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NIOBIUM OXIDE AS CATALYST FOR THE PYROLYSIS OF POLYPROPYLENE AND POLYETHYLENE PLASTIC WASTE

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Abstract. In the present work, the pyrolysis of polypropylene and polyethylene was evaluated with and without the addition of niobium oxide as catalyst by means of thermogravimetric analysis and experiments in a glass reactor. The results revealed that niobium oxide performed well in the pyrolysis of both polypropylene and polyethylene separately. For the mixture of polypropylene with polyethylene, the catalyst reduced the pyrolysis time.

Keywords: recycling, pyrolysis, polyolefin, catalyst, niobium oxide.

1. Introduction

Due to the increased use of plastic products in various sectors of industry, their consumption has increased in the recent decades, generating large volumes of waste. This plastic waste is a growing ecological concern, especially in the developed countries, since it is not biodegradable. Solutions to reduce this generation of waste plastics are reducing consumption, reuse and/or recycling. Among these solutions, recycling is most environmentally friendly. By recycling, materials and energy can be recovered [1-6].

Various methods for recycling plastic waste for use as raw materials have been proposed. Pyrolysis is a tertiary recycling method, which has promising potential applications [5, 7-10] especially for polyolefins, since it is one of the most effective methods to reduce use of oil resources and preserve the environment by reducing the volume of non-biodegradable waste [1, 2, 4, 11-13]. For commodity polymers such as polyolefins, mechanical recycling is not appropriate since it consumes water and energy to produce materials with inferior properties than those of pure resin.

Pyrolysis is considered a relatively low-cost process where a wide range of products can be obtained.

During this process, the materials are heated in an oxygen-free atmosphere and the organic compounds are decomposed into gaseous and liquid products. These products can be used as fuel and/or sources of chemicals. The solid fraction obtained consists of inorganic material present in the recycled sample. This fraction remains unchanged and can be recycled later [10, 14].

Thermal pyrolysis requires high temperatures and gives products with a wide distribution of carbon atoms. However, in the catalytic pyrolysis, the reaction temperature decreases and makes the distribution of carbon atoms narrower, reducing the cost and leading to higher value-added products [5, 8, 9, 15-22].

The use of catalysts promotes pyrolysis. The cracking efficiency of these catalysts depends both on their chemical and physical characteristics. These particular properties promote the breaking of C-C bonds and determine the chain lengths of the products obtained [10, 23].

Niobium oxide is an insoluble white solid that is stable in air, sometimes defined as amphoteric, but more often characterized as inert, including a mesoporous structure. Brazil has the largest reserves of niobium and produces about 92 % of the world's compounds containing niobium [24, 25]. Specifically, niobium oxide has numerous applications, among them a catalyst.

Studies of the synthesis, characterization and application of mesoporous materials containing niobium have been conducted due to their texture, structure, morphology and surface characteristics, such as ordered structure and high specific surface area [26]. The special properties (redox properties, photosensitivity, acidity and catalytic behavior) of materials containing niobium, such as niobium phosphate, niobium oxide and compounds containing niobium layers, have attracted interest in these compounds, as well as the understanding of their behavior and the use as catalysts [25].

There are many factors affecting the synthesis of mesoporous particles containing niobium, among them the presence of silicon, the presence and amount of niobium, type of surfactant, *etc*. The incorporation of niobium ions on sodium silicate as a silica source is favored, but a less ordered structure is obtained.

Lately interest in niobium oxide has been growing due to its mesoporous structure. It can be prepared only with niobium alone, niobium combined with elements (such as molybdenum, aluminum, and tungsten, thereby forming mixed oxides), and other catalysts (sulfides, nitrides and carbides).

This article is the first to report the use of niobium pentoxide hydrate as a pyrolysis catalyst of waste polypropylene (PP) and polyethylene (PE), individually or combined in blends.

2. Experimental

2.1. Raw Materials and Catalyst

Samples of PP and PE were obtained from municipal waste in the form of pellets. These were knife-milled for characterization. The catalyst niobium oxide (HY 340) was obtained from Companhia Brasileira de Metalurgia e Mineração (CBMM) and passed through a 200-mesh sieve.

2.2. Methods

Mixtures of the polymers and the catalyst were prepared using a Haake twin-screw Minilab mini-extruder in counter-rotating mode at 60 rpm and 453 K for 5 min, thus obtaining samples with 5 g of polymer with well-dispersed catalyst. For comparison, both reused PP and PE were also extruded without catalyst. In addition, blends containing 1:1 by mass of PP and PE were obtained with and without catalyst.

2.2.1. Material characterization

Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q-500 analyzer at the heating rate of 10 K/min to 973 K under nitrogen atmosphere. The XRD patterns were obtained with an X-ray diffractometer operating at the wavelength of 1.542 Å, corresponding to CuKα band at the speed of 1º (2θ)/min, with the step of 0.05º in reflectance mode and angular range from 2º to 80º (2θ) using a Miniflex diffractometer equipped with a radiation source generated at 30 kV and 15 mA.

The samples analyzed by energy-dispersive X-ray spectrometry (EDX) were in the form of powder, and the analysis was performed using a Shimadzu EDX-720 apparatus under vacuum for 320 s.

Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K) were employed and the Braunauer-Emmett-Teller (BET) equation was used to measure the external area (specific surface area) of solids through adsorption as inert gas (N_2) on the solid surface. The pore volume was obtained by the BJH method (Barrett, Joyner and Halenda) in the adsorption branch. The equipment was a Micromeritics ASAP 2020.

The films for FTIR analysis were obtained with a Carver laboratory press, in which the samples remained for 5 min at the temperature of 453 K. After this stage, Fourier-transform infrared (FTIR) analysis was performed with a Perkin Elmer 1720X spectrophotometer.

Differential scanning calorimetry (DSC) was performed with a TA Instruments Q-1000 apparatus, in which samples containing 3.0–4.5 mg were heated from 298 to 473 K at the heating rate of 10 K/min.

2.2.2. Pyrolysis experiments

The catalytic and thermal cracking were performed in 1:1 by weight mixtures of PP:PE containing 20 g. The amount of catalyst, when used, was 10 wt %.

Pyrolysis was performed under two different experimental conditions. The first occurred at the temperature of 673 K and the second at 703 K, both with the nitrogen flow of 60 ml/min. The samples were placed in a glass reactor inside a furnace under temperature control. The liquid fraction obtained from the pyrolysis was collected in a flask in ice bath, while the solid fraction was retained inside the reactor and the gas part was discarded.

The masses of the liquid and the solid fractions were weighed after pyrolysis, and the gas was quantified by the difference between the total mass of 20 g and the masses of the liquid and solid fractions discounting the mass of the catalyst (all weighed accurately) when the process was catalyzed. The liquid fraction was analyzed by gas chromatography with a flame ionization detector (GC-FID) in an Agilent 7890 detector. The column used was HP-5 (30 m x 530 μm x 1.5 μm). This technique was used to evaluate the composition of the liquid fraction obtained by pyrolysis.

3. Results and Discussion

The chemical elements present in the niobium oxide were identified by the EDX analysis (Table 1). Niobium oxide is an amorphous material, acquiring crystallinity at the temperatures above 573 K. Therefore, its diffraction (Fig. 1) does not have peaks of crystallinity, only amorphous halos. The absence of defined peaks reveals its amorphous character.

Results of EDX analysis for the catalyst niobium oxide

Catalyst	Components	Quantitative results, %
Niobium oxide	NbO	99.481
	Cl	0.519

Textural analysis of the catalyst

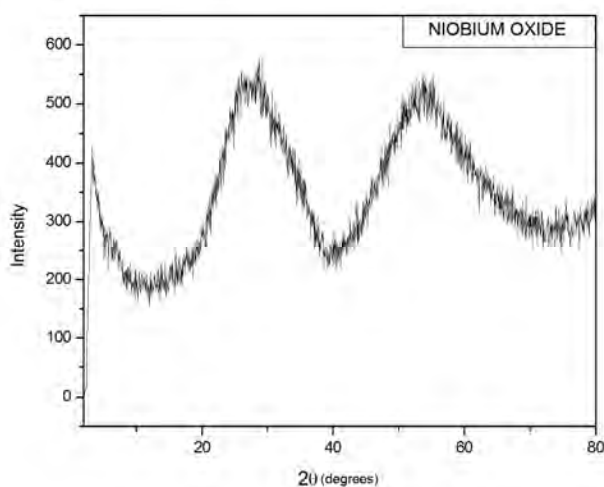| Catalyst	Specific surface area, $m^2 \cdot g^{-1}$	Pore volume, $m^3 \cdot g^{-1}$
Niobium oxide	150	$1.253 \cdot 10^7$

Fig. 1. X-ray diffractogram of the niobium oxide catalyst

The specific surface area and average pore volume of the catalyst were determined by the methods of Braunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH), respectively (Table 2). Materials with larger pore sizes tend to deactivate more easily during the pyrolysis of plastics, in contrast with materials with smaller pores [27-28]. This could lead to increased production of the solid fraction in the catalytic pyrolysis of PP and PE, because larger molecules can be deposited in these pores, forming coke and blocking the acid sites of the catalyst.

Consequently, this also would result in lower gas fraction. The process of molar mass decay begins on the outer surface of the catalysts, where macromolecules are cracked into smaller molecules that will diffuse to the inner pores of the catalyst [29-30].

While these pores are large and easily deactivated by the coke, smaller molecules do not reach the internal pores and are less effective in the next steps of cracking.

Another important factor that must be taken into consideration for catalyst efficiency is the specific surface area. The larger this area, the greater the number of pores

present. As mentioned earlier, it is known that this catalyst presents pores that are acidic sites for catalytic cracking to occur.

The polymeric materials used were municipal waste and the nature of their functional groups was determined by FTIR. Only the presence of aliphatic hydrocarbon was detected in their compositions (Fig. 2).

For the spectrum of the PP sample, we can highlight the following bands: those near 980 and 1370 cm^{-1}, corresponding to the angular deformation of CH_3 group; bands near 2870 and 2950 cm^{-1} related to the stretching of the group CH_3; absorptions in the range of 1370 and 1460 cm^{-1} related to the angular deformation of the methylene group; bands at 2840 and 2920 cm^{-1} corresponding to the normal vibrations of asymmetric and symmetric stretching of the CH_2 group, and finally the band at around 1170 cm^{-1}, related to deformation of the $CHCH_3$ group.

The spectrum of the PE sample contains the following bands: at 2920 and 2850 cm^{-1}, which correspond to asymmetric and symmetric stretching vibrations of the CH_2 group, and those near 1370 and 1460 cm^{-1}, associated to the angular deformation of the methylene bonds.

The maximum melting temperature for the PP sample was around 432 K. In the case of the PE sample, two endotherms were observed, one at 402 K and one with lower intensity at 436 K, which is possibly due to contamination of PP by PE in the original sample from recycling. For the PP:PE blend (1:1 w/w), as expected, two endotherms were observed, characteristic of PP and PE (Fig. 3).

The results of the TG analyses showed that the use of niobium oxide as catalyst for the pyrolysis of PP reduced T_{onset} and T_{max} (Table 3) compared with the decomposing polymer without catalyst. Niobium oxide has acid sites in its structure, which help in the cracking process, besides having high specific surface area and high average pore volume. This set of characteristics promotes the penetration of large molecules generated by the degradation of PP (Fig. 4).

The TG data were used to plot a curve of mass loss x 1000/reaction temperature (K). The slope of the resulting linear equation provides the activation energy (E_a) for each system. E_a is the minimum energy needed for the reaction to occur, *i.e.* if a certain material reduces the E_a of the process, the energy required for the process to occur will be lower, indicating the material acts as a catalyst (Table 4). The results showed that niobium oxide in fact reduced the E_a of the PP pyrolysis.
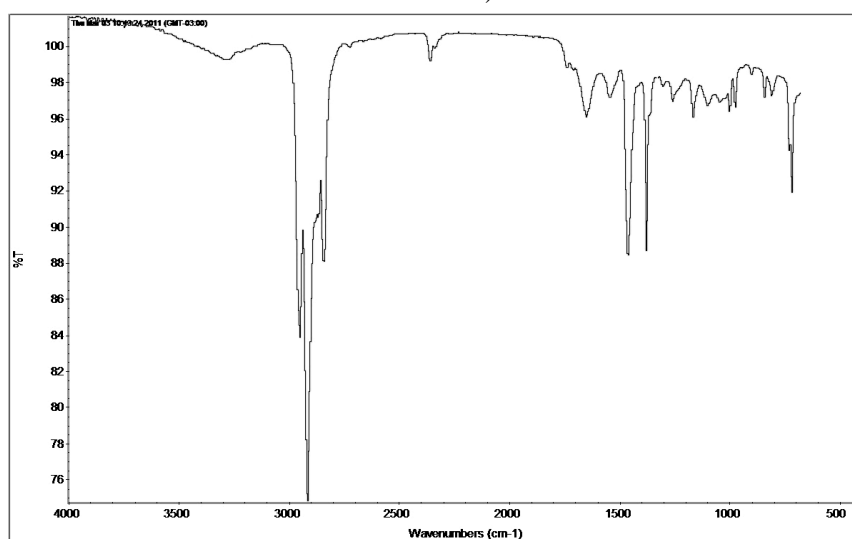
Table 3

TGA results for PP, PE and PP:PE mixture without catalyst and with niobium oxide

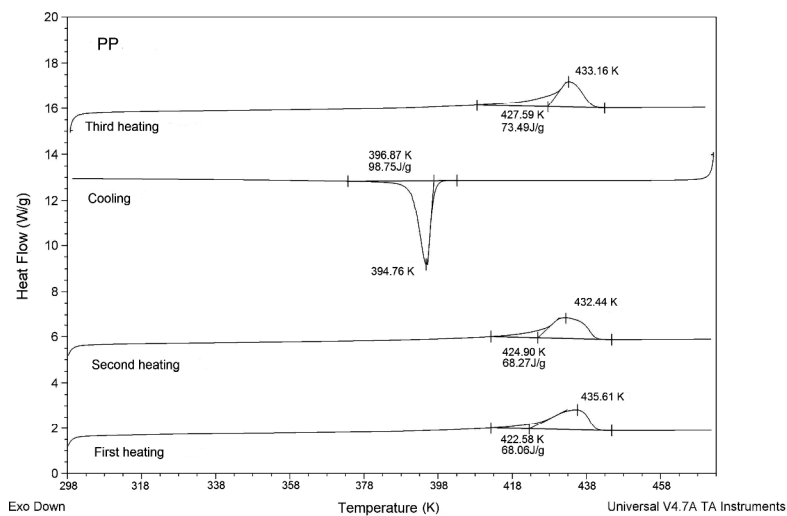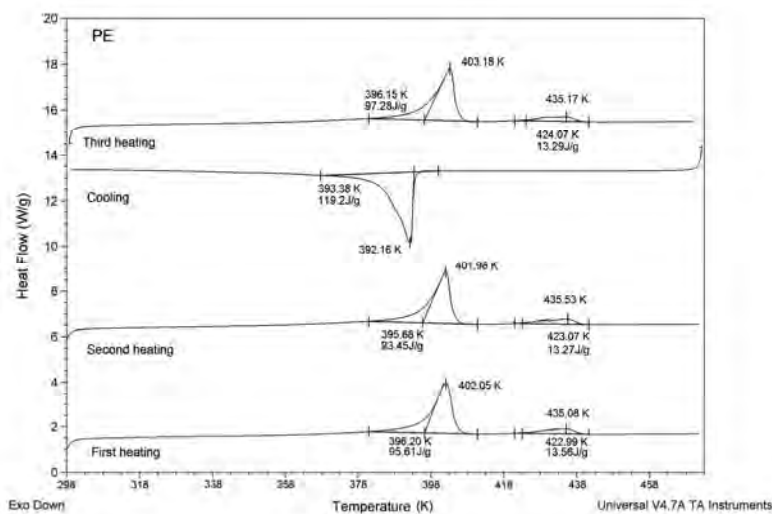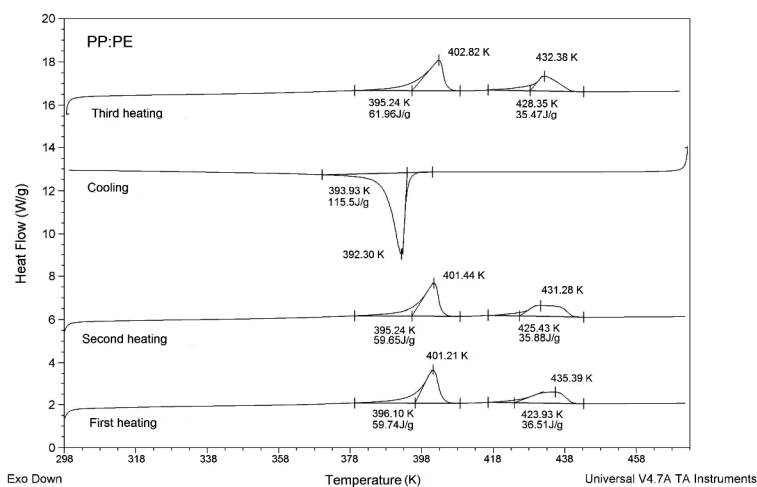| Polymer	Catalyst	T_{onset}, K	T_{max}, K	Mass loss, %
PP	–	659	707	100
	Niobium oxide	618	654	96
PE	–	711	731	100
	Niobium oxide	683	725	93
PP:PE (1:1 w/w)	–	655	712	99
	Niobium oxide	705	725	94
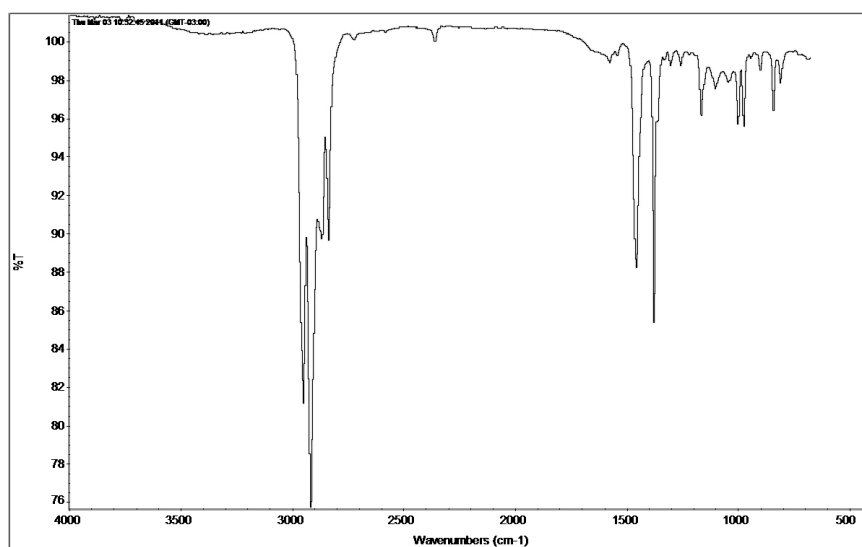
a)

b)

Fig. 2. FTIR spectra for the samples of waste plastics: (a) PP; (b) PE

a)

b)

c)

Fig. 3. DSC curves of the waste plastics: PP (a); PE (b) and PP:PE blend (1:1 w/w) (c)
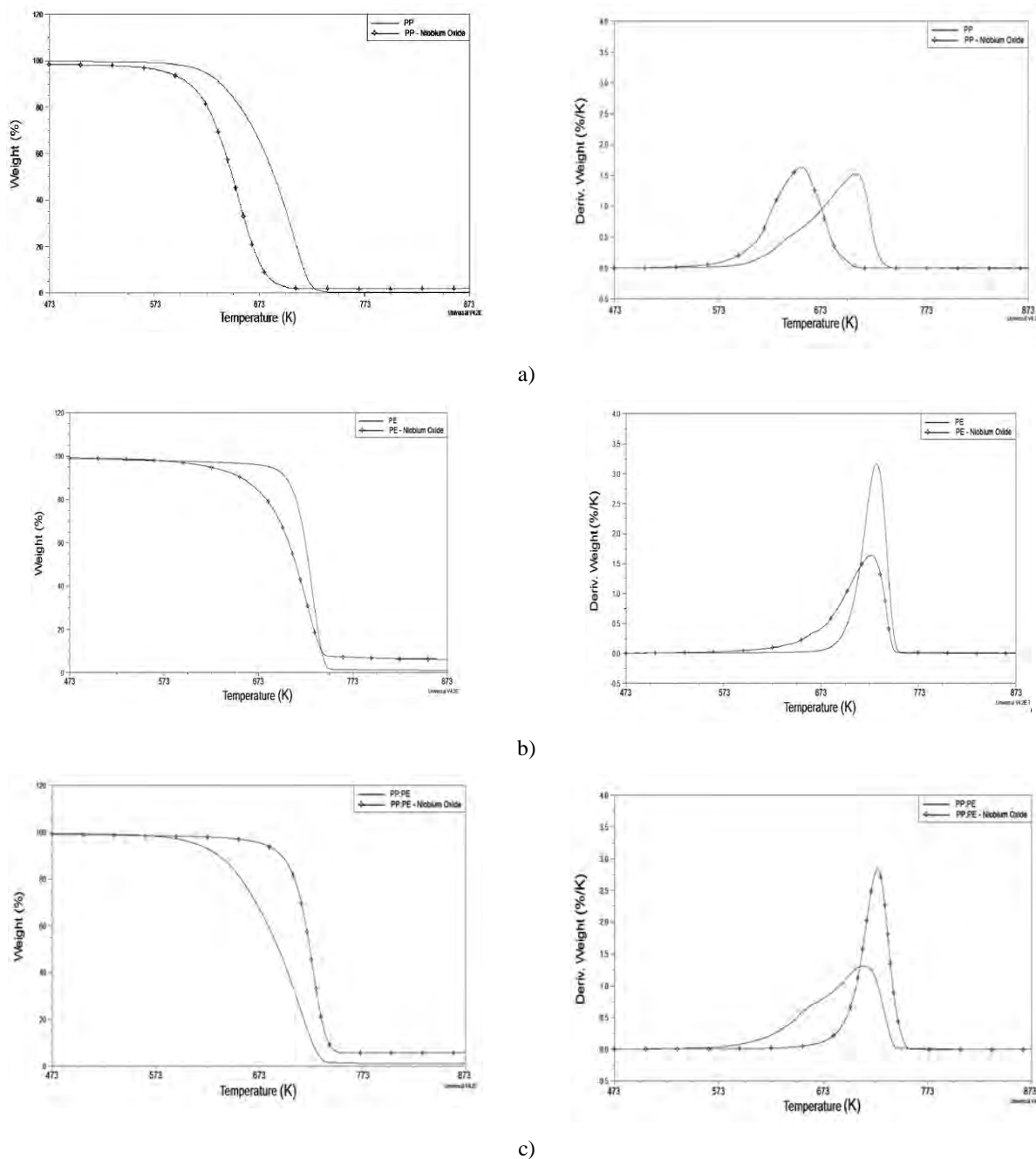
Fig. 4. TGA and DTG curves corresponding to samples without and with niobium oxide: PP (a); PE (b) and PP:PE blend (c)

Table 4

Activation energy for the pyrolysis

Polymer	Catalyst	Lineal Equation	R^2	Activation energy, $J \cdot mol^{-1}$
PP	–	$-613.97x + 945.83$	0.9902	5108
	Niobium oxide	$-592.19x + 965.86$	0.9964	4928
PE	–	$-502.89x + 783.01$	0.9998	4183
	Niobium oxide	$-665.77x + 987.57$	0.9851	5539
PP:PE (1:1 w/w)	–	$-842.05x + 1219.6$	0.9818	7004
	Niobium oxide	$-952.42x + 1370.8$	0.9727	7921

Table 5

Results of the pyrolysis performed at 673 and 703 K

T, K	Catalyst	Liquid fraction, g	Liquid volume, ml	Solid fraction, g	Gas fraction, g	Pyrolysis time, h
673	–	0.900	1.0	9.092	10.008	4
	Niobium oxide	1.445	7.0	6.452	10.103	3
703	–	5.143	10.0	2.064	12.793	3
	Niobium oxide	2.613	6.0	5.650	9.737	2

Percentage of carbon atoms in the liquid fraction for the pyrolysis at 703 K

Catalyst	C11, %	C12, %	C13, %	C14, %	C15, %	C16, %	C17, %	C18, %
–	3	2	47	0.4	21	1	8	17
Niobium oxide	9	5	17	13	23	12	2	9

Likewise, niobium oxide was effective in cracking the PP. It also reduced the T_{onset} and T_{max} of the pyrolysis of PE (Table 3). This is probably because this catalyst has acid sites in its structure that aid in the cracking process (Fig. 4). However, unlike what occurred in the PP sample, it did not reduce the activation energy of the system (Table 4).

The same experiment was conducted for the blend of PP:PE (1:1 m/m) in order to verify if there is any synergistic effect when pyrolyzing this polymer mixture.

Pyrolysis of PP:PE blend without catalyst resulted in a slightly lower decomposition temperature than that of the polymer with lowest T_{onset} (PP), *i.e.* there was synergy between the polymers, which accelerated the pyrolysis of the blend. One explanation is that the greater the proportion of tertiary carbons, as in the case of the PP, the faster the initial stage of decay. Thus, a lower initial temperature of pyrolysis was obtained.

Niobium oxide did not reduce the initial degradation temperature of the mixture. This was probably because this catalyst has a high pore volume, which favors the deposition of bulky molecules generated by the decomposition of PP. Thus, its pore system can be deactivated by the solid fraction produced in the pyrolysis of PP, which occurs first in the case of PE. Also, there was no reduction in the activation energy of the system with the catalyst (Table 4).

Both the thermal and catalytic cracking were performed with the blend of PP:PE containing 20 grams. For the catalytic pyrolysis, the amount of catalyst used was 10 wt %.

Pyrolysis was performed at two different temperatures, 673 and 703 K, both with the nitrogen flow of 60 ml/min. The samples were placed in a glass reactor inside a furnace with temperature control. The liquid fraction obtained from the pyrolysis was collected in a flask at 273 K and the solid fraction was retained in the reactor. The reaction time varied for each mixture, with the maximum of 4 h.

The mass of the solid fraction was obtained by weighing the residue remaining in the glass reactor after pyrolysis. In turn, the mass of the liquid fraction was obtained from the mass of the oil obtained, and the mass of the gas was calculated by the difference between the total mass and those of the solid and liquid fractions, after discarding the amount of catalyst.

Table 5 shows the results obtained for pyrolysis at two temperatures, including their reaction times. Although the niobium oxide catalyst did not reduce the initial degradation temperature of the PP:PE blend or the activation energy of the process, it reduced the reaction time to 1 h compared with the case without catalyst at 673 K. This is probably due to the specific surface area and average pore volume associated with the highly acid sites, which facilitated the pyrolysis process, thereby generating a high liquid fraction. Moreover, it generates a high solid fraction, because the larger pores also favor the formation of the solid fraction.

Increased temperature favors the pyrolysis process, decreasing the time and the amount of gas fraction, and also increases the liquid fraction content and reduces the solid fraction. For thermal pyrolysis, the increase in temperature caused significant changes such as reduced time, a considerable increase in the liquid fraction as well as reduction in the solid fraction. Analysis of the liquid product showed it is primarily composed of carbon chains of 13, 15 and 18 carbons. For C13 the percentages were 47 %, for C15 – 21 %, and C18 – 17 %.

The thermal cracking of polyolefins is described as occurring through a radical mechanism, *i.e.*, the polymer chain is broken into hydrocarbon radicals, which can contain any number of carbon atoms, generating hydrocarbons having a broad size distribution.

With increasing temperature, the niobium oxide raised the liquid fraction content. This was much less pronounced than in the catalyst-free process. However, the solid fraction content was higher than the uncatalyzed

process, and its gas fraction was lower. This catalyst decreased the reaction time by 1 h. The products in the liquid fraction had a slightly wider range than other zeolitic catalysts, such as HZSM-5 and HMOR, lying between C10 through C18. The largest quantities were 17 % for C13 and 23 % for C15.

Table 6 shows the distribution of the number of carbon atoms of the liquid fraction obtained in the pyrolysis at 703 K, ranging from C11 to C18. The carbon chains with fewer than 11 carbons are not reported because they contained very small amounts of the liquid fraction.

4. Conclusions

Niobium oxide has a structure with acid sites that facilitate the process of cracking polypropylene and polyethylene chains.

In the case of PP, the use of this material as catalyst reduced both the initial degradation temperature and the maximum degradation rate temperature when compared with the thermal process. The same behavior was observed for PE. However, this was not the case for the blend. The PP cracking occurs at lower temperature than for PE, so the solid fraction obtained from the PP can block the pores of the niobium oxide, hindering its action in PE cracking and retarding it.

For the pyrolysis of the PP:PE mixture, niobium oxide reduced the cracking time at both temperatures. Increasing the temperature caused an increase in the liquid fraction and a decrease in the solid and gaseous fractions.

Acknowledgments

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ОКСИД НІОБІЮ ЯК КАТАЛІЗАТОР ПІРОЛІЗУ ПОЛІПРОПІЛЕНОВИХ І ПОЛІЕТИЛЕНОВИХ ВІДХОДІВ

Анотація. Проведено піроліз в скляному реакторі і термогравіметричний аналіз поліпропілену і поліетилену з додаванням і без додавання оксиду ніобію як каталізатора. Показано, що оксид ніобію добре зарекомендував себе при піролізі окремо як поліпропілену, так і поліетилену. При використанні суміші поліпропілену з поліетиленом каталізатор зменшує час піролізу.

Ключові слова: утилізація, піроліз, поліолефін, каталізатор, оксид ніобію.