Acta Scientiarum
http://periodicos.uem.br/ojs/acta
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v41i1.37303

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CHEMICAL ENGINEERING

Synthesis of metal nanoparticles for use as nanocatalysts in pet recycling

Luciana Cristina Soto Herek Rezende[1*], Jean Halison de Oliveira[2], Vanessa Paola Miranda Zart[2], Murilo Pereira Moisés[2], Guilherme Piovezan Otto[2] and Sílvia Luciana Fávaro[2]

[1]Programa de Pós-Graduação em Tecnologias Limpas, Instituto Cesumar de Ciência, Tecnologia e Inovação, Centro Universitário de Maringá, Avenida Guedner, 1610, 87050-390, Maringá, Paraná, Brazil. [2]Departamento de Química, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900, Maringá, Paraná, Brazil. *Author for correspondence. E-mail: lucianarezende17@gmail.com

ABSTRACT. This study investigated the efficiency of nickel nanocatalysts in the degree of PET conversion, under different conditions. The nanocatalysts were synthesized by the Pechini method at 500, 700 and 900°C. PET depolymerization, via chemical glycolysis, was tested with varying time (3, 4 and 5 hours) and amount of catalyst (10, 35 and 60 mg). In order to evaluate the efficiency of these catalysts in PET depolymerization reactions, we followed a 2^3 factorial design with central point and applied a statistical analysis of variance (ANOVA). To optimize the degree of PET conversion, it was suggested to use 10 mg catalyst with 5h reaction time. Nickel nanocatalysts presented satisfactory results due to the possibility of using small amounts of catalyst, synthesized at low temperature, thus achieving a degree of conversion greater than 90%.

Keywords: poly(ethylene terephthalate); depolymerization; nickel.

Received on May 22, 2017.
Accepted on November 22, 2017

Introduction

PET (polyethylene terephthalate) is a thermoplastic polymer of commercial importance and has been widely used in several segments of the world industry, mainly in the production of plastics, fibers and films (Katoch, Sharma, Kundu, & Bera, 2012). This versatility is due to its excellent physical and chemical properties (Pacheco-Torgal, Ding, & Jalali, 2012).

Poly (ethylene terephthalate) can be produced from two initial reactions: by esterification, in which terephthalic acid (TPA) reacts with ethylene glycol (EG), and also by the transesterification reaction, by reacting dimethyl terephthalate (DTM) with ethylene glycol (EG) (Torrik, Nejati, & Soleimani, 2014).

Although the mechanical recycling is the most common, the chemical glycolysis of poly(ethylene terephthalate) is the most economical and environmentally friendly method, due to the possibility of obtaining and reusing its monomer, aiming at the use of the prepolymer in the repolymerization of PET. This prepolymer is reused in the production of plastics and/or other materials (Sinha, Patel, & Patel, 2010). Thus, a commercial value is added to the residue from the depolymerization reaction (Fernández-García, Martínez-Arias, Hanson, & Rodriguez, 2004).

Much attention has been given to glycolysis by ethylene glycol, and the effect of different parameters on the speed of the reaction is investigated (Chen, Chen, Lo, Mao, & Liao, 2001; Pingale, Palekar, & Shukla, 2010; López-Fonseca, Duque-Ingunza, Rivas, Arnaiz, & Gutiérrez-Ortiz, 2010). Glycolysis can occur both under pressure and atmospheric pressure (Abdelaal, Sobahi, & Makki, 2011). The use of tensoactive molecules in interfacial and superficial reactions is a good alternative for the chemical depolymerization processes of PET, being able to optimize the time and the reaction temperature (di Souza, Torres, & Filho, 2008; Vanini, Castro, Silva Filho, & Romão, 2013).

Glycolysis consists of a molecular depolymerization process by transesterification between the ester groups of PET and a diol (Duque-Ingunza, López-Fonseca, Rivas, & Gutiérrez-Ortiz, 2013; Vanini et al., 2013). The diol used in this study was ethylene glycol (EG) in order to obtain the bis (2-hydroxyethyl) terephthalate-BHET monomer.

Oxide nanoparticles may have unique chemical properties due to their reduced size and high density of surface sites (Ge, Zhu, Zhao, Li, & Liu, 2012). The glycolysis reaction can be catalyzed by metal salts such as acetate, carbonate, sulfate, chloride, etc. Researchers have recently made efforts to use oxide nanoparticles and composites (López-Fonseca, Duque-Ingunza, Rivas, Flores-Giraldo, & Gutiérrez-Ortiz, 2011; Bartolome, Imran, Cho, Al-Masry, & Kim, 2012; Imran et al., 2013). The advantages of oxide and composite nanoparticles are their high selectivity to convert PET into BHET and its reusability (Yue, Zhao, Ma, & Gong, 2012).

Nanocatalysts have a high specific area, which increases the contact between the reactants and the surface of the catalyst, allowing a great increase in the catalytic activity. In addition, they can be easily separable from the reaction medium due to their insolubility (Chaturvedi, Dave, & Shah, 2012).

Thus, the goal of this study was to investigate, under different conditions, the efficiency of nickel nanocatalysts in the chemical recycling of PET, via glycolytic reaction.

Material and methods

Synthesis of nanocatalysts

Nanoparticles were synthesized using the Pechini method (Costa, Vilar, Lira, Kiminami, & Gama, 2006). Initially, nickel nitrate (Sigma-Aldrich 97%) and citric acid (Anidrol PA) (1: 4) were added to a beaker, thus forming chelates between the metal salt and the hydrocarboxylic acid, resulting in a metal citrate. Then, the ethylene glycol (1:16) was added to promote the polymerization reaction with the citrate formed. The temperature of the system was raised to approximately 110°C. The reaction resulted in a highly viscous, gel-like polymer resin (Yue et al., 2012).

Gel was then transferred to a porcelain capsule, which was heated at 250°C in a muffle furnace for two hours. The material formed (called puff) was macerated. The capsule was then heated again at 500, 700 and 900°C for 5 hours. In this step, the formation of nanostructured metallic oxides occurred (Ribeiro & Souza, 2011).

Depolymerization of PET - polyethylene terephthalate

After synthesizing, nickel oxide nanoparticles were used as a catalyst in the depolymerization reaction of poly(ethylene terephthalate) via glycolysis. The work was developed following a 2^3 full factorial design with central point obtained through the Design-Expert® software. The applied variables were: the synthesis temperature of nanocatalysts, the time of depolymerization reaction and the amount, in mass, of nanoparticles used.

The depolymerization via glycolysis was performed in the presence of 100 mL ethylene glycol and a predetermined variable amount of the nanocatalyst. The mass of PET added was defined as 4 g. The reaction temperature was set at 185°C at ambient pressure.

At the end of the reaction, the solution was vacuum filtered, yielding the non-depolymerized poly(ethylene terephthalate). The remaining liquid, filtered, was stored for 24 hours at low temperature to precipitate bis (2-hydroxyethyl) terephthalate-BHET. This stored liquid was then filtered again, obtaining in the filter the solid BHET. Both products (non-depolymerized PET and BHET) were oven-dried at approximately 50°C for 24 hours, so that the masses were subsequently checked and analyzed.

Factorial design

In the factorial design (Barros Neto, Scarminio, & Bruns, 2001; Bussab & Morettin, 2003), we used as variables those applied in the depolymerization of PET. Each of these factors has two levels (upper and lower) with central point. Therefore, we used a 2^3 factorial design with central point, represented in Table 1.

The project was developed with the use of nickel nanocatalysts. The experiments were conducted in random order and in duplicate, totaling 20 experiments. Table 2 lists the conditions used for each experiment.

Table 1. Levels of factors used in the 2^3 full factorial design for PET glycolysis.

Factor	Name	Unit	Level (-1)	Level (0)	Level (+1)
A	Synthesis temperature	°C	500	700	900
B	Time	hours	3.0	4.0	5.0
C	Amount	mg	10	35	60

Table 2. 2^3 full factorial design, in duplicate, with central point.

Sample	(A) Temperature/ °C	(B) Time/ hours	(C) Catalyst/ mg
1 and 2	(-1) 500	(-1) 3.0	(-1) 10
3 and 4	(+1) 900	(-1) 3.0	(-1) 10
5 and 6	(-1) 500	(+1) 5.0	(-1) 10
7 and 8	(+1) 900	(+1) 5.0	(-1) 10
9 and 10	(-1) 500	(-1) 3.0	(+1) 60
11 and 12	(+1) 900	(-1) 3.0	(+1) 60
13 and 14	(-1) 500	(+1) 5.0	(+1) 60
15 and 16	(+1) 900	(+1) 5.0	(+1) 60
17 and 18	(0) 700	(0) 4.0	(0) 35
19 and 20	(0) 700	(0) 4.0	(0) 35

Characterization of nanocatalysts

The nickel oxide nanocatalysts were characterized by X-ray diffraction using a Shimadzu diffractometer model D6000, Cukα source with 30 mA and 40 kV, with velocity 2.0000 degrees/min, in the range of $10.000 \leqslant \theta \leqslant 80.000$.

Transmission electron microscopy analysis for the nanocatalysts was performed on a Shimadzu electron microscope JEM 1400.

Characterization of the product obtained (BHET)

Bis (2-hydroxyethyl) terephthalate (BHET) was characterized by infrared spectroscopy with attenuated total reflectance with Fourier transform (FTIR-ATR). The infrared spectrophotometer used, BomemMichelson MB - 100, was operated in the region of 4000 to - 0.5 cm^{-1}, with a resolution of 4 cm^{-1}.

BHET was also used by DSC using a DSC 20 equipment from TA Instruments.

Results and discussion

After determining the masses, the degree of conversion of the depolymerization via chemical glycolysis of the PET was calculated. The results obtained are presented in Table 3, with conversion values varying from 32 to 96%.

Table 4 lists the values obtained by the analysis of variance (ANOVA) of the 2^3 factorial, obtained from Design-Expert® software. P-values (Prob > F) of less than 0.0500 indicate that the terms of the model are significant. In this case, only the terms B and AB are significant for the model.

The F value of the model (7.67) implies that the model is significant. There is only 0.12% chance that the result was random, or due to noise, which is desirable. However, the values of F (104.71) and P (< 0.0001) of the 'lack of fit' indicate significance. However, a significant lack of fit is undesirable, since we want an adjustable model in order to obtain predictions.

Among the significant effects, the sum of squares indicate which are the most influential. It is observed from Table 4 that the effect B (time) is the most influential for the model, followed by the AB interaction.

The analysis of significance can be confirmed by the semi-normal graph, shown in Figure 1a, which shows that no factor is in the normal line, where the error estimate is represented. The most influential effects are at greater distances from the normal line. Time (B) is the most influential factor, positively influencing depolymerization. The interaction between temperature and time (AB) also influenced positively the degree of conversion, as well as the ABC interaction. Other factors and interactions had a negative effect n the degree of depolymerization of PET.

Figure 1b shows the residues obtained through analysis of variance (ANOVA). Data are distributed almost linearly within a normal analysis, which also proves the good conformation of the data. The values used for optimization of the PET depolymerization process using nickel nanocatalysts are presented in Table 5.

From these values, 100 solutions were found to maximize results. Two of them presented a greater degree of adequacy (Table 6). Solution 1 suggests the use of a catalyst synthesis temperature as 900°C, time of 5 hours and 10 mg catalyst, maximizing the degree of conversion.

Table 3. Degrees of conversion obtained in the experiments of the 2^3 full factorial design.

Nickel	Degree of Conversion / %	
Samples	Response 1	Response 2
1 and 2	64.45	59.03
3 and 4	52.74	44.63
5 and 6	95.38	93.02
7 and 8	96.14	93.62
9 and 10	63.59	71.78
11 and 12	32.00	32.41
13 and 14	80.94	75.53
15 and 16	79.18	80.00
17 and 18	92.14	85.23
19 and 20	93.40	89.77

Table 4. Summary of ANOVA for the 2^3 factorial.

Source	Sum of squares	Degrees of freedom	Mean squares	F-value	P-value
Model	6639.47	7	948.50	7.67	0.0012
A- Temperature	540.80	1	540.80	4.37	0.0584
B- Time	4663.69	1	4663.69	37.71	< 0.0001
C- Catalyst	436.50	1	436.50	3.53	0.0848
AB	639.65	1	639.65	5.17	0.0421
AC	118.21	1	118.21	0.96	0.3475
BC	107.25	1	107.25	0.87	0.3701
ABC	133.37	1	133.37	1.08	0.3195
Residual	1483.91	12	123.66		
Lack of fit	1342.83	1	1342.83	104.71	< 0.0001
Pure error	141.07	11	12.82		
Total	8123.38	19			

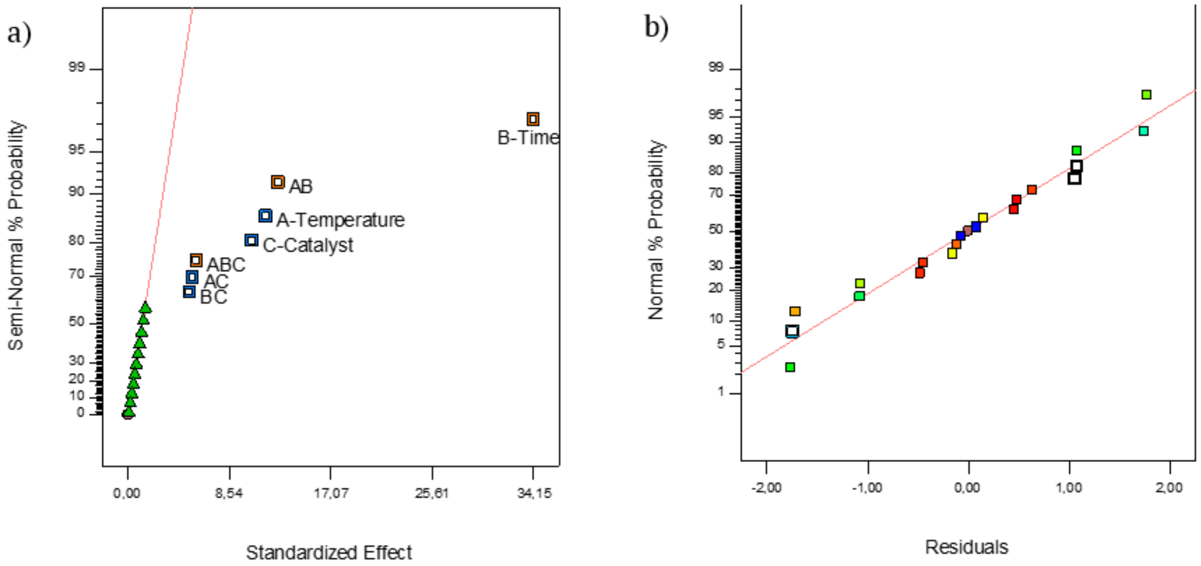


Figure 1. (a) Semi-normal graph of effects for the 2^3 factorial. (b) Normal plot of residuals.

Table 5. Values used for optimization.

Factors	Objective	Maximum limit	Minimum limit	Importance
A:Temperature	Within the range	500	900	3
B:Time	Within the range	3	5	3
C:Catalyst	Within the range	10	60	3
Conversion	Maximize	32	97	5

Table 6. Table de soluções para maximização dos resultados de conversão.

Solution	Temperature	Time	Catalyst	Conversion	Degree of adequacy
1	900.000	5.000	10.000	98.973	0.985
2	898.340	5.000	10.000	98.970	0.985

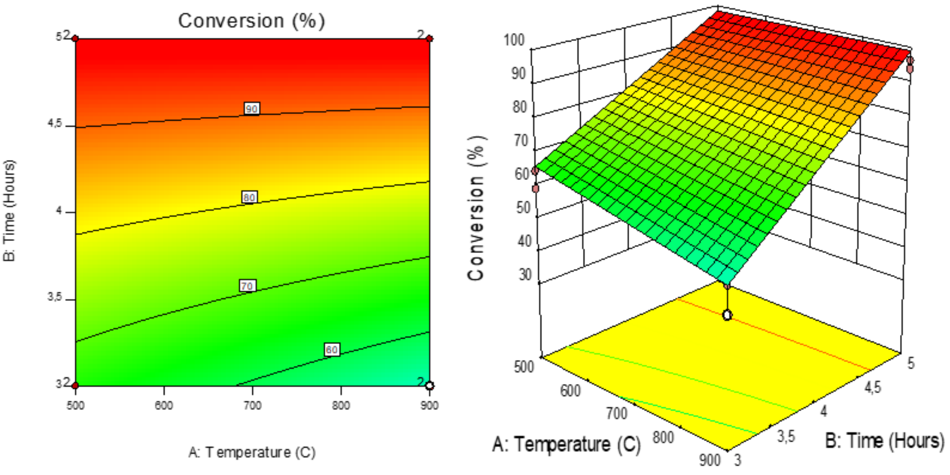
The contour response surface in Figure 2a, and the three axis response surface in Figure 2b indicate the degree of conversion (%) - time as a function of temperature. The amount of catalyst was set at 10 mg in order to obtain better results based on the solutions in Table 4. It can be verified, therefore, that the best degree of conversion (%) can be obtained in longer reaction times (5 hours).

However, even at longer reaction times, the temperature of synthesis of the nanocatalysts had no expressive influence. This can be seen in Figure 2a and b, where the reddish coloration represents a better degree of conversion of PET. It is thus perceived that the temperature was less influential than the time, as the gradient remained similar as the temperature increased. This can be confirmed by Table 3, which shows that factor B (time) was the most influential. At short reaction times, the temperature negatively influenced the degree of conversion of PET.

Characterization of metal catalysts

X-ray diffraction

Figure 3 shows the graphs of the XRD analysis for the NiO nanocatalysts, synthesized at 500, 700 and 900°C. In the three diffractograms, it can be observed a signal of greater intensity around 2θ = 41°, and other signals in approximately 2θ = 35°, 60°, 73° and 77°. These signals observed in the diffractograms refer to the nickel oxide with a cubic face-centered structure (containing one atom at each vertex and one atom at each face of the cube). The oxide formed showed light green coloring for the syntheses at 700 and 900°C, indicating the production of nickel oxide known as stoichiometric (Pingale & Shukla, 2008). The heating of the metal in oxygen can produce ash, which indicates the non-stoichiometry observed in the synthesis at 500°C. The narrow and intense peaks that can be observed in the diffractogram suggest that the material has high crystallinity and purity.



(a) (b)

Figure 2. (a) Contour response surface indicating the degree of conversion of PET (time x temperature). (b) Three axis response surface indicating the conversion (%) as a function of time and temperature.

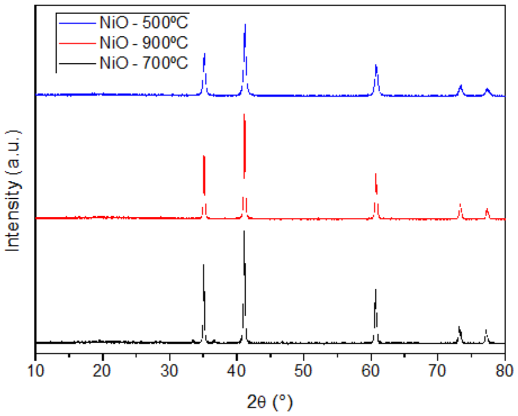


Figure 3. XRD spectra (diffraction angle 2 Theta) of nickel nanocatalysts calcined at 500, 700 and 900°C.

TEM – Transmission Electron Microscopy

Figure 4a, b and c shows the particle transmission electron microscopy analysis of samples of nickel nanocatalysts synthesized at temperatures of 500, 700 and 900°C respectively. A significant discrepancy was found in the size variation of the nanocatalysts prepared at 700°C, but not disfavoring the result of their catalytic activity.

It is observed that in all the syntheses, the particle shapes were the same, and these are clustered, thus, there was no variation in the crystalline structure of the particles at the different synthesis temperatures.

Characterization of BHET, monomer obtained

FTIR - ATR

Figure 5a shows the Fourier transform infrared (FTIR) analysis for the BHET samples obtained by PET depolymerization using nickel catalysts. All the samples had the same pattern of signals. Therefore, among all the products obtained through the depolymerization reaction, the one that presented the highest yield in the depolymerizations using NiO as a catalyst, were taken as references and their spectra are represented in Figure 5a.

In Figure 5b, it is possible to observe elongation vibrations around 3434 cm^{-1}, which come from the hydroxyl group. Intermolecular hydrogen bonds grow with increasing concentration of the solution and additional bonds begin to appear at lower frequencies (3550-3200 cm^{-1}) at the expense of the free hydrogen bonds present in the vapor phase and in very dilute solutions.

It is also observed some signals in the region of 2967 to 2880 cm^{-1}, from the absorption of vibrations of the C-H bonds in alkyl groups. These occur, in general, in the region of 3000 to 2840 cm^{-1}.

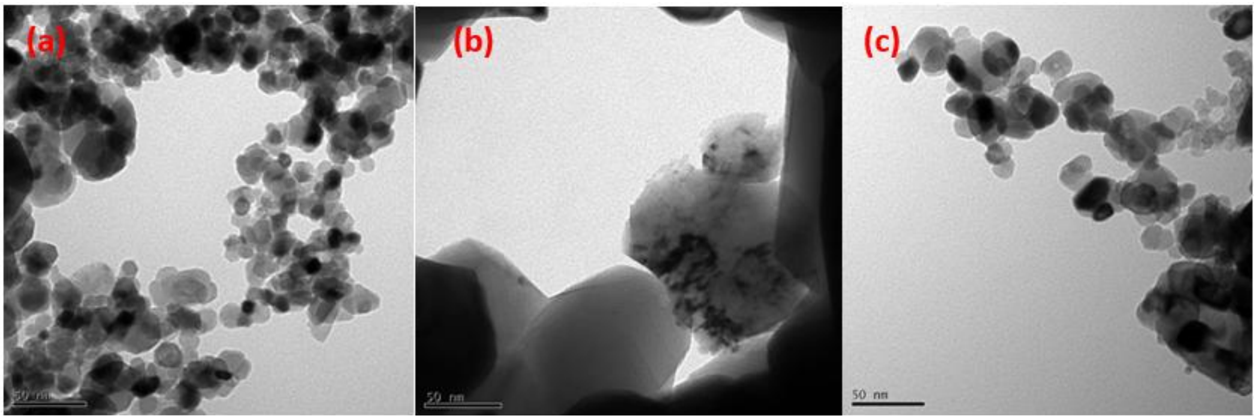


Figure 4. TEM of the nickel nanocalatysts calcined at: (a) 500; (b) 700 and (c) 900°C, and their corresponding size distribution.

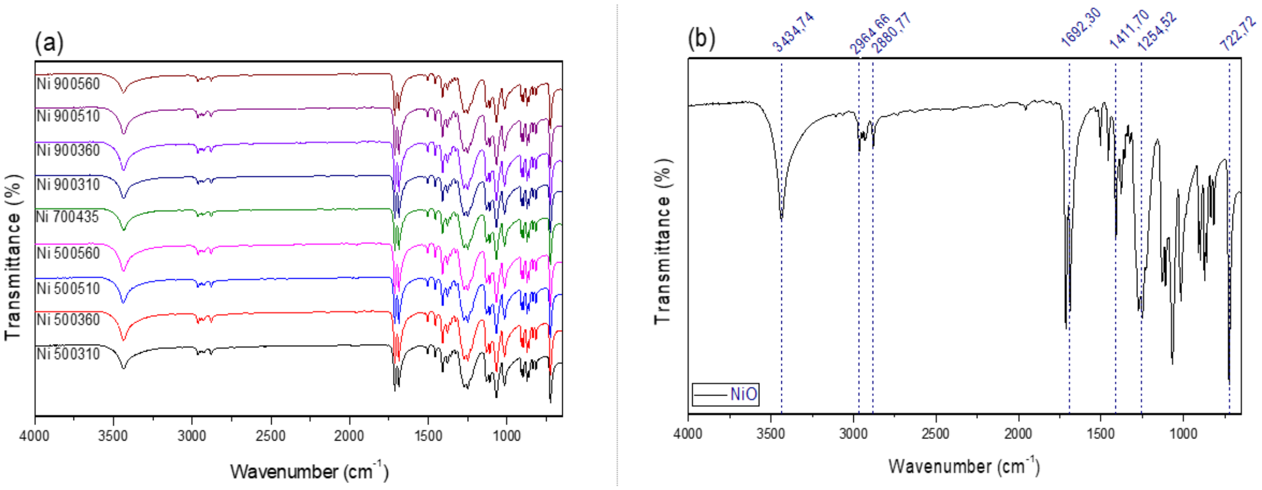


Figure 5. FTIR of products obtained for nickel nanocatalysts. (a) Products obtained at each depolymerization and (b) one of the products obtained.

The stretches of absorption bands of the carbonyl groups of the esters are observed close to 1700 cm^{-1}. The position of this signal is practically constant, of high intensity and is reactively free of interference.

There is a signal in the region of about 1410 cm^{-1}, which corresponds to the C-H bonds in the aromatic ring present in the molecule. The elongation vibrations at 723 cm^{-1} also come from the C-H bonds of the ring, but these refer to the 'off-plane' bonds.

The vibration spectra of asymmetric C-O-C bonds are close to 1255 cm^{-1}. The resonance, which results in the elongation of the C-O bond, is responsible for the change in the asymmetric absorption band.

The signals presented in the FTIR analyses of all BHET samples obtained through depolymerization using both nickel nanocatalysts were compatible with the commercial BHET spectra. Therefore, the product obtained is of high purity (Bemis, Dindorf, Harwood, & Samans, 1982; Bower & Maddams, 1989; Silvestein, Webster, Kiemle, & Bryce, 2014).

DSC

In Figure 6, for all BHET samples, a clear endothermic peak around 109°C was observed, coinciding with the known melting point of BHET. Other signals and ramps were observed around 250 to 300°C, which may indicate the presence of terephthalic acid, which can also be obtained through the depolymerization of PET (López-Fonseca et al., 2011; Dutta & Dolui, 2011; Bartolome et al., 2012).

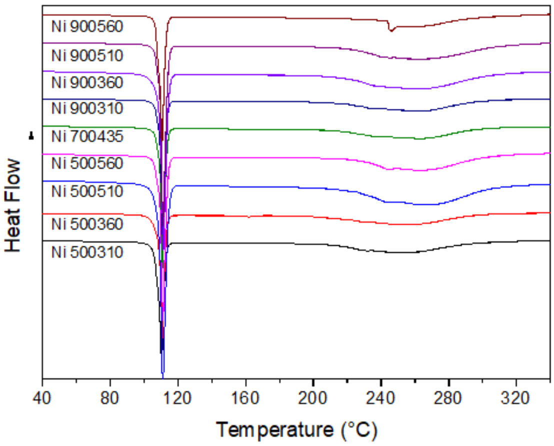


Figure 6. DSC of products obtained in each depolymerization for nickel nanocatalysts.

Conclusion

From the results obtained, it was observed that time was the most influential factor in the analyses.

The synthesis temperature had no strong influence in the depolymerization using nickel catalyst, also nickel obtained better results in the PET depolymerization due to its degree of conversion (~99%) using 10 mg of the catalyst at 500°C in a reaction time of 5 hours.

The product obtained (BHET) presented a high degree of purity according to the analyses carried out. This can be further applied in the production of plastics and/or other materials, thus adding a commercial value to the residue from depolymerization reaction.

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