Thermal Decomposition and Biodegradation of polyethylene-vinyl Acetate by *Zophobas atratus* larval: an economic viability study

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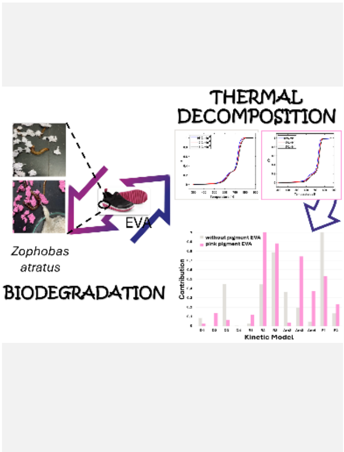


Thermal decomposition of polyethylene-vinyl acetate (EVA) generates toxic substances that directly impact the environment. Biodegradation is an alternative to minimize these implications. This study investigates the oxidative thermal decomposition process of Ethylene-Vinyl Acetate (EVA) and compares with biodegradation by *Zophobas atratus* larval. The thermal decomposition was performed using non-isothermal TG experiments and kinetic analysis by applying isoconversional method and artificial neural network to determine the kinetic triplet, which consists of activation energy, pre-exponential factor and the combination of mechanism to describe the process. The neural network results provide an adjustment in TG curves with residual error of 10^{-5} up to 10^{-8} and the R2 and F1 models as an appropriate combined mechanism to describe the thermal process for EVA without pigment and with pink pigment, respectively. The results provide information to understand and compare biodegradation and thermal decomposition processes in terms of costs and sustainability issues.

Introduction

Nowadays the environment receives a large account of plastic waste, mainly constituted by polyethylene-based polymer, especially the polyethylene-vinyl acetate (EVA) [1]. Conventional AOTs can be used to minimize this environment problem in fast reaction but generally they either uses reagents that can generate organic pollutants or only modify the surface of the polymers, as UV-ozone treatment [2]. Thermal decomposition and biodegradation are oxidative processes and can be an alternative process, without adding reagents to degrade polymers.

In this work, the kinetic of EVA thermal decomposition process was investigated together with the biodegradation process performed by Zophobas atratus larvae [3]. Additionally, economic viability was pondered to evaluate the costs of both processes.

The EVA used in this study was obtained from children's shoes industry and this work provides an innovative procedure to compare biodegradation and thermal decomposition processes, considering thermal decomposition mechanisms and biodegradation ways to promote waste reduction.

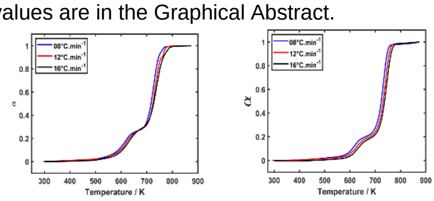
Material and Methods

The decomposition study was carried out with one sample of EVA without pigment and one sample of EVA with pink pigment, both are from children's shoes waste. The TG curves of these two samples were obtained using Shimadzu DTG60H thermobalance with heating rates of 08, 12 and 16°C.min^{-1} under a controlled atmosphere of 50ml.min^{-1} of N_2 and sample mass of about 2.0 mg, accurately measured. The non-isothermal experimental TG curves were analyzed by isoconversional method to determine the activation energy and frequency factor, and artificial neural network to determine the contribution of kinetic models that best fit the TG data [4].

The biodegradation of EVA by *Zophobas atratus* larval study was carried out by monitoring their mass over 45 days.

Results and Discussion

The non-isothermal experimental data of α(T) obtained with heating rates of 08, 12 and 16°C.min^{-1} for the two samples are presented in Figure 1. All curves were treated by the non-linear isoconversional method, and the activation energy values are in the Graphical Abstract.



(a) (b)

Figure 1. TG data for the EVA (a) without pigment and (b) with pink pigment.

TG curves indicate the thermal decomposition event occurred in two steps for both samples. The mean values of activation energy, rate constant and frequency factor, considering a global process, are presented in Table 1.

Table 1. Mean activation energy, rate constant and frequency factor of EVA samples.

Samples	Activation energy kJ.mol^{-1}	Rate constant 10^{-2} s^{-1}	Frequency factor ln (A) s^{-1}
Without pigment EVA	188.89	1.6029	31.090
Pink pigment EVA	1024.09	8.1232	172.11

For EVA without pigment, high values for activation energy (Ea) are required to start the thermal decomposition process at 10-30% of conversion, but it is observed these values decreases along the process. For EVA with pink pigment, it is necessary a high value for Ea to start the process, but interestingly, in 50% of conversion the process requires a greater amount of Ea. This value is almost 5.4 times superior to EVA without pigment.

These different values of Ea suggest the thermal decomposition process is strongly influenced by the pigment in the children's shoes. For the studied samples, it is noted that the pink pigment presented superior Ea than EVA without pigment, i.e. an additional energy must be supplied along the whole process in comparison to the EVA without pigment.

The neural network fit procedure presented residual error of 10^{-5} for EVA without pigment and 10^{-6} for EVA with pink pigment. These results were obtained assuming a combination of kinetic models, which the contributions are presented in Figure 2.

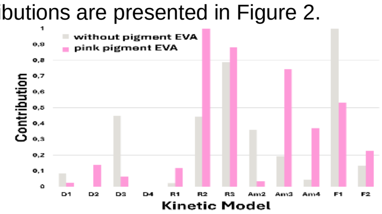


Figure 2. Normalized contribution of kinetic models.

Figure 2 shows the R2 model, area contraction, is the main mechanism to thermal decompose the EVA without pigment and the F1, first order model, is the main mechanism for EVA with pink pigment. The F1 model is related only to the homogeneity of the sample and the R2 model depends on the area contraction. The F1 model presents a superior rate constant for the process, Table 1. Although this mechanism present superior value to Ea, the frequency factor is more relevant. These results show the pigment accelerates the EVA thermal decomposition.

From the DTA curves, it was determined the heat required to thermal decompose the samples. It was noted that the total value of energy agrees with the sum of Ea determined, validating the kinetic analysis performed in this work. An economic study was carried out based on the heat required in the whole process, being 277 J.g^{-1} (during 2944 s) for EVA without pigment and 1938 J.g^{-1} (during 2905 s) for EVA with pink pigment. The costs are presented in Table 02, assuming R$1/KWh and the cost of the larvaes.

Table 2. Energy costs for thermal decomposition and biodegradation of EVA.

Samples	Energy cost R$ / kg of XPS
White EVA	0.27
Pink EVA	1.50
biodegradation	200.00

The EVA thermal decomposition on laboratory scale presents an energetic cost lower than to perform biodegradation. However, thermal decomposition process generates around 3.4 kg of CO_2 per kg of EVA, what should be considered in the global analysis. Despite biodegradation presents superior cost, it produces solid waste that can be reused in agricultural and food sectors. Comparing these methodologies with conventional OATs, thermal decomposition and biodegradation are promising processes in EVA degradation, since it does not require any organic pollutant as reagent.

Conclusions

EVA thermal decomposition is an oxidative process and its biodegradation by *Zophobas atratus* larval is a sustainable AOT because it does not produce organic pollutants. The thermal decomposition study shows that the EVA samples presented similar behavior in the TG curves and the kinetic analysis using neural network describes the process with maximum residual error of 10^{-5}. The calculated Ea showed the process requires significative amount of energy to start but decreases along the process and more energy is required to maintain the decomposition process for sample with pink pigment. The heat required for the process was determined from the simultaneous DTA/TG experiments and the Ea agrees with the heat required during the whole process, validating the kinetic study, that presents the R2 and F1 models as appropriate mechanisms to describe the thermal decomposition for EVA without pigment and with pink pigment, respectively. The biodegradation presented a higher cost than the thermal decomposition process, but sustainability is nowadays a mandatory issue.

Acknowledgments

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