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Delamination and deinking of colored multilayer flexible plastic packaging *via* selective aminolysis of polyurethane and acrylate based adhesives

Selective aminolysis of polyurethane- and acrylate-based adhesives was developed as a single-step method for simultaneous delamination and deinking of multilayer flexible packaging. The effects of amine properties and film type on deinking efficiency were modeled quadratically. This selective aminolysis approach enabled recovery of intact polymer layers without dissolution or degradation, supporting their reuse in closed-loop recycling.

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## Delamination and deinking of colored multilayer flexible plastic packaging *via* selective aminolysis of polyurethane and acrylate based adhesives

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The demand for efficient recycling processes towards closed-loop recycling of multilayer plastic packaging is increasing. Delamination enables recovery of intact polymer layers without degrading main materials, offering economic and environmental benefits. Yet, scientific studies on the mechanisms of delaminating and deinking multilayer packaging remain limited despite strong industrial interest. This work presents key findings on the delamination and deinking mechanisms of multilayer flexible packaging films using selective aminolysis of the polyurethane and acrylate based adhesives. While aminolysis is widely used in plastic recycling, this study provides first insights into its targeted use for depolymerizing adhesives without affecting the main polymer layers. To investigate the relationship between specific amine properties and their effectiveness in deinking various types of plastic films including chemically stable UV-based inks, a quadratic model was developed. Among different properties, heat capacity, boiling point as proxy for polarity and molecular weight, dipole moment, and polar surface area emerged as key properties influencing deinking efficiency across different plastic films. The mechanism of selective aminolysis of the adhesive was investigated through FTIR and NMR analyses. Kinetic tests, based on a central composite inscribed (CCI) design, were conducted using a selected amine to assess the effect of process conditions for the colored PET/PE multilayer sample. The optimal conditions were identified as 65 °C, a particle size of 0.5 cm, and an S/L ratio of 0.01 g mL<sup>-1</sup>. The impact of addition of chemical reagents on deinking and delamination efficiency was also explored, showing positive results depending on film composition.

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### Green foundation

1. This work presents a novel approach for the delamination and deinking of colored multilayer flexible plastic packaging, aiming to enhance closed-loop recycling and unlock both economic and environmental value of plastic waste.
2. This study provides first insights into selective aminolysis of polyurethane and acrylate based adhesives to recover constituent polymer layers of multilayer plastic packaging without any dissolution and degradation, paving the way for their reuse in closed-loop recycling.
3. The demonstrated single-step deinking and delamination process for a wide range of monolayer and multilayer plastic packaging is promising; however, future research should address solvent recovery and evaluate the environmental impact of the process to enable large-scale application.

## 1. Introduction

In order to advance towards a circular economy for plastics, policymakers are increasingly introducing regulations. For example, under the European Green Deal, the goal is to ensure that all plastic packaging placed on the EU market is recyclable

in an economically viable manner by 2030, with an additional target for packaging to contain at least 30% recycled content.<sup>1</sup> The demand for high-quality recyclates thus becomes increasingly imperative considering that globally only 9% of plastic waste is recycled.<sup>2</sup> Together with ambitious goals set by policymakers industry engagement is crucial to reduce reliance on virgin resources, advancing circular products and services, and minimizing environmental impacts.<sup>3–6</sup> Chemical companies both within and outside the EU are taking important steps toward a more circular economy.<sup>7–11</sup> For instance, BASF has launched a new Circular Economy Program aimed at increasing the use of recycled and renewable feedstocks, establishing new material cycles, and developing innovative business

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models.<sup>7</sup> Similarly, Henkel has relaunched its bonding and sealing portfolio with a new packaging concept designed to increase the recycled content of packaging materials.<sup>10</sup> Such initiatives are crucial to improving closed-loop recycling rates. It is obvious that the composition of plastic packaging is a determining factor of the recycling efficiency. Especially for post-consumer flexible packaging, closed-loop recycling is still rare. Inks are essential for packaging but hinder recycling, often resulting in dark, low-quality recyclates. Residual inks can degrade during processing, causing odors and affecting material properties. Deinking is key to improving recyclate quality, but it's challenging due to the complex and varied ink compositions comprising solvents, resins, colorants, and additives. While nitrocellulose is common, more stable resins like PU, polyester, or PVB are preferred for high-temperature uses. UV-cured inks use reactive resins such as epoxy or urethane acrylates, and overprint varnishes further complicate removal.

Inks are essential for packaging but hinder recycling, often resulting in dark, low-quality recyclates. Residual inks can degrade during processing, causing odors and affecting material properties.<sup>12,13</sup> To improve recyclate quality and marketability, interest in deinking technologies is growing. However, ink removal remains challenging due to the complex composition of printing inks, which include solvents, resins, colorants, and additives.<sup>14</sup> Ink composition varies by application, substrate, and printing method. While nitrocellulose is common, more stable resins like PU, polyester, or PVB are preferred for high-temperature uses. UV-cured inks use reactive resins such as epoxy or urethane acrylates, and overprint varnishes further complicate removal.<sup>15–17</sup> Furthermore, for quite some packaging applications, the ink layer is embedded between polymer layers to prevent leaching.<sup>18</sup> To simultaneously improve barrier properties of a packaging, such different layers can consist of different polymer types which causes incompatibility issues in recycling. In this context, there is a significant drive to develop 'mono-material multilayers' which contain at least 80% of a single polymer *e.g.* polyethylene or polypropylene.<sup>19</sup> While these multilayer films align with current mechanical recycling objectives to avoid incompatibility between polymers, they still contain adhesives/tie layers and inks in the middle layers, which still results in dark colored and odorous plastic recyclates. Therefore, delamination and deinking of monomaterial multilayers is still needed to remove the inks and adhesives. This indicates that a combined deinking and delamination process can become a key technology to boost closed-loop recycling of both monolayer and mono/multi-material multilayer printed plastic films which are typically difficult to deink and delaminate due to their chemical resistance and limited solvent diffusivity *e.g.* UV-based printed plastic films and polyolefin based monomaterial multilayer plastic films.

Current mechanical recycling practices is based on different steps such as sorting, shredding, washing, density separation, drying and finally regranulation. The washing process then typically relies on cold or hot water, whether or not in presence of caustic soda and/or surfactants.<sup>20</sup> Some surfactants can also

induce the removal of inks from plastic films.<sup>21–25</sup> Several initiatives already aim at commercialization of surfactant based deinking, such as the efforts by Keycycle, formerly called Cadel deinking.<sup>26</sup> Similarly, Sorema utilizes an advanced water-based washing system for the removal of inks.<sup>27</sup> Yet, a main drawback of surfactants is their limited effectiveness towards some ink structures *e.g.* UV-based crosslinked inks, and they are not able to penetrate into the polymer matrix, thus they are not always effective for removing inks from multilayer packaging.<sup>28</sup> Solvent-based purification (SBP) is also a widely used technique for recycling of plastic packaging.<sup>29</sup> In the context of deinking of plastic packaging, organic solvents were also widely studied for deinking of flexible plastic packaging. For example, the NorEC® process applies hot ethyl acetate to remove inks and some organic substances from polyolefins.<sup>30</sup> Similar to surfactants, ethyl acetate demonstrates limited effectiveness against cross-linked inks, especially when the ink layer is covered by polymer layers.<sup>31,32</sup> Alternatively, a polymer can be 'deinked' by dissolving the polymer in suited solvents, which allows to filter of the ink binder system which tends to stay solid.<sup>33–38</sup> This method has been applied in several industrial processes such as STAP, CreaSolv®, Newcycling®, and PureCycle.<sup>39–42</sup> However,<sup>33–38</sup> the effect of additives and inks on the purity of recovered polymers has hardly been considered in this process up to now. Furthermore, use of large solvent volumes increases the CAPEX of this technology, and it is a tedious process still facing processing problems such as high viscosity, gel formation and additive encapsulation.<sup>43</sup> Alternatively, delamination of multilayer structures by selective dissolution/depolymerization of the adhesive layer is a promising pathway for recycling of multilayer structures. This has been mainly applied on aluminum (Al) containing multilayers in acid media such as organic acids (*e.g.* acetic acid) or inorganic acids (*e.g.* nitric acid, phosphoric acid).<sup>44–47</sup> In general, only a few scientific papers have given attention to the mechanisms of delamination and deinking, studying for example the influence of different types of laminates such as covalent or hydrogen bonding between (corona treated) polymer layers and the adhesive *e.g.* polyurethane (PU) or acrylics.<sup>48–51</sup> These state-of-the art deinking and delamination processes are summarized in Table 1. Compared to current deinking and delamination methods, this study demonstrates a one-step process that can be applied to a wide range of monolayer and multilayer plastic packaging, including the removal of chemically resistant inks such as UV-cured inks.

In this study, selective aminolysis of adhesive and ink binders is proposed as a novel approach towards simultaneous deinking and delamination of monolayer and multilayer plastic films. To gain deeper insight in the mechanisms, a quadratic model is established that analyses the influence of amine properties and the type of plastic film on deinking efficiency for different plastic films. Furthermore, a specific case study is elaborated to analyse the delamination pathway of a printed multilayer film by focusing on the selective aminolysis of the PU adhesive. The parameters affecting the delamination and deinking process such as temperature, plastic flake size and solid/liquid ratio were assessed through a design of experiment.



**Table 1** State-of-the-art deinking and delamination processes of plastic packaging

| Medium type                             | Chemicals and conditions  | Process   | Applicable to  | Limitations   | Ref.          |
|---|---|---|--|---|---------------|
| Aqueous medium                          | Water based alkaline medium w/ and w/o surfactants at <i>T</i> range between 50° and 100 °C   | Deinking <i>via</i> solubilization of ink resin   | Monolayer packaging  | <ul style="list-style-type: none"> <li>• Not effective on deinking and delamination of many multilayer packaging, including monomaterial multilayers</li> <li>• Generally slow process or ineffective on many binders, especially UV based inks</li> <li>• Harsh acidic conditions</li> </ul> | 21–23 and 27  |
| Inorganic acids                         | Conc./diluted inorganic acids <i>e.g.</i> nitric acid, sulfuric acid at moderate <i>T</i>   | Delamination <i>via</i> degradation of adhesive/polymer, deinking surface printed packaging | Polyolefin (PO) and Al based monolayer and multilayer packaging  | <ul style="list-style-type: none"> <li>• Not applicable on PET</li> <li>• Limited delamination potential</li> <li>• High operation <i>T</i> for high yield</li> </ul>   | 46, 52 and 53 |
| Organic acids                           | Conc./diluted organic acids <i>e.g.</i> formic acid, acetic acid w/ and w/o organic solvents at <i>T</i> range between 20° and 140 °C | Delamination <i>via</i> solubilization of adhesive  | Mainly nonprinted PO and Al based multilayer packaging   | <ul style="list-style-type: none"> <li>• Not effective for deinking</li> <li>• Multiple process steps to recover each polymer</li> </ul>  | 44, 45 and 47 |
| Solvent-based medium – dissolution      | Organic solvents <i>e.g.</i> toluene, DMSO at <i>T</i> above 80 °C  | Delamination <i>via</i> selective dissolution-precipitation of polymer layers               | Multilayer packaging, surface printed monolayer packaging  | <ul style="list-style-type: none"> <li>• Need of high amount of antisolvent for polymer precipitation</li> <li>• Tedious process, beyond a 'wash'</li> </ul>  | 42, 54 and 55 |
| Solvent-based medium – chemical washing | Organic solvents <i>e.g.</i> ethyl acetate at <i>T</i> above 60 °C  | Deinking <i>via</i> solubilization of ink resin   | Monolayer packaging  | <ul style="list-style-type: none"> <li>• Limited delamination potential</li> <li>• Limited activity on many ink binder types</li> <li>• Not effective on removal of UV-based inks</li> <li>• Need of safe handling</li> </ul>   | 30 and 56     |
| Amine-based medium (this study)         | Different types of amines w/ and w/o chemical reagents  | Deinking and delamination <i>via</i> selective aminolysis of adhesive and ink binders       | Broad range of colored monolayer and multilayer packaging including UV-based printed plastic packaging | <ul style="list-style-type: none"> <li>• Potential odor issues at industrial level</li> <li>• Need of further research on solvent recovery and environmental assessment of the process due to potential ecotoxicity of the solvents</li> </ul>  | 57            |

Furthermore, addition of chemical reagents alongside amines such as solvents to enhance polymer swelling and catalysts *e.g.* KOH to accelerate aminolysis was explored to further improve the efficiency of the delamination and deinking processes.

## 2. Materials and methods

### 2.1. Printed plastic films, chemicals, and reagents

Various types of monolayer and multilayer printed plastic films (Table 2) were used during selection of the potential amine. These plastic films were supplied by Siegwark Druckfarben AG & Co. Films printed with UV-crosslinked acrylate is mainly used on rigid plastic packaging such as the

labels of PET bottles and in-mold labeling.<sup>58</sup> Sample 4 containing low migration (LM) ink can be used in nutrition, pharma and hygiene (NPH) applications compared to sample 1, 2 and 3.<sup>59</sup> Samples 5, 6 and 7 are mainly used for food packaging.<sup>60</sup> Among these samples, samples 1 to 6 were used to screen various types of amines, whereas sample 7 was employed to assess the effect of deinking conditions through kinetic experiments. Following amines were used in the tests: ethylene diamine (Fluka Analytical ≥99.5%), 1-pentyl amine (Thermo scientific, 98%), dibutylamine (Merck, ≥99.5%), *N*-ethyl *N*-butyl amine (Merck, >98%), *N*-ethylcyclohexylamine (Alfa Aesar, 97%), diisopropylamine (Merck, >99%), tripropylamine (Merck, ≥98%), *N,N*-dimethylcyclohexylamine (Merck, 99%), 1,6 diamino hexane (Merck, 98%), dicyclohexylamine (Thermo



**Table 2** Composition of monolayer and multilayer printed plastic films used in the tests

| Sample number | Printing type         | Layer 1          | Layer 2                                 | Layer 3                 | Layer 4                | Layer 5        |
|---------------|-----------------------|------------------|---|-------------------------|------------------------|----------------|
| 1             | Acrylate, crosslinked | OPP, white       | Cyan ink layer                          |                         |                        |                |
| 2             | Acrylate, crosslinked | OPP, white       | Cyan ink layer                          | Overprint varnish (OPV) |                        |                |
| 3             | Acrylate, crosslinked | OPP, transparent | White ink layer                         | OPP, transparent        | Cyan ink layer         |                |
| 4             | Acrylate, crosslinked | OPP, transparent | White ink layer, low migration (LM) ink | OPP, transparent        | Cyan ink layer, LM ink |                |
| 5             | Solvent-free PU       | OPP              | NC-magenta                              | SF-PU adhesive          | Transparent PE         |                |
| 6             | Solvent-free PU       | PET              | NC-black ink layer                      | PU-white ink layer      | SF-PU adhesive         | Alu-PP         |
| 7             | Solvent-free PU       | PET              | NC-violet ink layer                     | PU-white ink layer      | SF-PU adhesive         | Transparent PE |

scientific, 98%), *N,N*-dimethylbenzylamine (Merck, ≥99%), piperidine (Acros organics, 99%), triethylamine (Merck, ≥99.5%), and *N,N*-diethylcyclohexylamine (TCI, 98%).

To observe the impact of adding chemical reagents on the efficiency of deinking and delamination, the following chemicals were used in combination with *N*-ethyl *N*-butyl amine (EBA): ethanol (Merck, ≥99.5%), butanol (Merck, ≥99.4%), cyclohexane (Merck, ≥99%), and KOH pellets (Merck, >85%). During the tests, these chemicals were combined with EBA at varying volume ratios ranging from 25 v% to 75 v% at 60 °C for 4 hours. For KOH solution, a 1 w% KOH solution was prepared in water, and this solution was then mixed with EBA for the experiments. As a reference, the results obtained with EBA alone at 60 °C for 4 hours is given.

The generic chemical structures of acrylate and PU compounds used in the inks of the tested samples are given in the figure below (Fig. 1).

## 2.2. Delamination and deinking experiments

Samples 1 to 6 (given in Table 2) were cut to a 1 cm × 1 cm flake size. Three pieces from each sample were then brought into contact with different amines at 75 °C for 4 hours. After testing a range of temperatures between 50 °C and 75 °C, it was observed that higher temperatures accelerated the deinking of plastic films. However, to remain below the boiling point of the amine and to prevent any risk of polymer dissolution, the operating temperature was set at 75 °C. In order to detect the effect of different primary, secondary and tertiary amines (given in Table 3) on the deinking and delamination rate of different samples, each 30 minutes the changes on the samples were noted. Deinking percentage of printed plastic films in different amines were determined through a reflection densitometry approach which detects the amount of residual pigment on the plastic film by means of the intensity of the reflected light. The collected plastic films from the liquid medium were rinsed with water, dried, and scanned together with two reference samples: one sample was a fully colored plastic film, and the other was an unprinted plastic film. A regular image scanner (Canon CanoScan LiDE 400) with a



**Fig. 1** (a) Polyurethane chemical structure; (b) acrylate chemical structure (used as crosslinked ink for samples 1, 2, 3 and 4).

**Table 3** Amines and their corresponding properties used in the correlation matrix

| Class      | Amine                                 | Boiling point (°C) | Log <i>P</i> <sub>b</sub> | Log <i>P</i> at 25 °C | MW (g mol <sup>-1</sup> ) | C <sub>p</sub> (J K <sup>-1</sup> mol <sup>-1</sup> ) | Dipole moment (D) | Dipole polarizability (× 10 <sup>-24</sup> cm <sup>3</sup> ) | Polar surface area (Å <sup>2</sup> ) | Molar volume (cm <sup>3</sup> mol <sup>-1</sup> ) |
|------------|---------------------------------------|--------------------|---------------------------|-----------------------|---------------------------|---|-------------------|--|--------------------------------------|---|
| 1° amine   | 1-Pentyl amine                        | 104                | 3.40                      | 2.9                   | 87.2                      | 120.2   | 0.12              | 0.31   | 26.0                                 | 91.9  |
| 1° diamine | Ethylene diamine                      | 116                | 4.07                      | -2.0                  | 60.1                      | 78.2  | 0.19              | 0.14   | 52.0                                 | 60.8  |
|            | 1,6 Diamino hexane                    | 204.6              | 2.98                      | 0.4                   | 116.2                     | 158.8   | 0.23              | 0.49   | 52.0                                 | 114.7   |
| 2° amine   | Dibutyl amine                         | 159                | 2.61                      | 2.1                   | 129.2                     | 179.6   | 0.90              | 0.61   | 12.0                                 | 134.8   |
|            | <i>N</i> -Ethyl <i>N</i> -butyl amine | 107.5              | 3.31                      | 1.7                   | 101.2                     | 139.2   | 0.92              | 0.41   | 12.0                                 | 109.2   |
|            | <i>N</i> -Ethylcyclo hexyl amine      | 165                | 2.85                      | 1.0                   | 127.2                     | 156.4   | 0.88              | 0.42   | 12.0                                 | 96.9  |
|            | Diisopropylamino                      | 84                 | 2.93                      | 1.4                   | 101.2                     | 144.9   | 0.90              | 0.24   | 12.0                                 | 93.1  |
|            | Dicyclo hexylamine                    | 255.8              | 3.60                      | 2.7                   | 181.3                     | 214.4   | 0.88              | 0.64   | 12.0                                 | 158.2   |
|            | Piperidine                            | 106                | 2.78                      | 0.8                   | 85.1                      | 92.06   | 0.88              | 0.11   | 12.0                                 | 90.8  |
| 3° amine   | Tripropylamine                        | 156                | 3.35                      | 2.5                   | 143.3                     | 202.3   | 0.33              | 0.32   | 3.2                                  | 132.2   |
|            | <i>N,N</i> -Dimethylcyclo hexylamine  | 158                | 3.28                      | 2.3                   | 127.2                     | 157.1   | 0.53              | 0.34   | 3.2                                  | 125.6   |
|            | <i>N,N</i> -Dimethylbenzylamine       | 194                | 5.01                      | 1.9                   | 135.2                     | 154.7   | 0.62              | 0.79   | 3.2                                  | 173.5   |
|            | Triethylamine                         | 88.6               | 3.38                      | 1.6                   | 101.2                     | 141.5   | 0.56              | 0.15   | 3.2                                  | 92.7  |
|            | <i>N,N</i> -Diethylcyclohexyl amine   | 193                | 3.31                      | 2.7                   | 155.3                     | 198.5   | 0.57              | 0.47   | 3.2                                  | 174.3   |



resolution of  $2550 \times 3507$  pixels was used for scanning. The settings (brightness:  $-40$  units, contrast:  $+10$  units) were to optimize visibility of transparent deinked samples. Subsequently, the images were processed using a program written in Python V3.9 programming language with the Open Source Computer Vision Library (OpenCV V4.5.5). The average deinking percentage of each sample in each medium was utilized to compare the effectiveness of the mediums. Detailed processing steps of determining ink density on the plastic films are given in Ügdüler *et al.*<sup>32</sup>

### 2.3. Construction of quadratic model to estimate deinking efficiency

To investigate the relationship between amine properties and their effect on the deinking efficiency of plastic films with different compositions, a quadratic model was constructed for each type of plastic film (samples 1–6) listed in Table 2. To achieve this, various properties of amines relevant to deinking and delamination were gathered through the CONductor-like Screening MOdel for Realistic Solvents (COSMO-RS) molecular modeling. The properties of amines considered consists of boiling point,  $pK_b$  value,  $\log P$  value, molecular weight (MW), heat capacity, dipole moment, polar surface area, dipole polarizability and molar volume. To obtain these property values of different amines, COSMO-RS files were generated using Gaussian 16 and processed using Biovia Cosmotherm 20.0.0 (Dassault Systems). The properties of each amine gathered are in Table 3.

Afterwards, Pearson correlation coefficient matrix was examined to evaluate the correlation between the considered properties. The higher the absolute value, the stronger the correlation between the predictors. Therefore, predictors having coefficients with an absolute value higher than 0.7 were eliminated. The correlation matrix was created using the `cor()` function from the Stats package in R and is given in the SI, Fig. S1. Based on the correlation matrix, properties with high intercorrelation—such as volume, molecular weight (MW), dipole polarizability, and  $\log P$ —were excluded from further analysis to avoid redundancy. In the construction of quadratic model, it was seen that  $pK_b$  value and molar volume were not significant, thus they are not included. A quadratic model with the adjusted  $R^2$  value (0.71) was constructed for each plastic packaging based on the interaction of properties of boiling point, heat capacity, dipole moment and polar surface area. Residual analysis and Normal QQ plots given in Fig. S2 indicate that the identified outliers do not exhibit pronounced properties. Based on the significant amine properties, a quadratic model was constructed for each tested sample to estimate the deinking efficiency through following formula:

$$\%Deinking_{\text{sample}} = a \times X1 + b \times X2 + c \times X3 + d \times X4 + e \times X3^2 + f \times X4^2 \quad (1)$$

where,  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  refer to the coefficients and  $X1$ ,  $X2$ ,  $X3$ , and  $X4$  refer to the properties of boiling point, heat capacity, dipole moment and polar surface area, respectively.

### 2.4. Investigating the effect of process parameters and medium composition through kinetic tests

Additionally, kinetic studies were performed on the delamination and deinking of a violet colored PET/PE multilayer sample (sample 7 in Table 2) under different experimental conditions, as defined by central composite inscribed design (CCI). *N*-Ethyl *N*-butyl amine (EBA) was used as medium due to its high potential among the tested amines on this sample. The DoE was constructed based on three factors, namely temperature, particle size and solid/liquid (S/L) ratio as shown in Table 4. The limits of each factor were determined through exploratory experiments to adjust the parameters until a significant change in the delamination rate of MFPFs is observed. For example, while higher temperatures accelerate the deinking process of the plastic film, it was noted that the plastic film begins to curl at elevated temperatures, impeding effective delamination. Therefore, a maximum temperature of  $65^\circ\text{C}$  was chosen for the kinetic studies. The S/L ratio was set between  $0.01\text{ g mL}^{-1}$  and  $0.05\text{ g mL}^{-1}$ , based on the maximum concentration of SF-PU adhesive reaction products ( $490\text{ mg L}^{-1}$ ) observed after 2 hours of interaction with EBA at  $65^\circ\text{C}$ . The particle size range was selected between 0.5 cm and 4 cm based on the standards typically used in the plastic cleaning industry.<sup>61</sup> The experiments for the kinetic study were carried out in a round-bottom flask equipped with a condenser and an overhead agitator with 2-blade impeller, operating at 300 rpm for consistent stirring. The 100 mL flask containing EBA was placed into a thermal bath at room temperature (RT) and pre-heated to the target temperature based on DoE prior to the addition of multilayer plastic film (sample 7) in order to minimize the delays prior to reaching the specified temperature at atmospheric pressure. During the 120 minutes of reaction, a 4 mL aliquot of liquid sample was collected from the medium

**Table 4** Central composite inscribed experimental design (CCI) used to assess the effect of deinking and delamination conditions in *N*-ethyl *N*-butyl amine

| Run | X1     | X2     | X3     | T (°C) | T (K)  | Size (cm) | SL (—) |
|-----|--------|--------|--------|--------|--------|-----------|--------|
| 1   | -1     | -1     | -1     | 33     | 306.15 | 1.2       | 0.02   |
| 2   | 1      | -1     | -1     | 57     | 330.15 | 1.2       | 0.02   |
| 3   | -1     | 1      | -1     | 33     | 306.15 | 3.3       | 0.02   |
| 4   | 1      | 1      | -1     | 57     | 330.15 | 3.3       | 0.02   |
| 5   | -1     | -1     | 1      | 33     | 306.15 | 1.2       | 0.04   |
| 6   | 1      | -1     | 1      | 57     | 330.15 | 1.2       | 0.04   |
| 7   | -1     | 1      | 1      | 33     | 306.15 | 3.3       | 0.04   |
| 8   | 1      | 1      | 1      | 57     | 330.15 | 3.3       | 0.04   |
| 9   | -1.682 | 0      | 0      | 25     | 298.15 | 2.3       | 0.03   |
| 10  | 1.682  | 0      | 0      | 65     | 338.15 | 2.3       | 0.03   |
| 11  | 0      | -1.682 | 0      | 45     | 318.15 | 0.5       | 0.03   |
| 12  | 0      | 1.682  | 0      | 45     | 318.15 | 4.0       | 0.03   |
| 13  | 0      | 0      | -1.682 | 45     | 318.15 | 2.3       | 0.01   |
| 14  | 0      | 0      | 1.682  | 45     | 318.15 | 2.3       | 0.05   |
| 15  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |
| 16  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |
| 17  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |
| 18  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |
| 19  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |
| 20  | 0      | 0      | 0      | 45     | 318.15 | 2.3       | 0.03   |



(50 mL) at every 30 minutes. The collected sample was subsequently transferred into a vial and immersed in an ice bath to stop further reaction of the polyurethane (PU) adhesive. These samples were then subjected to UV-VIS measurements. Utilizing calibration curves developed by using pure cured PU adhesive in EBA, the quantity of adhesive reaction products *e.g.* urea derivatives was quantified as explained in section 2.5.

The influence of process parameters were assessed through analysis of the kinetic experiment results. The delamination % in *N*-ethyl *N*-butyl amine (EBA) after 90 minutes of reaction time served as the reference point for comparing experimental conditions. The initial step involved analyzing the experimental datasets to identify outliers, achieved through residual plots generated by the plot function in R software. Subsequently, the resulting datasets were utilized to establish a quadratic model, describing the relationship between the experimental factors (temperature, S/L ratio, and particle size) and the delamination % after 90 minutes of interaction time. During the construction of the quadratic model, non-significant terms ( $p > 0.05$ ) were incrementally removed, repeating this process until obtaining the quadratic model with the highest adjusted  $R^2$ . This iterative procedure was conducted using the Response Surface Methodology (RSM) package within the R environment. During the optimization, after excluding data points of experiment 2 as outliers, the adjusted  $R^2$  value was 0.90, and the Lack of Fit (LOF) value was 0.11. The following equation was constructed to elucidate the effect of process parameters on the formation of reaction products:

$$Y = \beta_0 + \sum_{i=1}^p \beta_i X_i + \sum_{i=1}^p \sum_{j=1}^p \beta_{ij} X_i X_j + \sum_{i=1}^p \beta_{ii} X_i^2 \quad (2)$$

where  $Y$  is the response (delamination %),  $\beta_0$  is the overall mean response,  $X_i$  and  $X_j$  refer to the  $i^{\text{th}}$  and  $j^{\text{th}}$  factor of the DoE, and  $\beta_i$ ,  $\beta_{ij}$ , and  $\beta_{ii}$  refer to the coefficients describing the main effects for each factor, the two-way interaction between the  $i^{\text{th}}$  and  $j^{\text{th}}$  factors, and the quadratic effect for the  $i^{\text{th}}$  factor, respectively.

### 2.5. Analytical techniques for monitoring adhesive aminolysis

The medium containing the reacted PU adhesive and *N*-ethyl *N*-butyl amine (EBA) was analyzed *via* UV/Vis spectroscopy on a UV-1280 multipurpose UV/Vis spectrophotometer with a scan range of 190–1100 nm. The collected 4 mL aliquots were transferred into a semi-micro quartz cuvette with an outer cell dimension of 12.5 mm × 12.5 mm × 45 mm and an optical pathlength of 10 mm. Pure EBA solutions were measured as a reference. For each sample, the optical spectrum measurements were repeated three times to ensure their consistency and repeatability. In the spectrum, the strongest absorption was recorded at 280 nm for SF-PU adhesive reaction product. Based on the Beer–Lambert law [38], calibration curves were elaborated by using pure SF-PU adhesive at known concentrations. These curves were used to calculate the delamination percentage by correlating the concentration of reaction pro-

ducts with reaction time during the kinetic tests. During calculation of the amount of adhesive reacted in kinetic tests, a correction was made by considering the total amount of adhesive present in the reaction flask in the beginning of the experiment. This was performed by considering the density of the SF-PU adhesive ( $1.1 \text{ g cm}^{-3}$ ) and the mass of the SF-PU adhesive layer per  $\text{cm}^2$  surface area of the violet colored PET/PE multilayer sample (sample 7) used in the kinetic tests ( $0.00033 \text{ g cm}^{-2}$ ). Afterwards, delamination % was expressed in terms of the mass of reacted adhesive which was calculated *via* the following equations:

$$M_A = \frac{M_{\text{Total}}}{M_{\text{sample}}} \times 0.00033 (\text{g cm}^{-2}) \times A \quad (3)$$

$$\text{Delamination (\%)} = \frac{M_t}{M_A} \times 100 \quad (4)$$

where  $M_A$  is the total mass of adhesive present in the multilayer sample used in the kinetic test (g),  $M_{\text{Total}}$  is the total mass of multilayer sample used in the kinetic test (g),  $M_{\text{sample}}$  is the mass of one multilayer particle (g),  $A$  is the surface area of one multilayer particle ( $\text{cm}^2$ ) and  $M_t$  is the mass of adhesive reacted in the solution medium at a specific time during kinetic studies (g).

In order to elucidate the mechanism of delamination and deinking, Fourier-Transform Infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (NMR) measurements were performed on the EBA solution containing SF-PU adhesive. To achieve this, an excess amount of multilayer plastic films, sample 7, around 2 grams, was brought into contact with 20 mL of *N*-ethyl *N*-butyl amine (EBA) at 65 °C, the highest temperature utilized during the kinetic tests, for a duration of 2 hours. Afterwards, the solution was concentrated by using the rotavapor and the obtained crude product was collected for characterization. The FTIR measurements were recorded using the Omnic software in the range of 4000–400  $\text{cm}^{-1}$ , at resolution of 4  $\text{cm}^{-1}$  and with 32 scans. For each FTIR analysis, automatic smooth and baseline correction was applied. 1D proton NMR and 2D homonuclear CORrelation Spectroscopy (COSY) spectra (Fig. S3) were recorded using Bruker Avance 400 Ultrashield at room temperature in deuterated dimethyl sulfoxide (DMSO- $d_6$ ). The spectra were analyzed using ACDLabs Spectrus Processor.

## 3. Results and discussion

### 3.1. Comparison of the effectiveness of different amines

To assess the impact of various amines on the deinking of different types of plastic films, six different plastic films given in Table 2 were tested in 14 different amines at 75 °C during 4 hours, after which a quantitative scan was taken on the deinked plastic film. Results are detailed in Table 5. Based on the experimental data, including replicates for each sample-amine combination, a two-factor ANOVA was conducted to assess the significance of differences among amines and film





$$\begin{aligned} \%Deinking_{\text{sample 4}} = & 110.7 + 3.7 \times X1 - 4.1 \times X2 - 28.0 \times X3 \\ & + 106.2 \times X4 - 39.4 \times X3^2 - 42.8 \times X4^2 \end{aligned} \quad (8)$$

$$\begin{aligned} \%Deinking_{\text{sample 5}} = & 147.1 + 41.1 \times X1 - 40.9 \times X2 - 26.9 \times X3 \\ & + 71.9 \times X4 - 39.4 \times X3^2 - 42.8 \times X4^2 \end{aligned} \quad (9)$$

$$\begin{aligned} \%Deinking_{\text{sample 6}} = & 151.9 + 17.7 \times X1 - 24.0 \times X2 - 9.1 \times X3 \\ & + 91.0 \times X4 - 39.4 \times X3^2 - 42.8 \times X4^2 \end{aligned} \quad (10)$$

where,  $X1$ ,  $X2$ ,  $X3$ , and  $X4$  refer to the properties of boiling point, heat capacity, dipole moment and polar surface area (PSA), respectively. The coded value of each property used to calculate the deinking efficiency based on the eqn (5)–(10) is given Table S3.

The generated quadratic equations were applied to validate the experimental results presented in Table 5. A consistent trend was observed between the model predictions and experimental deinking efficiency results for the various plastic films tested with different amines. For instance, *N,N*-diethylcyclohexylamine experimentally exhibited no deinking on samples 1, 3, and 4, while achieving the highest deinking efficiency on sample 5, followed by samples 2 and 6. The same deinking efficiency order was observed in the model predictions. The mean absolute error (MAE) between the modeled and experimental results, considering all tested samples and amines, was calculated to be 11.4%. The calculated deinking % values based on the quadratic equations and the calculation of the MAE are given in Table S4.

Based on these quadratic equations, the coefficients for boiling point and heat capacity of the amines are lower than those for dipole moment and polar surface area (PSA), indicating that their influence on deinking efficiency is less significant. In general, the positive coefficient of boiling point ( $X1$ ) in the quadratic models indicates that amines with higher boiling points are associated with increased deinking efficiency. This is somehow a strange result, but is potentially linked to the specific structure of the amines in scope. Indeed, increased boiling point in our amine series is mainly caused by increase in alkyl chain length within the same class of amines which thus results in increasing apolarity of the amines enhancing diffusion through the apolar structure of polyolefins. Notably, sample 5 (NC-magenta colored OPP/PE multilayer) showed a stronger correlation with boiling point (coefficient value of 41.1 compared to other samples), likely because its double polyolefin layers. Similar to boiling point, heat capacity of amines also has small contribution on the deinking efficiency of samples. For most samples, the heat capacity coefficient in the quadratic models is negative, indicating that amines with higher heat capacities tend to exhibit lower deinking efficiency. Since solvents with higher heat capacity absorb more heat before experiencing a temperature increase, this may slow down the aminolysis reaction of inks

and adhesives, especially due to the reaction's temperature-dependent rate. Exceptionally, sample 1 (monolayer OPP film with UV-based cyan ink) and sample 3 (OPP/OPP film with UV-based white and cyan ink) exhibited higher deinking efficiency with amines having a higher heat capacity. This could be attributed to the faster diffusion of amines, which facilitates deinking and delamination in these samples. Since these samples lack an OPV layer or low migration ink (LMI), the increased diffusion through the polyolefin layers in the presence of amines with higher heat capacity becomes a more determining factor for improving deinking efficiency compared to the aminolysis reaction itself. Among the various properties of amines, the dipole moment and polar surface area (PSA) showed the highest contribution to deinking efficiency. Since these two properties exhibit quadratic effects on deinking efficiency, their direct influence is not easily noticeable from the equation itself. Therefore, Fig. S4 illustrates the individual contribution of each amine property ( $X1$ ,  $X2$ ,  $X3$ , and  $X4$ ) to the deinking percentage, providing a more intuitive visualization of their impact. As seen in Fig. S4, for all samples an inverse correlation between dipole moment and deinking efficiency was observed. Similar to the effect of heat capacity, a lower dipole moment indicates a smaller separation of charge or a more symmetrical electron distribution, which corresponds to decreased molecular polarity. This enhanced apolarity facilitates swelling of the apolar polymer matrix, such as polyolefins, allowing the amine to diffuse more effectively into the film and contribute to both delamination and deinking. As indicated by the equations, the quadratic coefficients of dipole moment and polar surface area (PSA) are the same for all samples, suggesting that their contributions to deinking efficiency are comparable. Based on the quadratic equations, it is seen that the deinking efficiency of the plastic films correlates directly with the PSA of the tested amines. It can be observed in Fig. S4 that PSA ( $X4$ ) has quadratic impact on the response value for all the samples. Amines with higher PSA are able to interact more effectively with the polar adhesive and ink components, such as the polyurethane (PU)-based adhesive and nitrocellulose (NC)-based ink present in the tested samples. Despite the increased polarity of amines with higher PSA, amines like ethylene diamine, 1-pentyl amine, and 1,6-diaminohexane, which possess higher PSA, are primary amines, enabling them to diffuse more rapidly through the polymer layers. This combination of faster diffusion and stronger chemical interaction with adhesive and inks results in more efficient deinking and delamination of the plastic films. As shown, chemically resistant inks such as UV-based inks require harsher deinking conditions for effective removal. Therefore, developing new ink binders that incorporate reversible or cleavable bonds could enable easier removal of inks, including UV-based types, during recycling.<sup>62–64</sup>

### 3.2. Mechanism of delamination and deinking

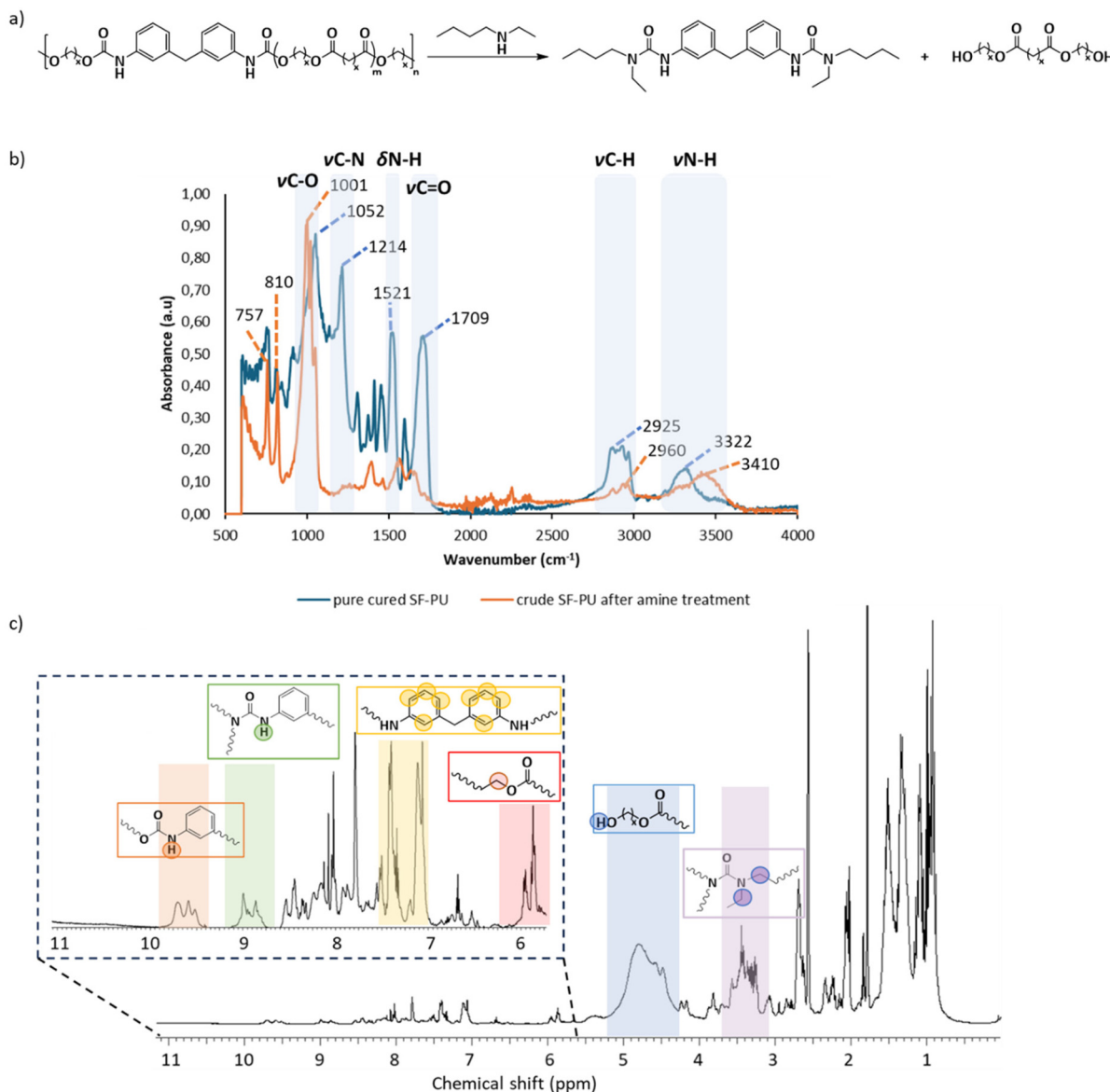
To investigate the underlying mechanism of the delamination of multilayer samples, the reactivity of the PU adhesive was studied. For this, the multilayer structure laminated through



the aromatic polyester PU adhesive (sample 7, Table 2) was treated with *N*-ethyl *N*-butyl amine (EBA) at 65 °C for 2 hours. As shown in Fig. 2a, it is expected that the PU adhesive will undergo aminolysis during delamination with the amine, yielding urea and polyol adducts. Therefore, changes in the chemical structure of the PU adhesive were monitored using FTIR and NMR measurements (Fig. 2b and c, respectively). Detailed FTIR peaks of the pure cured SF-PU adhesive together with their description and assignment are given in the SI, Table S1.

The FTIR spectrum provides clear evidence of polyurethane undergoing aminolysis. Initially, the polyurethane spectrum displays characteristic peaks such as a broad N–H stretching ( $\nu$ N–H) band around 3320  $\text{cm}^{-1}$ , a strong C=O stretching peak

near 1700  $\text{cm}^{-1}$ , and distinct C–N and C–O stretching vibrations at approximately 1220  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$ , respectively. Upon aminolysis, changes in the FTIR spectrum are observed. The N–H stretching peak shifted towards higher wavenumber ( $\sim$ 3400  $\text{cm}^{-1}$ ) indicating the breakdown of urethane linkages. Since the peaks associated with hydroxyl groups also appear around this wavenumber, only small decrease in the peak intensity can be attributed to the formation of alcohols. Furthermore, the C=O stretching peak decreased in intensity, reflecting the conversion of urethane groups into urea derivatives. It was also noticed that there is a substantial decrease in C–N stretching and N–H bending vibrations after the amine treatment (orange line in Fig. 2b). Aminolysis transforms the urethane groups into urea deriva-



**Fig. 2** (a) Chemical reaction scheme of aromatic polyester polyurethane (PU) with *N*-ethyl *N*-butyl amine (EBA); (b) FTIR spectra of the aromatic polyester polyurethane (PU) adhesive before and after EBA treatment; (c) NMR spectrum of the aromatic polyester polyurethane (PU) adhesive after EBA treatment.







**Fig. 3** Experimental kinetic data of delamination of the violet colored PET/PE multilayer sample (sample 7) through selective aminolysis of the adhesive in *N*-ethyl *N*-butyl amine (EBA) during 120 minutes. Detailed experimental data points are given in the SI, Table S2. The data points are connected with dashed lines for easier visualization. The standard deviation of delamination %, based on the 6 center points of DoE, is 5.97%.

higher temperature. This is due to the interaction between the experimental parameters which impacts the delamination rate. Therefore, the relationship between experimental parameters was described through Response Surface Methodology (RSM), as given in eqn (11) where  $X_1$ ,  $X_2$  and  $X_3$  refer to the coded values of temperature, particle size and S/L ratio, respectively.  $\epsilon$  represents the model error, calculated as twice the residual standard error (5.75%), resulting in an estimated error of 11.5% at a 95% confidence interval.

$$Y_{\text{Delamination \%}} = 2.9 + 1.4 \times X_1 - 15.5 \times X_2 - 7.7 \times X_3 + 2.9 \times X_1^2 + 9.2 \times X_2^2 + 9.2 \times X_3^2 + 2.5 \times X_1 \times X_2 + 3.6 \times X_2 \times X_3 \mp \epsilon \quad (11)$$

Using the quadratic equation and coefficients, it is possible to determine which parameter or interaction between parameters has the most pronounced effect on increasing delamination %. For example, among all the process variables, particle size ( $X_2$ ) makes the highest negative contribution (with a coefficient value 15.5), followed by S/L ratio ( $X_3$ ) for obtaining a higher delamination %. Similarly, in terms of interaction of the parameters, particle size and S/L ratio interaction plays a crucial role on increasing the delamination yield. The relationship between the experimental parameters and its effect on the delamination yield is visualized through the surface plots given in Fig. 4.

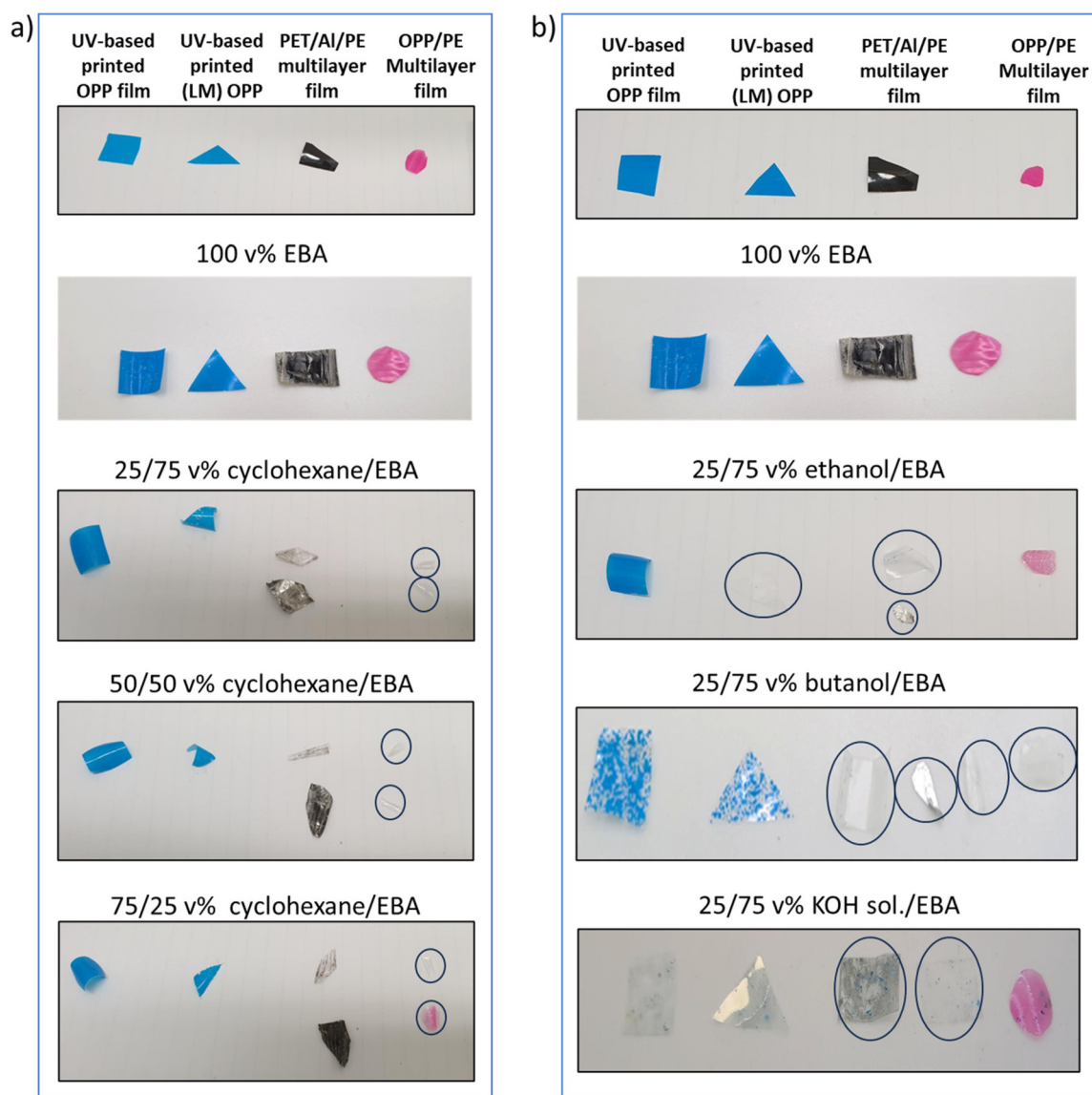
Fig. 4a shows that smaller particle size significantly enhance the delamination yield, even at lower temperatures. As the delamination rate was influenced by particle size, it suggests that lateral diffusion of the amine through the sides of the multilayer film can also play a significant role. In our research on the delamination and deinking of plastic films using carboxylic acids, there were indications that frontal diffusion of the acid was potentially more profound.<sup>66</sup> This may be attributed to the lower polarity of amines compared to short-chain carboxylic acids, which enhances polymer swelling and, in turn, increases the potential for lateral diffusion. The greater impact of reduced particle size on delamination yield,



**Fig. 4** Response surfaces of the delamination % as a function of (a) temperature (°C) and particle size (cm); (b) temperature (°C) and S/L ratio ( $\text{g mL}^{-1}$ ); (c) particle size (cm) and S/L ratio ( $\text{g mL}^{-1}$ ) for delamination of sample 7 through selective aminolysis of the PU adhesive layer. Delamination percentages exceeding 100% fall within the experimental error margin of the RSM model and are normalized to 100%.







**Fig. 5** Deinking and delamination of 4 different plastic films (a) in cyclohexane/*N*-ethyl *N*-butyl amine (EBA) mixture at different volume ratios; (b) in ethanol/EBA, butanol/EBA and KOH solution/EBA mixtures at 25/75 v% ratio after 4 h contact at 60 °C. Hourly visual progression of deinking and delamination of these samples in each medium is given in Fig. S5.

minimizing damage to the plastic and metallic layers. Ultimately, the careful selection and dosage of chemical reagents such as alkaline agents, solvents, or catalysts is essential to balance process efficiency with the preservation of material integrity. Tailoring the chemical environment to the specific composition of the plastic films ensures optimal performance of the delamination process without compromising recycle quality.

## 4. Conclusion

Delamination and deinking of plastic packaging is a key process in the circular economy of plastics. In this study, selec-

tive aminolysis of adhesive and ink binders is proposed as a novel approach towards simultaneous deinking and delamination of monolayer and multilayer plastic films. In general, amines, potentially with additions of some solvent or catalyst are able to delaminate and deink a wide array of printed multilayer flexible packaging.

Our study shows that it would be beneficial to align amine type, depending on the plastic film structure if possible, maybe in future, based on advanced sorting. Regarding sample composition, multilayer films printed with UV-cured inks exhibited significantly lower deinking efficiency ( $p < 0.05$ ) compared to other samples, with values below 10% for most amines. This is likely due to the high chemical resistance and crosslinked structure of UV-cured inks. Yet, primary amines









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