

Effect of using activated carbon and graphene oxide on the microwave assisted pyrolysis of expanded polystyrene waste

Pirólise assistida por micro-ondas de resíduos de poliestireno expandido utilizando carvão ativado e óxido de grafeno

Pirólisis asistida por microondas de residuos de poliestireno expandido utilizando carbón activado y óxido de grafeno

Received: 11/14/2022 | Revised: 11/26/2022 | Accepted: 11/28/2022 | Published: 12/05/2022

Davi Angelo Zancanaro

ORCID: <https://orcid.org/0000-0002-4920-355X>
Universidade de Caxias do Sul, Brazil
E-mail: dazancanaro@ucs.br

Matheus Poletto

ORCID: <https://orcid.org/0000-0003-2317-2713>
Universidade de Caxias do Sul, Brazil
E-mail: mipolett1@ucs.br

Abstract

Polymers are increasingly present in everyday life to replace other materials. Because they are cheap and have attractive mechanical properties, they were and still are produced on a large scale and, consequently, their large volumes in landfills present a challenge for their recycling. Thus, the objective of this study was to evaluate the depolymerization of expanded polystyrene (EPS) waste through the use of microwaves using two agents that have carbon in their constitution to assist in depolymerization: graphene oxide (GO) and activated carbon (AC). Different amounts of GO and AC (0.125, 0.25, 0.5 g) were used, always keeping the mass of the EPS sample constant at 1 g. The tests in the microwave oven were performed in 3 cycles of 4 minutes each, with a total time of 12 minutes per batch. Inside the oven, the sample was placed inside a round-bottomed flask wrapped with rock wool. To characterize the material obtained from depolymerization, a mass balance was performed to evaluate the depolymerization yields associated with Fourier Transform Infrared Spectroscopy (FTIR) and thermogravimetric analysis (TGA). For the sample containing 0.125 g of GO, it was observed the formation of a larger solid fraction, little gaseous fraction and no liquid fraction. The sample with 0.25 g of GO showed the best yield of volatiles, with 22.58% of volatiles, and it was possible to observe both the liquid and the gaseous fractions. When AC catalyst was used the depolymerization extension was lower than GO. Samples containing with 0.125, 0.250 and 0.5 g of AC yielded gaseous fractions of 5.13; 9.16; and 3.06, respectively. In FTIR analysis it was not possible identify the formation of new bands for samples treated with GO or AC, when compared with EPS. Some new degradation peaks, when compared with EPS, were observed in TGA for samples that used GO as catalyst; which can be associated with the formation of more volatile compounds after depolymerization. The samples treated with AC showed a less pronounced reduction in its thermal stability. This study suggests that the heat transfer from the dark particle to the EPS sample is more effective when GO is used which may contribute to the depolymerization of EPS wastes.

Keywords: Polystyrene waste; Catalyst; Waste treatment.

Resumo

Os polímeros estão cada vez mais presentes no cotidiano para substituir outros materiais. Por serem baratos e terem propriedades mecânicas atraentes, foram e ainda são produzidos em larga escala e, conseqüentemente, seus grandes volumes em aterros apresentam um desafio para sua reciclagem. Com isso, o objetivo deste estudo foi avaliar a despolimerização de resíduos de poliestireno expandido (EPS) através do uso de micro-ondas e, com o auxílio de dois agentes que possuem carbono em sua constituição para auxiliar na despolimerização: o óxido de grafeno (GO) e o carvão ativado (AC). Foram utilizadas diferentes quantidades de GO e AC (0,125, 0,250, 0,5 g), mantendo sempre a massa da amostra de EPS constante de 1 g. Os testes no forno micro-ondas foram realizados em 3 ciclos de 4 minutos cada, com tempo total de 12 minutos por batelada. Dentro do forno, a amostra foi acondicionada no interior de um balão de fundo redondo envolto com lã de rocha. Para caracterizar o material obtido da despolimerização, realizou-se o balanço de massa para avaliar os rendimentos da despolimerização associada com a Espectroscopia de Infravermelho com Transformada de Fourier (FTIR) e a análise termogravimétrica (TGA). Para a amostra contendo 0,125 g de OG observou-se a formação de uma maior fração sólida, pouca fração gasosa e nenhuma fração líquida. A

amostra com 0,25 g de GO apresentou o melhor rendimento de voláteis, com 22,58 % de voláteis, e foi possível observar tanto a fração líquida quanto a gasosa. Quando AC foi utilizado como catalisador a extensão da despolimerização foi inferior àquela obtida com GO. As amostras com 0,125, 0,25 e 0,5 g de AC renderam frações gasosas de 5,13; 9,16; e 3,06, respectivamente. Na análise de FTIR não foi possível identificar a formação de novas bandas para as amostras tratadas com GO ou AC, em comparação ao EPS. Diferentes picos de degradação, quando comparados ao EPS, foram observados no TGA para amostras que utilizaram GO como catalisador podem estar associados a formação de compostos mais voláteis após a despolimerização. As amostras tratadas com AC apresentaram uma redução menos acentuada na sua estabilidade térmica. Este estudo sugere que a transferência de calor da partícula escura para a amostra de EPS é mais efetiva com a utilização de GO, podendo contribuir para a despolimerização do EPS.

Palavras-chave: Resíduos de poliestireno; Catalisador; Tratamento de resíduos.

Resumen

Los polímeros están cada vez más presentes en la vida cotidiana para sustituir a otros materiales. Debido a que son baratos y tienen propiedades mecánicas atractivas, fueron y aún se producen a gran escala y, en consecuencia, sus grandes volúmenes en los vertederos presentan un desafío para su reciclaje. Así, el objetivo de este estudio fue evaluar la despolimerización de residuos de poliestireno expandido (EPS) mediante el uso de microondas y, con la ayuda de dos agentes que tienen carbono en su constitución para ayudar a la despolimerización: óxido de grafeno (GO) y activado carbono (CA). Se utilizaron diferentes cantidades de GO y AC (0,125, 0,250, 0,5 g), manteniendo siempre constante la masa de la muestra de EPS en 1 g. Las pruebas en el horno de microondas se realizaron en 3 ciclos de 4 minutos cada uno, con un tiempo total de 12 minutos por lote. Dentro del horno, la muestra se colocó dentro de un matraz de fondo redondo envuelto con lana de roca. Para caracterizar el material obtenido de la despolimerización, se realizó un balance de masa para evaluar los rendimientos de despolimerización asociados con la Espectroscopia Infrarroja por Transformada de Fourier (FTIR) y el análisis termogravimétrico (TGA). Para la muestra que contenía 0,125 g de GO, se observó la formación de una mayor fracción sólida, poca fracción gaseosa y ninguna fracción líquida. La muestra con 0,25 g de GO presentó el mejor rendimiento de volátiles, con 22,58% de volátiles, y se pudo observar tanto la fracción líquida como la gaseosa. Cuando se usó AC como catalizador, el grado de despolimerización fue menor que el obtenido con GO. Muestras con 0,125, 0,25 y 0,5 g de AC dieron fracciones gaseosas de 5,13; 9,16; y 3,06, respectivamente. El análisis FTIR para las muestras que contenían GO o AC no fue posible observar la formación de nuevas bandas en comparación con EPS. Se observaron diferentes picos de degradación, en comparación con EPS, en TGA para muestras que utilizaron GO como catalizador, lo que puede estar asociado con la formación de compuestos más volátiles después de la despolimerización. Las muestras tratadas con CA mostraron una reducción menos marcada en su estabilidad térmica. Este estudio sugiere que la transferencia de calor de la partícula oscura a la muestra de EPS es más efectiva con el uso de GO, lo que puede contribuir a la despolimerización de EPS.

Palabras clave: Resíduos de poliestireno; Catalizador; Tratamiento de desechos.

1. Introduction

The continuous increase in the generation of urban solid waste (MSW), together with the population increase, causes concerns regarding its management in order to promote a more sustainable society. Since polymeric materials are present in most things used, they comprise a significant fraction of the waste generated (Streit, 2016). The recycling of polymeric materials constitutes a constant challenge for governments around the world. Mechanical and thermal recycling are the alternatives generally adopted to promote sustainable options for polymer recycling because its incineration emits many harmful gases into the atmosphere, requiring a purification system downstream of the incineration equipment (Adnan & Jan, 2017).

Expanded polystyrene is one of the most used thermoplastic materials for packaging and thermal insulation (Morais & Vidigal, 2021; Silva et al., 2022). Due to its high demand for several industrial sectors, its production is forecast to grow by 5% each year until 2025 (Adnan & Jan, 2017). However, recycle large amounts of EPS wastes still being a challenge. Since, due to its low density, large volume and non-biodegradability, it can take up a lot of space in landfills if it is erroneously disposed of (Bartoli et al., 2015; Kumar et al., 2015). Currently, a viable way to EPS recycling is thermal depolymerization using microwave-assisted pyrolysis. However, this option requires peculiar conditions for obtained valuable products from EPS

waste. The time and temperature are critical parameters, as well as the addition of additives or catalysts (Marco & Poletto, 2022). The usage of materials with high thermal conductivity in the microwave range promotes the EPS waste depolymerization. These materials are normally composed by metals or carbonaceous compounds and are able to absorb the electromagnetic waves and transmit them to the polymer in the form of heat (Bartoli et al., 2015; Menéndez et al., 2010).

Rex et al. (2020) used activated carbon from biomass as catalyst to depolymerization of polystyrene and polypropylene wastes. Microwave pyrolysis occurred at 900 W with a polymer to absorbent ration of 10:1 during 10 min. The highest oil yield of 84.3 wt% was obtained when coconut sheath activated carbon was used as an absorbent. Suriapparao et al. (2021) evaluated the effect of microwave power (300 W, 450 W and 600 W) and graphite susceptor quantity (50 g, 200 g and 350 g) for waste polypropylene microwave pyrolysis. The authors observed that the microwave conversion efficiency (68.1%) is high at high microwave power (600 W) and low susceptor quantity (50 g). Marco and Poletto (2022) evaluated the effect of using carbon black as a catalyst in EPS waste depolymerization using microwave-assisted pyrolysis at 400W for 12 min. Five different catalyst/polymer ratios (0.0125:1, 0.125:1, 0.25:1, 0.5:1, 1:1) were tested. The authors observed that the highest yield of non-condensable gases was obtained at the ratio 0.25:1 with a gaseous yield of 53 wt%.

Based on the literature, the use of GO and AC as catalysts, proposed in this study, are viable alternatives to provide the depolymerization of EPS through microwave-assisted pyrolysis. Given these aspects, the objective of this work is to evaluate the effect of both catalysts and also the effect of different catalyst/polymer ratio to obtain recyclable products presenting a cleaner route for EPS recycling.

2. Methodology

2.1 Materials

Expanded polystyrene wastes were obtained from an industry located at Vila Flores city (Brazil). The powder activated carbon was supplied by Energy and Bioprocesses Laboratory (LEBio) located at University of Caxias do Sul obtained according the methodology adopted by Ferreira et al. (2017) from elephant grass (*Pennisetum purpureum*). Graphene oxide used in this work was previously synthesized by Oliveira et al. (2018) based on the Hummer's method.

2.2 Microwave assisted pyrolysis

The microwave pyrolysis experiment set up with an output power of 400 W. The EPS sample (1g) was added to a borosilicate quartz flask of 500 mL. To connect the borosilicate quartz flask to the condenser a borosilicate adaptor was used. To avoid heat loss the quartz flask was insulated with mineral wool and all joints were sealed using Teflon tape. The experimental setup used in this work is based on a previously published work (Marco and Poletto, 2022).

The effect of graphene oxide (GO) and activated carbon (AC) as catalysts on the microwave pyrolysis of EPS wastes were tested. Two different catalyst (GO or AC) to EPS polymer ratios (0.125:1, 0.25:1, 0.5:1) were investigated. The reaction time was composed by three uninterrupted cycles of 4 min each and totalized 12 min for samples treated with AC and treated with 0.125 g of GO. The samples treated with 0.25 g and 0.5 g were exposed to only one treatment cycle. The experiments were done in triplicate and the gas yield was determined by mass balance. A sample from the oil formed after microwave pyrolysis was collected from the top of the liquid fraction using a pipette.

2.3 Catalyst and product oil characterization

The morphology of each catalyst used in microwave-assisted pyrolysis was observed using scanning electron microscopy (SEM) analysis by means of SEM-FEG Tescan Mira 3 equipment. The surface area of each catalyst was

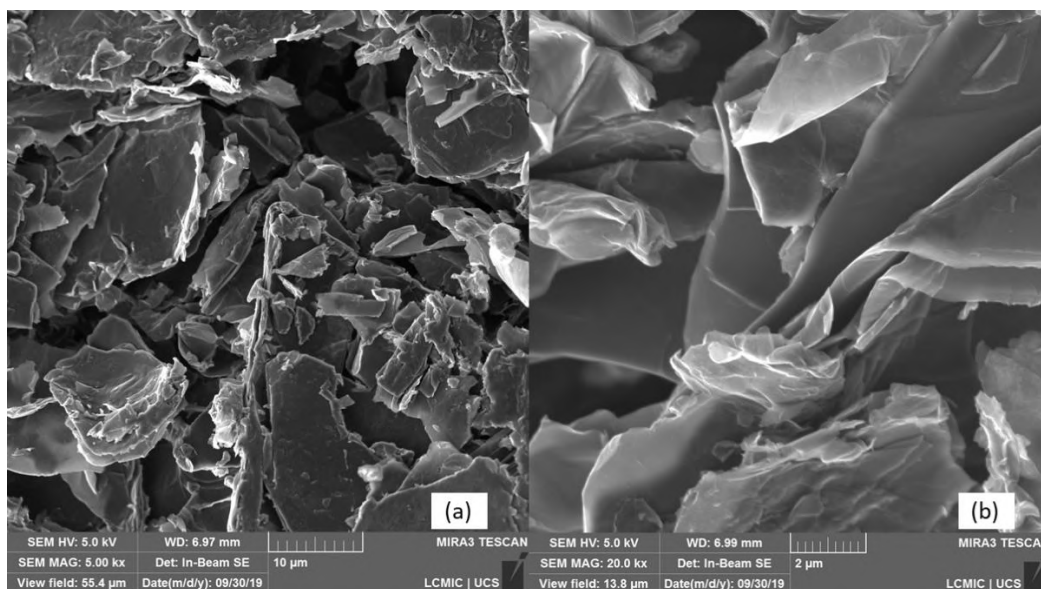
determined using the Langmuir and Brunauer-Emmett-Teller (BET) isotherms on a Quantachrome Instruments Nova 1200e by adsorption of N_2 at 77K. The oil obtained after depolymerization was evaluated by means of Fourier-transform infrared spectroscopy and thermogravimetric analysis. FTIR measurements were performed in a Nicolet IS10 Thermo Scientific instrument, in the range of 4000 to 400 cm^{-1} , through the average of 32 scans. TGA was carried out under a N_2 atmosphere, with a gas flow of 50 $mL \cdot min^{-1}$, at a temperature range of 25 to 800 $^{\circ}C$ using a heating rate of 10 $^{\circ}C \cdot min^{-1}$. The analysis was performed on a Shimadzu model TGA-50 instrument.

3. Results and Discussion

3.1 Catalyst characterization

Figure 1 (a) and (b) shows the SEM micrographs, with magnifications of 5,000 and 20,000 times, of the graphene oxide sample.

Figure 1 – Morphology of GO samples with magnifications of 5,000 (a) and 20,000 (b) times.

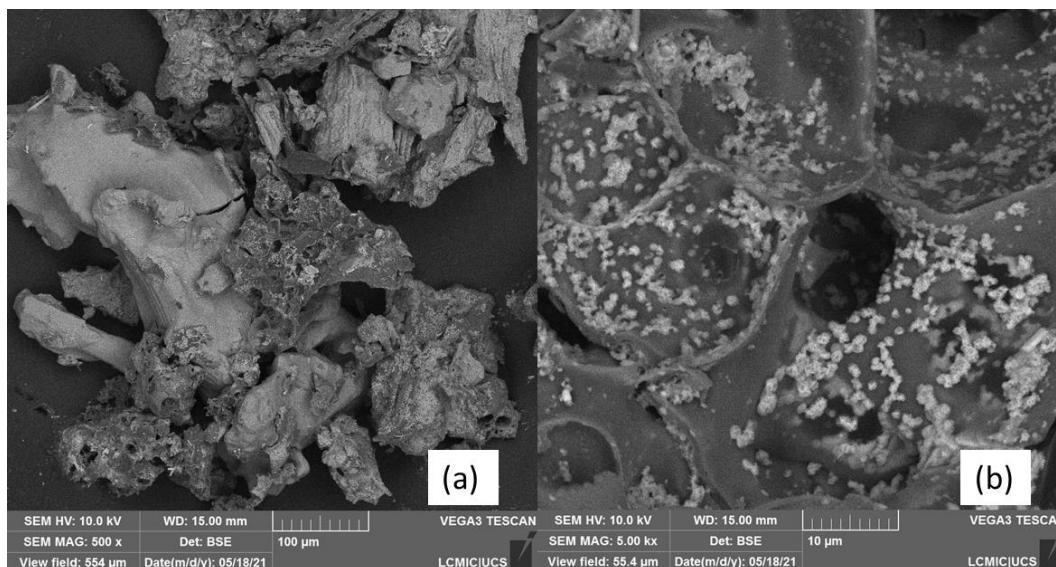


Source: Authors (2022).

As can be seen in Figure 1(a) the morphology of GO is composed by nanoplatelets. The GO is a material similar to a thin film, composed of several lamellae or nanoplatelets. This lamellar structure, with a high surface area, is characteristic of this type of compound (Oliveira et al., 2018).

Figure 2 shows the SEM micrographs, with magnifications of 500 and 5,000 times, of the activated carbon sample.

Figure 2 – Morphology of AC samples with magnifications of 500 (a) and 5,000 (b) times.



Source: Authors (2022).

It can be seen in Figure 2 that the morphology of the AC presented rough characteristics and a large number of pores, which give it a high surface area. This rough characteristic associated with a large number of pores is common in raw materials originating from lignocellulosic fibers, such as elephant grass (*Pennisetum purpureum*), and also by the thermal degradation processes (pyrolysis/gasification) that the sample is subjected to until obtaining activated carbon. Both the pyrolysis process and the gasification process involve high temperatures associated with the partial or total absence of oxygen which, under these conditions, favor the release of volatile matter present in the plant structure, thus conferring this characteristic structure. According to Pinto et al. (2013), the high number of pores gives activated carbon its high surface area which, in most coals, varies from 200 to 1500 m².g⁻¹.

Based on the results obtained from the BET analysis the superficial area of GO is 34 ± 2 m².g⁻¹ while AC presented a superficial area equal to 438 ± 6 m².g⁻¹. The AC presented a high surface area, about 10 times greater than the GO. This result is unexpected. However, a possible explanation for this result may be associated with a non complete separation of the GO nanoplatelets. Higher surface area may result in higher space for the incidence of energy from the microwave oven, allowing a greater amount for its transformation into heat (Bhattacharya & Basak, 2016; Rosi et al., 2018), which can result in a decrease of the time to promote EPS degradation during microwave assisted pyrolysis. The dielectric characteristic of the susceptor used can accelerate the depolymerization process and also generate uncontrolled reactions resulting in polymer degradation (Li et al., 2019; Hussain et al., 2012). One factor that affected the surface area of the GO was possibly the electrostatic attraction between the nanoplatelets, keeping them overlapping and, thus, generating a denser final structure (Oliveira et al., 2018, Lavoratti et al., 2019).

3.2 Microwave assisted pyrolysis results

The results of the gaseous fraction formed after microwave assisted pyrolysis were presented in Table 1. The utilization of 0.125 g of GO generated a volatile content of 1.43 ± 0.65 %, while the use of 0.250 g of GO generated a volatile content of 22.58 ± 2.24 %. The addition of 0.500g of GO promoted a severe EPS degradation. It was possible to observe small sparks inside the oven in the first seconds after the start of the test. An intense formation of gas was also observed, and the test was immediately stopped when these conditions were verified. Possibly due to the high amount of GO and its high radiation

absorption capacity and the subsequent transformation of microwaves into heat, the temperature inside the borosilicate quartz flask reached values above 300 °C, which were sufficient to volatilize the EPS even with a few seconds of testing, but it also generated enough heat to crack the borosilicate quartz flask and generate sparks during the experiment. Thus, it was decided not to use this test condition anymore during the experiments.

Table 1 – Gaseous fraction formed after microwave assisted pyrolysis.

Samples	Gaseous fraction (%)
EPS/GO0.125	1.43 ± 0.65
EPS/GO0.250	22.58 ± 2.24
EPS/AC0.125	5.13 ± 0.56
EPS/AC0.250	9.16 ± 0.69
EPS/AC0.500	3.06 ± 0.01

Source: Authors (2022).

The sample with the addition of 0.125 g of GO showed lower volatile yield. On the other hand, when 0.250 g of GO was added best results were obtained. A time of 4 min was used, which represents only one cycle of exposure to radiation, since the maximum time for each cycle used in the equipment is only 4 min. With this condition, it was possible to observe the formation of gas and small droplets inside the flask, in addition to the solid fraction. When the microwaves incident on the EPS GO mixture, the GO nanoparticles absorbed the energy and a localized raise in temperature and pressure around the GO nanoparticles occurs and promoting EPS decomposition with the release of pyrolysed compounds. Larger quantities of GO catalyst may generate an uncontrolled and excessive cracking of the feedstock (Suriapparao et al., 2021) in a short time which may result in the formation of undesirable reaction components and excessive polymer degradation. The results shows that GO is an efficient catalyst to promote EPS depolymerization in low microwave exposition time. In a previous study, Marco and Poletto (2022) using the same apparatus, but with carbon black catalyst, obtained a gaseous fraction of approximately 54% using a exposure time three times higher.

The AC was not so efficient to promote EPS depolymerization in the conditions used during the tests. The addition of 0.125, 0.250 and 0.500 g of AC to EPS sample generated a gaseous fraction of 5.13 ± 0.56%, 9.16 ± 0.69% and 3.06 ± 0.01, respectively. When 0.250 g of AC was used an increase in volatile content around two times higher than the sample with 0.125 g was observed. When the mass of coal added in the flask was increased twice the gaseous fraction also increase by the same factor. A high amount of AC may promote higher energy absorption from the microwave by the catalyst that can transfer its energy to the EPS sample. However, the addition of 0.500g of AC not increased the amount of volatiles generated, showing a non-linear behavior. As showed in Figure 2 AC is formed by a porous structure with higher internal pore area than GO. An increase in the AC content may not result in an increase of the specific incident energy on the catalyst particles due its porous structure reducing the gaseous fraction formed during microwave pyrolysis.

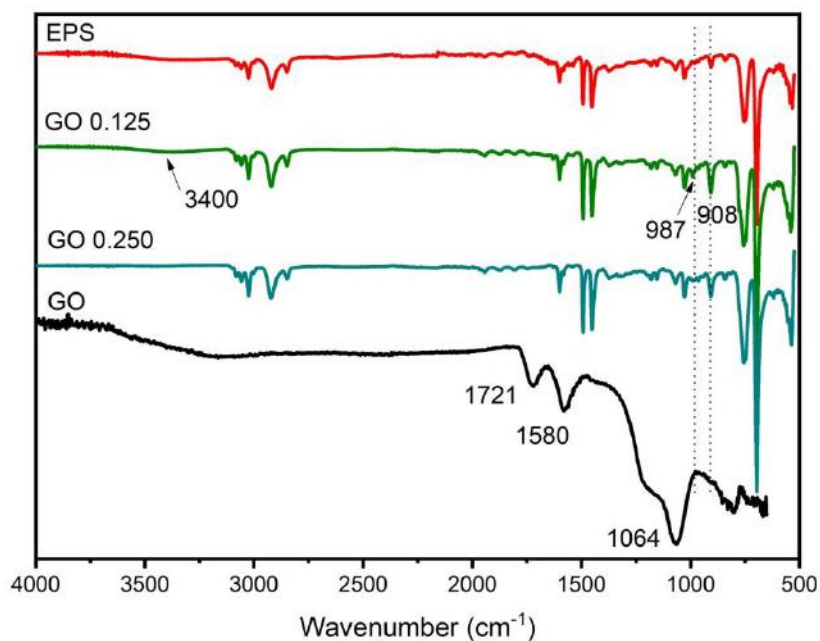
Bartoli et al. (2015) performed experiments involving the depolymerization of polystyrene by microwave-assisted pyrolysis with two depolymerization agents: a carbon powder from tires and silicon carbide. In a system with the control of factors such as pressure, nitrogen flow and microwave power, a yield of 94.3% of liquid fraction was obtained. In this test, 101.2 g of polystyrene and carbon powder were used at a ratio (PS/carbon) of 2.21, with a time of 28 min. The authors observed that a lower pressure inside the reactor increased the formation of liquid and gaseous fraction, as well as temperatures at around 800 °C. Prathiba et al. (2018) also carried out microwave assisted pyrolysis of EPS. The sample was placed in a quartz flask coated with glass wool, with a condensation system at the end of the process and the depolymerization agent also

was AC with surface area of $692 \text{ m}^2 \cdot \text{g}^{-1}$. A EPS/AC ratio of 10:1 was used at a temperature of $418 \text{ }^\circ\text{C}$ for 1 h, generating an oil yield of 93%. However, it can be observed that the yield of the gaseous fraction suffered a drop with the increase in the amount of the depolymerization agent and temperatures below $400 \text{ }^\circ\text{C}$ contribute even more to its decrease. Undri et al. (2013) also using microwave depolymerization with carbon as the depolymerization agent by varying microwave power, residence time and amounts of PS/charcoal. The authors obtained a liquid fraction of 66% of styrene with a reaction time of 22 min EPS/charcoal ratio of 2:1, reaching a temperature of $407 \text{ }^\circ\text{C}$. The authors reports that with lower microwave powers they help in the yield of the liquid fraction, while higher powers help in the formation of the remaining solid due to its high capacity to heat the sample.

3.3 FTIR characterization of liquid fraction

Figure 3 shows the FTIR spectra of EPS, GO and samples obtained after depolymerization. The EPS sample treated with 0.125 g of GO presented two new bands at 987 cm^{-1} and 908 cm^{-1} that are marked in Figure 3. The spectrum of the EPS sample treated with 0.250 g of GO are similar to that obtained using 0.125 g of GO.

Figure 3 – FTIR spectra of EPS waste, GO and liquid fraction samples after microwave pyrolysis.

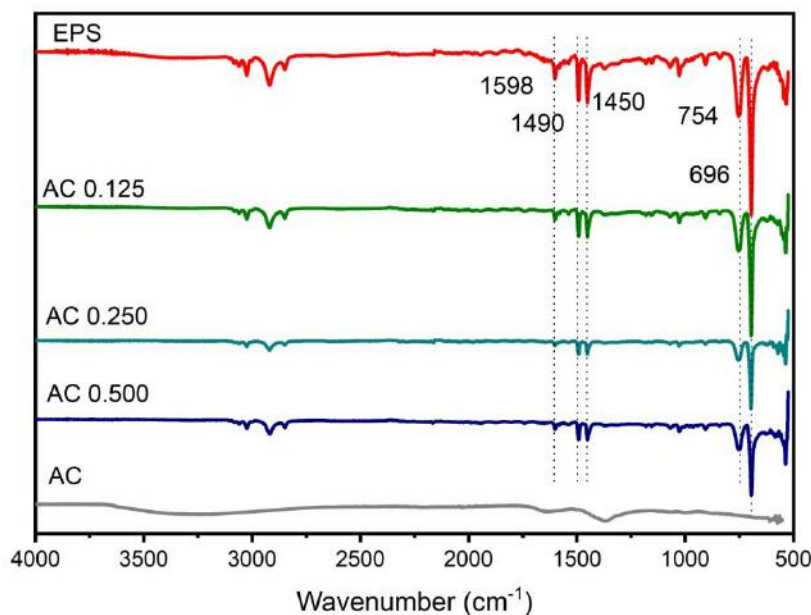


Source: Authors (2022).

The bands at 987 cm^{-1} and 908 cm^{-1} are assigned to the out-of-plane vinyl group C-H bond (Undri et al., 2013; Mo et al., 2013). The weak band at 3400 cm^{-1} for EPS sample treated with 0.125 g of GO are assigned to the hydroxyl groups (Undri et al., 2013) and may be associated with traces of GO in the EPS sample after depolymerization. The bands obtained for EPS sample and EPS samples after exposed to microwave radiation using GO as catalyst are basically the same. It was not possible to identify the formation of new band after microwave radiation treatment.

The FTIR results of EPS, AC and samples obtained after depolymerization can be seen in Figure 4.

Figure 4 – FTIR spectra of EPS waste, AC and liquid fraction samples after microwave pyrolysis.



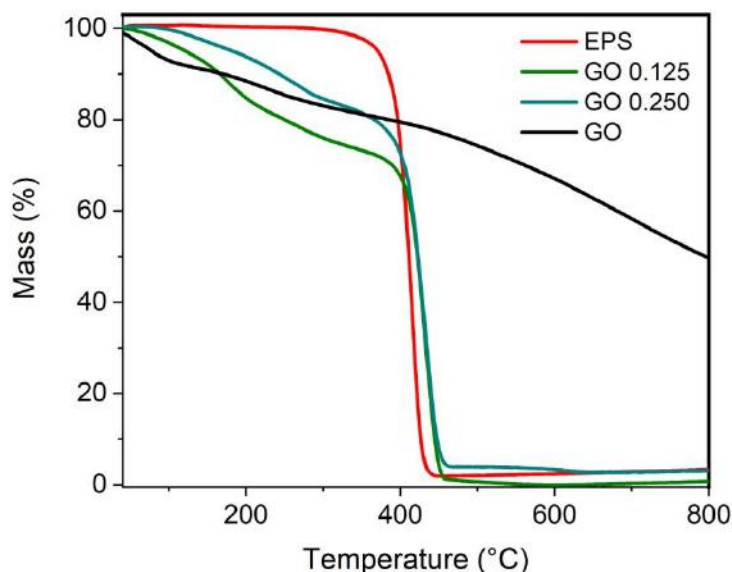
Source: Authors (2022).

The depolymerization of the samples containing AC presented bands practically identical to the EPS sample. Based on these results it is possible that did not occurred EPS depolymerization in the conditions tested or, at least, it was not possible to identify any type polymer depolymerization. This results is in agreement with the lower volatile yield obtained when AC was used, corroborating that AC was not so efficient to promote EPS depolymerization in the test conditions.

3.4 TGA characterization of liquid fraction

The thermogravimetric results for EPS, GO and samples treated with GO are showed in Figure 5. The samples treated with GO showed a decrease in thermal stability, when compared with EPS. After EPS depolymerization low molar mass compounds were formed and these compounds may volatilized at relatively low temperature, as can be seen in Figure 5. The sample treated with 0.125 g of GO showed a more pronounced decrease in its thermal stability than the sample treated with 0.250 g of GO. This result may be associated with the fact that sample treated with 0.125 g of GO was exposed to radiation for 12 min, while sample treated with 0.250 g of GO remained only 4 min in the microwave. As the time exposed to microwave radiation is higher for sample treated with 0.125 g when compared with sample treated with 0.250 g of GO, more time to initiate and propagate degradation reactions may generate chemical compounds with lower molar mass which result in lower thermal stability, as observed in Figure 5 for EPS sample treated with 0.125 g of GO.

Figure 5 – Thermogravimetric results of EPS, GO and samples treated with GO after microwave pyrolysis.



Source: Authors (2022).

It can also be seen in Figure 5 that the GO sample presented three mass loss events. The first between 25°C and 100 °C, the second between 100°C and 280 °C representing a loss of 10% of its mass and, finally, there is a slower degradation from 280°C to 800 °C with a loss of approximately 30%. These events are previously related to Oliveira et al. (2018) which can be associated with the loss of moisture in the sample, the degradation of hydroxyls, carbonyls or other groups and, the last one, with the combustion of aromatic rings, respectively. The EPS sample showed only one mass loss event between 300 °C and 450 °C. This event, typical of EPS, represents the decomposition of its structure (Prathiba et al., 2018).

Table 2 presented a detailed assessment of the TGA analysis for samples treated with GO. The $T_{3\%}$ is the temperature of 3% of mass loss for each sample. T_{Peak} is the peak temperature, that is, the temperature of maximum degradation of the sample. The samples depolymerized with GO presented a mass loss event at 177 °C for the GO 0.125 sample and for the GO 0.250 sample this event was shifted to 276 °C. The occurrence of a mass loss event at intermediate temperatures between the peak temperatures of GO and EPS indicates the formation of intermediate compounds. Probably were compounds with low molar mass in relation to EPS, which may have originated from its depolymerization.

Table 2 – Thermogravimetric results of EPS, GO and liquid fraction samples after microwave pyrolysis.

	$T_{3\%}$ (°C)	$T_{Peak 1}$ (°C)	$T_{Peak 2}$ (°C)	Ash at 800 °C (%)
EPS	358	---	421	3.3
GO	60	80	229	49.7
EPS/GO0.125	98	177	433	0.8
EPS/GO0.250	151	276	433	3.1

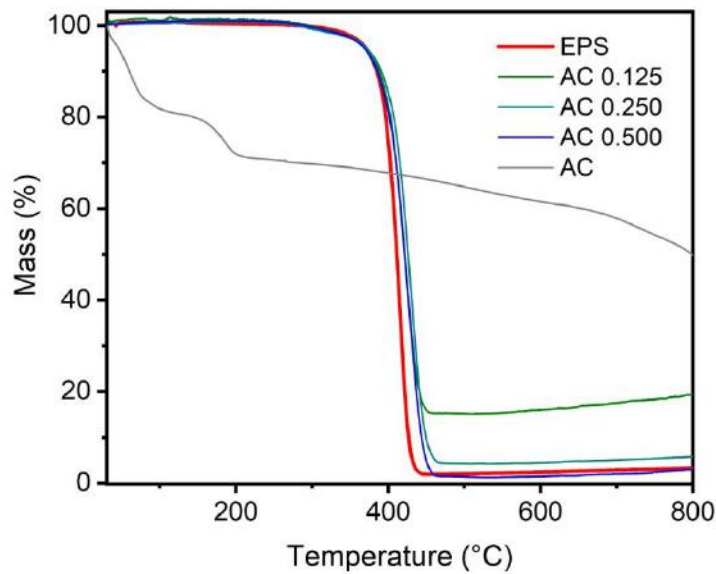
Where: $T_{3\%}$: temperature of 3 wt% of mass loss; T_{Peak} : peak temperature. Source: Authors (2022).

The higher peak temperature for the sample with 0.25 g of GO in relation to the sample with 0.125 g, may be related to the shorter depolymerization time to which the GO 0.250 sample was submitted. Thus, depolymerization occurred to a lesser extent, generating compounds of higher molar mass, which would lead to an increase in $T_{Peak 1}$. This fact may also be reflecting in the ash content, as shown in Table 2. $T_{Peak 2}$ did not vary between the samples that had the addition of GO, since variations

of $\pm 5^\circ\text{C}$ in the TGA can be the error of the equipment. This behavior may indicate that an amount of non-depolymerized EPS still remains, since this temperature is related to the maximum degradation temperature of EPS.

Figure 6 shows the thermogravimetric results for EPS, AC and samples treated with AC. The thermal stability of all samples treated with AC was quite similar to the EPS. A more pronounced thermal degradation for EPS and all samples treated with AC initiate at around 400°C , while AC presented three events of mass loss.

Figure 6 – Thermogravimetric results of EPS, AC and samples treated with AC after microwave pyrolysis.



Source: Authors (2022).

The AC sample presented a mass loss event from room temperature to approximately 110°C , with a mass loss equal to 20% and maximum degradation temperature at 60°C . A second event occurred between $110\text{--}210^\circ\text{C}$ with 10% of mass loss and maximum degradation temperature at 184°C . Finally, slower degradation occurs from 210°C to 800°C . Generally, the first event of mass loss is associated with the loss of moisture present in the sample and the others, according to Hayashi et al. (2002), are due to reactions between the carbon present and the K_2CO_3 used to promote the activation of the char. The other samples involving EPS with AC showed no differences in relation to the EPS sample. Table 3 presents a more detailed assessment of the TGA analysis of samples treated with AC.

Table 3 –Thermogravimetric results of EPS, AC and liquid fraction samples after microwave pyrolysis

	$T_{3\%}$ ($^\circ\text{C}$)	T_{Peak} ($^\circ\text{C}$)	Ash at 800°C (%)
EPS	358	421	3,3
AC	38	184	49,8
EPS/AC0.125	357	423	19.3
EPS/AC0.250	355	426	5.8
EPS/AC0.500	354	427	2.9

Source: Authors (2022).

Based on the results presented in Table 3 it was evident that no significant changes in decomposition temperatures were observed for EPS samples depolymerized with AC. Small differences can be attributed to equipment variations. The ash

content showed differences between the samples. The depolymerized samples may have been contaminated with inorganic salt, possibly K_2CO_3 , which is generally used to promote the activation of the char. As observed in FTIR results the TGA analyzes did not prove the depolymerization of EPS with the use of AC.

4. Conclusion

Microwave depolymerization is an alternative process for recycling expanded polystyrene, converting it into more attractive compounds. However, it needs some other material capable of absorbing the radiation and transforming it into heat so that depolymerization can occur, since the polymer in question lacks this characteristic by itself. In this work it was proposed the use of two catalysts to assist with the absorption of microwaves, graphene oxide and activated carbon. In principle, the results suggest that the heat transfer from the dark particle to the EPS sample is more effective with the use of GO.

The test with 0.25 g of GO generates the best condition with a yield of around 23% of volatiles, with the formation of a liquid and a dense gaseous phase. When AC was used a volatile content of 9% was obtained with the addition of 0.25 g of AC. EPS samples treated with GO also showed a decrease in their thermal stability. The results demonstrate that AC is not efficient to generate EPS depolymerization via microwave assisted pyrolysis in the condition used in the tests done in this work, while the usage of GO as a catalyst is viable option to convert EPS wastes into useful products.

Acknowledgments

The authors would like to thank Universidade de Caxias do Sul.

References

- Adnan, J.S. & Jan, M.R. (2017). Recovery of valuable hydrocarbons from waste polystyrene using zinc supported catalysts. *Journal of Polymers and the Environment*, Vol. 25, pp. 759-769.
- Bartoli, M., Rosi, L., Frediani, M., Undri, A., & Frediani, P. (2015). Depolymerization of polystyrene at reduced pressure through a microwave assisted pyrolysis. *Journal of Analytical and Applied Pyrolysis*, Vol. 113, pp. 281-287.
- Bhattacharya, M. & Basak, T. (2016). A review on the susceptor assisted microwave processing of materials. *Energy*, Vol. 97, pp. 306-338.
- Ferreira, S.D.; Bassanesi, G.R.; Lazzaroto, I.P.; Poletto, P.; Godinho, M. & Osório, E. (2017). Preparação e caracterização de carvão quimicamente ativado com K_2CO_3 a partir do biochar de capim elefante. *57º Congresso Brasileiro de Química*. Gramado-RS.
- Hayashi, J.; Uchibayashi, M.; Horikawa, T.; Muroyama, K. & Gomes, V.G. (2002). Synthesizing activated carbons from resins by chemical activation with K_2CO_3 . *Carbon*, Vol 40, n. 15, p. 2747-2752.
- Hussain, Z., Mohammed Khan, K., Perveen, S., Hussain, K., & Voelter, W. (2012). The conversion of waste polystyrene into useful hydrocarbons by microwave-metal interaction pyrolysis. *Fuel Processing Technology*, Vol. 94, No 1, pp. 145-150.
- Kumar, P.S.; Bharathikumar, M.; Prabhakaram, C.; Vijavam, S. & Ramakrishnan, K. (2015). Conversion of waste plastics into low-emissive hydrocarbon fuels through catalytic depolymerization in a new laboratory scale batch reactor. *International Journal of Energy and Environmental Engineering*, Vol. 8, pp. 167-173.
- Lavoratti, A.; Zattera, A.J.; Amico, S.C. (2019). Mechanical and dynamic-mechanical properties of silanized graphene oxide/epoxy composites. *Journal of Polymer Research*, Vol. 26, 140, pp. 1-10.
- Li, K., Chen, J., Chen, G., Peng, J., Ruan, R., & Srinivasakannan C. (2019). Microwave dielectric properties and thermochemical characteristics of the mixtures of walnut shell and manganese ore. *Bioresource Technology*, Vol 286, pp.121381.
- Marco, P.de. & Poletto, M. (2022). Microwave assisted pyrolysis of expanded polystyrene waste using carbon black catalyst. *Research, Society and Development*, v. 11, n. 11, p. e518111134058.
- Menéndez, J.A, Arenillas, A., Fidalgo, B., Fernández, Y., Zubizarreta, L., Calvo, E.G., & Bermudez Menendez, J. (2010). Microwave heating processes involving carbon materials. *Fuel Processing Technology*, Vol 91, pp. 1-8.
- Mo, Y., Zhao, L., Chen, C.L., Tan, G.Y.A., & Wang, J-Y. (2013). Comparative pyrolysis upcycling of polystyrene waste: thermodynamics, kinetics, and product evolution profile. *Journal of Thermal Analysis and Calorimetry*, Vol. 111, pp. 781-788.

Morais, M. de O. & Vidigal, H. (2021). The reverse logistics process applied to the EPS product (ISOPOR). *Research, Society and Development*, Vol. 10, n. 2, p. e52910212908.

Oliveira, M. de; Poletto, M. & Severo, T.C. (2018). Rota química para produção de óxido de grafeno a partir de oxidação do grafite comercial. *Revista Interdisciplinar de Ciência Aplicada*, Vol. 3. pp. 16-20.

Pinto, M.V.S.; Silva, D.L.; Saraiva, A.C.F. (2013). Obtenção e caracterização de carvão ativado de caroço de buriti (*Mauritia flexuosa* L. f.) para a avaliação do processo de adsorção de cobre (II). *Acta Amazonica*, Vol. 43, n. 1, p. 73-80.

Prathiba, R., Shruthi, M., & Miranda, L.R. (2018). Pyrolysis of polystyrene waste in the presence of activated carbon in conventional and microwave heating using modified thermocouple. *Waste Management*, Vol. 76, pp. 528-536.

Rosi, L., Bartoli, M., & Frediani, M. (2018). Microwave assisted pyrolysis of halogenated plastics recovered from waste computers. *Waste Management*, Vol. 73, pp. 511-522.

Silva, J. C. da ., Santos, L. J. da C. ., Lustosa, S. M. C. ., Silva, G. de A. ., Paz, G. M. da ., Viana, D. dos S. F. & Viana, V. G. F. (2022) Thermal and toxicological analysis of commercial polystyrene with recycled polystyrene, *Research, Society and Development*, Vol. 11, No1, p. e55911124904.

Streit, A.F.M. (2016). Resíduos Poliméricos: quantificação, caracterização, lavagem e tratamento do efluente gerado no processo. 2016. 126 f. Dissertação (mestrado em engenharia química) – Universidade Federal de Santa Maria. Santa Maria.

Suriapparao, D.V., Nagababu, G., Yerrayya, A., & Sridevi, V. (2021). Optimization of microwave power and graphite susceptor quantity for waste polypropylene microwave pyrolysis. *Process Safety and Environmental Protection*, Vol. 149, pp 234-243.

Undri, A., Frediani, M., Rosi, L., & Frediani, P. (2014). Reverse polymerization of waste polystyrene through microwave assisted pyrolysis. *Journal of Analytical and Applied Pyrolysis*, Vol. 105, pp. 35-42.

Rex, P., Masilamani, I.P., & Miranda, L.M. (2020). Microwave pyrolysis of polystyrene and polypropylene mixtures using different activated carbon from biomass. *Journal of the Energy Institute*, Vol. 93, No 5, pp .1819-1832.