



Understanding the complexity of deinking plastic waste: An assessment of the efficiency of different treatments to remove ink resins from printed plastic film

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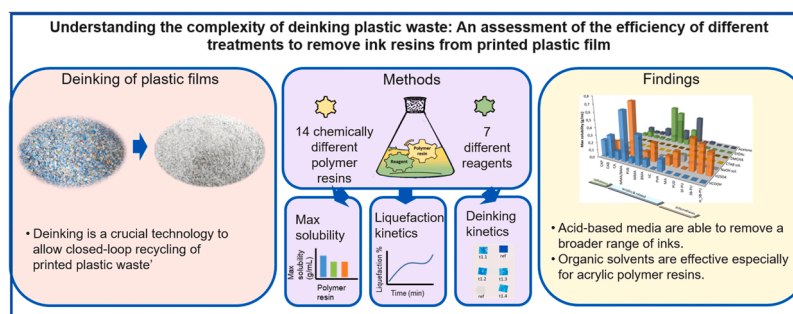
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HIGHLIGHTS

- Ink removal is key towards closed-loop recycling of printed plastics.
- Scientific insights into the effectiveness of different deinking techniques were provided.
- Acid-based media are able to remove a broader range of inks.
- Organic solvents are particularly effective against acrylic-based polymer resins.
- Basic cost and environmental impact analysis was given.

GRAPHICAL ABSTRACT



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ABSTRACT

Plastic packaging is usually heavily printed with inks to provide functional benefits. However, the presence of inks strongly impedes the closed-loop recycling of plastic films. Various media have already been studied for the deinking of plastic films, but there is little scientific insight into the effectiveness of different deinking techniques. Therefore, this study aims to obtain a systematic understanding by measuring the liquefaction and maximum solubility of 14 chemically different polymer resins in seven different media typically used in plastic deinking, such as acetone, ethyl acetate, sodium hydroxide solution, cetyltrimethylammonium bromide solution, formic acid, sulfuric acid, and N,N-dimethylcyclohexylamine. Our findings show that acid-based media are able to remove a broader range of polymer resins. Organic solvents are particularly effective against acrylics and

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related polymer resins. The deinking efficiency tests on pure resins are also confirmed by deinking four printed plastic films containing different classes of polymer resins. A basic cost and environmental impact analysis is given to evaluate scale-up potential of the deinking medium.

Environmental Implications

More than 50 % of plastic packaging remains landfilled and incinerated, resulting in devastating environmental effects, such as carbon dioxide emissions, soil and marine pollution, and release of toxic gases. As a result, stringent legislation is put in place on the recycling of plastic packaging. However, the presence of heterogenous compounds, such as printing inks, impedes the quality of recyclates, resulting in open-loop recycling. In this study, the removal efficiency of ink resins was studied to obtain understanding of the potential of deinking media to achieve clean recyclates with higher potential for closed-loop recycling.

Data Availability

Data will be made available on request.

1. Introduction

Plastic packaging is used in various fields, such as pharmaceutical, food, electronics, and construction. This is due to the ability of plastic packaging to offer various functional performances, depending on the field requirements, such as an oxygen, moisture, and light barriers, high printability, and longer food preservation [1]. However, the broad applicability of plastic packaging implies vast waste generation. Around 35 kg of plastic packaging waste was generated per person in 2019 by the European Union [2]. Due to suboptimal plastic waste management over the last decades, the general perception of plastic is far from positive, which pushes consumers toward using alternative packaging, such as paper, glass, and aluminum cans. Nevertheless, plastic is a great candidate material for a sustainable economy due to its thin film thickness typically somewhere in between 10 and 250 μm [3] and light weight, resulting in lower energy consumption during production and lower transport costs compared with alternatives. For example, plastic grocery bags consume 71 % less energy during production than paper bags [4]. However, to be a sustainable material, plastic recycling rates should increase through recycling design, better infrastructure for collection and advanced sorting, and new recycling technologies [5].

One of the components impeding the closed-loop recycling of flexible packaging is the use of printing inks. Plastic packaging is usually heavily printed with inks through different printing technologies, such as continuous inkjet and laser marking [6]. Printing inks provides plastic packaging with various functional benefits, such as including information about composition, presence of allergens and nutritional details, and making packaging visually more attractive to consumers for marketing purposes. Although inks seem to be a necessary component of plastic packaging, they are a significant source of contamination in plastic recycling. As all printed plastic films are generally collected and processed together, low-quality brownish, greyish, or black recyclates are obtained, making them only suitable for downcycled products [7]. The presence of ink tends to cause recycled films to be less stiff, weaker, and denser than the original material [1]. Furthermore, during reprocessing, residual ink can also decompose and produce gases, causing rancid odor formation and decreasing the physical properties of the raw material [8]. Therefore, the price of recycled films containing inks is considerably lower than that of transparent films [1]. To eliminate these problems and obtain high-quality recyclates, interest in deinking technologies is increasing.

For effective deinking, it is important to realize that the main

constituents of printing inks are resins, solvents, colorants, and additives [8]. Resins are high-molecular-weight polymers constituting 15–50 % of the ink composition, and they act as a binder for colorant stabilization and also for adhesion to the substrate [9,10]. Solvents account for the largest part of the ink formulation (up to 65 %), and they are used to dissolve the resins and keep the ink in a liquid state to allow proper ink transfer [9,11]. Colorants used to give the desired color to plastic packaging constitute 5–30 % of the ink composition [9,10]. In addition to colorants, lacquers, or overprint varnishes are uncolored printing inks that can be used to provide gloss and protection to the print [10]. Additives are generally used up to 10 % to improve the physicochemical properties of inks, such as adhesion, slip, and scratch resistance [12,13]. The composition of these ink components can differ considerably depending on the printing process and the substrate. For example, solvent-based inks in which organic solvents are used to solubilize polymer resins are preferred for applications in which sufficient substrate wetting and adhesion are crucial [14]. Contrary to solvent and water-based inks, in which the drying of inks is performed through the evaporation of the liquid medium, ultraviolet (UV) radiation is used for drying in UV-based inks. These UV-based inks require reactive resins, such as acrylates, which can react with free radicals created by UV radiation [10,11]. This extensive variety in ink compositions not only broadens the functionality and application area of plastic packaging but also increases the complexity of recycling, specifically the deinking process.

Various studies have focused on the removal of inks from plastic packaging. Among different deinking media, surfactants have been extensively studied as a potential deinking medium [15–19]. For example, Chotipong et al. (2007) found that cationic surfactants, such as cetyltrimethylammonium bromide (CTAB), were effective in removing water- and solvent-based inks [19]. Moreover, critical micelle concentrations (CMC), pH of the medium, temperature, and stirring were found to be important parameters for deinking efficiency [19]. Through a patented method (EP2832459B1), a cationic surfactant was used to remove inks from plastic packaging [20]. This method was demonstrated in a deinking plant with a treatment capacity of 100 kg/h [20]. The use of surfactants to deink plastic films was also described in another patent filed (EP1419829A1) [21] in which a mixture of organic solvents and non-ionic surfactant was used as a deinking medium. In addition to surfactants, organic solvents are also used as a deinking medium. For example, in the patented Nordenia Extraction and Cleaning (Norec®) process (DE19651571A1), ethyl acetate is used as a solvent-based extraction medium to remove a broad range of inks [22]. The Norec® process is currently applied in an industrial packaging plant in north Germany, with a capacity of 70,000 tons per annum [22]. Aside from deinking purposes, different liquid media are used for the pre-treatment of plastic packaging, such as delamination, deodorization, and removal of food remnants. For example, the polyethylene terephthalate (PET) bottle recycling industry generally utilizes a water medium containing 2–3 % sodium hydroxide (NaOH) and certain detergents to reduce surface contaminants and remove labels and glue [23]. For the delamination of multilayer plastic packaging, the performance of various organic solvents and acids has also been highlighted. Mumladze et al. used switchable hydrophilicity solvents (SHSs), such as N,N-dimethylcyclohexylamine (DMCHA), to recover each constituent polymer layer individually [24]. Similarly, in the patented method of Panagiotis et al., a cured composite laminate material is delaminated by soaking in one or more solvents, such as water, benzyl alcohol, acetone, methyl ethyl ketone, or a combination of one or more thereof [25]. Aside from organic solvents, organic acids, such as formic acid and acetic acid,

have also been extensively studied for the delamination of multilayer structures through the liquefaction of adhesive between the constituent polymer layers [26–29]. In addition, an inorganic acid-based method (WO 2021/198437) was developed that could remove ink structures from polyolefin-based plastic films.

Although various media have been studied in the context of resin removal from plastic film waste, there has been no systematic study that aims to understand the efficiency of these media in deinking various types of inks. As chemically different polymer resins are used in the production of printing inks, depending on the application purpose, it is questionable whether all treatments could remove all resins and how effective they could be. Although each commercial deinking process claims to have superior deinking performance, it is difficult to compare which deinking process is exactly how effective against a certain ink type. Therefore, the objective of this study was to gain a systematic understanding of the effectiveness of different media in different types of polymer resins. This is achieved by the following:

- The investigation of liquefaction % and maximum solubility of 14 chemically different polymer resins (i.e., cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB), cellulose acetate (CA), methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer, polyvinyl butyral (PVB), poly(methyl methacrylate), poly(n-butyl methacrylate), hydroxyl containing copolymer of vinyl chloride (VC) and acid esters, polyvinyl acetate (PVA), medium molecular weight (MW) acrylic polymer, polyurethane dispersion (PUD), medium-performance solvent-free polyurethane (PU), medium-performance solvent-based PU, and high-performance solvent-based PU (H₂SB-PU)) typically used in printing inks for plastic films in seven different media used in plastic pretreatment, such as acetone, ethyl acetate, NaOH solution, CTAB solution, formic acid, sulfuric acid and DMCHA. Note that the term liquefaction can refer to both dissolution and reaction, as the interaction mechanism of the different liquids is different;
- Confirming the findings on pure resins by deinking four printed plastic films containing different classes of polymer resins;
- Understanding the correlation between the chemical structure of the polymer resin and the deinking efficiency of the medium and proposing solutions for recycling design.

This systematic knowledge related to resin removal from plastic film is essential in the further development of deinking processes and recycling designs.

2. Materials and methods

2.1. Samples, chemicals, and reagents

Pure polymer resins were supplied by Allnex and Bostik companies in Belgium. The physical properties and chemical structures of these polymer resins are presented in Table 1.

The maximum solubility and liquefaction of these 14 polymer resins were quantified in seven liquid media: acetone, ethyl acetate, 2 w % NaOH solution, formic acid, sulfuric acid, an aqueous/caustic detergent solution (CTAB) and DMCHA. Acetone (≥ 99.5 %) and ethyl acetate (≥ 99.5 %) were supplied by ChemLab. DMCHA (99 %), formic acid (≥ 98 w %), sulfuric acid (96 w %–98 w %), CTAB powder (≥ 98 w %), and NaOH pellets (≥ 98 w %) were supplied by Sigma Aldrich (Merck). The caustic solution was prepared by dissolving 2 w % of NaOH pellets in water. A CTAB solution was prepared at a concentration of 0.92 mM (corresponding to 10 times the CMC) in basic medium using NaOH pellets (pH 13). The other liquids were used as received.

To analyze the effect of polymer resin on the deinking rate, kinetic tests were performed on plastic films printed with different types of water-based ink resins through gravure printing, as shown in Table 2. These printed plastic films were provided by Siegwirk Druckfarben AG

& Co. The plastic films were used in the kinetic tests as received at particle sizes of 2.5 cm × 3 cm without prior pretreatment.

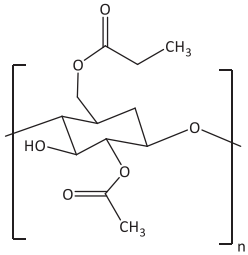
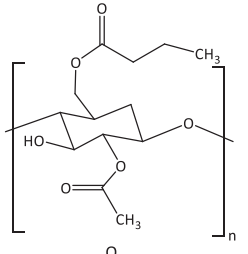
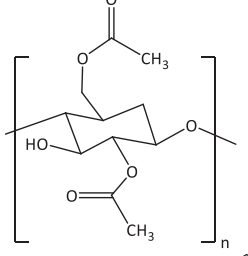
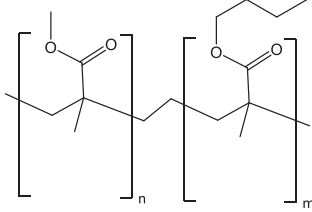
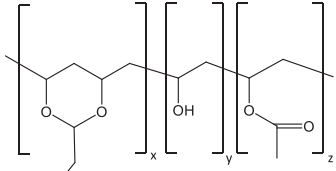
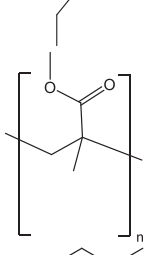
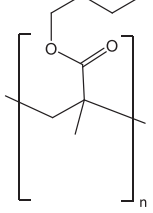
2.2. Solubility analysis and liquefaction tests

The maximum solubility of each polymer resin in seven different liquid media (i.e., acetone, ethyl acetate, NaOH solution, formic acid, sulfuric acid, CTAB solution, and DMCHA) was determined. An excess amount of polymer resin, which was examined through prescreening experiments, was brought into contact with 5 mL of the liquid medium and stirred at room temperature (RT) with a magnetic stirrer for 24 h. Afterwards, the undissolved polymer resins were separated through filtration, and the supernatant was analyzed using ultraviolet–visible spectroscopy (UV–vis) or thermogravimetric analysis with Fourier transform infrared spectroscopy (TGA-FTIR) by making calibration curves (Appendix Figure A-2–Figure A-8). Once the maximum solubility of each polymer in each medium was defined, kinetic tests were performed at RT to investigate the liquefaction rate of the polymer resins. Note that liquefaction can mean both dissolution and chemical reactions. The amount of polymer resin used in the kinetic tests was kept below the solubility limits of each resin to follow the liquefaction rate. To avoid an impact of the particle size in the kinetic analysis when comparing the different resins, sequential sieving was performed on the solid powder polymer resins, and a fraction with a particle size of 30–150 μ m was collected. During the kinetic tests, each polymer resin was treated with 40 mL of liquid medium at RT through continuous stirring at 150 rpm. The amount of each polymer resin used in the kinetics was determined based on maximum solubility. During 30 min of liquefaction, aliquots of 3 mL were collected at each specific time interval (i.e., at 1 min, 5 min, 10 min, 20 min, and 30 min). Thirty minutes interaction time was used as a typical residence time for washing lines in industry. For example, the residence time of post-consumer PET plastic washing with 2 w % NaOH is 30 min [30]. Furthermore, in previous studies in which some of the media used in this study were presented, the interaction time was kept below 30 min. For example, CTAB solution and DMCHA were contacted with plastic films during 15 min and 10 min, sequentially for removal of printing inks from plastic films [16,24]. Each experiment was repeated two times to obtain an indication of the standard deviation. Afterwards, the collected samples were analyzed using UV–VIS or TGA-FTIR for the quantification of the dissolved polymer resin during the kinetic tests.

To determine the correlation between the liquefaction rate of the polymer resin and the deinking rate of the plastic film printed with that specific polymer resin, kinetic tests were performed on the printed plastic films listed in Table 2. First, each printed plastic film was cut to a 2.5 cm × 3 cm size using an automatic cutting tool (Cricut adaptive tool system). The cut samples were brought into contact with 40 mL of liquid medium at RT by stirring at 150 rpm on a rotary shaker (GFL orbital shaker 3017). A control test was performed by bringing a printed plastic film in contact with water at RT for 5 h to observe the effect of friction between the plastic films on deinking. Although no deinking was observed after water treatment, there might be a risk that once the plastic films are treated with a medium having solvation power on the polymer resin, ink might detach faster from the plastic surface in the presence of friction. In order to measure deinking resulting only from the interaction with the medium and not from the friction between the plastic films, a separate beaker was used for each time interval (at 1 min, 5 min, 10 min, 20 min and 30 min). Yet, it should be noted that in industrial scale operations high shear might be applied causing friction between particles which could be beneficial for deinking. Four samples were analyzed at each time point to calculate the standard deviation. The collected samples were then scanned to calculate the remaining ink density on the plastic surface, thus following the deinking process of the printed plastic film in each medium. The sequence of the kinetic tests performed on the printed plastic films is illustrated in Fig. 1. The obtained deinking efficiency was calculated based on the amount of the

Table 1

The tested polymer resins and their corresponding chemical structures. The acronyms refer to the abbreviations of the polymer resins used throughout the manuscript.

Polymer resin no.	Acronym	Polymer resin	Chemical structure
1	CAP	Cellulose acetate propionate	
2	CAB	Cellulose acetate butyrate	
3	CA	Cellulose acetate	
4	MMA/ BMA	methyl methacrylate/ butyl methacrylate copolymer	
5	PVB	Polyvinyl butyral resin	
6	MMA	Low-molecular-weight poly(methyl methacrylate)	
7	BMA	Poly(n-butyl methacrylate)	

(continued on next page)

Table 1 (continued)

Polymer resin no.	Acronym	Polymer resin	Chemical structure
8	VC	Hydroxyl containing copolymer of approx. 75 w % vinyl chloride (VC) and approx. 25 w % carbon acid esters	
9	PVA	Polyvinyl acetate	
10	MA	Medium MW polyacrylic resin	
11	PUD	Polyurethane dispersion (PUD) with low viscosity	
12	SF-PU	Medium-performance solvent-free polyurethane	
13	SB-PU	Medium-performance solvent-based polyurethane	
14	H_SB-PU	High-performance solvent-based polyurethane	

Table 2

Tested plastic films printed with inks including a specific type of polymer resin.

Sample no.	Polymer resin class	Substrate	Layer 1	Ink layer thickness (mm)
1	Nitrocellulose	Transparent LDPE	Black	0.006
2	Acrylate	Transparent PP	Cyan	0.005
3	Polyvinyl butyral	Transparent LDPE	Cyan	0.007
4	Polyurethane	Transparent LDPE	Black	0.006

residual pigment obtained by means of the intensity of the reflected light. This procedure is explained in Section 2.4. In this study, it is considered that the medium only attacks the ink layer as it is stated in

literature that polyolefins which are also the substrates of printed plastic films used in this study, exhibit excellent resistance to acids, bases and aliphatic and aromatic hydrocarbons at RT [31].

2.3. Analytical techniques for the quantification of polymer resins in the medium

The dissolved amount of polymer resin in each liquid medium during the kinetic tests was analyzed through UV/VIS spectroscopy using a UV-1280 multipurpose UV/VIS spectrophotometer, with a scan range of 190–1100 nm. The collected 3 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 liquid media were measured as a reference. For each sample, the optical spectrum measurements were repeated three times to ensure consistency and repeatability. UV/VIS spectroscopy was also used to

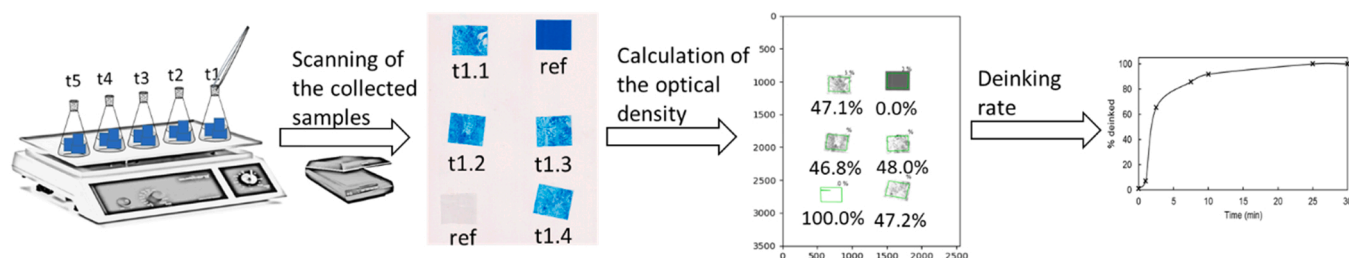


Fig. 1. Sequence of kinetic tests performed on printed plastic films to assess the deinking process.

determine the maximum solubility of the polymer resins in each medium. Some polymer resins resulted in a viscous solution during liquefaction. For these polymer resins, a NETZSCH TG 209 F3 Tarsus thermogravimetric analyzer coupled to a Nicolet™ iS20 Fourier transform infrared spectroscopy (TG-FTIR) was used to perform the analyses. As the FTIR unit allows the detection of the evolved gases derived from the sample decomposed within the TGA, as such quantification of the dissolved polymer resin was achieved by determining the mass change caused by the solvent and the polymer separately. A general temperature profile was developed for the analyses. The experiments started at a temperature of 30 °C and heated until 50 °C at a heating rate of 10 °C/min. This temperature was held for 10 min. Afterwards, the temperature was increased to 400 °C at a heating rate of 20 °C/min and kept at this temperature for 5 min, followed by an increase in temperature until 600 °C at a heating rate of 20 °C/min. An inert environment was established with nitrogen gas at a flow rate of 20 mL min⁻¹. Once the TG coupled to the FTIR unit, the off-gassing materials are directed through a transfer line to a gas cell, where the infrared light interacts with the gases. The transfer line was preheated till 280 °C for 4 h. The FTIR data were measured using OMNIC spectroscopy software and OMNIC Series time-base software. Before the data collection, background and Gram-Schmidt (GS) basis vector collection was performed at 4 cm⁻¹ resolution. GS allows to visualize the total change in the spectrum from the initial time. Afterwards, FTIR data collection of the sample was started at the same time with the TG measurement and the FTIR data were collected for 1 h. After the measurement, multi-component searching was performed by sending the OMNIC data to OMNIC Spectra where the evolved volatiles were analyzed in the FTIR range of 4000–400 cm⁻¹. Based on this temperature profile, mass change at 25–30 min was used to calculate the amount of polymer resin (Appendix Figure A-2–Figure A-8).

2.4. Quantification of ink density on printed plastic films during kinetic tests

To determine the deinking percentage of printed plastic films in different media, a reflection densitometry approach was used to measure the amount of residual pigment by means of the intensity of the reflected light. During the kinetic tests, the solid samples taken out of the medium at different time periods (1, 5, 10, 20, and 30 min) were rinsed with water, dried, and scanned together with two reference samples: one sample was a fully colored plastic film (top right), and the other was an unprinted plastic film (bottom left), as shown in Fig. 2. A regular image scanner (Canon CanoScan LiDE 400) with a resolution of 2550 × 3507 pixels was used for scanning. The setting (brightness: -40 units, contrast: +10 units) was adjusted to provide the highest visibility of transparent deinked samples. The images were then processed using a program written in Python V3.9 programming language with the Open Source Computer Vision Library (OpenCV V4.5.5). This library was used to automatically detect samples and localize them in the image coordinate system. The following steps were applied consecutively:

- The image was gray-scaled because the OpenCV functions only work with one channel;

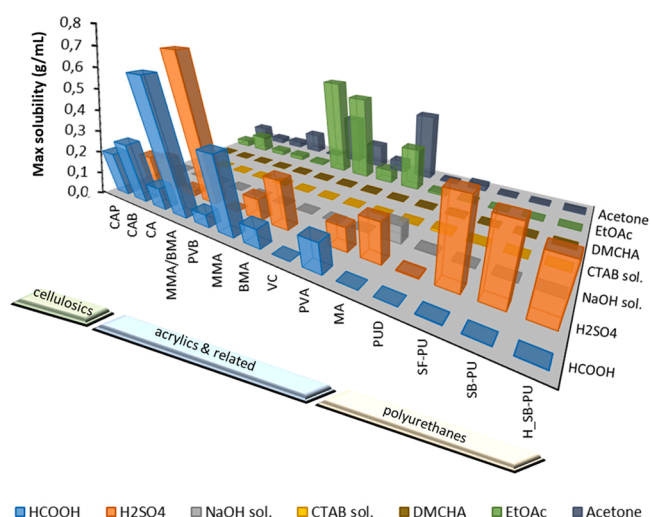


Fig. 2. Maximum solubility of different polymer resins in seven different media at RT (the detailed solubility numbers together with the standard deviation are shown in Appendix Table A-1.).

- Gaussian blur was applied to prevent partial segmentation of the samples. For the tested samples, a kernel of 25 × 25 pixels was experimentally found to be optimal;
- The adaptive threshold function was used to increase the recognition of a transparent plastic film and to prevent excessive noise. An adaptive threshold with a sub-region size of approximately double the sample size was found to be optimal for the tested samples;
- Size filtering was applied to ignore the small artifacts induced by noise, as the dimensions of the samples were kept constant. To merge the deinked areas on the plastic surface, a dilation function with a kernel of 5 × 5 pixels was used;
- The minimum area rectangle function was used to eliminate residual defects, such as the concavity of the obtained contour and wiped-out corners.

By following this procedure, the number of arrays with values from 0 (black) to 255 (white), representing the shades of gray, was obtained, which correlated with the amount of ink remaining on the plastic film. Based on this, the deinking efficiency (%) was calculated as follows:

$$\text{deinking efficiency}(\%) = \frac{d_{\text{sample}} - d_{\text{min}}}{d_{\text{max}} - d_{\text{min}}} \times 100 \quad (1)$$

where d_{sample} , d_{min} , and d_{max} are the average gray values of the collected sample, transparent plastic film, and fully printed plastic film, respectively.

3. Results and discussion

3.1. Solubility of polymer resins in different media

Deinking is the process of removing polymer resin from a plastic film and releasing colored pigment in the liquid. Solubility is an indication of the “capacity” of a liquid to deink a printed plastic film. If a liquid has high solubility for a certain resin, it can liquefy more resin and thus deink more plastic films. Thus, 14 different polymer resins (Table 1) at RT were investigated in seven different liquid media (i.e., acetone, ethyl acetate, NaOH solution, formic acid, sulfuric acid, CTAB solution, and DMCHA) typically used in plastic pretreatment. The results are shown in Fig. 2. The solubility, expressed as g resin per mL liquid of each polymer resin, together with the standard deviation, is shown in Appendix Table A-1.

As shown in Fig. 2, the tested polymer resins were categorized into three groups: cellulose, acrylics & related, and polyurethanes. Among these categories, polyurethanes generally exhibited the lowest solubility in most of the liquid media tested. This is mainly due to the high chemical resistance of polyurethanes, which requires harsh conditions such as oxidizing acids and/or catalysts to break the stable carbamate bond. Sulfuric acid was able to solubilize the tested polyurethanes to the highest extent. As shown in Fig. 2, the oxidation and hydrolysis capability of sulfuric acid also resulted in the solubility of a broader range of polymer resins. Another acid medium, formic acid, has also been tested for the solubility of different types of polymer resins. Formic acid is generally used for the delamination of multilayer plastic films through the liquefaction of tie layers, which are generally PU-based polymers [26,27,32]. Compared with sulfuric acid, formic acid does not have an oxidation capability and seems to have a lower liquefaction power for PUs. The literature also indicates that the solubility of PUs in formic acid is low [33,34]. However, formic acid is an efficient medium for solubilizing most cellulose and acrylic polymer resins. Among other tested media, organic solvents, such as acetone and ethyl acetate, have been shown to solubilize acrylic and related polymer resins. The high solubility of acrylates, such as poly(methyl methacrylate) in acetone, has also been shown in various studies [35–37]. Acetone has been used for the delamination of multilayer packaging composed of metallized PET and low-density polyethylene (LDPE) through the liquefaction of a two-component solvent-based polyurethane adhesive (SB-PU) layer [38]. In this study, acetone was able to dissolve the SB-PU adhesives to some extent, but their solubility in acetone was 10 times lower compared to the acrylic-based polymer resins (Table A-1). The ethyl acetate-based extraction process known as Norec® is applied industrially to remove dirt, soil, fatty and waxy pollutants, and some types of printing inks and odor components from plastics [39]. In this patented process [40], the removal efficiency of printing inks depending on the type of polymer resin was not stated, but as shown in Fig. 2, ethyl acetate showed a higher affinity to liquefy acrylic-based polymer resins due to its polar structure but had a relatively low capacity to liquefy PU-based resins. DMCHA is an organic solvent used for the delamination of multilayer plastic packaging, mainly due to its switchable hydrophilicity [41]. In the presence of a trigger in a medium, such as acid, base, or carbon dioxide, SHSs can reversibly turn their polarity by switching from a neutral form into an ionic liquid, thus allowing for the liquefaction and precipitation of the components in the same medium without the addition of a non-solvent [24]. As the neutral form of DMCHA has low polarity, it is generally used to solubilize apolar polymers, such as LDPE, to delaminate multilayer structures [41]. In this study, the apolar nature of DMCHA resulted in relatively low solubility for all the tested polymer resins which generally have a polar chemical bond. For example, the maximum solubility of all the tested polymer resins was below 0.0024 g/mL. Aside from solvent-based methods, a water-based deinking process is beneficial for industrial applications because it can be applied in the current recycling infrastructure. Currently, a 2 w % NaOH solution is used as a cleaning solution to

remove surface contaminants, such as dirt, oil, and soil, from plastics [30]. As NaOH is a strong base, it has the ability to hydrolyze polymer resins with functional groups, such as esters and amides [42,43]. However, high temperatures are applied to obtain hydrolysis in alkaline conditions. As in this study, the solubility of polymer resins was determined at RT to have a fair comparison over the different treatments; a NaOH solution resulted in the low solubility of polymer resins. Moreover, it is expected that the solubility of a polymer resin would be higher at elevated temperatures. Especially for deinking purposes, surfactants were used in an alkaline medium to reduce the surface or interfacial tension at the air/water, ink/water and plastic/water interface, thus allowing alkali to penetrate between the ink particle and the plastic film [17]. In this respect, cationic surfactants (e.g., CTAB at a critical concentration (10 CMC)) in alkaline conditions are industrially applied to remove surface-printed water-based and solvent-based inks from plastic films [20]. This was also confirmed in this study that the solubility of polymer resins, especially cellulose polymers and acrylates, in a CTAB solution was higher than that in a NaOH solution (Table A-1).

The solubility of polymer resins in each medium also differed in each polymer class. For example, in the cellulose class, the solubility of CAB was higher than that of CAP and CA. Increasing the aliphatic chain length of acetate side groups decreases the viscosity of the polymer, increases its flexibility during its application, and increases solubility in a broader range of solvents [44–46]. Conversely, in the acrylic class, an increase in alkyl chain length resulted in lower solubility. For example, the solubility of MMA in different media was higher than that of BMA. These results are in accordance with the literature which states that the lower solubility of BMA is attributed to its larger molecular size and branched structure compared with MMA [47–49]. In terms of media, an acid-based medium is efficient in solubilizing acrylic polymer resins. The solubility of acrylic resins in an acid-based medium (both sulfuric acid and formic acid) is more than 10 times higher than that in other media. Among these acrylic resins, PVB, and VC copolymers have higher solubility in ketones and esters (e.g., acetone and ethyl acetate), whereas a medium MW polyacrylic (MA) polymer resin prefers an alkaline medium. In the PU resin class, PUD showed the lowest solubility in the tested media due to its extremely high chemical resistance. For the other PU resins tested (SF-PU, SB-PU, and H₂SB-PU), the solubility of the solvent-free PU (SF-PU) resin was higher in sulfuric acid compared with that of the polymer resins of SB-PU and H₂SB-PU. This difference may originate from the curing technique used during polymer synthesis. For example, solvents are not used during the curing process of SF-PU adhesives, which makes these adhesives less vulnerable to chemicals [50, 51].

3.2. Liquefaction of polymer resins

Aside from the solubility capacity of a medium, its ability to liquefy polymer resins as quickly as possible is important to assess the efficiency of the medium. Especially for scaling up, the high liquefaction of polymer resins increases the economic feasibility of the method. Given the fact that plastic films take up much volume in a liquid phase, slow liquefaction means large residence times and thus large and capital-intensive deinking reactors. As 30 min interaction time is used as a typical residence time for washing lines in industry, the liquefaction process at RT was also investigated for 30 min at concentrations below their solubility limits. In Section 3.3, some resins were contacted with the medium longer to gain more insight into the longer-term liquefaction profiles. The results are shown in Fig. 3, along with the experimental standard deviation based on duplicate experiments. In order to give an indication on the reproducibility of the experimental data, we have performed 3 repetitions for three experiments. These experiments were performed at different time periods in different media. For these points average data with the corresponding standard deviation is given in Figure A-1. It is seen that standard deviation decreases substantially once three repetitions were performed.

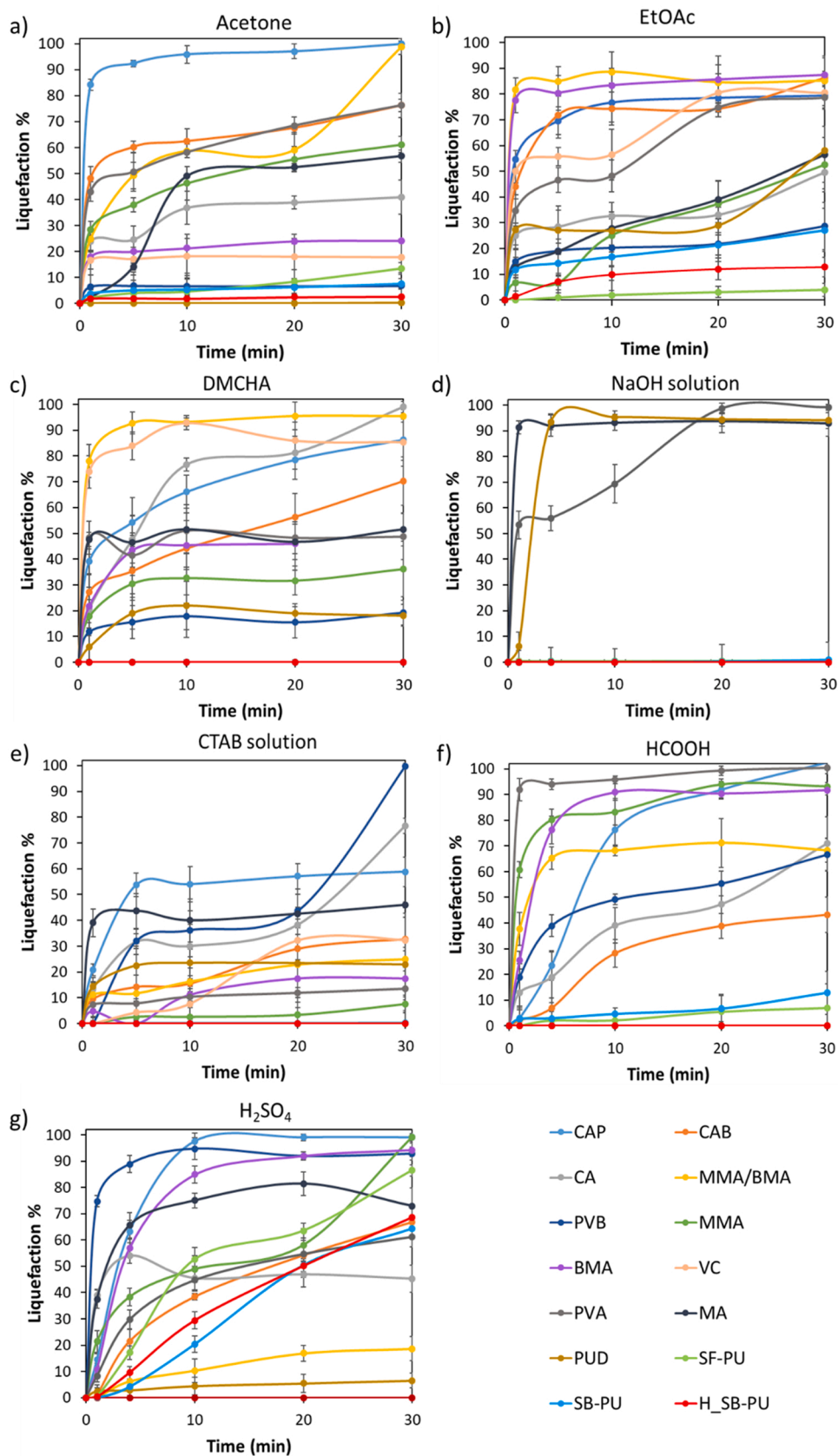


Fig. 3. Liquefaction % of 14 polymer resins in a) acetone, b) ethyl acetate, c) NaOH solution, d) CTAB solution, e) DMCHA, f) formic acid, and g) sulfuric acid during 30 min of interaction time at RT. Error bars shown at each experimental data point represent the standard deviation. Experimental data points are connected only for the purpose of improving visual interpretation.

As illustrated in Fig. 3, the polymer resins showed different liquefaction profiles due to their physicochemical differences. In the tested organic solvents (e.g., acetone, ethyl acetate, and DMCHA; Fig. 3a, b, and c, respectively), polymer resins such as CAP, CAB, MMA/BMA copolymer, and PVA reached more than 50 % liquefaction after 30 min of interaction time. Among the cellulosics, CA dissolved quickly in DMCHA, reaching 99 % in 30 min. This is mainly due to the less polar structure of CA compared with CAP and CAB. The acrylic-type polymer resins showed high solubility limits in organic solvents (Fig. 2), but as shown in Fig. 3, some acrylic polymer resins exhibited low liquefaction. For example, VC copolymer had high solubility limits, especially in ethyl acetate and acetone, but its liquefaction in acetone was quite low (18 %). Conversely, the VC copolymer reached 90 % liquefaction in 30 min in DMCHA, even though it had a relatively low solubility limit. In PU resins, liquefaction in organic solvents was low (below 10 % on average). The PUD resin was best dissolved in ethyl acetate, reaching 58 % liquefaction in 30 min of interaction.

In the alkaline medium (2 w % NaOH solution), most of the tested polymer resins showed the lowest liquefaction. Only PVA, medium MW polyacrylic (MA), and PUD resins showed liquefaction above 90 % in 30 min, while the liquefaction of other polymer resins were less than 1 %. Once the surfactant was used in the alkaline medium (10 CMC CTAB solution), the liquefaction of the polymer resins increased substantially. For example, almost 99 % of PVB liquefied in 30 min of interaction with a CTAB solution. The liquefaction of CAP and CA reached 58 % and 76 %, respectively. This shows that decreasing the surface tension of the medium using a surfactant improves not only the solubility capacity of the medium but also its solvation process.

Acidic media (formic and sulfuric acid) resulted in the highest liquefaction for the tested polymer resins (Fig. 3). For example, most of the polymer resins reached more than 80 % liquefaction at a 30-min time interval. In formic acid, the liquefaction of VC, MA, and PUD resins could not be determined because they are not soluble in formic acid at all. Higher liquefaction was obtained for PU resins in an acidic medium compared with the non-acidic media, but their liquefaction remained low (below 20 %). Compared with formic acid, sulfuric acid showed higher liquefaction (higher than 80 % in 30 min). This is mainly due to the dual ability (hydrolysis and oxidation) of sulfuric acid. In PU resins, more than 60 % liquefaction was obtained in sulfuric acid, except for the PUD resin. Liquefaction generally increases with increasing temperature for all treatments, but the temperature effect of all treatments should be the subject of further research.

3.3. Process of polymer liquefaction

The dissolution behavior of polymers is explained by two transport processes: solvent diffusion and chain disentanglement [52]. When a non-crosslinked, amorphous, glassy polymer is in contact with a solvent, the solvent diffuses into the polymer. This causes plasticization of the polymer, resulting in the formation of a gel-like swollen layer with two separate interfaces, one between the glassy polymer and the gel layer and the other between the gel layer and the solvent (Fig. 4) [53]. This process causes a delay in the dissolution of polymer, called induction

time. Therefore, an S-shaped, three-stage dissolution profile is observed for polymers [54]:

- 1) Period of solvent diffusion (induction time)
- 2) Dissolution of the polymer when in contact with the diffused solvent
- 3) Complete dissolution of the polymer, reaching a plateau

Although the three-stage dissolution profile indicates the ideal case, the dissolution profile of polymers is affected by various factors, such as residual solvent content, the presence of stirring during dissolution, the MW of polymers, and the thickness of the boundary layer [55]. As shown in Fig. 3, most of the polymers tested in this study did not show a three-stage liquefaction profile. Instead, at 5 min, the liquefaction % increased immediately, reached an intermediate plateau, and then increased again. In the literature, this kind of dissolution profile has been obtained as a result of the dissolution of low-MW polymers, dissolution without stirring, and the high thickness of the boundary layer [56]. If the MW of the polymer increases, the extent of the polymer chains in the entangled gel layer becomes higher than that of the gel-solvent interface. Therefore, the disengagement of the polymer chain from the entangled gel layers becomes restricted, resulting in disengagement-limited dissolution [57]. In this case, the diffusion of the disengaged chains to the bulk is higher than the disengagement rate; thus, no intermediate plateau is observed during dissolution. In the case of low-MW polymers, the disengagement rate is initially higher; thus, the dissolution rate increases to some extent. Once the diffusion of the disentangled polymer chains to the bulk becomes insufficient, the process becomes diffusion-limited, causing a decrease in the dissolution rate and resulting in an intermediate plateau [56]. Similarly, when the applied shear is insufficient during dissolution, the rate of diffusion decreases and the dissolution process becomes a diffusion-limited process rather than a disengagement-limited process, resulting in an intermediate plateau [58]. In addition, if the boundary layer thickness between the sol-gel and the liquid phase is higher, the dissolution process is initially disentanglement controlled and then becomes diffusion controlled after a certain time, resulting in an intermediate plateau [59]. A decrease in the boundary layer thickness results in faster transportation of the disentangled polymer chains, which makes dissolution a disentanglement-limited process; thus, an intermediate plateau is not observed [56]. Once the disentangled polymer chains go to the bulk, dissolution increases again.

In this study, an intermediate plateau was also observed in the liquefaction profile of the polymer resins. As explained above, this could be due to the presence of a lower MW of polymer resins and the high thickness of the boundary layer. Moreover, a rotary shaker was used during polymer liquefaction. It is shown in literature that stirring through turbulent mixing using a rotor is more efficient than the one through orbital mixing using a rotary shaker [60,61]. This difference in mixing might cause obtaining an intermediate plateau. In this study, the liquefaction of polymer resins was tested at 30 min of solvent interaction, as commonly practiced in the industry. The liquefaction % of polymer resins changes depending on the medium. For example, the VC copolymer reached 90 % liquefaction in DMCHA, whereas it reached

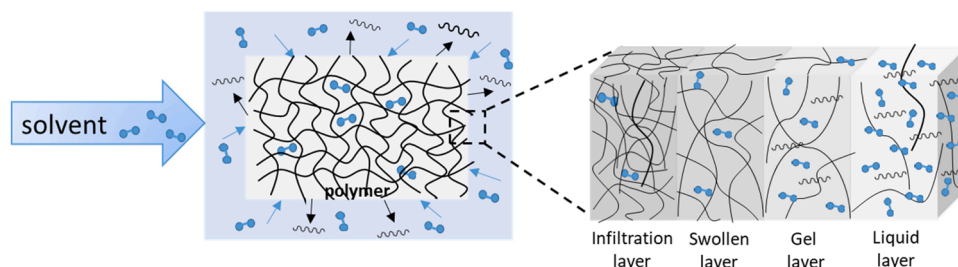


Fig. 4. Schematic representation of the polymer dissolution process (adapted and redrawn from [52]).

only 30 % liquefaction in a CTAB solution in 30 min. To make a better comparison between the liquefaction process of polymer resins in different media, a short interaction time was preferred. To determine whether a longer interaction time could change the liquefaction profile of the polymer resins, some of the polymer resins were kept in contact with the medium for 5 h, as shown in Fig. 5. In the figure, the MA and MMA/BMA polymer resins reached 100 % liquefaction after 5 h, while the liquefaction of the VC polymer resin reached only 35 %. As all the polymer resins were tested below their maximum solubility limits (after 24 h), obtaining an intermediate plateau did not indicate the saturation of the medium, but it was rather related to the mechanism of liquefaction, as explained above.

3.4. Deinking tests on printed plastic films

In order to confirm the solubility and kinetic tests performed on the pure resins, the deinking % were also determined on four plastic films printed with inks containing nitrocellulose (NC) polymer resin (sample 1), acrylate polymer resin (sample 2), PVB polymer resin (sample 3), and PU polymer resin (sample 4), respectively (Table 2). In these kinetic tests, each printed plastic sample was brought into contact with the seven different media separately during a 30-min time interval. During the kinetic tests, ink removed from the plastic surface was released into the medium. Fig. 6 shows the change in the color intensity of the medium and plastic film surfaces at each time interval.

During the 30 min of the kinetic test, samples were collected from the medium at each time point (1, 5, 10, 20, and 30 min), and the ink remaining on the plastic surface was measured using the reflection densitometry approach, as explained in Section 2.4. Deinking efficiency (%) as a function of time was calculated for each printed plastic film in each medium, and the results are shown in Fig. 7.

In Fig. 7a, more than 50 % deinking of sample 1 containing NC polymer resin was obtained within 5 min in sulfuric acid, formic acid, acetone, and ethyl acetate. This was also observed in the liquefaction process of the cellulosic polymer resins. As shown in Fig. 3a, b, f, and g, the highest liquefaction of the tested cellulosic polymers (CA, CAP, and CAB) were obtained in sulfuric acid, formic acid, acetone, and ethyl acetate. In DMCHA, cellulotics showed slower liquefaction process than these four media, but after 30 min of interaction, 85 % of the cellulosic polymer resins could be liquefied (Fig. 3c). Similarly, sample 1 showed slower deinking in DMCHA compared with sulfuric acid, formic acid, acetone, and ethyl acetate. Even after 30 min of interaction, only 48 % of sample 1 could be deinked in DMCHA. This difference between the liquefaction of cellulosic polymer resins (85 %) and the deinking percentage of sample 1 (48 %) in DMCHA could be due to the low solubility limits of cellulosic polymer resins in DMCHA. As shown in Fig. 2 (the actual values and their standard deviations can be found in Appendix Figure A-2), the maximum solubility of cellulosic polymer resins in DMCHA was more than 100 times lower than that of sulfuric acid, formic

acid, acetone, and ethyl acetate. Therefore, a relatively higher amount of DMCHA could be needed to increase the deinking of sample 1. The slowest deinking kinetics of sample 1 was obtained in NaOH and CTAB solutions. In the NaOH solution, deinking of sample 1 did not occur even after 30 min of interaction time. In the CTAB solution, deinking started much slower (only 20 % deinking in 10 min), but after 30 min, complete deinking was achieved. This was also observed in the liquefaction process of cellulosic polymer resins in basic media. As shown in Fig. 3d, cellulotics did not liquefy in the NaOH solution. The presence of CTAB substantially improved the liquefaction of cellulotics, resulting in 56 % liquefaction after 30 min.

Fig. 7b shows the deinking efficiency of sample 2 printed with the ink containing an acrylate polymer resin. Among the different media, sulfuric acid showed the highest deinking efficiency for sample 2, resulting in complete deinking in 5 min of interaction. Unlike in sample 1, the difference in the deinking efficiency of sample 2 between sulfuric acid and other solvents was much larger. This is also observed in Fig. 3g, which shows that the liquefaction of acrylate polymer resin (e.g., MMA) in an acidic medium (formic acid and sulfuric acid) was much higher than those in other media. The deinking efficiency of sample 2 in DMCHA was also high, resulting in 54 % deinking in 5 min of interaction. As shown in Fig. 3c, the liquefaction of acrylates in DMCHA was around 50 %. Regarding the basic media (NaOH and CTAB solutions), deinking of sample 2 in these media started much slower, especially in the NaOH solution, but after 30 min of interaction, around 90 % deinking was achieved in both media. As shown in Fig. 3d and Fig. 3e, the liquefaction of acrylates in basic media was also slower, and after 30 min of interaction, 30 % liquefaction was obtained. This is much lower than the deinking efficiency of sample 2 in basic media (> 80 % in 30 min). However, this difference could originate from the presence of other elements, such as pigments, additives, and substrates, which are also involved in the deinking process compared with pure polymer resin liquefaction. In organic solvents (ethyl acetate and acetone), the deinking of sample 2 started slowly. However, after 30 min of interaction, deinking efficiency reached 92 % in acetone but remained at 40 % in ethyl acetate. Although similar liquefaction efficiencies were obtained for acrylate polymer resins in organic solvents (Fig. 3), the deinking superiority of acetone over ethyl acetate could be related to its faster diffusion through the polymer due to its smaller molecular size.

Fig. 7c illustrates the deinking efficiency of sample 3 printed with the ink containing a PVB polymer resin in seven different media within 30 min of interaction. Among the tested media, sulfuric acid and formic acid showed superior deinking efficiency, reaching over 90 % deinking efficiency in 5 min of interaction. Conversely, the deinking rate of sample 3 in organic solvents (ethyl acetate and acetone) was quite slow, reaching around 5 % deinking efficiency in 10 min of interaction. After 30 min of interaction, deinking efficiency reached 62 % in ethyl acetate but remained at 25 % in acetone. Similar to ethyl acetate, in DMCHA around 60 % deinking efficiency was achieved after 30 min of interaction. In the basic media, sample 3 showed high deinking efficiency in the CTAB solution, reaching 80 % after 30 min, but in the NaOH solution the deinking of sample 3 was not achieved. These results are in accordance with the liquefaction of PVB resins. As shown in Fig. 3, the highest liquefaction of PVB resin was obtained in sulfuric acid, reaching 90 % in 5 min of interaction. In formic acid, its liquefaction process was slower, but after 30 min of interaction, 66 % liquefaction was obtained. In ethyl acetate, over 90 % liquefaction was achieved, whereas only 10 % liquefaction was obtained in acetone. Similarly, PVB resin showed slow liquefaction in DMCHA, reaching only 20 % liquefaction in 30 min (Fig. 3c). In the basic media, in the CTAB solution, liquefaction of PVB resin started slowly, but complete liquefaction was achieved after 30 min. PVB did not show any liquefaction within 30 min of interaction with NaOH solution, as confirmed in the deinking efficiency of sample 3.

In Fig. 7d, the deinking efficiency of sample 4 printed with the ink containing SB-PU polymer resin is presented. High deinking efficiencies were obtained in acidic media and organic solvents. For example, in

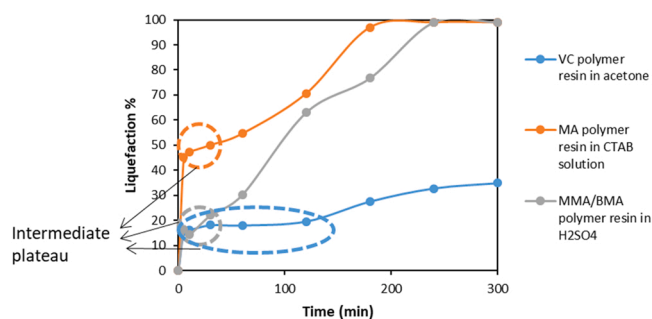


Fig. 5. Liquefaction % of the vinyl chloride (VC) copolymer in acetone (blue line), medium MW polyacrylic resin (MA) in a CTAB solution, and methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer in sulfuric acid (H₂SO₄) during a 5-h interaction.

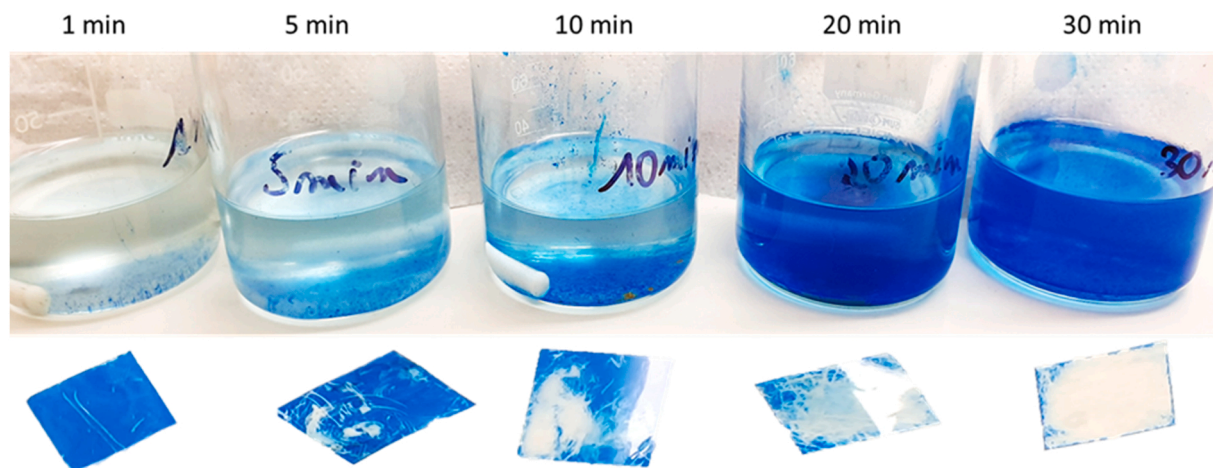


Fig. 6. Visual presentation of the medium during the deinking kinetic test of sample 2 in DMCHA and the collected plastic films from the medium at different time points after stirring was stopped.

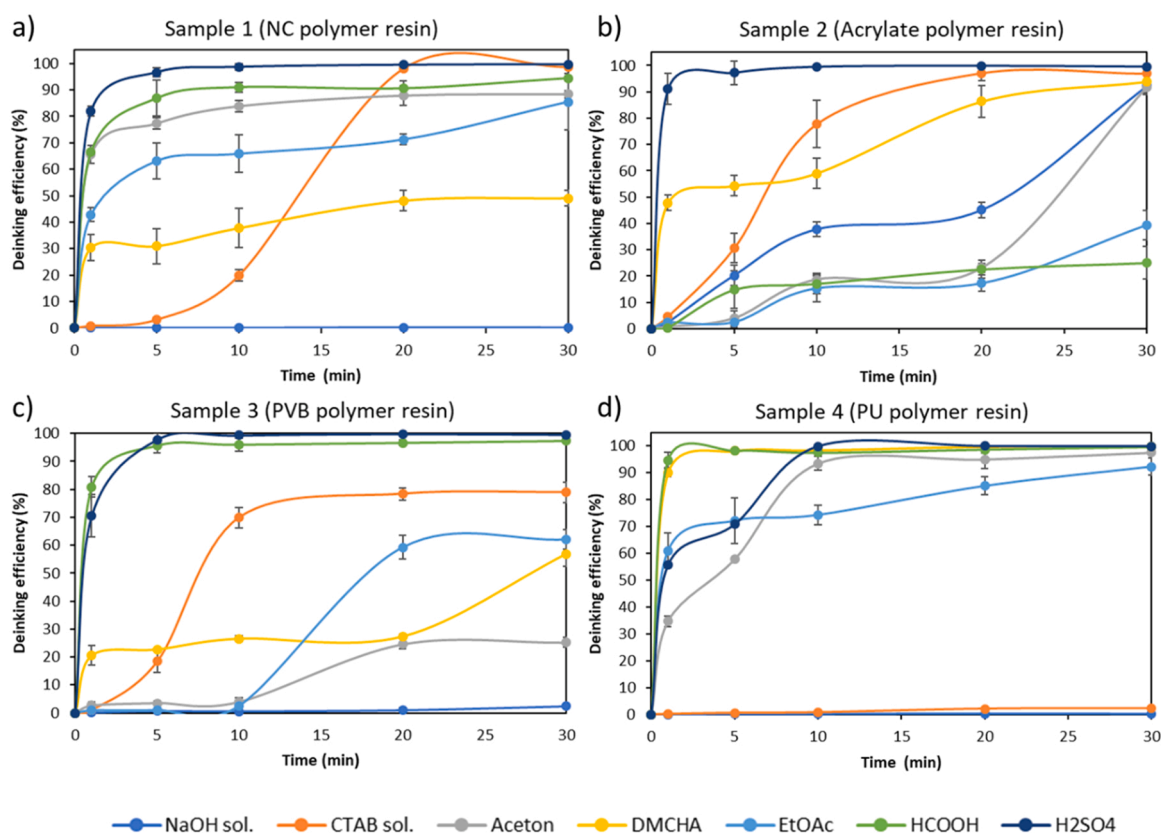


Fig. 7. Deinking efficiency of a) sample 1 printed with the ink containing NC polymer resin, b) sample 2 printed with the ink containing acrylate polymer resin, c) sample 3 printed with the ink containing PVB polymer resin, d) sample 4 printed with the ink containing PU polymer resin in 7 different media during 30 min of interaction at RT. The experimental data points are connected only for the purpose of improving visual interpretation.

formic acid and DMCHA, more than 90 % deinking efficiency was reached after 5 min of interaction. In sulfuric acid and acetone, the deinking rate was slower than that in formic acid and DMCHA, but complete deinking of sample 4 was achieved after 10 min of interaction. Similarly, in ethyl acetate, the deinking of sample 4 started slower, but 90 % of the ink could be removed successfully after 30 min of interaction. Basic media were not efficient in deinking sample 4. No deinking was observed in the CTAB and NaOH solutions. The liquefaction of SB-PU polymer resin was the highest in sulfuric acid, reaching 64 % after 30 min of interaction (Fig. 3). This was followed by ethyl acetate with 27

%, formic acid with 13 %, and acetone with 8 % liquefaction. Compared with the deinking efficiency of sample 4 in these media, the liquefaction of SB-PU polymer resin was lower. As the deinking rate is also affected by the interaction between other ink components, it is expected not to obtain exactly the same number for both the deinking efficiency and the liquefaction rate. This was clearly observed in DMCHA. Whereas complete deinking of sample 4 was achieved in DMCHA, the liquefaction of SB-PU resin was very low, reaching only 1 % within 30 min of interaction. This could be due to the physicochemical differences in the PU polymer resins, resulting in different liquefaction process. Regarding the

basic media, sample 4 could not be deinked in the CTAB and NaOH solutions. Similarly, no liquefaction was observed for the SB-PU polymer resin in these basic media.

3.5. Comparison of deinking media

As similarities in the liquefaction process were observed within each polymer resin class, the average solvation % of each medium is presented for each polymer resin class (cellulosics, acrylics & related and PUs) in Fig. 8. For this, the average liquefaction % at 30 min interaction time was taken per class of polymer resin. The liquefaction % of each polymer resin at 30 min interaction in each medium is given in Table A-2.

Among the three polymer resin classes, cellulosics showed the highest liquefaction in most of the tested media, followed by acrylics and PUs. As illustrated in Fig. 3, each polymer class showed different liquefaction process in diverse media. For example, cellulosics exhibited high liquefaction in DMCHA (85 %) but did not liquefy in the NaOH solution at all during 30 min of interaction. Unlike cellulosics, PUs showed the lowest liquefaction in DMCHA (4 %). Although PUs showed slow liquefaction process in most of the media, 56 % liquefaction was obtained in sulfuric acid. As the variety within the acrylic polymer class was broad, they showed diverse liquefaction process, but in average high liquefaction (above 45 %) was obtained for most of the tested media. Once the solvation processes of the different media were compared, the NaOH solution showed the lowest solvation %. The addition of a surfactant (10 CMC CTAB solution) to the NaOH solution improved the solvation process of the medium. For example, the average liquefaction of acrylics in the NaOH solution was 27 %, but this increased to 35 % in the CTAB solution. This was not the case for PUs, as their liquefaction in the NaOH solution was higher than that in the CTAB solution. This could be due to the that increase in CTAB concentration decreases the hydrolysis rate; thus, the reaction of PU slowed down in the presence of CTAB [62]. Organic solvents (i.e., acetone, ethyl acetate, and DMCHA) showed high solvation, except for PUs which generally require basic/acidic medium for liquefaction. Because printed plastic film waste consists of a mixture of different resin classes, the ability of the medium to exhibit high solvation for different resin classes is an important element in the selection of a potential medium. Among all the tested media, acid-based media, especially sulfuric acid, resulted in the

highest liquefaction % for the three polymer resin classes. This is mainly due to the hydrolyzing and oxidizing capability of sulfuric acid, allowing for the removal of even chemically attached cross-linked inks, such as PUs. Compared with water-based media, solvents are also effective in obtaining a high liquefaction, especially for cellulosics and acrylic-related polymer resins. As most polymer resins contain functional groups with apolar properties, water-based media create high surface tension, which impedes the liquefaction process of polymer resins. The addition of CTAB helps to reduce surface tension, which results in a more effective liquefaction.

Table 3 presents an overview of the comparison of different media in terms of their liquefaction ability and scaling-up potential. Aside from the efficiency of the medium to liquefy a broader range of polymer resins, its ability to liquefy high amounts of polymer resin also plays a crucial role in the selection of a potential medium. Among the different media, sulfuric acid can achieve the highest polymer resin solubility (0.73 g/mL), followed by formic acid (0.66 g/mL), ethyl acetate (0.51 g/mL), and acetone (0.36 g/mL). The solubility limits of polymer resins also determine the amount of liquid medium required for effective plastic pretreatment (e.g., deinking and delamination), which is crucial for the economic feasibility of the process. Table 3 shows the range of the volume of the medium required to deink 1 m² of printed plastic film. A printed plastic film contains each polymer resin separately, and it is calculated using the following formula:

$$M_r = A_p \times t_A \times d_r \quad (2)$$

where M_r is the mass of polymer resin in 1 m² of printed plastic film (g), A_p is the area of plastic film (cm²), t_A is the thickness of the polymer resin layer (cm), and d_r is the density of the specific polymer resin (g/cm³). The thickness of the polymer resin was considered to be 2 μm for all polymer resins.

As the maximum solubility of each polymer resin in each medium was determined (Fig. 2), the calculated mass of polymer resin (M_r) was used to obtain the volume of the medium needed (L) for deinking 1 m² of plastic film printed containing the specific polymer resin. As shown in Table 3, 0.002–0.364 L of sulfuric acid was sufficient to liquefy the different types of polymer resins, thus achieving the deinking of 1 m² of printed plastic film. Acetone is also an efficient medium because 0.007–1.849 L of acetone was sufficient for deinking the printed plastic film. The volume range of other media (formic acid, NaOH solution, CTAB solution, DMCHA, and ethyl acetate) required to deink 1 m² of plastic film was quite broad, starting from 0.003 L and reaching more than 15 L. Especially for the CTAB solution, the maximum volume increased to 40 L. In general, acidic medium showed a higher solubility capacity for a broader range of polymer resins (Fig. 2). However, formic acid, for example, showed low solubility, especially for PUs compared with acetone. This resulted in obtaining a higher volume of formic acid required for deinking the plastic film compared with acetone. It should be noted that temperature could increase solubility and strongly decrease the amount of liquid needed; thus, the above values should mainly be used to compare the media. Although sulfuric acid and acetone, among the tested media, could be economically beneficial for scaling up, the technical feasibility of the medium should also be considered. For example, sulfuric acid requires careful handling and the use of corrosion-resistant equipment. Moreover, there is a risk of attacking potentially present heteropolymers, such as PET and polyamide (PA), rather than selectively removing the polymer resin. Furthermore, acetone and ethyl acetate have a low flashpoint; thus, special care should be taken to manage their flammability. Also, during polymer resin liquefaction, the solution becomes viscous, especially in formic acid, CTAB solution, and ethyl acetate, which could hamper the post-treatment process (e.g., removal and washing of deinked plastic flakes). All these factors should be taken into account when selecting potential deinking media.

The cost of the liquid and its recovery are also crucial factors on the

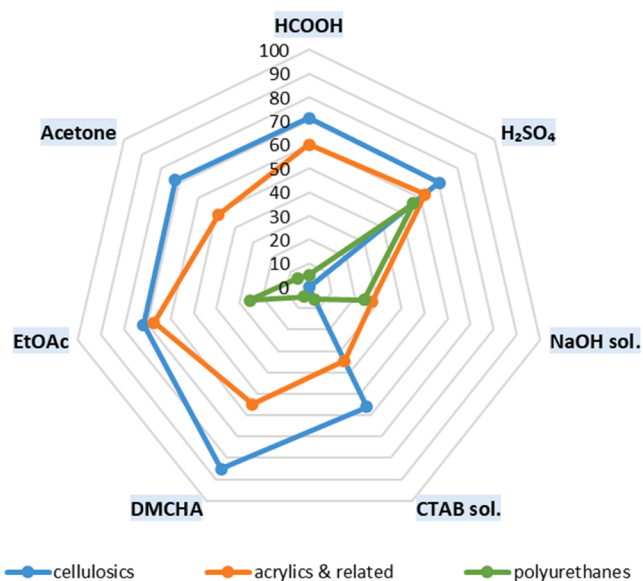


Fig. 8. Radar chart of the average liquefaction percentage of three polymer resin classes (cellulosics, acrylics & related, and polyurethanes) in seven different media in 30 min of interaction time at RT.

Table 3
Comparison of the different media in terms of liquefaction capability and scaling-up potential.

Liquid medium	Mechanism for resin liquefaction	Min resin Solubility at RT (g/mL)	Max resin solubility at RT (g/mL)	Good deinking medium for	Poor deinking medium for	Liquefaction process	Range of volume of medium needed for deinking of 1 m ² plastic film (L) at RT	Other remarks
Formic acid	Dissolution [33, 63,64]	0.0000	0.6609	Cellulosics (CAP, CAB, CA) and acrylates (MMA/BMA, MMA, BMA, PVA)	Acrylates (MA) and polyurethanes (PUD, SF-PU, SB-PU, H_SB-PU)	Fast for acrylates, slow for PUs	0.003–20.340	<ul style="list-style-type: none"> The resin solution turns viscous visually, especially for polyurethanes
Sulfuric acid	Hydrolysis and oxidation [65–67]	0.0000	0.7347	Cellulosics (CAP, CAB), acrylates (CA, MMA/BMA, MMA, BMA, PVA, MA), polyurethanes (SF-PU, SB-PU)	Acrylates (PVB, VC) and polyurethanes (PUD)	Fast for cellulosics and acrylates, slow for PUs	0.002–0.364	<ul style="list-style-type: none"> The resin solution turns brown Potential corrosion Risk of attacking heteropolymers
NaOH solution	Hydrolysis [68–70]	0.0001	0.0906	Acrylate (MA)	Cellulosics (CAP, CAB, CA), acrylates (MMA/BMA,PVB, MMA, BMA, VC, PVA) and polyurethanes (PUD, SF-PU, SB-PU, H_SB-PU)	Fast for MA, PVA, and PUD, slow for cellulosics and acrylates	0.021–26.667	<ul style="list-style-type: none"> Risk of attacking aluminum and heteropolymers, especially at high temperatures
CTAB solution	Micelle formation [17, 19]	0.0001	0.0111	Polyurethanes (PUD)	Cellulosics (CAP, CAB, CA), acrylates (MMA/BMA,PVB, MMA, BMA, VC, PVA, MA) and polyurethanes (SF-PU, SB-PU, H_SB-PU)	Fast for cellulosics, slow for acrylates and PUs	0.688–39.667	<ul style="list-style-type: none"> The resin solution becomes viscous
DMCHA	Aminolysis [71, 72]	0.0000	0.0030	Acrylates (PVB, BMA, VC)	Cellulosics (CAP, CAB, CA), acrylates (MMA/BMA, MMA, PVA, MA), and polyurethanes (PUD, SF-PU, SB-PU, H_SB-PU)	Fast for cellulosics and acrylates, slow for PUs	0.678–31.667	<ul style="list-style-type: none"> The resin solution turns yellowish Air-sensitive
Ethyl acetate	Dissolution [73, 74]	0.0001	0.5101	Cellulosics (CAP, CAB, CA) and acrylates (MMA, BMA, PVA)	Acrylates (MMA/BMA, PVB, VC, MA) and polyurethanes (PUD, SF-PU, SB-PU, H_SB-PU)	Fast for cellulosics and acrylates, slow for PUs	0.004–18.718	<ul style="list-style-type: none"> The resin solution becomes viscous, difficult sampling Low flashpoint
Acetone	Dissolution [75, 76]	0.0011	0.3574	Cellulosics (CAP, CAB, CA) and acrylates (MMA/BMA, MMA, BMA, PVA)	Acrylates (PVB, VC, MA) and polyurethanes (PUD, SF-PU, SB-PU, H_SB-PU)	Fast for cellulosics and acrylates, slow for PUs	0.007–1.849	<ul style="list-style-type: none"> The resin solution becomes viscous High volatility

Table 4
Basic cost assessment and the environmental impact of the tested medium.

Liquid medium	Cost assessment		Environmental impact of virgin chemical production			
	Chemical cost (EUR/m ³)	Range of chemical cost based on the volume of medium needed for deinking of 1 m ² plastic film (EUR/~100 kg plastic film)	Medium circulation cost (EUR/m ³)	Range of medium circulation cost based on the volume of medium needed for deinking of 1 m ² plastic film (EUR/~100 kg plastic film)	Impact on human toxicity (kg 1,4-DCB-eq)	Impact on climate change (kg CO ₂ -eq)
Formic acid	573.40 [81]	1.72–11662.96	3.46	0.01–70.35	0.7465	2.4813
Sulfuric acid	258.03 [82]	0.52–93.92	36.60	0.07–13.32	0.1002	0.1238
NaOH solution	12.90	0.27–343.95	12.60	0.26–335.95	0.0449	0.0442
CTAB solution	390.78 [83]	268.86–15501.00	390.48	268.65–15489.10	0.3041	0.3262
DMCHA	1197.09 [84]	811.63–37908.25	7.69	5.21–243.51	0.5602	3.4179
Ethyl acetate	954.51	3.82–17866.58	4.42	0.02–82.77	0.7692	2.8305
Acetone	760.51	5.32–1406.18	3.21	0.02–5.93	0.0298	2.2279

feasibility of the process. We have performed a basic cost assessment based on the raw chemicals costs and medium recirculation costs calculated through Aspen Plus® simulations. Raw chemical costs were taken from online available prices and databases. Regarding the medium recirculation, energy consumption during evaporation was calculated for formic acid, DMCHA, ethyl acetate and acetone via Aspen Plus® simulations. Energy costs were minimized by varying evaporation pressure based on a sensitivity analysis. For this, a flash unit in combination with a compressor was used to assess the required energy for evaporation. The compressed stream was sent through a series of 2 heat exchangers. The first set was at a dT of + 10 °C against the flash unit to determine the energy that could be recuperated for heating the flash unit, and the other heat exchanger was used to further cool down the media till 25 °C. The costs of sulfuric acid regeneration and water treatment were taken from the literature [77,78]. The electricity and gas prices considered in the energy consumption calculations during the liquid evaporation were taken from the recently updated online sources [79,80]. Furthermore, we have compared the environmental impact of the media in terms of CO₂-eq. emission and the human toxicity of the production of 1 kg virgin chemical using the Ecoinvent Database v3.1 in OpenLCA 1.9. Since the environmental impact of DMCHA does not exist in the Ecoinvent Database, the environmental impact of chemicals to produce DMCHA (stoichiometric ratio of dimethylamine and cyclohexanone at plant) was used. Similarly, the environmental impact of ethylenediaminetetraacetic acid (EDTA) was used instead of CTAB. The costs of chemicals and medium recirculation were calculated for the range of volume of medium needed for deinking of 1 m² plastic film as given in Table 3. The obtained results of cost and environmental impact analysis are given in Table 4.

As seen in Table 4, the range of detergent cost for deinking of around 100 kg plastic film is high, mainly caused by the low solubility of polymer resins in the detergent, which results in high volume requirements as given in Table 3. On the other hand, the volume of DMCHA needed to deink 1 m² plastic film is lower than that of detergent, but the high price of DMCHA increases the cost of deinking process significantly. This shows that both the price of chemical and its required volume for effective deinking have crucial impact on the cost of the deinking process. Regarding the cost of medium recirculation, it is seen that acetone recirculation results in the lowest cost, followed by sulfuric acid, formic acid and ethyl acetate, respectively. The optimization of the energy consumption by pressure adjustments during recirculation of solvent- and acid-based media show potential to lower the cost of medium recovery. Related to the water-based deinking methods, the large amount of water required induces high costs for water treatment. Regarding the environmental impact of the production of the chemicals, it is seen that ethyl acetate shows the highest human toxicity over its life cycle, followed by formic acid and DMCHA. In terms of the effect of chemical production on CO₂ emission, DMCHA shows the highest impact, followed by ethyl acetate, formic acid and acetone. It should be noted that these results are only indicative and depending on the deinking process conditions and type of polymer resins present in plastic waste feedstock, these results might change. With this basic cost and environmental analysis, it is aimed to show that the cost of chemicals, recovery of the medium, the volume of medium needed and the environmental impact of production these chemicals are equally crucial as selecting an efficient deinking medium towards potential upscaling of the process.

4. Conclusion

Deinking plastic films is a crucial pretreatment process to obtain clean and high-quality extrudates from flexible plastic packaging. However, deinking efficiency strongly depends on the medium used because of the huge variety of polymer resins applied in printing inks. Therefore, in this study, the effectiveness of a range of liquid media was systematically studied on various types of polymer resins used in

printing inks.

First, the maximum solubility of 14 chemically different polymer resins was determined at RT in seven different media typically used in plastic pretreatment (i.e., acetone, ethyl acetate, NaOH solution, CTAB solution, formic acid, sulfuric acid, and DMCHA). According to the results, acid-based media were more efficient in liquefying a broader range of polymer resins. Specifically, sulfuric acid showed the highest solubility capacity for different classes of polymer resins (> 0.1 g/mL on average). Compared with sulfuric acid, formic acid does not have oxidation capability; thus, it resulted in a lower solubility capacity, especially for PUs. Among the tested organic solvents (i.e., acetone, ethyl acetate, and DMCHA), acetone and ethyl acetate were more effective than DMCHA, specifically in the solubility of acrylic-related polymer resins. The apolar nature of DMCHA resulted in relatively low solubility (< 0.0024 g/mL) for all the tested polymer resins which have a relatively polar chemical bond. Regarding the water-based media (i.e., NaOH and CTAB solutions), the NaOH solution resulted in a low solubility of polymer resins (< 0.09 g/mL). The addition of the surfactant CTAB to the basic medium increased the solubility capacity, especially for the cellulose and acrylic-related polymer resins.

Second, the liquefaction processes of these 14 polymer resins were investigated in each medium at RT. Due to the physiochemical differences between polymer resins, they showed different liquefaction processes. Among the tested media, acid-based media (i.e., sulfuric acid and formic acid) resulted in the highest liquefaction for most of the polymer resins, reaching more than 80 % liquefaction at a 30-min interval. In the tested organic solvents (e.g., acetone, ethyl acetate, and DMCHA), the polymer resins CAP, CAB, MMA/BMA copolymer, and PVA reached more than 50 % liquefaction after 30 min of interaction time. In the alkaline medium, most of the tested polymer resins showed the lowest liquefaction process. Only PVA, MA, and PUD resins liquefied above 90 % in 30 min, while the liquefaction of other polymer resins stayed less than 1 %.

Lastly, the liquefaction data obtained on pure polymer resins were confirmed by deinking plastic films printed with inks containing NC polymer resin, acrylate polymer resin, PVB polymer resin, and PU polymer resin. The liquefaction results obtained with pure polymer resins were in accordance with the results of the deinking efficiency. For example, the highest deinking efficiency was also observed in the acid-based media, resulting in more than 60 % deinking efficiency within 5 min of interaction. Remarkably, formic acid showed low deinking efficiency for the printed plastic film containing acrylate polymer resin. Among the tested organic solvents, acetone showed high deinking efficiency for plastic films containing NC and PU polymer resins, reaching more than 80 % deinking efficiency in 10 min of interaction. Whereas DMCHA showed low liquefaction for various polymer resins, it presented high deinking efficiency for plastic films containing PU polymer resin. The basic media resulted in low deinking kinetics for the tested printed plastic films. The presence of CTAB substantially increased the deinking efficiency, especially for plastic films containing NC, acrylate, and PVB polymer resins.

Aside from the liquefaction of different media, some upscaling considerations were also made. Among the different media, the lowest amount of sulfuric acid (0.002–0.364 L) was sufficient to deink 1 m² of printed plastic film, followed by acetone (0.007–1.849 L). However, the technical feasibility of the medium, such as flashpoint, handling, and corrosiveness, are also crucial points to be considered for scaling up of the deinking process. The basic cost assessment for deinking around 100 kg plastic film showed that both the price of chemical and its required volume for effective deinking have crucial impact on the cost of the deinking process. The cost of recirculation of the medium would be lowered by optimization of the energy consumption via pressure adjustments. Regarding the environmental impact of the production of the chemicals, ethyl acetate shows the highest human toxicity and DMCHA exhibits the highest impact on CO₂ emission over their life cycle. These results are only indicative and depending on the deinking process

conditions and type of polymer resins present in plastic waste feedstock, these results might change.

This study provides systematic knowledge for the further development of deinking processes and recycling designs. Currently recyclers are mainly using water-based media during washing, eventually with NaOH and detergents. This is mainly due to the easy handling during processing in terms of safety and higher compatibility with equipment. The main original aim of the caustic addition is also not deinking, but it is a typical addition made to washing media for removal of grease among others. It is also used together with detergents in order to increase the effectiveness of detergents for deinking purposes. For example, it is shown that CTAB is more effective at high pH values. On the other hand, as shown in this study acid-based media would be more effective for deinking, but they require additional safety, corrosion mitigation measurements for equipment and post-treatment of the plastics. Furthermore, process optimization is required for some types of polymer resins, such as PU resin, to increase their solubility, thus achieving increased deinking efficiency. The differences in the solubility of polymer resins make the selection of an optimal medium more difficult, especially for post-consumer plastic waste containing various types of inks and adhesives. Increased chemical uniformity would be advantageous to make the deinking of plastic films more effective.

CRedit authorship contribution statement

Sibel Ügdüler: Conceptualization, Methodology, Writing - original draft, Visualization, Funding acquisition. **Tine Van Laere:** Investigation, Validation. **Tobias De Somer:** Software, Formal analysis. **Sergei Gusev:** Software. **Kevin M. Van Geem:** Writing - review & editing. **Andreas Kulawig:** Resources. **Ralf Leineweber:** Resources. **Marc Defoin:** Resources. **Hugues Van den Bergen:** Resources. **Dirk Boninck:** Resources. **Steven De Meester:** Conceptualization, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2023.131239](https://doi.org/10.1016/j.jhazmat.2023.131239).

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