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Study of the residual polymer-aluminum recycling process of carton packaging

Estudo do processo de reciclagem de polímero-alumínio residual de embalagens cartonadas

Estudio del processo de reciclaje de residuos de polímero-aluminio de envases de carton

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Abstract
The complexity of the structure of carton packs is one of the factors that hinder the development of processes for recycling after consumption. The few processes that are currently used do not manage to completely recycle all the materials used in these packages. The few economically viable processes are applied to the recycling of paper layers, leaving as a residue the combined layers of polyethylene and aluminum, known as polymer-aluminum residues (Poly-Al) from carton packs. In this context, a method for recycling polyethylene and aluminum present in Poly-Al residues from post-consumer carton packs was researched and developed using the alkaline aluminum digestion process. Solutions with different concentrations of NaOH were evaluated at an ambient temperature with a treatment time of 24 h. After the aluminum removal processes, the polyethylene films and the liquid and solid phases precipitated from the reaction medium were analyzed. Scanning electron microscopy (SEM/FEG), dispersive x-ray fluorescence energy spectroscopy (EDS), x-ray diffraction (XRD), inductively coupled plasma mass spectrometry (ICP) and calorimetry differential scanning (DSC) were used for the analyzes. The results indicated the removal of aluminum from polyethylene films from Poly-Al residues with good efficiency and without significantly compromising the thermal properties of the polymer.
Keywords: Carton packaging; Recycling; Polymer-Aluminum.

Resumo
A complexidade da estrutura das embalagens cartonadas é um dos fatores que impedem o desenvolvimento de processos de reciclagem após o consumo. Os processos utilizados atualmente não conseguem reciclar completamente todos os materiais utilizados nestas embalagens. Os poucos processos economicamente viáveis são aplicados para reciclagem das camadas de papel, deixando como resíduo as camadas combinadas de polietileno e alumínio, conhecidas como resíduos de polímero-alumínio (Poli-Al) das embalagens cartonadas. Nesse contexto, um método de reciclagem para polietileno e alumínio, presente nos resíduos de Poli-Al de embalagens cartonadas pós-consumo, foi pesquisado e desenvolvido utilizando o processo de digestão alcalina de alumínio. Soluções com diferentes concentrações de NaOH foram avaliadas em temperatura ambiente com tempo de tratamento de 24 h. Após os processos de remoção do alumínio, analisou-se os filmes de polietileno e as fases líquida e sólida precipitadas do meio reacional. Microscopia eletrônica de varredura (MEV/FEG), espectroscopia de energia de fluorescência de raios-X dispersiva (EDS), difração de raios-X (DRX), espectrometria de massa com plasma indutivamente acoplado (ICP) e varredura diferencial de calorimetria (DSC) foram usados para as análises. Os resultados indicaram a remoção do alumínio dos filmes de polietileno dos resíduos de Poli-Al com boa eficiência e sem comprometer significativamente as propriedades térmicas do polímero.
Palavras-chave: Embalagem cartonada; Reciclagem; Polímero-Alumínio.

Resumen
La complejidad de la estructura de los envases de cartón es uno de los factores que impiden el desarrollo de los procesos de reciclaje después el consumo. Los procesos que se utilizan actualmente no pueden reciclar por completo todos los materiales utilizados en estos envases. Los pocos procesos económicamente viables se aplican para reciclar las capas de papel, dejando como residuo las capas combinadas de polietileno y aluminio, conocidas como residuos de polímero-aluminio (Poly-Al) de los envases de cartón. En este contexto, se investigó y desarrolló un método de reciclaje de polietileno y aluminio, presente en los residuos de Poly-Al de envases de cartón posconsumo, utilizando el proceso de digestión alcalina de aluminio. Se evaluaron soluciones con diferentes concentraciones de NaOH a temperatura ambiente con un tiempo de tratamiento de 24 h. Después de los procesos de eliminación de aluminio, se analizaron las películas de polietileno y las fases líquida y sólida precipitadas del medio de reacción. Para los análisis se utilizaron microscopía electrónica de barrido (MEB), espectroscopia de fluorescencia de rayos X de dispersión de energía (EDS), difracción de rayos X (DRX), espectrometría de masas de plasma acoplado inductivamente (ICP) y calorimetría diferencial de barrido (DSC). Los resultados indicaron la eliminación de aluminio de las películas de polietileno de los residuos de Poly-Al con buena eficiencia y sin comprometer significativamente las propiedades térmicas del polímero.
Palabras clave: Envases de cartón; Reciclaje; Polímero-Aluminio.

1. Introduction

Carton packaging has long been applied in the food industry, especially for providing optimum conditions for thermal and microbiological protection, which helps extend the shelf life of packaged food and offers optimal conditions for transport and storage. However, studies reported that consumption of these packaging and the waste in the processes of manufacture negative impact the environment, which justifies the fact that these containers be also treated as large-scale waste after use and discard (Uemura & Comini, 2017).

Studies indicate that the percentage of carton packaging recycled in Brazil in the year 2016 was approximately 23.3% of the total waste produced, about 60,000 ton of recycled packaging (CEMPRE, 2019). Of these, the amount of approximately 76.7% of the packaging carton post-consumer is still destinated to landfills, leading to significant environmental impact (Jain, *et al*., 2016).

Carton packs are manufactured with combined multilayers of aluminum films (5%), polymers (24%) and paper (71%) (Cerqueira, n/d). These constituents end up becoming contaminating residues of the environment when the packaging is not properly disposed or treated after its use. This residue can threaten invertebrate species and plants that are the basis of the food chain mainly due to the presence of polyethylene that has long life cycle and high corrosion resistance (Chae & An, 2018; Wang, *et al*., 2019).

Due to the structure of a multilayer films formed by different materials, recycling carton packaging is a complex process (Fernandes, Danielewicz & Secco, 2014). However, can be found suitable recycling approaches for the waste generated by carton packs, the volume of waste, the corresponding disposal cost and environmental pollution can be reduced. In addition, promising approaches can result in conservation of natural sources and economic benefits (Mahinroostaa & Allahverdia, 2018).

The recycling process of the layers of carton packs can be economically viable in industrial scale, but still generates waste that needs to be properly disposed. These remaining materials, which are composed of polymeric films coated with metallic aluminum, generally referred to as Polymer-Aluminum residues (Poly- Al), are still used in the manufacture of several composite products, however with low added value (Neves, 1999). These composites are used for the manufacture of tiles, tanks, culverts (Cerqueira, 2007; Barrera, *et al*., 2017; Hassanin, *et al*., 2016) and articles for the civil construction sector (Quintero, *et al*., 2017). The widespread use of Poly-Al waste as a composite material in these low value-added products is due to the lack of viable processes for removing or separating aluminum coatings from polymeric films. Therefore, the separation of the layers of aluminum and polyethylene can provide use for each of the materials to the manufacture of products with greater added value.

The separation of the aluminum coating from the polymeric layers of carton packs can be carried out by using chemical solvents or processes with high temperatures, but these are processes with complex operations, high costs and significant environmental damage (Zang, *et al*., 2014; Xie, *et al*., 2016; Karaboyaci, *et al*., 2017). However, studies have been dedicated to the use of processes with low-cost reagents with less energy consumption and less environmental damage.

Considering that many studies have been dedicated to the alkaline digestion of aluminum oxide for the production of hydrogen gas, similar procedures can be applied to remove metallic aluminum from the polymeric layers of Poly-Al residues (Hiraki, *et al*., 2007; Chai, *et al*., 2014; Santos, *et al*., 2017; Pagliarini, *et al*., 2016).

From the alkaline treatment of Poly-Al waste, the polymer can be reused in the market for recycled plastics and aluminum in the market for non-ferrous materials, both with higher added value compared to Poly-Al composites (Castro, *et al*., 2017). Therefore, the main objective of this study was to evaluate the efficiency of removing aluminum coatings from Poly-Al residue from carton packs by an alkaline digestion process with NaOH solutions, aiming at the recovery of polyethylene with future application for polymer industries recycled.

2. Experimental Procedures

The research was classified according to the applied nature with a quantitative approach. As for the focus, it consists of explanatory research with technical procedures, classified as an experimental study (Pereira, *et al*., 2018).

2.1 Materials

For the alkaline digestion process, analytical purity NaOH was used, supplied by Vetec Química Fina Ltda, Brazil. The polyethylene-aluminum residues (Poly-Al) were supplied previously fragmented by the company Mercoplas Indústria e Comércio Ltda (Rio Grande do Sul, Brazil), coming from a primary recycling process that separates the paperboard layer from carton-type packaging, which were manufactured by the company Tetra Pak. The residues were used in the form of flakes with medium are different, but predominantly with rectangular shapes which had smaller area than or equal to 1 cm^2. The low-density polyethylene used as a reference for comparative studies was supplied by Braskem (Grade S1522).

2.2 Process of alkaline digestion of the aluminum coating of Poli-Al

The processes for removing the aluminum coating from the Poly-Al residue flakes were carried out by alkaline digestion. The studies were carried out on a laboratory scale in a 1 L glass reactor, with the aid of a Fisatom mechanical stirrer (model 711-40W).

The solutions for alkaline digestions were prepared with different contractions of NaOH in distilled water (1, 2 and 3 M). The definition by this granulometry for the flakes and the chemical route was based on the results of the study of alkaline aluminum digestion (Brazil, 2005).

Upon contact with the aqueous NaOH solution, aluminum reacts and releases hydrogen gas (H_2), forming sodium aluminate ($NaAl(OH)_4$) , described by Equation 1, and sodium aluminate can also dissociate and form aluminum hydroxide ($Al(OH)_3$), as described by Equation 2 (Brasil, 2005; Portela; Cho & Liu, 2016).

$$\mathbf{Al + 3H_2O + NaOH \rightarrow NaAl(OH)_4 + 3/2H_2} \qquad (1)$$

$$\mathbf{NaAl(OH)_4 \rightarrow Al(OH)_3 + NaOH} \qquad (2)$$

In alkaline digestion studies, 10 g of Poly-Al waste flakes and 300 mL of NaOH solution were used for each concentration at room temperature. The flakes of Poly-Al residues were added to the solution and stirred s for 10 min, in order to favor the dispersion of starting components, and then were kept at rest. With intervals of 24 h were collected the s sample of flakes, which were dang to s on an analytical balance (Shimadzu - BL-3200S model) for determining the weight aluminum metallic removed these residues Poly-Al.

For the calculation of the mass removed from metallic aluminum the fractions flakes removed to of the reactor were filtered on polyethylene filter and washed out with a distilled water solution, which had a corresponding volume to 50% of the volume of the solution of NaOH. The washed flakes were dried in an oven (Brand Cid, model 311 cg) with natural convection for 48 h and a temperature of 105 °C, being weighed again. The Poly-Al flakes that remained with aluminum impregnated on the surface were separated and weighed, as well as the clean polymer flakes that were then reserved for characterization.

Since the polymer is inert to concentrated NaOH solutions, the mass variation in the alkaline digestion process is referred to the aluminum mass present in the Poly-Al residue, which reacts with NaOH. In this way, the mass removed from aluminum was determined using Equation 3.

$$\mathbf{M_{remAl} = M_{1\ Poly\text{-}Al} - M_{2\ Poly\text{-}Al}} \qquad (3)$$

Where, M_{remAl} is the mass removed from the metallic aluminum coating, $M_{1\ Poly\text{-}Al}$ is the initial mass of the residue Poly-Al and $M_{2\ Poly\text{-}Al}$ is the post-process mass of the remaining residue of Poly-Al.

The polymeric characterization and the solid and liquid residues were performed only for the test products in which aluminum removal was more efficient.

2.3 Characterization of the alkaline solution after the Poly-Al residue digestion process

The solution of the alkaline digestion process, after the treatment of the Poly-Al waste flakes, was centrifuged at 3600 rpm with a centrifuge (FANEM Baby® I Model 206-BL), with the objective of separating the liquid phase from the solid phase: i) liquid phase constituted by the alkaline solution and, ii) solid phase constituted by precipitates resulting from the removal of the components present on the surface of the waste flakes.

The liquid phase of the alkaline digestion process, collected after the flake treatment, was subjected to chemical analysis with the metal quantification technique by ICP-MS (inductively coupled plasma mass spectrometry), following the 3120-B method. The analyzes were performed with the 3 M NaOH solution considering that it was the solution that showed total removal of the aluminum coatings from the surface of the Poly-Al waste flakes. The aliquots of the liquid phase of the digestion solution were adequately packed in polyethylene containers following the recommendations of the Laboratory of Water and Wastewater Analysis - LANAI/SENAI Blumenau, accredited by INMETRO for the analysis of ICP-MS.

2.4 Characterization of the solid phase of the alkaline digestion system

After the process of centrifugation of the solution precipitated the reaction medium resulting solid phase was dried in an oven at (Brand Cid, model 311 CG) to 105 °C to 48 h. The resulting solids were analyzed by scanning electron microscopy, energy dispersive spectroscopy fluorescence x-rays and diffraction x-rays.

The scanning electron microscopes were performed in a scanning electron microscope MEV/FEG (Philip XL-30), with the secondary electron and retro electron modes scattered. All samples were coated with thin gold films in order to conduct the surface for analysis.

X-ray fluorescence dispersive energy (EDS) spectroscopy was performed simultaneously with SEM/FEG analyzes. A Bruker probe was used for EDS analysis for chemical microanalysis and for mapping the chemical composition of the solid phase.

X-ray diffraction analyzes were performed on a Bruker x-ray diffractometer (model D8 Advance ECO) configured in Bragg-Brentano geometry with a copper anode X-ray source with a characteristic emission line of 1.54 Å/8.047 keV (Cu-Kα_1) - 1.0 kW.

2.5 Characterization of polymeric films after the process of alkaline digestion

Polymeric films after treatment with alkaline solution of 3 M NaOH were analyzed by scanning electron microscopy, energy dispersive spectroscopy X-ray fluorescence, diffraction of r tutors - X and differential scanning calorimetry.

The scanning electron microscopy (SEM) technique was used to assess the presence of aluminum or other residual elements of the alkaline digestion process on the surface of polymeric films. A SEM/FEG scanning electron microscope (Philip XL-30) was used, with secondary electron and retro electron modes scattered. All samples of the polymeric films were coated with thin gold films in order to conduct the surface for analysis.

Simultaneously to the scanning electron microscopy analyzes, X-ray fluorescence dispersive energy (EDS) spectroscopies were performed. Such analysis aims at the identification and semiquantitative evaluation of the chemical composition of possible residues impregnated on the surface of the polymeric films after treatment in alkaline solutions. For EDS analysis, a Bruker probe was used for chemical microanalysis and for mapping the chemical composition. The polymer film flakes were subjected to x-ray diffraction analysis and were performed on a Bruker x-ray diffractometer (model D8 Advance ECO) configured in Bragg-Brentano geometry with a copper anode X-ray source with characteristic emission line of 1.4 Å/8.047 keV (Cu-Kα_1) - 1.0 kW.

The s analysis s of thermal polymer films was performed with deferential scanning calorimetry. A Perkin Elmer - DSC 6000 thermal system was used, in a temperature range from 30 ºC to 150 ºC, with a heating rate of 10 ºC.min^{-1} and with a high purity nitrogen atmosphere, with a flow rate of 50 mL.min^{-1}. The first heating for all thermograms of DSC was not considered, in order to delete the information of the thermal history of the samples. F pray considered DSC thermograms for the second heating and for cooling of the polymeric film. DSC tests were performed at the LATEM Laboratory of Unochapecó.

2.6 Extrusion processing of polymeric films

The polymeric films that were made with 3M NaOH alkaline solution were processed with linear extrusion. The main objective was to evaluate the flow stability in comparison with the reference low density polyethylene (LDPE), the processability and the visual aspects of the extrudate. The process of extrusion are films was conducted in Materials Technology Laboratory - Unochapecó in one mono extruder - screw of L/D = 28 inch (D = 16 mm), with four heating zones and speed thread of 90 rpm. The temperatures established for the heating zones were 80 °C for feeding, 113 °C for plasticization, 120 °C for homogenization and 135 °C in the head. The reference LDPE was processed under the same conditions for comparison.

3. Results and Discussion

3.1 Tests for removing the aluminum coating from the Poly-Al films

The results indicate r m that the higher removal efficiency d the aluminum is obtained from the solution with 3M NaOH, applied for 24 h at room temperature on samples with 10 g ($m_{1Poly\text{-}Al}$) flakes of poly residue A1 (Table 1). In these conditions will, at the end of the digestion process to alkaline average mass of aluminum removed was 1.80 g. The tests carried out with the solutions with the concentrations of 1 M and 2 M of NaOH did not provide the complete removal of the aluminum layers.

Table 1 - Values of Poly-Al residue masses before and after treatment with solutions NaOH, applied for 24 h at room temperature, samples with 10 g of Poly-Al flakes residue.

C_{NaOH} (Mol.L^{-1})	Temperature (°C)	Time (h)	$m_{1\ Poly\text{-}Al}$ (g)	$m_{2\ Poly\text{-}Al}$ (g)	m_{remAl} (g)	Aluminum's presence
1	25	24	10	8.83	1.17	YES
2	25	24	10	8.43	1.57	YES
<u>3</u>	<u>25</u>	<u>24</u>	<u>10</u>	<u>8.20</u>	<u>1.80</u>	<u>NO</u>

Where: $m_{1\ Poly\text{-}Al}$: Poly-Al residue mass before alkaline treatment; $m_{2\ Poly\text{-}Al}$: Poly-Al residue mass after alkaline treatment; m_{remoAl}: aluminum mass removed from waste.
Source: Authors.

Figure 1 shows images of the flakes of the Poly-Al residue without the treatment of alkaline digestion and after the treatment of alkaline digestion with the 3 M NaOH solution, applied for 24 h at room temperature. The flakes of Poly-Al residues without the alkaline digestion treatment has notably their surfaces coated with metallic aluminum and flexographic printing inks with different colors, Figure 1(a). The different paint colors are indicative of the presence of different inorganic pigments and, consequently, the presence of different metallic chemical elements, in addition to aluminum, in the Poly-Al residue. Although the inks are not soluble in the alkaline NaOH solution, it is quite possible that a small fraction of the inorganic chemical elements will migrate and contaminate the liquid phase of the treatment system by alkaline leaching.

Figure 1(b) shows the flakes of Poly-Al residues after the process of treating alkaline digestion with the 3 M NaOH solution, for 24 h and at room temperature. The removal of the metallic aluminum coating is total, leaving only the coatings with the printing inks, as planned.

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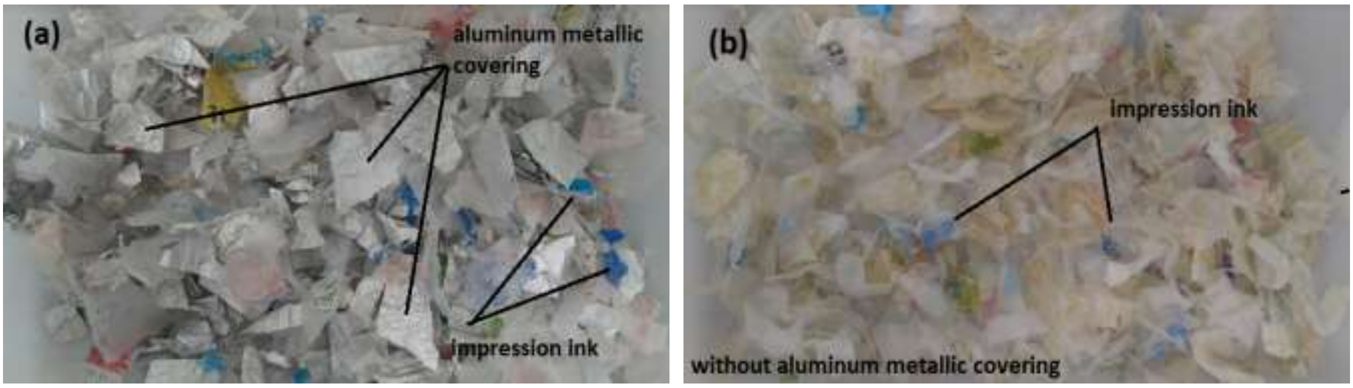
Figure 1 - Images of Poly-Al waste flakes. (a) without the treatment of alkaline digestion and (b) with the treatment of alkaline digestion with the 3 M NaOH solution and with 24 h at room temperature.



Source: Authors.

3.2 Characterization of the liquid phase after the alkaline digestion process

Table 2 lists the metals and their d - values the concentration identified in the liquid phase of the solution after alkaline digestion process of flakes Poly-Al residue. The expected maximum and permitted by Brazilian law contained in Resolution CONAMA 357-2005 (Brasil, 2005) in order to assess whether this solution meets the standards releases effluent co r pos water. Highlighted are chemical elements with concentrations higher than that provided for in the resolution.

Many metallic elements were detected in the liquid phase after the treatment of the flakes of the Poly-Al residue and with concentrations above those allowed by the CONAMA resolution. In particular, the high concentrations of zinc, molybdenum, iron, copper, antimony and aluminum are worth mentioning. The high concentration of aluminum in the solution is due to the dissolution of the metallic aluminum by the alkaline solution, which gives indicators of the high efficiency of removing the metallic aluminum coatings from the residues of Poly-Al by the process of alkaline digestion. The other elements meth originates possibly of pigments and inorganic fillers employed in flexographic printing inks and were applied on are polymeric films of the carton.

Table 2 - Elements detected and quantified by the ICP-MS technique in the liquid phase after the process of alkaline digestion of the residues of Poly-Al and the corresponding maximum values predicted and allowed by Brazilian law CONAMA resolution 357-2005 for the standard of discharge of effluents in water bodies.

Element	Concentration ($mg.L^{-1}$)	CONAMA 357/2005 ($mg.L^{-1}$)
Aluminum	24.954	0.100
Antimony	1.100	0.005
Arsenic	-	0.010
Barium	<0.200	0.700
Beryllium	<0.020	0.040
Boron	0.594	0.500
Cadmium	<0.001	0.001
Calcium	<0.050	-
Cobalt	<0.020	0.050

Copper	1.140	0.009
Chrome	<0.010	0.050
Iron	6.040	0.300
Lead	<0.010	0.010
Magnesium	<0.020	-
Manganese	0.227	0.100
Molybdenum	26.800	-
Nickel	0.185	0.025
Tin	<0.200	-
Titanium	0.225	-
Vanadium	1.070	0.100
Zinc	26.700	0.180

Source: Authors, adapted of CONAMA 357/2005 (Brasil, 2005).

The pigments are and inorganic dyes user settings to s in the inks employed in the process are flexographic printing of cartons are in a titanium dioxide composition, iron compounds, vanadium, titanium, nickel, copper, molybdenum, chromium, barium, while Mineral fillers have compounds based on calcium and magnesium (Gajadhur & Łuszczyńsk, 2017; Sonmez, 2011; Souza Santos, 1985). Although most of these compounds remain impregnated on the surface of the Poly-Al flakes after the processes of alkaline digestion, significant concentrations of these elements are detected in the liquid phase resulting from the digestion process, possibly released by leaching caused by the solution.

However, boron (Bo) is not a commonly used element in s formulation of s d the pigments and to their presence not the solution may be from detergents applied to the primary processes for recycling the carton for removing organic compounds (Souza Santos, 1985). It also may be a residue from the people reducer used in the process of paper bleaching the sodium borohydride ($NaBH_4$) (Parks & Edwards, 2005).

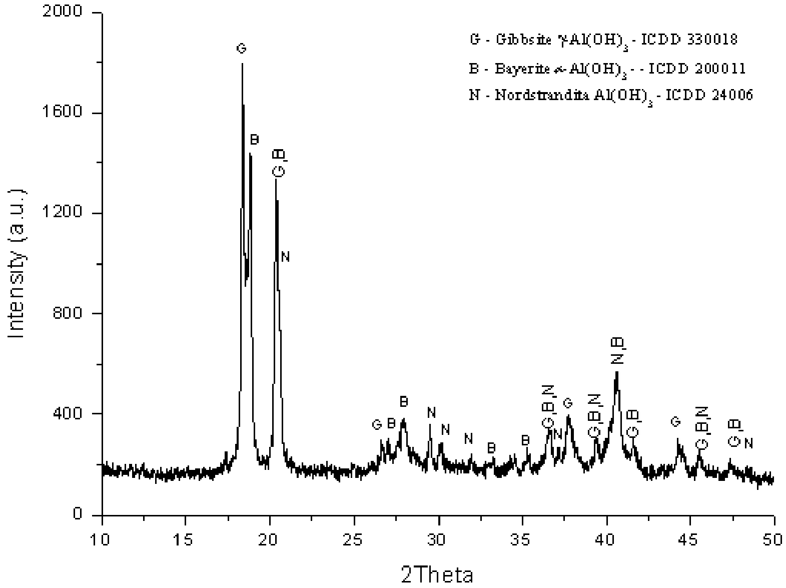
According to CONAMA Resolution No. 357-2005, which establishes the conditions and discharge standards and the effluent into water bodies in the country (Portela, Cho & Liu, 2016), the resulting liquid phase of the alkaline digestion process aluminum coating of waste Poly-Al is not compliant for disposal in water bodies. Concentrations above the limits established by Brazilian legislation, especially for aluminum, lead, boron, copper, iron, manganese, nickel, vanadium and zinc characterize the solution as unsuitable for disposal. For its proper disposal, studies dedicated to its chemical treatment are necessary in order to meet the required regulations.

However, these metals can be easily removed by electrochemical processes, including with selective criteria for separating the components (Wefers, 1990; Yu, Cheng & Zhang, 2019). It is possible that electrochemical processes are applied to remove these metals and also to recover aluminum, manganese and zinc, which are present in high concentrations and which have a relative commercial value.

3.3 Characterization of the solid phase after the treatment of alkaline digestion

The solid phase of the alkaline digestion system, obtained after the treatment of the residue flakes of Poly-Al, was submitted to evaluation by X-ray diffraction, as shown in Figure 2. The diffractogram reveals the majority presence of aluminum hydroxide in the Gibbsite, Bayerite and Nordstrandite phases (Wefers & Misra, 1987; Jaerger, *et al*., 2017).

Figure 2 - X-ray diffractogram of the solid phase of the alkaline digestion system, obtained after the treatment of the residue flakes of Poly-Al.



Source: Authors.

Gibbsite is defined as the γ-Al(OH)$_3$ phase and has a monoclinic crystalline system with lattice parameters a = 0.8684 Å, b = 0.5078 Å and c = 0.9136 Å. Among the aluminum hydroxides, Gibbsite for being the precursor compound of alumina powders applied in conventional ceramics and advanced ceramics. Also, because it has a catalytic character and is applied as a catalyst support, due to the absorption and adsorption capacity and the character of an anti-flame agent, it is therefore widely applied in the paper, rubber and plastics manufacturing industry (Wefers & Misra, 1987; Jaerger, *et al*., 2017).

Bayerite is defined as the α-Al(OH)$_3$ phase and has a crystalline system also monoclinic with network parameters a = 0.5062 Å, b = 0.8671 Å and c = 0.4713 Å, with density equal to 2.53 g.cm^{-3} and greater than Gibbsite, which has a density of 2.42 g.cm^{-3}. Bayerite can be transformed by a simple thermal process at Gibbsite (Wefers & Misra, 1987; Jaerger, *et al*., 2017).

Nordstrandite is the phase named simply by aluminum hydroxide (Al (OH)$_3$), and has a triclinic crystalline system with network parameters equal to aa = 0.5114 Å, b = 0.5082 Å and c = 0.5127 Å. Like Bayerite, Nordstrandita a can be transformed by a simple thermal process at Gibbsite (Wefers & Misra, 1987; Jaerger, *et al*., 2017).

The X-ray diffractogram does not indicate the presence of other chemical components in the solid phase of the alkaline digestion system, so that it can be considered a waste made up mainly of aluminum hydroxide and also as a product of commercial value. This information is extremely important for studies of technical and economic feasibility for the future application of the solid phase.

3.4 Characterization of polymeric flakes by SEM-EDS

The flakes of the Poly-Al residues treated with the 3 M alkaline NaOH solution visually presented the aluminum-free surface after the alkaline digestion process. Figure 3 shows electron microscopy images obtained from the surface of these polymeric flakes.

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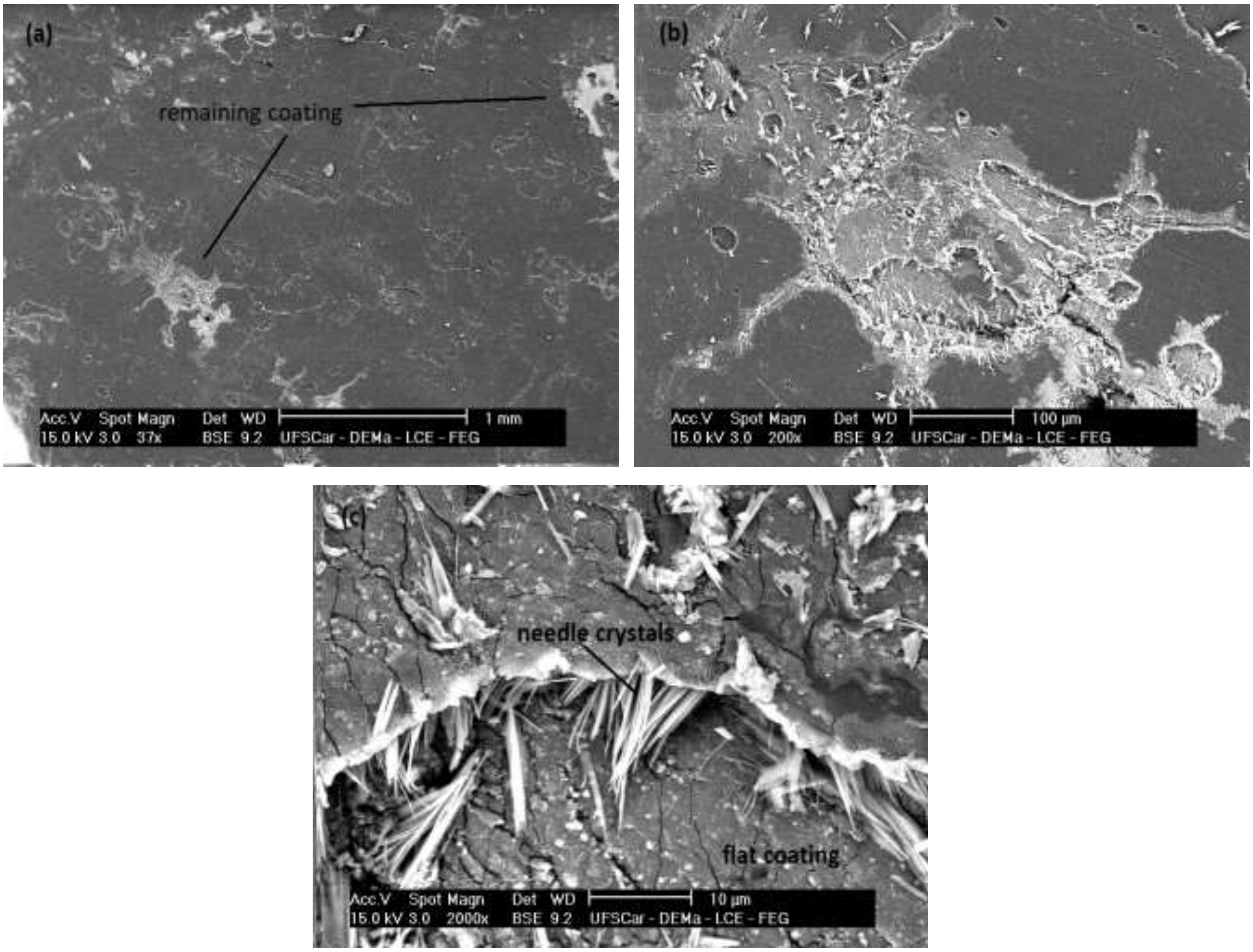
Figure 3 - Images obtained with scanning electron microscopy with retro electrons spread over the surface of flakes of Poly-Al residues after treatment in alkaline solution for 24 h with 3 M NaOH solution and at room temperature. (a) 37 times magnification, (b) 200 times magnification, and (c) 2000 times magnification.



Source: Authors.

The images reveal that the alkaline digestion process with 24 h with the 3 M NaOH solution promotes the removal of much of the aluminum from the polymeric surface of the Poly-Al residue, leaving only a few regions apparently with the metal, as shown in Figure 3. The lighter regions in the microscopy image indicate that the remaining coatings are made up of higher density chemical elements, possibly aluminum. Details of a region of the remaining deposit show that it is anchored on the surface of the polymer with needle-shaped crystals in the edge regions of the flake defects, Figure 3(b).

Figure 3(c) reveals the difference between the flake crystalline structures of the remaining deposit, which has a flat morphological surface, and the crystals that grow in the flake defect regions, which have a needle shape. These expressive differences are indications that the flat base of the flake and the crystals in the form of needles are made of chemically different materials.

Figure 4 shows the chemical distribution of the surface of the Poly-Al residue in the corresponding region shown in Figure 3(a), obtained by X-ray fluorescence dispersive energy spectroscopy (EDS). The analyzes reveal the presence of aluminum and sodium as constituents of the remaining material deposits, Figure 4(a) and Figure 4(b), respectively. The presence of aluminum indicates that a fraction of it was not removed with the treatment of alkaline digestion, probably requiring a longer

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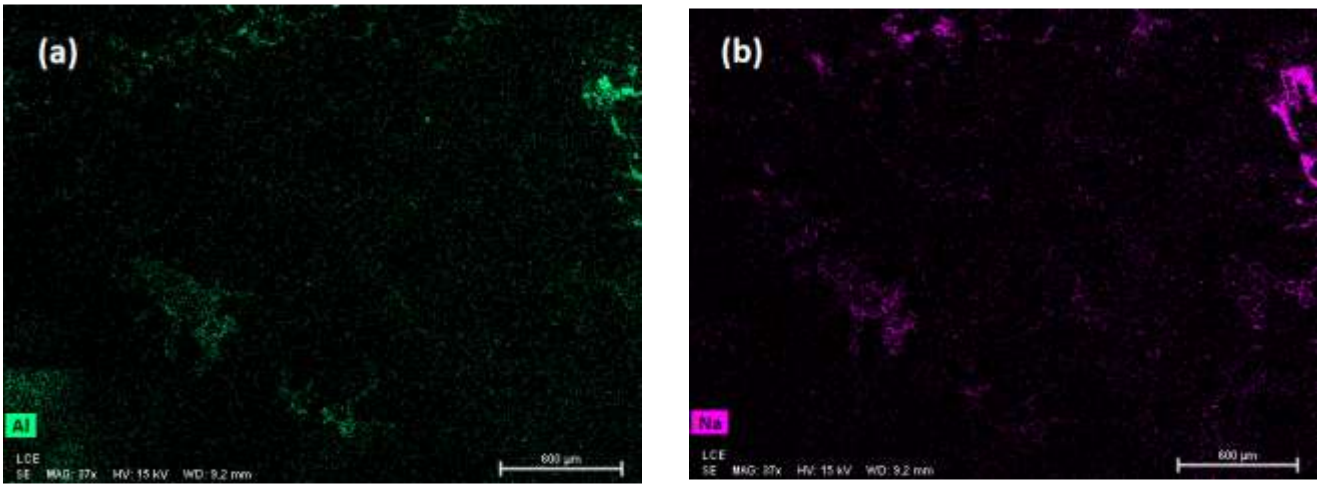
treatment time for total removal. The presence of sodium indicates that the washing process after digestion treatment has not completely removed the sodium from the alkaline solution. It is noticeable that in the regions of the aluminum film the presence of sodium is identified, which corroborates with the results of electron microscopy that the remaining deposits consist of a flat aluminum base and crystalline sodium in the shape of needles.

Figure 4 - Chemical distribution of the surface of the Poly-Al residue in the corresponding region shown in Figure 2 (a), obtained by X-ray fluorescence dispersive energy spectroscopy (EDS).



Source: Authors.

The results of X-ray fluorescence dispersive energy spectroscopy (EDS) also reveal the presence of other chemical elements on the surface of the Poly-Al residue with lower concentrations Table 3.

The results indicate, addition of aluminum and sodium, the presence of calcium, iron, oxygen, carbon and silicon. Carbon is associated with the polymeric structure of the Poly-Al residue, while the high oxygen presence is related to the oxidized polymer regions and the possible hydroxide or oxide structure of the alkali and metallic elements remaining on the residue surface after treatment.

The presence of calcium and silicon is due to the chemical constitution of the mineral fillers that are constituents of the formulations of flexographic inks, used in printing arts on carton packs, as well as iron. These conditions may be responsible for the presence of these contaminating elements which, although in small quantities, appear as contaminants on the surface of the residue of Poly-Al after the process of alkaline digestion.

Table 3 - Qualitative chemical composition determined with X-ray fluorescence dispersive energy spectroscopy (EDS).

Element	Concentration (%)
C	66,64
O	24,81
Na	4,39
Al	1,38
Ca	2,01
Si	0,50
Fe	0,28

Source: Authors.

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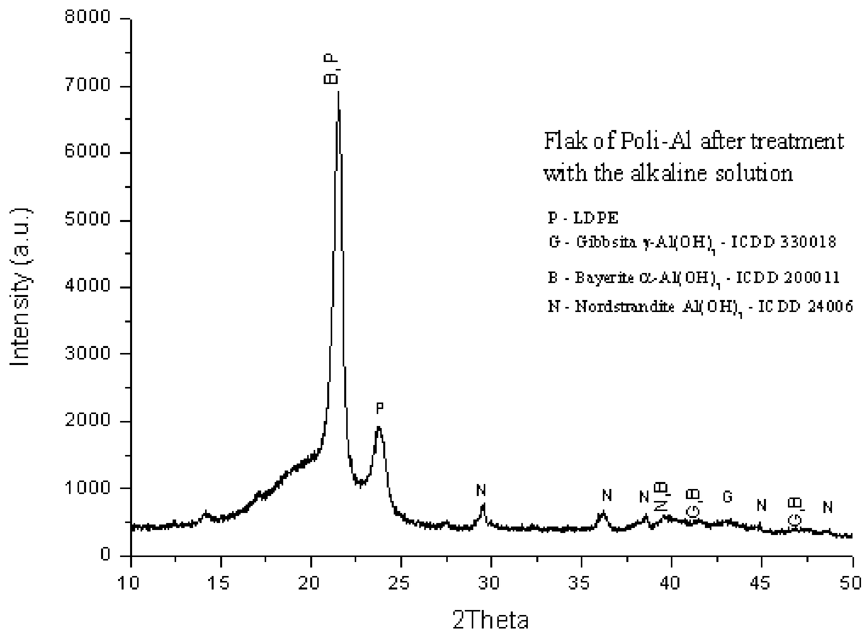
The results of electron microscopy and X-ray fluorescence dispersion spectroscopy prove the presence of small amounts of aluminum, sodium and other elements on the surface of the Poly-Al flakes.

3.5 X-ray diffraction (DRX) characterization of Poly-Al flakes

The Poly-A l flakes treated for 24 h with the alkaline solution with 3 M NaOH and at room temperature were subjected to x-ray diffraction evaluations, as shown in Figure 5. The diffractograms obtained are typical of a low polyethylene surface density, with characteristic peaks of 2θ equal to 21.54º and 23.74º.

Figure 5 - X-ray diffractogram obtained for the Poly-Al flakes after the alkaline treatment for 24 h in a 3 M NaOH solution at room temperature.



Source: Authors.

The diffractogram shown in Figure 5 indicates the presence of small amounts of aluminum hydroxide on the surface of the Poly-Al flakes, even after the alkaline digestion process. The aluminum residue is identified in the form of the phases of γ-$Al(OH)_3$ (Gibbsite), α-$Al(OH)_3$ (Bayerite) and $Al(OH)_3$ (Nordstrandite). These results are in accordance with the information obtained by scanning electron microscopy and by X-ray fluorescence dispersive energy spectroscopy, which also identify the presence of aluminum on the surface of the Poly-Al flakes after the alkaline digestion process.

The results indicate that a small fraction of the aluminum coating still remains on the polymer surface of the Poly-Al flakes after being treated with the alkaline solution with the highest concentration of NaOH.

In general, the results of X-ray diffraction reveal mostly the presence of LDPE and with small fractions remaining of aluminum coatings, which can be considered as a small fraction of polymer contamination. The results indicate that the alkaline digestion process is efficient for removing aluminum coatings and for recovering polymeric films from Poly-Al flakes.

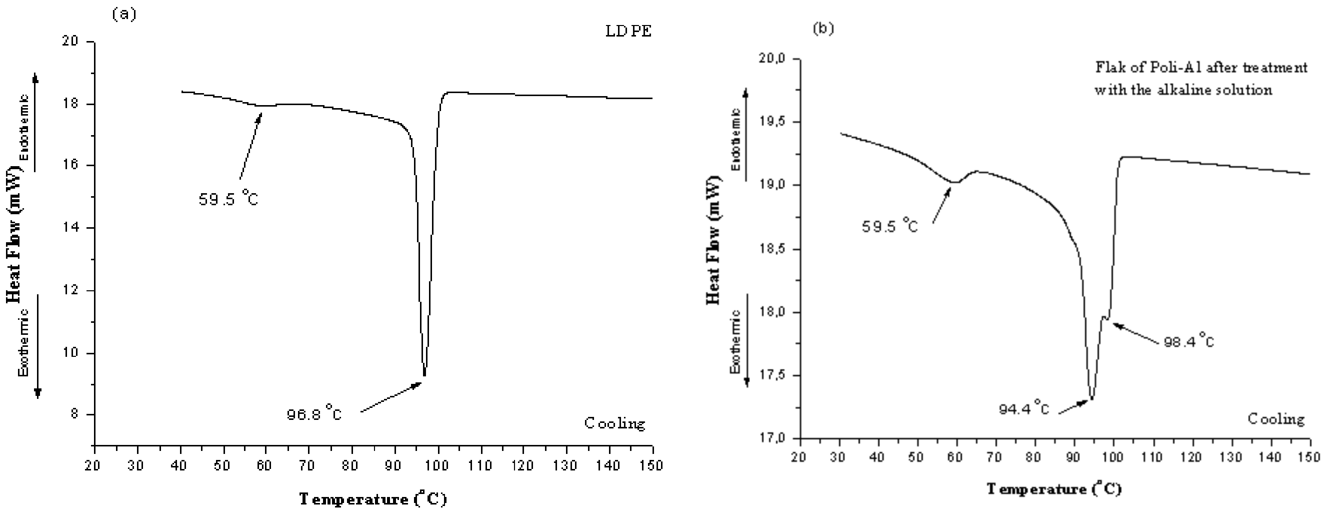
3.6 Thermal characterization (DSC) of Poly-Al flakes

Figure 6 shows thermograms obtained by differential scanning calorimetry (DSC) of the Poly-Al flakes after treatment with the 3 M alkaline NaOH solution. Figure 6(a) shows the cooling thermogram obtained for low density polyethylene (Braskem

- Grade S1522), which was defined as a reference. The thermogram shows two typical LDPE crystallization peaks, with average crystallization temperatures of 96.8 °C and 59.5 °C.

The thermogram obtained for the Poly-Al flake, after treatment with the alkaline solution, is shown in Figure 6(b). The two crystallization transitions corresponding to low density polyethylene occur with crystallization temperatures of 94.4 °C and 59.5 °C. However, an additional crystallization transition is identified with the temperature of 98.4 °C.

Figure 6 - Differential scanning calorimetry (DSC) thermograms obtained with a cooling rate of 10 °C.min^{-1}. (a) low density polyethylene (LDPE) - Braskem - Grade S1522. (b) f lake Poly-Al treated with alkaline solution of 3 M NaOH for 24 h at room temperature.

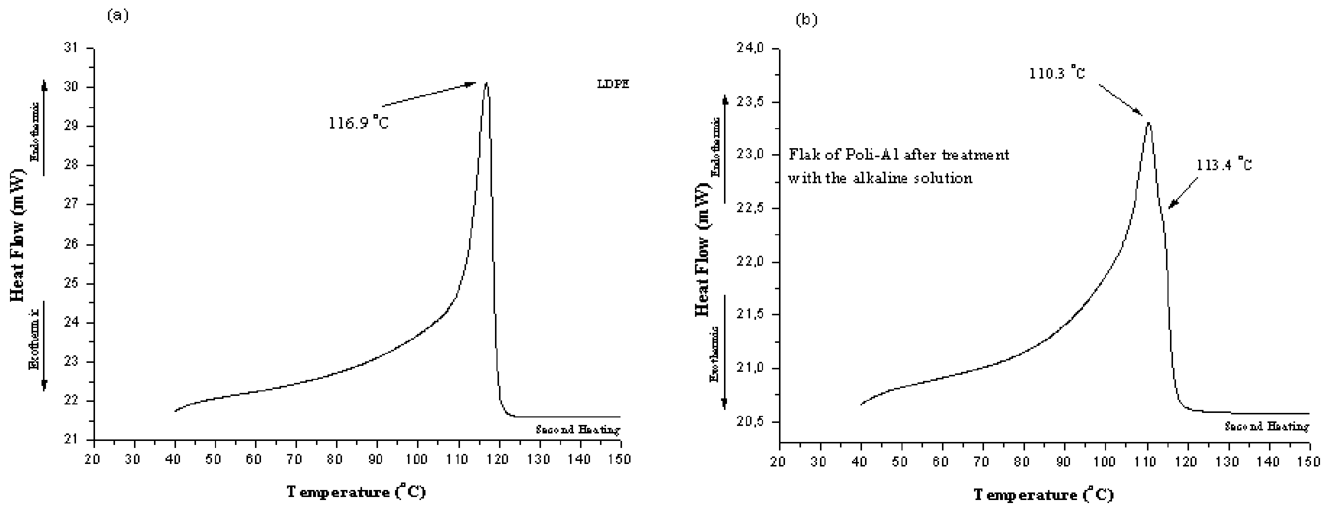


Source: Authors.

This additional transition indicates that the nucleation of a new crystalline phase is favored in the cooling of the fused Poly-Al flakes treated with the alkaline solution. This stage of crystallization occurs at temperatures above the pure polyethylene, an important indicator that the remaining fraction f in aluminum lakes of Poly-Al may be acting as a nucleating agent and promoting the solidification of the flakes melted. Jaerger, *et al.* (2017) showed that the addition of Ni/Al and Co/Al metallic compounds induced a new crystallization phase in low density polyethylene with higher temperatures, an effect similar to that shown by the cooling thermograms of the Poly-Al flakes after the alkaline digestion process. In this sense, the presence of a small fraction of remaining aluminum can be an important and positive factor for the use of the polyethylene recovered from the Poly-Al flakes, since a cooling at a lower temperature can be obtained in the transformation processes of low polyethylene. density, both in extrusion and injection processes.

The differential scanning calorimetry thermograms obtained in the second heating of the reference low density polyethylene (Braskem - Grade S1522) and the Poly-Al flake after the treatment in 3 M NaOH alkaline solution are shown in Figure 7. The thermogram for the reference polyethylene it has an endothermic peak typical of the fusion transition with an average temperature of 116.9 °C.

Figure 7 - Differential scanning calorimetry (DSC) thermograms obtained with a heating rate of 10 ºC.min^{-1}. (a) low density polyethylene (LDPE) - Braskem Grade S1522. (b) Poly-Al flake treated with 3 M NaOH alkaline solution, for 24 h and at room temperature.



Source: Authors.

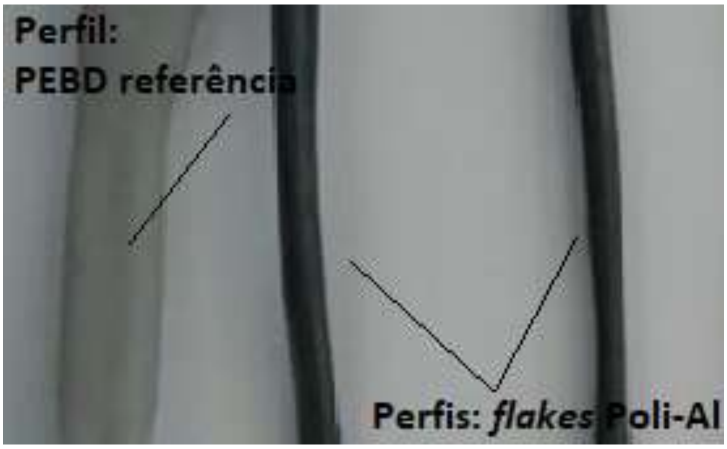
Figure 7(b) shows the heating thermogram obtained for the Poly-Al flake, which has two melting transitions with very close temperatures, 110.3 °C and 113.4 ºC, consistent with the additional formation of a crystalline phase indicated by the cooling thermogram. However, the two fusion transitions occur at lower temperatures in relation to the fusion of the reference polyethylene, which is an indication that in addition to aluminum acting as a nucleating agent, it must be providing a higher degree of crystallinity to the polyethylene and the formation of crystalline phases with lower spherulite sizes, which require lower thermal energy values and consequently lower temperature values for their fusion, according to results obtained by Yu, *et al.* (2019) who proved that the addition of metallic species, especially ZnO, provides a reduction in the value melting temperature of polyethylene.

3.7 Processability by extrusion of poly-Al flakes treated by alkaline digestion

For comparison, the reference LDPE and the flakes of the waste treated with the alkaline digestion process with the 3 M solution were extruded for 24 h at room temperature, with equal processing conditions. In Figure 8 are shown profiles you've got the s with extrusion of both materials. What is evidenced as the main difference is the color change of the profiles processed with the flakes of the translated Poly-Al residue in relation to the profile processed with the reference LDPE. The dark coloration of the profile is due to the mixture of pigments present in the imprinted residues that remained on the Poly-Al flakes even after the alkaline digestion process.

Although there are differences in color, the characteristics of the melt flow, such as flow and dimensional stability with processing time, remained constant. There was no need for changes in the temperatures of the extrusion process and the profiles showed ease of stretching for forming. The surfaces of the profiles produced with Poly-Al flakes translated with alkaline digestion are regular and can be considered to be of excellent finish and absent of signs of thermal degradation.

Figure 8 - Images of profiles obtained by extrusion processing. Details of a profile produced with the reference LDPE (Braskem - Grade S1522) and profiles produced with flakes of Poly-Al residue after the process of alkaline digestion with a solution of 3 M NaOH, for 24 h and at room temperature.



Source: Authors.

In general, the extrusion processability of Poly-Al waste flakes treated with the alkaline digestion process is effective. These results are indicative that the polyethylene obtained after removing the aluminum layer can be processed by conventional polymer transformation methods, proven by extrusion and possibly by injection. Based on the results obtained, it is possible to state that the alkaline digestion process is an effective method for the recovery of polyethylene from post-consumer carton packs.

4. Conclusions

The process parameters that showed a greater removal of aluminum from the Poly-Al flakes from carton packaging waste were obtained when a 3 M NaOH solution was used for 24 hours at room temperature.

The analysis by microscopy indicated the presence of residual aluminum, sodium and other metal species on the surface of lakes Poly-Al after treatment with alkaline digestion solution of higher efficiency. However, the residual percentage is very low, to the point of not significantly compromising the thermal properties of the polymer that constitutes the Poly-Al treated flakes.

From thermal analysis, it was found that the LDPE recovered from the Poly-Al flakes, after treatment with the alkaline digestion solution, shows small variations in the thermal characteristics in relation to the LDPE adopted as a reference. It is worth mentioning the change in the melting temperature, since two melting transitions at 110.3 ° C and 113.4 °C are observed for the recovered LDPE, while only a melting temperature, with a value lower than 116.9 °C, is observed for the reference LDPE. These changes in thermal characteristics are indicators that the presence of metallic species still present after treatment with the solution of alkaline digestion may be acting as nucleating agents and modifying the crystalline phases of the LDPE recovered from the Poly-Al flakes.

The presence of metallic residues in the liquid phase, Cu, Zn, Fe, Ni, V, Mn, with concentrations above the limit allowed by Brazilian law (CONAMA), makes its direct disposal improper. For its proper disposal, it is necessary to treat it in the sense of removing metallic species and conditioning it according to the provisions of Brazilian legislation.

As for the solid phase precipitated after the alkaline digestion process of the Poly-Al flakes, it was found that it consists mostly of $Al(OH)_3$. $Al(OH)_3$ has an added market value and is an input for several large-scale industrial segments. For its proper destination and application, it is still necessary to its complete chemical and physical characterization.

In general, the results obtained indicate that with the process parameters adopted in this study it is possible to perform the polymeric recovery of carton packaging waste, previously devoid of paper. The recycled polymer has favorable characteristics for the recyclable materials industry. The formation of $Al(OH)_3$ and the presence of metals in a concentration higher than that indicated by CONAMA in the liquid phase, indicates that for the purposes of environmental control and disposal both require prior treatment.

Some suggestions for future work include evaluating the mechanical properties of the recovered polyethylene, in addition to carrying out an evaluation of possible processes for the treatment of the effluent generated in this process.

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