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Recycling of multilayer packaging waste with sustainable solvents

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Abstract

De-pulped multilayer packaging waste containing low-density polyethylene (LDPE) and aluminium was separated into its single components by using sustainable solvents capable of solubilizing LDPE under mild conditions. LDPE and aluminium of high purity and quality were recovered with biodiesel, 2-methyl tetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME). The recovered LDPE has been characterized by thermal and mechanical analysis, confirming its similarity to the polymer before the dissolution process, while the recovered aluminium was analysed by X-Ray Photoelectron Spectroscopy (XPS) depth profiling, confirming the non-oxidative behaviour of the tested solvents. The mass balance of the recovered materials and solvents at the end of the dissolution process was close to 100%.

Keywords: flexible metalized packaging; plastic recycling; low-density polyethylene; aluminium; bio-based solvents

1. Introduction

Plastic recycling is a pillar of the EU's plastic strategy adopted in 2018 and a key tool for achieving the transition toward a circular and carbon-neutral economy that protects the environment and reduces greenhouse gas emissions and dependence on non-renewable resources. In particular, EU rules on plastic packaging waste aim to face the increasing quantities of post-use plastic materials by promoting reuse, recycling and other forms of recovery, instead of the final disposal in landfills; according to the Directive 2005/20/EC of European Parliament and the Council, the target will be 55% of recycling within 2030. About 2 Mt/y of plastic packaging currently in use in the EU is composed of multilayer materials that combine functionalities of distinct materials, like barrier performance, thickness, mechanical strength, and heat tolerance (Kaiser et al., 2018). However, if such a combination of different materials offers advantages in the manufacturing of superior packaging, it also represents a challenge for existing recycling systems (Soares et al., 2022). Food and beverage cartons are composed of flexible packaging where a thin aluminium foil is laminated as a barrier material to plastics like linear low-density polyethylene, LLDPE and low-density polyethylene, LDPE, or polypropylene, PP, or cardboard, in a variable number of layers according to the type of food/beverage. The current recycling approach of these multilayer materials foresees a partial deconstruction through hydropulping that removes the paper layer, while plastic and aluminium are not furtherly separated and are typically sent to incineration exploiting the high heating value of plastics, or used as a blend in the cement industry (Georgiopoulou et al., 2021). The recycling of both the polymeric and metal layers as separated entities is virtually feasible by delamination, thus by breaking the adhesion bonds that keep the layers together, or dissolution of plastic through organic solvents and removal of the non-dissolved material through filtration (i.e. Selective Dissolution-Precipitation, SDP) (Soares et al., 2022). Both the delamination and the SDP approaches can play a role in the chemical recycling/upcycling technologies for multilayer packaging materials, crucial in moving toward a circular economy for plastics, but some requirements are needed to evaluate their real sustainability and feasibility. First of all, the quality of recycled polymers is mandatory for their application in the plastic market: the recycled polymeric chains should not be damaged/shorten thus keeping a quality that meets that of their virgin counterparts (avoiding down-cycling). The market for recycled plastics is continuously growing, although polymer quality and contamination remain major barriers, and the demand/supply can be affected by various independent factors such as legislation and technological availability (Gu et al., 2020). The prices of recycled and virgin PE in 2022 (for the quarters ending in June and September 2022) are currently similar (global average of 1.4-1.7 €/kg vs 1.5-2 €/kg, respectively) (www.chemanalyst.com), but even when the price spread between the two increases, downstream plants decide which feedstock to use according to the desired product performances, independently of cost savings. Secondly, recycled aluminium should maintain the same quality as primary aluminium, thus avoiding reducing its economic value. As for recycled plastics, the price of aluminium scraps depends on the quality, and mixed aluminium scrap contaminated with other materials like plastic residues constitutes poor scrap quality (Frees, 2008). While rigid/semi-rigid aluminium scraps (i.e. cans) have a high aluminium content and therefore a high market value, flexible packaging waste has a very low aluminium content, difficult to be recovered without changing its oxidation state: under high-temperature processes like pyrolysis, incineration and thermal plasma techniques, aluminium is completely oxidized. The market price of aluminium oxide is much lower than metallic aluminium i.e. 0.3 €/kg vs > 2.3 €/kg (October 2022, www.lme.com/en/Metals). Lastly, hazardous solvents and antisolvents used to precipitate the polymer should be avoided (Vollmer et al., 2020).

Recently, PE solubilization and aluminium separation from de-pulped food and beverage cartons have been demonstrated by using *N*,*N*-dimethylcyclohexylamine (Samorì et al., 2017), xylene (Georgiopoulou et al., 2021), or methylcyclohexane (Wohnig et al., 2016), without downgrading the properties of the recovered materials. Also, waste vegetable oil has been used for this purpose, and to the best of our knowledge, this is the only example in which non-hazardous bio-based solvents have been applied to the recycling of multilayer packaging materials (Rodríguez-Gómez et al., 2015). However, low PE and aluminium purities were observed (73 and 85%, respectively) due to the high viscosity and density of waste vegetable oil that remained on the recovered materials compromising their quality (Rodríguez-Gómez et al., 2015).

Herein we aimed at exploring the dissolution capacity of neoteric sustainable solvents towards LDPE for the recycling of de-pulped multilayer packaging waste from food and beverage cartons and recovering of high-quality aluminium and LDPE. Among the tested solvents we included well-established green candidates like bio-based esters (ethyl lactate, γ-valerolactone), bio-based alcohols (ethanol, butanol), and alkyl carbonates (dimethyl carbonate), but also more unconventional options like biodiesel, 2-methyl tetrahydrofuran (2-MeTHF) and cyclopentyl methyl ether (CPME). The results achieved with the tested solvents in terms of LDPE solubilization and aluminium separation from flexible metalized packaging waste have been compared with cyclohexane use, chosen as the benchmark of fossil-based volatile organic solvents capable of solubilizing LDPE. To the best of our knowledge, none of these solvents nor other sustainable solvents have been used before for any application related to plastic recycling. Moreover, since the maximization of both recovery ratios and quality of the recovered materials is scarcely investigated, the degree of oxidation of aluminium, the mechanical properties of the recovered LDPE, and the purity of both have been also evaluated.

2. Materials and methods

2.1 Chemicals and materials

2-Methyl tetrahydrofuran (Viridisol ® M) was kindly provided by Pennakem (FR), while biodiesel from rapeseed oil was kindly provided by a local supplier. All the other chemicals/solvents used in this study were obtained from Sigma-Aldrich (purities ≥ 98%) and used without purification. Flexible metalized packaging waste (i.e. de-pulped food and beverage packaging waste) was kindly provided by Lucart S.p.A. (IT).

2.2 Characterization of multilayer packaging waste

Samples of flexible metalized packaging waste were embedded in KBr and cross-sectioned by dry polishing according to the literature (Mazzeo et al., 2007).

Sample cross-sections were observed under optical microscopy to acquire visible and fluorescent images and study the stratigraphic morphology. Attenuated total reflection (ATR) analyses were performed using a Thermo Scientific Nicolet iN 10MX spectrometer and a germanium ATR crystal. Spectra were recorded in the range of 4000 to 675 cm^{-1} with an optical aperture of 150×150 μm, a spectral resolution of 4 cm^{-1} and 64 scans. Transmission spectra were recorded using a Thermo Nicolet Nicolet iS50 spectrometer. Spectra were collected by dispersing the sample in KBr medium (ratio 1:150) and preparing transparent pellets by applying a pressure of 5 tons for 1 min. The spectra were recorded in the range of 4000-400 cm^{-1} with a spectral resolution of 4 cm^{-1} and 64 accumulations per spectrum.

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was performed on the flexible metalized packaging material from which a layer of LDPE was mechanically removed. The analyses were performed with a Jeol 6400 Scanning Electron Microscope equipped with an Oxford EDS (Energy Dispersive System) microprobe. Microprobe analysis operating conditions were 20 kV and 1.2 mA current, ∼1 mm beam diameter and 60 s counting time; several analytical points and chemical maps per sample were done. SEM images were obtained using both back scattered and secondary electron detectors.

The degree of oxidation of the aluminium before the solubilization process was determined on the same samples prepared for SEM-EDS through X-ray Photoelectron Spectroscopy (XPS) depth profiling. The XPS experiments were carried out by using an ESCALAB 250 Xi spectrometer (Thermofisher Scientific, UK), equipped with a monochromatic Al X-ray source and a 6-channeltrons detection system. The spectra were collected in magnetic lens standard mode and constant pass energy of 50 eV. The base pressure in the analyser chamber was p = 1 x 10^{-10} mbar and it was increased to p = 1 x 10^{-8} mbar during the depth profile. The depth profile was performed alternating spectra acquisition and cycles of ion (Ar^+) sputtering by EX06 ion source. The binding energy scale was calibrated positioning the adventitious carbon contribution (before ion sputtering) at BE = 285.0 eV. The accuracy of the binding energy (BE) scale was ±0.1 eV. All samples were attached to the sample holder by a metallic clip. All data were acquired and processed by Avantage software v.5.979

2.3 LDPE and aluminium recovery from multilayer packaging waste

2.3.1. LDPE solubilization with biodiesel

The solubilization of LDPE was performed at a small and medium scale by using 6 mL and 80 mL of biodiesel, respectively. In both cases, pieces (1x1 cm) of flexible metalized packaging waste were charged in a round bottom flask with biodiesel and the system was stirred at 150°C for 10 min in the case of the small scale, or 1.5 h in the case of the medium scale. Different sample loadings were tested: 1, 2, 4 and 6 wt%. Aluminium pieces were filtered through a metallic grid (mesh size of 0.1 cm) while the system was still at high temperature, and then it was left to cool down. The LDPE-biodiesel solution was filtered overnight at rt over a Gooch filter under vacuum, and a gel containing 20% of LDPE was obtained. The process was repeated a second time on the aluminium fraction to ensure the complete removal of the polymer. Ethanol was added as an antisolvent to wash LDPE gel from the residual biodiesel; 6 mL and 80 mL of ethanol were used for the small and medium scale, respectively (LDPE gel/ethanol weight ratio of 9%), and the mixture was stirred at rt overnight. The recovered aluminium was also washed at rt with ethanol and both washing phases were distilled under vacuum to separate and recover ethanol and biodiesel. The amount of the recovered LDPE and aluminium at the end of the dissolution process was expressed based on the amount of the multilayer waste in input to the process itself (w/w, %).

2.3.2. LDPE solubilization with sustainable organic solvents

2-Methyl tetrahydrofuran (2-MeTHF), cyclopentyl methyl ether (CPME), cyclohexane, butanol (BuOH), ethanol (EtOH), ethyl acetate (EtOAc), ethyl lactate, γ-valerolactone (GVL), and dimethyl carbonate (DMC) were tested as solvents for solubilizing LDPE in a preliminary screening test. The solubilization of LDPE was performed at a small scale by using 6 mL of all the solvents, and at a medium scale by using 80 mL of 2-MeTHF, CPME and cyclohexane. In all cases, pieces (1x1 cm) of flexible metalized packaging material were charged in a round bottom flask with the solvent and the system was stirred at various temperatures according to the solvent (see Table 1). The sample load was 1.5 wt%, thus about 0.09 g of multilayer waste in 6 mL of solvent, or 1.2 g of multilayer waste in 80 mL of solvent. Aluminium pieces were then filtered through a metallic grid (mesh size of 0.1 cm) while the system was still at high temperature, while LDPE was recovered by distilling under vacuum the solvent at the solvent boiling point. The process was repeated a second time on the recovered aluminium to ensure the complete removal of the polymer. The amount of the recovered LDPE and aluminium at the end of the dissolution process was expressed based on the amount of the multilayer waste in input to the process itself (w/w, %).

2.4 Characterization of the recovered materials

2.4.1. Purity and degree of oxidation of the recovered aluminium

The quantification of LDPE residues on the recovered aluminium was performed through calcination at 550°C for 5 h, attributing the weight loss to traces of polymer. Only in the case of biodiesel, a further GC-MS analysis was done to quantify solvent residues: the recovered aluminium (2 mg) was placed in dichloromethane (0.5 mL), adding methyl nonadecanoate as the internal standard (50 µL of a 1000 ppm solution); the solution was then analysed by GC-MS using an Agilent HP 6850 gas chromatograph connected to an Agilent HP 5975 quadrupole mass spectrometer. Analytes were separated on an HP-5MS fused-silica capillary column (stationary phase poly[5% diphenyl/95% dimethyl]siloxane, 30 m, 0.25 mm i.d., 0.25 µm film thickness), with helium as the carrier gas (at constant pressure, 36 cm s^{-1} linear velocity at 200 °C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s^{-1} within the 12-600 m/z range. The injection port temperature was 250°C. The temperature of the column was increased from 50 to 220°C at 50°C min^{-1}, then from 220 to 265°C at 5°C min^{-1} and finally from 265 to 325 °C at 50°C min^{-1}.

XPS depth profiling analyses were performed as described in Section 2.2 to confirm the presence of C and the degree of oxidation of the recovered aluminium.

2.4.2. Thermal and mechanical analysis of the recovered LDPE

Thermogravimetric analyses (TGA) were carried out using a TGA Q500 thermogravimetric analyzer (TA Instruments). Analyses of the multilayer waste were performed from room temperature to 600°C, at a heating rate of 10°C min^{-1}, under air-flow. Hi-ResTM Thermogravimetric analyses were performed on recovered LDPE from room temperature to 600°C, at a heating rate of 50°C min^{-1} and a resolution index of 4, under airflow. The onset decomposition temperature was defined as the temperature at 5% weight loss (T_d, 5%), while the % residue at 600°C was used to determine the inorganic impurities present on the recovered LDPE. 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^{-1}, from -90 to 155°C, to erase the polymer thermal history. The samples were then cooled at 10°C min^{-1} and a second heating scan was applied. The melting temperature (T_m) was taken at the peak maximum of the melting endotherm from the second heating curve. The crystallinity degree (X_c, %) was calculated as follows:

$$X_C = 100 \times \frac{\Delta\mathrm{H}_m}{\Delta\mathrm{H}^0}$$

where ΔH_m is the melting enthalpy of the sample (J g^{-1}) and ΔH^0 is the melting enthalpy of 100% crystalline polymer (J g^{-1}). For LDPE, ΔH^0 was considered equal to 294 J g^{-1} (Fischer and Hinrichsen, 1966).

Tensile stress-strain measurements were carried out on LDPE films produced by compression moulding starting from the recovered LDPE. The polymer was placed between two polytetrafluoroethylene plates, with an appropriate spacer, at 150°C for 1 min under a pressure of 2 ton m^{-2} (Carver C12, laboratory press). An Instron Tensile Testing Machine 4465 was used at an extension rate of 5 mm min^{-1} for the mechanical testing of dog-bone specimens (width 5 mm, gauge length 20 mm) die-cut from hot-pressed samples (180°C, film thickness 0.2 mm). The average specimen thickness, measured by using a digital micrometer, was used to construct the stress-strain curves from the raw load-displacement data. The stress was measured with a standard 100N cell while the deformation was precisely monitored. The elastic modulus was calculated from the initial slope of the stress-strain curve. The statistical significance of the differences among the tensile stress-strain values was tested by one-way analysis of variance (ANOVA). Once ANOVA resulted significantly, Dunn’s post-hoc test was carried out to identify which LDPE samples were significantly different from each other.

2.5. Hansen solubility parameters and Relative Energy Distance (RED) calculation

The Hansen solubility parameters (dispersion δD, polar δP and hydrogen-bonding δH) for the tested solvents and LDPE were found in the literature and reported in Table 1S in ESI (Rasool and Vankelecom, 2019; Yara-Varón et al., 2016).

The Relative Energy Distance (RED) number, has been calculated as follows:

$$RED = \frac{Ra}{Ro}$$

where R_o is the radius of a Hansen solubility sphere of LDPE (7.35), and R_a is the distance of a solvent from the centre of the Hansen solubility sphere that measures polymer-solvent affinity (i.e. small values of R_a indicate good compatibility), given by:

$$Ra = \sqrt{4(\delta D\_A - \delta D\_B)^2 + (\delta P\_A - \delta P\_B)^2 + (\delta H\_A - \delta H\_B)^2)}$$

Where A is LDPE and B the solvent (see Figure 1S in ESI).

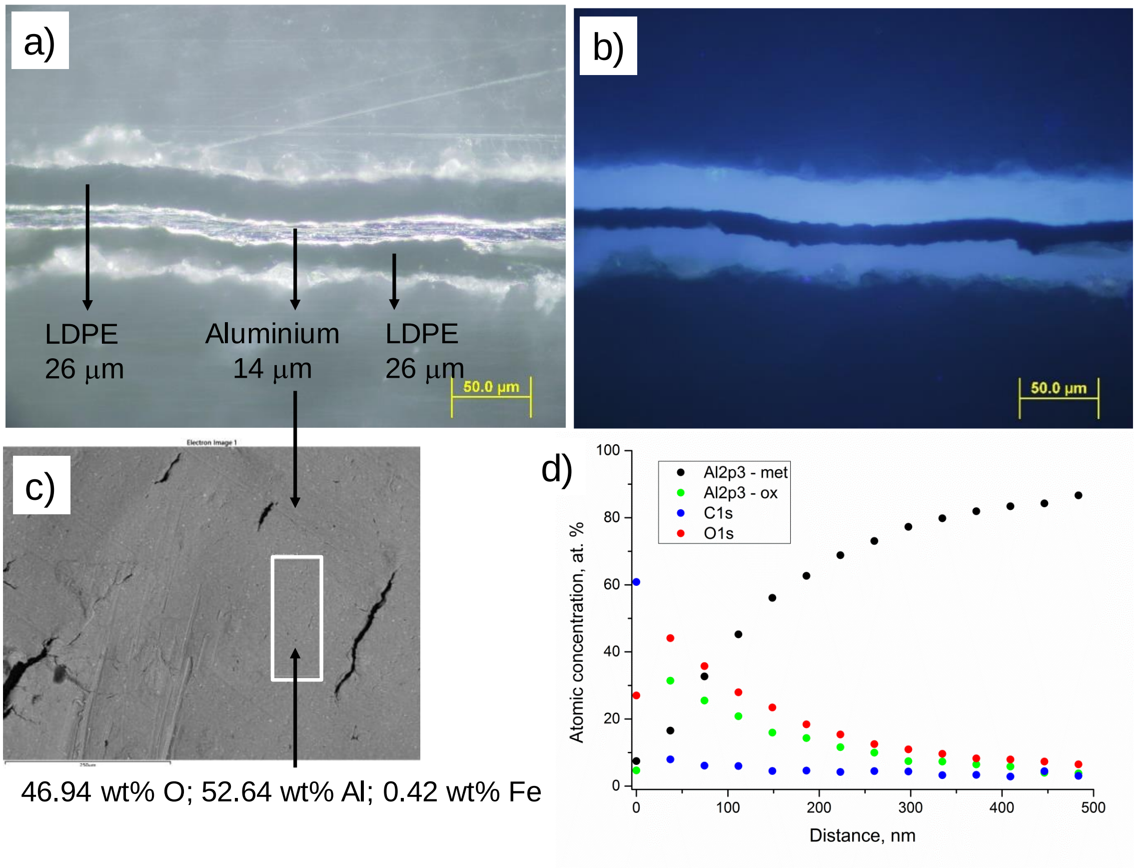
3. Results and discussion

3.1 Characterization of multilayer packaging waste

The flexible metalized packaging waste here used was previously de-pulped through hydropulping, thus it contained LDPE, a minor amount of LLDPE, and aluminium. The material was highly heterogeneous and composed on average of two layers of LDPE of 26 μm each, and a layer of aluminium with a thickness of 14 μm, partially oxidized on the surface. XPS depth profiling and SEM-EDS analysis testified the presence of 15% aluminium oxide within the first 100 nm of aluminium samples (Figure 1; ATR and TGA of the polymeric layers have been reported in Figures 2S and 3S in ESI). The total amount of aluminium and LDPE was 26.9±4.1% and 70.8±7.2%, respectively.

Figure 1. Microscope images of flexible metalized packaging waste sample before the solvent treatment under visible (a) and UV light (b), composition of

the surface (100 nm) of the metallic layer using SEM-EDS analysis (c) and XPS depth profiling (d). For SEM-EDS and XPS depth profiling analysis, one layer of LDPE was mechanically removed from the sample.



3.2 LDPE and aluminium recovery from multilayer packaging waste

3.2.1 Screening of LDPE solubilization with sustainable solvents

Some of the most promising sustainable/bio-based solvent groups currently available on the market were initially screened in terms of LDPE solubilization at a small scale (6 mL of solvent). To this purpose ethers (2-MeTHF and CPME), alcohols (BuOH and EtOH), esters (EtOAc, ethyl lactate, GVL, and biodiesel), and carbonates (DMC) were tested at the 1.5 wt% multilayer waste/solvent weight ratio (Table 1). The results were compared with the solubilization process performed with cyclohexane chosen as a model of traditional volatile organic solvents capable of solubilizing polyethylene

Alcohols and carbonates did not delaminate nor solubilize LDPE, even after a prolonged time; just partial delamination was observed with butanol.

Among the bio-based esters, GVL and ethyl lactate did not work, EtOAc gave the delamination of one LDPE layer, while biodiesel solubilized LDPE at the tested conditions (150°C). Vegetable oils have already been explored for solubilizing PE from multilayer packaging waste but the high viscosity of these unusual solvents makes the recovery of low-contaminated materials challenging (Anand et al., 2010; (Rodríguez-Gómez et al., 2015). At the same market price (1.8 €/kg for biodiesel *vs* 1.0-1.4 €/kg for palm and rapeseed oil, October 2022, www.neste.com), biodiesel is 10-time less viscous than vegetable oils. For this reason, deepening on the behaviour of biodiesel was performed: at 100°C, the polymeric layers were not completely solubilized, and the presence of LDPE "flakes" hampered an efficient filtration of the aluminium in the work-up. When the multilayer waste/solvent weight ratio was increased (2, 4 and 6 wt%), LDPE solubilization occurred as well and aluminium was filtered from the solution; however, the solution was very viscous at 4 and 6 wt%, and this was reflected in the higher amount of biodiesel impurities on the recovered aluminium (13-14 wt%). The best parameter combination was obtained by treating a solution of biodiesel with 2 wt% loading of multilayer waste (0.12 g of multilayer waste on 6 mL of biodiesel) at 150°C, for two cycles of 10 min each: on the input material weight basis, the amount of the recovered LDPE achieved after polymer precipitation with ethanol was 71% (0.09 g of LDPE on 0.12 g of material in input), while the amount of the recovered aluminium was 27% (0.03 g of aluminium on 0.12 g of material in input). The amount of residual biodiesel on the recovered LDPE and aluminium was 0.1 and 0.5 wt%, respectively. The recovery of biodiesel and ethanol was 82 and 89%, respectively, presumably because of the small scale on which the dissolution process was performed.

Both the tested ethers behaved similarly: 2-MeTHF showed a clear temperature-dependent behaviour since it did not work at rt, it delaminated one layer of LDPE at 50-65°C, while it gave complete polymer solubilization at 75°C in 15 min. On the input material weight basis, the amount of the recovered LDPE with 2-MeTHF was 70% (0.08 g of LDPE on 0.12 g of material in input), while the amount of the recovered aluminium was 27% (0.03 g of aluminium on 0.12 g of material in input). Analogously, CPME gave complete polymer solubilization at 70°C in 15 min, with a mass balance of the recovered materials close to 100%. Cyclohexane behaved like both 2-MeTHF and CPME.

Biodiesel, 2-MeTHF, CPME and cyclohexane are all characterized by low polarity (logP > 1) and Relative Energy Distance (RED) values, calculated from the Hansen solubility parameters, largely lower than 1 (Table 1) (Amadi-Kamalu et al., 2020; Gårdebjer et al., 2016; Gonzalez et al., 2007; Rasool and Vankelecom, 2019; Yara-Varón et al., 2016; Zuorro, 2020). It is known that Hansen solubility parameters are a numerical estimation of the interactions between materials, and similar values of (δ) for polymer and solvents are an indication that polymer is likely to be soluble in these solvents. The closer LDPE and solvents in the Hansen space, the greater the possibility of dissolving into each other, as testified by the values of the solvents here used (see Table 1S and Figure 1S).

Table 1. LDPE solubilization at a multilayer waste/solvent weight ratio of 1.5 wt%, and RED values for the tested solvents (+: solubilization of LDPE; +/-: delamination of one of the two LDPE layers; -: no solubilization of LDPE).

Solvent	**Waste loading (wt%)**	**Time (min)**	**T (°C)**	**LDPE solubilization**	**Solvent residues on LDPE/Al (wt%)**	**RED value**
Biodiesel	1.5	10 (×2)	150	+	0.6/0.5	0.60
Biodiesel	2	10 (×2)	150	+	0.1/0.5	
Biodiesel	2	10 (×2)	100	+/-		
Biodiesel	4	10 (×2)	150	+	0.2/12.7	
Biodiesel	6	10 (×2)	150	+	0.3/14.0	
BuOH	1.5	180	100	+/-		1.95
Cyclohexane	1.5	15	80	+	- [a]	0.37
CPME	1.5	15	70	+	- [a]	0.52
DMC	1.5	>300	110	-		1.33
EtOH	1.5	120	80	-		2.58
EtOAc	1.5	>300	90	+/-		1.04
Ethyl lactate	1.5	>300	70	-		
2-MeTHF	1.5	>300	rt	-		0.61
2-MeTHF	1.5	120	50-65	+/- [a]		
2-MeTHF	1.5	15	75	+	- [a]	

GVL	1.5	>300	75	-	1.06

[a] No traces of solvent on LDPE and aluminium.

3.2.2 Scale-up of the selective dissolution precipitation process and characterization of the recovered materials

Given the promising results obtained with biodiesel, 2-MeTHF and CPME, the scale of the process was increased by about 10-times (80 mL of solvent) and compared with the performances of cyclohexane. The multilayer waste/solvent weight ratio was kept constant at 1.5 wt%, and just biodiesel was tested also at 2 wt%. A temperature of 150°C for biodiesel and 100°C for the other three solvents were set based on the results obtained on a small scale; the time was kept constant for 2-MeTHF and CPME, while increased to 1 h for biodiesel since two cycles of extraction of 10 min each were not enough to solubilize all LDPE probably because of a less efficient stirring (data not shown).

LDPE was recovered as described for the small scale: the separation of biodiesel from the extracted LDPE was accomplished by using ethanol that worked as an antisolvent for LDPE, while in the case of 2-MeTHF, CPME and cyclohexane the separation occurred through solvent distillation. The recovery of biodiesel from ethanol was performed by distillation, giving 95% of biodiesel and 92% of ethanol used in the dissolution process, while the recovery of 2-MeTHF, CPME and cyclohexane was more than 97%.

A complete mass balance of the recovered LDPE and aluminium was obtained with each solvent, while their “purity”, intended as solvent residues on LDPE or solvent/LDPE residues on aluminium, varied with the solvent used (Table 2).

Table 2. Organic residues on the recovered LDPE and aluminium after the treatment with the selected solvents under optimized conditions.

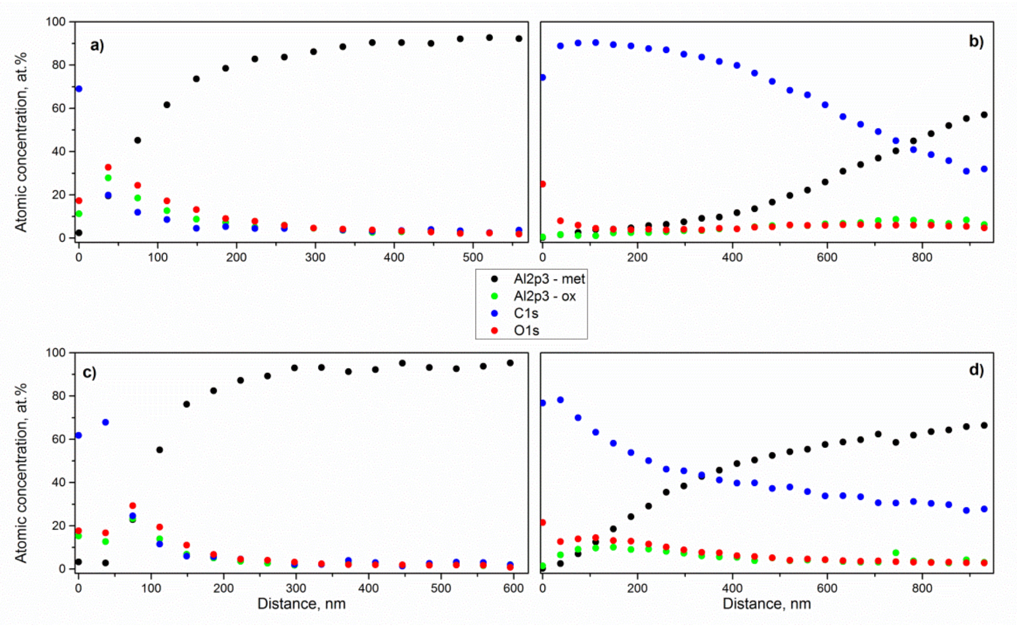
Entry	**Solvent**	**Time (min)**	**Solvent residues on LDPE (wt%)**[a]	**LDPE residues on Al (wt%)**[b]
1	Biodiesel[c]	60(×2)	1.0	2.4[d]
2	Biodiesel	60(×2)	0.4	0.8
3	2-MeTHF[e]	15(×2)	-	3.7
4	2-MeTHF[e]	60(×2)	-	2.4
5	CPME	15(×2)	-	1.2
6	Cyclohexane	15(×2)	-	8.1
7	Cyclohexane	60(×2)	-	8.8

[a] Determined by GC-MS; [b] determined by calcination for 5 h at 550°C; [c] 2 wt% multilayer waste/solvent weight ratio; [d] 0.5 wt% of biodiesel quantified by GC-MS and 1.9 wt% of LDPE; [e] 8-9% of LDPE was delaminated but not solubilized, independently of the tested conditions.

Biodiesel residues on LDPE and LDPE and/or biodiesel residues on aluminium were lower by operating under a multilayer waste/solvent weight ratio of 1.5 wt% than 2 wt% (entries 2 and 1, respectively); similar aluminium contamination by residues of LDPE (about 1 wt%) was achieved by using CPME (entry 5). On the other hand, 3-8 wt% of LDPE residues were found on the recovered aluminium with both 2-MeTHF (entries 3 and 4) and cyclohexane (entries 6 and 7), even after two cycles of extraction of 1 h each. Since 2-MeTHF and cyclohexane are highly volatile, we excluded the presence of a solvent on the recovered aluminium and we identify LDPE as the major organic contaminant. These results were confirmed by XPS analysis (Figure 2) that clearly showed a large presence of C after the depth profile (1000 nm) on the aluminium recovered with 2-MeTHF (Figure 2b, 30 atomic %) and cyclohexane (Figure 2d, 25 atomic %) with a cross between the Al and C profiles at 770 and 335 nm, respectively. The thinnest overlayer between the Al and C profiles (~ 40 nm) was obtained with biodiesel (Figure 2a), suggesting a lower presence of organic contamination on the surface of aluminium, easily removed by ion sputtering; the cross between the Al and C profiles in the sample obtained with CPME felt at ~100 nm and after that Al metallic became predominant.

The amount of metallic aluminium in the recovered material is a crucial parameter for determining its commercial value after an industrial re-melting process, and all of these values testified that the chemical recycling of multilayer materials containing aluminium through the tested solvents is a “friendly” approach in terms of aluminium quality. The recovered aluminium samples were analysed by XPS (see Table 2S in ESI): they were characterized on the surface by the presence of C, O and Al in metallic and oxide states. During the depth profile (Figure 2), the atomic concentration of all species decreased except for metallic Al, which became predominant. It is worth noting that the concentration of aluminium oxide found in all the samples after the ion sputtering process was below 10 atomic % (Figure 2), suggesting a non-oxidative behaviour of the tested solvents.

Figure 2. XPS depth-profiling analysis of aluminium recovered with a) biodiesel, b) 2-MeTHF, c) CPME, d) cyclohexane.



The recovered LDPE, after compression moulding, were tested under stretching (Table 3, and Figure 4S in ESI). The first significant result was that the LDPE mechanically removed from the multilayer waste showed far less homogeneous mechanical properties than those of LDPE recovered by dissolution (strain at break in the range 22-175%, stress at break in the range 5.3-8.6 MPa, Young's module in the range 99-138 MPa). This finding suggested that the solvents here used contributed to improving the purity of the polymeric matrix, conferring mechanical characteristics that cannot be achieved through a manual recovery of LDPE. Within the LDPE samples recovered with different solvents, the polymers recovered with biodiesel and 2-MeTHF displayed lower Young's moduli and higher strain at break than those recovered with CMPE and cyclohexane. This difference may be related to the presence of traces of biodiesel (0.4 wt%, see

Table 2, entry 2) and 2-MeTHF in the recovered LDPE that could work as a plasticizer (Saad et al., 2019), thus reducing Young's modulus and increasing the strain at break.

Table 3. Thermal and mechanical properties of recovered LDPE determined by TGA and DSC analysis, and tensile stress-strain measurements. The results of the Dunn post-hoc statistical test for pairwise comparison of strain at break, Young's module and the stress at break are reported between brackets: values sharing the same letter were not significantly different.

Recovered LDPE	**T_d 5% (°C)**	**Residue @600°C (%)**	**T_m (°C)**	**T_c (°C)**	**ΔH_m (J/g)**	**X_c (%)**	**Strain at break (%)**	**Stress at break (MPa)**	**Young's Module (MPa)**
Biodiesel	343.9	1.6	106.3	97.3	109	37	283±35 (a)	8.4±0.5 (a)	109±7 (ab)
2-MeTHF	340.9	1.5	105.8	96.6	106	36	247±34 (ab)	7.4±0.3 (b)	100±7 (b)
CPME	342.1	1.7	105.3	96.1	105	36	147±42 (bc)	7.9±0.1 (ab)	136±21 (a)
Cyclohexane	338.2	1.7	105.3	96.1	103	35	115±23 (c)	7.5±0.2 (b)	124±6 (a)

Thermal analysis of the LDPE recovered through the different solvents (Table 3) indicated that the onset of the degradation temperature (Td, 5%) ranged between 338 and 344°C, in line with the value reported for virgin LDPE (399±10°C, Mark, 2009) and the residue at 600°C of such samples, useful for quantifying the presence of inorganic additives/impurities, was below 2 wt%, as already reported in the literature (Georgiopoulou et al., 2021). This was an indication that the dissolution process had a positive effect in removing additives like $CaCO_3$, used as filler, and silicones, used during the preparation of the multilayer packaging, whose presence was detected in the samples before the dissolution process by SEM-EDS (see Figure 5S in ESI). No printed ink was present on the original samples (see Figure 2S in ESI).

The melting peak for all the recovered LDPE was found from the DSC analysis at 105-106°C, and it fell within the range reported for virgin LDPE and LDPE recovered by the solvent dissolution processes (Georgiopoulou et al., 2021). Similar crystallinity fraction values found for the recovered LDPE (35-37%, slow cooling; Mark, 2009) confirmed that all the tested solvents did not alter the polymeric fraction nor the aluminium initially present in the multilayer packaging waste.

3.3 Comparison between biodiesel, CPME and 2-MeTHF

The use of biodiesel, 2-MeTHF, and CPME for PE solubilization has never been reported before, even if their potential for extracting lipophilic matrices has been widely documented (de Gonzalo et al., 2019; de Jesus et al., 2019; Samorì et al., 2019; Wan Mahmood et al., 2017). In particular, the use of biodiesel as an industrial solvent is a recent application, explored in parallel to its more consolidated use as a fuel for cleaning and degreasing, resin cleaning and removal, and cleaning up of oil spills. For comparing the three solvents in terms of process performance and sustainability, we considered two groups of parameters: (eco)-toxicological and process parameters (Table 4). Three (eco)toxicological criteria were selected according to the CHEM21 solvent selection guideline (Prat et al., 2015), proposed in the last years to compare the “greenness” of solvent-based processes or syntheses: Safety, Health and Environment, each one scored from 1 to 10 (10 is the highest hazard in each category) and with a colour code associated (green for 1-3, yellow for 4-6, and red for 7-10).

Table 4. Comparison between the tested solvents in terms of (eco)-toxicological and process parameters.

	Safety	**Health**	**Environment**	**Aluminium quality**	**Viscosity/ affinity**	**Energy consumption**
Biodiesel	1	1	7	1	6	7
2-MeTHF	6	5	3	4	4	4
CPME	7	2	5	1	1	2

The CHEM21 guideline already includes neoteric solvents like 2-MeTHF and CPME: 2-MeTHF has been evaluated as “yellow” for the Safety and Health criteria, while “green” for the Environment since it is synthesised from renewable resources, it is easy degradable in the environment and it has no H4xx phrases after full REACh registration; these features make the environmental footprint of 2-MeTHF better than the traditional fossil-based ethers.

CPME has been evaluated as “red” for Safety-because of its resistivity associated with the low auto-ignition point < 200°C, “green” for Health given the lower formation of peroxides than traditional ethers, and “yellow” for Environment given its petrochemical origin and because it is harmful to aquatic life with long-lasting effects.

According to the CHEM21 approach, biodiesel has been evaluated as “green” for the Safety and Health criteria since it has no H2xx, H3xx and H4xx statements after full REACh registration; in fact, it is not classified as dangerous according to the criteria of the Dangerous Substances Directive, 67/548/EEC, and CLP, Regulation CE 1272/2007. However, even if it is fully bio-based, faster biodegradable and safer for aquatic and terrestrial organisms than most of the common organic solvents (Hu et al., 2004), its boiling point above 200°C makes the recycling not easy and complicates the work-up and downstream; therefore, as glycerol in the CHEM21 guideline, it has been evaluated “red” for the Environment.

By using the same color-coded classification, the solvents were also evaluated in terms of three process parameters; the mass balance of the recovered materials, the multilayer waste/solvent weight ratio, the recovery of the solvents or antisolvent, and the thermal and mechanical properties of the recovered LDPE were not included since all the solvent performed similarly:

- aluminium quality in terms of organic residues measured by calcination at 550°C: biodiesel and CPME ranked better (“green”) than 2-MeTHF (“yellow”) since they both gave a higher aluminium purity (see Table 2);
- solvent viscosity as a rough indication of the possibility to treat higher multilayer waste/solvent weight ratios, coupled with the RED value (Table 1): 2-MeTHF and CPME have a lower viscosity than biodiesel (about 0.5 *vs* 8.5 cp at 20°C), and the RED values suggest CPME as the solvent more compatible with LDPE among the three (it has the smallest value of Ra that indicates better compatibility), followed by biodiesel; moreover, preliminary

solubility data highlighted that there is the possibility to use more concentrated LDPE solutions, thus lowering the consumption of solvent and antisolvent: the maximum LDPE concentrations processable at the lab-scale were 20 wt% with biodiesel and CPME, and 10 wt% with 2-MeTHF, in line with the concentrations reported for xylene. According to all these considerations, CPME was evaluated as “green”, while biodiesel and 2-MeTHF as “yellow”;

- energy consumption for heating the solvent from room temperature to the process temperature, and for recovering the solvent (or the antisolvent) by evaporation: 2-MeTHF and CPME have a lower heat capacity than biodiesel and they solubilized LDPE at a lower temperature; moreover, the latent heat of vaporization of ethanol (the antisolvent for biodiesel process) is higher than that of 2-MeTHF and CPME. In particular, the chemo-physical characteristics of CPME facilitate its recovery through distillation (Watanabe et al., 2007). The energy consumption for heating CPME at 100°C and recovering the solvent by evaporation is 2- and 3-times lower than that of 2-MeTHF and biodiesel, respectively (see Table 3S in ESI). Therefore, CPME was evaluated as “green”, followed by 2-MeTHF (“yellow”) and biodiesel (“red”).

According to the colour code and the score given to each parameter (Table 4), CPME was the best solvent among the tested ones for performing LDPE solubilization and recycling both aluminium and LDPE from metalized packaging waste, followed by biodiesel and then 2-MeTHF. Biodiesel got the lowest score in the (eco)-toxicological criteria, meaning a higher sustainability profile, but the use of an antisolvent for recovering LDPE worsened its overall performance. Despite some parameters like LCA, economic considerations and scaling up should still be analysed and considered for proposing these neoteric solvents as feasible industrial tools for processing metalized multilayer materials, the results here presented contribute to widen the number of solvents potentially usable for chemically recycling plastic waste, and at the same time, widen the applicability of biodiesel, CPME and 2-MeTHF in the field of plastic recycling.

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Author Contributions

C.S.: conceptualization, writing- original draft preparation, writing- reviewing and editing, supervision. W.P., M.V. and T.C.: methodology, data curation, investigation. E.C. and L.M.: data curation. C.G. and A.M.: writing- reviewing and editing. P.G.: supervision, funding acquisition, writing- reviewing and editing.

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