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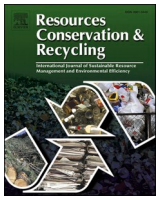

Full length article

The delamination of metalized multilayer flexible packaging using a microperforation technique

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ABSTRACT

Multilayer flexible packaging waste is a critical issue in the field of waste management as it is considered a non-recyclable material. One of the solutions to increase its recyclability is the delamination, which allows the recycling of the different polymer layers separately. This study investigated the optimization of the delamination by microperforating this plastic. The diffusion model was described by Fick's first law. The delamination process was tested at three different temperatures (50, 65 and 80 °C) with caustic soda. In addition, the influence of other parameters such as the thickness of aluminium layer, the presence of inks and the use of surfactants was tested. As a result, the microperforation technique improved the delamination rate by decreasing the residence time by 83% at the optimum conditions studied, being the thickness of the metal and the temperature essential factors affecting the process. However, the presence of inks and surfactant had no effect.

1. Introduction

Multilayer flexible packaging (MFP), in which different materials are combined in a layered structure, is widely used in different sectors such as food agriculture and cosmetics, since its good protection and preservation of the product are considered as economic advantages. MFP is made with different materials such as paper, plastics and metals joining together making a sandwich-like structure. The polymer in the package is laminated with aluminium (Al) foil and /or paper board and other polymer types, each layer contributing in its own way to achieve the technical functionality desired by this packaging. For example, polyethylene terephthalate (PET) is often used for water and gas barrier and it improves the mechanical strength, while polyethylene (PE) is often used because of its excellent sealing properties, water barrier properties, and low-temperature performance (Delva et al., 2019). The paperboard, which is considerably thicker than the other layers, bears the load when the package is filled, folded and gripped, while the Al-film isolates the liquid inside from light and diffusion (Shafiqul, 2016), protects the product from UV light and avoids the photo-oxidation reaction. The adhesion between layers is obtained by co-extrusion or by adhesives (Garrido-López and Tena, 2010). Depending on the use of this packaging and the protection needed for the product to be packaged, the number of layers in the packaging can be up to 12 layers.

The packaging of aromatic products such as coffee is one of the sectors most using laminated packaging, this latter being designed to minimize the transmission of oxygen, moisture and aromas. It is generally formed from a sheet of metal foil, various layers of known plastics and adhesives. A conventional coffee package may have a laminate structure (from the inner layer to the outer layer) of PE, inner PET, metal foil (Al), and outer polyester, such as PET. A printed ink layer is often reverse printed on the PET layer.

Around 25.8 million tons of plastic waste is produced in Europe each year, 59% of which is plastic packaging (European Commission, 2018). At present, multilayer flexible packaging waste (MFPW) represents the largest proportion of non-recyclable packaging, accounting for around 20% of all flexible packaging (Kaiser, 2020). As the European Union makes a target that 55% of all plastic packaging must be recycled by 2030, the packaging products should move towards a circular economy where packaging made from recycled material and renewable energy should be used in their manufacture.

However, the recyclability of multilayer flexible packaging is difficult because it is composed of different layers of polymer of different types, inks, paper, and metal. These materials are joined together by typical manufacturing technologies for multilayer materials (lamination and co-extrusion). In the case of co-extrusion, the different plastic materials are melted in an extruder, and then co-extruded layers bond

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directly to each other. In some cases, a so-called extrudable adhesive might be applied between materials as a third polymer, such as anhydride-modified PE or anhydride-modified ethylene-vinyl acetate (EVA) (Lahtela et al., 2020). These materials have different physical-chemical properties, and they are thermodynamically immiscible with each other, which makes the usual recycling process difficult because the reprocessing of these mixtures leads to the degradation of some components, since their properties are different and thus, the separation of their layers is economically and technically difficult (Kaiser, 2020; Pauer et al., 2020). Furthermore, the separation of the polymeric fraction from aluminium foils of composite packaging still remains the main challenge for the circular economy (CE), especially since the performance and quality of all CE stages depend entirely on the recycling stage. Average plastic packaging recycling rate in the EU is still rather low, since it was 41% in 2019 (Eurostat, 2021).

Accordingly, in order to increase the recycling rate of MFPW different research and efforts should focus on developing new recycling techniques for MFPW with high recovery rates. One of the methods proposed in the literature is the compatibilization, which is applied when using additives that allow the different polymers to blend and stabilize, but this method is not efficient due to fluctuations of the materials composition (Kaiser et al., 2018; Lahtela et al., 2020). Focusing on finding a more effective way has led to think about the separation of the different layers, so that each type of layer can be recycled separately by current recycling techniques. This separation process is called delamination, which consists of the dissolution of the inner layers (adhesives or metal) that join the polymers using a different solution. The problem in this method is that it is suitable for a limited amount of MFPW. The optimization of these methods makes them the optimal solution for a sustainable economy instead of energy recovery and landfilling, which are currently used for these plastic types.

Interestingly, focusing on optimizing the delamination process has led to the idea that modifying the plastic surface can improve this process. The most prominent idea to enhance the delamination is the microperforation of the plastic surface. The purpose of this innovative idea, developed by our research group at the University of Alicante, is to facilitate the removal of adhesives, inks and metal present in the interlayer of MFPW (Fullana, 2021). 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. Microperforation technique is used in the plastic industry and precisely in plastic packaging of fresh food products to improve the shelf life of the product, thanks to the continuous transmission of gas between the inner and outer atmosphere of the packaging. The perforation of the food packaging shows an increase in the gas transmission rate between the food product and the environmental area (Boonthanakorn et al., 2020; Winotapun et al., 2015). The perforated films can offer calibration of oxygen and carbon dioxide exchange between the surrounding and the inside of the package, increasing the permeability and the breathability of the plastic film (Allan-Wojtas et al., 2008).

In this research, we devoted our study to improving the delamination of MFPW using microperforation. We hypothesized that this technique would enhance the diffusion of the dissolving agent through the layers to dissolve the adhesive or/and metal that join the other layers, thus decreasing the processing time and improving the techno-economic efficiency of this process.

A fundamental understanding of the delamination mechanism and its improvement by this technique was investigated in this paper. Various parameters which can affect the efficiency of microperforation were studied, as well as the theoretical aspect of the delamination such as the diffusion of caustic soda through the different polymer layers for micro-perforated samples and without perforation (control).

The study also included the improvement of the delamination process by using surfactants. As well as this, the presence of inks in the plastic packaging was also taken into consideration to investigate its influence on the micro-holes during the delamination process.

2. Materials and methods

2.1. Materials and chemical agents

The majority of metalized multilayer flexible packaging uses Al as a metal layer. This Al layer is made in two different ways depending on the properties of the packaging needed. The first type is packaging with an Al foil layer (the average Al layer thickness is about 3 μm), which can be printed or unprinted. The second type of metalized MFP is metalized PET. Here in this packaging the Al powder is sprayed on the inner surface of PET, and in this case the Al layer is very thin (about 1 μm). The choice of these types of MFP for this research was done for the purpose of better following the process and its improvement, since after the dissolution of the Al, for other MFP it would have been difficult to follow the process because of the diversity of the components that contain this type of materials and the poor information present about those components. However, this technique could be applicable for other MFPW without metal.

The unprinted MFPW with Al foil was collected from personal domestic coffee packaging waste, whereas the printed MFPW with Al foil was supplied from Carte Noir company, and metalized PET from Tramonto Antonio SRL company.

The dissolving agent used in this study was a 10% sodium hydroxide (NaOH) solution. Also, cationic or nonionic surfactants were added to the solution to investigate their influence on the process expecting to improve the attack solution by these chemical components.

As previously mentioned, the barrier layer (Al layer) in MFP is located between two polymer layers, namely the outer layer and the sealing layer (inner layer); the barrier layer is connected with these layers by two types of bonding: chemical (molecular attraction) and mechanical (friction). They are formed during the lamination process whereby the plastic materials and barrier layer are oxidized through high-temperature extrusion or corona discharge treatment, which supports the formation of polar groups (the van der Waals bonds) on their surfaces. These bonds are parallel to the cross-section of the plastic (Garrido-López and Tena, 2010; Mumladze et al., 2018). Therefore, the delamination or the separation of the polymer layers (outer and inner layer) consists of the dissolution of the barrier layer (Al layer).

MFPW samples: All MFPW were first microperforated mechanically using a laboratory perforation roller. Three different densities (μP/cm^2) of μP were carried out in the films (5, 31 and 76 μP/cm^2) and part of the plastic film was left without microperforation as a control sample. All samples were then cut into small flakes of 2 × 2 cm^2.

In order to quantify the surface structures of the microperforated plastic and of each perforation to characterize their microstructure and determine their size range, the distance between them and the distribution of these micro-holes in MFPW, the analysis of microscopic images by scanning electron microscope (SEM) involved the determination of these parameters. The way of diffusion of the solution inside the layers was also observed by SEM.

The scanning electron microscope used was a Hitachi S3000N. This microscope is equipped with a Bruker model XFlash 3001 X-ray detector for microanalysis (EDS) and mapping.

2.2. The delamination process

The delamination of the MFPW involves the dissolution of the Al layer, since when this metal is totally dissolved the two polymeric layers delaminated. For all the experiments, two main parameters were studied: the temperature and the microperforation density in the plastic film (number of holes in the film per surface area). We performed the separation of the Al from the polymer layers in a beaker of 250 mL using a 10% NaOH solution. The solution was under agitation and the temperature was maintained constant using a heated magnetic stirrer. The experiments were carried out at three temperatures (50, 65 and 80 °C) for samples with different microperforation densities (0, 5, 31 and 76

μP/cm^2). At each experiment four identical samples with the same microperforation density were introduced in the beaker. The delamination of both the printed films with Al foil layer samples and samples with a lower thickness (metalized PET) was carried out to investigate the effect of temperature and microperforation density in both cases. Furthermore, a reflexion on the optimization of the process led to try to improve the attack solution by improving the surface tension between the aqueous solution and the plastic film by adding a surfactant. Two types of surfactants were tested (cationic and non-ionic). These types of surfactants are currently used for the deinking of plastic films; thus, we assumed that they could improve the delamination process. Table 1 summarizes all the parameters studied.

2.3. Reaction and model

2.3.1. Reaction

The delamination of a multilayer flexible package involves the combined process of diffusion of the chemical solution through the polymer layers and the dissolution of the metal layer when in contact with the basic solution. The description of the dissolution kinetics of the multilayer polymer is essentially based on the phenomena of diffusivity and solubility. Three steps take place on the delamination of MFPW: the transfer of the attack solution into the MFPW, the dissolution of the substance through the chemical reaction and the transfer of the reaction products ($Al(OH)_4^-$) to the outside.

The dissolution of the Al foil by the aqueous NaOH solution is described by the following reaction:

$$Al_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 2Na^+_{(aq)} + H_{2(g)}$$

The concentration change of Al in the aqueous solution was measured by Inductively coupled plasma mass spectrometry (ICP-MS-Agilent 7700X). The samples in aqueous solution were acidified with 2% HNO_3 in order to avoid the precipitation phenomenon. When the concentration of Al in the solution was constant, we assumed that the layers of MFPW material were totally delaminated, after checking that this constant concentration was not the concentration of saturation.

Before studying the process of dissolution of Al inside the MFPW, we examined the dissolution of Al foil in the same solution used for the delamination process (NaOH 10%) at 25 °C. The Al foil samples had the same size as the MFPW with Al foil (2 × 2 cm^2). The dissolution process of the solid in the solvent involves two steps: the surface reaction kinetics (1) and the diffusion process expressed in (2) using Fick's first law (Gao et al., 2021).

$$\frac{dm}{dt} = K \cdot S_d \cdot (C_s - C_b) \quad (1)$$

Table 1
Parameters studied.

Parameters	MFPW with Al foil layer (unprinted)	MFPW with Al foil layer (printed)	Metallized PET
Microperforation (μP/cm^2)	0 5 31 76	0 76	0 5 76
Temperature (°C)	50 65 80	50 80	50
Solution	NaOH (10%) NaOH (10%) + cationic NaOH (10%) + non-ionic	NaOH (10%) NaOH (10%)+ cationic NaOH (10%)+ non-ionic	NaOH (10%) NaOH (10%) + cationic NaOH (10%) + non-ionic
Thickness	Film = 99 μm Al layer = 3 μm	Film = 105 μm Al layer = 3 μm	Film = 101 μm Al layer = 1 μm

$$\frac{dm}{dt} = \frac{D}{h} \cdot S_{ext}(C_s - C_b) \quad (2)$$

Where m represents the mass of undissolved solute (Al) *(g)*, C_s is the concentration of the solute on the surface of the solute (it is supposed to be the concentration of saturation) *(g/L)*, C_b represents the bulk concentration and is considered negligible ($C_b = 0$), S_{ext} represent the total surface of the solid (side x side of sample) *(cm^2)*, S_d represent the solid surface area accessible to dissolution (side x thickness of sample) *(cm^2)* (the surface in both expressions is supposed constant), K represent the dissolution kinetic coefficient *(cm/s)*, D is the diffusion coefficient *(cm^2/s)* and *h* is the thickness of the Al foil *(cm)*. The factor $\frac{dm}{dt}$ is the slope of the kinetic curves of the dissolution.

The saturation concentration C_s was calculated by dissolving $Al(OH)_4^-$ on the aqueous solution until the saturation of the solution by this component, obtaining $C_s = 936$ *g/L* at 25 °C.

From Eq. (1), we obtained $K = 0.13$ cm/s and from Eq. (2), $\frac{D}{h} = 6.34\ 10^{-5}$ cm/s. Thus, the results obtained showed that the reaction kinetic is very fast, and as $K >> \frac{D}{h}$ we concluded that the diffusion was the mechanism that controls the dissolution process. According to this result, the process of dissolution of Al inside the MFPW can be controlled and improved by following the evolution of the diffusion coefficient using Fick's first law.

2.3.2. The diffusion model

Different models can be developed to describe this process depending on the representation adopted. The simplest one is to calculate the apparent diffusion coefficient using Fick's first law (Ügdüler et al., 2021):

$$D = \frac{dC}{dt} \cdot \frac{\Delta x}{S.(C_s - C_b)} \quad (3)$$

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 ($C_s = C_{saturation}$) of the solute (Al). It was calculated at 50, 65 and 80 °C by dissolution of sodium aluminate in the aqueous solution until saturation. C_b represents the bulk concentration and is considered negligible ($C_b = 0$). C is the concentration of Al diffused to the solution during the time t. It was measured by ICP-MS.

S: specific surface (S_{ext}/ volume of sample) (cm^2/cm^3)
Δx: half the thickness of plastic film (*cm*)
dt: differential of time (*s*)
D: diffusion coefficient (cm^2/s)

The mechanism of transport is considered to be molecular diffusion in both edges and every hole. González et al. (2008) confirmed that the interchange through the holes is due to molecular diffusion, which obeys the Fick's law. It was verified that the diffusion of $Al(OH)_4^-$ from the inner layers of MFPW to the bulk solution was 10 times lower than the diffusion of NaOH solution through the layers, so for this reason the controlling step was the diffusion of $Al(OH)_4^-$ to the solution.

The diffusion through the plastic layers was checked to be negligible. It was verified in the laboratory that the permeation rate through the PE and PET layers (both sides of the MFPW) was very low. A MFPW sample was introduced into a permeation test chamber. Then, only one surface of the film (one side) was on contact with the aqueous solution of NaOH, and the diffusion of the solution through the sample from the other side was controlled during 5 h. The results showed that no NaOH migrated through the MFPW sample. Thus, the diffusion was assumed to take place only through the edges of the samples and through the micro-holes in the case of the micro-perforated samples.

The diffusion of NaOH through the polymer and the holes depends on temperature, described by an Arrhenius type equation (Seymour et al., 1984):

$$D = D_o\, e^{\frac{-E}{RT}} = f(T) \quad (4)$$

where D_o is the maximal diffusion coefficient constant of a specific polymer layer (cm^2/s), E is the activation energy of the diffusivity (J/mole), R is the gas constant (8.314 J/(mole K)) and T is the absolute temperature (K).

3. Results and discussions

3.1. Separation mechanism

The interest here is in the way that the Al layer is dissolved in both cases, the focus on the sample edges (Fig. 1a) and the micro-holes in the surface area of the flakes (Fig. 1b,c), in order to examine the improvement of the delamination by the microperforation. Once the samples were treated with the NaOH solution, the solution started to penetrate inside the plastic film through the edges as shown in Fig. 1a and through the micro-holes and sample edges as seen in Fig. 1b,c. Then, the bonds started to weaken and the Al in contact with the solution started to dissolve through the edges and the micro-holes. When the Al was totally dissolved by NaOH, all bonds that joined the two plastic layers, adhesive and Al were broken and the two polymer layers were separated one from the other. When microperforation was not applied, the solution diffused only from the edges towards the centre of the sample. Thus, the microperforation of the Mfpw allowed the diffusion and penetration of the attack solution from the edges and from a different position in the surface and therefore, the microperforation made the MFPW more permeable and penetrable by the attack solution.

3.2. Characteristics and microstructure of MFPW microperforated surface

3.2.1. Characteristics of the microperforation

The deep focus in the micro-holes showed a distinct microstructural characterization. The size and the shape were different from one hole to another. The holes took the form of a volcano (Fig. 2a,c) as the perforation was made from the upper and the lower surface, so this form was shown to the inside in some cases and to the outside in others (Fig. 2b (200 μm) and a (250 μm)). The rims of some of the holes were sealed, but in most cases the rims had a ragged form. The holes ranged from being mostly open (Fig. 2a (250 μm)) to being completely obstructed by plastic debris of various forms (Fig. 2c (200 μm)). These debris were in continuity with the film, since they occurred during mechanical perforation of the film. This observation can be explained assuming a bad perforation of the film, since the needle did not go through the whole film in these cases, but it just went through half of the film. Another observation noticed after the deep focus in the micro-holes showed mechanical delamination of the plastic layers in the edges of the hole resulting from the microperforation of a multilayer film. This initial delamination may be explained by the failure of the aluminium–polyethylene joint as a result of the breaking of H-bonds between polar functional groups on oxidized Al and PE surfaces (Garrido-López and Tena, 2010). The initial delamination may have helped the attack solution to diffuse easily from this opened area to the insider layer (Al layers).

The microstructure of the microperforation during the reaction

SEM images for the film during the delamination process showed that the solution diffused from the holes to the inner area of the film, being the diffusion in all directions surrounding of the pore (Fig. 2d). From Fig. 2e,f we observed that the obstruction in the holes was remarkable. This obstruction may have been caused by the bad microperforation as it was said before. Another explanation for this observation is that due to the dissolution of the Al layer in this area of the sample, the two polymer layers are in direct contact and agitation of this solution caused the movement of one layer in that area of the film that obstructed the hole. This is best seen in Fig. 2f. We can notice that it looks like another convex film inside this hole.

3.3. The dissolution kinetics of the Al foil

3.3.1. The influence of microperforation in the delamination time

The mechanical modification of plastic by microperforation is supposed to improve the delamination process of MFPW. Fig. 3 shows the results obtained of Al dissolution in micro-perforated samples with different perforation densities in comparison with no microperforated samples. When the dissolution kinetic curve achieved the steady-state, that meant that all Al was dissolved and the plastics were totally separated.

The comparison of the results shown in Fig. 3 confirmed that the delamination time decreased with the increase of the microperforation of the surface. Thus, the delamination process was faster for all microperforated samples in the interval [9–15 min] compared to the control film M-0 (50 min), and the time decreased when the density of microholes in the samples increased. It was observed that the increase in the density of micro-holes led to a slow increase in the delamination rate, since total delamination for M-76 was noticed at 9 min against 15 min for M-5 (Fig. 3). The dissolution evolution of M-31 was more or less similar to M-76 at T_1 (50 °C), and all micro-perforated samples showed an improvement of the delamination process. The results found by Boonthanakorn et al. (2020) indicated that films with a higher number of micro-holes per surface area were responsible for higher gaseous transmissions properties which confirm our results. However, the heterogeneity of the film (Al foil, adhesive, thickness, etc.) and a bad perforation in some area as it was noticed by SEM can lead in some cases to increase the delamination time.

The micro-holes in sample surface allowed the penetration of the aqueous solution not only by the edges of the samples but also by different points of the surface of these samples. Some studies that worked in microperforated films related the permeability of the film to the density of area of perforation in the film, and they concluded that a

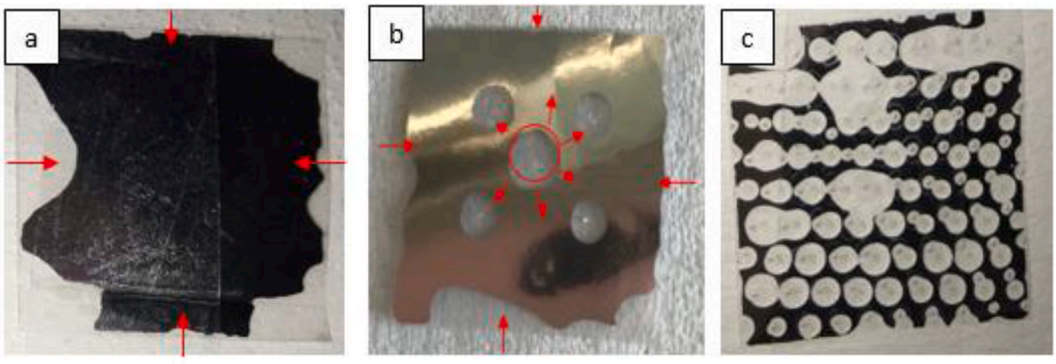

Fig. 1. Photographs of the delamination mechanism of MFPW for no-microperforated (a) and microperforated ((b) 5 μP/cm^2 and (c) max μP) samples.

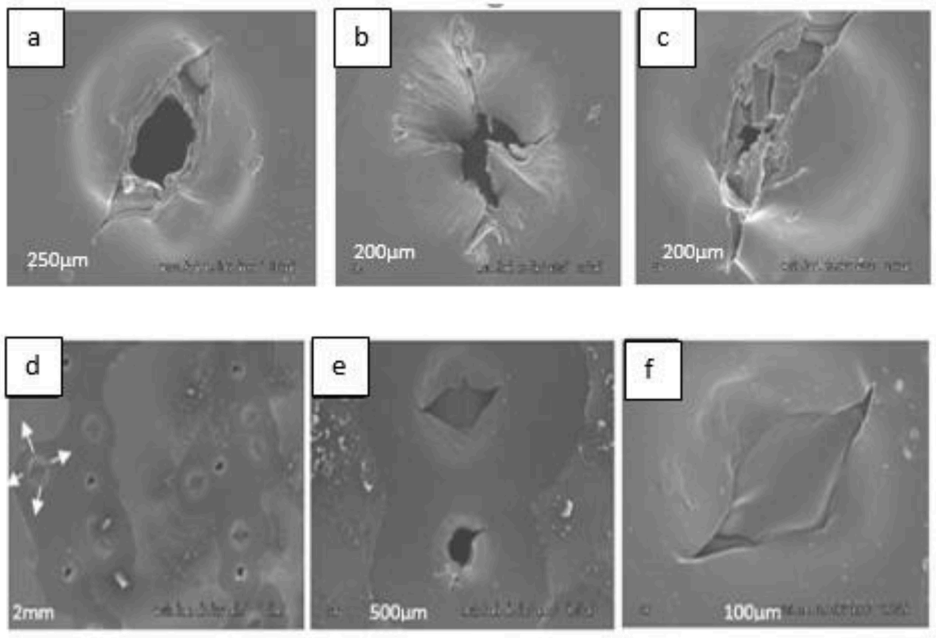

Fig. 2. The SEM images of the micro-perforated film: before delamination mechanism (deep focus of the holes (**a: 250 µm; b and c: 200 µm**); after contact with alkaline solution (low focus in **d: 2 mm**; medium focus in **e: 500** µm and deep focus in **f: 100 µm**).

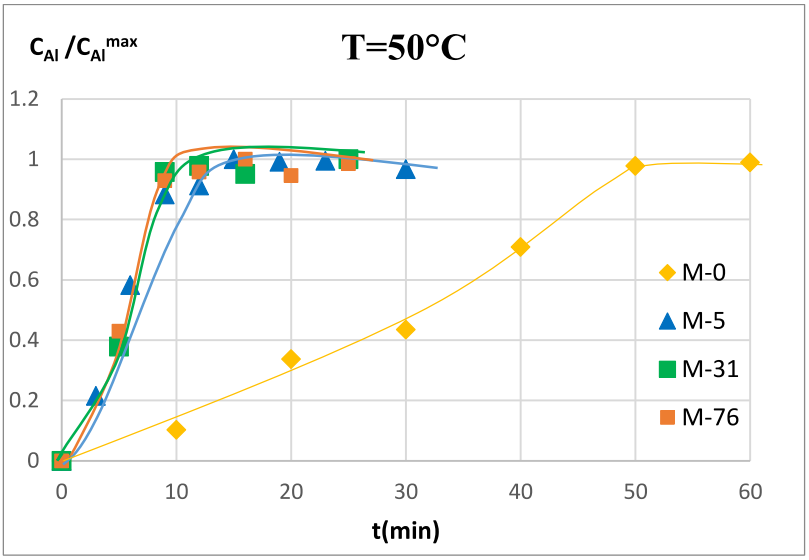

Fig. 3. Kinetics of the dissolution of Al for **M-0**: no microperforation samples; **M-5**: 5 µP/cm^2; **M-31**: 31 µP/cm^2 and **M-76**: 76 µP/cm^2 at T_1 = 50 °C.

higher density of perforation area improves the permeability coefficient of the gas (Ozdemir et al., 2005). This confirms the results obtained in this study.

3.3.2. *The influence of the temperature on the delamination*

The delamination time depended on the dissolution kinetics of Al present between layers. When the caustic soda solution diffused through the polymer layers and reached the Al layer, it started to dissolve Al, the delamination process started and a total delamination was achieved when all Al was dissolved. This dissolution was affected by the reaction temperature. In order to check the influence of temperature in the delamination three different temperatures were tested, as already mentioned (T_1 = 50 °C, T_2 = 65 °C and T_3 = 80 °C).

From all the results shown in Table 2, it can be concluded that the dissolution of Al increased with the temperature and thus, the fastest dissolution was obtained at temperature 80 °C for all samples. The time needed for the delamination was reduced to half when we passed from 50 to 80 °C. As known, the solubility of most solids increases when the solution temperature increases. This is explained by the fact that the

Table 2
The total delamination time of MFPW samples in three temperatures: T_1 = 50 °C, T_2 = 65 °C and T_3 = 80 °C, for M-0, M-5, M-31 and M-76. R represent the delamination time in minutes.

R (min) T (°C)	M-0	M-5	M-31	M-76
50	52	15	10	9
65	23	10	8	5
80	20	8	5	2.5

average kinetic energy of molecules that make up the solution increases with the temperature, and this increase in kinetic energy allows the solvent molecules more effectively to break apart the solute molecules that are held together by intermolecular attractions. The molecules at higher temperature have more thermal energy and are more likely to collide that molecule with less energy (Laidler, 1987).

3.3.3. The diffusion coefficient

The diffusion coefficient was calculated for each experiment using the Fick's equation (Eq. (3)). As mentioned before, due to the low permeability of the plastic films it is considered that the diffusion of the solution through the plastic surface area of the MFPW samples was negligible.

The diffusion coefficient increased when the temperature increased as it is seen in Fig. 4. The highest value of this coefficient was observed for M-76 (maximum μP) and at the temperature of 80 °C for all samples. At the lowest temperature (50 °C) for all microperforated samples a slow increase of the diffusion coefficient (9.91, 11.9 and 17.3 × 10^{-10} cm^2/min) was noticed when the microperforation density increased from 5 to 31 and 76 μP/cm^2, respectively, the diffusion was not significantly improved according to the increase in the density of microperforation. As the temperature increased, we noticed from the data in Fig. 4 that the diffusion coefficient increased significantly with increasing microperforation density.

According to the study of (Türker and Erdoğ du, 2006), the increase in the temperature favours the extraction by improving the solubility, which explains the results obtained, so it has been confirmed that the diffusion coefficient calculated is sensitive to the temperature. The dependence of the diffusion with the temperature was verified using the Arrhenius model (Fig. S1 from appendices). This was also observed in other papers (Ügdüler et al. (2021). They found that the diffusion of formic acid through the plastics layers increased with the temperature. Mahajan et al. (2008), also found that the transmission of the water vapor through the holes increased significantly when the temperature increased.

From Fig. 4, it was also observed that we obtained higher values of the diffusion coefficient when the packaging samples had a higher number of micro-holes per surface area. As an example, at 50 °C this coefficient was twice for samples with 76 μP/cm^2 (M-76) compared to samples with 5 μP/cm^2 (M-5), and it was five-time higher compared to its value for samples without microperforation (M-0). This can be explained considering that the microperforation density increased the number of diffusion paths for the solution towards the Al layers.

The microscope observation of the microperforation showed that the distance between the holes is variable, and the diameter and the distribution of these holes are also variable. According to other research, the important parameters being decisive to enhance the quality of the absorption in microperforated material are the diameters of the hole, the thickness and the surface of the material, and the density of the holes in the film (Patsouras and Pfaffelhuber, 2000; Ucherek, 2001), so the high variability of these parameters can affect the diffusion phenomena.

3.3.4. The influence of the thickness of Al layer

The thickness of the Al layers in the packaging was also a parameter affecting the time needed for the delamination. As explained in the section of the experiments the total dissolution of the Al layer led to the delamination of the multilayers. Thus, if the thickness of this layer is lower, this could decrease the time needed and vice versa. The results of experiments carried out in packaging with a thin Al layer of 1 μm thickness (metalized film), three times thinner than ordinary package (Al foil about 3 μm thick) proved this supposition. The delamination time of samples without microperforation was 20 min for this packaging with 1 μm of Al layer against 50 min for MFPW with Al foil (3 μm) for samples without microperforation. Similar results were found for samples with microperforation (76 μP/cm^2), since the time of the process decreased from 10 min for samples with a thickness of 3 μm of Al layer to 4 min for samples with a thickness of 1 μm of Al layer (Fig. S2 from appendices). Thus, it was concluded that the dissolution of the Al layer in the MFPW increased when the thickness decreased.

3.3.5. The influence of the inks in the delamination time

The MFP, as mentioned in the previous section, may contain ink (printed film), and this latter can affect the delamination process by acting as a barrier that prevents the attack solution from diffusing to the inside of the different layers, consequently decreasing the dissolution rate of Al. In order to confirm this hypothesis, a comparison of Al dissolution for a printed film with the non-printed film, under the same conditions, was carried out at two different temperatures to determine if the inks had an effect when the temperature increased.

The dissolution kinetics of printed MFPW (printed film-76) was quite similar to the ordinary packaging (unprinted film), since a very low decrease in the delamination rate was noticed for the printed packaging in both lower and higher temperatures (50 and 80 °C). As a result, the presence of inks in the package did not make a barrier against the diffusion of the solution through film layer and micro-holes as was supposed, and the increase of temperature did not affect the inks layer to react and deteriorate the process (Fig. S3 from appendices). Therefore, it was concluded that the presence of inks in the MFPW did not affect the time needed for the delamination.

3.3.6. The effect of surfactants on the delamination rate

The majority of plastic packaging is printed for consumer product

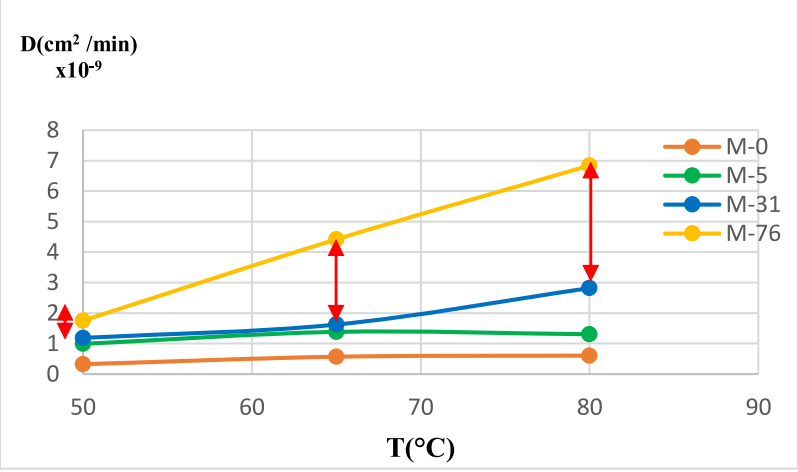

Fig. 4. The diffusion coefficient as a function of temperature D=f(T) for: **M-0; M-5; M-31** and **M-76**.

information and safety precautions as well as for marketing purposes. At the stage of material recovering, the inks should be removed. According to some research, inks removal from the plastic is best done using surfactants (cationic and non-ionic surfactant) (Gecol et al., 2001; Songsiri et al., 2002). These are generally used for de-inking in the recycling of printed MFPW, since they improve the surface tension between the liquid and the solid, so it is possible that they can increase the access of the dissolving solution through the layers of MFPW in the delamination process. It was supposed that the surfactant could decrease the plastic/water interfacial tension by adsorption mechanism making the detachment of the layers thermodynamically favourable, thus increasing the diffusion of the solution inside the different layers of the polymer.

In order to know the effect of surfactant in the dissolution of Al for μP samples, as a first step, we added to the solution of NaOH (10%) 2 g of a cationic surfactant, and on the other hand 2 g of non-ionic surfactant to the solution of NaOH (10%).Then, we proceed in both cases to the delamination of microperforated samples (printed MFPW) at the temperature of 50 °C. The delamination of the samples with 76 μP/cm^2 was performed in both solutions with cationic and non-ionic surfactants, and the data obtained were compared to the ones obtained when the solution was only with 10% of NaOH (control). According to the results obtained of the dissolution kinetics of Al in the presence of surfactants, the two surfactants had no effect in increasing the dissolution of Al (Fig. S4 from appendices).

4. Conclusion

The delamination of multilayer flexible packaging is difficult due to the bonding's strength between layers. However, the mechanical modification of the plastic surface by microperforation was proved to be a promising way to optimize the delamination process, since the surface modification can allow the separation of different layers easily by increasing the diffusivity of attack solution through the layers, consequently reducing the delamination time.

The microperforation of the MFPW improved significantly the delamination mechanism by reducing the processing time. A maximum microperforation (76 μP/cm^2) decreased the process time to 5 times less than without perforation, and even for minimum microperforation (5 μP/cm^2) a decrease of more than three time less than for the control samples (M-0) was achieved. The diffusion phenomenon was improved and the diffusion coefficient was five times higher when a maximum microperforation was applied to the plastic than when there was no microperforation. For the microperforated samples, it was noticed that the diffusion was significantly improved at 80 °C. The time needed for the delamination process decreased when the thickness of the Al layer decreased.

As expected, a higher temperature led to a decrease in the delamination time up to more than two times less for all samples when it increased from 50 to 80 °C, thus improving the diffusion.

The inks present in the majority of the packaging did not deteriorate the delamination process, since the results found for this type of packaging were more or less similar to the no printed packaging. Moreover, the presence of cationic or non-ionic surfactant in the delamination process of this material did not enhance the delamination, so they had no effect in the process.

Finally, the heterogeneity of the size, number, and distribution of the micro-holes may be responsible for the variability of the delamination time in some cases. For instance, the high permeability of the film was observed for the film with the higher density of perforation M-76, and the diffusion coefficient value was 10 times higher in this case than that of M-0.

As a conclusion, the microperforation technique is considered as a pretreatment that could be used at industrial scale in the mechanical recycling process. It can be placed after the separation and sorting of plastic waste and the pre-washing process, in order to improve the permeability of the multilayer plastic packaging before going to the delamination process and the deep washing of this type of material. Currently, there are many industrial microperforating machines on the market that are used at different industries. These machines can be used also for industrial pretreatment of MFPW, and according to our results, the main factors to be considered would be the microperforation density that these machines supply and ensuring that they provide a good microperforation through all MFPW layers.

CRediT authorship contribution statement

Imene Berkane: Methodology, Investigation, Writing – original draft, Visualization. **Andrea Cabanes:** Methodology, Conceptualization. **Oksana Horodytska:** Methodology, Conceptualization. **Ignacio Aracil:** Validation, Writing – review & editing, Supervision. **Andrés Fullana:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2022.106744.

References

Allan-Wojtas, P., Forney, C.F., Moyls, L., Moreau, D.L., 2008. Structure and gas transmission characteristics of microperforations in plastic films. Packag. Technol. Sci. 21 (4), 217–229. https://doi.org/10.1002/pts.804. Retrieved from.

Boonthanakorn, J., Daud, W., Aontee, A., Wongs-Aree, C., 2020. Quality preservation of fresh-cut durian cv. 'Monthong' using micro-perforated PET/PE films. Food Packag. Shelf Life 23. https://doi.org/10.1016/j.fpsl.2019.100452. Retrieved from.

Delva, L., Deceur, C., van Damme, N., Ragaert, K., 2019. Compatibilization of PET-PE blends for the recycling of multilayer packaging foils. AIP Conf. Proc. 2055 https://doi.org/10.1063/1.5084815. Retrieved from.

Eurostat. (2021). Recycling rates of packaging waste for monitoring compliance with policy targets, by type of packaging. data code ENV_WASPACR. Retrieved 05 24, 2022, from https://ec.europa.eu/eurostat/databrowser/view/ENV_WASPACR_custom_1512763/default/bar?lang=en.

European Commission. (2018, 01 16). Une stratégie européenne sur les matières plastiques dans une économie circulaire. Retrieved 05 28, 2021, from https://eur-lex.europa.eu/legal-content/FR/TXT/HTML/?uri=CELEX:52018DC0028&from=DA.

Fullana, A. (2021). Method for removing adhesives and /or interlaminar inks on laminated plastic material. Application number WO/2021/089895. WIPO-PCTThe International Patent System. Retrieved from https://patentimages.storage.googleapis.com/d5/cf/7a/6a1a1d40a703b5/WO2021089895A1.pdf.

Gao, Y., Glennon, B., He, Y., Donnellan, P., 2021. Dissolution kinetics of a BCS class II active pharmaceutical ingredient: diffusion-based model validation and prediction. ACS Omega 6 (12), 8056–8067. https://doi.org/10.1021/acsomega.0c05558.

Garrido-López, Á., Tena, M.T., 2010. Study of multilayer packaging delamination mechanisms using different surface analysis techniques. Appl. Surf. Sci. 256 (12), 3799–3805. https://doi.org/10.1016/j.apsusc.2010.01.029. Retrieved from.

Gecol, H., Scamehorn, J.F., Christian, S.D., Grady, B.P., Riddell, F., 2001. Use of surfactants to remove water based inks from plastic films. In. In: , 189. Colloids and Surfaces A: Physicochemical and Engineering Aspects 1, pp. 55–64. Retrieved from. https://doi.org/10.1016/S0927-7757(01)00591-X.

González, J., Ferrer, A., Oria, R., Salvador, M.L., 2008. Determination of O_2 and CO_2 transmission rates through microperforated films for modified atmosphere

packaging of fresh fruits and vegetables. J. Food Eng. 86 (2), 194–201. https://doi.org/10.1016/j.jfoodeng.2007.09.023. Retrieved from.
Kaiser, K.M., 2020. Recycling of multilayer packaging using a reversible cross-linking adhesive. J. Appl. Polym. Sci. 137 (40) https://doi.org/10.1002/app.49230. Retrieved from.
Kaiser, K., Schmid, M., & Schlummer, M. (2018). Recycling of polymer-based multilayer packaging: a review. J recycling, 3(1). Retrieved from https://doi.org/10.3390/recycling3010001.
Lahtela, V., Silwal, S., Kärki, T., 2020. Re-processing of multilayer plastic materials as a part of the recycling process: the features of processed multilayer materials. Polymers 12 (11), 1–10. https://doi.org/10.3390/polym12112517. Retrieved from.
Laidler, K.J., 1987. Chemical Kinetics, 3rd ed. Pearson Education Inc. bydoi:ISBN0-06-043862-2.
Mahajan, P.v., Rodrigues, F.A.S., Leflaive, E., 2008. Analysis of water vapour transmission rate of perforation-mediated modified atmosphere packaging (PM-MAP). Biosyst. Eng. 100 (4), 555–561. https://doi.org/10.1016/j.biosystemseng.2008.05.008. Retrieved from.
Mumladze, T., Yousef, S., Tatariants, M., Kriukiene, R., Makarevicius, V., Lukošiute, S.I., Bendikiene, R., Denafas, G., 2018. Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents. Green Chem. 20 (15), 3604–3618. https://doi.org/10.1039/c8gc01062e. Retrieved from.
Ozdemir, I., Monnet, F., Gouble, B., 2005. Simple determination of the O_2 and CO_2 permeances of microperforated pouches for modified atmosphere packaging of respiring foods. Postharvest Biol. Technol. 36 (2), 209–213. https://doi.org/10.1016/j.postharvbio.2004.10.008. Retrieved from.
Patsouras, D., Pfaffelhuber, K., 2000. Flexible sound absorption by microperforation. In: Proceedings of the 29th International Congress and Exhibition on Noise Control Engineering-France. Retrieved from. http://www.conforg.fr/internoise2000/cdrom/data/articles/000648.pdf.
Pauer, E., Tacker, M., Gabriel, V., Krauter, V., 2020. Sustainability of flexible multilayer packaging: Environmental impacts and recyclability of packaging for bacon in block. Clean. Environ. Syst. 1, 100001 https://doi.org/10.1016/j.cesys.2. Retrieved from.
Seymour, R.B., Charles, E., Carraher, 1984. Structure Property Relationships in Polymers. Labriry of congress Cataloging in Publication Data. https://doi.org/10.1007/978 -1-4684-4748-4.
Shafiqul, I.M., 2016. Shear Fracture and Delamination in Packaging Materials: A Study of Experimental Methods and Simulation Techniques. Department of Mechanical Engineering Blekinge Institute of Technology, SWEDEN.
Songsiri, D., Min, S., Scamehorn, J.F., Osuwan, S., Ellis, J.W., 2002. Use of cationic surfactant to remove solvent-based ink from rigid high density polyethylene surfaces. In Colloids Surf. A: Physicochem. Eng. Asp. 204, 261–269. Retrieved from. https://doi.org/10.1016/S0927-7757(02)00003-1.
Türker, N., Erdog˘du, F., 2006. Effects of pH and temperature of extraction medium on effective diffusion coefficient of anthocynanin pigments of black carrot (Daucus carota var. L.). J. Food Eng. 76 (4), 579–583. https://doi.org/10.1016/j.jfoodeng.2005.06.005. Retrieved from.
Ucherek, M., 2001. How to design perforated polymeric films for modified atmosphere packs (MAP). Packag. Technol. Sci. 14 (6), 253–266. https://doi.org/10.1002/pts.557. Retrieved from.
Ügdüler, S., de Somer, T., van Geem, K.M., Roosen, M., Kulawig, A., Leineweber, R., de Meester, S., 2021. Towards a better understanding of delamination of multilayer flexible packaging films by carboxylic acids. ChemSusChem 14 (19), 4198–4213. https://doi.org/10.1002/cssc.202002877. Retrieved from.
Winotapun, C., Kerddonfag, N., Kumsang, P., Hararak, B., Chonhenchob, V., Yamwong, T., Chinsirikul, W., 2015. Microperforation of three common plastic films by laser and their enhanced oxygen transmission for fresh produce packaging. Packag. Technol. Sci. 28 (4), 367–383. https://doi.org/10.1002/pts.2108. Retrieved from.