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THERMAL CONVERSION KINETICS IN THE PYROLYSIS OF POLYETHYLENE/ALUMINUM FROM VACUUM PACKAGING WASTE
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Abstract. *The industrial production of fuels from organic sources can follow different thermal routes. Among them, pyrolysis could be a viable route to reduce environmental impacts due to polymer discharges. However, the wide polymeric variety and the presence of addition elements and fillers pose challenges to process control. This work studied the effects of thermal parameters on the pyrolysis of polyethylene/aluminum metallic (PE/Al) from vacuum packaging waste. Kinetic parameters were evaluated as a function of the heating rate between 10 and 40 °C/min until 750 °C. An isoconversional kinetic model was applied to the results of Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). The PE/Al pyrolysis product showed only the inert material while the organic material was volatile (about 92.5% of the initial mass), fraction intended for energy purposes. The activation energies of the different samples were determined by the isoconversional method with Starink's simplification: (153.8±13.3) and (76.8±3.6) kJ/mo[1] for PE and PE/Al, respectively. The reduction in the activation energy value demonstrated the catalytic influence of the presence of metallic aluminum in the pyrolysis of this class of materials.*

Keywords: *polyethylene, pyrolysis system, thermal degradation, activation energy*

1. INTRODUCTION

The processes of obtaining thermal or electric energy through conventional sources, such as oil, natural gas and coal, cause great environmental impacts, which combined with exploration and economic problems, encourage the search for alternative forms of energy. Therefore, to reduce harmful emissions and overcome the problem of energy scarcity, the search for new resources, renewable or sustainable, has become fundamental (Jayaraman *et al.*, 2018).

Among the different thermochemical treatments used for this purpose, the following stand out: combustion, hydrogenation, gasification and pyrolysis, the latter receiving the most attention from researchers (Zhang *at al.*, 2017; Baetge and Kaltschmitt, 2018; Darmawan *et al.*, 2018; Karaca *et al.*, 2018). This is due to the operational and environmental advantages, according to Al-Salem *et al*. (2017), it provides and for being a flexible process, as its process parameters can be manipulated to optimize the product's performance based on preferences.

Pyrolysis is a chemical transformation process of materials induced by the contribution of thermal energy to a heated compound to moderate temperatures (400 to 700 ° C), in an atmosphere with partial or total absence of an oxidizing agent, with the possibility of using catalytic agents or not (Santos *at al.*, 2012; Sogancioglu *et al*., 2017). The result of this process is to obtain products that have important destinations for engineering. According to Bridgwater (2012), an example is the case of condensed fraction used in boilers, turbines, and diesel engines. Pyrolysis is often applied in polymers cracking, which has been studied by several authors (Adrados *et al*., 2012; Wong *et al.*, 2015; Miandad *et al*., 2016; Kunwar *et al*., 2016; Sharuddin *et al*., 2017; Ratnasari *et al*., 2017).

The intention of many researchers is to use pyrolysis in polymers to convert them into liquid fuel to reduce the consumption of fossil fuel, since the energy sources constituted by polymeric residues have similar properties to fossil fuels. According to Kunwar *et al.* (2016) this is since they have hydrocarbons from the same source as the oil fraction. Unlike sources provided from biomass, the absence of oxygen and the higher content of carbon and hydrogen in fuels of

polymeric origin avoid the need for further treatment and result in a non-acidic and non-corrosive fuel. Besides the absence of water in these fuels presents high calorific value (Lago *et al*., 2017).

However, the conversion of fuels by pyrolysis of products with the presence of additives or fillers has become a challenge, according to Yang *et al*. (2012), as they present different thermochemical behaviors inherent to its constituents. The food industry is one of the sectors that use this material composition technique, through its long-life packaging and vacuum packaging. These structural composites are made from the combination of polymeric films and metallic aluminum, junction that is the object of studies that seek the maximum reuse, to obtain products that can return the investment of its materials and reduce the extraction of raw materials to preserve resources and reduce environmental impact.

To analyze the quality of the products generated by the pyrolysis, the thermal parameters of the process are fundamental for the compression of the relationship of these parameters with the kinetics of thermal degradation (White *et al*., 2011; Miranda, 2011; Alvarenga, 2012; Ansah *et al*., 2016; Zhu *et al*., 2017; Siddiqui *et al*., 2018; Majoni and Chaparadza, 2018). The kinetics of thermal conversion of polymers is of great importance in obtaining information about the mechanism of chemical reactions. The measure of the speed with which the reactions occur indicates the possible chemical and physical transformations of the system as a function of time, according to Alvarenga (2012). The kinetics of pyrolysis can be studied by means of thermal analyzes in conjunction with a kinetic model that considers that for each break in the chemical bond, a certain amount of energy is required.

Based on statistical analysis and highly significant correlation coefficients, the kinetic modeling by means of isoconversional reactions is adequate to estimate the kinetic parameters of the thermal conversion of polymers (Alvarenga, 2016; Vidal, 2017). In the isoconversional reactions model, it is possible to estimate the activation energy by measuring it through the temperature change that occurs due to the change in the heating rate without the need to know the decomposition route or the reactions' order (Santos *et al*., 2012; White *et al*., 2011; Alvarenga, 2016; Xavier, 2016).

Considering what has been exposed, the present work studies the thermal transformation by pyrolysis of composite material of polyethylene / aluminum (PE/Al) from vacuum packaging waste under different thermal conditions. The main objective of the study is to analyze the kinetic parameters of the process in this class of materials. The research represents a deepening in the kinetic studies associated with the thermal degradation of polymers and multilayer composite materials. For this purpose, a system of simultaneous thermal analysis: Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) and isoconversional reaction models will be used to determine the thermal behavior of the isolated polyethylene and the composite in its integral form. Thus, it is possible to analyze the quantitative influence of metallic aluminum on the activation energy in the polymeric degradation.

2. MATERIALS AND METHODS

2.1 Sample Material

Among the varieties of plastic waste often discarded in the urban environment, which for the purpose of this work show energetic and economic potential, it was opted for the compounds made of metallic aluminum layers in polymeric film, free of mineral charges and contaminating phases. We also sought a material that was composed of polyethylene, because it is a single chain hydrocarbon, facilitating the analysis and because it is the most widely used synthetic plastic in the world (Ungvarsky, 2019). Thus, the exemplar of this class of material is the vacuum packaging.

For each stage of the experiments, this material went through different chemical procedures. For the first stage of experiments, the polyethylene layer was isolated, completely removing all other layers with a solution of sodium hydroxide (NaOH) with a concentration of 97% and distilled water in a proportion of 20 g/mL, often agitated. However, in previous studies carried out in the laboratory, it was identified the possible presence of a thin layer of polyamide between polyethylene/aluminum. Therefore, to eliminate polyamide residues, Formic Acid PP.A. (CH_2O_2) was used with a concentration of 85% for 8 hours. Figure 1 illustrates the sample of vacuum packaging after these chemical treatments.

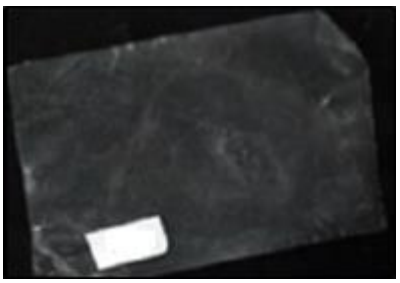


Figure 1**.** Sample of the isolated polymeric layer from vacuum packaging, after being exposed to separation chemical treatments.

For the second stage of testing, with the polyethylene/metallic aluminum composite, only the paint layer was removed from the packaging so that it did not influence the result. For this, Acetone PP.A. (CH3)2CO with a concentration of 99.5% was used. To complete all the processes, alcohol was used to remove traces of chemicals on the sample surface.

2.2 Sample Characterization

2.2.1 Composition of polymeric sample

To confirm the expected composition of the vacuum packaging sample, it was evaluated using FTIR on a Shimadzu IR Spectrometer. Spectra were recorded in the region of 4000 to 400 cm^{-1}, using a resolution of 4 cm^{-1} and a minimum number of scans of 32 spectra. The results of these analyzes were compared with standard spectra of polymeric materials found in the literature. The composition was identified from the comparison of bands.

2.2.2 Fusion temperature

The vacuum packaging sample was analyzed by DSC as for the fusion of the existing polymeric phases. The test was carried out on the equipment model DSC-60, of the Shimadzu brand, in which the sample was heated from room temperature to 250 °C and cooled to 30 °C, using the rate of 10 °C/min for both processes. This procedure was performed in 3 cycles. A mass of approximately 8 mg (± 0.1 mg) was used, duly verified with the aid of the high precision scale model AUW220D of the Shimadzu brand, in an aluminum crucible and nitrogen atmosphere.

2.2.3 Pyrolysis behavior study

The thermal analysis was successful in two moments: without the presence of metallic aluminum and later polymer/aluminum. The procedure was performed in triplicate. The kinetic profile was determined with the isolated polymeric film exposed to a schedule of 10, 20 and 40 °C/min until reaching 750 °C, under argon flow at a rate of 20 mL/min.

The tests were carried out in a thermogravimetric analyzer coupled to differential exploratory calorimetry (TG-DSC) by heat flow model LABSYS evo, from the brand Setaram. The thermal tests were performed with a mass of approximately 20 mg (± 0.1 mg) of sample, duly verified with the aid of the high precision scale model AUW220D, of the Shimadzu brand. The reference and sample crucibles were composed of alumina and were kept open during the experiments. For each test performed, a blank experiment was executed with the empty crucibles to act as a baseline, to cancel any influence of the equipment.

To understand the possible catalytic action of aluminum during PE pyrolysis and to obtain technological responses for thermal conversion of residues in the form of multilayers, the samples of the PE/Al composite were subjected to the same pyrolysis conditions.

2.2.4 Isoconversional Kinect Model

The entire equation described below was based on research already carried out on the cracking kinetics of polymers, with the necessary adaptations (White *et al.*, 2011; Miranda, 2011; Siddiqui *et al.*, 2018; Majoni and Chaparadza, 2018; Alvarenga, 2016; Vidal, 2017). The isoconversional model characterizes the reaction kinetics based on the principle that the speed of the conversion reaction is exclusively a function of temperature. Thus, the thermal decomposition rate ($d\alpha/dt$) can be described as a function of two parameters, see Eq. (1):

$$\{d\alpha/dt\} = \{K(T)\}\{f(\alpha)\}, \quad (1)$$

where α is the decomposition rate, $f(\alpha)$ is the reaction model and $K(T)$ is the temperature dependent kinetic constant. The decomposition rate of the reaction (α) can be determined from sections of TG, such as fractional mass loss, according to Eq. (2):

$$\{\alpha\} = \{m_0 - m\} / \{m_0 - m_f\}, \quad (2)$$

where m is the mass at each time monitored, m_0 and m_f represent the initial and final mass of the sample, respectively.

The Eq. (1) can be translated following the expression of Arrhenius in Eq. (3):

$$\{d\alpha/dt\} = \{K_0\}\{e^{(-E_a/RT)}\}\{f(\alpha)\}, \quad (3)$$

with K_0 being the pre-exponential factor, Ea the activation energy, R the universal gas constant and T the temperature.

Under dynamic conditions, thermal conversion occurs with a linear increase in temperature ($T = T0 + \beta t$), with a heating rate (β) given by Eq. (4) where the temperature varies with time:

$$\{\beta\} = \{dT/dt\}, \quad (4)$$

Thus, rearranging Eq. (2) and using Eq.(4), we obtain the expression of decomposition rate, represented by Eq.(5):

$$\{d\alpha/f(\alpha)\} = \{k_0/\beta\}\{e^{(-E_a/RT)}\}\{dT\}, \quad (5)$$

The function $f(\alpha)$ depends on the amount of solid and the temperature, separately. Integrating Equation (5), from the conditions: initial temperature (T_0) corresponding to the zero conversion until the inflection temperature (T), coinciding with the conversion (α), there is the function of the conversion rate, expressed by Eq. (6):

$$\{g(\alpha)\} = \{integrate(0 \rightarrow \alpha)\}\{d\alpha/f(\alpha)\} = \{k_0/\beta\}\{integrate(T \rightarrow T0)\}\{e^{(-E_a/RT)}\}\{dT\}, \quad (6)$$

There is a possibility to simplify the form of the function $f(\alpha)$ if the reaction follows first order kinetics ($n = 1$). Therefore, $f(\alpha) = (1 - \alpha)\, n$, where $(1 - \alpha)$ corresponds to the remaining fraction of volatile material in the sample.

There is a divergence as to the method of approximating the integration of Eq. (6) with equations developed by different authors (Kissinger, 1956; Ozawa, 1965; Akahira and Sunuse, 1971; Starink, 1996). Among the elaborated simplification options, it has been demonstrated, in the literature, that the Starink's method has greater precision, as it is an adaptation of the previous ones and reproduces the activation energy with minimal variations in the reactions [25,26,32]. Thus, Starink's simplification for Eq. (6) was applied, generating Eq. (7):

$$\{\ln(\beta/T^{1,8})\} = \{-1{,}007 - 1{,}2\times10^{-5} Ea\}\{Ea/RT\}, \quad (7)$$

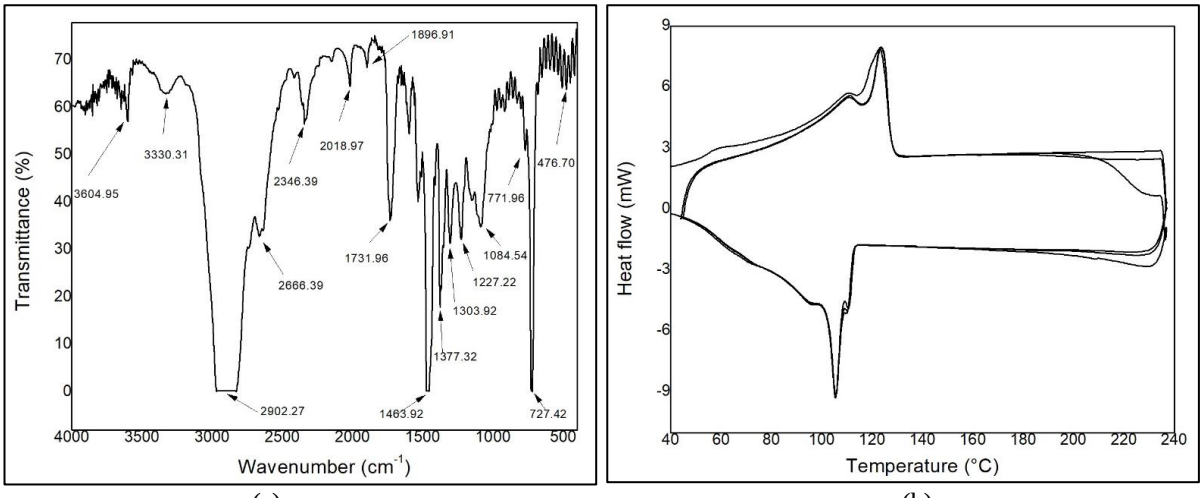
with β representing the heating rate, T temperature, Ea activation energy and R the universal the universal gas constant.

To establish a possible catalytic effect of aluminum on PE in pyrolysis, the activation energies of the polymeric film and the polymer/aluminum film were calculated separately as a function of the transformation temperature.

3. RESULTS AND DISCUSSION

3.1 Sample characterization by FTIR and DSC

After the vacuum packaging sample went through chemical treatments, the material was analyzed by infrared (FTIR) to check the chemical composition, using the generated spectrogram, shown in Figure 2 (a). The band in the spectrogram was found in the range of 2900 cm^{-1} referring to the linear bonding of primary and secondary aliphatic carbon and hydrogen, close to 1460 cm^{-1} for the angular deformations of methylene groups and around 720 cm^{-1}, which represents the repetition of the carbon-hydrogen bond. These bands and the spectrogram configuration are characteristic of polyethylene. Furthermore, it can be stated that polyamide was no longer present together with polyethylene because it was not observed the bands at 3500 and 1690 cm^{-1} referring to ketone's carbonyls (Paiva, 2010).



(a) (b)

Figure 2. (a) Spectrogram of the polymeric layer isolated from the vacuum packaging and (b) Heat flow curve of the polymer layer heating and cooling cycle.

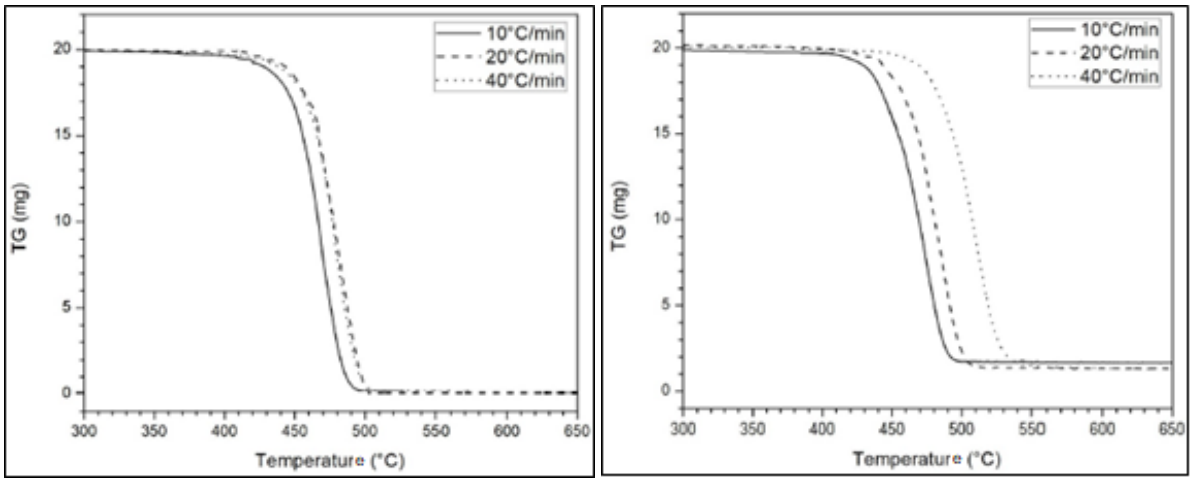
To collaborate with the FTIR analysis, a complementary DSC analysis was performed to better understand the existence of phases and to verify whether the polymer sample still had contaminants. The curve generated in the DSC, seen in Figure 2 (b), did not show any different type of polymer, confirming it to be low density polyethylene and reaffirming the information obtained in the FTIR technique performed previously. This is because there are no peaks of fusion of the PA in the range of 220 to 250 °C. The peaks at 110.8 and 123.5 °C can be associated with low density polyethylene and low linear density polyethylene, respectively. These values are consistent with the literature (Canevarolo, 2002; Canevarolo, 2007; Menczel and Prime, 2008).

As there was no significant presence of other polymers, which could generate specific reactions in pyrolysis, the work proceeded with the kinetic analysis of thermal conversion, considering the polymeric sample without aluminum as a homogeneous material with saturated chains typical of polyethylene.

3.2 Kinects of thermal conversion in PE pyrolysis

3.2.1 Mass analysis

From the experimental result of Thermogravimetry (TG), information was obtained on the mass variation of the PE and the PE/Al composite as a function of temperature, while subjected to heating rates of 10, 20 and 40 °C/min. Figure 4 shows the curves for the samples loss of mass as a function of the heating rate.



(a) (b)

Figure 4. Loss of mass of (a) PE and (b) PE/Al as a function of the heating rate.

It was found that the mass conversion occurred only in one stage of volatilization, both for the polymeric sample and for the composite. When evaluating the final pyrolysis mass, carbonaceous residues were not observed for the PE sample, as shown in Figure 4 (a), indicating that the polymer conversion occurred in its totality. However, for the PE/Al sample, there was a portion of residues in Figure 4 (b), which represents the fraction of aluminum in the composite. Calculating the ratio between the final mass of the two samples, it was determined that the aluminum mass was 7.5%.

The curves referring to the mass loss rate (dTG) as a function of the heating rate are shown in Figure 5 and some important temperatures of this behavior are presented in Table 2. For both samples, the thermal conversion started at temperatures higher than 290 °C with little loss of mass until reaching 370 °C. Above 400 °C the thermal degradation was intense with significant mass loss. This value is in accordance with the temperature ranges present in the literature on the thermal degradation of polyethylene (Alvarenga, 2016; Sinfrônio, 2005).

Table2. Temperatures of mass loss as a function of heating rate.

Sample	Heating rate [°C/min]	Initial temperature [°C]	Maximum mass loss temperature [°C]	Final temperature [°C]
PE	10	396.7 ± 15.3	478,1 ± 0,9	493.3 ± 20.8
	20	399.7 ± 5.8	486,3 ± 2,0	526.7 ± 5.8
	40	406.7 ± 5.8	500,8 ± 7,7	546.7 ± 3.3
PE/Al	10	393.3 ± 5.0	476.2 ± 0.9	509.7 ± 3.5
	20	403.6 ± 10.7	486.8 ± 1.7	534.2 ± 1.,5
	40	418.8 ± 9.0	507.9 ± 0.6	557.4 ± 9.2

As detailed in Table 2, there is an increase in the transformation temperatures as the heating rate increases. The values found for the maximum thermal conversion of the polymer were in line with the literature (Alvarenga, 2016; Menczel and Prime, 2008; Sinfrônio, 2005; Saha *et al*., 2008).

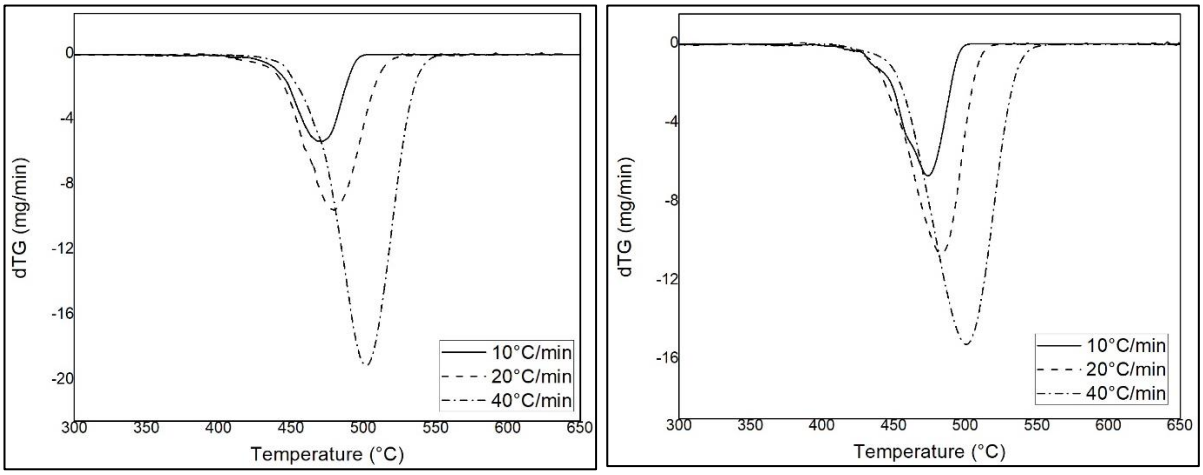


Figure 5. Mass loss rate of (a) PE and (b) PE/Al as a function of the heating rate.

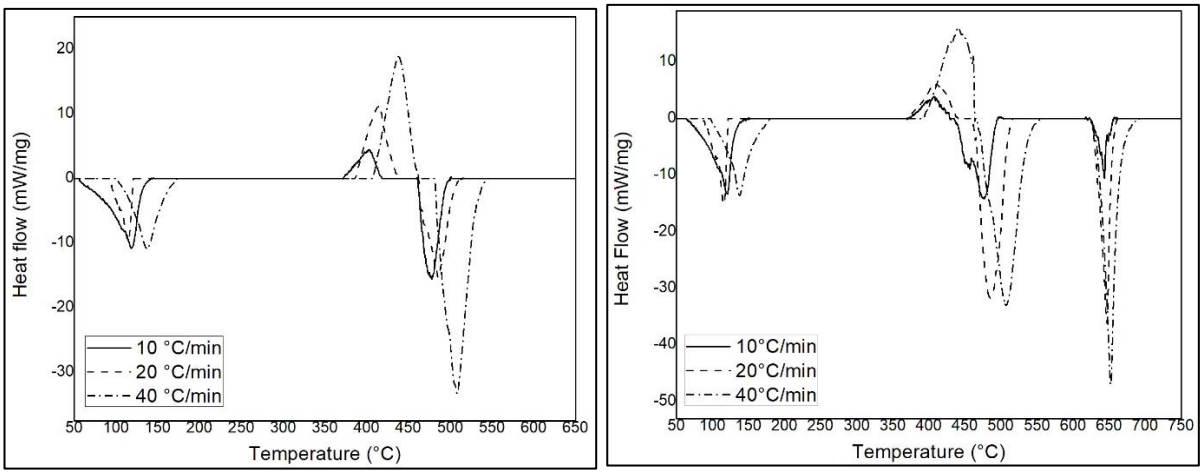
3.2.2 Calorimetric analysis

The Figure 6 shows the energy curves resulting from the conversion of samples as a function of temperature, at rates of 10, 20 and 40 °C/min. By convention, peaks in the positive energy value represent exothermic events and with negative value, endothermic events. The data reaffirm the DSC results previously obtained at low temperatures, in which the presence of polyamide was not observed. Note that even in the PE/Al sample, in Figure 6 (b), it is not possible to detect the presence of another polymer.

The thermal delay, mentioned in the previous analysis of TG, is also observed in the samples with the change in the heating rate. The striking difference in the number of thermal events between the PE sample and the PE/Al, in Figure 6, are the endothermic peaks close to the range of (644.5 ± 1.2), (642.6 ± 6.6) and (654.8 ± 2.4) °C for heating rates of 10, 20 and 40 °C/min, respectively. These temperature values are in accordance with the melting temperature of aluminum, a well-known value in the literature.

The first endothermic event for the PE occurred in the temperature range of (118.7 ± 0.9), (119.3 ± 0.5) and (124.6 ± 3.2) °C and for PE/Al in the range of (119.2 ± 1.1), (117.1 ± 2.3) and (138.2 ± 1.2) °C at heating rates of 10, 20 and 40 °C/min, respectively. These temperature values are consistent with the melting point of the polyethylene (Canevarolo, 2007; Menczel and Prime, 2008). In this range, according to Menczel and Prime (2008), the first order phase transition occurred, in which the crystalline state of the polyethylene changed to the molten state, generating an increase in the disorder of the system accompanied by an increase in entropy. After passing through the PE melting point, the energy gradually increases with the increase of temperature to a maximum, which marks the beginning of the material's mass conversion. This is due to the exothermic event in the temperature range of (401.6 ± 1.2), (414.0 ± 3.0) and (426.0 ± 10.4) °C for PE and in the range of (408.5 ± 2.4), (419.5 ± 7.6) and (443.5 ± 1.9) °C for PE/Al at heating rates of 10, 20 and 40 °C/min, respectively. In this stage, covalent bonds split, and the production of a stable molecule occurs, which caused the release of energy (Canevarolo, 2007; Menczel and Prime, 2008).

Then there was another endothermic event in the temperature range of (478.1 ± 0.9), (486.3 ± 2.0) and (500.8 ± 7.7) °C for PE and in the range of (476.2 ± 0.9), (486.8 ± 1.7) and (507.9 ± 0.6) °C for PE/Al at heating rates of 10, 20 and 40 °C/min, respectively. At this point, the thermal conversion of the polymer chains into the gas fraction began, significantly losing mass. This temperature range is in accordance with the literature and with the analysis of TG, in which the maximum loss of mass of the samples occurs (Canevarolo, 2002; Menczel and Prime, 2008; Sinfrônio, 2005). Furthermore, it was observed that the increase in the heating rate caused an increase in the energy variation with the temperature. This quantitative increase in thermal conversion energy can be seen in Table 3, demonstrating the energy difference in thermal events.



(a) (b)

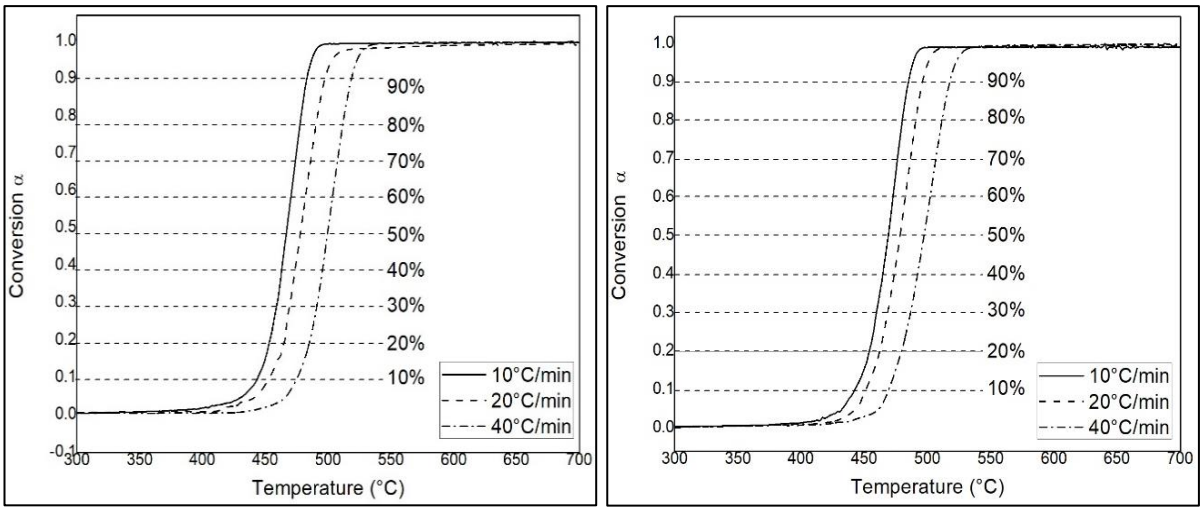
Figure 6. Transformation energy curve of (a) PE and (b) PE/Al as a function of the heating rate.

Table3. Transformation energies as a function of the heating rate.

Sample	Heating rate [°C/min]	Fusion energy [mJ/mg]	Thermal degradation energy [mJ.mg-1]	
			Exothermic	Endothermic
PE	10	322.9 ± 16.7	131.2 ± 14.0	633.1 ± 11.1
	20	345.6 ± 10.0	286.5 ± 11.3	792.2 ± 22.7
	40	377.5 ± 20.0	548.9 ± 9.6	986.0 ± 14.0
PE/Al	10	354.2 ± 41.9	155.6 ± 25.5	908.5 ± 23.7
	20	391.6 ± 29.5	237.0 ± 19.0	1135.5 ± 38.3
	40	415.7 ± 13.1	543.6 ± 10.6	1291.0 ± 21.3

3.2.3 Activation energy of PE and PE/Al samples

To find the value of the activation energy required in the transformation of the samples, the behavior of the material's conversion rate as a function of temperature, shown in Figure 7, was analyzed.



(a) (b)

Figure 7. Conversion rate as a function of the temperature of (a) PE (b) PE/Al.

From this conversion rate, the conversion temperature values from 10 to 90% were extracted, depending on the heating rate. Then, these temperature values were plotted on a graph with their axes defined by the Starink's equation, exposed by Eq. (10). The linearization graphs of the conversion of the PE and PE/Al sample, with the respective values and identifications, can be seen in Figure 8.

In both the PE and PE/Al samples, the lines obtained in the linear adjustment significantly showed parallelism, in the range of 20 to 90%, which denotes a similar kinetic behavior. In this way, it can be said that the reaction mechanism in

this conversion interval occurs equally. However, it can be observed that the 10% line was not parallel, indicating change in the reaction mechanism at lower temperatures.

The linear regression angular coefficient, shown in Figure 8, was used to calculate the activation energy using the isoconversional method. For each line, an activation energy was found, so the average was performed. These data are shown in Table 5.

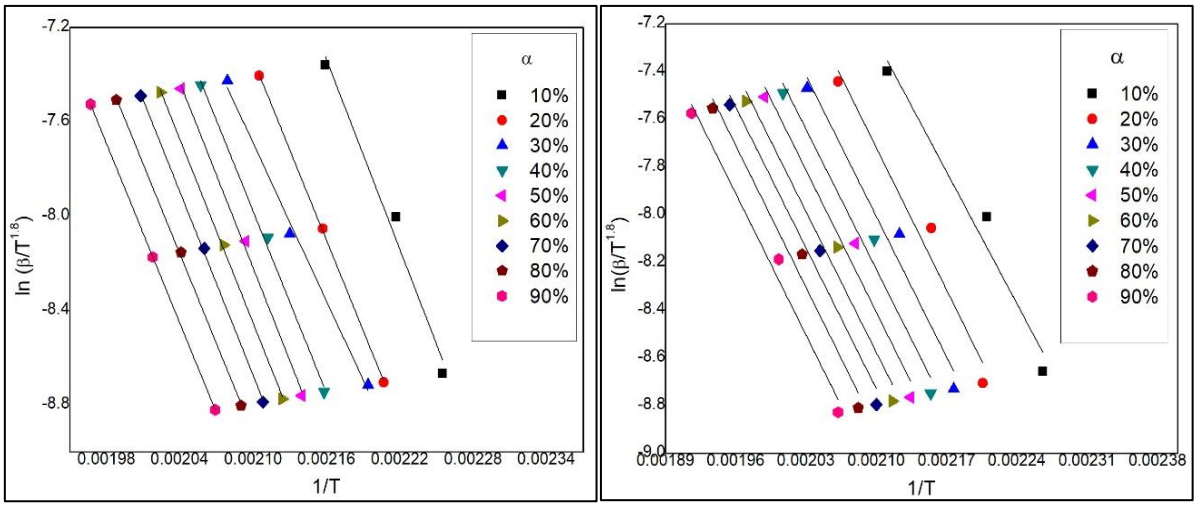


Figure 8. Linear regression of the conversion rate of (a) PE and (b) PE/Al as a function of the heating rate and temperature by the Starink's equation.

Table5. Activation energy as a function of the conversion rate.

Sample	Conversion rate [%]	Slope	Activation energy [kJ/mol]	Determination coefficient
PE	0.1	21.64	178.58	0.96
	0.2	19.44	160.42	0.99
	0.3	15.74	129.89	0.99
	0.4	18.98	156.63	0.99
	0.5	19.32	159.43	0.99
	0.6	18.82	155.31	0.99
	0.7	18.59	153.41	0.99
	0.8	17.75	146.48	0.99
	0.9	17.45	144.00	0.99
Average			153.80	
Standard deviation			13.33	
PE/Al	0.1	9,31	76.82	0,94
	0.2	10,16	83.84	0,93
	0.3	9,69	79.96	0,95
	0.4	9,37	77.32	0,95
	0.5	9,45	77.98	0,95
	0.6	9,11	75.18	0,96
	0.7	8,99	74.19	0,96
	0.8	8,95	73.86	0,96
	0.9	8,70	71.79	0,97
Average			76,77	
Standard deviation			3,61	

There was a great correlation, greater than 0.93 of the values for the activation energy as a function of the conversion rate in pyrolysis. Thus, the mean values of activation energy obtained by the isoconversional method and by the Starink's equation were (153.8 ± 13.3) and (76.8 ± 3.6) kJ/mol for polyethylene and polyethylene/aluminum, respectively. The polyethylene activation energy value approached the value presented in the literature (Alvarenga, 2016). As a result of this difference of values, it can be observed that there was a clear influence by the presence of aluminum in reducing the

activation energy in the thermodynamic conditions used in pyrolysis. Thus, it is concluded that, in the present work, there was a catalytic influence by the presence of aluminum in polymeric pyrolysis.

4. CONCLUSION

This work evaluated the thermal transformation by pyrolysis of a polyethylene/aluminum (PE/Al) composite under heating rates of 10, 20 and 40 °C/min to obtain the thermal degradation kinetic parameters of this category of materials. Initially it was identified that the vacuum packaging was suitable for the development of this research because it is composed of layers of polyethylene and metallic aluminum.

Through Thermogravimetry it was possible to determine that the mass conversion occurred in a single stage of volatilization for both samples. With the increase in the heating rate, the maximum thermal decomposition started to occur at higher temperatures. It was also observed that with the increase in the heating rate, the conversion speed increased.

The thermal conversion peaks of the material were defined by the Differential Scanning Calorimetry. For both PE and PE/Al samples, the same endothermic and exothermic peaks were observed, except for the PE/Al sample, in which an endothermic peak was observed regarding the aluminum melting close to 650 °C. There was no significant difference in the temperature ranges in which the physical-chemical transformations occurred for the PE and PE/Al samples. The transformation started at 396.7 to 406.7 °C for the PE sample and at 393.3 to 418.8 for the PE/Al sample. The melting temperatures of polyethylene ranged from 118.7 to 124.6 °C and from 117.1 to 138.2 °C for the PE and PE/Al samples, respectively.

In both samples, an exothermic peak was observed that marks the random split of covalent bonds and the origin of new chains resulting in the release of energy. The thermal event peaked at 401.6 to 426.0 °C for the PE sample and 408.5 to 443.5 °C for the PE/Al sample. In sequence, another endothermic peak was observed, showing the polymer thermal conversion into the gas fraction with significant loss of mass. The process peaked at 478.1 at 500.8 °C for the PE sample, while for the PE/Al sample it occurred at 476.2 to 507.9 °C. It was possible to observe that the increase in the heating rate caused an increase in the variation of total conversion energy with temperature. There was also an increase in the conversion rate with an increase in the heating rate. When applying these pyrolysis conditions to PE/Al, the organic material that became gaseous (92.5% of the initial mass) while only aluminum remained as a solid fraction. In a thermal conversion limit situation of these technological materials, this work suggests a processing temperature of 550 °C for a heating rate of up to 40 °C/min in an inert atmosphere.

Using the Starink's isoconversional method, the estimated activation energy in the pyrolysis of the PE and PE/AL sample was (153.8 ± 13.3) and (76.7 ± 3.6) kJ/mol, respectively. It was possible to observe that there was a clear influence by the presence of aluminum in reducing the activation energy in the thermodynamic conditions used in pyrolysis. Therefore, it is concluded that in the present work there was a catalytic influence by the presence of aluminum in pyrolysis.

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