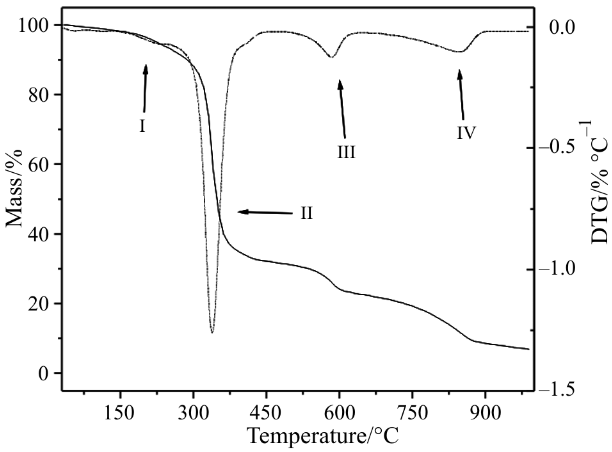

Fig. 4 TG and DTG curves of flame retarded (FR) composite

tion [5]. This can be confirmed by the higher char content of 28.3% for FR composite (with the previous subtraction of the inorganic residue, that was estimated as 2.6% by X-ray fluorescence), compared to the N composite with a char content of 5.6%. This explanation is in agreement with the results obtained by UL-94V flammability test. The final residue, at 1000°C, obtained for these samples were zero (composite S) and 6.89% (composite SR).

Table 1 shows the mass loss steps for all composites with their respective temperature ranges.

Flammability test

The polyester/sisal composite, submitted to the UL-94V test, burned completely while the flame retarded samples self-extinguished in 0.42 s, thus achieving V-0 classification, a very high safety standard for polymeric systems. The efficiency of a flame retardant on a given system is inversely proportional to its self-extinguishing time. The UL-94V flammability test was performed in order to assess and classify the flame resistance of the composites. The behavior of the composites without anti-flame system addition (S) presented ignition and self-propagation of the flame. These materials burned completely and did not achieve classification. On the other hand, a carbonaceous residue was formed on the surface of the flame-retarded composites (SR) which caused flame self-extinguishment in about 4 s after flame removal, thus achieving V-0 classification according with UL-94V standard. This is though to indicate that the anti-flame system acted on the surface of the polymer matrix.

Pyrolysis

The evolved gas analysis of the pyrolysis products showed the same main organic substances for flame retarded and non-flame retarded composites, i.e, styrene and phthalic anhydride, as showed in Fig. 5.

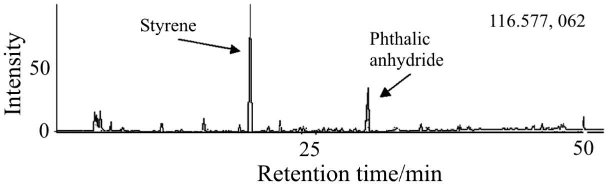

Fig. 5 Representative GC/MS spectrum for all composites

For all samples small quantitative variations in the chemical composition of the products were observed (Table 2). This indicates the potential use of pyrolysis as a promising technique for the partial recycling of thermoset composites, as it allows the reuse of the main evolved components. In the case of FR composites, the generated toxic compounds must be recovered by a separation system.

Conclusions

The flame retardant polyester/sisal composites can be enhanced by the addition of a flame retardant system based in 7.5% decabromine oxide associated antimony trioxide in 3:1 molar ratio. This is confirmed by UL-94V flammability test, where the composite containig flame retardant system obtaining the major classification (V-0).

The main evolved organic products observed as a consequence of the pyrolysis, for both flame retarded and non-flame retarded composites, were styrene and phthalic anhydride. This fact suggests the potential use of pyrolysis as a promising technique for recycling thermoset composites, as it generates molecules which may be used as raw materials.

Table 2 Degradation products obtained during pyrolysis test

Composites	Degradation products/%					
	propene	benzene	toluene	styrene	α-methyl styrene	phthalic anhydride
SR	2.35	1.00	2.35	23.21	0.94	17.43
S	1.55	1.00	1.61	37.01	1.53	18.12

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