Circular economy approach to plastic waste – kinetic studies

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Abstract

Plastic packaging represents one of the largest end-use market of plastic. Waste of these materials is in high growth worldwide and contributes extensively to the pollution of coastal areas. In this thesis, the thermal pyrolysis in a thermogravimetric differential scanning calorimetric (TG/DSC) is studied, using common plastic straws, consisting essentially of polypropylene, which can be easily found in marine environments. The influence of various procedures applied to samples that aimed to recreate the aging of waste exposed to environmental conditions was studied. The results showed that virgin PP decomposes only in one peak whereas PP from plastic straws, without previous treatment, shows two peaks of degradation with the first associated to the additives degradation. Most of the samples subjected to pre-treatment also showed only a peak of degradation, which means that the exposure of plastics to environmental conditions promotes the additives degradation. The kinetic study showed that the activation energy values associated with the degradation of each samples are not related with the implementation or not of pre-treatment. Although there were some differences regarding the degradation of the two types of samples, they are not significant enough to state that the plastic waste collected in the marine environment will have to be treated differently from others when recycling. Thus, to be able to apply a circular economy approach to plastics coming from coastal areas, they must be subjected to the same recycling process as other plastic packages made of polypropylene.

Keywords: Packaging waste, Thermal Pyrolysis, Kinetic Study, Polypropylene, Circular Economy

1. Introduction

Plastic was one of the major inventions, which has contributed to improve the quality life of populations. Due to its high durability and versatility, this material is present in most of industries, being used to replace other less resistant and durable materials [1]. However, in recent years plastic consumption has fastest increased worldwide. In 2018, around 360 million tons of plastic were produced of which 17% corresponds to Europe, the third biggest producer [2]. Plastic packaging represents one of the main plastic markets, corresponding, in 2018, to 40% of the final use of plastic. Polyolefins, especially polypropylene (19,3%) and polyethylene (17,5%) are the most used polymers in the plastic end-use markets [2]. In 2018, 17,8 million tons of plastic packaging were collected to be treated [2]. Recycling appears as the first option to plastic waste treatment. A circular economy will only be possible if there is zero landfilling. The concept of circular economy means a system of production and consumption of materials in which waste is recycled, recovered and reused, that is, the material is converted into a new product with economic value [3]

1.1 Plastic Production

World plastic production rose from 2 million tonnes in 1950 to 359 million tonnes in 2018, of which 51,2 million tonnes was produced in Europe [2] [4]. Analysing the distribution of plastic use in Europe is easily noted that plastic packaging corresponds to the main end-use market for these materials (40%), in 2018 [2]. However, coupled with this increase in production is an increase in the amount of plastic waste, which has strongly led to environmental problems, mainly due to degradation time associated with these materials [5].

1.2 Plastic Waste Treatment

To reducing the adverse effects caused by plastic waste, efforts have been made to increase the recovery of waste to recycling. Chemical recycling allows recovery of material quality, leads to the production of raw materials, and supports the reuse of plastic [3] [6]. This type of recycling is a process that converts polymeric waste, changing its chemical structure, to produce substances that are used as raw materials for the manufacture of new products and supports the reuse of plastics, excluding the production of fuels and means of power generation [7]. All these advantages are linked with the aim of achieve a circular economy.
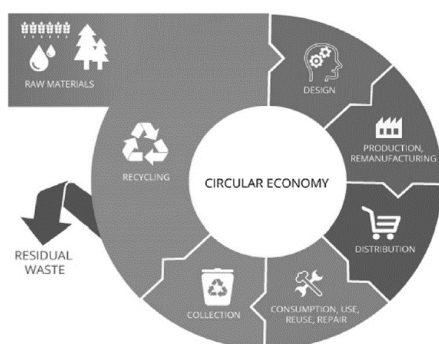

Figure 1 Circular economy principles [6]

1.2.1 Pyrolysis

Pyrolysis is a chemical and thermal decomposition technology of organic plastic waste in the absence of oxygen [8]. The pyrolysis process gives the possibility of adjusting the product obtained by varying the type of reactor, the operating conditions, and the use of catalysts [9] [10]. This is a very advantageous feature for the process economy.

This process can be considered economically viable since it uses discarded material to produce products with high energy value.

Plastic pyrolysis is a complex endothermic process that involves breaking bonds, transforming the polymer chains into small ones. The break occurs at the most unstable bonds in the molecular structure [8] [11].
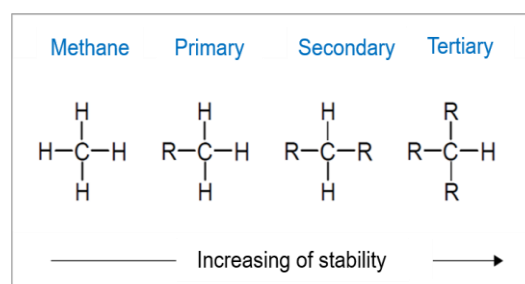

Figure 2 Order of carbon stability. Adapted from [15]

1.2.2 Degradation mechanisms

The thermal decomposition reactions are mainly by a radical process. It can be as follow: 1) unzipping: decomposition into monomer units; 2) random fragmentation; 3) combination of unzipping and random fragmentation; 4) elimination of simple, stable molecules from adjacent atoms; 5) elimination of side-chains, followed by cross-linked [8].

The mechanism of primary degradation of plastic polymers consists of polymeric chain scission, side group reaction and recombination. This degradation is usually initiated by free radical formation.

The thermal decomposition of polypropylene occurs through a radical mechanism, and the final product depends on the type of dominant radical at the beginning of decomposition process. This degradation starts with the homolytic breaking of a C-C bond in its primary chain giving rise to a primary and a secondary radical [12]. The products obtained are alkanes, alkenes, dienes and aromatic compounds [13] [14].

2. Materials and Methods

2.1 Polymer Materials

The plastic materials used in experiments was propylene from common plastic straws. All the straws used were white and yellow. The straws were cut into smaller pieces with approximately 5 cm and pre-treated or not according each experiment performed. After treatment, straws were cut again to guarantee even smaller samples (6mm). For each test samples with approximately 10 mg of weight were used. A test using virgin PP was also carried-out. The virgin PP used is identified as HF420FB and was supplied by Repsol.

2.1.1 Treatments Performed

Four different types of samples were analysed, which are: untreated, pre-treated in water + salt, pre-treated in unsalted water and pre-treated in water + salt and washed later. Three temperatures of pre-treatment were used: 80ºC, 60ºC and 40ºC. All the pre-treatments performed lasted 6h. These treatments aimed to simulate the action of staying in salt for more or less long periods of time. It was also considered that the permanence in salt water could have an impact on the thermal degradation of the samples due to the presence of residual salt in the samples. Thus, some of the samples that were pre-treated in salt water were washed before being analysed on TG/DSC. The different temperatures used in the pre-treatment of straws, as well as the presence or absence of salt allowed to evaluate the influence of these two factors on degradation kinetics of polypropylene.

The saltwater solution was prepared by adding 800mL of water and 29,02g of salt in a cup. The amount of salt to be used was calculated considering an average salt concentration in sea water (3,5 % w/w), according to the National Oceanic and Atmospheric Administration (NOOA). In addition to these tests, as the straws used were painted with a yellow dye, it also became important studying the influence of the white/yellow colour on plastic degradation curve. Thus, two tests were carried out, using an untreated straw sample, whose pieces contained only one of the colours.

2.2 Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) analysis

TG/DSC experiments were carried-out in a Perkin-Elmer STA 6000. The samples were put in an alumina pan and, before the runs, the equipment was equilibrated at 40ºC with constant gas flow and maintained for 10 min. Then, the temperature was raised with heating rate of 10ºC/min until 700ºC, which was maintained for 10 min. After that the equipment was cooled.

3. Results and Discussion

3.1 TG/DSC analysis

Degradation starts when a certain temperature is reached – T_{onset}. This value of temperature is obtained through the TG curve. In addition, the $T_{máx}$ and T_{fusion} can be obtained from the DTG and DSC curves. The melting temperature corresponds to the first peak observed in the heat flow curve, which is not accompanied by loss of mass.

3.1.1 Thermal Pyrolysis

The DSC curves shown in Figure 3 show the existence of a degradation peak for virgin PP and two degradation peaks for PP from straws, while DTG curves (Figure 4) show only one degradation peak for each sample.
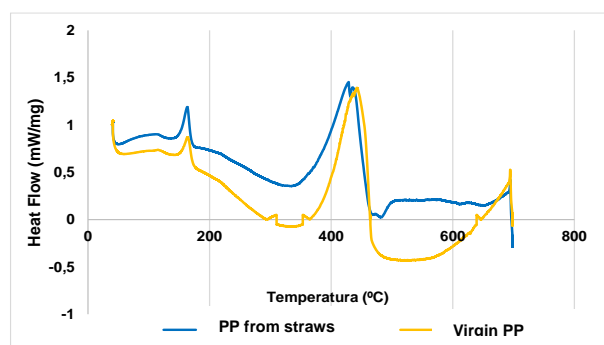

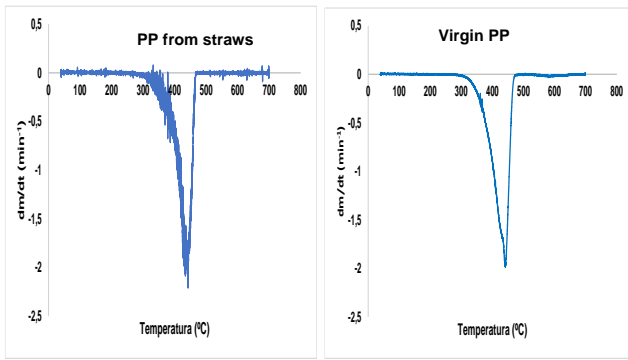*Figure 3 Comparison between DSC curves obtained for virgin PP and PP from untreated straws*

Figure 4 Comparison between DTG curves obtained for virgin PP and PP from untreated straws

PP from the plastic straws starts to degrade earlier than virgin PP samples. This maybe happens because the straws have a streak painted with yellow dye, which may have influence on their degradation behavior. The TG curves for both samples are shown in Figure 5.
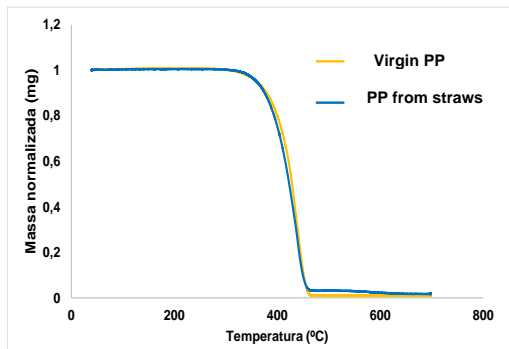

Figure 5 Comparison between TG curves obtained for virgin PP and PP from untreated straws

Analyzing the TG curve of untreated straw sample, it is possible to observe the existence of residue at the end of the curve. However, this residue does not appear on the virgin PP degradation curve. For this reason, the influence of color in plastics degradation was studied. On the Figure 6 are shown the TG curves obtained for each test: white samples, yellow samples, and whole straw sample.
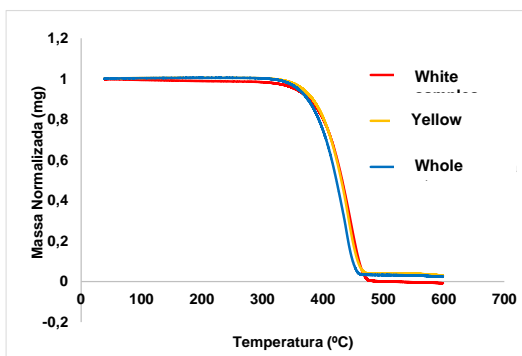

Figure 6 Comparison between TG curves obtained for white samples, yellow samples and whole straw

The degradation curves obtained for the various tests show that samples of different colors do not behave in the same way. The yellow samples start degradation at a higher temperature than white samples and whole straw. Furthermore, it should be noted that white samples have no residue in the end of curve, contrary to yellow samples and whole straw. As for the whole straw, the colored samples also showed two peaks of degradation on DSC curve (Figure 7).
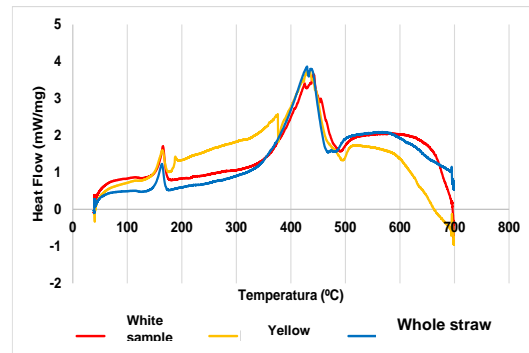

Figure7 Comparison between DSC curves obtained to white samples, yellow samples and whole straws

The T_{onset} values obtained for each test with samples treated in saltwater shows that there is no consistency, nor a direct relationship between the treatment temperature and T_{onset}. Samples pre-treated at 60ºC show a higher value when compared to samples pre-treated at 80ºC, and a smaller value than samples pre-treated at 60ºC. Furthermore, it is possible to observe that this samples have a higher T_{onset} than untreated samples. DSC curve shows that most of the samples subjected to pre-treatment show one peak of degradation as virgin PP, Figure 8.
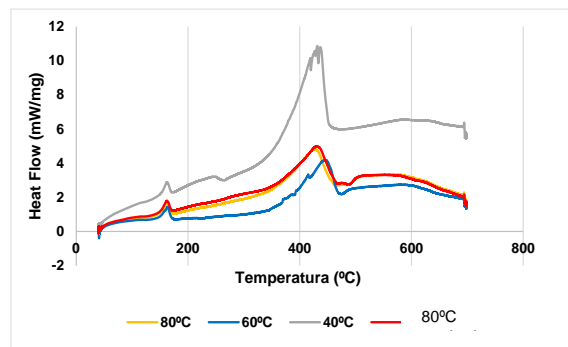

Figure 8 Comparison between DSC curves obtained to samples subjected to pre-treatment

Contrary to what was verified for samples pre-treated in saltwater, most of the samples pre-treated in unsalted water show two degradation peaks in DSC curve, as it shown on Figure 9.

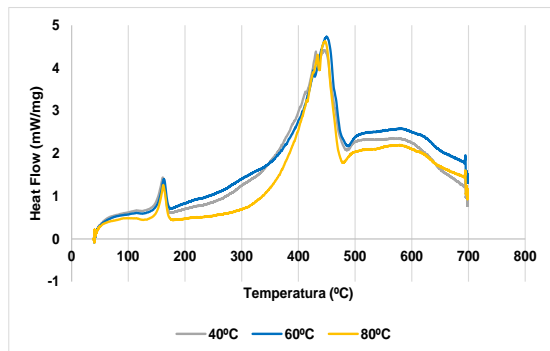Figure 10 Comparison between DTG curves obtained to samples subjected to pre-treatment with salt

Figure 9 Comparison between DSC curves obtained to samples subjected to pre-treatment without salt

DTG curves obtained for all tests carried-out with pre-treated samples show only one degradation peak, Figures 10 and 11.
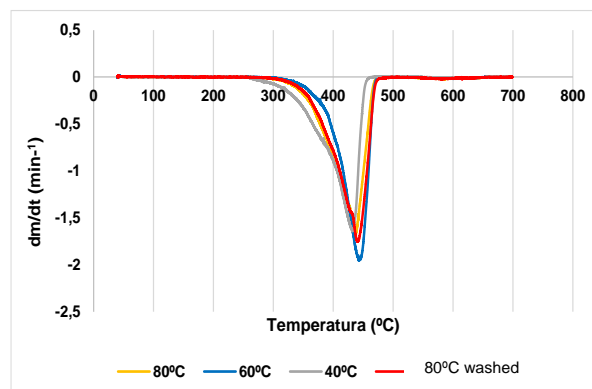

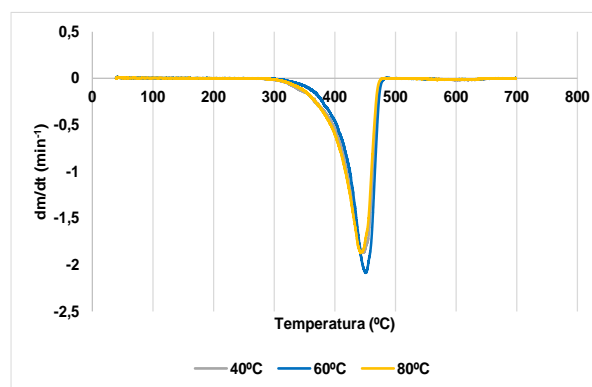Figure 11 Comparison between DTG curves obtained to samples subjected to pre-treatment without salt

Table 1 T_{onset}, $T_{máx}$ and T_f values obtained for thermal pyrolysis of samples

Samples	DTG		DSC		
	T_{onset} (ºC)	$T_{máx}$ (ºC)	T_f (ºC)	$T_{máx1}$ (ºC)	$T_{máx2}$ (ºC)
Virgin PP	410,7	442,6	164,2	442,8	-
PP from untreated straws	381,2	441,5	163,5	428,8	435,8
White samples	392,4	447,2	164,7	424,5	440,0
Yellow samples	406,6	442,0	162,8	428,5	434,4
80ºC + saltwater	398,4	436,2	162,3	427,5	-
60ºC + saltwater	410,9	442,6	163,2	445,2	-
40ºC + saltwater	389,7	434,4	162,1	433,4	438,6
80ºC + saltwater washed	401,8	440,6	162,2	429,8	-
80ºC + unsalted water	408,5	442,6	161,7	434,3	447,1
60ºC + unsalted water	418,6	450,8	163,1	450,0	-

40ºC + unsalted water	410,8	447,4	160,8	430,9	446,6

Table 1 shows that samples subjected to pre-treatment starts degradation at higher temperatures than samples untreated. This happens because the exposure of materials to environmental conditions leads to the loss of plasticizers and additives in the matrix making it difficult to decompose.

3.1.2 Combustion

To better understand the behaviour of the samples when subjected to thermal degradation, tests were carried-out under the same conditions as some of the previous tests, but this time, under an atmosphere of reconstructed air instead of nitrogen.

Thus, tests are performed using samples containing only the white and yellow part of the straw and samples containing whole straw.
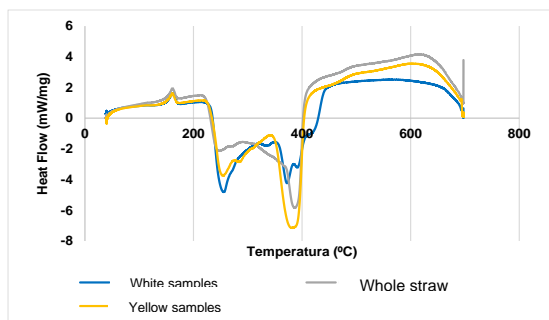

Figure 12 Comparison between DSC curves obtained to combustion of samples
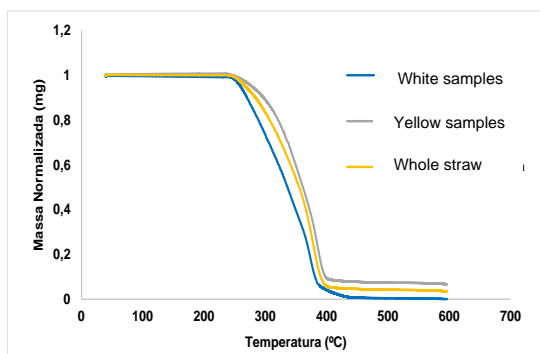

Figure 13 Comparison between TG curves obtained to combustion of samples

Once again it appears that the two colours behave differently and that, even in the case of combustion

instead of pyrolysis, the white sample starts to degrade before the yellow one. Comparing the results obtained for pyrolysis and combustion, it shows that the samples have a different behaviour in degradation under nitrogen or under air. In addition, it appears that when degradation occurs in an air atmosphere (combustion), the degradation of materials starts at lower temperatures.

3.2 Kinetic Model

The rate law with the Arrhenius equation was used to describe the experimental data. To calculate the sample fraction, the Euler Method was used. The model was adjusted to the experimental mass degradation curve. Equations 1 and 2 were used to describe experimental data.

$$\frac{dW}{dt} = -kW^n \qquad (1)$$

$$k = k_0 e^{\frac{-Ea}{RT}} \qquad (2)$$

Kinetic parameters were estimated using a least squares procedure, using the sum of the squares of the residuals over the fraction as an objective function (Equation 3) to be minimized.

$$O.F. = \sum_{all\ data\ points}\left(Fraction_{experimental} - Fraction_{computed}\right)^2 \quad (3)$$

3.2.1 Model considering 2 pseudo components

Thermogravimetric analysis performed previously revealed, in some tests, the existence of two peaks of degradation. For this reason, the application of the kinetic model to virgin PP considered the existence of two pseudo components in the sample.

The analysis of obtained curves shows a good fit of the model to the experimental data, which leads to the conclusion that this model will be able to describe the thermal degradation of virgin PP. Since considering two pseudo components a good fit was achieved, the kinetic model considered was applied to other samples. The model represents a good fit to the experimental data in almost the entire curve except in the final part where the existence of residue in the studied samples is evident in relation to the model. Thus, to ascertain whether the model was plausible to be applied to these samples, the corresponding kinetic parameters were calculated. The results obtained are shown on Table 2. The values obtained for the fractions of each pseudo component show that one of them has a much more expressive presence than the other, regardless of the treatment to which the sample has been subjected. Thus, it was considered the possibility that the PP from straws is composed only of one pseudo component + residue, instead of two pseudo components.

3.2.2 Model considering 1 pseudo component

The application of the model considering only one pseudo component revealed a good fit of it to the experimental data referring to the samples of PP from straws. Kinetic parameters obtained to these tests are present on Table 3. Considering the differences observed in the degradation curves of the samples performed with white or yellow part of the straw, as well as the influence of colour on the degradation of the PP used, the kinetic model was also applied to these tests. As observed in the Thermogravimetric Analysis carried out, the two colours present different behaviour, and consequently a fit to model. Analysing the results obtained for the kinetic parameters, it is observed that the activation energy associated with the yellow samples presents a higher value than white samples.

Table 2 Kinetic parameters obtained to model considering 2 pseudo components

Samples	Activation Energy (kJ/mol)		k(s^{-1})		Fraction	
	PP1	PP2	PP1	PP2	PP1	PP2
PP from untreated straws	27,1	156	5,71 x 10^{-3}	1,23 x 10^{-1}	0,03	0,97
80ºC + saltwater	23,5	148	6,85 x 10^{-3}	1,33 x 10^{-1}	0,04	0,96
60ºC + saltwater	23,1	190	7,78 x 10^{-2}	6,56 x 10^{-3}	0,04	0,96
40ºC + saltwater	0,37	123	4,54 x 10^{-3}	1,93 x 10^{-1}	0,03	0,97

Table 3 Kinetic parameters obtained to model considering 1 pseudo component

Samples	Activation Energy (kJ/mol)	k(s^{-1})	Fraction
	PP1	PP1	PP1
PP from untreated straws	153	1,21 x 10^{-1}	0,98
80ºC + saltwater	145	1,30 x 10^{-1}	0,97
60ºC + saltwater	190	7,91 x 10^{-2}	0,96
40ºC + saltwater	118	1,84 x 10^{-1}	0,99

White samples	149	$9,52 \times 10^{-2}$	0,98
Yellow samples	160	$9,87 \times 10^{-2}$	0,97

Considering the two adjustments made, it is observed, in the model considering two components, that one of them is residual. So, the model considering 1 pseudo component is the one that best fits the plastic straws.

4. Conclusion and future perspectives

The results showed that degradation of the samples subjected to pre-treatment in saltwater at different temperatures shows only a peak of degradation, as seen for the sample of virgin PP. Comparing the maximum degradation temperatures obtained for virgin PP and straws subjected to pre-treatment in saltwater, it is observed that these are slightly higher in the second case. Regarding the T_{onset} it was found that the samples subjected to pre-treatment start the degradation after untreated samples. The tests subjected to combustion showed, in DSC curve, two degradation peaks and degradation temperatures lower than those obtained for pyrolysis. The kinetic parameters obtained revealed that the pre-treatment of samples does not have a direct influence on the activation energy. In summary, the results showed that pre-treatment of the samples does not have a great influence on their behaviour during degradation, so that the plastics collected in the marine environment can be treated in the same way as those which are not exposed to environmental conditions.

The following actions could be developed to complement the work presented: thermal degradation of plastics effectively collected in the marine environment, catalytic pyrolysis of packaging wastes from coastal areas, application of this study to another type of plastic packaging.

5. References

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