



Improvement of multilayer plastic delamination using surface modification

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ABSTRACT

Multilayer flexible packaging waste (MFPW) represents a critical issue in the field of waste management. The heterogeneous composition of this type of plastic makes its recyclability challenging. In this context, the delamination process appears to be a promising way to recycle the polymers layers separately. However, this process is still limited for a few MFPW.

This work propose an innovative way to improve the delamination process using three surface modification techniques (mechanical and laser microperforation (μ P), and abrasion) on the MFPW surface in order to accelerate the diffusion of the dissolving agent. The delamination was tested in a 10 % sodium hydroxide solution at 25°C.

Under this study, the mechanical μ P and the abrasion gave the best results of delamination compared to the laser μ P (total delamination in 25 min vs 45 min, respectively). It was concluded that the distance between the microholes was an important factor in both μ P techniques.

1. Introduction

Nowadays, plastic packaging is the main application of plastic representing more than 40 % of the total plastic demand in Europe (Plastics Europe, 2021), and multilayered flexible plastics (MFP) have become the most used materials in fast-moving consumer goods and packaged-food industries. These MFPs are used once and discarded (Gayathri Devi, 2020). Besides this, multilayer flexible plastic packaging waste (MFPW) is constantly increasing due to the increase in consumption because of population growth.

According to European Commission (European Commission, 2018), plastic packaging waste represents 59 % of the total plastic waste generated in Europe. In 2017, only 42 % of all plastic packaging waste was recycled in the EU (European Union) (European Commission, 2018), and the rest was sent to energy recovery or landfilled. These may cause environmental problems by releasing hazardous chemicals, including dioxins and acid gases (European Bioplastics, 2015; Ragaert et al., 2017). Therefore, energy recovery processes and landfilling must be highly controlled and monitored (Jiang et al., 2020). In addition, 18 % of the total greenhouse gas emissions caused by the plastics value chain come from the processing of plastic waste. It has been estimated that 1 kg of plastic product will result in 2.7 kg of emissions when it is discarded or if it is incinerated (Vanderreydt, 2021). In the EU, 27.36 Mt CO₂-eq were produced from incineration of plastic waste against only

3.02 Mt CO₂-eq generated from plastic recycling (Vanderreydt, 2021). Thus, the incineration contracts the efforts directed toward reaching the goals of a circular economy which states to reduce gas emissions by 40 % by 2050 and to make plastic waste as a material in circulation and keep it in use (Morlet et al., 2019).

MFPW is still a major challenge in the recycling of plastic waste, and it is considered as an undesirable plastic for recycling due to the difficulties that could appear in the recycling chain (Lahtela et al., 2020; Walker et al., 2020). The main problem remains at the composition of this plastic packaging, since the different polymeric and no polymeric layers, adhesives, and inks that make up the MFP have different physical-chemical properties and they are thermodynamically immiscible, which makes their recycling very difficult to proceed by the current technology used for mechanical recycling of plastic (Kaiser, 2020; Pauer et al., 2020).

The main issue that arises when recycling a plastic is that polymers will degrade under certain conditions (Ragaert et al., 2017). This problem could be more important when the plastic to be recycled is a mix of polymers, due to the different physicochemical properties of the different polymers. During the mechanical recycling of polymers, the predominant type of degradation is the thermomechanical degradation of polymers occurring during reprocessing, particularly in extrusion cycles, which reduces their recycling possibilities after four extrusion cycles (Ragaert et al., 2017; Badía et al., 2009), and this yields

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downcycling material with lower quality. This problem is more important when the plastic waste also contains other components apart from polymeric substances such as metals and papers. According to Schmidt et al. (2022), it is estimated that 95 % of the value of plastic packaging is lost after the first phase of use. This is due to the use of mechanical recycling to reprocess mixed plastic waste streams, which leads to a decrease in molecular mass due to the thermal-mechanical degradation which could occur during the reprocessing as a result of overheating and thus limits the number of possible reprocessing processes. However, recycling of single layers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), or polyethylene terephthalate (PET) films, is technically solvable (Mumladze et al., 2018).

Therefore, the challenge in the recycling of this type of waste is mainly in the detection and separation of the different layers in order to get recycled by the usual mechanical recycling techniques and achieve the target set by the EU that 55 % of all plastic packaging must be recycled by 2030. In order to reach this goal, it is essential to focus on the optimization of the mechanical recycling of this type of material to reduce the downcycling, incineration and landfilling allowing plastic waste to be recycled into an upcycling material that could be used in the same sector that was used as the first use, in order to move from linear flow to circular.

The delamination technology is a promising method that can be used as a pretreatment for the separation of MFPW into single materials, since it could allow the recovery of this multilayer material by the traditional mechanical recycling. It consists of the separation of the layers of MFPW by the dissolution of the inner layers such as adhesive or metal using an attack solution. This solution consists of a solvent base solution that can separate one layer from the packaging composite. Mumladze et al. (2018) studied the delamination of the layers using switchable hydrophilicity solvents (SHSs) to break the chemical and mechanical bonding between the layers. Other different techniques were also developed using solvent for the separation of the layers. For example, APK AG developed a technique that can separate the polymers of multilayer films that also contain aluminum foil by stepwise dissolution in methylcyclohexane of PE and PP (Vollmer et al., 2020). Other separation techniques using solvents were developed by Saperatec in Germany and by PVC Separation in Australia, the separation of the different layers of MFPW was also feasible using carboxylic acid (Ügdüler et al., 2022, 2021), nitric acid (Sleiniūtė et al., 2023) and aqueous solution of sodium hydroxide (Berkane et al., 2023). These techniques may not be effective because they do not require a full dissolution of the polymers (Vollmer et al., 2020), and the process could be very long due to the poor permeability of the MFP, which makes the penetration of the solution to the inner layers go only from the edges of the MFP flakes and thus causes the separation process of the different layers take more time.

When focusing on enhancing the delamination process by improving the permeability of MFPW and accelerating the penetration of the solution through the layers apart from using chemical compounds as solvent, this leads to think about the mechanical surface modification of the MFPW as a new way to improve the permeability of this latter. The surface modification of the plastic packaging by microperforation was already used in the food packaging manufacturing to increase the gas transmission rate between the food product and the environmental area in order to improve the shelf life of the food product (Allan-Wojtas et al., 2008; Boonthanakorn et al., 2020). The act of microperforation involves the formation of small holes in the plastic films, and the material studied may be punctured in various ways with the use of lasers, punch, pin or needles.

A mechanical microperforation technique was already developed in our research group (Berkane et al., 2023), and the results obtained by this technique were promising, staying on the same concept. In the present work different techniques for the surface modification of MFPW have been investigated with the purpose of enhancing the delamination process. These techniques consisted, firstly, of mechanical microperforation using microneedles and laser microperforation. The deep

focus in the mechanical modification led to investigate also as a third method mechanical fractures in the MFPW surface by abrasion using sanding paper and a metallic broch. The use of these techniques are considered as an innovative idea in the plastic recycling field with the purpose of facilitating the separation of the different layers of MFPW.

The resulting samples obtained after those techniques were applied were then subjected to delamination in a solution, for the aim to improve the process and make it more effective by identifying the best technique that improves the penetration of the delamination solution through the plastic layers. As mentioned before, the delamination process is limited by the long processing time, so using these techniques before the starting of any delamination methods might decrease that processing.

2. Materials and methods

2.1. Materials

The MFP used for this study was metalized PET supplied from Tramoto Antonio SRL company. This material consisted of two polymeric layers of PET and PE laminated with a barrier layer of aluminum. These aluminum layers are joining together the polymeric layer making a sandwich-like structure. This type of MFP is used in various packaging applications such as food and cosmetics packaging. The dissolution of the metal layer allows the separation of the two plastic layers.

The dissolution of the aluminum layer is easy and fast compared to the dissolution of adhesives joining the plastic layer in the MFP without a metallic layer, since in this case, the dissolution time is very long. For this reason, this type of material was chosen to better follow the delamination process.

The delamination solution used to dissolve the aluminum inside the MFP was an alkaline solution of 10 % sodium hydroxide.

2.2. Surface modification techniques

All samples for which the three treatment techniques were applied were cut into small flakes of 2.3 x 2.3 cm². This metalized MFPW had a thickness of 107 µm.

Microperforation: The perforation technique consists of creating diffusion channels in the plastic surface. These channels allow the penetration of gas or liquid to go through this material. Plastic packaging has a narrow range of permeability for gases (Kwon et al., 2013) and liquids. In the case of multilayer packaging the separation of the different layers by delamination is difficult because of the weak permeability of this material. Furthermore, in some cases the adhesives that join the layers of MFP are very hard to be dissolved. Thus, these microperforations or channels allow the liquid to act as a dissolution agent to penetrate through the different layers, which improves the diffusion and accelerates the delamination process.

Mechanical microperforation: MFPW samples were firstly microperforated mechanically using a laboratory perforation roller. Five different microperforation densities (µP/cm²) were applied in films (6, 22, 30, 46 and 61 µP/cm²). The diameter of the holes ranged from 76 to 168 µm. This technique was patented by Fullana (2021).

Laser microperforation: The laser cutting machine used for the microperforation was a K40 40 W 200 mm x 300 mm Portable CO₂ Laser Engraver Cutter Engraving Machine 40 W L. Before introducing the MFPW sample in the laser machine, the distribution of the microholes in the plastic film, the diameter of the holes and the distance between the holes were adjusted using the Inkscape software. The same microperforation density as that made for mechanical perforation was made by laser microperforation. The diameter fixed by the Inkscape was 100 µm. The laser microperforation is a technique already used in food packaging manufacturing. The intensity of the laser power and the laser speed was adjusted in order to get the required microperforation. Thus, the laser machine could give holes with a bigger diameter than the one fixed with

Inkscape. This is because the polymer layer melted, and the perforation of this type of MFPW through all the film thickness needed a higher power and lower laser speed. In this case, it was adjusted in laser power 100 % and speed of 8 mm/s. However, for microperforation only in one surface (one layer) the speed was fixed at 20 mm/s.

Mechanical abrasion: For the mechanical abrasion of the surface of the MFPW sanding paper and a metallic broch were used. A random sanding was carried out by these two instruments.

In order to quantify the surface structures of the modified surfaces and characterize their microstructure, analysis of scanning electron microscopy (SEM) was used in the determination of these parameters. The scanning electron microscope used was a Hitachi S3000N model. This microscope was equipped with a Bruker model XFlash 3001 X-ray detector for microanalysis (EDS) and mapping. Atomic force microscopy (AFM) was used to analyze the modified surface by abrasion of the MFP sample.

2.3. Experimental study

As said before, the delamination process involves the dissolution of the aluminum layer. When this layer is totally dissolved the two polymeric layers are separated. Since it is supposed that the permeation of the two polymer layers (PE and PET) is negligible, the delamination mechanism is carried out by the penetration of the solution only from the lateral edges of the samples. When no modification is applied on the samples surface, it is expected that the mechanical surface modification will improve the surface permeability of the two polymeric layers by creating access of the solution from the surface to the inner layer. The process carried out consisted of introducing the MFPW samples with surface modification in a beaker of 250 mL with a stirred aqueous solution (10 % sodium hydroxide), and the processing temperature was fixed at 25 °C. The subsequent delamination process of the different samples consisted of the measurement of the quantity of Al being dissolved in the solution during time. The concentration change of Al in the aqueous solution was measured by inductively coupled plasma mass spectrometry (ICP-MS-Agilent 7700X). The samples in the aqueous solution were acidified with 2 % HNO₃ in order to avoid the precipitation phenomenon. When the concentration of Al in the solution was constant (steady state of dissolution kinetic curve), the layers of MFPW material were assumed to be totally delaminated.

2.4. Characterization of the MFPW sample

The determination of the MFPW composition and the thickness of each layer was made by using Fourier-transform infrared and Raman

spectroscopy (Raman/FTIR) and SEM to identify the structure of the MFPW samples. The analysis of the cross-section of a sample is shown in Fig. 1. The characterization clearly showed the presence of three layers: a thick layer of PE film of 86 μm thickness, a very thin layer of Al with 4 μm and a thin layer of PET with 17 μm of thickness. The Raman analysis did not show the presence of an adhesive layer. This could be due to the very thin thickness of the adhesive. Nevertheless, the FTIR analysis gave a PE spectrum and other unknown spectrum which is a thin layer about 20 μm that makes its characterization difficult by Raman/FTIR. This layer could be the PET layer containing the nanoparticles of Al (aluminum) and the adhesive.

3. Results and discussion

3.1. Microstructure of the samples after surface modification by the three different techniques

The mechanical perforation using a microneedle roller produced a total microperforation on the film surface. The SEM images showed that the perforation was done through all the film layers, and Fig. 2a and b showed that the hole was totally open from both sides of the film making a volcano shape. These holes had an irregular shape and size and their diameter ranged from 76 μm to 168 μm. Another observation noticed after a deep focus in the microholes showed mechanical pre-delamination of the plastic layers in the edges of the hole, best seen in Fig. 2b resulting from the breakup in the multilayer film. This initial delamination may be explained by the failure of the aluminum–polyethylene joint due to breaking H-bonds between polar functional groups on oxidized Al and PE surfaces (Garrido-López and Tena, 2010).

Fig. 2c and d obtained by SEM of the laser microperforated samples showed that the holes formed in the MFPW sample surface had a regular shape and size. The hole diameter was about 500 μm and the holes were regularly distributed in the sample surface contrarily to mechanical μP which has a random distribution. However, a deep focus showed that perforation was not done totally through all the film (from the upper to the lower surface), but it was made only in the side of the application of the laser, so the laser light did not go through all the film. This is best seen in Fig. 2d Another observation noticed that the plastic layer where the laser was applied was melted and the Al was burned (Fig. 2d). The melted plastic made obstruction in the perimeter of the microperforation which might close in some point the access of the solution to the Al layer.

The SEM analysis of the sample surface with abrasion using a metallic broch presented in Fig. 2e and f showed a scribble on the sample surface, and the analysis of the cross-section did not show any fissures in

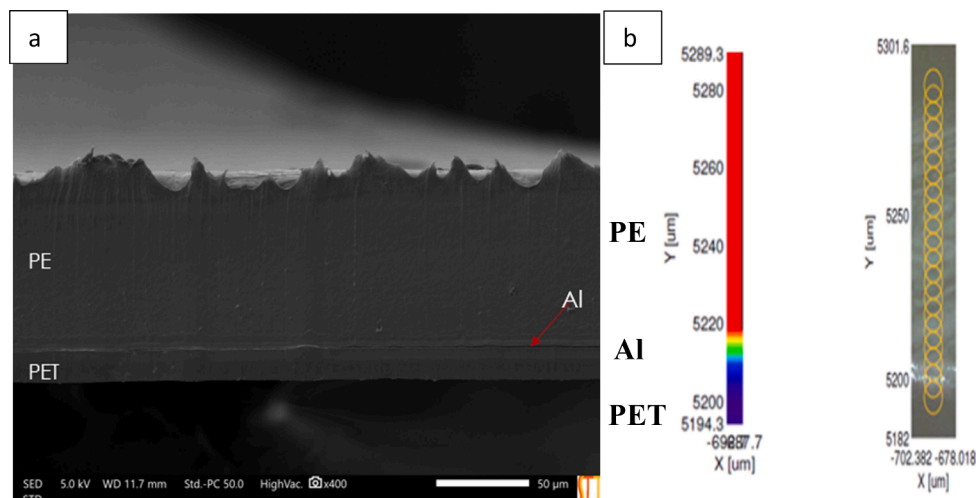


Fig. 1. SEM image (a) and Raman imaging (b) of the cross-section of MFPW sample.

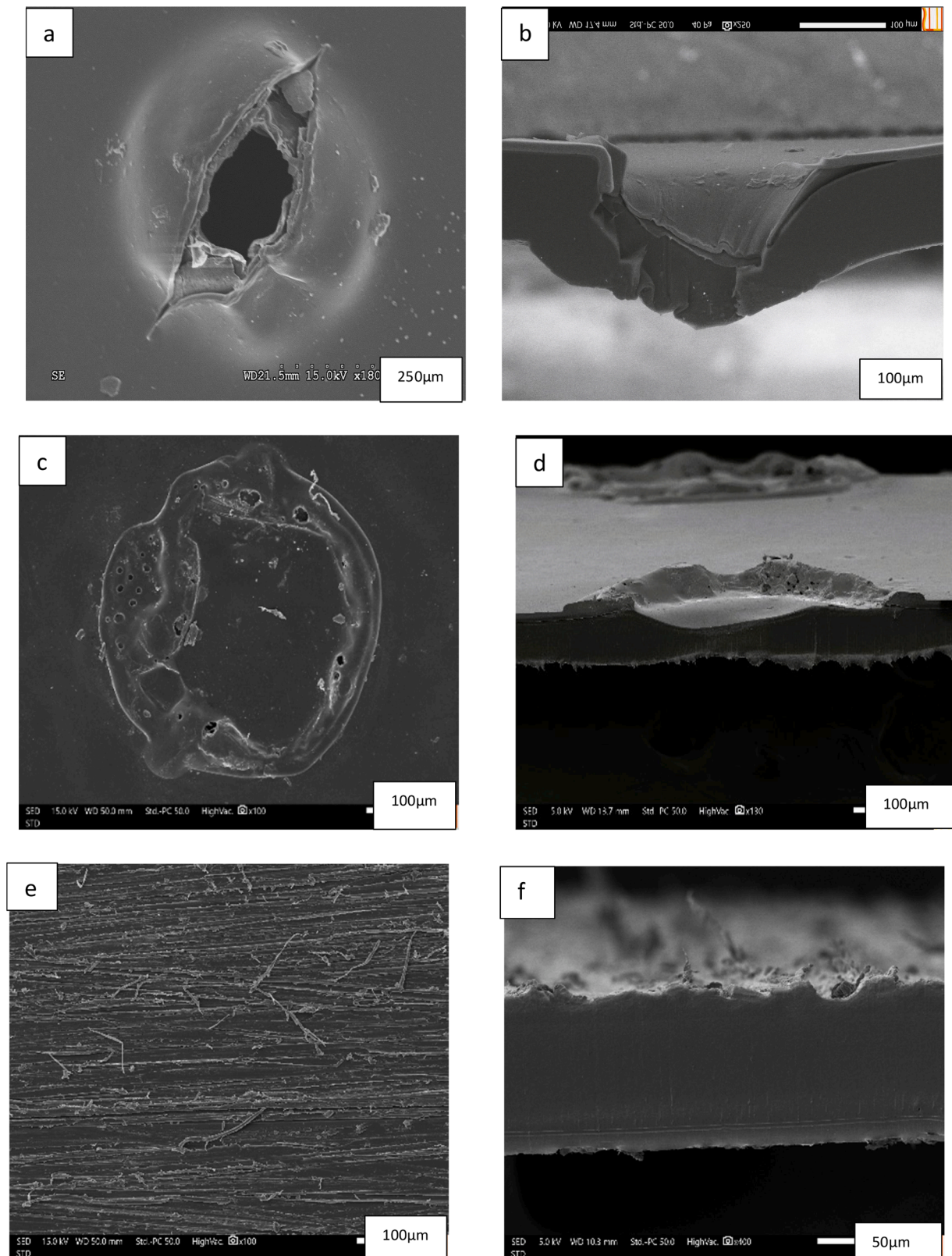


Fig. 2. SEM images for samples with mechanical μ P (a: the surface view and b: cross-section view); laser μ P (c: surface view and d: cross-section view) and samples with abrasion (e: view of the surface and f: cross-section view).

the cross-section surface. There was not a modification in the transverse section (Fig. 2f), but the modification was done only on the outer surface of the samples. According to this observation, the mechanical modification using a metallic broch did not break up the sample layers.

However, it was observed that during the delamination process the dissolution solution penetrated also from some areas on the surface. According to this, there was some kind of modification and reduction of the thickness of the samples, but the SEM analysis could not show this

modification.

3.2. The dissolution kinetics of Al in mfpw samples with surface modification

The surface modification of the MFPW could be an innovative technique for the enhancement of the delamination process. The mechanical microperforation had been already tested in our research group with promising results (Berkane et al., 2023). For the same purpose, the laser microperforation and surface modification by sanding the surface could also improve the recyclability of the MFPW as well as mechanical microperforation. In this section, a comparative study of the three techniques is presented in Fig. 3.

The evolution of the delamination process was monitored by the dissolution kinetics of the Aluminum layer. A total delamination of the polymeric layers was achieved when Al was totally dissolved (steady state of the dissolution curve). The microperforation density of mechanical and laser microperforation technique chosen for the comparison with the abrasion technique was the maximum density (61 $\mu\text{P}/\text{cm}^2$), and the abrasion of the MFPW samples was made in one direction forming parallel lines in both surfaces of the samples (maximum lines were made in the sample surface). From the comparison of the dissolution kinetic curves obtained by the three techniques shown in Fig. 3, it can be concluded that the samples subjected to laser μP (M-L) gave the slowest processing time of the three techniques, and the total delamination was achieved after 45 min. However, the mechanical μP (M-MC) and the surface modification with abrasion (Ms) gave better results and a similar evolution of dissolution, since a total delamination was achieved after 25 min for mechanical μP and after 30 min for samples with abrasion. In comparison to control samples without surface modification (M-0), the results showed a significant improvement in the delamination process with the three techniques.

As said before, the mechanical μP gave better results than the laser μP . This may have been due to differences in the microstructure of the microholes formed by these two techniques as shown in the SEM (Fig. 2). The penetration of the solution into the Al layer from the rims of the holes formed by mechanical μP was in all directions of the hole perimeter. However, for the laser microholes the access from the holes was lower compared to the mechanical μP . The molten plastic formed a barrier at certain points of the perimeter of these holes as shown in SEM images (Fig. 2d), which made the permeability of the film lower compared to the holes made by mechanical μP and so the penetration of the solution into the Al layer from the surrounding area of these holes was obstructed. Moreover, the pre-mechanical delamination formed during the mechanical perforation might have facilitated the accessibility of the solution to the Al layer, making this technique better than the laser μP . Regarding the good results obtained by abrasion, this technique was supposed to increase the roughness of the surface and

made fissures in some points of the surface, which increased the diffusivity of the solution to the inner layer of Al.

Regarding the literature, the MFPW was placed into the dissolving agent directly without any pretreatment of the plastic surface. Generally the process is carried out at high temperature (higher than 50 °C) to accelerate the process. In this work, we proposed a new way to accelerate the process and improve the diffusion of the dissolving agent to the inner layers of adhesive or metal by applying a surface modification in the MFPW samples. The comparison of the results of the delamination obtained here when any of the three techniques were applied in the plastic surface with the existing results in the literature without applying any modification in the plastic samples shows that the three techniques could improve significantly the process. O'Rourke et al. (2022) obtained the delamination of different polyamide/polyolefin multilayer films in diethylene glycol (DEG) at 150 °C after about three hours. However, the delamination of different types of MFPW using carboxylic acids was obtained after about two hours at 75 °C (Ügdüler et al., 2021). Moreover, Vagnoni et al. (2023) studied the delamination of polyolefin/Al at 90 °C in anionic surfactant and the delamination was obtained in half an hour for coffee bags and three hours for the other polyolefin/Al samples. From these results we can notice that the processing time in these works was significantly high even at high temperatures (75–150 °C) compared with the results obtained in this study, and in the previous results the high temperature was the factor accelerating the delamination process. By using the surface modification techniques the processing time is reduced significantly as mentioned before, so we can consider these techniques as an accelerating factor of the delamination process. Thus, using the surface modification allows decreasing the temperature and the time of the process.

3.3. The microperforation technique

3.3.1. Effect of microperforation density in the delamination process

The delamination time decreased significantly when any microperforation technique was applied to the plastic waste, and this time decreased as a function of the increase in the perforation density.

The evolution of the delamination time (R) vs the microperforation density for mechanical and laser perforation samples is shown in Fig. 4a. It was noticed that applying microperforation decreased the delamination time when both techniques were used. For only 2 $\mu\text{P}/\text{cm}^2$ applied on the sample surface the time decreased from 300 min to 190 min for laser μP and to 130 min for mechanical μP . A significant decrease to the half in the delamination time of the process was observed when the μP density increased from 6 $\mu\text{P}/\text{cm}^2$ to 22 $\mu\text{P}/\text{cm}^2$. Then the decrease in the time started to be slow with the increase in the μP density. As an example, going from microperforation of 22 $\mu\text{P}/\text{cm}^2$ to 30 $\mu\text{P}/\text{cm}^2$ decreased by only 10 min the processing time for both techniques. This means that the diffusion increased more slowly for perforation densities higher than 22 $\mu\text{P}/\text{cm}^2$.

The distance between the microholes decreases when increasing the μP density and that decrease was the factor causing the decrease in the delamination time. In this case, it was supposed that the diffusion through the microholes was lateral diffusion from the perimeter of the holes to the inside area of the surface.

Assuming that the MFPW samples were square in shape and that the microholes were regularly distributed inside the surface area of the sample, with the same number of holes along both perpendicular directions of the surface of the square shape sample, with the consideration that in 1 x 1 cm^2 we have N $\mu\text{P}/\text{cm}^2$ so in 1 cm we have \sqrt{N} $\mu\text{P}/\text{cm}$, under this condition the distance d between two consecutive holes was estimated as a function of the μP density, using the following expression:

$$d = \frac{1}{\sqrt{N}} - \emptyset \quad (1)$$

being N the microperforation density in $\mu\text{P}/\text{cm}^2$ (in this case $N \neq 0$) and \emptyset

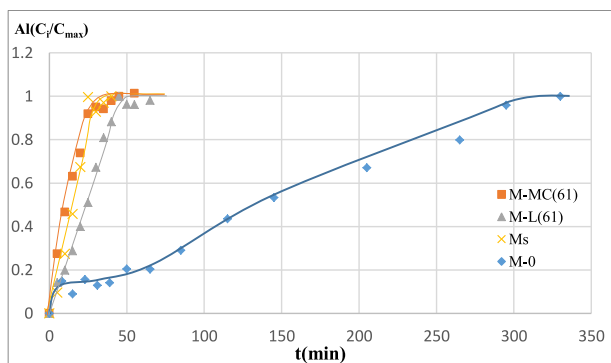


Fig. 3. The dissolution kinetics of MFPW samples with different surface modification techniques: M-MC: mechanical μP , M-L: laser μP , and Ms: by sanding the surface of MFPW samples.

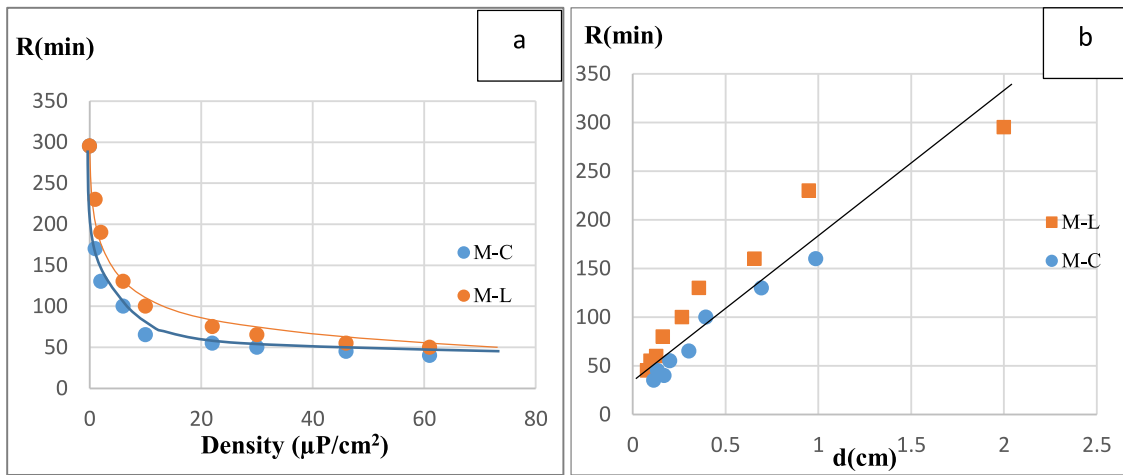


Fig. 4. (a): delamination time R of MFPW samples with mechanical (M-C) and laser (M-L) microperforation vs microperforation density at $T = 25^{\circ}\text{C}$; (b): delamination time vs distance between microholes at $T = 25^{\circ}\text{C}$.

the diameter of one hole in cm. In the case of the no microperforated sample the distance d was considered to be the side of the sample a (in the case of our samples, $a = 2$ cm).

The results seen in Fig. 4b showed that the delamination time fitted properly with a linear function of the distance d above defined. These results proved that the diffusion in the case of microperforated samples was a lateral diffusion from the microholes perimeter to the inner surface. The diffusion phenomenon of the process was described using Fick's first law (Ügdüler et al., 2021) as follows:

(2)

The concentration diffused to the solution (C_s) is the concentration at the boundary layer, which is supposed to be equal to the concentration of saturation ($C_s = C_{\text{saturation}}$) of the solute (Al); C_b represents the bulk concentration and is considered negligible ($C_b=0$); C is the concentration of Al diffused to the solution at any time t ; A is the specific surface (cross sectional area of diffusion S / volume of the diffusion V) (cm^2/cm^3); Δx is defined as half the thickness of plastic film (cm); and D is the diffusion coefficient (cm^2/s).

In the case of the lateral diffusion, the cross-sectional area of the diffusion flow from the microholes (S) is not constant (Eq. (3)), since each microhole has a diameter \varnothing , but the diffusion takes place until a maximum distance of $d/2$, being d the initial distance between the walls of two consecutive microholes, as shown in Fig. 5. Thus, the specific surface of the diffusion is not constant, and it depends on the distance d that the dissolution travels from the walls of the microholes through

Aluminum while is dissolved at time t_i (Eq. (5)).

$$S = \pi (\varnothing + 2d_i)e_{Al} \tag{3}$$

$$V = \pi \left(\left(\frac{\varnothing + 2d_i}{2} \right)^2 - \left(\frac{\varnothing}{2} \right)^2 \right) e_{Al} \tag{4}$$

$$A = \frac{S}{V} = \frac{(\varnothing + 2d_i)}{\left(\frac{\varnothing + 2d_i}{2} \right)^2 - \left(\frac{\varnothing}{2} \right)^2} \tag{5}$$

with $0 \leq d_i \leq d/2$

Moreover, from the results of Fig. 4b it was noticed that the three lower distances for both mechanical and laser microperforation that corresponded to the μP density 61, 46 and 30 $\mu\text{P}/\text{cm}^2$ were more or less constant (there was a variation of 0.05 cm). This very small variation might have been the reason for a lower decrease in the residence time of delamination noticed previously from Fig. 4a. Therefore, when the reduction in the distance between the holes was not significant, the diffusion of the dissolving agent to the inner Al layer was constant.

3.3.2. Limitation of laser microperforation

In food packaging manufacturing, the perforation of the packaging by laser machines allows the formation of total holes or only on the surface depending on the needs of the breathability of the film for each food product to improve the gas transmission. The application of this

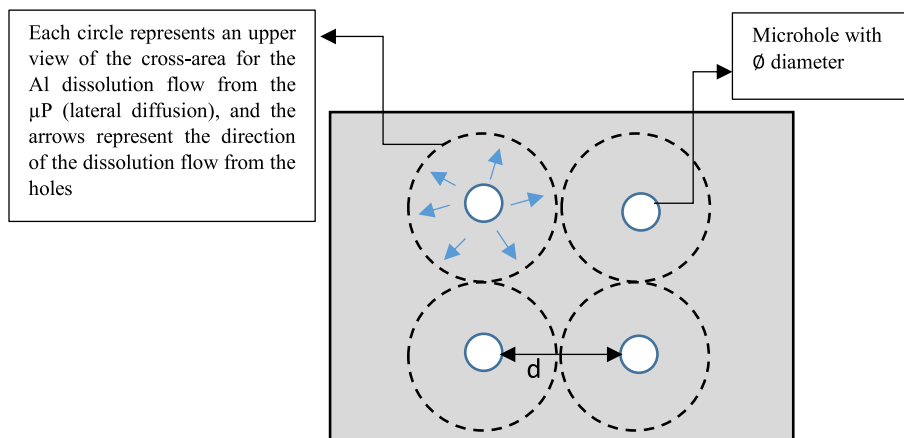


Fig. 5. Illustration of the surface A and the direction of the diffusion from the μP in a microperforated MFPW sample.

technique to increase the permeability of MFPW to liquid (dissolving agent) to enhance the delamination process might not be applied as in food packaging production.

Laser microperforation is based on the accumulation of focused light at a very small point in space. This energy is so big that it can vaporize materials such as polymers, metals, and even ceramics. In our case, this has been done in a controlled way at a small point to make microholes in the material surface (Atria Innovation, 2020). Thus, the laser perforation of a polymeric material generates a melted polymer in the borders of these microperforations, and depending on the thickness of the plastic material and the laser power pulsation this microperforation could be only at the surface (not a total hole) or through all the material deepness (total hole). This technique could be used as mentioned previously to increase the penetration of the dissolving agent to the inner layer of MFPW from the perimeter of this micro perforation. However, contrary to mechanical perforation the access here was not from all the perimeter but only from a few accesses, due to the presence of melted plastic in this area generated during laser perforation which made a sealing of the layers in some point of perimeter, according to the results obtained in Fig. 6. The higher the power of the laser pulse, the greater the presence of the sealing at the holes, since it was observed that when the power pulsation of the laser was increased to get a total microperforation the delamination time was higher compared to the samples with superficial microperforation (210 min vs 175 min for μP from PE side and 160 for μP from PET side).. It was also noticed from the results that the samples with μP on the thin layer took less time to be delaminated compared to samples with μP on the thick layer, since a decrease of 15 min was observed. This was due to the quantity of the melted plastic at the microperforation perimeter. Thus, the μP on the thick layer generated more melted plastic than in the case of the thin layer, which meant less area for the solvent to access the inner layer.

3.4. Surface modification by abrasion of the MFPW surface

The abrasion of the MFPW samples was made in only one direction, which formed on the sample surface like parallel lines as shown in Fig. 7. After following the delamination process and the dissolution of the Al layer inside the MFPW sample by controlling the experiment each minute of processing after 10 min of dissolution, the samples were taken out from the solution and the distances that the dissolution took from the four sides of the sample were measured (Fig. 7a) using a caliper. The experiment was repeated three times, and from the comparison of the dissolution distances ("a" and "b" in Fig. 7b), it was observed that the dissolution of Al through the sample edges was faster at the two sides of the sample in the direction of abrasion or sanding ("a" in Fig. 7b) compared to the direction perpendicular to sanding ("b" in Fig. 7b), being the distance "a" of the dissolution from edges in the direction of

abrasion bigger than the distance "b" of the dissolution perpendicular to the direction of abrasion ($a > b$, Fig. 7b). The abrasion of the surface samples, contrarily to the μP , led to make only few access areas from the plastic surface in a random position on the surface as shown in Fig. 7a and b. This technique led also to reduce the thickness of the plastic layers as shown in Fig. 7c and d. However, the residence time of the delamination was quite the same as that of the mechanical microperforation of $61 \mu\text{P}/\text{cm}^2$.

The SEM analysis of the cross-section of the sample with sanding did not show any modification through the thickness (see Fig. 2e and f), and the abrasion was observed only on the outer surface. However, AFM analysis of the height profile (Fig. 8a) showed that this abrasion decreased the thickness of the plastic layer at some area in the cross-section (where the abrasion was made) compared to the control sample (Fig. 8b). All the surface area of the modified sample ($6 \times 9 \text{ mm}^2$) was analyzed by AFM by analyzing an area of $100 \mu\text{m}^2$. This showed that the thickness decrease of the analyzed layer (PET layer of $17 \mu\text{m}$) ranged from 0 to $17 \mu\text{m}$. However, the thickness reduction at the other side of the sample (PE layer of $86 \mu\text{m}$) was lower compared to its thickness. This surface modification might have weakened the aluminum-plastic layers joint and make some access on the surface of the samples. This could be the reason for the improvement in the penetration of the solution observed at the edges of the samples. Also, this surface modification increased the specific surface of the sample and its roughness. The increase of the surface roughness of the plastic could decrease the hydrophobic properties of PE and PET layers and improve the wettability of the surface, thus making the immersion in the aqueous solution easier than in the control sample. Encinas et al. (2010) studied the improvement of the wettability and adhesion properties of HDPE, LDPE, PP and silicone by abrasion of the surface of these polymers, and they found that this mechanical treatment enhanced the wettability of the polymers.

Results also showed that the sanding of the sample from both sides was important (Fig. 9a), since the dissolution kinetics was faster when the abrasion was made on both sides of the samples. A significant decrease in the processing time was also observed when the abrasion was made on the thin layer (PET layer of $17 \mu\text{m}$) compared to the processing time obtained when the abrasion was made only on the thick layer of the sample (PE layer). The total delamination time of the sample with abrasion only on the thick layer was about 190 min against 70 min obtained when the abrasion was made only on the thin layer. This could be due to the significant decrease in the thickness by abrasion of the thin layer (PET) compared to its thickness. As shown in Fig. 8a, the thickness decrease by abrasion in the PET layer went from 0 to $17 \mu\text{m}$. This made access in some areas on the surface which led to accelerated dissolution. When the abrasion was made in both sides (thin and thick layer) the delamination time was around 25 min, although the abrasion of the thick layer (PE) did not reduce the thickness and create accesses from the surface, but its application reduced the delamination time to up to half compared to the sample with abrasion only in the thin layer side. These results proved that the enhancement of the specific surface and the roughness of the surface improved the immersion and the spread of the solution on the samples surface, which involved a fast diffusion of the dissolving agent to the inner layer of Al from the edges of the sample. It was also noticed that the Al dissolution was faster from the edges in the direction of the abrasion ("a" direction in Fig. 7b). Thus, the valleys (parallel lines) formed by abrasion improved the diffusion through the edges of the sample. The results obtained in Fig. 9b for the sample with abrasion along two perpendicular directions confirmed these results, since the abrasion along both directions increased the specific surface of all the cross-section area of the sample. However, the abrasion along one direction increased the specific surface only in the cross section in direction of abrasion. The delamination time decreased to the half when the abrasion was made in the two directions of the sample compared to the experiment when the abrasion was made in one direction. It was supposed that in the case of the abrasion technique both lateral diffusion (from the accesses created on the surface to inner area of sample surface)

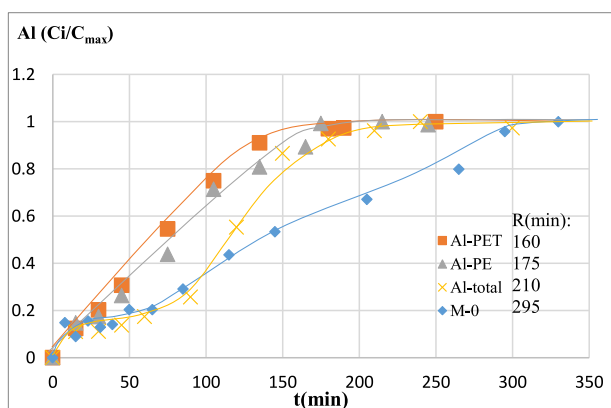


Fig. 6. The evolution of the dissolution kinetics of the Al layer for samples with laser microperforation with different intensities of the laser application.

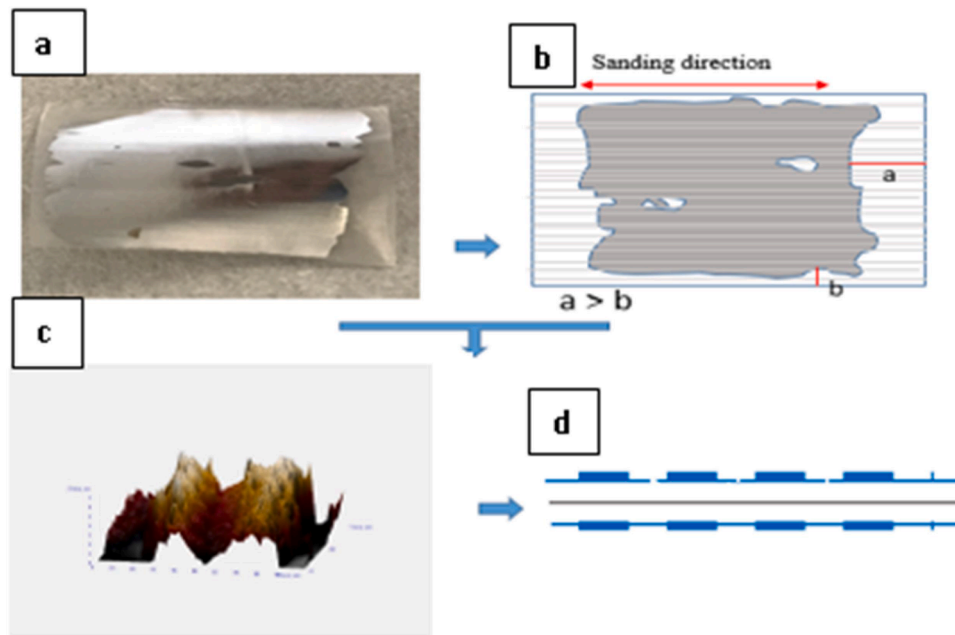


Fig. 7. (a) represent the sample with abrasion after 10 min of dissolution, (b): represent an illustrative diagram of figure (a) describing the way of Al layer dissolution in sample the shaded area represents the non-dissolved Al and the transparent area the dissolved Al area, an illustration of the cross-section of the sample by AFM microscope (c), and a representation of the cross-section (the reduction of the layers thickness) (d).

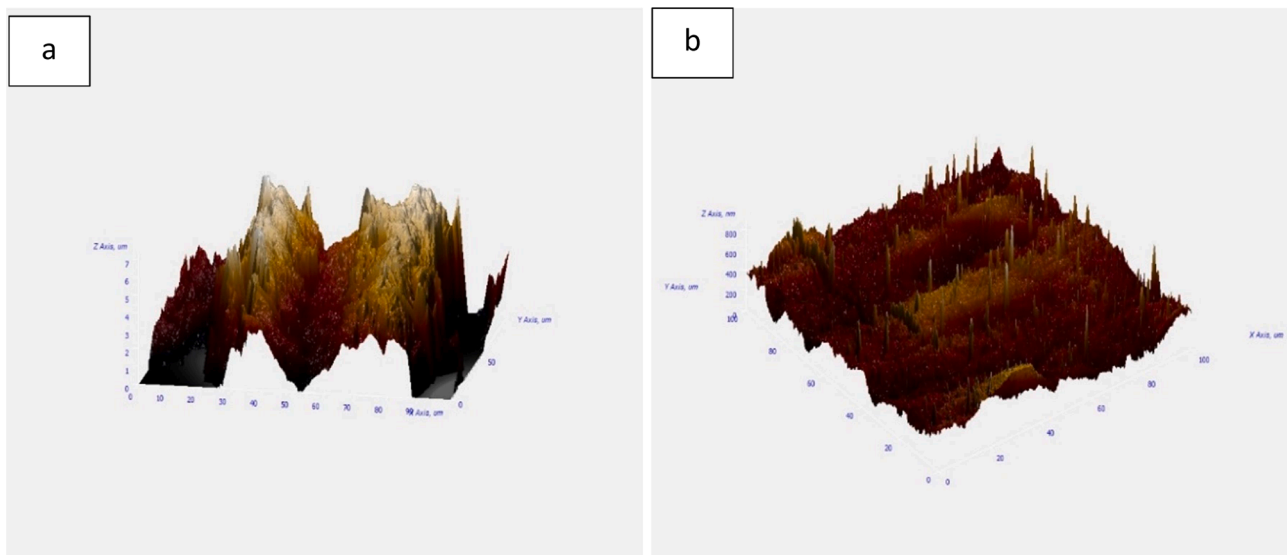


Fig. 8. AFM 3D image of MFPW samples: (a) sample with abrasion, (b) control sample without abrasion.

and frontal diffusion (from the edges of the sample) happened. The lateral diffusion was at the samples surfaces in the access area (cracks formed due to the strong abrasion). Here it was expected that the diffusion was similar to the diffusion through the microholes, but it was slower than in the microperforated samples due to the small number of accesses compared to the number of accesses in the microperforated sample. However, the frontal diffusion through the edges of the sample was faster when the abrasion was applied to the samples than in the control sample or the microperforated sample (the frontal diffusion was supposed to be the same in both microperforated and control samples).. From these results it was concluded that the abrasion technique was affected by the thickness of the MFPW layers. If the polymers layers were too thick the application of abrasion did not decrease significantly the thickness and did not create accesses on the surface of the samples (the

case of PE layer). The specific surface improvement could be lower in this case. Thus, the enhancement of the delamination by this technique is related to the reduction of the thickness compared to the thickness of the polymer layer.

4. Conclusion

Separating the different polymer layers from the MFPW remains a challenge due to the difficulties that must be encountered in the separation process. The dissolution of the coating layer of metal joining the polymeric layer together is often a very long process because of the low diffusivity of this plastic material. The mechanical surface modification of the MFPW waste could be a promising way to improve the diffusivity of the plastic film to the dissolving agent and fasten the delamination

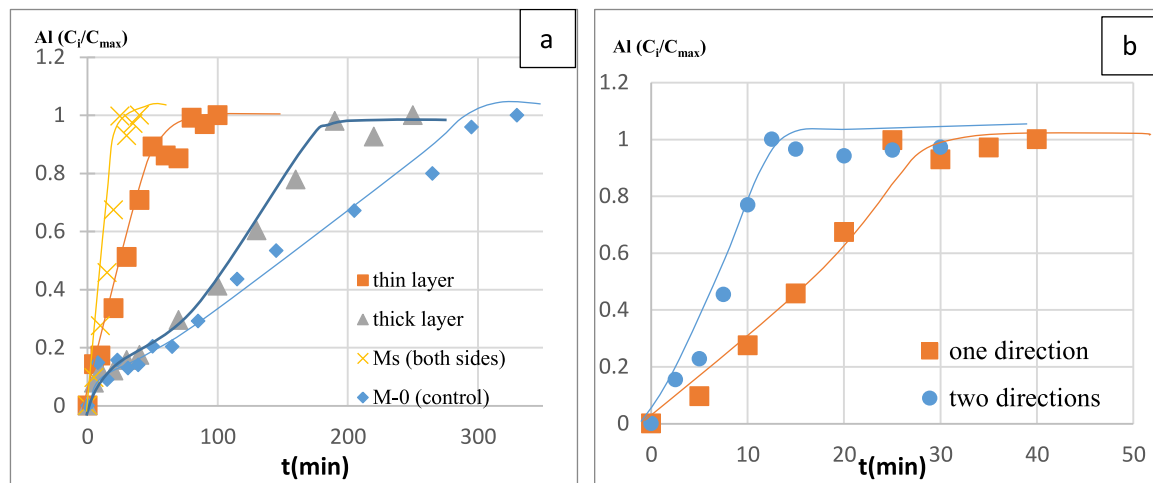


Fig. 9. Dissolution kinetics of the Al layer in MFPW samples: a) when only the thin layer of polymer was sanded, only the thick layer sanded and when both sides were sanded Ms (the abrasion was made in one direction) in comparison to control sample M-0, and b) two directions of the abrasion was made in the sample surface compared to abrasion made in one direction (in both experiments the abrasion was made in both sides of the sample).

process and enhance the effectiveness of this process.

All three surface modification techniques studied gave a significant improvement of the process compared to the control samples. A decrease from 295 min to 45 min in the delamination time was obtained for laser microperforation at room temperature. Both the mechanical μ P and the surface modification by abrasion gave the best results compared to the laser μ P, and the delamination time of the process decreased to 25 min by these two techniques at room temperature.

It was found that the delamination process of the metallized MFPW was size-dependent, and the decrease in the distance between the microholes led to decrease the delamination time.

The laser μ P of the MFPW waste should not be totally made through all the depth of the film to avoid the sealing problem of the different layers in the surrounding area of the microholes. Thus, superficial laser μ P of only the thin layer of the film gave better results than total laser μ P through all the sample. Therefore, both μ P techniques (mechanical and laser μ P) improved the lateral diffusion of the dissolving agent through the holes to the inner layer of Al by enhancing the permeability of the MFPW surface to the liquid.

The surface modification by abrasion of the MFPW surface led to increase the specific surface of the surface and the cross-section area. This technique also allowed the formation of some access in the sample surface, which improved the frontal diffusion of the dissolution agent through the edges of the sample (cross-section area) and the diffusion from the surface to the inner layer of Al.

The surface modification techniques by microperforation and abrasion could be an innovative technique investigated for the first time in this research to enhance the delamination process by improving the diffusion of the dissolving agent and the MFPW samples, which lead to accelerate the delamination process. Thus, the application of these techniques might decrease the energy consumption of the delamination process by decreasing the processing time and the temperature. This technique is a promising way to increase the recycling rate of MFPW.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this manuscript, artificial intelligence was not used.

CRediT authorship contribution statement

Imene Berkane: Conceptualization, Investigation, Methodology, Visualization, Writing – original draft. **Ignacio Aracil:** Project

administration, Supervision, Validation, Writing – review & editing. **Andrés Fullana:** Conceptualization, Methodology, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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