INNOVATIVE DIGITAL WATERMARKS AND GREEN SOLVENTS FOR THE RECOVERY AND RECYCLING OF MULTI-LAYER MATERIALS

Funding scheme: European Union's Horizon 2020 Research and Innovation programme

Call identifier: H2020-SC5-2020-2

Theme: CE-SC5-24-2020: Improving the sorting, separation and recycling of composite and multi-layer materials

Grant Agreement: 101003532

Project start date: June 1st, 2021

Duration: 36 months

DELIVERABLE N°5.3

Report on Solvent Recycling Protocols

Due date of deliverable: 31/08/2023	Actual submission date: 07/12/2023	Lead Beneficiary: TWI

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1 Introduction

Sol-Rec² project targets the development and implementation of ground-breaking strategies for improving the sorting, separation and recycling of pharmaceutical blister packs and flexible laminate packaging waste which comprise multiple layers of plastics, adhesives, inks and aluminium. Although widely used for the protection and preservation of pharmaceutical and food produce across the globe, such packaging materials present significant challenges for established recycling infrastructure and, therefore, our future with a circular economy.

Experience from the field of ionic liquids (ILs) and deep eutectic solvents (DESs) has been leveraged to develop a toolbox of novel green solvent systems that delaminate multilayer packaging material to facilitate separation and recovery of high purity commodity plastics, such as, poly(ethylene) (PE), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC), as well as the valuable barrier materials such as aluminium foils. In parallel, innovative digital watermark technologies are being further developed and progressed through to successful demonstration of rapid and efficient sorting of multilayer packaging; a key step towards proper inventory management of complex mixed waste streams.

Work Package 5 (WP5) of Sol-Rec² project has centred on the scale-up of processes and procedures from laboratory bench-top studies to a 1 L laboratory reactor vessel. The activity has enabled partners to produce, study and improve both the quantity and quality of delaminated materials and manage the recovery and recycling of solvents.

In Deliverable 5.3 we discuss the recovery and recycling procedures for used ILs and DESs. The work carried-out aligns with the overarching goals of WP5 to establish methods for high-yield polymer recovery, cost-effective aluminium separation, recovery and recycling of IL and DES solvent systems, and generation of high-purity recycled materials for high-value end-applications. Deliverable D5.3 serves as a bridge for technology transfer to pilot-plant implementation phase in WP6.

As the project advances, these tasks contribute to the refinement of Sol-Rec² technology, propelling it closer to its full potential.

2 Methods

2.1 Delamination of Packaging Laminates

The intermediate scale-up of delamination processes using a 1 L reactor filter reactor vessel was the focus T5.1 and, for a full account of the experiments undertaken and details of process optimisation, the reader is referred to Deliverable D5.1.

A brief summary of the solvent systems, packaging materials and delamination experiments from the previous work in WP5 is presented in the following sub-sections.

2.1.1 Ionic Liquids and Deep Eutectic Solvents

The short-list of three IL and DESs selected for the scale-up of Sol-Rec² processes (see D4.2) is given in Table 1.

Table 1 Short-list of ionic liquids and deep eutectic solvents established in WP4.

Partner	Solvent System	Ratio	Type	Reference
TWI	Alcohol:Organic Acid	1:1	DES	DES1 – TWI
ULEIC	Phenol:Organic Acid	1:1	DES	DES2 - ULEIC
SOL	Amine:Organic Acid	1:1	IL	IL3 - SOL

2.1.2 Multilayer Packaging

Three types of aluminium containing laminate consumer packaging materials were sourced by PLASTIGRAM and subsequently shredded by AIMPLAS, including PE/ALU, ALU/PE/PAPER and PE/ALU/PET. To facilitate an assessment of the size dependence of material sorting and recovery efficiency, two size fractions were created for each film in separate processes using 25 mm and 5 mm screens.

Pharmaceutical blister pack material based on PVC/ALU was obtained and provided by MIKROLIN. The materials were shredded at MIKROLIN using an industrial grinder equipped with a 9 mm mesh.

2.2 Reactor System

The laboratory reactor system set-up and commissioned at TWI as part of the Sol-Rec² Project for WP5 is shown in Figure 1. The system comprises: (i) a frame mounted 1 L jacketed reactor filter vessel; (ii) a heater/chiller unit for temperature control; (iii) overhead stirrer; (iv) temperature and pH probes and; (v) AVA Lab Control software.

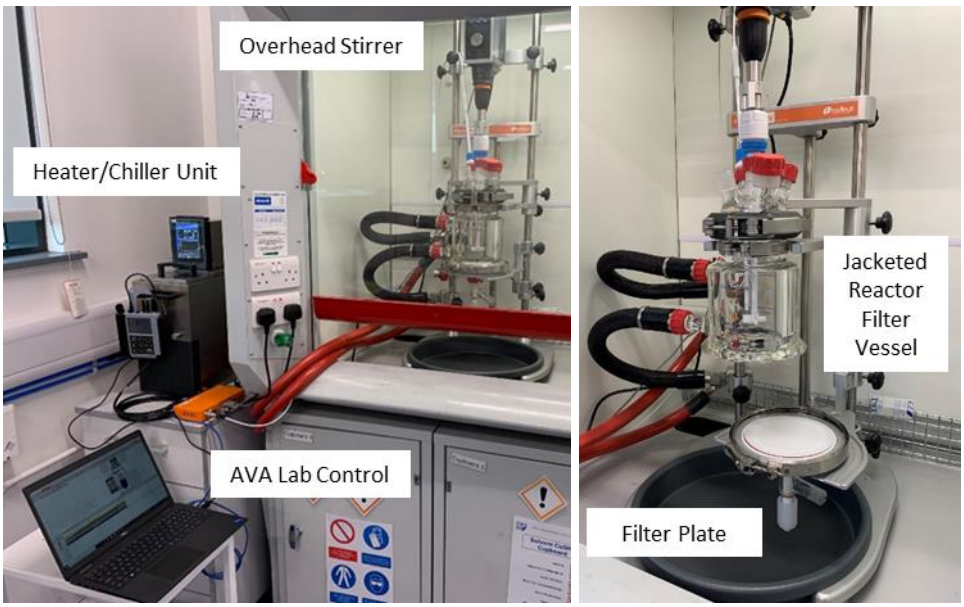

Figure 1 1 L reactor vessel system commissioned at TWI.

The filter plate was fitted with a P100 sintered glass disk (pore size 40-100 µm) with appropriate filter materials or meshes placed above, such as PET fabrics or steel wire mesh sieves with known pore sizes.

To extract solvents through the filter plate at the end of each experiment or rinse cycle, a receiver flask was attached to the outlet of the reactor vessel via PTFE tubing and then connected to a vacuum pump fitted with a regulator. The set-up is shown in Figure 2.

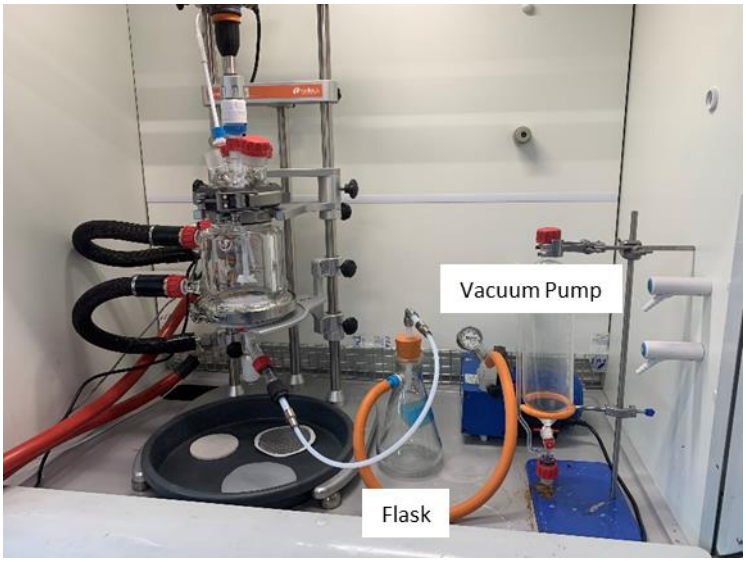

Figure 2 1 L filter reactor vessel system with receiving flask attached via PTFE tubing and further connected to a vacuum pump with a regulator.

2.2.1 Delamination Experiments

A brief summary of the delamination experiments performed in T5.1 using the aforementioned solvent systems and packaging materials is shown in Table 2. The experimental conditions in terms of temperature and duration were chosen to ensure complete delamination of the respective packaging materials. At the conclusion of the delamination step the solvent was extracted to a receiver flask and retained (as the set-up illustrates in Figure 2). The mix of delaminated plastic, paper and/or aluminium films within the reactor vessel was then rinsed, first, with either deionised water or organic acid, depending on the hydrophilic or hydrophobic nature of the solvent system, followed by three subsequent rinses with deionised water.

After each trial, the quantities of solvent and organic acid rinse recovered from the vessel were measured to determine losses, that is, the extent to which solvents were retained by the mass of delaminated materials. The filtered solvents and acetic acid rinse were then replenished and re-used for further delamination trials with the same packaging material in order to assess the ability of the solvents to be used again over successive trials.

Table 2 Table of Experiments A-G detailing solvent system, packaging material, size fraction of shredded material denoted by screen size, solids loading in the solvent and number of replicate trials for each set of experiments.

REF	SOLVENT SYSTEM	PACKAGING MATERIAL	SHREDDED SIZE FRACTION (denoted by screen aperture) (mm)	SOLIDS LOADING (g L^{-1})	NO. OF TRIALS
A	IL3 - SOL	PE/ALU	25	30	5
B	IL3 - SOL	PE/ALU/PET	5	30	5
FC	IL3 - SOL	PVC/ALU	9	150	1
D	DES2 - ULEIC	PE/ALU	5	30	5
E	DES2 - ULEIC	PE/ALU/PET	25	30	5
F	DES1 – TWI	ALU/PE/PAPER	25	30	5
G	DES1 – TWI	PE/ALU/PET	25	30	5

After 5 repeat uses, the contaminated solvents were provided to SOLVIONIC to investigate methodologies for purification and recycling. The quantities of recovered solvent are listed in Table 3.

Table 3 Table of recovered solvents and 1st rinses with organic acid.

REF	SOLVENT SYSTEM	MATERIAL	SOLVENT RECOVERED (av. 5 uses)	1st RINSE	RINSE RECOVERED (av. 5 uses)
A	IL3 – SOL	PE/ALU	900 ± 20 g	WATER	n/a
B	IL3 – SOL	PE/ALU/PET	920 ± 10 g	WATER	n/a
C	IL3 – SOL	BLISTER PACK	428 g	WATER	n/a
D	DES2 – ULEIC	PE/ALU	880 ± 30 g	ORGANIC ACID	999 ± 1 g
E	DES2 - ULEIC	PE/ALU/PET	920 ± 10 g	ORGANIC ACID	991 ± 1 g
F	DES1 – TWI	ALU/PE/PAPER	850 ± 10 g	ORGANIC ACID	971 ± 8 g
G	DES1 – TWI	PE/ALU/PET	910 ± 10 g	ORGANIC ACID	979 ± 3 g

2.3 Solvent Recycling

2.3.1 Recycling Methods

SOLVIONIC received batches A, B and C which were composed of an amine and organic acid. NMR analysis upon receipt showed a minor evolution of component ratio (see Table 5, Table 8 and Table 10. Further delamination tests were performed with the solutions as received, to age them until the loss of their efficiency towards delamination. The demonstration of the recovery process has been performed with the IL – SOL, as it was the first available. Performing the demonstration on one of the solutions was representative for the three of them.

To perform the additional delamination trials, solutions and consumer packaging were added in a 2 L bottle. The solution was then stirred at 300 rpm in an oil bath, heated at 70 °C for 30 min. The solution was then left to cool down for 30 min and then vacuum filtered on a Büchner using a 0.45 µm nylon filter. A dry ice bath was used to minimize

solution loss (Figure 3). Further delamination tests were conducted with recovered solutions. Results are assembled in (Table 4). It is worth noting that such tests were stopped due to the lack of remaining solution for the IL and of remaining packaging samples for DESs, rather than due to the loss of their efficiency.

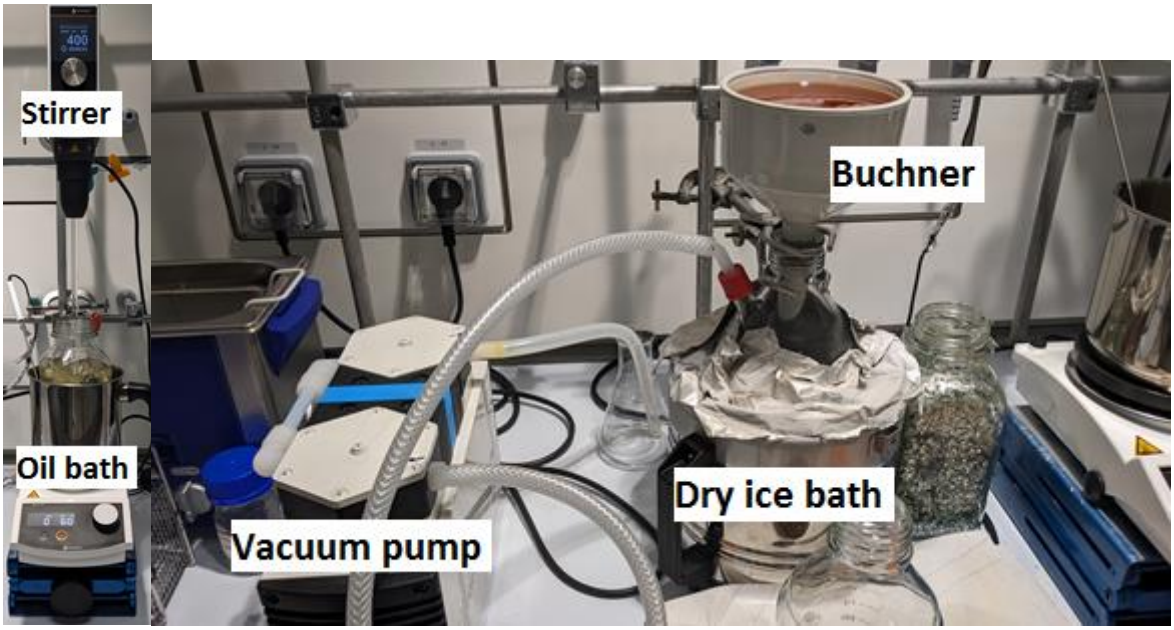

Figure 3 : Set-up for delamination tests and filter solution at SOLVIONIC

Table 4 Table of delamination tests for batch A, B and C at SOLVIONIC

REF	SOLVENT SYSTEM	MATERIAL	SHREDDED SIZE FRACTION (denoted by screen aperture) (mm)	SOLIDS LOADING (g L^{-1})	NO. OF TRIALS	TOTAL MATERIAL DELAMINATE (g)
A	IL3 - SOL	PE/ALU	25	25	10	400
B	IL3 - SOL	PE/ALU/PET	5	50	13	800
C	IL3 - SOL	LISINOPRIL	10	110	1	260

After delamination tests as described above, solutions turned yellowish, with different degrees of intensity. Coloration may have two causes: solution oxidation and the packaging ink dissolution (this explains the more intense coloration effect prior to purification and the remaining coloration after solvent recycling). For the PE/ALU/PAPER, an opaque liquid was obtained at the end of the test, due to paper particles in suspension.

After those observations, solutions were recovered to their initial state using purification processes according to Solvionic know-how (trade secret – quality characteristic described in section 3.2) and, thereafter, by adjusting the components to their initial 1:1 ratio.

2.4 Analytical Methods

2.4.1 ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) (Magritek Spinsolve 80 MHz) was used as the main tool to determine the component ratios of the solvent systems. ^{1}H and ^{13}C NMR spectra were obtained from the solutions used for delamination and compared to those of freshly made solutions.

^{13}C-NMR allowed to determine the presence of the unaffected components, as well as the presence of impurities (polymers, aluminium particles for instance) due to the delamination process. ^{1}H-NMR allowed to calculate approximatively the component ratio by integration of the spectral peaks. Such analyses were performed on TWI batches as received and the results are assembled in Table 5 below.

Table 5 Table of concentration for batch A, B and C after TWI's tests

COMPONENT	CONCENTRATIONS (mol %)			
	Blank Solution	Batch A after 150 g (PE/ALU)	Batch B after 150 g (PE/ALU/PET)	Batch C after 150 g (Blister Pack)
Amine	49	48.8	48.5	47.6
Acid	51	51.2	51.5	52.4

Delamination of 150 g of blister pack led to the biggest loss of the amine concentration. As seen later in the text, the additional delamination experiments conducted at Solvionic led to the same tendency. Due to the confidentiality of the solution's compositions, NMR spectra are not included in this report and are at the disposal of the reviewer upon request.

2.4.2 Fourier Transform Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy (SHIMADZU FTIR IRaffinity-1S) was used to complement NMR analyses. Freshly made solutions were used as blanks. The spectra of individual components were also obtained for better understanding of the formulation spectra. Unfortunately, due to the large number of constituents present in the mixture (including but not limited to impurities) no valid interpretations could be extracted from the (noisy) spectra obtained.

2.4.3 pH

pH of the solutions was determined to confirm the evolution of the acid concentration during the delamination cycles (Mettler Toledo SD23, pH InLab Expert Go electrode). This method was employed to complement the NMR results confirming the concentrations observed.

In addition to the solutions used to delaminate samples at TWI, tests were performed on solvents and acetic acid rinses used by TWI for T5.1 delamination experiments. Specifically, rinsing solutions of batch D, E, F and G, were also analysed.

3 Results

3.1 Delamination

3.1.1 IL3 – SOL

Results of the experiments described above are assembled in the following tables.

Table 6 Concentration of components of IL3 - SOL for batch A, B and C after TWI+SOLVIONIC delamination tests

COMPONENT	CONCENTRATIONS (mol %)			
	Blank Solution	Batch A after 400 g (PE/ALU)	Batch B after 800 g (PE/ALU/PET)	Batch C after 260 g (Blister Pack)
Amine	49	40	44.8	44
Acid	51	60	55.2	60

According to results of Table 6, the process involving batch B (PE/ALU/PET) was more efficient than that of batch A (PE/ALU), due to the size of particles, which was smaller for B than A, even if PE/ALU/PET is more difficult to delaminate than PE/ALU (3 layers instead of 2).

pH analysis confirmed the continuous loss of amine in the solution, as shown in Table 7 below.

Table 7 pH for batch A, B and C after TWI+SOLVIONIC tests

	Blank Solution	Batch A (PE/ALU)		Batch B (PE/ALU/PET)			Batch C (Blister Pack)	
Material delaminated (g)	0	150	400	150	400	800	150	260
pH	4.81	4.77	4.53	4.80	4.77	4.63	4.78	4.71

Colour change was also observed, as shown in Figure 4. Intensity increased through the several delamination tests for every batch. It can be explained by the degradation of the components and the dissolution of the ink in the case of batch B.

Figure 4 Colour of batch - in order: Blank solution, Batch B (150 g), Batch B (400 g), Batch B (800 g), Batch A (150 g) and Batch A (400 g).

Batch C was a particular case. For batch C, the blister packwas indeed composed of PVC which reacted with IL3 - SOL, as observed by ^{1}H-NMR, which showed PVC peaks in the solution after delamination. The PVC turned white/opaque and rigid after delamination, suggesting a more complex interaction than for the other plastics.

3.1.2 DES2 – ULEIC

As opposed to IL3 - SOL, DES2 - ULEIC solution was affected by the loss of the acid component, rather than by the loss of the amine (Table 8).

Table 8 Concentration of components of DES2 - ULEIC for batch D, E and acid rinse after TWI tests

COMPONENT	CONCENTRATIONS (mol %)				
	Blank solution	Batch D after 150 g of PE/ALU	Batch E after 150 g of PE/ALU/PET	Batch D Rinse	Batch E Rinse
Phenol	50	57	68	10	11
Acid	50	43	32	90	89

Table 9 shows the increases of pH due to the loss of acid. Batch E is the most basic one with the higher loss of acid. Batch E is also the most coloured due to the ink in the packaging (Figure 5).

Table 9 pH for batch D and E after TWI tests

	Blank Solution	Batch D after 150 g of PE/ALU	Batch E after 150 g of PE/ALU/PET
pH	1,36	1,38	2,35

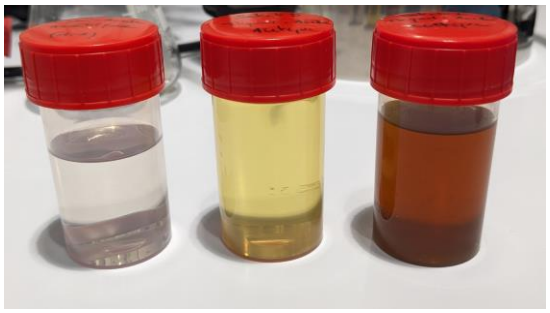

Figure 5 Blank solution - Batch D - Batch E

3.1.3 DES1 – TWI

Acid is also consumed during delamination tests with DES1 – TWI. In that case, ^{13}C-NMR revealed the presence of a third compound where the acid and alcohol reacted together to form an ester. It means that the component ratio of this solution will be more difficult to equilibrate after delamination.

Table 10: concentration of components of DES1 - TWI for batch F, G and acid rinse after TWI tests

COMPONENT	CONCENTRATIONS (mol %)				
	Blank Solution	Batch F 150 g of PE/ALU/Paper	Batch G 400 g of PE/ALU/PET	Batch F Rinse	Batch G Rinse
Alcohol	50	52	53	29	12
Acid	50	48	47	71	88

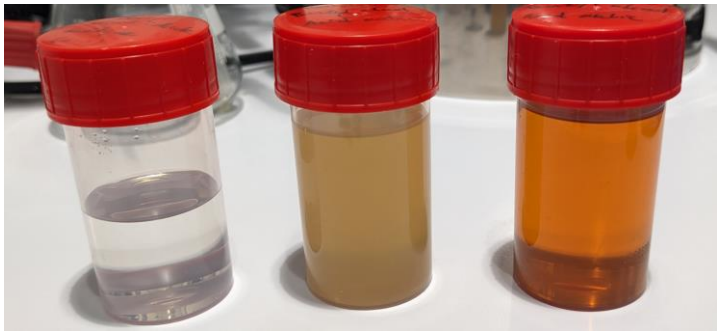

Figure 6 Blank solution - Batch F - Batch G

3.2 Solvent Recycling

Solvionic has developed expertise in the production process of ionic liquids and similar products over the last 20 years. This know-how is regularly upgraded with new techniques and knowledge and is intellectual property owned by Solvionic who have selected to maintain it as a trade secret. Purification techniques are used as the final step of the production process to obtain customer and legislation required product quality.

Recycling an ionic liquid or related product, that has been used in a device or a process, is the process of removing any contaminant, to recover to initial state and properties. SOL has thus applied their know-how to assess the recyclability of IL3 – SOL, which was chosen as the case study.

New chemicals, coming from product chemical degradation during the delamination process, packaging laminates particles, and atmosphere contaminants (i.e., water) are possible impurities for removal. As some of them are in solid-state, filtration is one of the applied techniques. Other techniques to remove contaminants may combine distillation, crystallisation, extraction etc. The reader will understand that details on this core technology of SOL will not be given. However, IL3 – SOL has been recycled using the scheme of Figure 7 Figure 1below.

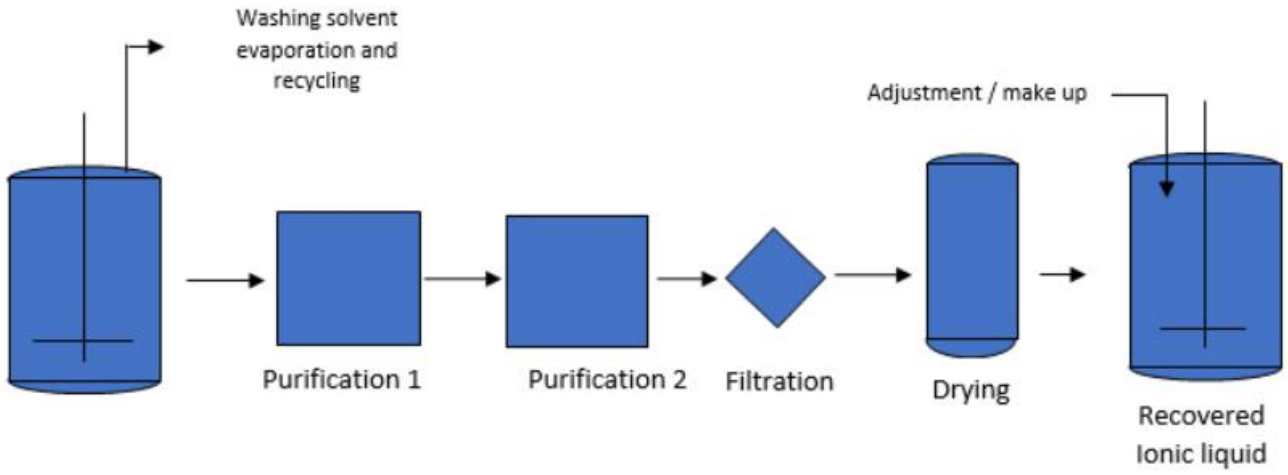

Figure 7: recycling process used to recover IL3-SOL

As explained above in the report, after several delamination cycles, one of the solution perturbations is the slight deviation of the bicomponent solution molar ratio from 1:1 mol. to non-equivalence, which results in an excess of base or acid. The last step is thus to add the missing component to recover the initial 1:1 molar equilibrium.

Product purity and 1:1 molar ratio was confirmed by H-NMR, as shown in Figure 8 below. As explained above, NMR spectra are not detailed in this report. Analyses details are at the disposal of the reviewer upon request.

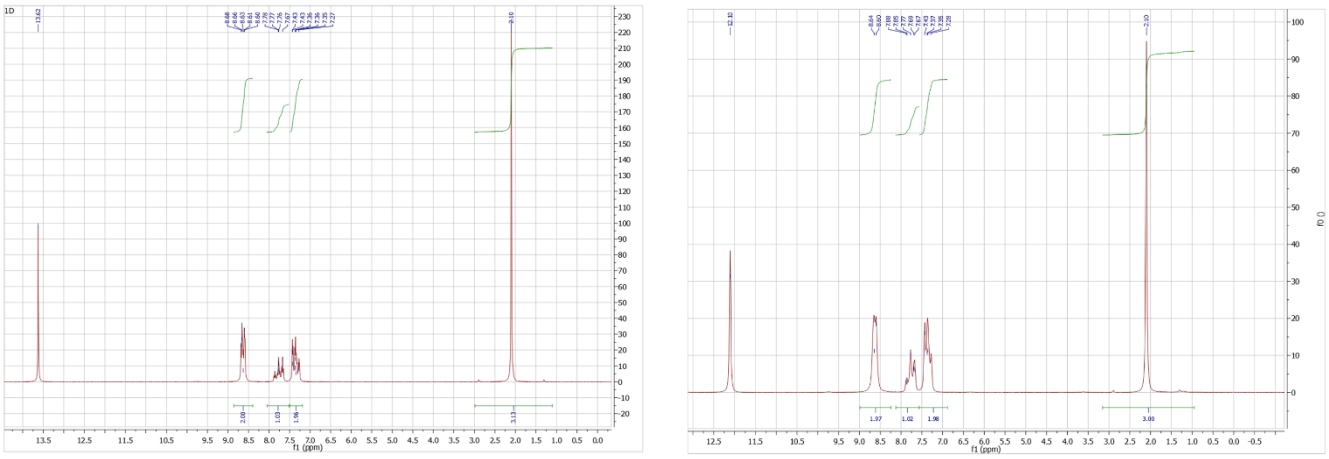

Figure 8 H-NMR spectra of freshly made IL3 – SOL (left) and of the recycled one (right)

Figure 9 below is the visual result of such purification process applied to IL3 – SOL used for batch B.

Figure 9 Batch B (800 g of PE/ALU/PET) before (left) and after (right) recycling

To confirm the efficiency of the recycled solution, a new delamination test was performed, which resulted in successful delamination. The yellow colour of the recycled solution did not affect its efficiency regarding delamination.

Also explained above in the report, the delamination experiments were stopped due to the lack of remaining solution after several cycles, rather than due to the decrease of its efficiency. The non-optimised laboratory scale process led to too much solution loss between to delamination cycles. In view of WP6, an upscaled process that would solve this solution loss can be pictured as follows in Figure 10 below.

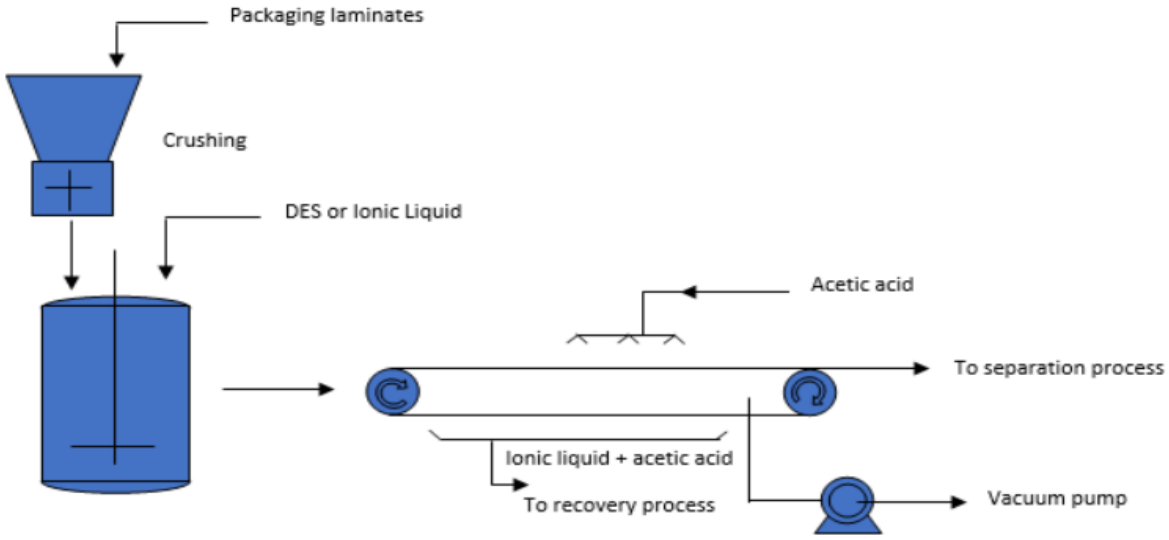

Figure 10: design of a possible upscaled recycling process

As it is seen on Figure 10**Erreur ! Source du renvoi introuvable.**, once the delamination process is completed, a vacuum belt filter can be used to separate the solution from solid compounds. While the isolated polymers and aluminium pieces are rinsed with acetic acid (which is one of the components of IL3 – SOL), the solution is pumped onto a filter cloth. While the solution goes through the filter cloth, polymers and aluminium pieces are rinsed and continuously evacuated to their reception container.

IL3 – SOL and acetic acid excess are then recovered using a closed-loop distillation technique which allows the acetic acid excess to be used again for the rinsing step and the IL3 – SOL to be reinjected in the delamination bath.

4 Conclusions

This report has presented the analysis of three short-listed Sol-Rec^2 solvent systems following use in a series of delamination cycles with four different types of packaging laminate. Analytical methods including, NMR, FTIR and pH measurements have shown that each solvent system is affected to a different extent as a result of the delamination cycles. The proprietary processes of Solvionic have been applied in the successful purification and recycling of the solvents to remove dissolved polymers, adhesives, inks and paper residues.

Through extended delamination cycles it has been shown that IL3 – SOL produces effective and efficient delamination with PE/ALU and PE/ALU/PET. After 800 g of packaging delamination, the solution remains efficient, although the concentration of the amine in the solvent system gradually decreases with an increasing number of delamination cycles. The maximum amount to be delaminated with the same solution before necessary recycling is still to be optimized. As it was the loss of solution that ended the delamination cycles, the optimisation has to do with the process rather than with the solution efficiency, which is a very good sign. It is believed that this solution loss will be reduced by the up-scaled size of the pilot plant reactor. The efficiency of IL3 – SOL has been shown and it is a good candidate for the prototype process.

With the solvent system, DES2 – ULEIC, after 150 g of delaminated packaging there was a loss 7 % of acid for batch D and 18 % for batch E. Therefore, this solution will consume more of the chemical components to maintain the 1:1 ratio than IL3 – SOL. Moreover, it has been noted that the solid-state of the phenol at room temperature can lead to more challenging processing due to the inherent instability of the solution. This has been observed between delamination cycles when the solvent cools down and it precipitates.

The third solvent system, DES1 – TWI, after 150 g of delaminated packaging experienced lower losses of acid for both batches F and G (~ 3 %) when compared to DES2 - ULEIC. However, the production of a third element (an ester from the reaction of acid and alcohol due the heat of the delamination process) after 5 repeat uses affects the 1:1 ratio of the component solution and presents an additional challenge to maintain the purity of the solvent.

IL3 – SOL is seen as the most promising formulation in terms of efficiency and ease of use. However, one of its components was classed as a CMR (carcinogenic, mutagenic and reprotoxic) in the past. Even if it was recently removed from this list, some end-users still prohibit its use in industrial processes, for the sake of branding, caution and workers acceptance. It has then been excluded from the final candidate list by the consortium (see minutes of consortium meeting in Valencia, November 14th, 2023). On the other hand, DES2 – ULEIC's solid-state behaviour will be too challenging when upscaling the process. It has been thus also excluded from the final candidate list. **Consequently, DES1 – TWI has been selected for the upscaling activities in WP6**.