A new dynamic model of thermal degradation of polymer binary mixes submitted through pyrolysis

Un nuevo modelo dinámico de degradación térmica de mezclas binarias de polímeros sometidas a través de pirólisis

Um novo modelo dinâmico de degradação térmica de misturas binárias de polímero submetido através da pirólise

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Abstract

Introduction: This article is the product of the review "A new dynamic model of thermal degradation of polymer binary mixes submitted through pyrolysis", developed in the University Pedagógica y Tecnológica de Colombia – UPTC-, carried out during 2020. This paper shows the validation process of a dynamic model proposed to represent the one-step thermal degradation reaction of individual components in polymer mixtures.

Problem: It is complicated to model the process of thermal degradation of polymer mixtures inside pyrolysis reactors. Inside the MPW reactor, the distribution of polymeric components in the mixture is shuffled.

Objective: The objective is to validate a proposed dynamic model to represent the thermal degradation of binary polymer mixtures from the thermograms of each individual component.

Methodology: A comparison is made between real data provided by TGA of binary mixes of plastic and the result of simulated thermal degradation obtained using a differential equation of the model for thermal degradation of the same plastics.

Results: The simulation results showed a reasonable degree of approximation with a mean square error of less than 5%.

Conclusion: The results of the simulation provide a good approximation of the loss of mass of the real samples submitted to TGA tests in the entire temperature range of the process. Consequently, it is not necessary to segment the process into sub-ranges to look for parameters in each of them.

Originality: The differential equation proposed as a dynamic model for the thermal degradation of a single polymer is extended to also represent the degradation of a mixture composed of two types of plastic for the first time in this paper.

Limitations: The number of samples allowed for thermogravimetric analysis was limited to five due to the institutional regulations of the UPTC for research projects attached to doctoral theses.

Keywords: polymer thermal degradation, thermogravimetric analysis, dynamic model, polymer pyrolysis simulation.

Resumen

Introducción: Este artículo es producto de la revisión "Un nuevo modelo dinámico de degradación térmica de mezclas binarias de polímeros sometidas a pirólisis", desarrollada en la Universidad Pedagógica y Tecnológica de Colombia - UPTC-, realizada durante 2020. Este artículo muestra la validación proceso de un modelo dinámico propuesto para representar la reacción de degradación térmica en un solo paso de componentes individuales en mezclas de polímeros.

Problema: Es complicado modelar el proceso de degradación térmica de mezclas de polímeros dentro de los reactores de pirólisis. Dentro del reactor MPW, se baraja la distribución de componentes poliméricos en la mezcla.

Objetivo: El objetivo es validar un modelo dinámico propuesto para representar la degradación térmica de mezclas de polímeros binarios a partir de los termogramas de cada componente individual.

Metodología: Se realiza una comparación entre los datos reales proporcionados por TGA de mezclas binarias de plástico y el resultado de la degradación térmica simulada obtenido mediante una ecuación diferencial del modelo de degradación térmica de los mismos plásticos.

Resultados: Los resultados de la simulación mostraron un grado razonable de aproximación con un error cuadrático medio menor al 5%.

Conclusión: Los resultados de la simulación proporcionan una buena aproximación de la pérdida de masa de las muestras reales sometidas a pruebas TGA en todo el rango de temperatura del proceso. En consecuencia, no es necesario segmentar el proceso en subrangos para buscar parámetros en cada uno de ellos.

Originalidad: La ecuación diferencial propuesta como modelo dinámico para la degradación térmica de un solo polímero se amplía para representar también la degradación de una mezcla compuesta por dos tipos de plástico por primera vez en este trabajo.

Limitaciones: El número de muestras permitidas para análisis termogravimétrico se limitó a cinco debido a la normativa institucional de la UPTC para proyectos de investigación adjuntos a tesis doctorales.

Palabras clave: degradación térmica de polímeros, análisis termogravimétrico, modelo dinámico, simulación de pirólisis de polímeros.

Resumo

Introdução: Este artigo é o produto da revisão “Um novo modelo dinâmico de degradação térmica de misturas binárias de polímeros submetidas por pirólise”, desenvolvido na Universidade Pedagógica y Tecnológica de Colombia - UPTC-, realizada em 2020. Este artigo mostra a validação Processo de um modelo dinâmico proposto para representar a reação de degradação térmica em uma etapa de componentes individuais em misturas poliméricas.

Problema: É complicado modelar o processo de degradação térmica de misturas de polímeros dentro de reatores de pirólise. Dentro do reator MPW, a distribuição dos componentes poliméricos na mistura é embaralhada.

Objetivo: O objetivo é validar um modelo dinâmico proposto para representar a degradação térmica de misturas poliméricas binárias a partir dos termogramas de cada componente individual.

Metodologia: É feita uma comparação entre os dados reais fornecidos pela TGA de misturas binárias de plásticos e o resultado da degradação térmica simulada obtida por meio de uma equação diferencial do modelo de degradação térmica dos mesmos plásticos.

Resultados: Os resultados da simulação mostraram um razoável grau de aproximação com um erro quadrático médio inferior a 5%.

Conclusão: Os resultados da simulação fornecem uma boa aproximação da perda de massa das amostras reais submetidas aos testes de TGA em toda a faixa de temperatura do processo. Conseqüentemente, não é necessário segmentar o processo em subfaixas para procurar parâmetros em cada uma delas.

Originalidade: A equação diferencial proposta como modelo dinâmico para a degradação térmica de um único polímero é estendida para representar também a degradação de uma mistura composta por dois tipos de plástico pela primeira vez neste trabalho.

Limitações: O número de amostras permitidas para análise termogravimétrica foi limitado a cinco devido às normas institucionais da UPTC para projetos de pesquisa vinculados a teses de doutorado.

Palavras-chave: degradação térmica de polímero, análise termogravimétrica, modelo dinâmico, simulação de pirólise de polímero.

1. Introduction

Municipal plastic waste (MPW) is becoming an environmental concern due to its fast accumulation in landfills and dumps [1], [2]. Artificial polymers derived from petroleum have many applications in modern life: from packaging and wraps to protect food to primary material in the manufacturing of equipment and structures [3, p. 39-41].

MPW is increasing at a higher speed than can be reintegrated into the biological cycle, and several alternatives have been contemplated; from the use of biological agents that contribute to polymer decomposition, to their substitution for biodegradable and environmentally friendly alternatives [4]. Packages, wraps and containers are discarded on a daily or weekly basis, but they can take centuries to reintegrate back into the environment. The main reason is that polymers derived from oil do not react chemically with the substances in soil and landfills.

1.1. Investigation Background

Plastic pyrolysis is the chemical decomposition of macromolecules due to a rise in temperature in a partially or totally oxygen-starved environment [5, p. 15, 140, 144, 157, 323]. Pyrolysis is an alternative means of treating waste that is not suitable for primary recycling. In this process, polymer chains are decomposed into another with smaller molecular weight. The resulting hydrocarbons can be reused as direct substitutes for fossil fuels or after they are submitted to some refining process [6]–[12].

A MPW reactor is a container in which plastic material is degraded through heating from a heat source [8], [10], [11], [13]. At an industrial level, it is used as raw material, a mix of various plastics in fluidized bed reactors [14], [15, p. 2601-2609]. It is disposed of via a procedure to reduce polluting substances of the process and to improve the quality of the derived products.

The thermogravimetric analysis (TGA) or thermogravimetry is a technique in which the loss of mass of a plastic sample submitted to a regulated temperature program is studied [16], [17]. That analysis is made in a thermobalance that contains technology and instrumentation to register the behavior of the residual mass as a function of the temperature. The result is shown through a thermogram, which is a plot where the process behavior can be interpreted. TGA can provide a complete and reliable register of the loss of mass and phase changes thanks to the precise instrumentation used and the uniform heat transfer as the result of a sufficiently small sample size.

The raw material that is submitted to pyrolysis in an industrial-scale reactor is a heterogeneous mixture of several plastics with a random distribution of the different components [16], [18]–[22]. It is complicated modeling a stochastic process, far from the deterministic nature of the TGA. Inside the MPW reactor, the distribution of polymeric components in the mixture is shuffled. High-temperature gradients occur and it is difficult to achieve a uniform heat transfer. All these factors always make it complicated to predict where in the process and within the material inside reactor that the degradation reactions occur and the specific presence of hydrocarbon of interest can be found.

The focus of this work is to validate a dynamic model proposed to represent thermal degradation. A comparison is made between real data provided by TGA of binary mixes of plastic and the result of simulated thermal degradation obtained using a differential equation of the model for thermal degradation of the same plastics. A dynamic model for a specific plastic was developed in [23], and this paper is a continuation extended for a binary mix. The polymer used in this study was Expanded Polystyrene (EPS) and Low-Density Polyethylene (LDPE). These specific plastics were chosen based upon an empirical test of the residues found in the trash of the largest cafeterias inside the UPTC. Matlab Simulink ® was used to simulate the degradation process. This paper is one of the products of an investigation project whose aim is to control the pyrolysis process of MPW. This stage corresponds to the modeling and simulation of the thermal degradation of the plastic mixture.

2. Materials and methods

2.1. Theoretical Analysis

The ideal raw material to use in the pyrolysis process of MPW is composed of polymers; each of them is crushed down to a size that is negligible compared to the internal volume of the reactor, constituting a homogeneous mix. The total mass m_0 of the mix in *kg* at the moment of introduction in a hermetic metallic container, is given by:

$$m_0 = \sum_{i=1}^{n} m_{0i} \qquad (1)$$

Where m_{0i} is the mass of each polymer that is a part of the mixture. The unitary fraction of -th polymer regarding total mass is given by:

$$f_i = \frac{m_{0i}}{m_0} \tag{2}$$

Based on the TGA of each polymer of thermal degradation of one-step and applying the systematic procedure proposed in [23], a dynamic model is obtained for the thermal degradation of plastic:

$$\frac{dm_{pi}}{dT} = A_i(m_{pi} - m_{pfi})\, e^{-\frac{1}{2}\left(\frac{T-T_{fxi}}{\sigma_i}\right)^2} \tag{3}$$

A_{i}, T_{fxi}, σ_{i}, are parameters of each polymer deduced from its own TGA. Equation (3) assumes that all of the plastics of the mixture have the same instantaneous temperature, and evolve according to heat transfer. Residual mass of each polymer left behind in the process as char m_{fi}, and m_{pi} is the instantaneous residual mass of a particular polymer expressed as a percentage of the initial mass of the polymer:

$$m_{pi} = \frac{m_i}{m_{0i}} \times 100\% \tag{4}$$

Moreover, the residual mass of the mix is given by:

$$m = \frac{m_0}{100}\sum_{i=1}^{n} f_i m_{pi} \tag{5}$$

2.2. Simulation

The block diagram in Figure 1 represents the thermal degradation process by TGA on both EPS and LDPE polymers. Both "Thermal Degradation" blocks contain code based on Equation (3) but with different parameters for each plastic; EPS and LDPE. The internal code applies the 4th order Runge-Kutta's algorithm to the numerical resolution of the equation. The "mtotal" block uses Equations (1), (2), (4), and (5) to determine the instantaneous total percentage of residual mixture mass. The "Tref" block represents the heating rate as it occurs inside the real thermal analyzer with linear behavior increasing from environmental temperature up to the maximum temperature in the process.

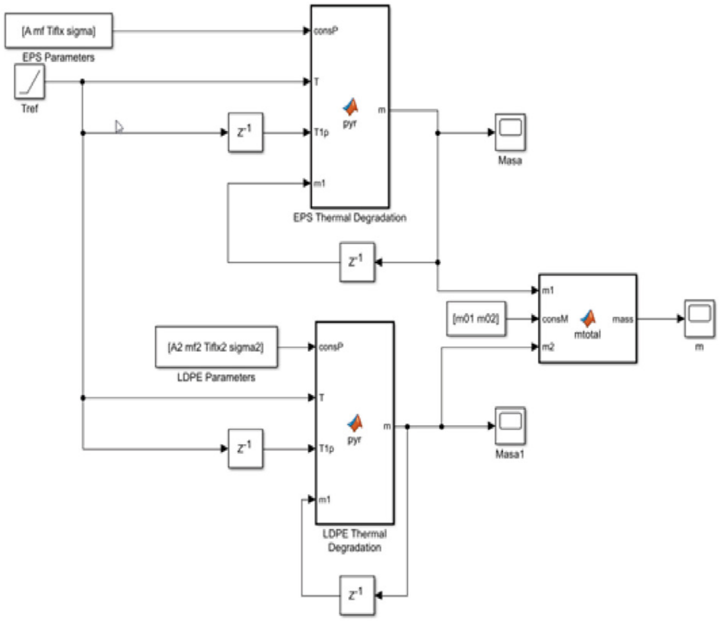
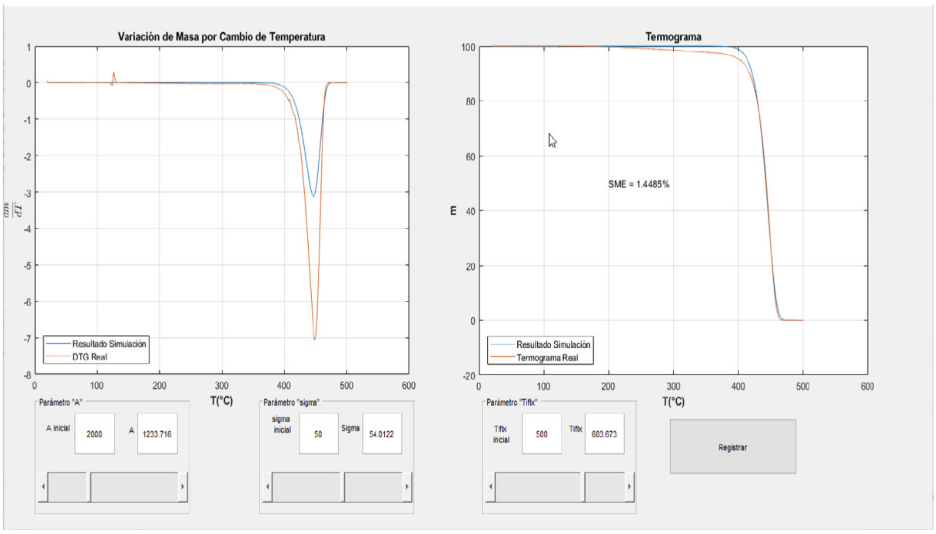


Figure 1. Block diagram on Matlab Simulink to simulate the thermal degradation of MPW.
Source: own work

Also, the software was designed to improve the determination of the parameters A_i, $T_{fxi,}$ and . The authors proposed the method in [23] as a starting point, but there are some restrictions related to the possibility of obtaining complex values. For that reason, the executable program gives the chance to modify these parameters manually until it reduces square medium error below . Figure 2 shows the graphical user interface (GUI) of the software to adjust the individual polymer parameters.



Parámetro "A"
A inicial 2000
A 1233.716

Parámetro "sigma"
sigma inicial 50
Sigma 54.0122

Parámetro "Tifix"
Tifix inicial 500
Tifix 683.673

SME = 1.4485%

Figure 2. Executable program to determine the individual polymer parameters

Source: own work

2.3. 2.3 Thermogravimetric Analysis

The TGA was made using a Simultaneous Differential Technique SDT Q600 Thermal Analyzer at the INCITEMA Institute at the UPTC facilities in Tunja, Colombia (Figure 3). The analysis ran into the atmosphere with Argon (Ar) at a constant flow of at a heat rate of starting at and finishing at . An available comercial bag made of LDPE and cut into small pieces was used as a polyethylene source. EPS came from a food dish bought at an ordinary store which was then clipped into small round pieces. First, the TGA analysis was conducted using samples of 100% EPS and then 100% LDPE. After that, several TGA were performed on three different samples of binary mixes LDPE+EPS corresponding to 25% LDPE + 75% EPS, 50% LDPE + 50% EPS, and 75% LDPE + 25% EPS. For each sample, it resulted in a respective thermogram. Crucibles made of Alumina carried the samples inside the thermal analyzer. Figure 4 shows the appearance of the original plastic samples. Figure 5 corresponds to the microbalance to prepare the samples for each test.

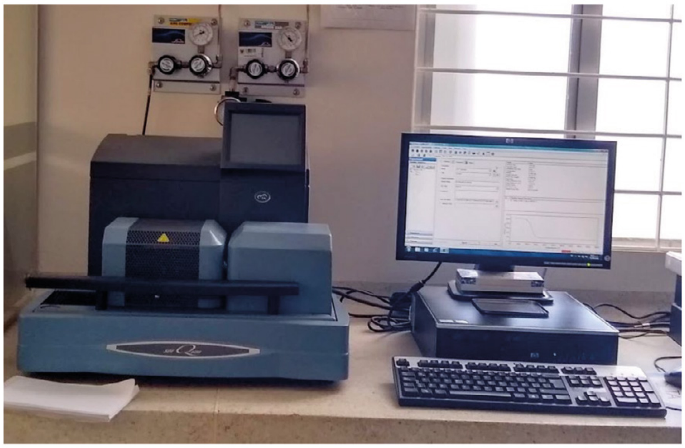


Figure 3. Thermal analyzer equipment SDT-Q600 used to run TGA at UPTC INCITEMA institute

Source: own work

The resulting thermograms for 100% LDPE and 100% EPS were used to obtain the parameters , , and for LDPE and EPS, according to Bellon et.al. After that, the software developed by the authors improved upon these parameters for a better simulation. With the use of Equation (3) and the particular values extracted from both thermograms, the simulation was run to predict the behavior of thermal degradation of plastic binary mixtures with the proportions previously indicated.

The SDT-Q600 Thermal Analyzer provided a series of files through its connection with a computer. A total of ten records were produced with five of them corresponding to pdf files with detailed thermograms for each sample. The remainder were text files containing information about test parameters and the configuration of the equipment and all the data. The data was organized as numerical values in seven columns and 18997 rows. The text files were processed using Microsoft Excel in order to accommodate the variables of interest: time, temperature, and mass. Finally, the resulting Excel files were imported into Matlab software as a vector for each variable mentioned before. Matlab has the necessary tools to generate plots to compare with the original TGA results.

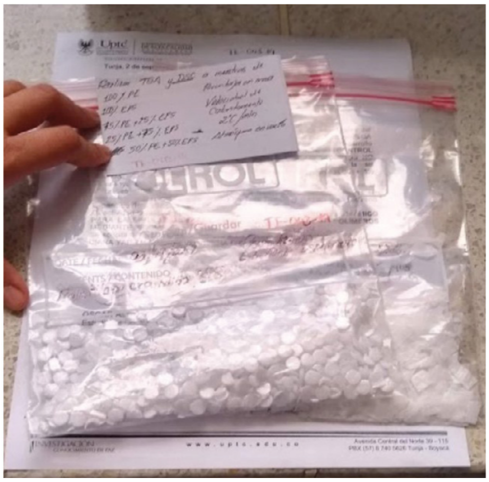


Figure 4. LDPE bag and EPS samples submitted to TGA
Source: own work

Results

Figures 5 to 9 show comparisons between the TGA of plastic binary samples described above and the resulting simulated data.

Based on the results of the EPS TGA (Figure 5) and in the procedure proposed by Bellon and Muñoz [23] the particular differential equation for this polymer was:

$$\frac{dm_1}{dT} = 0.3945m_1 * \exp\left(\frac{1}{2}\left(\frac{T - 417.0311}{20.7932}\right)^2\right) \qquad (6)$$

Equation (3) served as the basis for the simulation, and is the residual mass of EPS

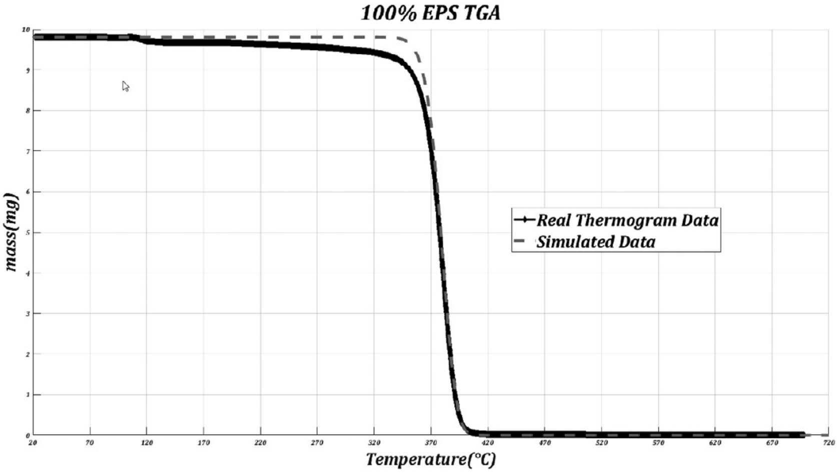


Figure 5. Comparison between real data from 100% EPS thermogram with data from the Simulink block diagram model
Source: own work

In turn, the TGA of LDPE presented interesting behavior (Figure 6). The thermogram looked like the LDPE sample was composed of two single elements with a one-step degradation reaction to each one of them. Treating them that way, the particular differential equations of every component were:

$$\frac{dm_2}{dT} = 1234m_2 * \exp\left(\frac{1}{2}\left(\frac{T-683.7}{54.01}\right)^2\right) \tag{7}$$

$$\frac{dm_3}{dT} = 0.048(m_3 - 0.42m_{f3}) * \exp\left(\frac{1}{2}\left(\frac{T-651.6}{35.82}\right)^2\right) \tag{8}$$

Where $\mathbf{m}_2$ is the residual mass of pure LDPE of the sample taken from the plastic bag, corresponds to the residual mass of the third element, and $\mathbf{m}_{f3}$ varies in the range of fractions of the initial mass of the sample taken from the plastic bag.

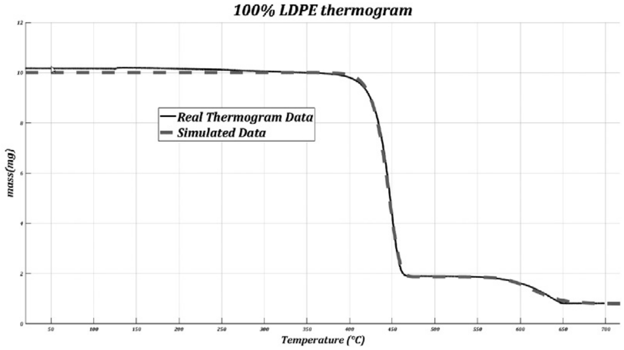


Figure 6. Comparison between real data from the thermogram of LDPE (taken from a plastic bag) with data from the Simulink block diagram model simulation

Source: own work

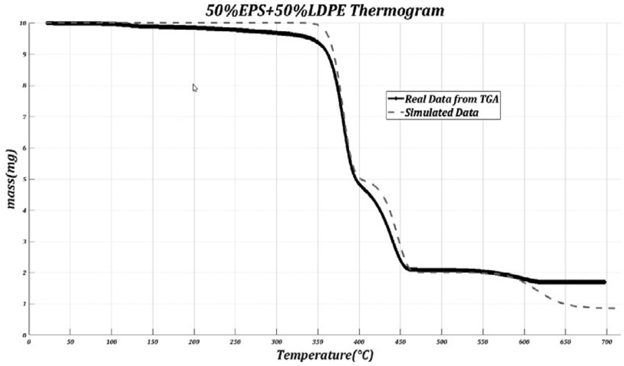


Figure 7. Comparison between data from TGA of 50%EPS + 50%LDPE mix and data provided by the Simulink block diagram model simulation

Source: own work

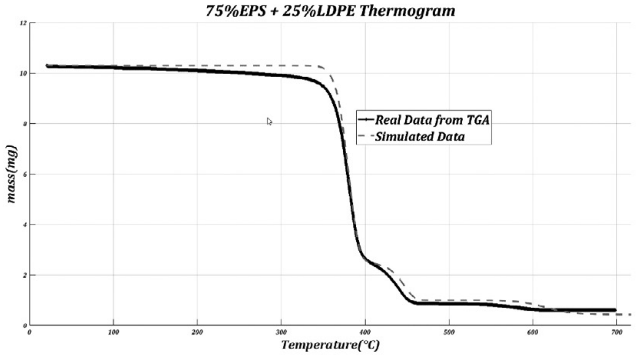


Figure 8. Comparison between data from TGA of 75%EPS + 25%LDPE mix with data from Simulink block diagram model simulation

Source: own work

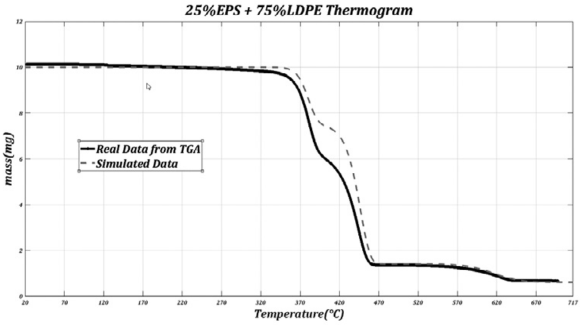


Figure 9. Comparison between data from TGA of 25%EPS + 75%LDPE mix and data from Simulink block diagram model simulation
Source: own work

$$m = m_1 + m_2 + m_3 \tag{9}$$

The total residual mass obtained because of the simulation is given by:

Table 1. contains information about the samples used for the TGA test and to simulate with the same parameters as the real mix of plastics. The SME column indicates the mean square error defined as:

$$SME = \frac{1}{n}\sum_{i=1}^{n}(\breve{m}_{\iota} - m_i)^2 \tag{10}$$

$$SME\% = SME * \frac{100\%}{m_{max} - m_{min}} \tag{11}$$

Where:

n: the size of the mass data vector.
i: the i-th element of the vector.
$\breve{m}_i$: the estimated mass at a temperature T_i throughout equation (3).
m_i: the i-th element of the mass vector took from the TGA data.
m_{max}: the maximum value in the mass vector.
m_{min}: the minimum value in the mass vector.

Table 1. Characteristics of the plastic mix samples, and the SME obtained.

Sample	EPS mass (mg)	LDPE mass (mg)	SME%
1	9.81	0	0.37
2	0	10.17	0.102
3	5.1	4.9	1.37
4	7.7	2.6	1.65
5	2.5	7.5	2.45

Source: own work

3. Discussion

The thermogram from the LDPE taken from a plastic bag looks like it would have two components mixed (Figure 6). A process was performed to deduce and separate those components and treat them as a binary plastic mixture. In this way, a set of parameters , and was obtained for that unexpected third component in the mix. Comparing with the results of other authors regarding LDPE thermograms [24], [25] indicate that a pure sample of this polymer has a one-step degradation reaction. The thermograms from the TGA of polymer mix samples shown in Figures 9-11 so not adjust to a fixed proportion between LDPE and the third component but are well suited for the EPS in each mixture.

LDPE samples were taken from bags used in the UPTC cafeterias. The supplier of these bags confirms that in addition to LDPE they contain additives, such as: stabilizers, pigments and flexibilizers. For this reason, the thermograms of the samples with some percentage of LDPE revealed the presence of other elements that also presented thermal degradation. That is, the presence of a third component can be determined in addition to LDPE and EPS.

The mix from the plastic bag does not have a homogeneous composition. It was necessary to modify the proportion between LDPE and the unknown third element to obtain simulated results according to real samples of the mixes. A variable proportion between LDPE and the hidden element better models the three samples of LDPE + EPS. In that case, while the mass of the EPS was maintained fixed, the mass of the plastic bag was distributed into different proportions between LDPE and the third component. The results of the simulation will improve with the manipulation of this variable based on the next assumption:

$$m_{PB} = m_2 + m_3 = (f_a + f_b) m_{PB} \tag{12}$$

$$f_a = \frac{m_2}{m_{PB}}\ ; \qquad f_b = \frac{m_3}{m_{PB}} \tag{13}$$

Where $_{mpb}$ is the mass of the sample taken from the plastic bag .

The usefulness of this model is that it presents a good approximation over the entire temperature range in which the process works. For control applications, it is advisable to have a model that can be used as a reference in all the points of the process. In this way, predictions about thermal degradation and mass loss can be extended over a broader time window. To make a reliable prediction, it is also necessary to have a precise characterization of the raw material.

The largest SME occurs in the temperature range in which volatilization happened. For EPS polymers, volatilization starts around and ends at almost . For LDPE polymers, that phenomenon is around approximately. The third unknown element also presents the one-step degradation reaction in the range of .

4. Conclusions

The thermal degradation process of LDPE and EPS mixtures can be represented as the sum of the individual one-step degradation reactions modeled through Equation (3). The results of the simulation provide a good approximation for the loss of mass of the real samples submitted to TGA tests over the entire temperature range of the process. Consequently, it is not necessary to segment the process into sub-ranges to look for parameters in each of them.

Future work will have to incorporate other factors that are part of the process of pyrolysis of MPW. This work allows us to model thermal degradation and volatilization of the raw material inside the pyrolysis reactor. However, the work so far does not consider the thermal characteristics of the reactor. It will be necessary to perform an experimental test to identify the thermal parameters. In addition to temperature, the pressure is another factor that affects the process.

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