Sustainable Delamination of Multilayer Plastic Films for Advanced Recycling

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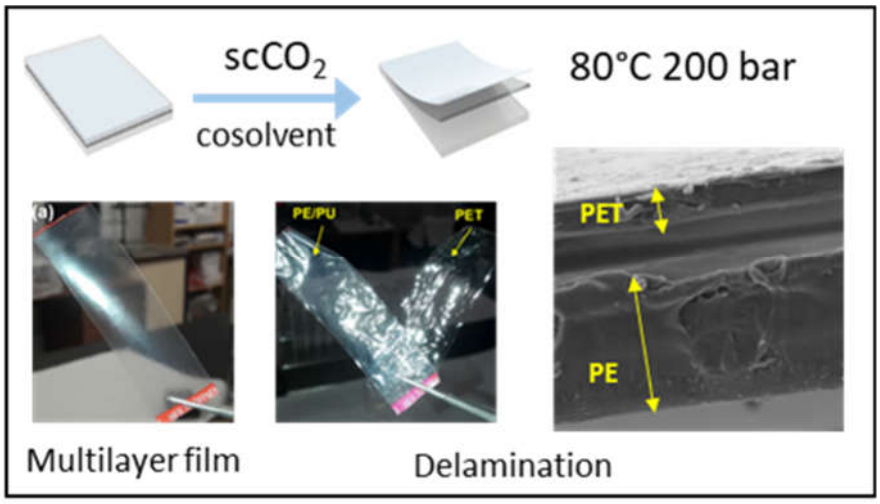
GRAPHICAL ABSTRACT



Highlights

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- A new sustainable delamination process for multilayer plastic films is proposed
- The method involves supercritical CO2 treatment and rapid depressurisation
- Small amounts of cosolvents are added to facilitate the process
- Delamination of commercial PE/PET, MDO-PE/PE and PolyAl is achieved.
- A multiple mechanism for the process is proposed

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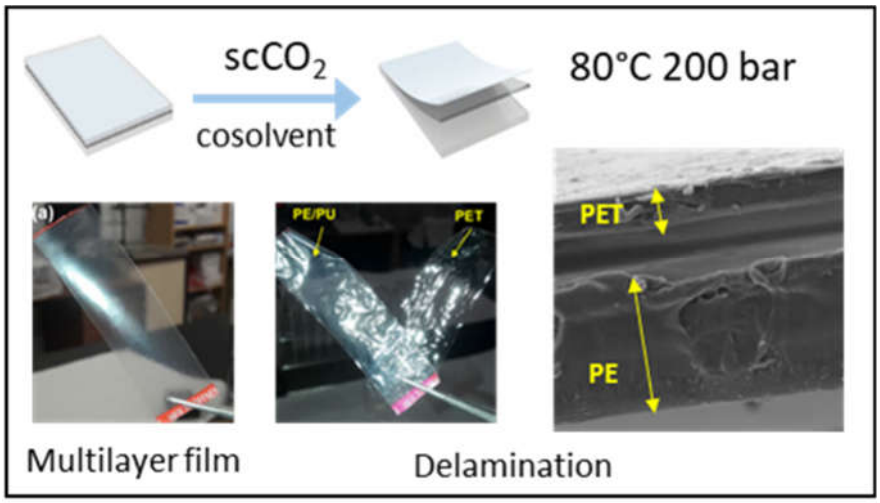


ABSTRACT

A novel delamination process for multilayer plastic films using supercritical CO_2 is proposed as a sustainable alternative to facilitate their recycling. The method involves exposing the films to pure CO_2 or CO_2 modified with a small amount of cosolvent under mild conditions (40–80 ºC, up to 200 bar), followed by rapid depressurisation. As proof of concept, the delamination of three commercial films used in food packaging is presented. The starting material and the delaminated layers were analysed by ATR-FTIR, TGA, DSC and SEM microscopy. Multilayer polymer films formed by polyethylene (PE) and polyethylene terephthalate (PET) or PE and Machine Directed Oriented PE (MDO-PE) prepared with polyurethane adhesive (PU) were delaminated at the PET/PU and MDO-PE/PU interfaces. Furthermore, PolyAl from an aseptic beverage carton delaminated partially, releasing a thin PE layer and an aluminium-enriched PolyAl composite. DMSO and methanol showed the highest delamination efficiency among the cosolvents, while acetone and water were ineffective under the conditions studied. A multiple mechanism for the process is proposed: (1) mechanical stress due to CO_2-induced polymer swelling and rapid depressurisation; (2) selective adhesive debonding via cosolvents. Further studies are needed to corroborate the mechanism, validate the process across varied materials, and optimise its performance. This technology could contribute significantly to a more circular and sustainable economy.

1. INTRODUCTION

Synthetic polymers (plastics) are among the most ubiquitous materials in current society. The accumulation of plastic waste, due to pollution and the presence of microplastics, causes serious environmental and public health problems.

Furthermore, there has been a worldwide paradigm shift in waste processing in recent decades. This change aims to reincorporate the constituent materials of products that have reached the end of their useful life to ensure a circular economy. For that, innovative, effective and low-cost strategies are needed in each of the steps of plastic recycling [1, 2].

In 2022, the European plastic production was 58.7 million tonnes (Mt), where 7.7 Mt of plastics were recycled, which represented 16 % of plastic production [3]. The EU has demanded that at least 25 % recycled material should be added to plastics production from 2025 onwards. Thus, the European Commission's 'Circular Plastics Alliance' aims to incorporate 10 million tonnes of recycled plastics by that date.

The food industry generates the largest volume of plastic waste. Plastics are used primarily in food packaging (primary wrapping) as one of the most effective ways to address food safety issues [4]. They also provide protection during transport (secondary and tertiary wrapping).

Multilayer films consist of two or more layers of different materials. They are essential for primary food packaging due to their specific properties and advantages, such as barrier properties, mechanical strength, lightweight, flexibility and other functional properties [5]. The combination of different layers improves the barrier properties against gases, water, oil and ultraviolet light, which helps to preserve the freshness, flavour and quality of food while preventing its oxidation. They can also incorporate layers with active functions, such as antimicrobial and antioxidant properties, which contribute to food safety and extended shelf life [6]. A well-known example of multilayer film is the Aseptic Beverage Cartons (ABC), more commonly known as Tetra Brik®, which consists of several superimposed layers of polyethylene, cardboard and aluminium.

Different overlapping polymeric layers form other composites. The most common multilayer films involve low-density or high-density polyethylene (PE), polyethylene terephthalate (PET) and/or polypropylene (PP). A polyurethane (PU) adhesive can be used to bond the layers together.

Multilayer plastics, which make up about 20 % of flexible packaging [7], are difficult to recycle due to their diverse polymer compositions and inadequate detection and collection systems. The current recycling techniques used for multilayer packaging have been recently reviewed [7]. The pollution

characteristics of typical waste plastic recycling plants have also been analysed [8]. Physical recycling of multilayer materials can be performed by the selective dissolution/precipitation technique. In this method, each polymer is dissolved or melted selectively, to be later precipitated and reused. Although effective, this method requires using toxic organic solvents that are dangerous to the environment and/or high temperatures, so it is not considered sustainable. Furthermore, organic solvent residues may be left in the recycled polymer, restricting its use. The process can be coupled with chemical recycling of the recovered layers to get the corresponding monomers.

Selective degradation of some of the layers (chemical etching) can also be carried out. For example, PET combined with PE can be selectively depolymerised to recover terephthalic acid in concentrated H_2SO_4 [9]. However, this process generates a large amount of aqueous liquid waste that needs to be further treated before disposal.

Delamination of multilayer films has also been attempted. Dissolution of the adhesive between layers has been described using nitric acid or bases [10]. However, the process is highly polluting and can also partially degrade the layers. Although mechanical delamination of multilayer films is rarely attempted due to the strong binding between the individual layers in the multilayer film, the delamination of multilayer PE/PU/PET films subjected to hydrostatic pressure has been previously reported [11]. The authors attributed this phenomenon to interfacial stress associated with the different mechanical properties of the films, PET being the hardest. After delamination, separation based on different layer densities, electrostatic charge or melt can be performed.

During the ABC recycling process, the cardboard and outer PE films are easily separated, dispersing the cellulose fibres by hydropulping. The remaining material is a composite of polyethylene and aluminium layers commonly known as PolyAl, which contains around 15 % aluminium. PolyAl can be recycled mechanically to produce a wide variety of composite materials used in construction by a combination of techniques such as agglutination, extrusion, moulding, etc. Other possible recycling techniques, such as pyrolysis, selective dissolution and solvent delamination, typically require high temperatures or harmful solvents [12].

The application of supercritical fluids to plastic recycling is an expanding area [13]. Supercritical fluids have a solvation power like liquids, but their transport properties (diffusivity, viscosity) are more similar to those of gases. Supercritical CO_2 ($scCO_2$) stands out because it is cheap, non-combustible, innocuous, has moderate critical parameters (31.0 ºC and 73.8 bar), is a gas at ambient temperature and does not leave any residue. CO_2 solubilises very well in the amorphous regions of polymers, swelling them and causing a decrease in their glass transition temperature (T_g). Rapid depressurisation of the swollen polymer

can lead to foaming. CO_2 also decreases the melting temperature of polymers [14]. These properties can be used favourably in physical recycling processes. In addition, CO_2 can improve mass transfer between polymer chains by increasing reactivity, which also favours chemical recycling processes. Thanks to their high diffusivity, supercritical fluids can penetrate solid matrices easily, making them excellent extraction agents and, therefore, useful for the removal of impurities in polymers [15] and in polymer decontamination [16]. Finally, sterilisation of biological plastic residues for reuse and/or recycling is also possible [17].

In this paper, we propose using $scCO_2$ alone or modified with cosolvents to delaminate multilayer packaging films. The starting hypothesis is that the different polymer films in a multilayer system swell differently in contact with CO_2, generating mechanical stresses between the films and, therefore, inducing separation/delamination of the layers. The addition of a cosolvent can help in the process, and partial dissolution or degradation of the polymer at the interface could take place.

There is enough evidence in the literature to support both effects. The Supercritical Carbon Dioxide Resist Removal (SCORR) process, developed at Los Alamos Laboratory in 1998 to clean semiconductor remnants from the lithographic process, was based on using liquid or $scCO_2$ to solubilise into the polymer residues [18]. Swelling of the residual polymeric photoresist, followed by a sudden depressurisation, led to the separation of the polymer from the substrate. A cosolvent could also be added to CO_2 to facilitate separation. The application of CO_2 pressure pulses facilitated the process [19].

More recently, Aymonier and Slostowski [20] patented a method to delaminate multilayer systems, including at least one organic layer, using $scCO_2$ modified with non-reactive solvents. They provided different examples of delamination of interest in the photovoltaic industry and proposed that the method could be applied to the food, pharmaceutical and cosmetic industries. Delamination was always performed between a polymeric material in contact with a non-polymeric one (glass, metal, or cardboard). This approach has been further studied by Briand *et al.* in the recycling of photovoltaic panels [21-23]. Swelling of the encapsulated polymer following rapid depressurisation led to polymer foaming and mechanical stress and promoted loss of adhesion at the interface. Delamination was also observed by Sumey *et al.* in the foaming of polystyrene and poly(methyl methacrylate) multilayer thin films [24]. Separation of metal–polymer composites using CO_2-induced bubble nucleation has been recently proposed for aluminium–polycarbonate composites [25]. Furthermore, CO_2 exfoliation processes based on the binder dissolution have been employed in the recycling of lithium-ion batteries [26, 27].

Despite extensive research indicating $scCO_2$ efficacy for delamination, a significant knowledge gap exists regarding its application to multilayer polymer

composites used in packaging. This study aims to address this gap by presenting exploratory research, demonstrating for the first time the feasibility of $scCO_2$ delamination on three commercial multilayer composites: two polymer films and a PolyAl composite. A plausible mechanism for the delamination process in CO_2 is proposed.

2. MATERIALS AND METHODS

2.1. Chemicals and polymer films

Carbon dioxide (CO_2) (99.995 % pure) was provided by Air Liquide. Ethanol (Scharlau, ≥ 99.9 %), methanol (Fisher Chemical, ≥ 99.8 %), dimethyl sulfoxide (DMSO) (Fisher Chemical, ≥ 99.9 %), acetone (Honeywell, ≥99.8 %) and deionised water were used as cosolvents. All reagents were obtained from Spanish providers and employed as received without further purification.

The multilayer polymer films used for food packaging were kindly donated by Plastigaur S.A. (Gipuzkoa, Spain). Samples were formed by a stack of PE and PET or PE and Machine Directed Oriented PE (MDO-PE) using polyurethane (PU) as adhesive.

Low-density PE films are flexible, soft, transparent, shiny, and highly resistant to moisture, tearing, and chemicals. PET films are more rigid and provide good barrier properties. MDO-PE (harder than conventional PE) is proposed as a replacement for PET in multilayer films to ease recycling.

For the two commercial multilayer polymer films, the thickness of the PET layer was 12 μm. PE and MDO-PE layers were 50 μm and 25 μm, respectively. Films had a 2 μm thick PU-based PL272A+CF-60 adhesive from Morchem S.A. (Guadalajara, Spain). The two multilayer composites are designated according to their structure as PE/PU/PET and MDO-PE/PU/PE. Each of the PE commercial layers is, in fact, a multilayer blown film made of 3 or 5 sub-layers of different densities (see **Figure S1**, Supplementary Material).

Additionally, simpler PE/PU and PET/PU stacks were prepared by applying a thin layer of a PU adhesive on PE and PET films. For the application of the adhesive, we follow the provider's instructions (see Supplementary Material, Section 2). Before the application of PU adhesive, PE films were subjected to a corona treatment, which is a surface modification technique that uses a low-temperature plasma discharge to improve adhesion by increasing the polarity and roughness of the films. Samples were cut into small pieces with sizes from *ca.* 3 x 1 cm^2 to 1 x 1 cm^2 for analysis.

PolyAl films were obtained from a commercial orange juice Tetra Brik® carton. The material was cut into pieces and treated in distilled water at 60-70 ºC for 2 h under stirring, simulating the hydro pulping process. The PolyAl fragments were separated from the cardboard, washed and dried in an oven overnight.

2.2. Supercritical fluid delamination process.

Experiments were performed in a *ca.* 60 mL custom-made high-pressure reactor previously described [28]. The high-pressure set-up includes inlet and outlet high-pressure valves (SS-OV-S2), a pressure gauge and a safety relief valve (SS-4R3A) to prevent overpressure (all Swagelok components). The reactor was housed in an aluminium block heated by heating cartridges controlled using a PID controller and mounted on a stirring plate. The temperature within the reactor was measured using a type J thermocouple placed into the reactor.

Several pieces of different plastic films (250-500 mg) were introduced into the reactor. In the experiments using cosolvents, 5 mL of an organic solvent (methanol, ethanol, acetone and DMSO) or water was also placed into the reactor in a small vial with a magnetic stirrer, so it is kept separated from the films. The reactor was closed, and the heater was set at the desired temperature. After the temperature was reached, CO_2 was introduced into the reactor from a Teledyne ISCO syringe pump thermostated at the temperature of the experiments, up to the desired pressure. When cosolvents were used, the reactor was stirred to speed up the mixing of CO_2 and the cosolvents. The system was kept at these conditions for 2 h and depressurised rapidly, opening manually the outlet high-pressure valve. Experiments were performed at 40 ºC and 80 ºC, and 200 bar. Depending on the temperature, the depressurisation time varied from 20 to 30 s. Assuming a linear depressurisation profile, depressurisation rates between 10-7 bar/s were employed. Cosolvent proportions in the supercritical CO_2 phase as well as bibliographic sorption values of CO_2 in the polymers are reported as mass percentages (%)

After cooling, the reactor was opened, and the samples were removed from the reactor for further analysis. The samples were dry, except for the experiments performed using DMSO and water, where the samples appeared wetted by the solvent. This is related to the lower miscibility of these solvents with CO_2, due to their much lower vapour pressures and higher boiling points in comparison to the other organic solvents used as cosolvent. Samples wetted by DMSO were further washed with distilled water. Experiments were performed in triplicate.

To identify possible substances eluted with the CO_2 upon depressurisation, the experiments with DMSO were repeated using the deuterated solvent and depressurising the reactor through a small vial containing deuterated DMSO. For collection purposes, the depressurisation rate was kept low at ca. 2 bar/min. Sample was analysed by ^{1}H NMR (Bruker AV 250MHz BACS60).

2.3 Characterisation techniques

Multilayer films were characterised before and after the CO_2 treatment using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-

FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

ATR-FTIR spectra were collected using a Perkin Elmer Spectrum 100 apparatus at a spectral resolution of 4 cm^{-1} between 4000 and 650 cm^{-1} and 16 accumulations.

DSC of the films was performed using a Q20 TA Instrument. Measurements were performed in dry N_2, flowing at 10 mL/min. The temperature and enthalpy of the calorimeter were previously calibrated using standard samples of Indium (99.999 %). Films were heated from -40 to 270 ºC at a heating rate of 10 ºC/min. Glass transition temperatures, melting temperatures and heats of fusion were determined from the first heating cycle using the Universal TA Analysis software.

TGA analysis of the films was performed using an SDT- Q600 from TA from 35 to 600 ºC at a heating rate of 10 ºC/min under 100 mL/min N_2 flow.

SEM was performed using two JEOL microscopes: JSM IT700HR and JSM-7600. Cross-sections for analysis were prepared by cooling the samples with liquid N_2 before fracturing with a pair of scissors. Samples were analysed before and after the supercritical treatment. Additionally, the internal face of some delaminated samples was studied under the microscope. Samples were gold-coated. Images from both secondary and backscattered electrons were recorded. Energy Dispersive X-ray (EDX) analysis was also performed in different regions of the films for identification purposes.

3. RESULTS AND DISCUSSION

First, the delamination behaviour of custom-made bilayer systems formed by PET or PE and a PU adhesive layer was evaluated, focusing on the influence of temperature and density during the $scCO_2$ treatment. The success of these experiments led us to attempt the delamination of more complex commercial multilayer films. In this case, different cosolvents were introduced to identify the most effective one, based on delamination performance, toxicity, and recyclability. The composition of the resulting layers and the interface where delamination occurred were analysed using FTIR, DSC and SEM techniques.

3.1. Delamination of lab-prepared bilayer polymer films

The first experiments were performed on the PE/PU and PET/PU lab-prepared films. PE and PET polymers are the most common materials used in packaging. Experiments were performed at 40 and 80 ºC at 200 bar using pure CO_2, followed by sudden depressurisation.

Visual inspection of the PET/PU samples after the CO_2 treatment, followed by rapid depressurisation, showed bubble formation and partial delamination of the

films (**Figure 1a**). In contrast, PE/PU films did not show appreciable changes after the CO_2 treatment at the same conditions.

Using a pair of tweezers, PET and PU layers could be easily separated (**Figure 1b-e**). Additionally, films curved when exposed to CO_2, indicating a different interaction of CO_2 with the different layers. The convex side of the curved films corresponded to the PU adhesive. The best results were obtained at 40 ºC and 200 bar, conditions of higher CO_2 density. Rapid depressurisation was essential to promote delamination. Thus, it was clear that CO_2 has a physical effect on the polymer films.

This was somehow surprising as the interaction of PET with the PU adhesive is expected to be stronger than the interaction of PE and PU. PET and PU can interact through covalent or hydrogen bonding, whilst the interaction of PE and PU, even after the introduction of some functional groups following the corona treatment, may be weaker. In fact, blends of PU and PET have been prepared, indicating good polymer compatibility and strong interface adhesion [29]. In contrast, the low surface energy and wettability of PE require corona and chemical treatments to improve the PU adhesion [30].

To understand the different behaviour of PET/PU and PE/PU interfaces when exposed to CO_2, the effect of CO_2 on the different polymers should be considered. It is well known that CO_2 dissolves appreciably in the amorphous domains of semicrystalline polymers, causing polymer plasticisation and swelling [14]. The effect depends on the chemical composition of the polymer and its interaction with CO_2, as well as on the crystallinity and mechanical properties of the polymers that may restrict polymer dilation.

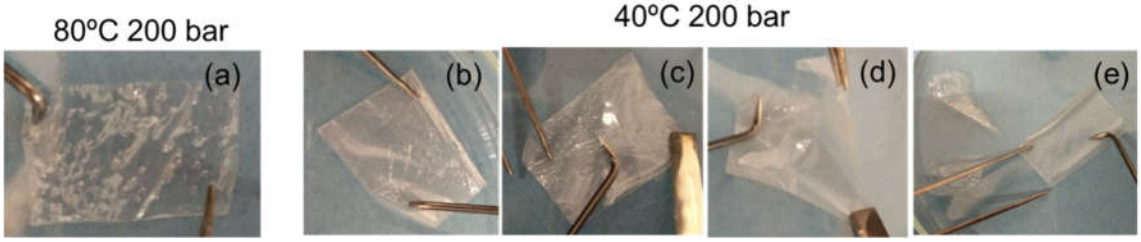


Figure 1. Photographs of PET/PU films treated with supercritical CO_2: (a) 80 ºC and 200 bar, (b–e) 40 ºC and 200 bar. The images show partial delamination at the adhesive interface, evidenced by the manual separation of the layers using tweezers.

The sorption of CO_2 in PET at 40 ºC and 150 bar is ca. 8 %, although the swelling is almost negligible at these conditions due to the high rigidity and crystallinity of PET [31]. At 80 ºC and 200 bar, the CO_2 sorption is lower than 3 %, but a small swelling between 2 and 3 % is reported [32]. Comparatively, the sorption of CO_2 in low-density PE films is smaller than that in PET at the same conditions [33].

However, the swelling is slightly larger. For example, at 60 ºC and 200 bar, a 4-5% swelling of PE has been reported [34].

In contrast, for the PU adhesive with different molecular weights and cross-linking densities, values for CO_2 sorption and swelling at 80 ºC and 150 bar are between 7-30% and 20-30%, respectively [35]. Thus, the PU adhesive, although highly cross-linked, may sorb a larger CO_2 quantity and swell appreciably, in comparison to PE and PET, promoting the film delamination in PET/PU, where the mismatch in swelling and mechanical properties is larger.

3.2. Delamination of commercial multilayer polymer films

Experiments were conducted using the commercial multilayer polymer films PE/PU/PET and MDO-PE/PU/PE. Experiments were performed at 40 and 80 ºC and 200 bar. In both samples, exposure to pure CO_2 failed to induce delamination, although some bubble formation was observed in the films. Best results were obtained at 80 ºC. In contrast to the PET/PU samples prepared in the lab, commercial samples had a much thinner PU layer sandwiched between the other polymer layers.

Further experiments were performed at 80 ºC and 200 bar, adding 5 mL of methanol as cosolvent, which corresponded to 11 %. At these conditions, CO_2 and methanol were fully miscible [36, 37]. PE/PU/PET films followed by rapid depressurisation were successfully delaminated into two layers and separated easily using a pair of tweezers, as shown in **Figure 2a.** The FTIR analysis of the different layers is presented in **Figure 2b**. Layer B was identified as PET, showing the characteristic strong bands at 1712 cm^{-1} associated with the carbonyl stretching and 1250 cm^{-1} to the ester group, in both the outer and inner faces of the layer. FTIR of the outer layer A showed two sharp and intense absorption bands at 2800 – 2900 cm^{-1} ascribed to the CH_2 asymmetric and symmetric stretching bands and medium and sharp bands at 1463 and 719 cm^{-1} corresponding to the bending and rocking of PE. The inner face of layer A showed the PE characteristic bands superimposed to bands associated with PU, particularly the band at 1222 cm^{-1} due to C-N stretching, the band at 1725 cm^{-1} due to carbonyl stretching (urethane moiety) and a broad band at 3334 cm^{-1} due to N-H stretching. FTIR-ATR beam penetration was enough to detect both the PU thin layer and the PE outer layer. Thus, as shown in **Figure 2c**, delamination took place at the PET/PU interface.

Similarly, MDO-PE/PU/PE films treated at 80 ºC and 200 bar followed by rapid depressurisation, were also easily separated using a pair of tweezers (**Figure 3a**). In this case, the commercial sample was coloured. The PE layer appeared white due to the presence of TiO_2 particles, while the MDO-PE side exhibited a magenta colour, resulting from the application of magenta ink printed on the inner surface of the PE film.

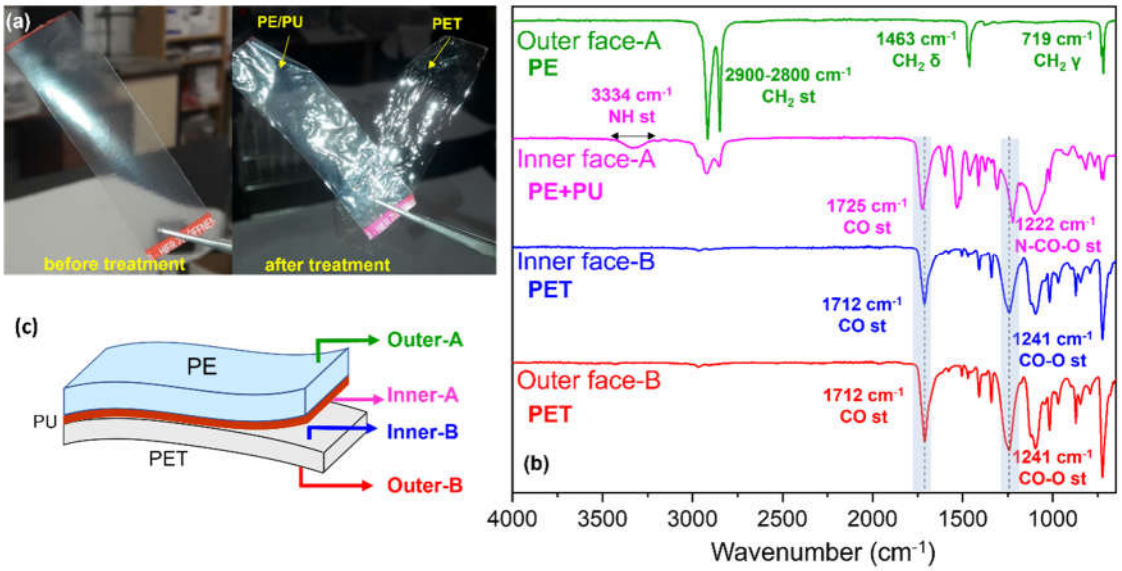


Figure 2. (a) Photographs of PE/PU/PET films before and after treatment with CO_2 modified with 11 wt% methanol as cosolvent, at 80 ºC and 200 bar. (b) ATR-FTIR analysis of the different layers and their identification. (c) Schematic of the delamination process according to FTIR.

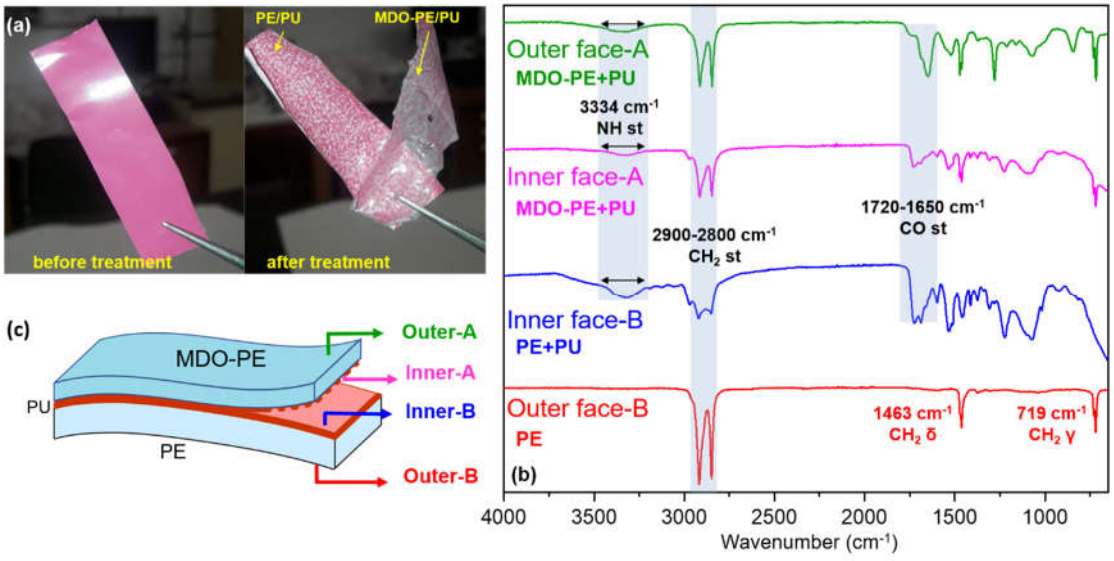
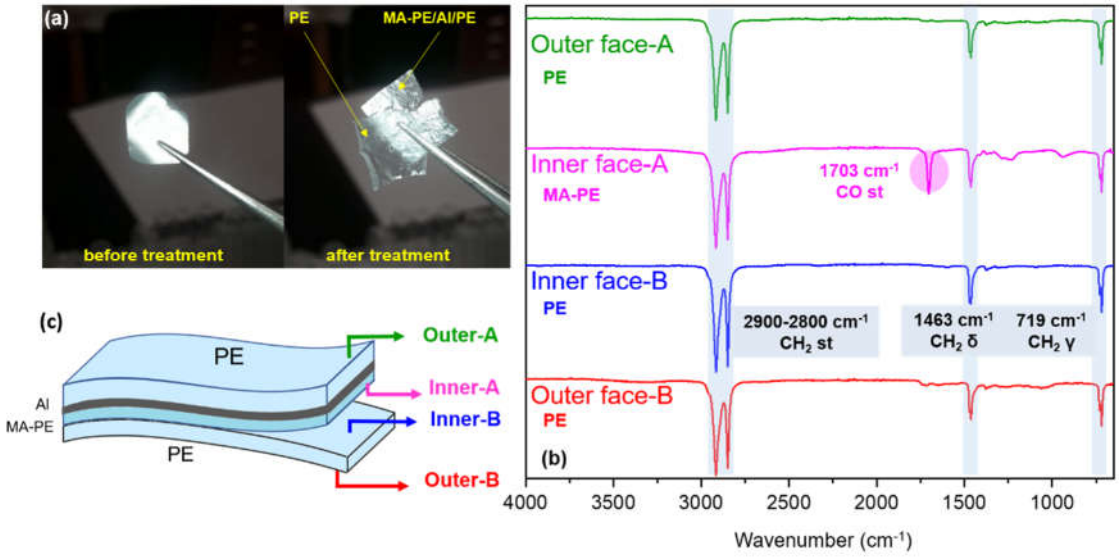


Figure 3. (a) Photographs of the MDO-PE/PU/PE film before and after the treatment with CO_2 modified with 11 wt% methanol as cosolvent at 80 ºC and 200 bar. (b) ATR-FTIR analysis of the different layers and their identification, and (c) schematic of the delamination process according to FTIR.

After delamination, A and B layers were analysed by FTIR (**Figure 3b**). Both layers exhibited the characteristic bands of PE. Outer layer B only showed these bands, but outer layer A presented additional bands that were associated to the pigments and additives of the magenta ink. FTIR analysis of the inner part of layers A and B showed bands due to the PU adhesive or other additives superimposed to those of PE. Pictures of the layers after delamination showed that, in this multilayer film, separation was not clean, resulting in partial material transfer between layers. Adhesive and pigment residues remained on both delaminated surfaces, as shown in **Figure 3c**. The broad band below 750 cm^{-1} visible in both inner faces was ascribed to TiO_2 present in the PE layer [38]. Differences in the levels of CO_2 sorption within the MDO-PE and PE layers are expected due to their different crystallinity.

Experiments were also performed using PolyAl multilayer films. Although PolyAl is formed by a complex multilayer structure, after the CO_2 treatment, two different layers could be separated using tweezers (**Figure 4a**). FTIR analysis of A and B layers (**Figure 4b**) showed bands due to PE in both the inner and outer faces. At the inner face of layer A, a relatively strong band at 1701 cm^{-1}, along with weak bands at 1200-1300 cm^{-1}, and 940 cm^{-1} associated with carboxylic acid groups, were identified. These peaks appear in PE films doped with maleic anhydride or in ethylene methacrylic acid copolymers that are used to improve adhesion with the Al layer (MA-PE).

Assuming the PolyAl is a composite of four layers whose structure is PE/Al/MA-PE/PE (from outer to inner), the delamination took place at the MA-PE/PE interface to yield a layer of PE and a PE/Al/MA-PE composite that can be envisaged as a PolyAl with a higher proportion of aluminium. The much higher CO_2 sorption and swelling of acrylic polymers[39] in comparison to PE would partially explain why delamination took place at the MA-PE/PE interface [33, 34].



388

389 **Figure 4.** (a) Photographs of PolyAl film before and after the treatment with CO_2
390 modified with 11 wt% methanol as cosolvent at 80 ºC and 200 bar, (b) ATR-FTIR
391 analysis of the different layers and their identification. (c) Schematic of the
392 delamination process according to FTIR.

393 Samples of the individual PE and PET plastic sheets used for the lamination of
394 PE/PU/PET were also obtained from the supplier. The area density of the sheets
395 was determined by weighing pieces of known area of each sheet. The area
396 densities for PE, PET and PE/PU/PET were 4.53, 1.69 and 6.37 mg/cm^{2,}
397 respectively. Assuming that the thickness of the sheets did not significantly
398 change upon lamination, an estimated area density for the PU adhesive layer of
399 0.16 mg/cm^2 was calculated. Using the layer thicknesses reported previously,
400 volumetric densities of 0.91 and 1.41 g/cm^3 for PE and PET were obtained. These
401 densities agree well with values from the literature (Low density PE: 0.91-0.93
402 g/cm^3, PET: 1.33-1.45 g/cm^3) [40]. Thus, the density of PU adhesive was
403 estimated as 0.8 g/cm^3. The lower density of PU indicates a larger free volume
404 that may lead to higher CO_2 sorption and swelling.

405 For the PolyAl, the proportion in mass of the different layers obtained after
406 delamination using CO_2 modified with methanol was 59 % PE/Al/MA-PE and 41
407 % PE. Then, the PE/Al/MA-PE layer would contain 25 % of aluminium. This
408 enriched PolyAl opens new possibilities to use this material in construction [12].

409 The successful delamination of the multilayer films and the composition of the
410 films analysed by FTIR was further confirmed by thermal analysis. DSC was
411 performed on the multilayer commercial films, some of the single component
412 films, PU adhesive and the delaminated A and B layers of each multilayer film
413 (**Figures 5-7**).

Table 1 summarises the thermal transitions found in each case. It shows the melting temperatures (T_m), and heats of fusion (ΔH_m) in the films and different polymer layers. The results confirm the layer identification performed by FTIR. The transition temperatures of the delaminated layers matched those detected in the composite and the starting layers. Molar enthalpies were lower for the composites because of the lower proportion of the crystalline material.

Table 1. Thermal transitions observed in the multilayer materials, PET and PE films and the different layers after the CO_2 + methanol treatment.

Film	Layer A		Layer B		Exothermic peak
	T_m (ºC)	ΔH_m (J/g)	T_m (ºC)	ΔH_m(J/g)	T (ºC)
PE/PU/PET	111	79	256	10	174
PE	113	118	-	-	191
Layer A (PE + PU)	113	113	-	-	196
Layer B (PET)	-	-	258	47	170
PET	-	-	257	47	188
MDO-PE/PU/PE	126/135	105	126	105	176
MDO-PE	127/133	150	-	-	-
Layer A (MDO-PE + PU)	126/132	151	-	-	174
Layer B (PE + PU)	-	-	126	123	-
PolyAl (PE/MA-PE/Al/PE)	-	-	108	80	190
Layer A (MA-PE/Al/PE)	97	22	-	-	-
Layer B (PE)	-	-	107	101	190

Figure 5 presents the DSC of a PET film, showing the expected T_m for this polymer at 258 ºC [40]. Additionally, two very weak T_g associated possibly to additives were observed at 52 and 128 ºC. The same transitions were identified in layer B (PET) after delamination. Similarly, the DSC of a PE film showed a very wide melting transition that started almost at room temperature and had a peak at 112 ºC. This broad transition corresponded to the melting point of a mixture of different high and medium-density PE layers (**Figure S1**, Supplementary Material). DSC of layer A (PE + PU) showed the same transitions. The PE /PU/PET film showed the transitions of both PE and PET. These results support the successful delamination of the layer according to **Figure 2**.

An additional narrow and small exothermic peak was found in all the commercial films studied at a temperature between 170-195 ºC. However, TGA analysis of the PE/PU/PET film (**Figure S2**, Supplementary Material) did not show a clear mass loss in this temperature range. This peak seems to indicate the presence of very low quantities of polymer additives or other compounds used to aid processing in the commercial films.

A piece of PU adhesive prepared by mixing the different adhesive components according to the vendor's instructions (**Section 3,** Supplementary Material), was

also studied by DSC. A T_g at ca. 5 ºC was observed in the sample, followed by other minor and unclear thermal events (**Figure S3**, Supplementary Material). However, this T_g transition was not observed in layer A (PE + PU), most likely due to the exceedingly small proportion of PU in the layer.

Although it has been previously reported that the solubilisation of CO_2 into the amorphous regions of polymers can cause polymer crystallisation [41], the heats of fusion in A and B layers after CO_2 delamination were very similar to those of the single-component films, indicating no changes in the crystallinity of the samples.

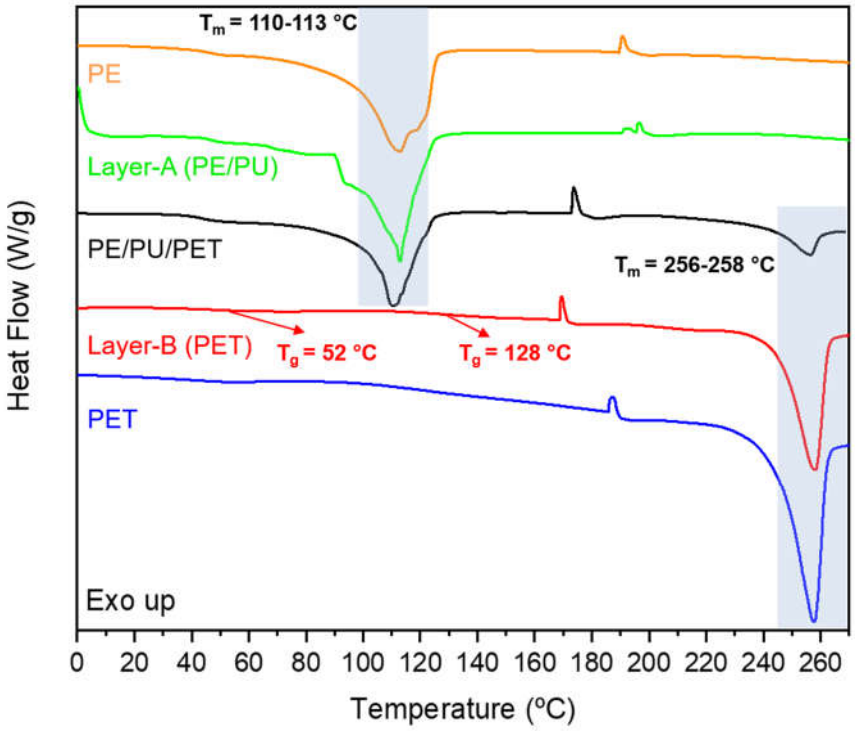


Figure 5. DSC thermograms of PE/PU/PET, PET and PE films and the layers obtained after the CO_2 + methanol treatment, indicating the different T_g and T_m transitions.

Multilayer films were weighed before and after the CO_2 treatment, showing, within the experimental error, that there is no substantial mass loss during the delamination process. Furthermore, TGA analysis of the PE/PU/PET multilayer films, the separated layers A and B (Table 1), and the PU adhesive was also performed (**Figure S2**, Supplementary Material). Layer A (PE + PU) and layer B (PET) decomposed mostly between 420-500 ºC and 375-500 ºC, respectively, whilst PU decomposed between 225ºC-500 ºC. The PE/PU/PET film

decomposed primarily between 350-500 ºC. As expected in PE/PU/PET and Layer A (PE + PU), there was a small mass loss between 200 ºC to 400 ºC, related to the PU decomposition. In contrast, weight loss in this range for layer B was negligible, confirming the absence of PU.

The DSC thermogram of an MDO-PE film in **Figure 6** showed two endothermic peaks between 120 and 135 ºC. These two melting peaks indicated the presence of two different crystalline domains in MDO-PE: one less ordered with a T_m similar to Linear Low Density Polyethylene (LLDPE, T_m = 125 ºC) and the other at a higher temperature (T_m = 133 ºC) associated with oriented PE domains [40]. The double peak may be related to the multilayer structure of this film.

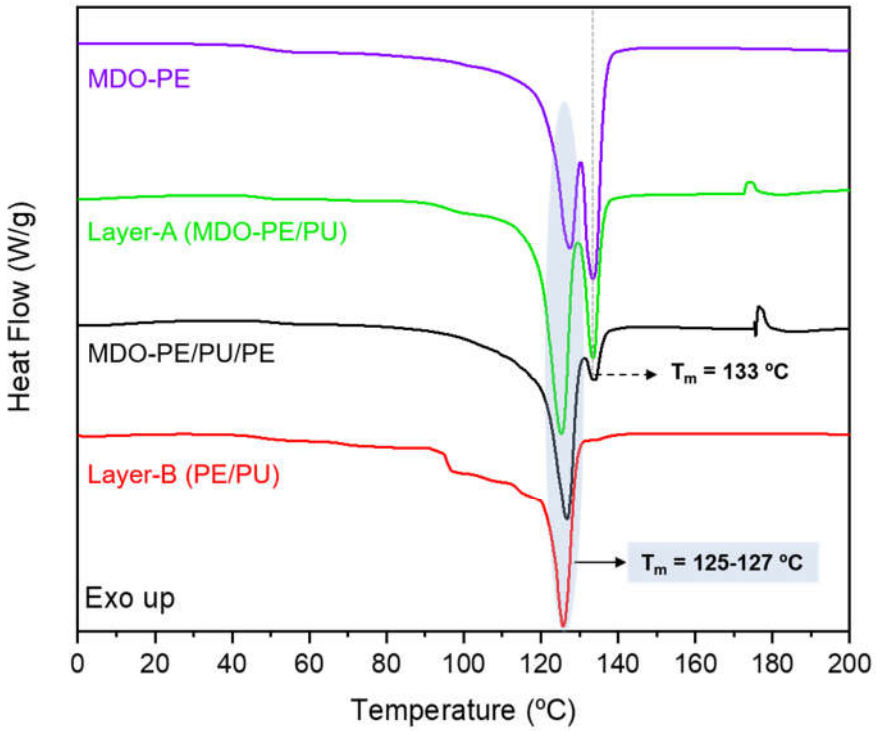


Figure 6. DSC thermograms of MDO-PE/PU/PE and MDO-PE films and the layers obtained after the CO_2 + methanol treatment, indicating the different T_m transitions.

The same transitions were observed in the MDO-PE/PU/PE film and the delaminated layer A (MDO-PE). The relative intensity of the two peaks was, however, different. In the MDO-PE/PU/PE film, the peak at higher temperature was weaker due to the lower percentage of MDO-PE in the composite material. Comparison of the thermograms of layer A and MDO-PE showed the same transitions, although the relative intensity of the second melting peak at the elevated temperature was slightly lower in layer A than in pure MDO-PE. This

suggests that the delamination process was not clean. In contrast, DSC of layer B showed only a single endothermic peak at 125 ºC that corresponded to LLDPE [40].

The exothermic peak at approximately 175 ºC was only present in the thermograms of multilayer MDO-PE/PU/PE and layer MDO-PE/PU.

The T_g of PU was not evident in any of the thermograms. PE and MDO-PE in both single-component and MDO-PE/PU/PE multilayer films started to melt at room temperature.

In the case of the PolyAl system, DSC thermograms of the composite system before treatment and the delaminated layers are compared in **Figure 7**. Regarding PolyAl, a broad endothermic peak was observed between 106-110 ºC. This low melting point is in accordance with the melting point of LDPE [40]. This peak was also observed in the delaminated layer B (PE). A similar endothermic peak was observed in layer A but shifted to 96-97 ºC. The lower melting point could be related to the carboxylic acid groups present in the MA-PE. This is in agreement with the FTIR results. Once more, there is an exothermic peak, this time at 190 ºC, which may be attributed to fillers or additives incorporated into the composite material.

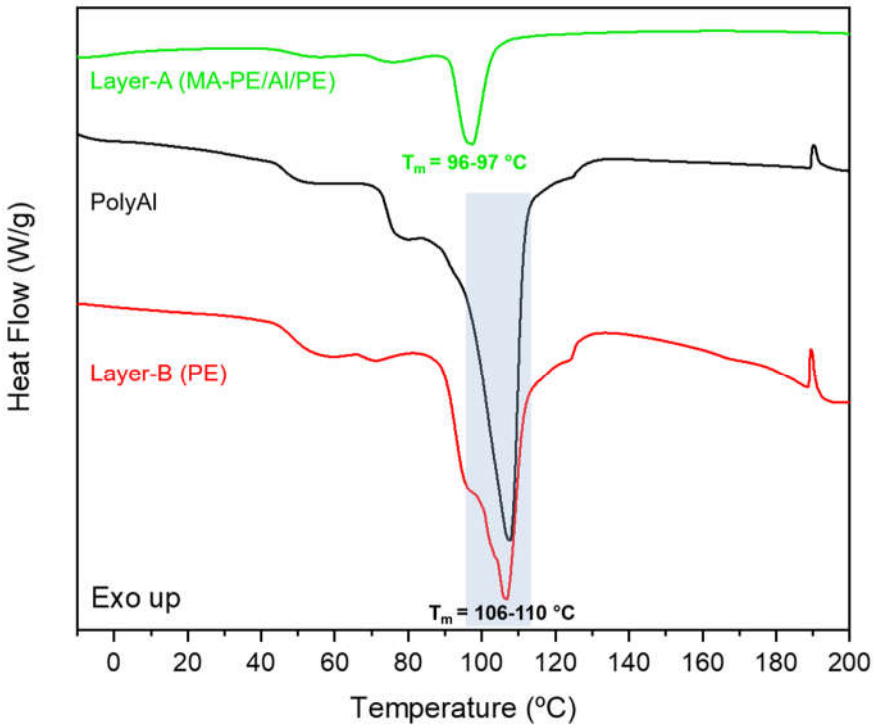


Figure 7. DSC thermogram of PolyAl multilayer film and the layers obtained after the CO_2 + methanol treatment, indicating the different T_m transitions.

Figure 8 presents SEM micrographs of the commercial PE/PU/PET sample, where the distinct PE, PU, and PET layers can be clearly identified with thicknesses of approximately 50, 2, and 12 µm, respectively (Figures 8a, 8c, and 8d). These values are consistent with the specifications provided by the manufacturer. During SEM sample preparation, a slight separation between the PET and PU layers occurred as a result of the freeze-fracture procedure (Figure 8a). In contrast, **Figure 8d** shows a sample delaminated with CO_2. The film thickness of the PE and PET films remained unchanged after CO_2 delamination, whilst PU adhesive was not clearly observed.

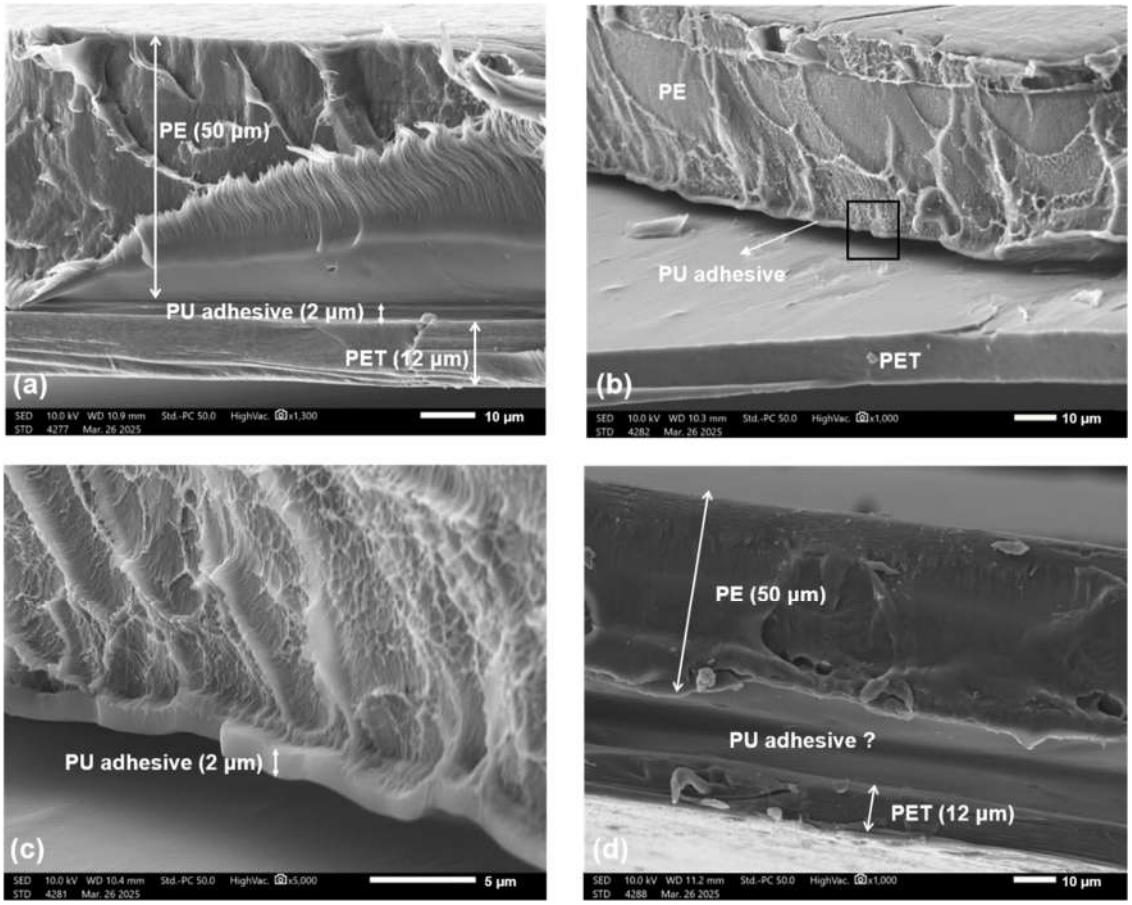


Figure 8. SEM images of: (a) PE/PU/PET film fractured using liquid N_2, (b) region delaminated due to liquid N_2 where PE, PU and PET are distinguished, (c) a closer view (black square in (b)) near the delamination place (PE/PU above and PET below) showing the PU adhesive, and (d) PE/PU/PET delaminated film after the CO_2 + methanol treatment.

SEM images for the MDO-PE/PU/PE film are shown in **Figure 9**. During sample preparation for SEM by freezing fracture, delamination occurred, resulting in a

thicker layer (PE) and a thinner layer (MDO-PE). The thickness measurements in **Figure 9a** matched well the values provided by the company.

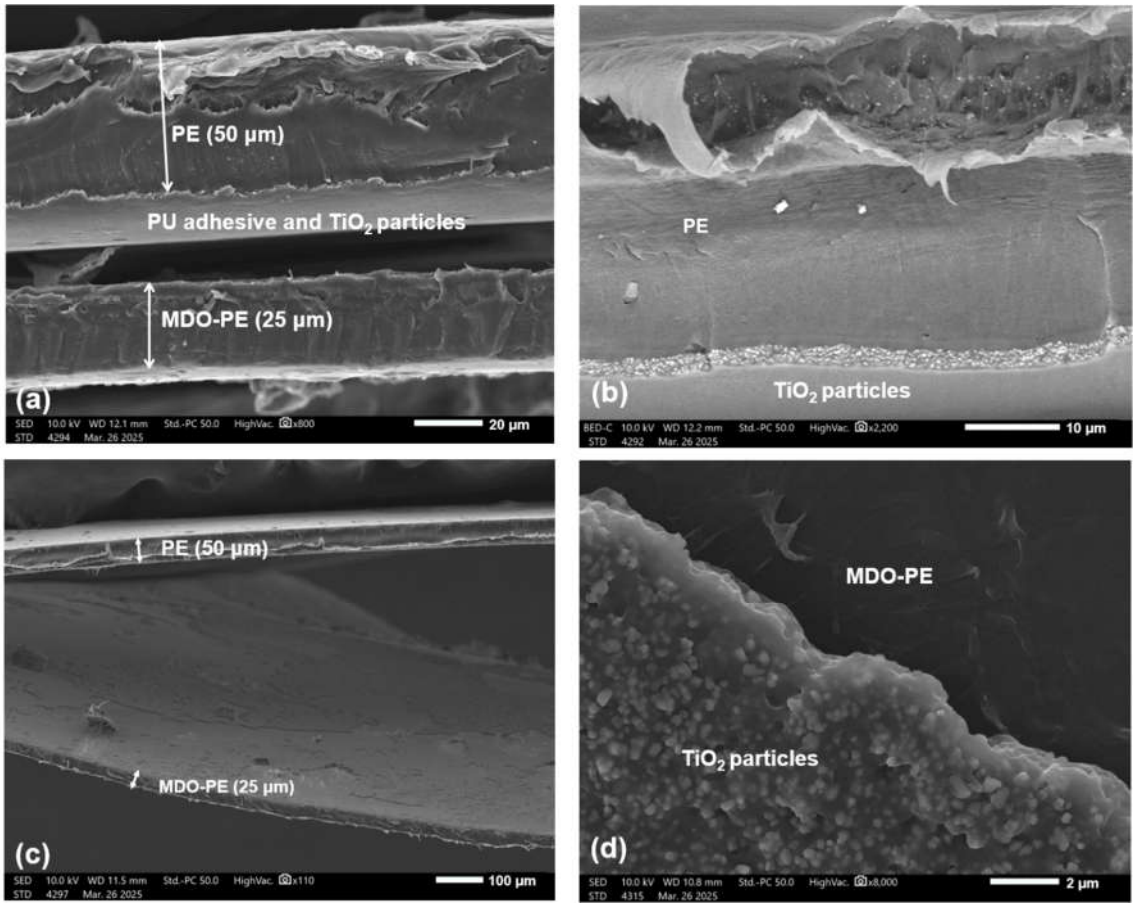


Figure 9. SEM images of: (a) MDO-PE/PU/PE film fractured using liquid N_2 (slightly delaminated), (b) back Scattering image of the PE layer in the MDO-PE/PU/PE multilayer film showing TiO_2 nanoparticles, (c) MDO-PE/PU/PE delaminated system after the CO_2 + methanol treatment, and (d) a front view of the MDO-PE delaminated layer.

Small and bright spherical particles were observed in the SEM images of the MDO-PE/PU/PE film. EDX analysis allowed their identification as TiO_2 (Supplementary Material, **Figure S4**). TiO_2 particles were used to provide the white colour to the PE film. Although the TiO_2 particles were originally introduced in the internal part of the PE film, SEM images showed that during lamination, particles migrated to the PU layer (**Figure 9b**).

SEM images of the CO_2 delaminated material are also presented in **Figure 9c** and **9d**, clearly showing the PE and MDO-PE layers. A close inspection of the inner face of the MDO-PE layer after delamination showed the presence of domains formed by TiO_2 particles, indicating that delamination took place at the

TiO_2/PU layer interface but not in a clean way. Similarly, SEM images of the PE inner layer revealed the presence of TiO_2 nanoparticles embedded into a polymer matrix. Thus, during delamination in CO_2, TiO_2 particles and PU were distributed between both layers.

These results agree with the ATR-FTIR results in **Figure 3c**. The spectra of the inner surfaces of both delaminated layers exhibited characteristic PU signals and a broad band starting at 700 cm^{-1}, attributed to TiO_2. It is worth noting that the MDO-PE layer appears slightly pink due to TiO_2 residues retained on the magenta-printed surface (see **Figure 3a**).

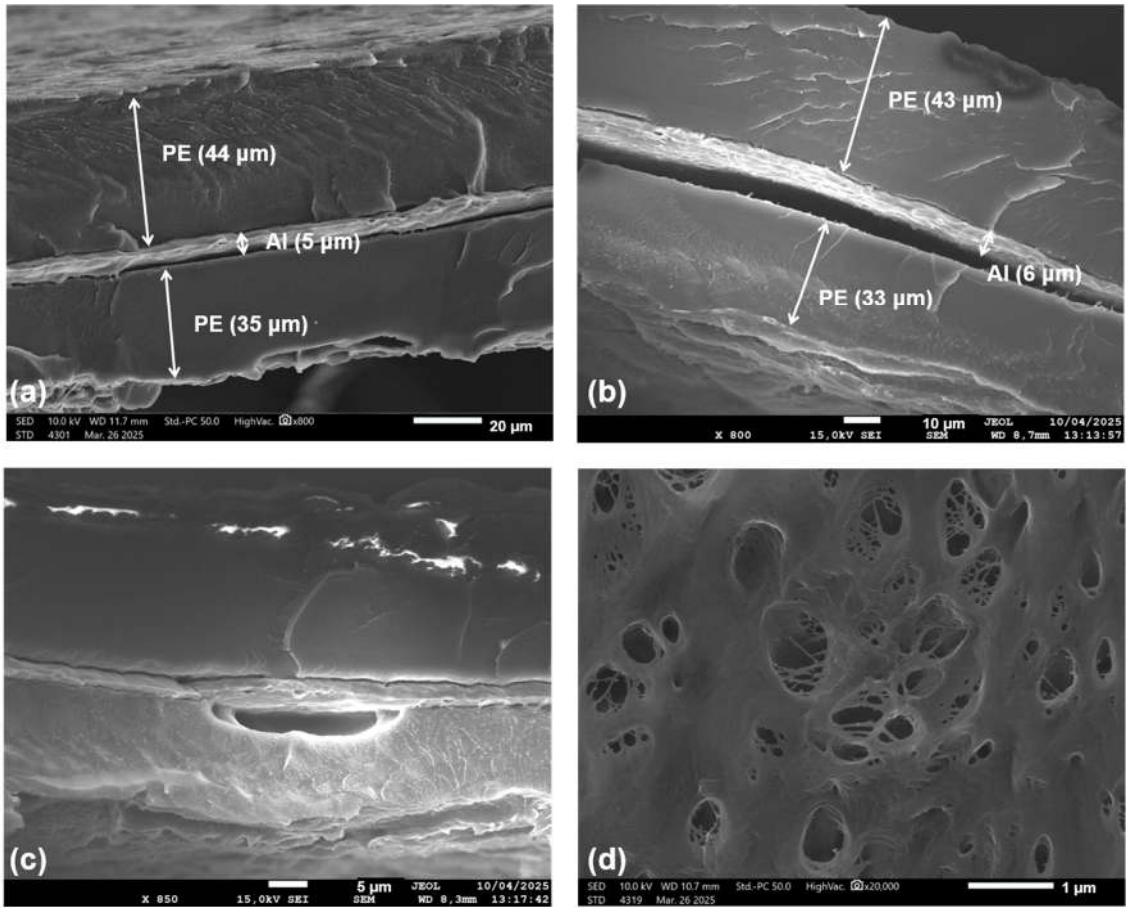


Figure 10. SEM images of: (a) PolyAl film fractured using liquid N_2, (b) PolyAl delaminated system after the CO_2 + methanol treatment, (c) localised delamination site (bubble) observed between the Al and PE layers, (d) a front view of the MA-PE layer.

Figure 10 shows SEM images of the PolyAl samples. In the untreated PolyAl sample (**Figure 10a**), at least three different layers were identified (one Al layer between two PE layers). **Figure 10b** shows an SEM image of the sample after the CO_2 treatment. The thickness of the layers remains almost the same before

and after the CO_2 treatment. **Figure 10c** highlights a possible delamination site in the form of a bubble. **Figure 10d** shows a front view of the MA-PE layer after delamination (CO_2 treatment), where several “bubble holes” are spread along the surface. This fact demonstrates that there is a mechanical modification of the film before delamination.

It is interesting to note that, during sample preparation for SEM, most samples partially delaminated during fracture at the same interface as samples delaminated with CO_2, which evidenced that delamination always took place at the weakest interface.

3.3. Delamination of commercial multilayer polymer films with $scCO_2$ and different cosolvents

Further experiments were conducted using additional cosolvents besides methanol, including ethanol, acetone, DMSO, and water. The amount of cosolvent was always equal to 5 mL, that is 8.3 % in volume and corresponds to mass percentages between 10.7 and 10.8% for acetone, methanol and ethanol, 13.3% for water and 14.5% for DMSO. The approximate mass calculation was performed, considering the volume of the reactor and the density of CO_2 at 80 ºC and 200 bar and neglecting the volume of mixing. At 80 ºC and 200 bar the CO_2 + organic cosolvent system remained in the one-phase region [36, 37, 42-45]. However, the solubility of water in CO_2 was much lower than the amount added. In particular, at 80 ºC and 200 bar, it is close to 0.75 % mass [46]. The presence of cosolvents is expected to change the swelling of the polymers as compared to pure CO_2. **Table 2** summarises the results.

A qualitative comparison of the cosolvent effect was performed, establishing a scale ranging from 1 to 4, meaning: (1) no delamination or visible separation between layers, (2) slight delamination with partial interfacial weakening observed; layers can only be minimally separated at the edges or with external force, (3) moderate delamination with a clear separation over a significant portion of the interface; delamination can be manually extended with moderate effort, but some adhesion zones remain, (4) complete delamination leading to full interfacial separation; layers detach easily and cleanly with minimal force (e.g., tweezers).

Table 2. Delamination degree of the different films with CO_2 modified by different cosolvents, ranging from (1) no delamination, (2) slight (minimal, edge-limited), (3) moderate (partial, extended), (4) complete delamination.

	PE/PU/PET	MDO-PE/PU/PE	PolyAl
DMSO	4	4	4
methanol	4	4	3
ethanol	4	3	1

acetone	2	2	1
water	2	1	1

603

604 The degree of delamination varied with the cosolvent and the multilayer film.
605 DMSO was the best cosolvent for the CO_2 delamination of all films. Methanol was
606 also a good cosolvent. The higher delamination efficiency of DMSO can be
607 partially related to its higher mass concentration in the experiments. DMSO is
608 highly soluble in CO_2. Although it has the highest boiling point of all cosolvents
609 used (T_m = 189 ºC), it could be very easily recovered from the CO_2 stream by
610 distillation with near-complete recovery, as demonstrated for the separation of
611 ethyl acetate-CO_2 [47]. Therefore, both CO_2 and the cosolvent could be efficiently
612 recycled in a simple loop. CO_2 would only require recompression and thermal
613 adjustment to restore process conditions. Moreover, DMSO is classified as a
614 Class 3 solvent according to ICH (International Council for Harmonisation)
615 guidelines, indicating low toxicological concern and enabling broader application
616 in environmentally responsible processes.

617 In contrast, acetone and water were bad cosolvents. Ethanol behaved differently
618 for each system; it helped in the delamination of PE/PU/PET and MDO-
619 PE/PU/PE, but not for PolyAl. In systems where both methanol and ethanol
620 successfully promoted delamination, ethanol would be a more suitable cosolvent
621 due to its lower toxicity (Class 3 vs. Class 2), despite its generally higher industrial
622 cost, particularly in its non-denatured form, owing to production methods and
623 taxation. **Figure 11** shows images of the films delaminated using CO_2 and the
624 four additional cosolvents.

625 Miscibility of the polymers and cosolvents was studied using the Hansen theory
626 [48]. The Hansen solubility parameters calculated from the dispersion, polar and
627 H-bonding forces (shown in **Tables S1** and **S2**, Supplementary Material)
628 indicated that acetone was the best solvent for PU and PET (slightly worse for
629 PET). DMSO was also a good solvent for PU and PET. In contrast, acetone and
630 DMSO were bad solvents for PE. Methanol, ethanol, and water were bad solvents
631 for all the polymers, water being the worst. Although water and alcohols are bad
632 solvents for the polymers involved, they are protic solvents, which could promote
633 the hydrolysis of PU. In the case of water, despite being a protic solvent, it may
634 have failed in the delamination due in part to its low solubility in scCO_2.The fact
635 that there is no correlation between the mutual solubility of the polymer and the
636 cosolvent and the delamination behaviour, strengthens the role of CO_2 in the
637 process.

638

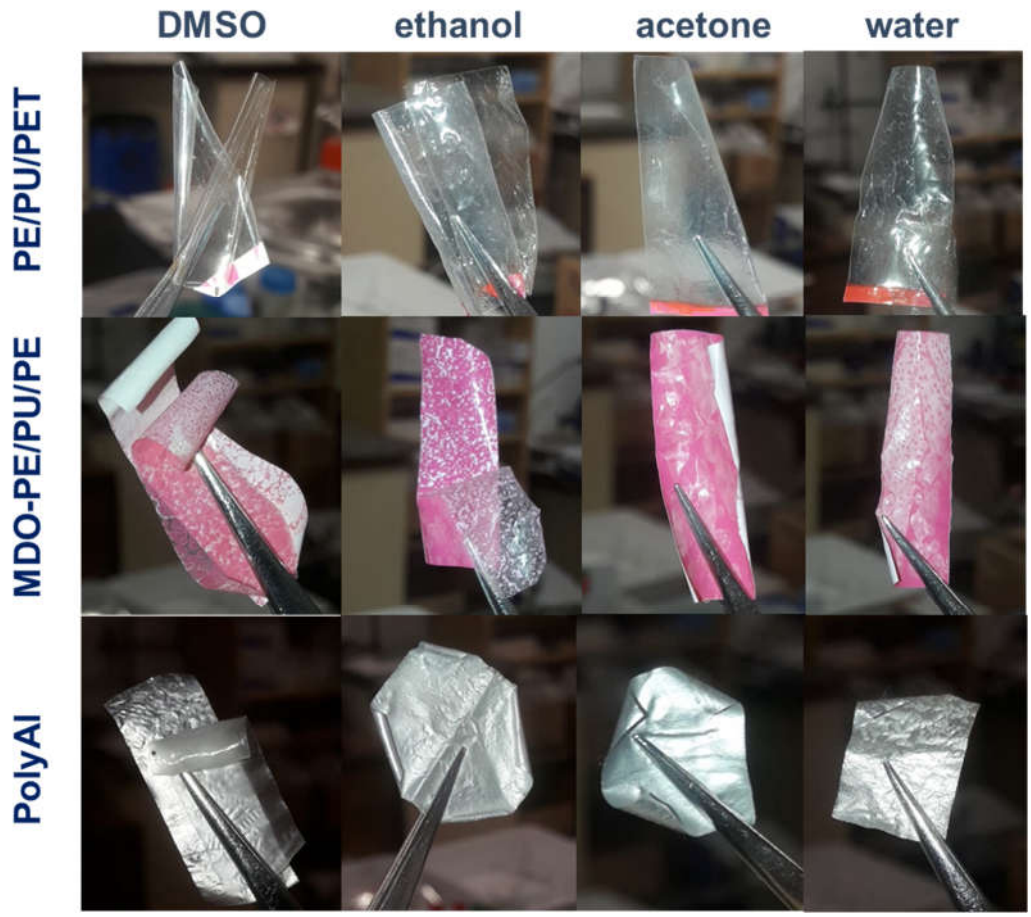


Figure 11. Images of the commercial films delaminated using CO_2 modified with the different cosolvents. Sample size for PE/PU/PET and MDPO-PE/PU/PE and PolyAl (DMSO) ca. 3 x 1 cm^2 and for PolyAl (ethanol, acetone, water) 1.5-1.0 x 1.5 cm^2.

In summary, although the treatment of a PET/PU multilayer material prepared in the lab with pure CO_2 followed by sudden depressurisation led to the separation of the PET and PU layers, successful delamination of other commercial and complex multilayer films was only possible when organic cosolvents were used. However, the success in the delamination using CO_2 and cosolvents did not follow the expected trend considering the mutual solubility of the polymers and cosolvents, so additional effects may take place.

The effluents of the delamination from PE/PU/PET films in pure CO_2 and CO_2 modified with DMSO were collected in deuterated DMSO. ^{1}H NMR of the samples (**Figure S5**, Supplementary Material) showed minor bands at 1.2 ppm, ascribed to aliphatic CH_2 groups. Due to the extremely low solubility of PE in CO_2 [49], these bands may indicate the extraction by CO_2 of oligomers, additives, polymerisation aids or unintended added substances present in the films [50]. No aromatic signals between 6.5 and 8.0 ppm due to PET or PU monomers or oligomers were observed.

Thus, we propose for the CO_2 delamination process a multiple mechanism involving (1) the generation of mechanical stress induced by the sorption of CO_2 into the polymers and preferential polymer swelling, followed by the sudden depressurisation, (2) the selective dissolution of the adhesive or the weakening of interfacial interactions between polymers induced by cosolvents. Previous research indicates that at higher temperatures, foaming of the polymers at the interface could also induce delamination [23, 24]. We envision that the separation between the PE layer and the PU adhesive using CO_2 may be possible by employing different conditions. The technique can also be combined with other physical or chemical recycling processes. Further studies are required to elucidate the exact delamination mechanism in CO_2 to be able to extend the process to other complex multilayer materials of interest.

4. CONCLUSIONS AND OUTLOOK

A new delamination process for multilayer plastics using supercritical CO_2 was demonstrated as a promising and sustainable alternative to current recycling technologies. Given the increasing concern around the environmental impact and technical challenges of recycling these materials, there is an urgent need for innovative approaches that are efficient, scalable, and environmentally friendly.

As a proof of concept, three commercial multilayer films, PE/PU/PET, MDO-PE/PU/PE and PolyAl, were treated using supercritical CO_2 at 80 ºC and 200 bar in the presence of various cosolvents, followed by rapid depressurisation. Selective delamination mainly occurred at the adhesive interfaces, depending on film composition. ATR-FTIR, DSC, and SEM analyses confirmed the release of distinct polymer layers.

Differences in the delamination efficiency were observed among the cosolvents used. DMSO and methanol showed the highest delamination efficiency, particularly at the PU-based adhesive interfaces, while acetone and water were ineffective under the tested conditions. DMSO is preferred due to its lower toxicity and the ease with which it can be separated from CO_2 by distillation for subsequent recycling.

A general mechanism for the CO_2 delamination process is proposed, considering both mechanical and chemical effects. The different degree of swelling induced by $scCO_2$ and the cosolvents in the polymers, followed by rapid depressurisation, can cause mechanical stress and/or foaming, promoting delamination. The selective dissolution of the adhesive or weakening of the interaction at the interface caused by the cosolvents is also possible.

Further investigation is needed to fully understand the delamination mechanism and enable broader application to other multilayer materials. Using several cycles sequentially at the same or different conditions could allow the delamination of

complex multilayer materials. Solvent-based methods show the highest delamination efficiency but carry the highest environmental and disposal concerns. Mechanical and thermal methods are simple but limited in efficiency and compatibility. The $scCO_2$ method combines the advantages of physical and chemical methods at less aggressive conditions, reducing substantially the amount of organic solvent used.

Furthermore, the $scCO_2$ method aligns with key principles of Green Chemistry, such as the use of safer solvents and waste prevention. It also complies with energy efficiency due to the mild operation conditions and simple sample recovery. Furthermore, it offers added benefits, such as the possible extraction of CO_2-soluble contaminants and the potential sterilisation of post-consumer waste plastics simultaneously with the separation process.

We are currently studying the effect of the sample size and mechanical stirring in the delamination process. After delamination, a density-based separation of the polymers could be performed. The method still requires optimisation, and a full life cycle assessment must be conducted to evaluate its environmental performance. However, given its mild operating conditions and important process advantages, the process holds strong potential for scale-up. Notably, numerous supercritical CO_2-based technologies have already been implemented at commercial scale under similar conditions. Engineering know-how and industrial expertise in supercritical fluid processing are well established, and several specialised companies could readily design and construct large-scale installations. If validated, this technology could help shift the paradigm in plastic recycling and contribute meaningfully to a more circular, sustainable economy.

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Supplementary Material

Sustainable Delamination of Multilayer Plastic Films for Advanced Recycling

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1. Structure of commercial multilayer films.

The commercial multilayer films provided by Plastigaur Company have several sub-layers. The arrangement is illustrated in **Figure S1**.

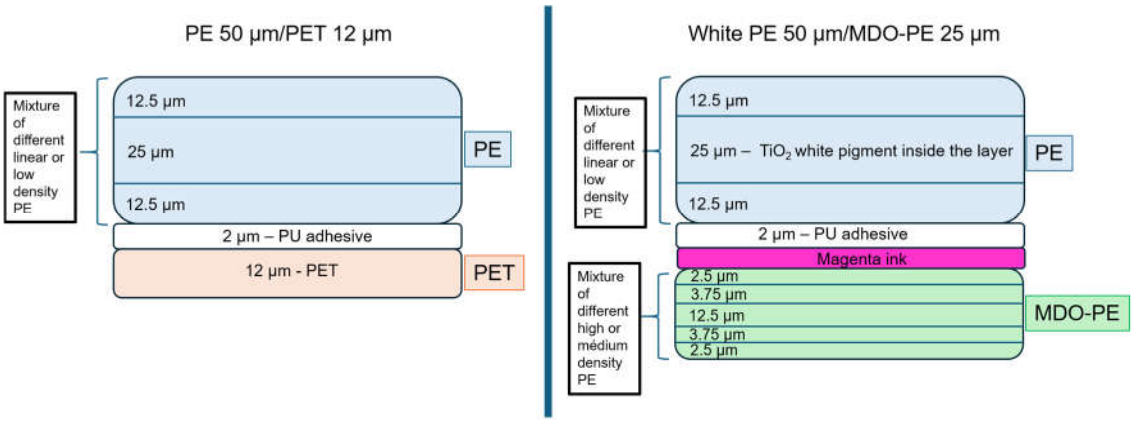


Figure S1. Multilayer structure of commercial films showing sub-layers: (a)PE/PU/PET and (b)PE/PU/MDO-PE system.

2. Thermogravimetric Analysis

TGA analysis of the PE/PU/PET multilayer films, the separated layers A and B (Table 1), and the PU adhesive prepared according to the vendor's instructions was also performed and is shown in **Figure S2**.

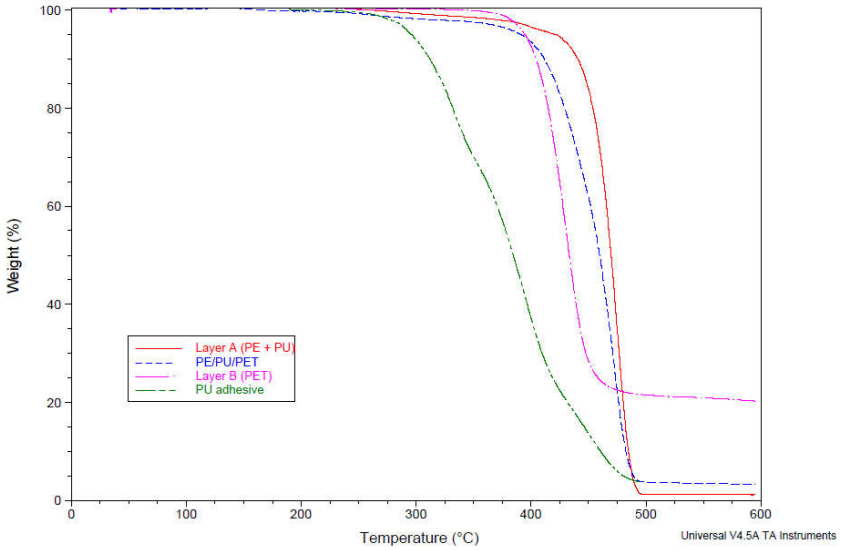


Figure S2. TGA analysis of the PE/PU/PET multilayer film, the separated layers: A (PE + PU) and B (PET) and the PU adhesive

Layer A (PE + PU) and layer B (PET) decomposed mostly between 420-500 ºC and 375-500 ºC, respectively, whilst PU decomposed between 225ºC-500 ºC. The PE/PU/PET film decomposed between 350-500 ºC. As expected in PE/PU/PET and Layer A (PE + PU), there was a small mass loss between 200 ºC to 400 ºC, related with the PU decomposition. In contrast, weight loss in this range for layer B was negligible, confirming the absence of PU.

3. .PU Adhesive preparation (Morchem PL272A+CF-60)

The adhesive preparation was performed in the laboratory following the supplier's instructions. The polyurethane adhesive is formed by mixing the separate components: PL272A (the glue) and CF-60 (the hardener). The mixture ratio used was 100 to 70, respectively. Prior to the mixing process, the components were thermostated at 40 ºC in a water bath. Then, 0.23 g of CF-60 was added using a 1 mL syringe to a 25 ml flask containing 0.32 g of PL272A, which had previously been weighed with a magnetic stirring bar. After that, stirring was initiated, and the temperature was maintained at 40 ºC for 45-60 minutes. Finally, the mixture was placed in an oven at 50 ºC for further drying and hardening for 24 hours.

The DSC of the PU adhesive prepared is shown in **Figure S3.** A T_g at ca. 5 ºC was observed in the sample, followed by other minor and unclear thermal events.

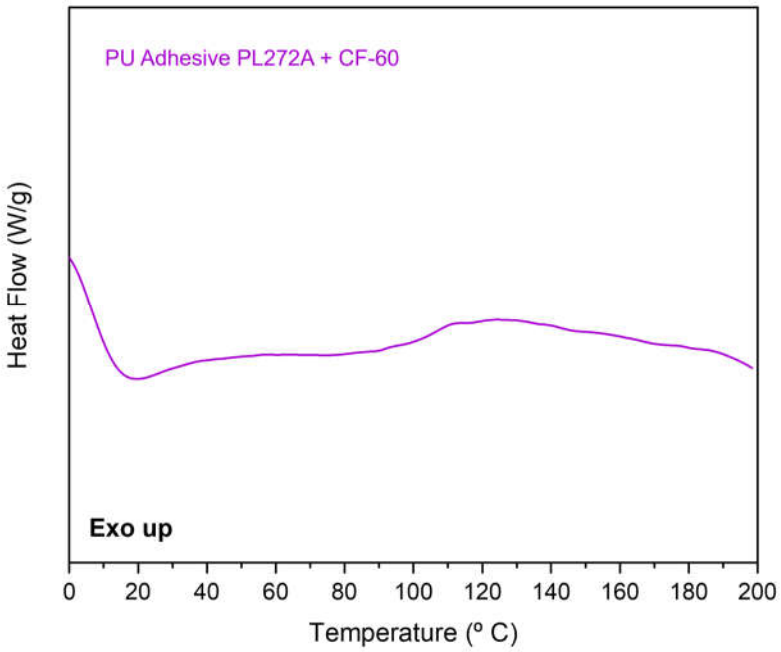
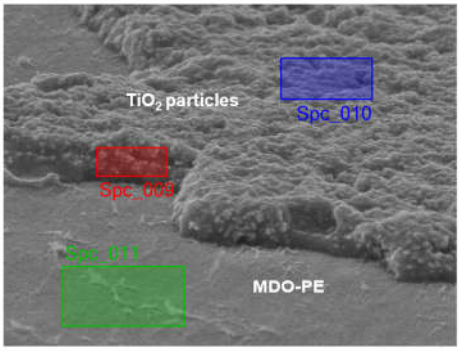
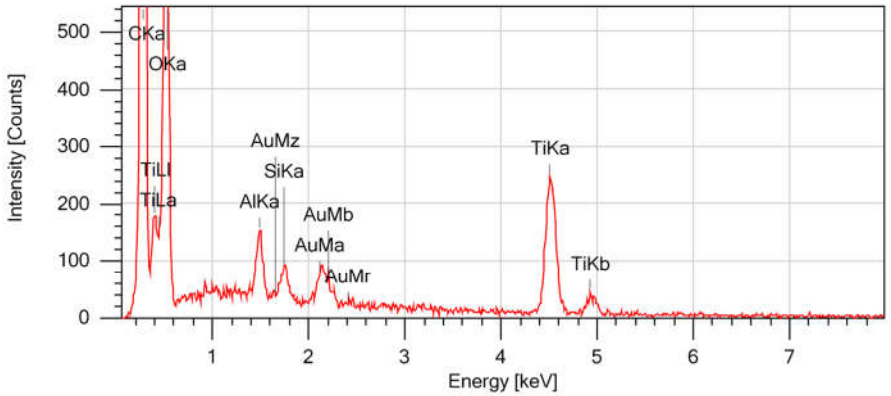


Figure S3. DSC thermogram of the adhesive prepared in the lab.

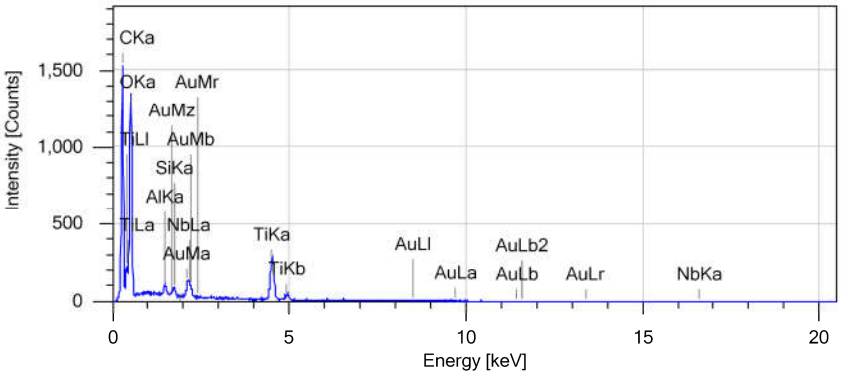
4. Characterisation of MDO-PE by EDX.

Energy-dispersive X-Ray spectroscopy (EDX) was conducted on the SEM images. **Figure S4** shows a SEM image and the spectra taken at three different locations. Analysis of the red and blue zones indicated the presence of Ti with a high mass percentage of ca. 24.8 % in both zones. Analysis of the green zone, however, did not show Ti. Therefore, titanium is present in the interphase zone of the laminates in a considerable quantity, as a different layer. This analysis confirms the identification of TiO_2 and the delamination place.

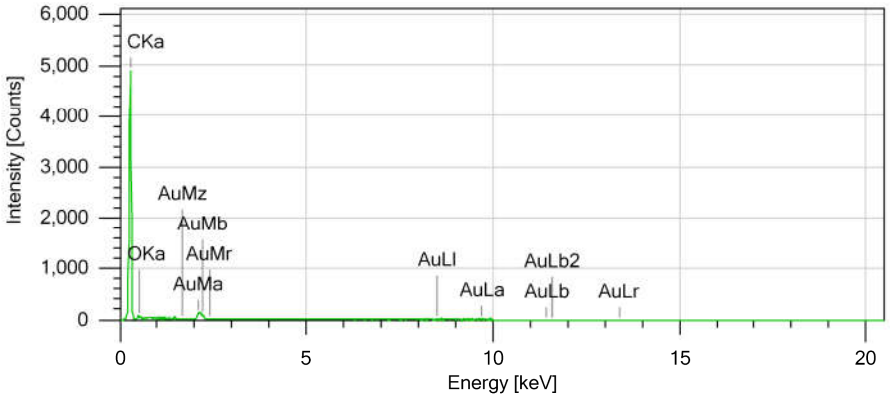




Element	Line	Mass%	Atom%
C	K	40.63±0.35	58.60±0.50
O	K	28.37±0.67	30.71±0.72
Al	K	1.45±0.11	0.93±0.07
Si	K	0.73±0.09	0.45±0.05
Ti	K	24.77±0.92	8.96±0.33
Au	M	4.05±0.33	0.36±0.03
Total		100.00	100.00
Spc_009			Fitting ratio 0.0334



Element	Line	Mass%	Atom%
C	K	31.32±0.30	47.87±0.46
O	K	35.62±0.69	40.87±0.79
Al	K	0.80±0.08	0.54±0.05
Si	K	0.72±0.08	0.47±0.05
Ti	K	24.68±0.87	9.46±0.33
Nb	L	1.45±0.22	0.29±0.04
Au	M	5.42±0.38	0.50±0.04
Total		100.00	100.00
Spc_010			Fitting ratio 0.0452



Element	Line	Mass%	Atom%
C	K	89.36±0.46	98.11±0.51
O	K	1.56±0.17	1.28±0.14
Au	M	9.09±0.45	0.61±0.03
Total		100.00	100.00
Spc_011			Fitting ratio 0.0130

Figure S4. SEM image and EDX spectra of MDO-PE layer in three different zones (red, blue and green highlighted in the micrograph).

5. Hansen solubility parameters

Solubility of the cosolvents into the different polymers was studied using the Hansen solubility parameters (HSP) approach [1]. Table S1 shows the Hansen solubility parameters (δ_D, δ_P, δ_H) for the solvents and the polymers used in the calculation.

Table S1. Hansen solubility parameters for the solvents and polymers used in this study.

	δ_D (MPa^{-1})	δ_P (MPa^{-1})	δ_H (MPa^{-1})
MeOH	14.7	12.3	22.3
Water	15.5	16.0	42.3
Acetone	15.5	10.4	7.0
Ethanol	15.8	8.8	19.4
DMSO	18.4	16.4	10.2
PET	18.2	6.4	6.6
PE	16.0	0.8	2.8
PU	18.1	9.4	4.5

These parameters were used to calculate the parameter distance between two molecules, R_a, as the measurement of how alike they are according to (1). The smaller R_a, the more likely they are to be compatible.

$$R_a^2 = 4(\delta_{D1}-\delta_{D2})^2 + (\delta_{P1}-\delta_{P2})^2 + (\delta_{H1}-\delta_{H2})^2 \quad (1)$$

Table S2. R_a values of the different polymers and cosolvents

	R_a(acetone) (MPa^{-1})	R_a(ethanol) (MPa^{-1})	R_a(methanol) (MPa^{-1})	R_a(DMSO) (MPa^{-1})	R_a(water) (MPa^{-1})
PET	6.7	13.9	18.2	10.6	37.4
PE	10.5	18.4	22.8	17.9	42.3
PU	5.9	15.6	19.3	9.1	38.7

Solvents with R_a values lower than 10 (or close to this value) for a given polymer are considered good solvents. From the R_a values, only acetone and DMSO are considered good solvents for PU and PET (slightly worse for PET), whilst they are bad solvents for PE. The rest of the solvents are bad solvents for all the polymers, with water being the worst.

6. ^{1}H NMR analysis of the effluent

The effluents of the delamination from PE/PU/PET films in pure CO_2 and CO_2 modified with DMSO were collected in deuterated DMSO. ^{1}H NMR of the samples showed bands of the solvent DMSO (2.5 ppm) along with water (3.3 ppm) as an impurity, and in some samples bands of acetone (2.1 ppm) used to clean the reactor. Minor bands at 1.2 ppm, ascribed to aliphatic CH_2 groups, were also found in both samples. Due to the extremely low solubility of PE in CO_2[2], these bands indicate the extraction by CO_2 of oligomers, additives, polymerisation aids or unintended added substances present in the films[3]. No aromatic signals between 6.5 and 8.0 ppm due to PET or PU monomers or oligomers were observed.

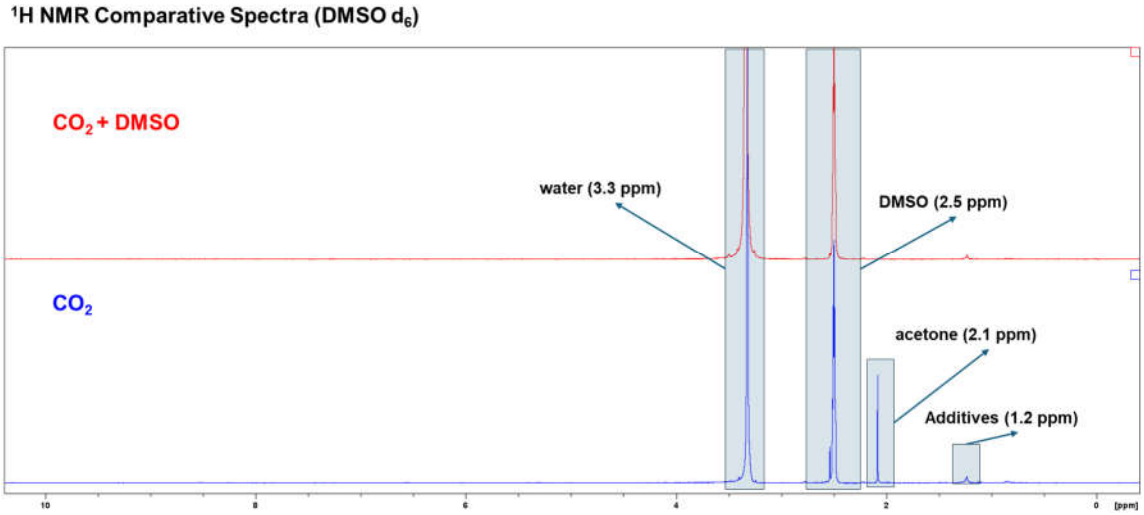


Figure S5. ^{1}H NMR analysis of the effluent collected after the delamination of PE/PU/PET films in CO_2 and CO_2 modified with DMSO.

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