

Article

Recycling of Multilayer Flexible Packaging Waste Through Delamination with Recoverable Switchable Hydrophilicity Solvents

Roberta Mastroddi , Chiara Samorì , Martina Vagnoni, Chiara Gualandi , Paola Galletti and Emilio Tagliavini *

Dipartimento di Chimica “Giacomo Ciamician”, Alma Mater Studiorum—Università di Bologna, Via P. Gobetti 85, 40129 Bologna, Italy; roberta.mastroddi2@unibo.it (R.M.); chiara.samori3@unibo.it (C.S.); mavagno@gmail.com (M.V.); c.gualandi@unibo.it (C.G.); paola.galletti@unibo.it (P.G.)

* Correspondence: emilio.tagliavini@unibo.it; Tel.: +39-3474430781

Abstract: Multilayer flexible packaging wastes (MFPWs) consist of complex materials composed of multiple plastic films, which are often laminated with aluminum foil, and they constitute a large portion of packaging waste. The use of several polymeric layers is essential to achieve the desired technical and mechanical performance of the packaging; however, this makes layer separation and recycling challenging. Currently, this type of waste is predominantly incinerated or landfilled; non-industrial recycling processes have recently been developed, but they mostly rely on traditional solvent-based treatments, which can be problematic. We present a versatile process for recycling MFPWs using switchable hydrophilicity solvents (SHSs). By treating waste with SHSs through a temperature-controlled process, we efficiently recovered the polymeric layers as sorted transparent films, effectively removing all additives while preserving the original properties of the polymers. Aluminum was recovered as well. *N,N*-dimethylcyclohexylamine was the best solvent for the delamination of the 26 different packaging materials tested, containing polypropylene, polyethylene, polyethylene terephthalate, and aluminum. The main advantage of this method is the straightforward recovery of the different components that can be efficiently delaminated and easily removed from the solvent, even from highly variable input material. Moreover, by exploiting the CO₂-triggered switchable behavior of the solvent, its purification and recovery can be achieved, maintaining its delamination efficacy over several cycles.

Keywords: switchable solvents; delamination; multilayer flexible packaging waste; recycling; CO₂



Academic Editors: Silvia Fraterrigo Garofalo and Giuseppe Pipitone

Received: 15 January 2025

Revised: 4 February 2025

Accepted: 6 February 2025

Published: 11 February 2025

Citation: Mastroddi, R.; Samorì, C.; Vagnoni, M.; Gualandi, C.; Galletti, P.; Tagliavini, E. Recycling of Multilayer Flexible Packaging Waste Through Delamination with Recoverable Switchable Hydrophilicity Solvents. *Separations* **2025**, *12*, 45.

<https://doi.org/10.3390/separations12020045>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Plastics represent essential and revolutionary materials in modern society because of their versatility, durability, lightweight, and low cost. Despite the extensive range of applications, which spans all production sectors, the packaging industry has become one of the fields most positively impacted by plastic innovation. Nearly 40% of plastic demand comes from packaging, making it the world’s largest plastics market, valued at USD 454.89 billion in 2024, with an average annual growth rate of about 4% [1]. Particularly, multilayer flexible packaging materials (MFPMs) are a hallmark of this innovation, combining the properties of various polymers, along with non-polymeric components (e.g., paper or aluminum foils), to create materials with exceptional characteristics, such as strength; barrier properties against moisture, light, and oxygen; and flexibility. MFPMs currently represent 17% of the

global film production, and they are primarily used in food, snack, and beverage packaging, accounting for 54% of the total packaging. They also find application in medicine, health care, chemical packaging, fabrics, and electrical appliances [2]. The most commonly used polymers are polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET), followed by polyamide (PA), polystyrene (PS), and polyethylene vinyl alcohol (EVOH) [3]. Their combination results in materials containing from 2 to 17 polymeric layers, often with aluminum (Al) foil or powder in between, to improve the mechanical resistance and oxygen-barrier properties, using different manufacturing technologies (e.g., extrusion, coating, or lamination) [4]. Despite numerous technological advantages, the disposal of plastic waste is becoming an increasingly significant challenge for industrialized societies, primarily due to its environmental persistence and global distribution, often as micro- and nanoparticles. In line with circular economy strategies, recycling polymeric materials is a priority. In Europe, the recycling rate of plastic packaging waste reached its maximum in 2022, with only 38% of the total 18.5 Mt of collected waste being recycled, while the majority was either incinerated (45%) or landfilled (17%) [1]. A worse scenario is observed in the US, where landfilling is currently the most common disposal approach (77% of plastic waste) [5]. The biggest challenges encountered in the recycling of multilayer flexible packaging wastes (MFPWs) consist of the sorting and separation of single components, requiring material-selective mechanical or chemical treatments, which must be efficient at separation, cost-effective, and, at the same time, able to preserve the initial properties of the individual recycled materials. Solvent treatment, although not yet implemented in industrial applications, is a useful strategy for separating and recovering the layers of MFPWs, and the following two main strategies have been proposed [6,7]: (i) selective dissolution–precipitation and (ii) delamination. The first approach consists of the use of a solvent able to selectively dissolve specific polymeric components, which can afterwards be collected by re-precipitation with an anti-solvent. Xylene–isopropanol [8], toluene–hexane [9] and dichloromethane–methanol [10] combinations have been exploited. Delamination, instead, involves the dissolution of adhesives and coating layers present in the material, allowing for the separation of the main polymeric or metallic layers. Solvents like xylene, acetone, hexane, and ethanol have been used [11].

These methods face several drawbacks, namely, VOC emissions, the toxicity of certain solvents, and the costly, environmentally impactful process of distilling solvents for their purification and reuse. These challenges have driven research seeking greener alternatives. Strategies utilizing alternative, greener solvents have emerged, including processes based on waste vegetable oil [12], ethylene glycol [13], carboxylic acids [14], deep eutectic solvents (DESs) [15], biodiesel, cyclopentyl methyl ether, and 2-methyl tetrahydrofuran [16]. Most of them have lower toxicity and higher biodegradability than traditional organic solvents. However, in many cases, separation, purification, and recycling are affected by the high energy demand required for distilling at the solvent's boiling point (e.g., cyclopentyl methyl ether and 2-methyl tetrahydrofuran) or by the addition of anti-solvents in the case of compounds that are either non-volatile or have too-low volatility to be distilled (e.g., DES, waste vegetable oils, and biodiesel). For example, the accumulation of impurities and aluminum after each delamination cycle, with the consequent need for a purification step with an additional solvent, has been reported for DESs; the same holds for biodiesel or vegetable oils, for which the use of ethanol as an anti-solvent for precipitating the solubilized polymers is needed. To overcome these issues and minimize the energy requirements of the solvent recovery process, innovative approaches based on “smart” solvents, such as switchable solvents, have recently been proposed. Particularly, switchable hydrophilicity solvents (SHSs) are known for their ability to reversibly switch from a non-polar and hydrophobic state to a more polar, hydrophilic one upon the input of CO₂, and this property has mainly been

exploited in separation and extraction protocols [17–22]. Notably, SHSs permit bypassing of the energy consumption step in distillation for recovering the solvent, as they can be readily separated from the polymers and components of the treated sample, as well as easily purified and reused, through the CO₂-triggered switch in polarity. Limited exploitation of this methodology for MFPWs has appeared in the literature, which, to the best of our knowledge, is often limited to specific classes of materials, such as aseptic packaging made of PE and aluminum [23] and pharmaceutical blisters [24]. One example of a broader application, developed by Mumladze et al., in 2018 [25], uses *N,N*-dimethylcyclohexylamine (DMCHA) under sonication allowing for the efficient recycling of MFPWs containing PET, Al, and PE or EVOH, Al, and PE. This method combines both the delamination and solubilization approaches, requiring an additional step to precipitate the solubilized polymer from the solvent, resulting in PE recovery after partial degradation and reduced mass weight.

Herein, we explore the use of SHSs for the recovery of PE, PP, and PET, in the form of transparent polymeric films, and aluminum (when present as foil) from MFPWs, developing a process entirely based on selective, temperature-controlled delamination. The goal is to efficiently sort and separate the single components, preserve their intrinsic properties, and optimize the recycling and reuse of the SHS. Both commercially available and newly synthesized SHSs are evaluated, and the process is applied to 26 types of MFPWs, also simulating a model of a mixed-waste scenario as closely as possible to real urban waste. The separation efficiency, properties of the recovered materials, and solvent recovery and reuse are thoroughly evaluated.

2. Materials and Methods

2.1. Materials and Waste Collection and Classification

All chemicals/solvents used in this study were obtained from Sigma-Aldrich—Merck (Darmstadt, Germany) and used without purification (purities $\geq 98\%$), except for *N,N*-dipropylcyclohexylamine, which was synthesized as described in the Supporting Material, Figure S1.

The MFPW samples were collected from local Italian shops or received from Itene—Technologic Institute for Packaging, Transport, and Logistics (Valencia, Spain)—and they consist of packaging for chips, snacks, biscuits, nuts, ice cream, coffee, soup, and pet food. The samples were classified into three categories according to the types of polymers present:

- Group 1 (mixture of PP- and Al-based packaging): 9 different packaging materials containing only polypropylene as a polymeric component and aluminum in the form of nebulized powder;
- Group 2 (mixture of PET-, PE-, and Al-based packaging): 9 different packaging materials containing both polyethylene and polyethylene terephthalate as polymeric components and aluminum in the form of a layer;
- Group 3 (mixture of PET-, PP-, and Al-based packaging): 8 different packaging materials containing both polypropylene and polyethylene terephthalate as polymeric components and aluminum in the form of a layer or nebulized powder;

This classification was made possible through a comprehensive characterization of these materials detailed in our previous work [26] and summarized in the Supporting Material (Table S1).

2.2. General Procedure for the Delamination of MFPWs with SHSs

The waste sample was cut into small pieces with a scissor (about 1 × 1 cm) and transferred into a round-bottomed flask equipped with a stirring bar and a water refrigerator on top. During the solvent screening and method optimization phase, a small scale was

employed, using 0.04 g of sample (approximately 4 to 5 pieces). For the mixed waste delamination experiments with DMCHA, a larger scale was employed, with sample weights ranging from 0.1 to about 0.5 g (equivalent to 16–18 pieces), depending on the type of mixed material. The solvent was added to the flask in a volume corresponding to the desired sample loading, and the mixture was then heated (for a time and at a temperature dependent on the type of sample and solvent) while being stirred, according to what is reported in Tables 1–3. Different sample loadings (1, 1.5, 2, 3, 4, and 5 wt%) were initially tested (Table S2 in Supporting Materials), and a sample loading of 1 wt% was selected for the larger-scaled experiments. After the delamination, consisting of the dissolution or dispersion of sealing and coating layers (clearly observable by noting the change in color and the increase in opacity of the solution), the floating polymers and aluminum chips or powder were removed from the solution. For the one polymer type-containing sample, this operation was performed by filtering the solution through a metallic grid with a mesh size of 0.1 cm. When treating different polymer type-containing samples, the delaminated polymers were mechanically removed by flotation (i.e., exploiting their buoyancy due to the lower density) and separated from the non-delaminated ones; the delamination step of the remaining sample, followed by recovery through flotation, was then repeated within the same process cycle at different polymer-specific temperatures. After each step, the collected single-polymer layers were washed with acetone to remove eventual traces of SHS, dried in an oven at 50 °C, and then weighed. The aluminum powder on the filter or the collected aluminum flakes were also washed with acetone, dried, and weighed.

2.3. General Procedure for SHS Recycling

After the delamination was completed, the remaining solution, containing the solvent with dissolved inks and additives, was cooled at room temperature and water was added at a 1 to 1 *v/v* ratio. After cooling the mixture at 0 °C with an ice bath, CO₂ was blown into the biphasic mixture using a needle connected to a CO₂ cylinder. After 0.5 h (small scale) or 1 h (larger scale), a single solvent phase was obtained with the separation of a distinct upper layer with a sludge consistency and a dark color, containing inks and other additives. The two layers were separated using a separatory funnel. Finally, the back-switch of the water/solvent phase was performed by heating to approximately 70 °C for 1.5 h (small scale) or 2 h (large scale) under vigorous stirring, with a water refrigerator placed on top of the system. After the reformation of the biphasic water/solvent system, the water was separated and set aside for reuse in the next cycle. A new delamination cycle was then carried out using the recycled solvent and the method described above.

2.4. Analyses of Recovered Materials and SHSs

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on the recovered polymeric films (PET, PE, and PP) were performed, using manually delaminated samples as a comparison.

Thermogravimetric analysis was carried out using a TGA thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) the high-resolution mode (Hi-Res™) from room temperature to 700 °C, at a heating rate of 50 °C/min and a resolution index of 4, under airflow.

Thermal transitions were measured using a differential scanning calorimeter (DSC Q2000; TA Instruments) equipped with a refrigerated cooling system (RCS). Samples, under nitrogen flow, were subjected to a first heating scan at 20 °C/min from −90 to 220 °C for the PE and PP samples and to 285 °C for the PET. The samples were then cooled to −90 °C at 10 °C/min and a second heating scan was applied. The glass transition temperatures (*T_g*)

were determined at the midpoint of the step-change in the DSC trace. Melting temperatures (T_m) were determined at the minimum of the most prominent endothermic melting peak.

Fourier transform infrared spectroscopic analysis (FTIR) was carried out on the recovered polymers (PET, PE and PP) using an FT-IR ATR Agilent (Santa Clara, CA, USA) Cary 630 spectrometer, with manually delaminated samples as a comparison.

Elemental analysis (CHNS) was conducted on recovered aluminum flakes using an elemental analyzer (Thermo Scientific, Waltham, MA, USA; Flash2000, Organic Elemental Analyzer) through the flash combustion technique.

The ^1H NMR analysis carried out on the recovered DMCHA was recorded on a Varian-Agilent (Santa Clara, CA, USA), Varian 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the TMS, with the residual protonated solvent resonance as the internal standard, as follows: deuteriochloroform (CDCl_3) = 7.26 ppm.

3. Results and Discussion

3.1. SHS Screening in MFPW Delamination

Various SHSs (Figure 1) were initially evaluated through qualitative experiments to assess their delamination efficacy and recoverability. All of them have a switchable hydrophilic behavior triggered by CO_2 , since they can be reversibly converted into a highly water-soluble ammonium salt when CO_2 is added and return to a neutral, less hydrophilic or hydrophobic form after CO_2 removal (Figure 1 and Figure S2 in Supporting Material). The tested solvents included tertiary amines—triethylamine (TEA); *N,N*-diisopropylethylamine (DIPEA), *N,N*-dimethylcyclohexylamine (DMCHA), *N,N*-dipropylcyclohexylamine (DPCHA), and triethanolamine (TEOA); secondary amines—dicyclohexylamine (DCHA), diisopropylamine (DIA), and di-*sec*-butylamine (DSBA); and amidines—1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

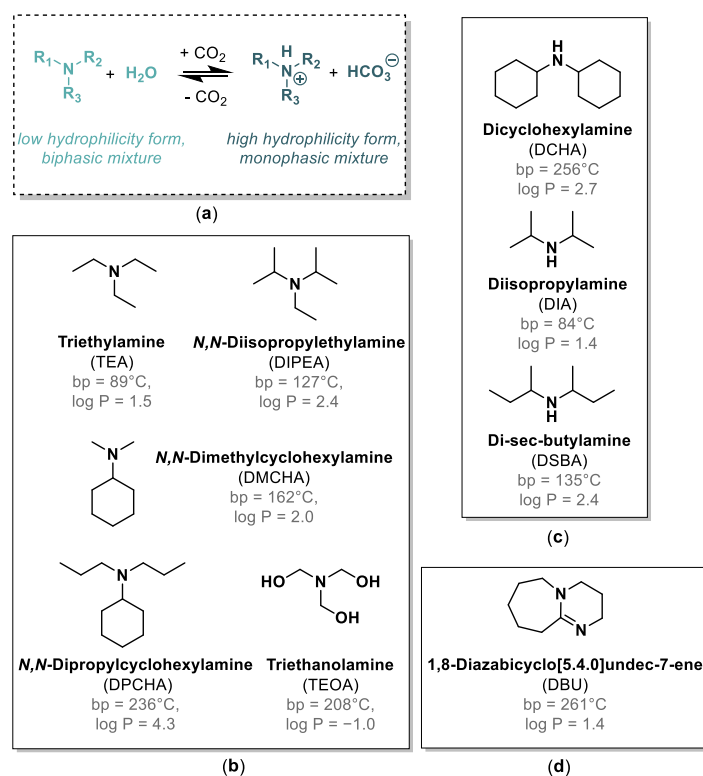


Figure 1. (a) CO_2 -triggered conversion of a generic switchable solvent–water mixture; structures and physical properties of various switchable solvents—(b) tertiary amines, (c) secondary amines, and (d) amidines—tested during the delamination process.

The results, as presented in Table 1, are based on the following three representative waste samples with different compositions:

- Sample A: “Gran Cereale[®]” biscuits packaging, containing only PP as polymeric material and Al powder between the layers;
- Sample B: “Pericaff[™]” coffee bag, with PE and PET as polymeric materials and an Al foil between these two layers;
- Sample C: “Oreo[®]” biscuits packaging, where PP and PET are the polymers with Al powder between the layers.

Table 1. Delamination results of different SHSs tested on the three samples.

Entry	SHS	Sample	T (°C) ¹	Time (h) ²	Delamination ^{2,3}
1	TEA	A	80	5	Incomplete
2	TEA	B	40	0.5	Yes
			80	4	No
3	TEA	C	80	4	Incomplete
4	DIPEA	A	90	5	Incomplete
5	DIPEA	B	40	0.5	Yes
			130	4	No
6	DIPEA	C	90	4	Incomplete
7	DMCHA	A	80	2	Yes
8	DMCHA	B	40	0.25	Yes
			130	2	Yes
9	DMCHA	C	90	2	Yes
10	DPCHA	A	90	5	Incomplete
11	DPCHA	B	40	0.5	Yes
			130	4	Yes *
12	DPCHA	C	90	4	Incomplete
13	TEOA	A	90	3	Incomplete
14	TEOA	B	40	0.5	Yes
			130	4	No
15	TEOA	C	90	3	Incomplete
16	DBU	A	75	3	Yes
17	DBU	B	40	0.5	Yes
			130	4	Yes
18	DBU	C	90	4	Yes
19	DCHA	A	90	4	Yes
20	DCHA	B	40	0.5	Yes
			130	4	Yes *
21	DCHA	C	90	4	Yes
22	DIA	A	80	5	No
23	DIA	B	40	0.5	Yes
			80	4	No
24	DIA	C	80	4	No
25	DSBA	A	90	5	No
26	DSBA	B	40	0.5	Yes
			130	4	No
27	DSBA	C	90	4	No

¹ When two values are reported, the second refers to the successive treatment of the sample at a higher T. ² When two values are reported, they refer to the first treatment at a lower temperature (for performing PE delamination) followed by a second treatment at a higher temperature (for performing PET delamination). ³ “Yes” corresponds to total delamination and transparency of the sample; “Incomplete” refers to partial detachment of the layers or delamination of part of the total number of sample pieces; “No” indicates no delamination. * Inks retained on the films.

The initial screening revealed that the three solvents were able to delaminate all of the following materials: DMCHA, DBU, and DCHA. DMCHA led to the best results in the shortest time (entries 7–9), providing transparent films, while the films recovered from

sample **B** through DCHA still retained the inks. The amidine DBU displayed comparable results in a slightly longer delamination time than DMCHA (entries 16–18). On the other hand, the secondary amines DIA and DSBA (entries 22–27) performed the worst among the tested solvents; no layer separation was obtained for samples **A** and **C** and only a partial delamination was observed for sample **B**. The TEA (entries 1–3), DIPEA (entries 4–6), DPCHA (entries 10–12), and TEOA (entries 13–15) performed slightly better than DIA and DSBA on samples **A** and **C**, as partial delamination was achieved, but worse than DMCHA, DBU, and DCHA. It was evident that additives, glues, and inks were better dissolved by tertiary amines of average lipophilicity (log *p*-value of around 2) and boiling points much higher than the delamination temperatures (>160 °C vs. a working temperature of 90–130 °C). Compounds that were too lipophilic or hydrophilic, like DPCHA (log *p*-value of 4.3) or TEA and TEOA (log *p*-values of 1.5 or –1), respectively, or amines with boiling points that are too low like DIPEA (b.p. of 127 °C) did not work efficiently. Indeed, temperature was a crucial parameter for the efficiency of the process, as follows: polyolefins were delaminated between 40 and 50 (PE) and 80 and 90 °C (PP), while PET was delaminated at 130 °C. The limitations associated with the boiling points of the solvents explain the reduced effectiveness observed with low-boiling-point (<130 °C) solvents in treating samples **B** and **C**, containing PET.

In addition to the recycling of the packaging waste components, the possibility of recovering and recycling the solvent by exploiting the CO₂-triggered conversion (as previously shown in Figure 1) was also evaluated. According to the best results in the delamination, three solvents were selected for the recyclability test: DMCHA, DCHA and DBU. After completing a delamination cycle using the representative sample **B**, the solvents underwent both the “switch” (i.e., addition of CO₂) and “back-switch” (i.e., removal of CO₂) processes (see the general procedure outlined in Section 2.3). The results of the recovery are presented in Table 2.

Table 2. Recycling experiments of the most efficient delaminating solvents.

SHS *	Switch Time (h)	Back-Switch Time (h)	Solvent Recovery (%)	Additive Separation
DMCHA	0.5	1.5	89	Yes
DCHA	0.25	1.5	95	No
DBU	0.2	4	-	Yes

* 5 mL with 1 wt% sample loading.

DMCHA was highly recyclable, allowing for complete separation from the additives and a solvent recovery of 89%. The loss of 11% is mostly attributed to evaporation and the small-scale of the experiments. It is foreseeable that using a properly engineered apparatus could strongly improve this drawback. DCHA exhibited a shorter switch time and a higher solvent recovery rate, likely due to its lower volatility and poor water solubility. However, the separation from the additives and effective solvent recycling was not successful; indeed, during the switch phase, the high polarity form of the solvent turned into a solid salt that was insoluble in water, even when the water volume was doubled. Additives precipitated as a solid sludge, and their separation from the solid salt was challenging. Although the neutral liquid form of the solvent could be restored, partial re-solubilization of the additives occurred, preventing the recovery of a clean solvent. Regarding DBU, a very rapid reaction with CO₂ was observed, thanks to its higher basicity compared to amines. However, the back-switch was ineffective even with the extended time; the neutral DBU could not be restored under standard conditions. While the combination of DBU/1-octanol is a well-known switchable solvent system [27], the mixture of DBU/water was not reversible upon the addition and removal of CO₂; thus, it was ultimately discarded.

DMCHA was selected as the best delaminating solvent and investigated over multiple MFPW delamination cycles. Specifically, successive delamination tests using the recycled solvent were conducted on sample **B**, demonstrating that solvent **C** be recycled without any loss of delamination efficiency for up to seven cycles (Table S3 in Supporting Material).

3.2. Delamination of Model Mixed-Waste Samples with DMCHA

DMCHA was tested in the delamination for the more representative and complex sample systems, Groups 1, 2, and 3 (see Section 2.1 for sample details), each consisting of mixtures of different packaging types of MFPWs having the same composition. Additionally, a further experiment was conducted on a sample composed of a mixture of all the samples from the three groups (MIX). Only clean and additive-free (i.e., transparent) recovered layers were weighted and evaluated for the results. The solvent recycling was also performed using the switch/back-switch procedure. The results and details are presented in Table 3.

Table 3. Delamination results of different composition model mixed samples with DMCHA.

Sample	Temperature, Time	Initial Sample Weight (g)	Clean Recovered Polymers Weight (Type) (g)	Clean Recovered Al (g)	Overall Material Recovery (%) *	Solvent Recovery (%)
Group 1 (PP/Al)	90 °C, 2 h	0.130	0.095 (PP)	0.006	78	95
Group 2 (PE/Al/PET)	50 °C, 0.5 h 130 °C, 2 h ¹	0.417	0.175 (PE) 0.075 (PET)	0.018	64	89
Group 3 (PP/Al/PET)	90 °C, 1 h 130 °C, 2 h ¹	0.205	0.061 (PP + PET)	0.006	33	90
MIX	50 °C, 0.5 h 90 °C, 1 h ¹ 130 °C, 2 h ²	0.559	0.088 (PE) 0.136 (PP + PET)	0.024	44	92

* Obtained as a percentage of the initial sample weight. ¹ Temperature and time of the second delamination step. ² Temperature and time of the third delamination step.

Delamination of the polymeric layers and aluminum was successfully achieved for all of the systems evaluated, accompanied by excellent solvent recovery. Notably, the best results were obtained with the samples in Group 1, where 78% of the material was recycled along with 95% of the solvent, and with the samples in Group 2, achieving a 64% material recovery and 89% solvent recovery. In the case of the samples in Group 3 and MIX, the delamination was successful, but, in some cases, the recovered layers retained some inks, additives, or aluminum powder, and these are not included in the reported recovery results. However, the solvent's recovery remained at higher than 90%. Moreover, the residues could be removed by mechanically scratching the surface of the "dirty" films, confirming the potential and versatility of this delamination strategy, even for very complex mixed samples, similar to actual plastic waste. It is worth underlining that this method enables the selective delamination of the different polymers present in the materials by carefully controlling the temperature of the process; PE was always delaminated at 50 °C, followed by PP at 90 °C and by PET at 130 °C (except for materials containing PET and PP with Al in the powder form, where delamination occurs simultaneously). This allows for the sorting of the recovered material flows instead of the production of a plastic mix that is difficult to reuse.

Figures 2 and 3 show pictures of the materials separated and collected after delamination and the appearance of the solvent during the process and the recovery phases, respectively.

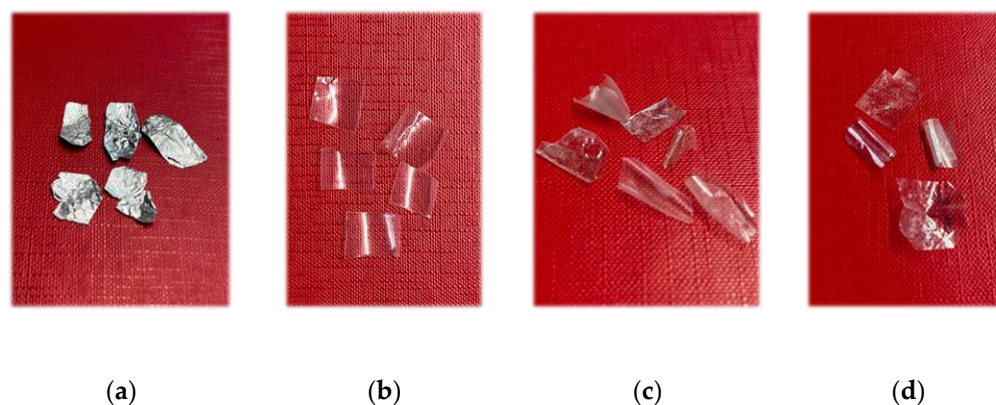


Figure 2. Recovered materials after the delamination process: (a) aluminum flakes; (b) PE films; (c) PP films; (d) PET films.

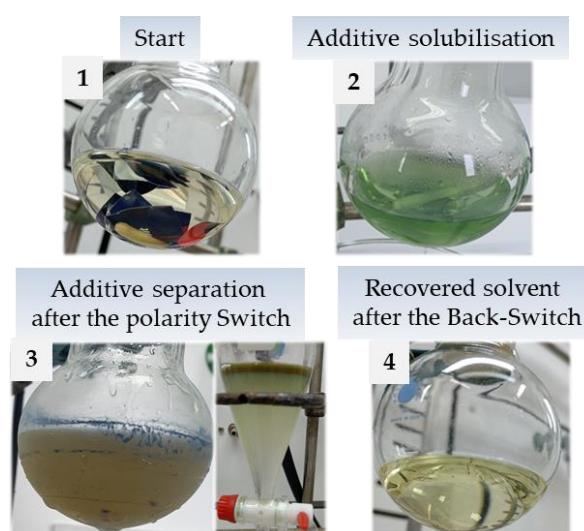


Figure 3. DMCHA in the delamination and recovery phases: before delamination (1), after delamination and additives solubilization (2); after the switch and additive separation (3); recovered DMCHA after the back-switch (4).

3.3. Characterization of Recovered Materials

Qualitative and quantitative analyses were carried out to determine both residual solvent and possible degradation of the recovered polymers. Thermal analyses of the recovered samples were compared with the corresponding reference samples. Calorimetric data, determined by DSC (2nd heating scan), are reported in Table 4, and the corresponding DSC curves are shown in Figure S2 in the Supporting Material.

Table 4. Thermal properties of the recovered PE, PET, and PP, as determined by the TGA and DSC analyses. The PE, PET, and PP references correspond to the untreated reference samples.

Sample	T _g (°C)	T _m (°C)	ΔH _m (J/g)
PE recovered	n.d. *	111	123
PE reference	n.d. *	111	121
PET recovered	80	247	47
PET reference	78	252	48
PP recovered	−11	163	90
PP reference	−8	161	80

* n.d. = not detectable.

Thermal transitions (T_g and T_m) and melting enthalpies (ΔH_m) of the recovered PE, PET, and PP samples were found to be almost identical to the corresponding reference, confirming the identity of each material and indicating that the delamination with the solvent did not alter their thermal properties.

The thermal degradation profiles (TGA curve reported in Figure S3 in the Supporting Material) of the recovered PE, PP, and PET films strongly overlap with those of the corresponding reference samples. This suggests that the recovered materials were not subjected to a previous degradation phenomenon possibly occurring during the recovery steps. In the case of the recovered PET sample, a small weight loss of approximately 2 wt% was noted at ca. 160 °C, corresponding to the boiling point of DMCHA, suggesting an almost negligible solvent contamination. This weight loss was not observed in the TGA of the PE and PP samples.

The FTIR-ATR analysis of the recovered polymers demonstrated full correspondence with the reference polymers (Figure S4 in Supporting Material).

Elemental analysis (CHNS) performed on the recovered aluminum flakes to determine the solvent contamination revealed a nitrogen content of 0.55 wt%, corresponding to a residual amount of DMCHA between 3 and 4 wt%.

Finally, ^1H NMR analysis confirmed that the recovered DMCHA showed no contaminants or alterations after the process (Figure S5 in Supporting Material), apart from the residual water solubilized during the recovery phase (the water solubility in DMCHA at 20 °C is about 21.4 wt%) [28].

4. Conclusions

This study has demonstrated the potential of developing an efficient and versatile process for the delamination and recycling of a wide variety of multilayer flexible plastic wastes (MFPWs) using switchable solvents. Through method optimization, DMCHA emerged as the most effective solvent for delamination compared to other tertiary and secondary amines and amidines, likely due to its favorable chemical and physical properties. It exhibited high delamination efficiency for all tested materials, regardless of type, together with optimal recyclability.

A key advantage of this approach is the ability to sort different polymeric layers during the delamination process. Effective sorting of all types of MFPWs containing Al in the form of foil is always possible, exploiting the polymer-specific temperature step. With mixed material inputs, PE layers can always be consistently separated from PP and PET by implementing an initial treatment at 40 °C. However, sorting PP and PET after delamination is only partially successful. For samples containing aluminum foils, separation is efficiently achieved, because PP delaminates from Al at 90 °C and PET at 130 °C. On the other hand, when aluminum is in the powder form, the sealing and coating layers require solubilization at 130 °C, leading to the simultaneous delamination of both polymers. Either way, post-process identification using infrared (IR) analysis can be employed to readily distinguish and separate PET from PP.

Despite these minor refinements, the method proves to be highly efficient and practical, offering a general strategy that ensures effective recycling of waste materials and low-energy solvent recovery. This aligns seamlessly with a circular economy model, promoting a sustainable and resource-efficient solution for recycling one of the most produced and challenging plastic wastes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations12020045/s1>, Figure S1: General procedure for the synthesis of *N,N*-dipropylcyclohexylamine and characterization; Figure S2: Chemical structures of the switchable solvents before and after CO₂ addition; Figure S3: DSC curves of the recovered polymers and the

corresponding references—(a) PE; (b) PET; (c) PP; Figure S4: TGA curves of the recovered polymers and the corresponding references. (a) PE; (b) PET; (c) PP; Figure S5: FTIR spectra of the recovered polymeric layers and the corresponding references—(a) PE reference; (b) PE recovered; (c) PET reference; (d) PET recovered; (e) PP reference—(f) PP recovered; Figure S6: ¹H NMR spectrum of recovered DMCHA after the switch and back-switch procedures. Table S1: Classification and features of the three waste categories treated; Table S2: Delamination of sample **B** with DMCHA varying the sample loading; Table S3: Delamination of sample **B** with recycled DMCHA.

Author Contributions: Methodology, data curation, investigation, writing—review and editing, and writing—original draft preparation, R.M.; Conceptualization, supervision, and writing—review and editing, C.S.; Methodology and investigation, M.V.; Investigation and writing—review and editing, C.G.; supervision, funding acquisition, and writing—review and editing, P.G.; supervision, funding acquisition, and writing—review and editing, E.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union’s Horizon 2020 Research and Innovation Programme, under grant agreement No 101003883 (MERLIN—Multilayer packaging recycling waste).

Data Availability Statement: The data supporting the findings of this study are available from the corresponding author upon request.

Acknowledgments: The authors acknowledge the Itene Institut for the furnished waste samples and the student Silvia Torrisi for contributions to the experiment.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Plastics Europe. Available online: https://plasticseurope.org/wp-content/uploads/2024/03/CEreport_executivesummary_2024.pdf (accessed on 9 January 2025).
2. Tartakowski, Z. Recycling of Packaging Multilayer Films: New Materials for Technical Products. *Resour. Conserv. Recycl.* **2010**, *55*, 167–170. [CrossRef]
3. Joint Research Centre—European Commission. *Guidance for the Identification of Polymers in Multilayer Films Used in Food Contact Materials: User Guide of Selected Practices to Determine the Nature of Layers*; Publications Office of the European Union: Luxembourg, 2016.
4. Wagner, J.R. Blown Film, Cast Film, and Lamination Processes. In *Multilayer Flexible Packaging*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 137–145. ISBN 978-0-323-37100-1.
5. Tumu, K.; Vorst, K.; Curtzwiler, G. Global Plastic Waste Recycling and Extended Producer Responsibility Laws. *J. Environ. Manag.* **2023**, *348*, 119242. [CrossRef]
6. Kaiser, K.; Schmid, M.; Schlummer, M. Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling* **2018**, *3*, 1. [CrossRef]
7. Li, T.; Theodosopoulos, G.; Lovell, C.; Loukodimou, A.; Maniam, K.K.; Paul, S. Progress in Solvent-Based Recycling of Polymers from Multilayer Packaging. *Polymers* **2024**, *16*, 1670. [CrossRef] [PubMed]
8. Georgiopoulou, I.; Pappa, G.D.; Vouyiouka, S.N.; Magoulas, K. Recycling of Post-Consumer Multilayer Tetra Pak® Packaging with the Selective Dissolution-Precipitation Process. *Resour. Conserv. Recycl.* **2021**, *165*, 105268. [CrossRef]
9. Achilias, D.S.; Roupakias, C.; Megalokonomos, P.; Lappas, A.A.; Antonakou, E.V. Chemical Recycling of Plastic Wastes Made from Polyethylene (LDPE and HDPE) and Polypropylene (PP). *J. Hazard. Mater.* **2007**, *149*, 536–542. [CrossRef]
10. Achilias, D.S.; Giannoulis, A.; Papageorgiou, G.Z. Recycling of Polymers from Plastic Packaging Materials Using the Dissolution–Reprecipitation Technique. *Polym. Bull.* **2009**, *63*, 449–465. [CrossRef]
11. Cervantes-Reyes, A.; Núñez-Pineda, A.; Barrera-Díaz, C.; Varela-Guerrero, V.; Martínez-Barrera, G.; Cuevas-Yañez, E. Solvent Effect in the Polyethylene Recovery from Multilayer Postconsumer Aseptic Packaging. *Waste Manag.* **2015**, *38*, 61–64. [CrossRef]
12. Rodríguez-Gómez, J.E.; Silva-Reynoso, Y.Q.; Varela-Guerrero, V.; Núñez-Pineda, A.; Barrera-Díaz, C.E. Development of a Process Using Waste Vegetable Oil for Separation of Aluminum and Polyethylene from Tetra Pak. *Fuel* **2015**, *149*, 90–94. [CrossRef]
13. O’Rourke, G.; Houbrechts, M.; Nees, M.; Roosen, M.; Meester, S.D.; Vos, D.D. Delamination of Polyamide/Polyolefin Multilayer Films by Selective Glycolysis of Polyurethane Adhesive. *Green Chem.* **2022**, *24*, 6867–6878. [CrossRef]
14. Ügdüler, S.; De Somer, T.; Van Geem, K.M.; De Wilde, J.; Roosen, M.; Deprez, B.; De Meester, S. Analysis of the Kinetics, Energy Balance and Carbon Footprint of the Delamination of Multilayer Flexible Packaging Films via Carboxylic Acids. *Resour. Conserv. Recycl.* **2022**, *181*, 106256. [CrossRef]

15. Nieminen, J.; Anugwom, I.; Kallioinen, M.; Mänttari, M. Green Solvents in Recovery of Aluminium and Plastic from Waste Pharmaceutical Blister Packaging. *Waste Manag.* **2020**, *107*, 20–27. [[CrossRef](#)] [[PubMed](#)]
16. Samorì, C.; Pitacco, W.; Vagnoni, M.; Catelli, E.; Colloricchio, T.; Gualandi, C.; Mantovani, L.; Mezzi, A.; Sciotto, G.; Galletti, P. Recycling of Multilayer Packaging Waste with Sustainable Solvents. *Resour. Conserv. Recycl.* **2023**, *190*, 106832. [[CrossRef](#)]
17. Soudham, V.P.; Raut, D.G.; Anugwom, I.; Brandberg, T.; Larsson, C.; Mikkola, J.-P. Coupled Enzymatic Hydrolysis and Ethanol Fermentation: Ionic Liquid Pretreatment for Enhanced Yields. *Biotechnol. Biofuels* **2015**, *8*, 135. [[CrossRef](#)]
18. Naemullah; Shah, F.; Kazi, T.G.; Afridi, H.I.; Khan, A.R.; Arain, S.S.; Arain, M.S.; Panhwar, A.H. Switchable Dispersive Liquid–Liquid Microextraction for Lead Enrichment: A Green Alternative to Classical Extraction Techniques. *Anal. Methods* **2016**, *8*, 904–911. [[CrossRef](#)]
19. Phan, L.; Brown, H.; White, J.; Hodgson, A.; Jessop, P.G. Soybean Oil Extraction and Separation Using Switchable or Expanded Solvents. *Green Chem.* **2009**, *11*, 53–59. [[CrossRef](#)]
20. Samorì, C.; López Barreiro, D.; Vet, R.; Pezzolesi, L.; Brilman, D.W.F.; Galletti, P.; Tagliavini, E. Effective Lipid Extraction from Algae Cultures Using Switchable Solvents. *Green Chem.* **2013**, *15*, 353. [[CrossRef](#)]
21. Anugwom, I.; Mäki-Arvela, P.; Virtanen, P.; Willför, S.; Sjöholm, R.; Mikkola, J.-P. Selective Extraction of Hemicelluloses from Spruce Using Switchable Ionic Liquids. *Carbohydr. Polym.* **2012**, *87*, 2005–2011. [[CrossRef](#)]
22. Jessop, P.G.; Kozycz, L.; Rahami, Z.G.; Schoenmakers, D.; Boyd, A.R.; Wechsler, D.; Holland, A.M. Tertiary Amine Solvents Having Switchable Hydrophilicity. *Green Chem.* **2011**, *13*, 619–623. [[CrossRef](#)]
23. Samorì, C.; Cespi, D.; Blair, P.; Galletti, P.; Malferrari, D.; Passarini, F.; Vassura, I.; Tagliavini, E. Application of Switchable Hydrophilicity Solvents for Recycling Multilayer Packaging Materials. *Green Chem.* **2017**, *19*, 1714–1720. [[CrossRef](#)]
24. Yousef, S.; Mumladze, T.; Tatariants, M.; Kriūkienė, R.; Makarevicius, V.; Bendikiene, R.; Denafas, G. Cleaner and Profitable Industrial Technology for Full Recovery of Metallic and Non-Metallic Fraction of Waste Pharmaceutical Blisters Using Switchable Hydrophilicity Solvents. *J. Clean. Prod.* **2018**, *197*, 379–392. [[CrossRef](#)]
25. Mumladze, T.; Yousef, S.; Tatariants, M.; Kriūkienė, R.; Makarevicius, V.; Lukošiuūtė, S.-I.; Bendikiene, R.; Denafas, G. Sustainable Approach to Recycling of Multilayer Flexible Packaging Using Switchable Hydrophilicity Solvents. *Green Chem.* **2018**, *20*, 3604–3618. [[CrossRef](#)]
26. Vagnoni, M.; Pitacco, W.; Arpaia, V.; Catelli, E.; Gualandi, C.; Mastroddi, R.; Mezzi, A.; Samorì, C.; Sciotto, G.; Tagliavini, E.; et al. Recycling of Multilayer Packaging Waste with Switchable Anionic Surfactants. *Resour. Conserv. Recycl.* **2023**, *198*, 107141. [[CrossRef](#)]
27. Phan, L.; Chiu, D.; Heldebrant, D.J.; Huttenhower, H.; John, E.; Li, X.; Pollet, P.; Wang, R.; Eckert, C.A.; Liotta, C.L.; et al. Switchable Solvents Consisting of Amidine/Alcohol or Guanidine/Alcohol Mixtures. *Ind. Eng. Chem. Res.* **2008**, *47*, 539–545. [[CrossRef](#)]
28. Berry, R.T.; Dach, E.; Melhorn, J.A.; Yip, N.Y.; Soh, L. Assessing the Temperature-Dependent Tunable Polarity of *N,N*-Dimethylcyclohexylamine (DMCHA) and Water Mixtures. *ACS Sustain. Chem. Eng.* **2022**, *10*, 3726–3734. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.