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Application of switchable hydrophilicity solvents for recycling multilayer packaging materials†

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A new procedure based on switchable hydrophilicity solvents (SHS) was proposed for polyethylene and aluminium recovery from food aseptic packaging. Treatment with *N,N*-dimethylcyclohexylamine (DMCHA) allowed very high material recovery (>99% for aluminium and >80% for polyethylene), without compromising the quality in terms of oxidation or polymer degradation. Moreover, the results from a simplified and preliminary life cycle analysis confirm the potential environmental benefits of a SHS approach compared with other treatment and disposal scenarios.

1. Introduction

Switchable hydrophilicity solvents (SHS) can provide significant improvements related to energy saving and sustainability in the field of extraction processes where high volumes of volatile, flammable, and toxic solvents are usually employed.¹ SHS, in fact, are peculiar solvents that can reversibly turn their polarity through the addition and removal of CO₂, switching from a neutral form (secondary or tertiary amines) into an ionic liquid (ammonium hydrogen carbonate or carbamate). This CO₂-promoted switching allows the separation of SHS from the extracted products at the end of the extraction process without consuming energy for evaporation. The application of SHS-based systems has been demonstrated for various separation processes, among which the extraction of lipids or other valuable compounds from vegetable and algal biomasses is very promising.^{2–5} In the field of polymer recovery, Jessop *et al.* have proposed the use of one of the best performing SHS, *N,N*-dimethylcyclohexylamine (DMCHA), for the recovery of polystyrene foam as a high-density material.⁶

In this paper the application of DMCHA is proposed for the separation and recovery of low density polyethylene (LDPE) and aluminium from multilayer packaging materials.⁷

Multilayer packaging systems are highly versatile materials largely exploited in the food industry as aseptic packaging for various goods. With the increase of the number of their everyday-life applications, the volume of these laminated products in municipal solid waste has continuously increased and their recyclability has become an environmental and socio-economic issue. These composite materials are made of several laminated layers, including paper (75% by weight, composed of long fibres that provide stiffness), aluminium (5%, which prevents the penetration of air and light, thus assuring the preservation of food contents) and LDPE (20%, for making the packaging impermeable and for preventing the contact of food with the aluminium layer). The recycling is industrially accomplished by recovering paper fibres by means of a hydra pulping process, whereas the remaining 25% fraction (LDPE and aluminium) can be treated by agglutination and extrusion to obtain a composite usable in the fabrication of injection-moulded pellets (polyAl). Recently, several pilot plants or lab techniques have been developed for the separation of LDPE and aluminium; they can be grouped into thermal, mechanical, and chemical processes. The thermal approach (*e.g.* incineration, plasma⁸ or pyrolysis^{9,10}) aims at generating energy and at recovering only aluminium, whose quality, however, can be hampered by a high level of oxidation and/or char residue. The mechanical technology is mainly based on exfoliation of the multilayer material with the aid of separating fluids/chemicals such as mixtures of water, surfactants and hydrotropes,^{11,12} organic solvents¹³ or acid solutions.^{14,15} Finally, the chemical strategy foresees the solubilisation of LDPE and the precipitation of aluminium, followed by LDPE recovery by evaporation of the solvent or after the addition of an anti-solvent. The solvents able to effectively dissolve LDPE, however, are few and usually “problematic” (*e.g.* toluene, xylenes); among them, vegetable oil¹⁶ represents one of the most environmentally

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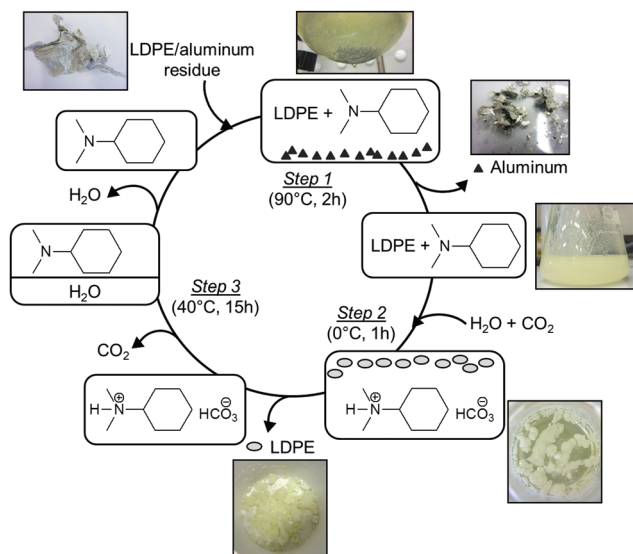


Fig. 1 Process steps and rationale.

friendly options, but chloroform or alcohols are necessary for removing oily contaminations from both LDPE and aluminium. The quality and purity of the outcomes (Al and LDPE), in fact, strongly affect their commercial value, and this holds true especially for the chemical processes for which too harsh conditions can hamper the extrudability of the recovered LDPE or the melting of aluminium flakes.

The protocol presented here (Fig. 1) belongs to the chemical approaches; it aims at treating multilayer packaging waste after the removal of a paper layer (de-papered residues) to separate LDPE and aluminium. Specifically, it exploits DMCHA's peculiarity of tuning its polarity through CO₂ addition and removal, switching from a neutral solvent (suitable for LDPE solubilization) to an ionic liquid (in which LDPE is no more soluble and thus can be recovered).

2. Experimental

2.1 Chemicals and materials

All solvents and chemicals used were obtained from Sigma-Aldrich (purities $\geq 98\%$) and were used without purification.

2.2 SHS-process

Multilayer “de-papered” residue (1 g) was cut into small pieces (squares of 1 cm side length) and charged in a round-bottom flask. DMCHA (80, 40, 20, 10 or 5 mL, corresponding to a residue/DMCHA ratio of 1.25, 2.5, 5, 10 and 20 wt%) was added and the mixture was heated at 90 °C (or rt and 50 °C in the case of 2.5 wt%) for 2 h. After that, the “milky” solution of LDPE and DMCHA was separated and residual aluminium was washed with acidic H₂O (5 mL, achieved by bubbling CO₂ in H₂O until pH 5) to remove DMCHA traces. The mixture of LDPE and DMCHA was added to a double volume of H₂O and cooled in an ice bath; then CO₂ was bubbled into the mixture

for 1 h while the flask was vigorously shaken. The floating LDPE was filtered and washed with the same acidic H₂O used for washing aluminium. Finally, removal of CO₂ from the residual water solution was achieved by stirring and heating at 40 °C overnight. In this way, a complete phase separation was achieved and the organic DMCHA layer was recovered on the top. Each extraction condition was repeated in duplicate.

2.3 Analysis

Calcination at 550 °C for 5 h was used to determine the amount of aluminium in the de-papered residues; LDPE content was calculated by difference. The residual amount of DMCHA in the recovered aluminium flakes and the elemental composition of recovered LDPE were determined using an elemental analyzer (Thermo Scientific, Flash2000, Organic Elemental Analyzer) by means of the flash combustion technique. FTIR/ATR spectra were recorded on a Nicolet iN10.Mx infrared spectrometer with a germanium crystal. The purity of DMCHA after a switching cycle was detected by ¹H NMR spectroscopy by using a 5 mm probe on a VARIAN Mercury 400 spectrometer in CDCl₃. The amount of metal oxides in the recovered aluminium was determined through microwave-assisted acid digestion with hydrochloridric acid (ISO/DIS 14869-3 protocol)¹⁷ and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, ISO 11885:2007 protocol).¹⁸

2.4 Life cycle analysis

Life Cycle Assessment (LCA) is a standardized methodology^{19,20} worldwide recognized as a valuable screening tool to support basic and applied research, in the field of environmental studies and green chemistry.^{21–24} Specifically, its application to the end-of-life management of composite packaging materials represents a consolidated way to evaluate improvements, reached because of a process implementation, or to compare several viable treatment solutions.^{14,25–27} Moreover, companies working in this field well recognized its adoption to implement research choices and disclose the environmental footprints.^{28–31}

A simplified life cycle analysis was applied to determine the environmental performances of the SHS-based system described above and make a comparison with three alternative protocols: landfill disposal (a), formic acid treatment (b) and pyrolysis (c). Although disposal procedures are the worst waste treatment solution according to the European Member States (EU waste regulation),³² they still are a common procedure in many countries. Therefore, landfill was chosen as a benchmark to simulate the less environmentally-friendly alternative. One ton of multilayer packaging material (paper/PE/Al) sent to treatment was chosen as a functional unit (FU) necessary to refer to the input–output within the system boundaries investigated.¹⁹ The analysis was limited within the physical boundaries of each treatment plant (Fig. 2), including: (i) all process requests (considering the renewable and fossil resources extraction to satisfy energy and utility needs) and (ii) the main outflows, in terms of emissions and avoided products due to

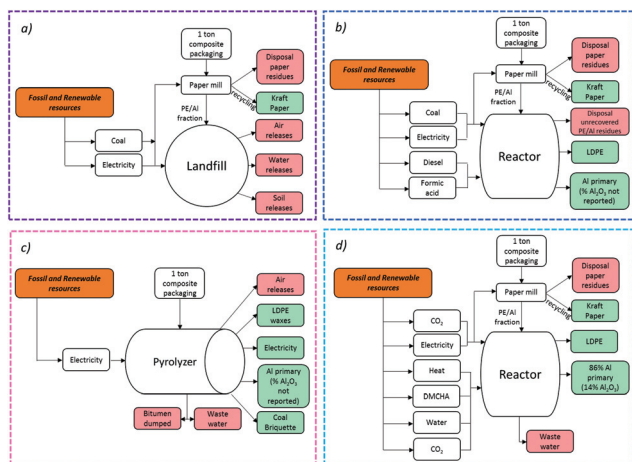


Fig. 2 System boundaries of the four treatment scenarios: (a) landfill, (b) formic acid process, (c) pyrolysis and (d) SHS route.

recoveries. A cradle-to-gate approach was used (the cradle being represented by the set of processes needed to cover plant requirements in terms of auxiliaries and energy, and the gate by all the outputs from the treatment system such as mass/energy recovery and releases into the environment).

The emissions (into air, water, and soil) and production of solid wastes due to each technology have been highlighted with red boxes, whereas the recoveries (avoided processes by LCA) have been highlighted in green. The inventory stage for the SHS-process (main scenario) was completed using primary data collected at the lab scale. In order to make a comparison with other possible scenarios, already published data for a life cycle analysis of the landfill and formic acid processes were adopted.¹⁴ To the best of our knowledge, no LCA studies on the pyrolysis of the composite packaging have been reported in the literature. Therefore, data from Korkmaz *et al.*⁹ were modeled to create the input-output model for this scenario, evaluating the energy requirements by enthalpy balance. As depicted by the boundaries, scenarios (a), (b) and (d) assume the disposal or recovery of the LDPE/Al fraction after the treatment of the multilayer packaging material within the paper mill to recover kraft paper. These scenarios include all the inputs/outputs from the paper mill process in terms of mass, energy, emissions and chemicals. On the other hand, scenario (c) was modeled if the entire packaging is used to feed the pyrolyzer, without mill pre-treatment.

The Ecoinvent database³³ was adopted as a reference library to complete all inventories in terms of energy, auxiliary production, and emissions for all stages involved. Where default processes were not available, dedicated software^{34,35} and literature data^{36,37} were used to fill the gaps (see Tables S1–S4 in the ESI† for the complete inventory of each scenario). Transportation was intentionally omitted due to the lack of reliable data for SHS and pyrolysis processes. In addition, to be more conservative, the same geographical boundaries were assumed, selecting China as a reference country to set up the technologies. The analysis was carried out to address environ-

mental concerns at the midpoint level. Six impact categories were chosen among the whole set of eighteen, because of their relevance to the study: climate change (CC), ecotoxicity (ET), fossil fuel depletion (FD), human toxicity (HT), land occupation (LO) and particulate matter formation (PMF). Moreover, the ReCiPe method was selected because of its capability of directly collecting all categories within the same single score indicator (point, Pt) to show the cumulative burden reached by each scenario. SimaPro software (v. 8.0.4.30)³⁸ and the ReCiPe method (World H/A, v.1.11)³⁹ were used to run the impact assessment stage.

3. Results and discussion

3.1 SHS extraction protocol

The protocol presented here (Fig. 1) exploits the fact that the neutral form of DMCHA has a low polarity, suitable for solubilizing LDPE at moderate temperature (Step 1), leaving residual aluminium pieces on the bottom of the flask. After the addition of water and CO₂ bubbling, the high polarity of the ammonium salt solution causes the separation of apolar LDPE that floats on the surface of the flask (Step 2). Finally, the removal of CO₂ regenerates neutral DMCHA as a separate phase from water (Step 3) that can be used for treating another stock of LDPE/aluminium multilayer waste. In the setup of the extraction protocol different temperatures (r.t., 50 °C and 90 °C) and residues/DMCHA ratios (1.25, 2.5, 5, 10 and 20 wt%) were investigated (Table 1). The solubilization of LDPE did not occur below 90 °C, the temperature at which it was possible to entirely recover the aluminium foil (>99%) with all residue/solvent ratios (1.25, 2.5, 5 and 10 wt%) apart from 20 wt%: in this case in fact a paste of LDPE/DMCHA formed immediately when the flask was removed from the hot silicon bath, preventing the separation of DMCHA phase from aluminium flakes. After the treatment with DMCHA (Step 1), aluminium was washed with acidic H₂O (obtained by bubbling CO₂ until pH 5) to remove residual traces of DMCHA. The DMCHA/LDPE solution was added to H₂O (volume ratio 1/1 or 1/2) and blown with CO₂. After the switching of DMCHA into the corresponding ammonium salt, LDPE separated as floating

Table 1 Tested process parameters, aluminium and LDPE recovery (%)^a

Residues/ DMCHA (wt%)	<i>T</i> (°C)	Al recovery (%)	LDPE recovery (%)	DMCHA/H ₂ O volume ratio
1.25	90	>99	93 ± 3	1/2
2.5	rt	—	—	—
2.5	50	—	—	—
2.5	90	>99	87 ± 2	1/2
2.5	90	>99	69 ± 4	1/1
5	90	>99	79 ± 2	1/2
10	90	>99	72 ± 16	1/2
20	90	—	—	—

^a The initial amount of aluminium in the treated residues was 25.3 ± 0.3 wt% (determined by calcination at 550 °C for 5 h); the remaining 75 wt% was assumed to be LDPE.

flakes on the surface of the aqueous solution, recovered by filtration (Step 2) and washed with the same acidic H₂O used for washing aluminium. The recovered LDPE amount ranged from 70 to 90% (Table 1) but it could be increased by reducing mechanical losses due to the small scale of the experiments. The experiment performed with 10 wt% residue/solvent ratio was scarcely reproducible in terms of LDPE recovery because a viscous solution of DMCHA and LDPE was formed at rt, preventing an efficient recovery. The lowest recovery (69%) was obtained when the DMCHA/H₂O volume ratio was 1/1 instead of 1/2 (in the case of 1/1, LDPE separated in a “paste” mushy form, difficult to filter).

The switching back of the DMCHAH⁺HCO₃⁻ ammonium salt into DMCHA (Step 3) was achieved by stirring and heating at 40 °C the aqueous solution.⁴⁰ At the end of this process, the amount of DMCHA recovered as separated, water insoluble phase was 80%; for achieving better amine separation, an increase of pH by addition of KOH was necessary. At pH 11, more than 96% of the initial amine could be recovered.

The recovered DMCHA did not contain detectable impurities (checked by ¹H NMR spectroscopy) and thus it could be used without any further purification for another extraction cycle.

3.2 Aluminium and LDPE characterization

Fourier transform infrared (FTIR) attenuated total internal reflection (ATR) spectra showed that on both faces of recovered Al pieces, residual LDPE was still present (Fig. 3): the bands related to the symmetric and asymmetric stretching modes of CH₂ (2916 and 2847 cm⁻¹) were clearly detectable as well as the bending and rocking modes of CH₂ at about 1460 cm⁻¹ and 725 cm⁻¹, respectively.

The contamination by LDPE of the recovered aluminium pieces (Table 2) decreased with increasing DMCHA to LDPE–Al ratio; the aluminium obtained from the most diluted extraction system (1.25 wt%) contained less LDPE (below 2%), around 4 times lower than what was achieved from the 10 wt% system.

No traces of nitrogen were detected on the recovered Al, confirming that washing with acidic H₂O effectively removed DMCHA traces as an ammonium salt. The percentage of metallic aluminium in the recovered material, a crucial parameter

Table 2 Contamination detected in the recovered aluminium and LDPE (C and N % determined by elemental analysis)

Residue/ DMCHA (wt%)	N in LDPE (%)	DMCHA cont. in LDPE (wt%)	C in Al (%)	LDPE cont. in Al (wt%)
1.25	0.21 ± 0.02	1.9	1.6 ± 0.1	1.9
2.5	0.12 ± 0.04	1.1	2.4 ± 0.3	2.8
2.5 ^a	0.14 ± 0.05	1.3	2.4 ± 0.6	2.8
5	0.13 ± 0.05	1.2	4.5 ± 0.3	5.2
10	0.40 ± 0.01	3.9	7.0 ± 0.2	8.1

^a DMCHA/H₂O volume ratio of 1/1.

for determining its commercial value after an industrial re-melting process, was 86%. This high value confirmed the non-oxidative behavior of DMCHA in the developed process.

The contamination by DMCHA in LDPE, calculated from the amount of N detected in the recovered LDPE, was low (around 1–2 wt%). The highest value of DMCHA (4 wt%) was obtained in the case of 10 wt% residue/DMCHA ratio, indicating that the viscous DMCHA/LDPE solution formed at rt at the end of the experiment affected both the recovery and the separation of DMCHA from LDPE itself. The recovered LDPE had similar thermostability properties to standard LDPE polymers when subjected to a thermal degradation in air (Fig. 4): its weight was stable until 250 °C (weight losses <0.1%), with a strong weight loss between 250 and 410 °C; the main difference with standard LDPE polymers was a solid residue (4.5 wt%) obtained at the end of the thermal treatment (600 °C). This finding confirms that the treatment with DMCHA did not alter significantly the quality of both aluminium and LDPE.

3.3 Life cycle assessment

Table 3 and Fig. 5 depict the main results from the impact assessment stage. The overall single scores indicated that when technologies are based on mass and/or energy recovery (formic acid, pyrolysis, and SHS-route), the avoided impacts largely exceed the potential burdens on the environment (most LCA studies refer to the avoided impacts using negative scores: the higher the absolute values, the greater the benefits). On the contrary, in the case of landfill the potential benefits are

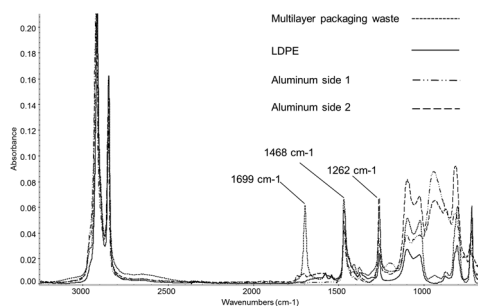


Fig. 3 ATR spectra of multilayer “de-papery” residue, recovered aluminium pieces and recovered LDPE.

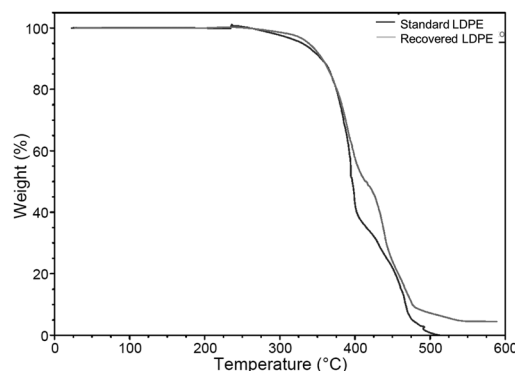


Fig. 4 Comparison of TGA profiles of recovered and standard LDPE.

Table 3 Results of the cradle-to-gate analysis per impact category: climate change (CC); human toxicity (HT); particulate matter formation (PMF); environmental toxicity (ET); land occupation (LO); fossil fuel depletion (FD)

Impact category	Unit	Landfill	Formic acid	Pyrolysis	SHS
CC	kg CO ₂ eq.	−1.0	−576.1	−225.2	−648.2
HT	kg 1,4 DB eq.	−308.0	−513.3	−251.4	−562.3
PMF	kg PM 10 eq.	$−3.0 \times 10^{-1}$	$−1.0 \times 10$	$−8.3 \times 10^{-3}$	$−1.2 \times 10$
ET	kg 1,4 DB eq.	18.1	−17.8	−4.2	−17.4
LO	m ² a	−6122.7	−6120.8	8.5	−6123.7
FD	kg oil eq.	137.4	−181.0	−430.2	−199.2
Single score	Pt	−26.4	−105.4	−75.2	−114.1

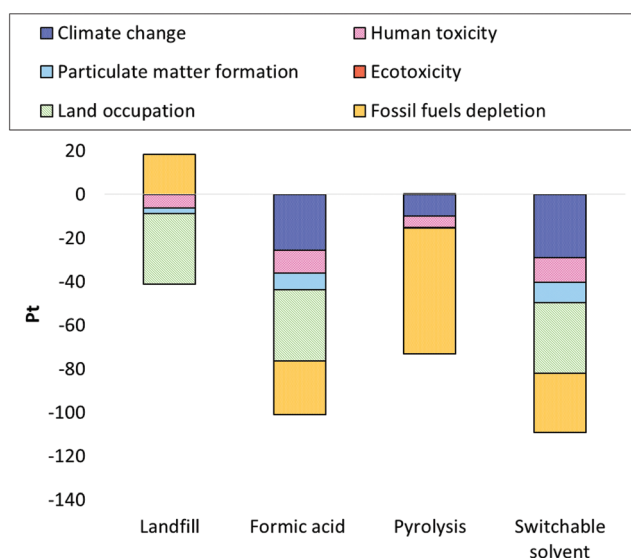


Fig. 5 Cradle-to-gate analysis in terms of ReCiPe single score.

associated with the paper recycling at the mill only, since the dumping procedure does not lead to environmental impacts mitigation (no mass and energy recovery). However, even if the recycled paper produces benefits in terms of HT, PMF and LO, it leads to negative effects in terms of FD due to the mill requirements: around 301 kg of coal and 379 kWh per ton of composite packaging.¹⁴ As further confirmation of the benefits due to paper recycling, impacts on LO have quite similar trends for each scenario in which a PE/Al fraction treatment follows the mill procedures. Pyrolysis requires only an energetic input and it can recover both electricity and coal briquettes.

These energetic recoveries lead to a higher reduction in terms of FD, estimated at around −313 kg of oil eq. of the total −430 (64% from electricity and the rest from briquettes), and for the PMF category (around −3.0 kg of PM10 eq.). Reduction of PMF is mainly driven by the lower amount of substances emitted during fuel combustion to produce process steam at thermoelectric plants. The energetic recoveries lead to relevant benefits also in terms of CC (−1077 kg of CO₂ eq.) and HT (−266 kg 1,4 DB eq.). Additionally, since metallic aluminium and good-*M_w* (molecular weight) LDPE waxes are obtained from pyrolysis,⁹ a replacement of virgin materials can also be

assumed, providing additional benefits for the categories of CC (−832 and −392 kg of CO₂ eq.), FD (−195 and −293 kg oil eq.) and HT (−341 and −5 kg 1,4 DB eq.) (scores for Al and LDPE, respectively). Data about the percentage of oxidized aluminium (Al₂O₃) have not been reported in the literature.

Cumulative impact achieved by pyrolysis was estimated at around −75 Pt, lower than the environmental benefits achieved by the formic acid process (−105 Pt).

On the other hand, although formic acid treatment is more resource-consuming (coal, diesel, electricity, and formic acid) and leads to a lower amount of recovered aluminium (36 kg vs. 49 kg), it guarantees greater LDPE recycling (196 kg vs. 125 kg), influencing the CC and FD for −411 kg of CO₂ eq. and −307 kg oil eq. Also in this case, data about the percentage of oxidized aluminium (Al₂O₃) have not been reported in the literature. Differently from the thermal valorization of the entire packaging waste, the combined cycle (also including paper recovery) saves 660 kg of kraft paper per ton treated. This last saving avoids the paper production from virgin cellulose, with a great effect on LO (−6121 m² subtracted), CC (−558 kg of CO₂ eq.) and FD (−164 kg oil eq.). This combination leads to greater cumulative benefits of formic acid-based treatment, when compared with the pyrolysis.

Although the amount of kraft paper recovered is the same, overall scores reached by the SHS-route are quite higher in terms of avoided impacts (−114 Pt). A further analysis (Fig. S1 in the ESI†) run for the recovery treatments alone (landfill is not included) reveals that the main contributions to the impacts mitigation are due to the LO (28%), CC (25%) and the avoided usage of fossil fuels (24%). In fact, recovering LDPE and Al prevents their production from virgin raw materials and guarantees a saving of −389 kg of oil eq. per ton treated. A reduction greater than −267 kg of oil eq. (around 70% contribution) is achieved thanks to the avoided manufacture of 187 kg of virgin LDPE, in which fossil-based resources are used both in the production of energy and feedstocks. Fig. S2a and b in the ESI† shows the network of the results for FD and CC categories. The avoided impacts are depicted using green arrows: the thicker the flows, the higher the avoided burden to the global scores. On the contrary, red arrows reflect the opposite situation of increasing the burdens. Since the Al recovery achieved by using a SHS-approach was close to 99%, and 86% is metallic Al, around 43 kg of primary Al are recovered with a contribution of −122 kg oil eq. (Fig. S2a†) (14% of aluminium

is obtained in an oxidized form with no sensible environmental and economic contribution). These results highlight the importance of recovering aluminium in the primary form, because of the intense energy requirements during its manufacturing chain, evaluated at around 190–230 MJ kg⁻¹.⁴¹ The energy saving could have relevant benefits also in terms of environmental issues. Looking at the contribution to the CC, –521 kg of CO₂ eq. are due to the recovery of virgin Al. This trend is well depicted by Fig. S2b in the ESI,[†] which confirms a contribution of 80% of the overall value for the greenhouse gas (GHG) emissions (–648 kg of CO₂ eq.). In both cases (FD and CC), the networks depict that the main incidence is related to the electricity consumptions involved in the electrolysis, a process necessary to obtain the virgin metal. The energy saving is also the main driver for the avoided impacts on the PMF and HT categories (8% and 10% contribution on the overall single score, see Fig. S1 in the ESI[†]). In fact, the prevented release of gases and particulates, on the one hand, and of heavy metals on the other (mainly due to the disposal procedures within the entire chain) leads to sensible reductions in both categories. Inventories of the avoided substances, together with the percentage contributions, are reported in Table S5 in the ESI.[†]

Even if the results from the simplified LCA show a positive trend for the SHS process, some considerations are mandatory. First, landfill represents a common option and the recovery with formic acid is already developed in China. This means that the Technology Readiness Levels (TRLs) for these two scenarios are higher than the invention presented in this paper, only developed on the laboratory scale. Then, the LCA should be considered as a good approximation of a simplified early stage analysis, carried out using preliminary data provided by experiments (automatically affected by uncertainties). However, different from the formic acid technology, the SHS-route was proposed in Italy. Therefore, assuming the same energy requirements, but substituting the China electricity mix with the Italian one and assuming the replacement of coal (used in the paper mill) with natural gas, a greater reduction up to –142 Pt could be achieved. This is a further confirmation of the potentiality of the SHS-route proposed here, which represents an interesting alternative to recover value from composite packaging.

4. Conclusion

The SHS system based on a lipophilic tertiary amine, such as DMCHA, can be successfully applied for processing multilayer packaging materials with the aim of recovering both LDPE and aluminium. The use of such systems was highly effective, without compromising the quality of the recovered materials; this holds true particularly for Al, whose recovery rate was >99%, with a great efficiency for the metallic form (86%). The mild process conditions (room pressure and temperature below 100 °C) and the possibility of recycling the solvent just by adding and removing CO₂ underline the greenness of the

entire process. The results achieved by the simplified life cycle analysis in comparison with other waste treatment technologies confirmed this finding: the overall reduction of the global environmental load could vary from –8% up to –35% if a different energy mix was adopted. Several interesting aspects came out from a preliminary environmental assessment; a further analysis on the pilot scale is mandatory to verify in detail all the economic and environmental advantages and drawbacks associated with the process. However, the results presented in this paper represent further confirmation of the importance of the Green Chemistry principles at the early design stage to minimize the production of waste (the use of a recyclable solvent) and increase the process efficiency.

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