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Research Paper

Beyond the Landfill: A critical review of techniques for End-of-Life Polyvinyl chloride (PVC) valorization

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ABSTRACT

Polyvinyl chloride (PVC) is a polymer comprised of more than 50% chlorine that offers unmatched versatility at low expense. PVC is irreplaceable in several applications, such as construction materials, medical applications, and cables. This versatility and tunable properties come at the cost of complex formulations for the product and challenging end-of-life (EoL) options for PVC waste. Pure collected and sorted PVC is already recycled successfully to some extent, yet, when PVC ends up in a mixed plastic waste stream, it can be detrimental to the recycling process. PVC waste and its effects at various concentrations remain a focal point for both scholars and policymakers. In this review, the narrative begins at the naissance of PVC and continues to investigate the EoL valorization options when the products are inevitably discarded. Strategies for PVC waste recycling and the technical and legal challenges regarding each method are discussed, focusing on the European recycling market. An effective solution to handle EoL PVC requires a combination of policies and schemes for proper collection and sorting of specific waste streams and considering all available technologies to select the right tools. This review can support appropriate policies and the selection of suitable methods of recycling PVC waste.

1. Introduction

Polyvinyl chloride (PVC) is one of the most controversial plastics, considering the constant scrutiny from society associated with its production, lifetime, and end-of-life (EoL). Yet, PVC offers unparalleled qualities such as longevity and versatility in many applications. Thanks to its chemical, mechanical, and electrical properties as well as flame retardancy, it is used in applications ranging from construction material (e.g., pipes, electrical wires, window profiles) to medical devices (Najafi and Abdollahi, 2020; Schiller, 2015a). Fig. 1 shows the variety of PVC applications in different categories.

However, for this vast range of applications to be possible, PVC is often mixed with numerous additives to achieve the required characteristics for the specific application (Akovali, 2012). The main additives include plasticizers, stabilizers, flame retardants, and colorants. When PVC recycling is considered, the presence of these additives in the feedstock can drastically affect the choice of applicable techniques (Lewandowski and Skórczewska, 2022). In applications such as flexible PVC products where the total content of these additives is typically higher, their nature and content will be particularly impactful on the process. Fig. 2 shows that PVC resin can account for 30 to more than 80 % of the product, depending on the application (Gilbert and Patrick, 2017). This variation in PVC content can make the recycling process challenging, since any process designed for the recycling of only PVC may only account for less than half of a given feedstock.

Although reducing consumption is the most effective solution to mitigate plastic waste accumulation, "reduce" or "reuse" is not always possible, which can also be deducted from a continuously growing demand for plastics and subsequent waste accumulation (ChemAnalyst, 2023). Recycling must thus be considered a valuable tool in our arsenal to valorize the EoL plastics (Chen et al., 2020). Plastic recycling can be categorized in various ways. Al-Salem et al. (2010) classify plastic

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recycling into four overall categories: primary recycling (re-extrusion of scrap parts), secondary recycling (physical), tertiary recycling (chemical), and quaternary recycling (energy recovery). While the first three categories focus on recovering the material in different ways, quaternary recycling is distinctive because it focuses on recovering the energy content. In this review, the recycling methods are categorized based on their principle of action, resulting in physical (mechanical and solvent-based) recycling which preserves the chemical structure of the polymer, and chemical recycling aiming at the chemical degradation of the polymer into smaller compounds. Furthermore, energy recovery is discussed as a separate recovery method, distinctive from other recycling methods as it only attempts to recover the energy and not the material.

Mechanical recycling methods require relatively "clean" feedstocks, and the dominant polymer species will determine the process conditions (Jeswani et al., 2021). Regardless, chlorine in waste, usually derived from PVC, is a challenging element for most processes (Dogu et al., 2021; Persson et al., 2007; Yuan et al., 2020). Therefore, depending on the chlorine content and the recycling technique, the chlorine is either neutralized or the PVC remains intact for further valorization (Tukker, 1999). As discussed, PVC waste stems from various streams, including medical plastics, construction and demolition, and so on (Du et al., 2014; Purnomo et al., 2021; Sormunen and Kärki, 2019; Vouvoudi and Achilias, 2020), each with different logistical and compositional complexities for viable PVC recycling (Schuyler et al., 2022).

In 2018, PVC was the least recycled plastic in municipal solid waste (MSW) as reported by the Environmental Protection Agency (Merrington, 2024). However, in total, PVC waste has shown recycling rates as high as 10 % globally (Lorang et al., 2022). In Europe, higher recycling rates (i.e., 27 %) have been achieved chiefly thanks to the mechanical recycling of specific waste streams (VinylPlus, 2023). Fig. 3 shows the total tonnage of mechanically recycled PVC in Europe within the VinylPlus framework since 2018 (VinylPlus, 2020, 2021a, 2022, 2023, 2024). While the total recycling rates are also dependent on external factors, rigid applications have consistently higher recycling rates compared to flexibles. Furthermore, the breakdown of the recycled quantities from the year 2020, shows the higher share of recycled pre-consumer waste in the annual values. Even though PVC's complex formulation is partly responsible, poor thermal and photostability makes mechanical recycling challenging and contributes to the poor recyclability of PVC waste (Sadat-Shojai and Bakhshandeh, 2011).

In this work, the characteristics of PVC as a polymer, a product, and a feedstock for a recycling process are discussed. The advantages and shortcomings of each recycling technology are addressed. While none of the available technologies for recycling PVC waste are complete, a great number of advancements are made in this field every day. This comprehensive review of different practices and technological advances in PVC waste recycling indicates that the various technologies should be employed in a complementary approach, rather than competing with each other.

2. PVC production

Production of PVC starts with the production of its monomer, i.e., vinyl chloride (VCM). VCM is synthesized by adding chlorine gas to ethylene, usually produced from fossil sources, to generate ethylene dichloride via direct chlorination. Ethylene dichloride is cracked to yield VCM and HCl. The HCl is then combined with oxygen and ethylene to yield more ethylene dichloride and steam through a catalytic process known as oxychlorination. These two steps can be employed jointly (known as the balanced VCM process) as both result in ethylene dichloride and have complementary effects. Alternatively, hydrochlorination may be employed to produce VCM from HCl and acetylene (Ma et al., 2020). While the production method of VCM is not particularly impactful on the final product, the following steps in PVC resin manufacturing can result in a variation of properties. These polymerization processes can be divided into four major processes: suspension, emulsion, bulk, and solvent (Wheeler, 1981). The manufacturing process predetermines the polymerization agents and the physicochemical properties of the PVC resin and, by extension, the PVC product. These, in turn, also affect the recycling process of PVC waste (Endo and Emori, 2001). Table 1 summarizes the characteristics of these processes.

Suspension (S-PVC) – This technique accounts for the majority of PVC resin production (~80 %) worldwide and involves a suspension of VCM in a solvent, typically water, with a suspending aid and an initiator (Wheeler, 1981). After the reaction reaches the desired conversion, the unreacted VCM will be recovered from the product mix, and the products will be dewatered and dried before packaging (Tacidelli et al., 2009).

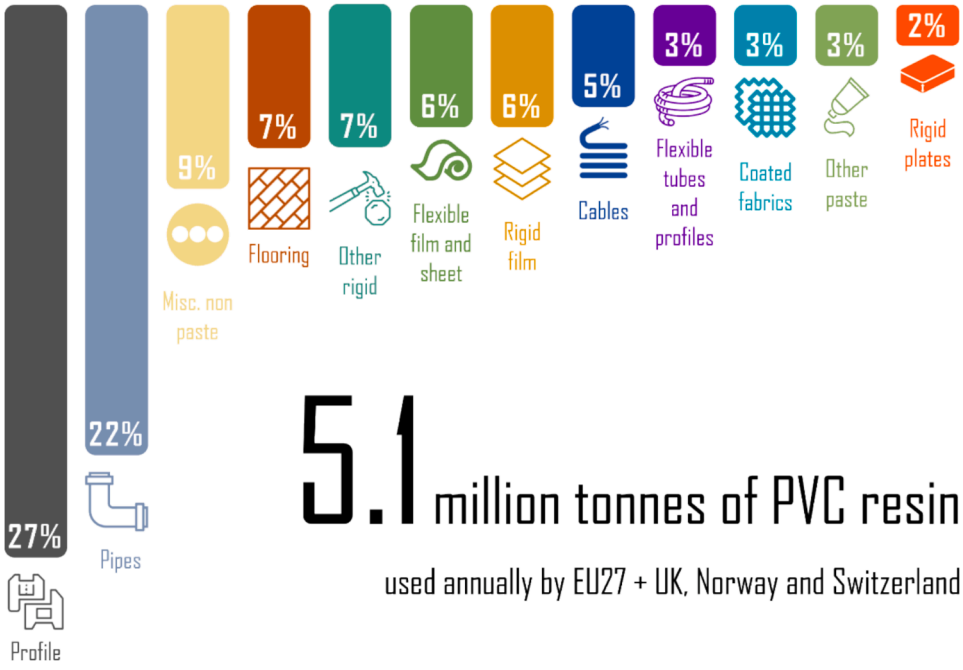

Fig. 1. Annual PVC use in EU27 + UK, Norway, and Switzerland broken into categories. PVC accounts for 10 % of all plastic used in Europe (ECVM, n.d.).

Emulsion (E-PVC) – Having a 10–12 % share in PVC resin production, emulsion polymerization is the second most common method for PVC resin production (Wheeler, 1981). VCM is mixed with water, a surfactant, and an initiator (water-soluble or oil-soluble) before it is sent to a reactor. Finally, the monomer is recovered and the PVC particles are dried and usually pulverized (Savrık et al., 2010).

Bulk (B-PVC) – Unlike the other methods, the bulk process (sometimes referred to as mass) does not require water or other solvents. The process is conducted by mixing VCM with an initiator in a reactor until ~ 10 % conversion is achieved (pre-polymerization), and the second step of polymerization is continued in a different reactor for a conversion of 80–85 %. After separating the unreacted monomer, the products are stored (Schoultz et al., 1977).

Solvent – With a small contribution to PVC worldwide production, the solvent process was developed by Union Carbide Corporation (now Dow®) (Shah and Poledna, 2002). This process is predominantly used to produce copolymers of PVC. VCM, the copolymer and a catalyst enter the reactor, where they are dissolved in the solvent and proceed to polymerization. After the stripping of the monomer, the resin is recovered with water and dried before storage.

3. PVC article formulation

Unlike most other plastics, high amounts of additives and mix-ins are often a characteristic of PVC articles. These additives include plasticizers, stabilizers, fillers, colorants, and other agents and can be present in very variable quantities, depending on the application (Ügdüler et al., 2020). For example, the content of PVC in a product such as cable can be less than 50 wt.%, while plasticizers and inorganics (e.g., calcium, aluminum, lead) make up the remaining half (Weil et al., 2006). On the contrary, a rigid application like window profile will typically contain up to 85 % PVC and no plasticizers. The remaining fraction will consist of mineral salts and other additives. To understand the complexity of PVC recycling, it is vital to identify these additives and their possible effects on the different recycling options. Fig. 2 shows the composition of some PVC articles.

3.1. Plasticizers

Pure PVC that is unplasticized (PVC-u or U-PVC) is a rigid material with a relatively high glass transition temperature (T_g) compared to that of polyolefins (~80 °C for PVC compared to ca. −10 °C for PP and −110 °C for PE) (Maddah, 2016; Omnexus, n.d.). One of the proxies used to describe PVC resins is the k-value, a simplified reference to the average chain length of PVC polymers in the resin. Higher k-values correspond to a larger average chain length due to lower polymerization temperatures (Schiller, 2015a). Different applications of PVC require different k-values ranging from 57 (e.g., blow film, calendered rigid film, foam technical profile) to 75 (e.g., water stops, cable insulation, automotive crash pad). The high T_g, accompanied by the relative thermal instability, makes the application of unplasticized PVCs with k-values of 70–74 difficult as they start to degrade at the process conditions (Schiller, 2015a). Therefore, for applications where different mechanical properties are crucial, PVC is plasticized either internally or externally. In internal plasticization, VCM is copolymerized with another monomer to alter its properties, whereas, in external plasticization, PVC homopolymer is mixed with plasticizers (usually esters) to reach the desired properties such as melt viscosity, elastic modulus, or glass transition temperature (Beirnes and Burns, 1986; Daniels, 2009). For instance, a content of less than 25 % di(2-ethylhexyl) phthalate (DEHP) is shown to reduce the T_g to approximately 0 °C (Martin and Young, 2003).

Plasticizers are used in applications other than p-PVC (i.e., plasticized PVC), but about 95 % of their 6.4 Mt annual global market (in 2011) belongs to PVC products (Schiller, 2015b). Wypych (2023) reports that the market size of plasticizers is more than double the consumption of flame retardants, impact modifiers, heat stabilizers, and antioxidants combined. These plasticizers are used in a variety of applications, such as floorings and walls, films and sheets, wires, and cables. For PVC products, phthalates, dicarboxylic acids, benzoates, adipates, and chlorinated paraffins are some of the commonly used plasticizers. In the case of phthalates, recent EU legislations and public health concerns have limited their presence (e.g., maximum 1000 ppm DEHP (EU Commission, 2021)) in new products, and their removal from waste products has become a challenge in PVC recycling (ECHA, n.d.; Hartmann, 2018). Most common phthalates that are found in plasticized PVC consist of alcohols bonded to (tere-, iso-) phthalic acid to create compounds such as diisooctyl phthalate (DOP), diisononyl phthalate (DINP), and dibutyl terephthalate (DBT). Recently, new plasticizers have been studied to address some of the environmental and health challenges. Morgan and Mukhopadhyay (2022) reported on bio-based plasticizers that could also be employed for their flame-retardant properties, thereby reducing the need for other chemicals. The search for sustainable plasticizers has become an important topic in research.

3.2. Fillers

Fillers are commonly used additives that are inexpensive and thus

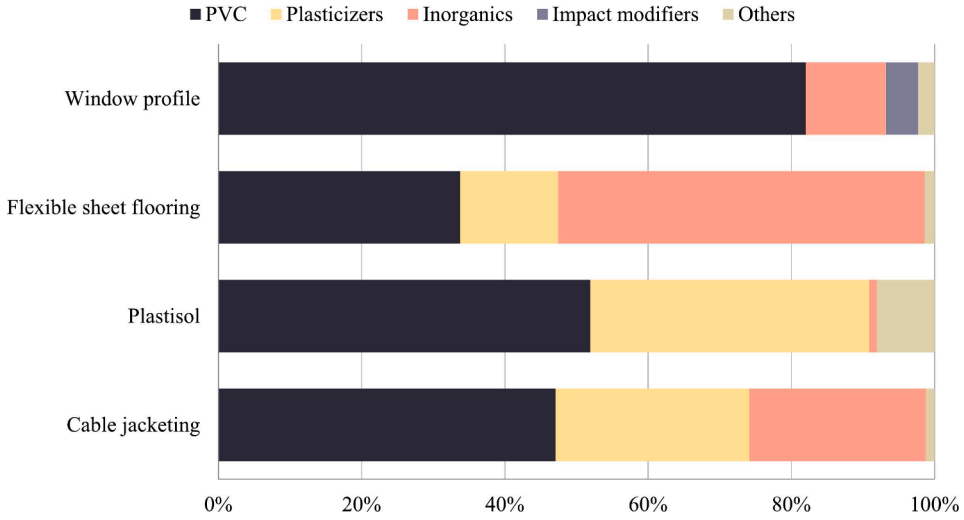

Fig. 2. Approximate PVC formula for different PVC products (Gilbert and Patrick, 2017).

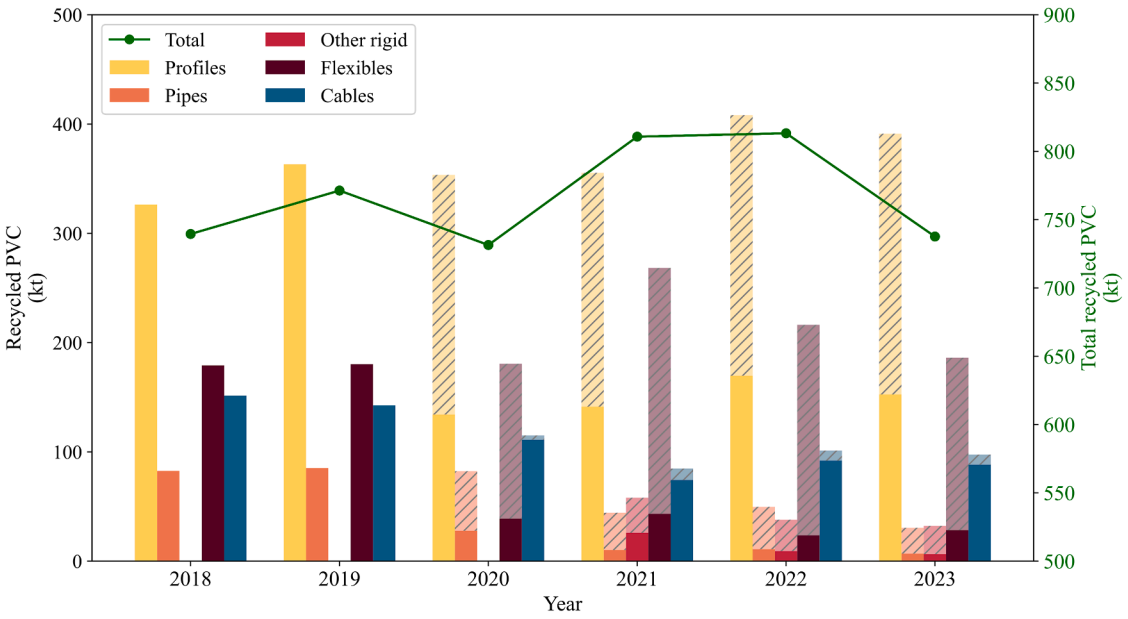

Fig. 3. Total annual tonnage of recycled PVC in Europe within the VinylPlus framework (VinylPlus, 2020, 2021a, 2022, 2023, 2024). Hatched lighter colors from 2020 represent pre-consumer waste.

reduce the market price of the plastic product and simultaneously can induce special functions such as density modification, EMI shielding, and abrasion resistance, among others (Wypych, 2020a). These fillers can include calcium carbonate, sand, and aluminum fiber. Some applications of PVC can have even 60 wt.% of fillers, such as chalk, in their formulation, so the importance of this group of additives in designing a recycling process is evident (Schiller, 2015a).

3.3. Stabilizers

Due to the presence of heteroatoms in the chain, when in contact with heat, radiation, or stress, PVC can start degrading. The mechanism of degradation initiates and propagates via the formation and involvement of HCl, the primary degradation product. PVC stabilizers aim to capture and neutralize the HCl (Wypych, 2015). This has led to the application of products such as metallic soaps (e.g., lead, cadmium, barium, and zinc stearates), organotins (e.g., alkyl- or dialkyl tins, and organotin mercaptides), and phosphites, among others. Some of the metallic stabilizers, such as cadmium and lead, have now been declared dangerous to human health and the environment by legal entities such as the European Chemicals Agency (ECHA)(ECHA, 2022). These "legacy additives" are usually difficult to separate from the waste and create challenges in valorizing the waste in recycling (Sevenster, 2012). The REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulations have thus allowed 0.1 wt.% of Cd and 1 wt.% of Pb in recovered PVC waste as an exemption as opposed to 0.01 and 0.1 wt.% in virgin material, respectively (ECHA, 2021; EU Commission, 2023). Although processes for removing such additives have been proposed, their implementation comes at the cost of complicating the overall recycling process or limiting the products or the choice of operation (Jaksland et al., 2000; Tsunekawa et al., 2011).

Despite the dominance of lead-based stabilizers in Europe until 2010, soon before they were phased out in 2015, organotin compounds were extensively uses in North America (among others) as another group of stabilizers (Schiller, 2015a). Recently, organotins have been under scrutiny in Europe due to concerns regarding the leaching of heavy metals (Commission and Environment, 2022). Tin stabilizers exist in many forms, such as (di-, tri-)alkyl tins or mercaptides (thiotins). Due to the toxicity of trialkyl tin chlorides and ethyl and propyl tins, as well as the ineffectiveness of aryl and branched alkyltins, methyl, butyl and octyl alkyltins are more common (Fisch et al., 1999). The mechanism of stabilization provided by organotins is similar to previously discussed stabilizers, i.e., through capturing the released HCl. Mercaptides, however, provide a secondary effect by releasing alkyl thioglycolates (Tahira et al., 2014). Braun (1981) proposes a mechanism whereby the mercaptide forms a bond with the PVC chain by reacting with the double bond resulting from dechlorination. This effect further stabilizes the chain and prevents further degradation. On the other hand, the alterations in the chemistry of degradation can pose a challenge in the recycling process, where intentional degradation of the chain is the main aim.

3.4. Flame-Retardants and smoke suppressants

PVC is a naturally flame-retardant plastic due to HCl being the primary degradation product and charring propensity; these features drive its widespread use in construction (Levchik and Weil, 2005). Nevertheless, flame retardants and smoke suppressants are added to the plastic in order to improve these features. Sb_2O_3, $Al(OH)_3$, $Mg(OH)_2$, molybdenum compounds, copper compounds, and zinc borate are some of these flame retardants and smoke suppressants (William Coaker, 2003). Ning and Guo (Ning and Guo, 2000) described the mechanism of action of zinc borate and aluminum trihydrate by lowering the activation energy of dechlorination and promoting the charring through cross-linking. Increased charring tendency is a challenge when chemical recycling is concerned.

3.5. Other additives

Apart from the abovementioned additives, PVC typically contains other additives such as lubricants, processing aids, impact modifiers, and colorants, albeit in smaller quantities (less than 3 wt.%) (Ügdüler et al., 2020). Table 2 summarizes the additives commonly found in PVC products.

3.6. Effect of additives on recycling

Due to their ubiquitous presence and chemical activity, understanding the additives used in PVC products is of utmost importance in PVC waste management. The amount of these additives in PVC waste

Table 1
Characteristics of each PVC resin manufacturing process (Savrık et al., 2010; Schoultz et al., 1977; Shah and Poledna, 2002; Tacidelli et al., 2009; Wheeler, 1981).

Process	Share (%)	Product specs.	Reagents	Pros/Cons
Suspension	82–85	Resin particles 50–150 μm	Suspending aid, initiator	+ High productivity + Flexibility regarding polymer composition and particle characteristics + Granular nature of the product − Large resin particles (50–150 μm) − Reactor fouling
Emulsion	10–12	Resin particles ~ 30 μm	Surfactants + water-soluble initiator, surfactants + organic peroxide initiator	+ Fine and uniform particle size suitable for paste and coating applications + Cheaper equipment for mixing with plasticizers and additives − Reactor fouling − Less flexible regarding different process conditions − Costly production
Bulk	5	Resin particles 50–150 μm	Initiator	+ Uniformity of particle size + Simplicity + High porosity of particles +Purity of products + No need for drying − Less flexible in product mix − Higher amount of residual monomer
Solvent	2	Resin particles ~ 75 μm	Comonomer, catalysts	+ High porosity + Free of soaps and suspending agents + Minimal residual monomer − Requires high investment

can render its recovery/recycling less economically feasible. In mechanical recycling methods, where the composition of the material is preserved, legacy additives can pose health and legal issues (ECHA, 2021; EU Commission, 2021). Regardless, soft PVC articles containing a host of additives have been reported to be mechanically recyclable with minor losses in mechanical properties (Janajreh et al., 2015; Yarahmadi et al., 2003). However, depending on their nature, the additives can alter the recycling process, specifically in chemical recycling.

The contribution of plasticizers in the chemical degradation of PVC waste is mostly through evaporation and degradation of the plasticizers producing oxygenated compounds (Saido et al., 1984). However, the presence of PVC and plasticizers under degradation conditions leads to interactions between the plasticizers and PVC and its degradation products. Phthalates, for instance, begin to degrade at lower temperatures in the presence of PVC producing products such as phthalic anhydride and other oxygenates (Saido et al., 2003). Furthermore, the plasticized samples produce higher quantities of chlorinated organic substances (McNeill et al., 1995). Phthalates such as DOP are also found to decrease the dechlorination temperature and yields (Jiménez et al., 1997). The decrease in dechlorination temperature depends on the plasticizer used. Marcilla and Beltrán (1996) reported the difference in

Table 2
Summary of common PVC additives.

Additive	Examples
Plasticizers	DOP, DINP, DBT, dibutyl sebacate, chlorinated paraffins, adipates
Fillers	Chalk, talc, aluminum fiber, carbon fiber, mica, sand, dolomite, wood fiber, kaolin, antimony trioxide, Mg $(OH)_2$
Stabilizers	Calcium stearate, magnesium oleate, epoxides, lead oxide, cadmium stearate, titanium dioxide
Flame retardants and smoke suppressants	Sb_2O_3, aluminum trihydrate, $Mg(OH)_2$, Mb compounds, Cu compounds, zinc borate
Lubricants	Fatty alcohols, paraffin waxes, metal soaps, oxidized PE waxes
Processing aids and impact modifiers	Polymethyl methacrylate, precipitated calcium carbonate, acrylic impact modifiers, ethylene vinyl acetate
Blowing agents	Hydrochlorofluorocarbons, hydrocarbons, liquid CO_2, 5-phenyl tetrazole, sodium bicarbonate
Antistatic	Aliphatic amides, organic phosphates, glycerol monoacyl esters
Foaming agents	Ammonium sulfate, substituted ureas
Biocides	Copper, zinc, tin, and mercury soaps, organotins
Colorants	Anthraquinone, azo, carbon black, metallic flakes, naphthol red, titanium dioxide, zinc oxide

Adapted from Schiller (Schiller, 2015b; Ügdüler et al., 2020).

the degradation temperatures for different plasticizers and ascribed the differences to two explanations: (1) the addition of polar substances to PVC has been shown to reduce its stability, and (2) more plasticizers result in higher viscosity of the melt hindering HCl diffusion, thereby affecting its autocatalytic effect. Results from hydrothermal degradation of plasticized PVC show similar degradation products (benzaldehyde, acetophenone, and 2-ethyl-1-hexanol) from DEHP (Xiu et al., 2020a; Xiu et al., 2023a). Gasification of PVC pyrolysis residue demonstrated higher conversion rates and reactivity of the flexible PVC residue compared to rigid PVC (Morishita et al., 2004).

Mechanical recycling of blends and composites is inherently more challenging than pure substances (Zhao et al., 2022). As PVC is often blended with substantial quantities of fillers or used with reinforcement materials, the impact of such agents on recycling is important. While PVC articles containing various additives including fillers have been mechanically recycled (e.g., cable and flooring (Janajreh et al., 2015; Yarahmadi et al., 2003)), a comparison between the total recycled tonnage of PVC articles with high additive content compared to less additive content articles (Fig. 3) illustrates the technical challenges in the mechanical recycling of more complex feeds.

Karayildirim et al. (2006) investigated the effect of common fillers, such as calcium carbonate on the degradation of PVC and found an increase in the maximum temperature of dechlorination and a lower rate of mass loss in the presence of carbonates. Their results suggest a decreased rate of decomposition to benzene due to acid scavengers. As HCl plays an autocatalytic role in the degradation of PVC, its absorption to inorganic fillers such as $CaCO_3$ reduces the reaction rate. Furthermore, the formation of $CaCl_2$ crystals leads to a lower porosity in the solid and hinders PVC pyrolysis (Li et al., 2023a). Moreover, the presence of sorbent materials in the pyrolysis environment is associated with higher chlorine content (Hubáček et al., 2022). However, the latter is contested by the results from Karayıldırım et al. (2005). Other additives such as SiO_2 and Al_2O_3 have been shown to be more effective in absorbing the HCl and encouraging the dechlorination (Saeki et al., 2001). Similarly, in the gasification of PVC waste, Kasteren and Slapak (2001) reported a decrease in carbon-to-gas conversions in the presence of fillers. Additionally, the reaction of the HCl with the fillers in chemical recycling, renders a meaningful portion of the hydrogen chloride unusable as a product.

The potential effects of stabilizers in recycling, similar to plasticizers, is on two levels: the legal, health, and environmental aspects, and the

technical challenges. As some of the legacy stabilizers such as lead and cadmium now face legal thresholds in Europe and are known to pose health and environmental hazards, their presence in PVC waste further limits their recycling. This is particularly severe in mechanical recycling where the composition is unchanged. Wiesinger et al. (2024) reported significant levels of hazardous substances such as lead in 16 % of the samples investigated and attributed this to uncontrolled recycling of the contaminated waste materials. Stabilizers are partially consumed during the lifetime of PVC (Braun, 2002). As a result, recycled PVC often needs to be restabilized to prolong its lifetime, thereby increasing its stabilizer content (Pfaendner et al., 1995). However, the increased protection against degradation can be considered a drawback in chemical recycling. PVC containing stabilizers exhibits longer induction times and higher temperatures of degradation (Atakul et al., 2005). Saeed et al. (2004b) found higher chlorine content in the char remaining from lead-containing PVC samples. Furthermore, the benzene yield from the pyrolysis of PVC was diminished in the presence of zinc stabilizers due to crosslinking, whereas tin stabilizers produced a comparable amount of benzene (Suzuki et al., 1972).

Lastly, flame retardants affect the chemical degradation of PVC by promoting char formation and participating in the degradation mechanisms chiefly in the first step of PVC degradation (Levchik and Weil, 2005; Wang et al., 2023a). Increased charring diminishes the total usable products in pyrolysis processes.

Due to the diversity and smaller quantity of those additives in PVC products, other PVC additives and their effect on recycling processes have not been investigated thoroughly. Nevertheless, the extent of such effects caused by PVC additives cannot be overstated. Therefore, a comprehensive understanding of the feed and appropriate waste management is imperative in handling PVC waste.

4. PVC waste

At the end of an often long lifetime, PVC products are inevitably disposed of as waste. Since PVC content in waste streams is directly linked to the complications in the waste treatment method, understanding the streams, sorting methods, and their effects on the strategy for an effective recycling process is necessary.

4.1. Waste Generation

In Europe, the most significant fraction of PVC post-consumer waste among specific sectors is from the building and construction sector (more than 40 %), followed by packaging (~20 %), electrical/electronic equipment (~8%), and automotive (~2%) (ECHA, 2023). Only a small fraction of MSW is comprised of PVC (usually below 4 wt.%, (Adrados et al., 2012; Gao et al., 2023)). Indeed, the majority of PVC waste is produced in specific sectors, where separate collection and sorting strategies are implemented. Yet, even after separate collection, further separation techniques are still necessary to separate PVC from other components of the waste, including glass, metals, and, most importantly, other polymers.

4.2. Sorting

The process of sorting PVC waste often starts with a shredding step. Following that, the separation process can be realized through one or a combination of technologies to reach a certain purity of the components required for the specific downstream process. These techniques each utilize a specific quality of the different components, such as the physical (specific gravity and melting point), electrical, and chemical (spectroscopy, selective dissolution, and wettability) properties (Ruj et al., 2015).

While metals can be separated in an earlier stage thanks to their magnetic properties or considerably higher specific gravity, the separation of different plastics from each other can be rather challenging due to their relatively close densities (Adhikari, 2021). Flotation techniques are an example of these methods, whereby a liquid medium of a specific gravity separates the waste into a sinking and floating fraction. Here, polyolefins (HDPE, LDPE, and PP) set themselves apart from the rest owing to densities of less than 1 $g.cm^{-3}$. PET and PVC products have a wide range of densities depending on their formulation (Ragaert et al., 2017)., typically between 1.15–1.55 and 1.3–1.45 $g.cm^{-3}$, for PVC and PET respectively. These can thus be easily separated in water from the polyolefins, but not from each other. Modifications to the separation medium or the surface of the polymers are needed to distinguish the rest (such as PVC and PET, two plastics that can often be found together) (Phengsaart et al., 2023). Pneumatic separation methods, centrifugation, hydrocyclones, and hybrid-jigs (i.e., separation based on settling velocity in a water bath through fluidization via air injection (Ito et al., 2019)) are other methods developed with the same principle (Choi and Yoo, 2007; Hori et al., 2009). Melt separation can also be used by taking advantage of the difference between the melting points of different plastics, however, in heat-sensitive polymers (such as PVC), various degrees of polymer degradation can be expected as a downside. Physical separation methods come with limitations, such as requiring a media, substantial energy demand for operation, and imperfect separation of products with close or overlapping densities. Nevertheless, the simplicity, low cost and potentially high throughput make them an attractive option as a part of the sorting process (Jiang et al., 2023).

For further separation, the electrical properties of the materials can be exploited. Electrostatic and triboelectric separation techniques rely on the affinity of materials to electrons. Particles of different materials are first charged using triboelectric charging, either by rubbing against each other or an external body (Bendimerad et al., 2009). By choosing the appropriate charger material based on the tribo-series of polymers, the plastic components in the waste can be charged differently. For instance, by choosing PP as a charger material, PVC will be charged negatively and PET will be charged positively, while by switching to a HIPS charger material, ABS can be separated from PET and PVC (Jiang et al., 2023; Park et al., 2007). Corona chargers can also be employed to charge the waste particles for the separation of different kinds of materials, including metals and non-metals (Phengsaart et al., 2023). The charged particles are later subjected to an electric field to separate the positively charged particles from those with a negative charge.

Lastly, the chemical properties of the distinct waste components create a host of separation options, including spectroscopic methods. Near-infrared (NIR), X-ray fluorescence (XRF), (laser-induced breakdown spectroscopy (LIBS), laser-induced plasma spectroscopy (LIPS), Raman spectroscopy, and UV–vis are some of the relevant spectroscopic methods (Adarsh et al., 2022). For PVC waste, the presence of chlorine as a heteroatom aids the characterization by acting as a proxy for PVC polymer. In an automatic waste sorting facility, after effective characterization of each particle using spectroscopic methods, the particle is separated into sorted streams using an air jet or via other mechanical means (Gundupalli et al., 2017). Among the spectroscopic methods, NIR has received significant attention both in the research and commercial stages thanks to its reliability, speed, and simple implementation (The Association of Plastic Recyclers, 2018; Freitag et al., 2000). The NIR technique is used in combination with a library in order to distinguish polymers based on their unique infrared spectra. NIR has been reported to separate PVC with up to 100 % accuracy among other polymers in dry, un-contaminated, or clean samples, but challenges remain in detecting black particles (Bassey et al., 2021; Zheng et al., 2018). Additionally, hand-held NIR devices have the potential to be used in rapid identification and inspection of samples on smaller scales with high precision (Schmidt et al., 2020). Rani et al. (2019) presented an application of a microNIR on urban plastic waste and reported no significant loss of accuracy due to contamination. Due to the inherent nature of PVC and the existing schemes for collecting major PVC waste streams, sorting technologies such as NIR are mostly used for flakes from a plastic mixture, and bulky items are sorted manually. Nevertheless, the

advancement of sorting technologies can further reduce the PVC content in waste streams prior to the waste treatment step.

The process of identification followed by separation can be categorized as an indirect separation method. This is unlike the previously discussed techniques where the separation act itself relies on the properties of the component. Most reported spectroscopic techniques can handle plastic waste of high diversity and result in high accuracy. However, an effective separation might require a multi-sensor detection equipped with artificial intelligence (AI) algorithms to identify complex waste streams at high speed (Strollo et al., 2020).

4.3. Energy recovery

Often referred to as quaternary recycling, energy recovery is the last resort among recycling options where material recovery is not practically or economically feasible (Al-Salem et al., 2010). Although energy recovery is usually synonymous with incineration, other technologies, such as chemical looping combustion, are emerging for this purpose, primarily due to the environmental concerns of PVC incineration (Buekens and Cen, 2011).

4.3.1. Incineration

Incineration is combusting a feedstock in an oxygen-rich environment to utilize the energy produced as heat, while eliminating the solid waste that would otherwise take up considerable landfill space. This solution is becoming increasingly adopted by the industry as it accepts a wide range of feedstock, uses simple, low-cost technology, and utilizes copious amounts of plastic waste accumulated in landfills to generate energy. However, incineration has always been a point of debate when it comes to PVC.

There are several reasons for the controversy around PVC waste incineration. The reported production of dioxins and chlorinated products from the incineration of PVC is a severe concern regarding human health in surrounding areas (Park et al., 2007). Moreover, the volatilization of heavy metals in PVC products is also an environmental threat. The inevitable toxic HCl gas production is a regulated emission product (less than 2–8 mg/Nm^3 in the EU for existing plants (EU Commission, 2019)) and causes corrosion to the equipment. Since chlorine constitutes more than 50 % of the PVC polymer, the organic content of this waste is relatively less and energy recovery from combustion is, therefore, much smaller than that of other carbon-rich polymers. As a result, PVC content in the waste stream is often considered a challenge for incineration plants and incineration has not yet been considered a serious contender in PVC waste management.

However, in specific cases such as medical waste, where PVC is used, incineration is a widely accepted practice due to the health risks stemming from the contaminated waste material (Jang et al., 2006). However, various issues such as the abovementioned pollutants have made the incineration of medical waste challenging due to its PVC content (Attrah et al., 2022). Concerns regarding PVC incineration emissions and the loss of the material have led scholars to suggest alternative strategies involving appropriate sorting and pretreatments followed by a chemical recycling method in order to valorize this waste stream effectively (Joseph et al., 2021; Su et al., 2021).

Despite the public view on PVC incineration, Scott (La Mantia, 1996) claims that this concern is less than valid as most modern incinerators can handle the problems concerning effluent in order to minimize emissions, especially when the PVC is present in smaller amounts. Zhang et al. (2015) reiterate that dioxins and other toxins are particularly problematic only if the incineration is not performed well, as is the case with open fires (e.g., landfills or backyard burning). In contrast, controlled incineration simultaneous with the employment of neutralizing salts are generally safe. Although other authors report dioxin production from organic and inorganic chlorides, incineration at 1000 °C has been shown to reduce the total dioxins by 99.9999 % (Shibamoto et al., 2007). The addition of inorganic reagents is another solution proposed for reducing dioxin formation. Copper wires and TiO_2 nanohybrides reduce total dioxin formation by 55 and 70 % (Kim et al., 2008; Yasuhara et al., 2005). However, Sun et al. (2003) found adverse effects of TiO_2 mixed with PVC and suggested a combination of $CaCO_3$ for reduction of dioxins in the gas and TiO_2 for photocatalytic decomposition of trapped dioxins in the ash after incineration. Another approach, which will be discussed further in the following sections, can be the dechlorination of the waste prior to incineration. Depending on the amount of PVC in the waste stream, such as for PVC-contaminated feedstocks, dechlorination could be deemed a reasonable approach for PVC mixes by reducing the problems caused by the chlorine radicals in the subsequent steps and by realizing a controlled release of HCl product (Joseph et al., 2021). Overall, the modernization of incineration plants and the employment of appropriate pretreatments and agents are reported to be necessary in addressing the major problems associated with this technique.

4.3.2. Chemical looping combustion

Incineration is not the only technology available for combustion of plastic waste. Chemical looping combustion (CLC) has proven interesting for this application recently. CLC is especially useful for polymers such as PVC, which reportedly diminishes dioxin production (Yaqub et al., 2023). CLC utilizes oxygen-carriers such as metal oxides to oxidize the feed into CO_2 and water and the consumed oxygen-carrier is then oxidized back to its initial form via air/O_2 (Yaqub et al., 2021).

As oxygen carriers are fundamental to this process, research has focused on this aspect to optimize further the CLC of PVC, particularly the dechlorination step. Modification of iron ore is a popular area of study, as reflected in the work conducted by Jiang et al. (2022), which used alkali metals and alkali earth metals to improve HCl removal. Combining this method of combustion with other methods of recycling, such as gasification or pyrolysis, has also been explored (Bi et al., 2015b; Ma et al., 2019a). The literature on the CLC of PVC consistently claims lower emissions of toxic compounds produced during the process and a better-controlled operation (Bi et al., 2015a).

5. PVC recycling

PVC waste recycling is highly dependent on the amount of PVC polymer in the waste stream. PVC can often be found compounded with other polymers or mixed in a waste stream with other plastic waste. That means that the amount of PVC resin in the waste can vary from a fraction of a percent to tens of percent. Each waste stream calls for different processing and offers different values, posing different challenges. Hence, several recycling technologies have been proposed over time to address PVC waste. Fig. 4 shows the trend of scientific literature on some of these technologies discussed herein. Nevertheless, PVC waste recycling, much like any other plastic waste recycling, can be divided into two categories: physical and chemical. Each of these methods is discussed, and their specific advantages and disadvantages are presented.

5.1. Physical recycling

5.1.1. Mechanical recycling

The process of mechanical recycling usually refers to a series of steps involving mechanical operations that turn plastic waste into new articles. As Ragaert et al. (2017) describe, the process of manufacturing new articles with solid plastic waste includes separation and sorting, baling, washing, grinding, compounding, and pelletizing, and the new plastic product can be fashioned into articles (Fig. 5). Mechanical recycling is currently the most common and widely applied recycling method. In 2022, out of 11.6 Mt (19.7 % of total plastics) of so-called *circular* (i.e., recycled or bio-based and bio-attributed) plastic production in Europe, almost 94 % were mechanically recycled from pre- and post-consumer plastics (Plastics Europe, 2023). This process is often known for its simplicity but also for its main disadvantages, which are products with

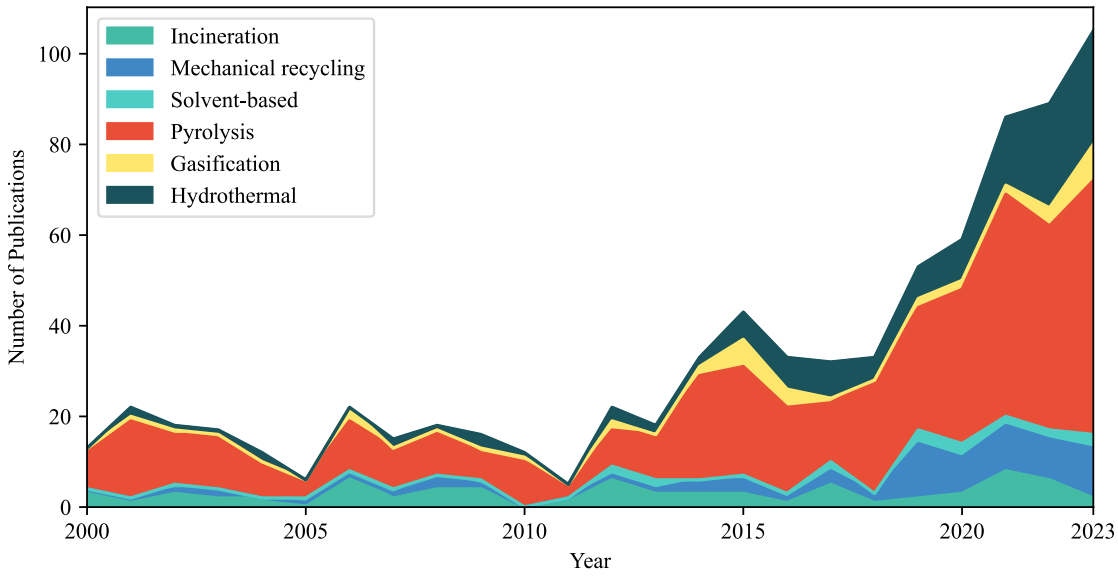

Fig. 4. Number of scientific publications, in English since 2000 on PVC waste end-of-life solutions. The number of publications has been obtained from Scopus database with the following keywords in the abstract: "PVC Waste" as well as "Incineration", "Mechanical Recycling OR Extrusion OR Aggregate", "Dissolution AND Solvent AND NOT Chemical Recycling", "Pyrolysis", "Gasification", "Hydrothermal OR Supercritical Water OR Subcritical Water" (searched on 21 May 2024).

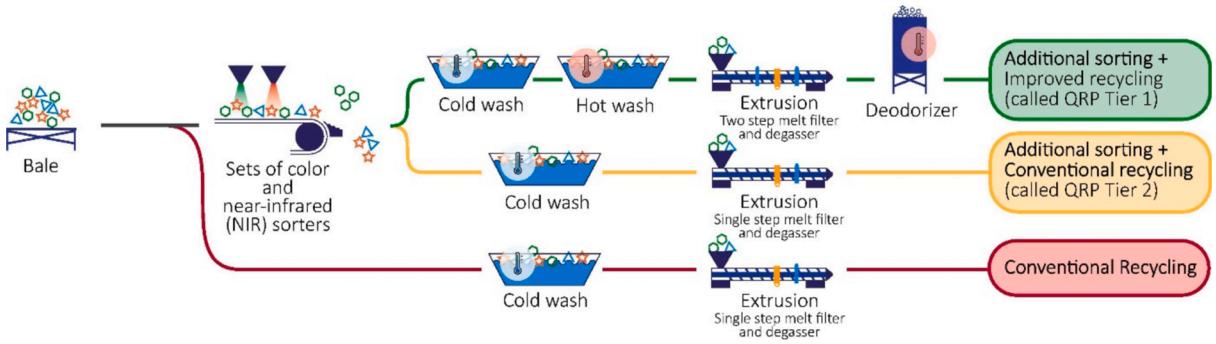

Fig. 5. Mechanical recycling of plastic waste using current schemes (bottom) and improved scenarios. Reproduced with permission from Elsevier (Bashirgonbadi et al., 2022).

inferior properties compared to the initial material and its inability to handle heterogeneous plastic products (e.g., multi-layered) (Jeswani et al., 2021). Mechanically recycled PVC (inferior rheological properties) is often blended with virgin PVC resin (superior rheological properties) to achieve the desired qualities (Schyns and Shaver, 2021). In rigid applications, ratios of up to 50 % recycled material blended with virgin resin have been reported to showcase comparable mechanical properties (Popovska-Pavlovska et al., 2000). Moreover, experiments by Ditta et al. (2004) suggested high recyclability from U-PVC from old buildings (20 years old) via re-extrusion based on mechanical and rheological properties. The re-extrusion of window profile regrinds up to three times resulted in an elongation at break slightly lower than Pb-stabilized virgin PVC in the first two extrusions and higher after the third re-extrusion. The authors attributed the initial decrease and eventual increase in elongation at break to changes in the degree of gelation. This is while the tensile strengths of the regrind after three cycles of extrusion remained consistently higher than Pb-stabilized U-PVC due to the effect of aging in creating crosslinkages and chain enlargement.

Blending with other polymers (e.g., SAN and ABS) is also reported as a method to achieve better mechanical and thermal properties (Garcia et al., 2006). Jaidev et al. (2020) reported significant benefits from blending recycled PVC from wires with recycled ABS and HIPS in the physical characteristics of recycled PVC independent of the source of the recycled materials. Their study suggests the role of released HCl from PVC in forming crosslinkage in the polymeric blend and thus, increasing the impact strength. In a different approach, Grigoryeva et al. (2005) successfully utilized chemically-uncrosslinked PVC/PU blends both as a polymer plasticizer (instead of DOP) and a polymer modifier in plasticized PVC application. In a similar endeavor, Sukkaneewat et al. (2024) blended recycled PVCs across applications using cling film and PVC pipes to toughen pipes and increase elongation with the use of cling film as a self-plasticizer agent. Mechanical recycling methods can also be employed in addition to other forms of physical recycling to improve the tensile properties of the product by improving the gelation and mixing of the additives (Kelly et al., 2005).

Composites are another field where mechanical recycling of PVC waste has found application. For an instance of such applications, PVC waste can be used as aggregate in construction material (Boutlikht et al., 2023; Karboua et al., 2023; Rafiq Bhat and Vikram, 2023). Fine aggregates from PVC pipes were reported to enhance the mechanical behavior of clay soils (Karboua et al., 2023), while fibers made from discarded PVC pipes improved the mechanical properties of concrete such as compressive strength (Boutlikht et al., 2023). In a comparison with PP fibers, PVC cable waste increased the compressive strength of concrete more and decreased the slump value (Rafiq Bhat and Vikram, 2023). The latter highlights the possibility of incorporating soft applications of PVC for this application and achieving superior mechanical properties. Noor

Azline et al. (2023) point out that the slump measurements are not sufficient to conclusively prove that the addition of PVC in concrete decreases the workability of fresh concrete. Their review underlines the influence of physical properties of the aggregate such as size on the final properties of the concrete and concludes that PVC plastic aggregate may replace coarse aggregate up to 30 %. Singh et al. (2023) enumerate some of the challenges associated with the use of plastics in bricks such as heat and UV sensitivity and overall susceptibility to degradation. Given the durability expected of construction materials such as bricks and concrete, these concerns must be investigated to ensure safety in using plastic waste in this sector.

One key issue with the latter two approaches (i.e., blends and composites) is the recyclability of the recycled products. Composite materials and polymer blends often exhibit higher degrees of complications in recycling due to more complicated chemistry and composition and difficult separation of constituents (Tomatis et al., 2023). Depending on the blend and its characteristics, specialized processes may be necessary for their effective recycling (Dorigato, 2021). When designing a recycling process, it is crucial to be mindful of the recyclability of the recycled good in order to avoid contributing to the problem of plastic waste.

Currently, in the EU, several schemes and companies in various countries are tasked with PVC recycling. The majority of these schemes operate within a narrow range of products in order to limit contamination in the feedstock and maintain a higher quality of the final product as a result. Table 3 summarizes some of the companies active in the field

Table 3
Examples of schemes and companies operating in the field of PVC mechanical recycling (ACR+, 2006).

Company/initiative	Countries	Capacity (tons/yr)	Feed
AgPR	Germany		Flooring
VEKA	Germany, UK, France	100,000	Window frame
Roofcollect (AfDR)	EU		Roofing
Rewindo	Germany	44,000	Window frame
KRV	Germany		Pipes
K&F Global	Germany		Films
Hundhausen	Germany		Pipes
WUPPI	Denmark	12,000	Rigid PVC
BIS (Bureauleiding)	Netherlands		Pipes
VKG Keurmerk	Netherlands		Window frame
Deceuninck	Netherlands, Belgium, Luxemburg	40,000	Window frame
RAFF Plastics	Belgium	70,000[a]	Medical PVC
Construction Plastic Recycling Scheme	Australia		Pipes and fittings
RecoMed	UK	8	Single-use medical PVC
JP Industrial	USA		Not specified
Ecotile	USA		Flooring
ScrapManagement	USA		Scraps
PVC Enterprise	Canada		Not specified
Nanchang Yuxiang Zaisheng Ziyuan Co. Ltd	China		Not specified
Zibo Chiding Petrochemical Co., Ltd	China		Not specified
AVS Cables & Compounds Industries	India		Soft PVC
AVSL Industries Ltd	India		PVC scraps
Acar Plastik	Türkiye		Not specified
Nova Recicla Plásticos	Brazil		Not specified
Compuestos y Derivados, S.A.	Guatemala		Not specified
Distribuidora Famaplast	Mexico		Post-industrial PVC

[a] Combined capacity for PVC, PP, HDPE, and PS.

of PVC mechanical recycling. These schemes are usually comprised of careful collection of specific waste streams that are deemed recyclable with a reasonable quality (e.g., no adhesives or similar contaminants) followed by sorting and extraction of non-PVC elements (e.g., metals, rubbers, glass) and regrinding. The regrind is then sold to PVC converters or used in-house for the manufacture of new PVC products. Due to the fundamental nature of mechanical recycling when used alone, and higher content of stabilizers in rigid applications used within these schemes, the content of legacy substances in the recycled material obtained has been the subject of discussion. In the EU, where the content of lead stabilizers, for instance, is limited to 0.1 % in all PVC products sold inside the union, a derogation was permitted by the commission for recycled rigid PVC to allow for lead content of up to 1.5 % until 2033 (EU Commission, 2023).

Mechanical recycling has not been widely adopted for post-consumer flexible PVC waste (ECHA, 2023). The inherent characteristics of PVC articles, such as generally considerable amounts of additives and plasticizers compared to other plastics, as well as high thermal instability, make the mechanical process challenging for this type of waste (La Mantia, 1996). Regardless, a few groups have investigated this technology so far, mainly on specific PVC articles. Cable insulation material and post-consumer flooring material are reported as examples of flexible applications that have the potential for mechanical recycling without considerable loss of quality (Janajreh et al., 2015; Yarahmadi et al., 2003). Nevertheless, the chemical changes in the PVC during the recycling process have been a point of concern, especially when superior longevities are expected of the product (such as in construction). Yarahmadi et al. (2001) investigated the expected lifetime of a Ca/Zn stabilized virgin PVC sample after several re-extrusions and reported a three-fold loss of lifetime after five re-extrusions. However, the results until the fourth extrusion suggest that the extrusion could still serve as a viable option for this application.

The simple nature of mechanical recycling combined with a product-to-product approach makes it an attractive option for the industry, both economically and technologically. Mechanical recycling can be very convenient for feedstocks such as off-cuts produced during the manufacturing of PVC articles and/or installation sites (Schuyler et al., 2022). However, complex waste streams, especially those with legacy additives or mixed nature, can prove challenging. Stichnothe and Azapagic (2013) showed great environmental savings from mechanical recycling of window frames with 200 kt CO_2 eq./yr savings for 100 kt/yr of window frame waste. However, several issues persist along the way. Appropriate identification methods are required to evaluate the legacy additives in each feed and subsequent decisions must be made based on the legal framework. Moreover, advanced sorting techniques and efficient and effective collection strategies are crucial in employing mechanical recycling.

5.1.2. Solvent-based methods

While the objective of mechanical recycling is to turn waste from PVC articles into new PVC articles, solvent-based recycling (material recycling) herein focuses on extracting, or rather purifying, the PVC resin or other components of the waste without intentionally altering the chemical structure of the polymer (Collias et al., 2021).

Dissolution/recovery is among the technologies that have been considered for the recycling of PVC as a form of physical recycling that retains the chemical properties of the polymer. Fig. 6 illustrates a simplified implementation of this technique. Depending on the waste stream and the main goal, several solvents have been proposed by the literature for this project. Vinyloop® is a process developed and patented by Solvay that uses solvents to purify PVC compounds from contaminants in a closed loop (Sadat-Shojai and Bakhshandeh, 2011). In this process, a combination of methyl ethyl ketone, hexane, and water (82, 13, and 5 %, respectively) was used to selectively dissolve PVC. The solvent was subsequently evaporated by injecting steam to precipitate the purified PVC compound, which was recovered as a slurry in an

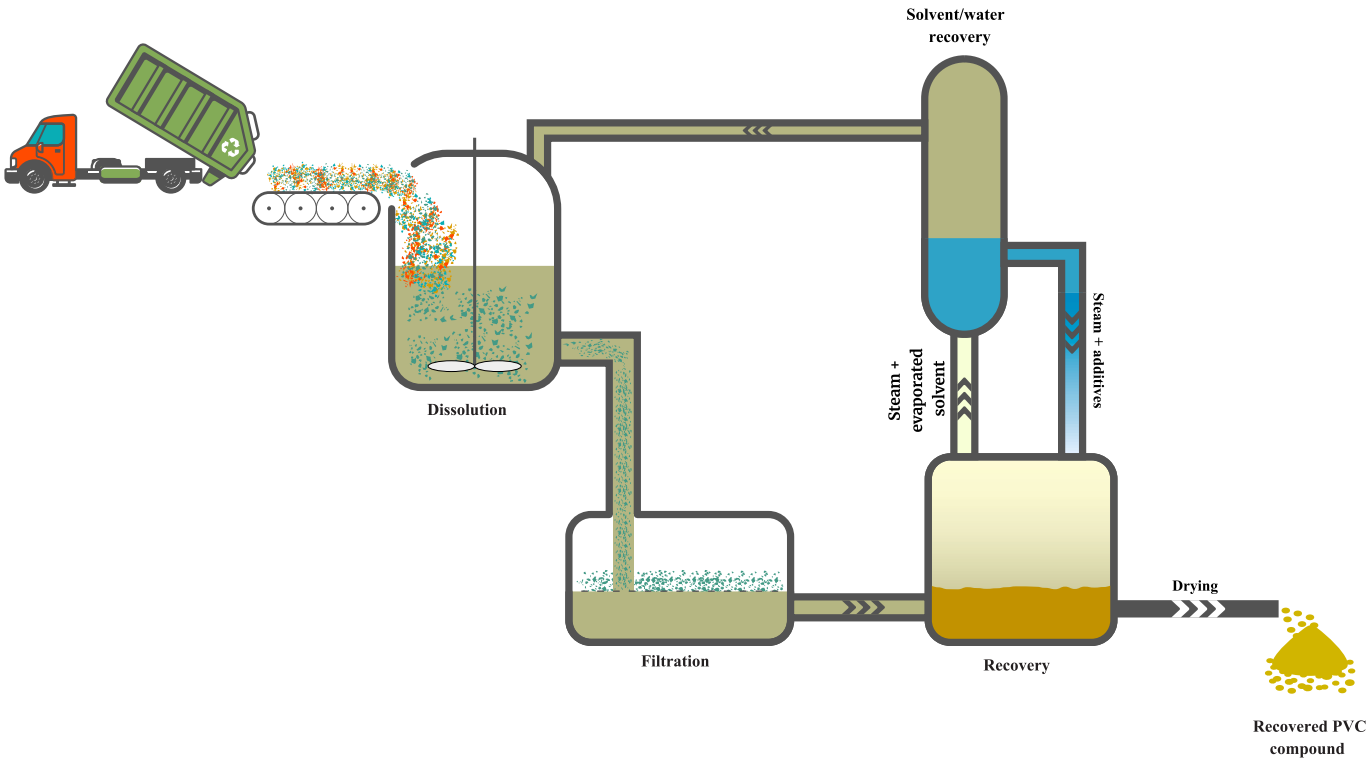

Fig. 6. Simplified scheme of the dissolution/recovery process used in a closed-loop (Sherwood, 2020).

aqueous phase (Sherwood, 2020). An industrial plant, Vinyloop® Ferrara SpA, was constructed in Ferrara (Italy) and was running between 2002 and 2018. However, the recycling plant was closed in June 2018 after the new legislation by the EU's REACH outlawed higher contents of heavy metals and specific phthalate plasticizers, including DEHP, DBP, DIBP, and BBP, most of which can be found in abundance in older PVC articles (ECHA, n.d.; Hartmann, 2018).

In an earlier attempt, Kampouris et al. (1986) succeeded in recovering rigid PVC from bottles up to 95 % using a cyclohexanone/n-hexane solvent couple, while retaining favorable chemical and mechanical characteristics such as molecular weight and tensile strength. Unfortunately, the study focuses only on rigid PVC and fails to adequately address the role of plasticizers or additives in the process. In a later study by the same research group, Papaspyrides and colleagues included pipes in the experiments and optimized the solvent mixture by reducing the required hexane and introducing water with an organic adduct (Papaspyrides and Diakoulaki, 1986). The optimization resulted in recovery rates as high as 97 % for bottles and 92 % for pipes. In the case of pipe samples, they reported a recycled grade with lower mechanical properties compared to that of the virgin polymer but better than the pipes, presumably due to the retention of some of the plasticizers and additives in the process of recovery in the polymer matrix.

In 2009, Achilias et al. (2009) investigated the concept of dissolution/reprecipitation of model polymers and packaging materials. The study found high PVC recovery from both dichloromethane/methanol and toluene/methanol solvent/non-solvent systems at temperatures ranging from 25 to 50 °C with the former system being highest at 50 °C with a small advantage over the others. The study reported 98.1 % recovery from detergent packaging, 90.5 % from pill bottles, 63.1 % from blister packs, 82.7 % from food membranes, and up to 98.2 % from model PVC. Furthermore, their results were consistent with the findings from other groups in that an increase in glass transition temperature was observed after recycling, attributed to the (partial) removal of additives such as plasticizers in the process.

In general, two points are essential when considering the solvent-based recycling of PVC articles. The first point is regarding the complexity of the PVC mixture. Dissolution/recovery processes have limitations in removing the additives, and there is much-needed work to be done on this topic in order to better understand the effect of this process on specific additives and their recovery rate. The second issue is the limiting nature of this technology. The recovered polymer has the same or slightly lower chemical properties, which makes the product useful in similar applications in most cases. Therefore, the process is less flexible in terms of the products, and it is not suitable for taking in a wide range of products with different chemical specifications (e.g., molecular weight).

5.1.2.1. Extraction of additives. Some have approached the concept of physical recycling of PVC articles from another end, which is the recovery of the additives more than the resin itself. Surely, the additives-extracted resin will be a product of such operation, but the main goal is, nevertheless, to extract the additives, including plasticizers, stabilizers, impact modifiers, etc. This process, which is closely pertinent to the recycling of PVC, often yields valuable plasticizers and purified PVC, which can be modified/recycled through other means for any specific application, leading to a higher degree of flexibility. In the case of PVC, as Ügdüler et al. (2020) summarized in their review of additives extraction methods, Soxhlet, ultrasonic, microwave-assisted, supercritical fluid extraction, accelerated solvent extraction, and dissolution/precipitation methods have been adopted with the help of solvents such as THF, methanol, and hexane in order to extract plasticizers and other additives.

Braun (2002) describes an analytical procedure for PVC material used in roofing which can be used as an example for designing a process with a more holistic approach. In his procedure, plasticizers are first separated via Soxhlet extraction in diethyl ether. There is enhanced value in plasticizers' separation, both in the compounds themselves and in the fact that the product can be more aligned with the newer regulations since some of the older additives are now declared prohibited. Next, the fibrous material in the potential composite is filtered after dissolving the material in THF. Finally, through centrifugation, other

insoluble additives in THF (e.g., inorganic additives and crosslinked PVC) are removed and PVC polymer is left in the solution. The inorganics can be analyzed after the ash test and the rest is assumed to be crosslinked PVC.

Beneš et al. (2006) removed DOP plasticizer from PVC cable insulation material up to 70 % after 30 min of ultrasonic treatment in n-hexane without dissolving the PVC. A five-minute ultrasonic treatment in THF was successful by 98–99 % in removing the DOP, but the PVC was also dissolved. They observed very low efficiency with cyclohexane and higher efficiency (compared to that of cyclohexane) with dichloromethane accompanied by partial dissolution.

Supercritical fluids have been employed in the extraction of a variety of components in different fields. Despite their recent boom, supercritical fluid extraction (SFE) of PVC additives has been reported as early as the 1990 s (Hunt et al., 1991; Marín et al., 1996). Marín et al. (1996) proposed an optimized set of extraction conditions using supercritical CO_2 between 90 and 100 °C which obtains higher efficiencies at shorter times compared to the traditional Soxhlet method. Later experiments suggested the effectiveness of SFE of benzoates and citrates from PVC under similar conditions (Guerra et al., 2002a; Guerra et al., 2002b). Moreover, through utilizing supercritical CO_2, Versteeg et al. (2024) achieved more than 98 % efficiencies in extracting DEHP resulting in 99.5 % PVC purity in the final product. By combining the supercritical fluid extraction and conventional ether extraction of plasticizers, Wang et al. (2024) employed liquified dimethyl ether with and without THF to extract DEHP and PVC in colored PVC waste samples. SFE promises remarkable recovery rates without the high consumption of organic solvents and the difficulty of solvent removal at shorter times. However, Cano et al. (2002) questioned the effectiveness of SFE when compared to microwave-assisted extraction and reported higher extraction rates of adipates using this technology compared to SFE.

In general, solvent-based methods face challenges such as technological barriers in handling complex formulations, limitations in the quality of the products, and solvent and energy consumption. While research on this topic is ongoing, more needs to be discovered, particularly regarding the removal of legacy additives before this technology can be employed. Furthermore, the numerous fractions in PVC articles may require multiple dissolution/recovery steps to achieve higher purities (for legal compliance or wider applications) thereby increasing the environmental and financial costs of the operation (Braun, 2002; Sherwood, 2020). Therefore, further improvements and development of new solvent systems are imperative in making this technology an attractive option for PVC waste recycling.

5.1.3. Melt filtration

Another technology that can be used to purify PVC is melt filtration, whereby the polymer melt is filtered prior to processing to remove unwanted contaminants in small concentrations, such as metals, paper, or other polymers (Markarian, 2008). For PVC waste, this technique can be applied to remove the remaining PET contamination or metallic compounds used as stabilizers (Boo et al., 1992). Sadowski and Shaw (1992) obtained low contents of 0.2 wt.% PET and 0.1 wt.% each paper and aluminum after melt filtration of contaminated PVC and concluded that the method is viable for application in the industry, provided the filter screen is changed frequently enough.

Similar to solvent extraction, melt filtration can be particularly valuable in mechanical recycling by allowing more waste to be recycled after the removal of the contaminants (Ooms and Cuperus, 2013). An example of such an application is Remadyl, the European initiative for removing legacy substances from PVC waste through extraction and melt filtration (Centexbel et al., 2024).

5.2. Chemical recycling

Chemical recycling aims at chemically retrieving the material/monomer/components used to produce the resin in the first place or chemically altering the polymer structure in order to manufacture a new product (Al-Salem et al., 2009). This makes chemical recycling a favorable option in many cases where the waste stream is less uniform or where the quality of the final product with the different physical recycling approaches is of particular concern. Chemical recycling is arguably the most researched method for recycling PVC due to the complex nature of PVC articles and the inherent vulnerability of the resin itself when exposed to the conditions required for other recycling methods (Bhaskar et al., 2003).

Chemical recycling of PVC is unique in that unlike most other plastics, the products of such operation are never the monomer units. Instead, depending on the process, several other valuable products, including but not limited to HCl, aromatics, and syngas, are produced (Zakharyan et al., 2020). Fig. 7 summarizes the main chemical pretreatment and recycling methods.

5.2.1. Dechlorination and thermal degradation

Thermal degradation of PVC has been the focus of many studies as it is a concern in all processes regarding PVC. At temperatures below 200 °C and short exposure times, PVC exhibits no significant degradation or mass loss, while heating to higher temperatures results in rapid degradation. Several TGA/DTG studies have described the mass loss of PVC at different heating rates and report an onset temperature of ca. 230 °C for pure PVC under pyrolysis conditions where the first step of the mass loss (i.e., dechlorination) takes place (Özsin and Pütün, 2019; Soudais et al., 2007). The dechlorination is of specific importance as it not only is a major mass loss step (~56 wt.% of PVC resin is chlorine), but it also forms active species (radicals or carbonium ions), which determine the following steps to a great extent. Therefore, speculations regarding the mechanisms and the kinetics of this step have received considerable attention both for recycling and for PVC product manufacturing and stabilization. PVC is usually stabilized with inorganic salts or organometallic compounds to capture the produced HCl from the PVC degradation in the manufacturing plant and throughout its use (Garcia et al., 2004). As Braun (2002) suggests, there is a heat stability capacity in PVC that constantly lessens over its lifetime and can be assessed by measuring the induction time – the delay in HCl release from heating PVC.

The inherent properties of a PVC grade could also affect the thermal stability of the polymer, which is usually synonymous with the rate of dechlorination. An example of such properties is the tacticity of the PVC polymer. Although commercial PVC does not have a regular tacticity due to the nature of free radical polymerization at an sp^2 hybridized orbital, by lowering the polymerization temperature, the rotation around the carbon center and, therefore, the tacticity can be controlled (Sörvik, 1977). By changing the stereochemistry of the elimination reaction, tacticity impacts the rate of the dechlorination reaction. A more syndiotactic resin, for instance, increases the dechlorination rate mainly due to a more stable polyene product, even though the initiation is more favorable in atactic chains (Martínez et al., 1978; Millan et al., 1980).

Similar to other polymers, chain defects in PVC can act as initiation sites for the degradation process (Cruz et al., 2021). Although PVC is ideally a uniform chain of head-to-tail VCM units, several defects could arise from potential head-to-head polymerization, hydrogen abstraction, and elimination reactions leading to 1,2-dichloro groups, branches, and allylic chlorines, among others (Daniels, 2009). Van Cauter et al. (2007) summarized the experimental data on the frequency of occurrence of each defect. Table 4 shows these defect types, their frequency of occurrence, and the mechanism of formation. Among all these irregularities, tertiary chlorine is, by many researchers' accounts, the most important as it is present in relatively higher frequencies and has a 10^4-fold elimination rate compared to that of secondary chlorine (Bacaloglu and Fisch, 1994a). The mechanism of this elimination would likely involve a strong polarization of the C–Cl bond, which is facilitated in polar solvents due to the ionization of chloroalkane (Bacaloglu and Fisch, 1994b).

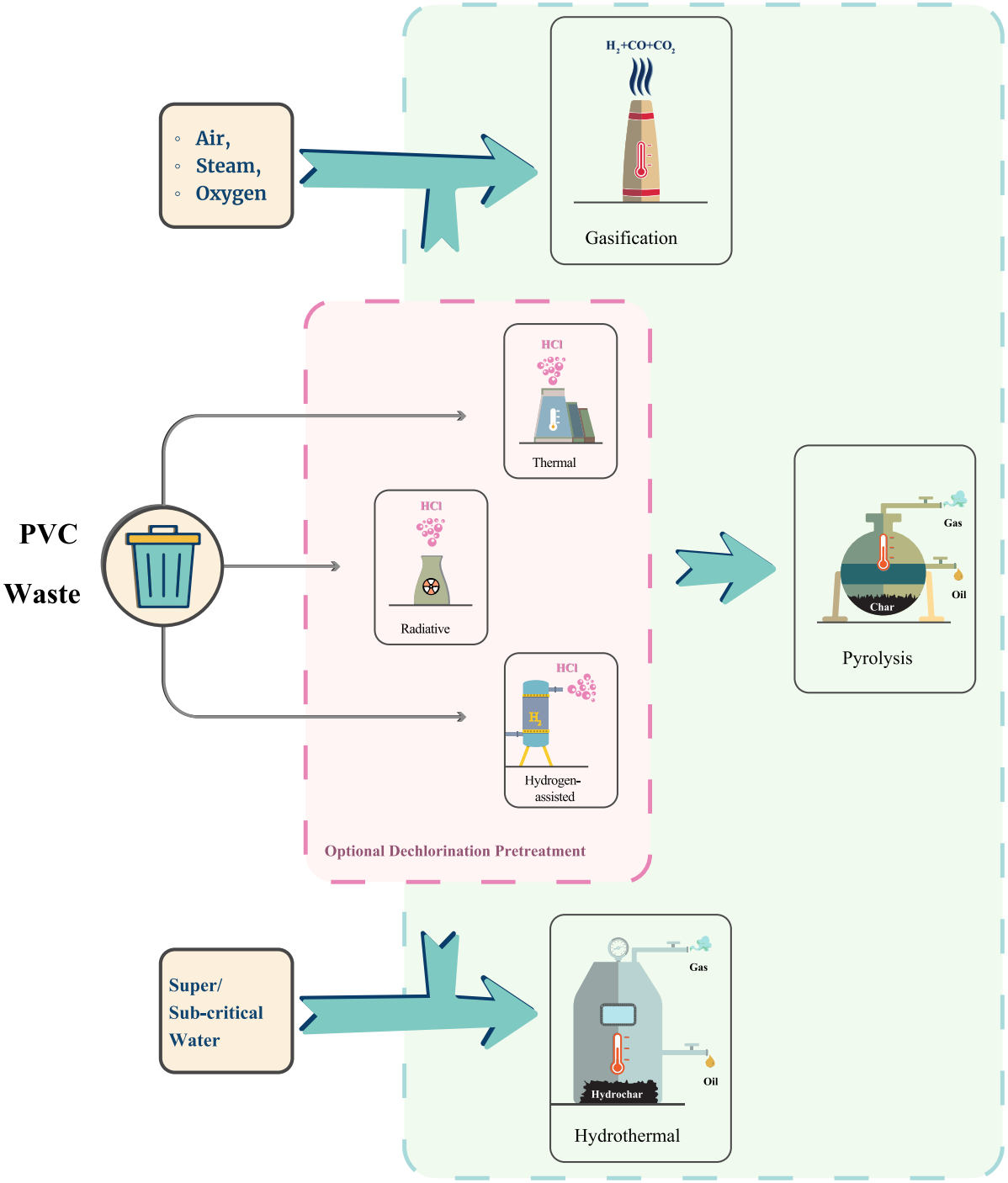

Fig. 7. Summary of the main chemical pretreatment and recycling methods described in the literature.

Double bonds in the polymer chain are also influential defects, as their presence is a sign of allylic chlorine (Wypych, 2020b). Allylic chlorine is one of the more vulnerable defects with a similar constant of dechlorination to that of tertiary chlorines (Bacaloglu and Fisch, 1994a). The importance of this defect is that over the lifetime of the PVC product, dechlorinations that occur in response to environmental triggers, such as heat or UV radiation, leave unsaturations behind, which in turn will decrease the stability of the PVC resin and its quality even after highly efficient physical recycling. The effect of this irregularity is also determined by its configuration (cis/trans), as the elimination of allylic chlorine is significantly faster in cis configuration owing to the formation of a six-member transition state suggested by Fisch and Bacaloglu (1999) (see Fig. 9.d). However, the proposed transition state for the thermolysis of PVC has been disputed by Starnes and colleagues (Starnes et al., 1996). Starnes, in a later study, suggests that the mechanisms governing this elimination are either ionic or quasi-ionic, even though radicals do form during the dechlorination (Starnes, 2002). Conversely, Marongiu et al. (2003) proposed a kinetic mechanism able to quantitatively describe the dechlorination and subsequent evolution of the polyene structure. According to the authors, dechlorination takes place because of both concerted quasi-ionic reactions and radical propagation pathways. These pathways have been studied with a high level of detail for gas-phase chloro-alkyl compounds (Ahubelem et al., 2014; Burgess Jr. and Manion, 2012; Mora et al., 2012; Rajakumar and Arunan, 2003).

Table 4
Reported occurrence of PVC chain defects and their mechanism of formation. Adapted from Van Cauter et al. (2007). Copyright 2007, American Chemical Society.

Defect	Mechanism of formation	Occurrence (per 1000 VCM unit)
chloromethyl branch (tertiary H)	Head-to-head	3.3–4.8
2,4-dichloro-n-butyl branch	Backbiting	0.5–1.7
1-chloro-2-alkene end group	Head-to-head	0.45–0.95
1,2-dichloroalkane end group	Radical transfer to VCM	0.8–0.9
1,2-dichloroethyl branch	Head-to-head	0.14–0.55
internal allylic bond	Backbiting	0.0–0.6
long chain branch (tertiary Cl)	Radical transfer to polymer	0.07–0.14
long chain branch (tertiary H)	Radical transfer to polymer	0.03–0.07
long chain branch	Radical transfer to polymer	0.1–0.2
1,3-dichloroalkane end group	Radical transfer to polymer	<0.75

Considering appropriate solvation corrections (Chung and Green, 2023; Marongiu et al., 2007), these studies can be employed to estimate dechlorination rates.

Overall, the dehydrochlorination step in PVC degradation can be broken down into two steps: initiation and propagation of the polyene. Defects in the polymer chains are important to initiate the degradation, which results in the conjugated double bonds along the chain. These reaction intermediates act as defects, lowering the activation energies required for the subsequent dechlorination steps (Huang et al., 2018; Papanikolaou et al., 2023). Similarly, the resonance stabilization on the neighboring allylic hydrogens results in a high selectivity of H-abstractions to form allyl-like radicals. These, in turn, decompose to release Cl radicals forming an additionally conjugated double bond. HCl has been observed to also play an *auto-catalytic* effect on the degradation (Wypych, 2020b). That is, indeed, why sequestering of this product is important in the kinetics of the reaction and the mechanism it follows. As some fillers in PVC adsorb HCl, their presence may alter the chemistry of PVC degradation (Karayıldırım et al., 2005). Some existing propositions for initiation and propagation reactions are illustrated in Fig. 8 and Fig. 9, respectively.

As PVC products frequently contain considerable amounts of metals and metallic salts, the effect of the reaction between the dechlorination product, HCl, with these metals on the stability of the product has been the focus of several studies. Wypych (2020b) concludes that while chlorides of Al, Sb, Cd, and Zn accelerate the dechlorination, Ca, Ba, K, and Na do not meaningfully impact its rate. In articles such as cable, copper could play a key role in the reactions occurring in the PVC. Grimes et al. (2006) investigated the effect of copper and copper (II) oxide on PVC pyrolysis and reported decreased yields of degradation products, particularly of aromatics, and increased production of aliphatics.

The dechlorination step results in the formation of a polyene structure characterized by conjugated double bonds. This structure has high thermal recalcitrance due to the high activation energies required to form vinyl radicals (Blanksby and Ellison, 2003; Linstrom and Mallard, 2001). Therefore, these conjugated structures undergo molecular and radical reticulation to form aromatic clusters.

The most important cyclization processes involve uni- and bi-molecular Diels-Alder reactions. The former is entropically favored but involves higher energy barriers, while the latter prevails at lower temperatures (Lattimer and Kroenke, 1982). As with the dechlorination, the unimolecular reaction rate is influenced by the stereochemistry of the reactant (Grimme et al., 1981). Similar reactions occur through radical

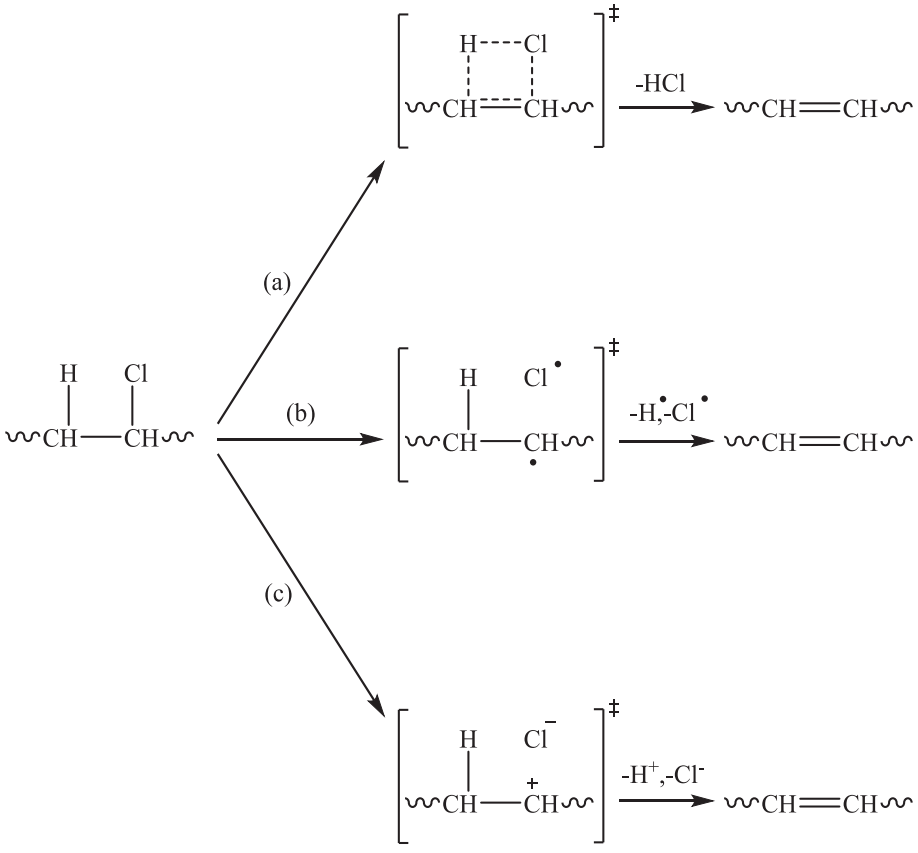

Fig. 8. Initiation of PVC degradation through (a) quasi-ionic, (b) radical, and (c) ionic mechanism (Starnes, 2002).

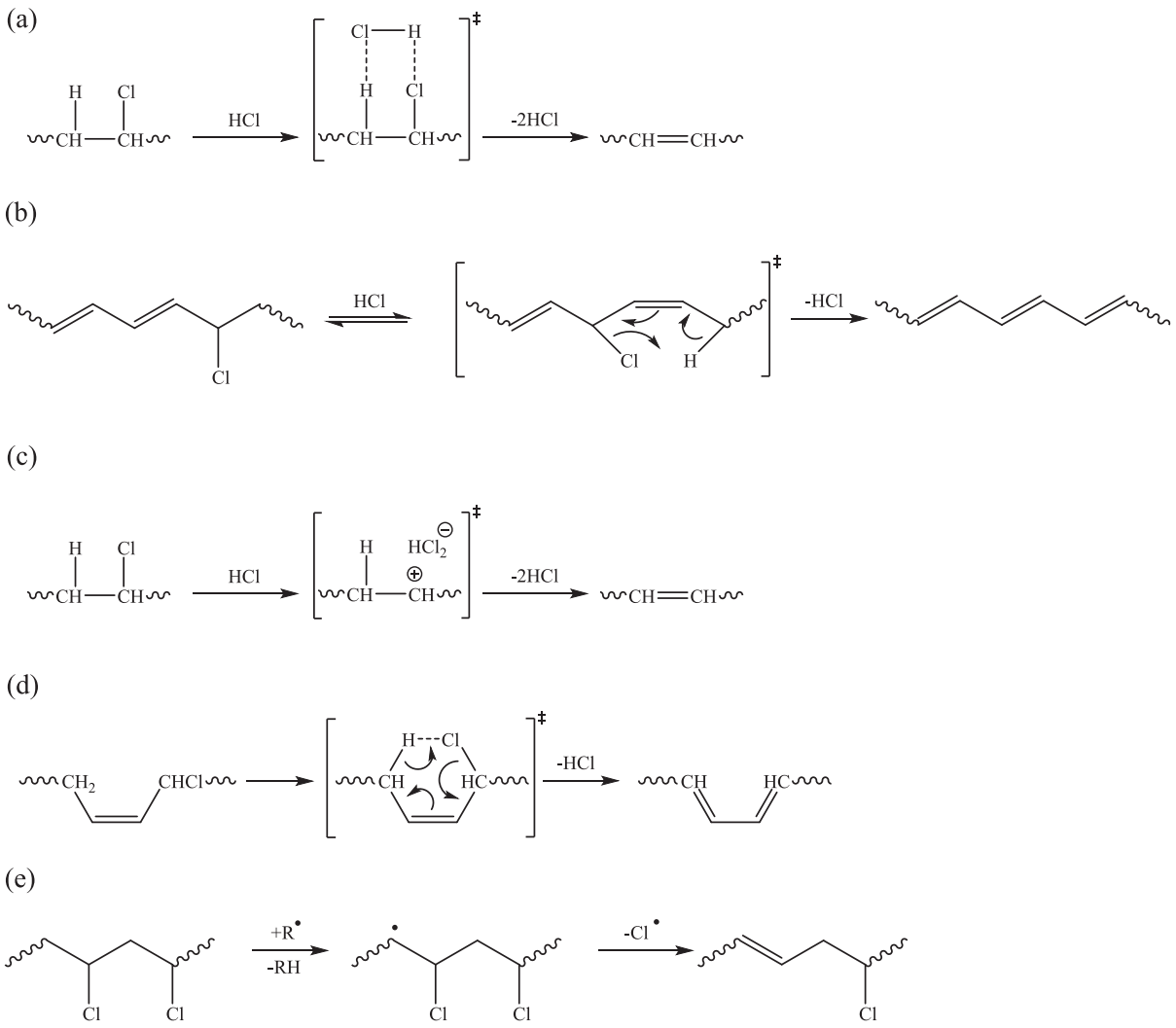

Fig. 9. Proposed mechanisms for HCl auto-catalytic effect and propagation of polyene chain. (a) auto-catalysis through molecular mechanism, (b) auto-catalysis through six-centered concerted mechanism, (c) auto-catalysis through ionic mechanism (d) polyene propagation through six-centered concerted mechanism, (e) polyene propagation through radical mechanism (Krongauz et al., 2011; Starnes, 2002; Wypych, 2020b).

additions on the double bonds. While addition reactions have low activation energies, they are relevant only at high temperatures due to the increase in the radical concentration (Nobili et al., 2022). The resulting cyclic structure can undergo dealkylation reactions, releasing small fragments (Lea-Langton et al., 2015; Singh et al., 2012). These decomposition pathways are enhanced by residual amounts of chlorine (Marongiu et al., 2003). Indeed, as highlighted by Knümann and Bockhorn (Knümann and Bockhorn, 1994), the dechlorination process is associated with the release of small amounts of monoaromatics. This is believed to occur due to the electronic delocalization of the Cl on the carbon–carbon bonds. As the chlorine content decreases, condensation of the alkyl-aromatic structures prevails. These reactions result in the formation of polyaromatic compounds, which are released as tars or undergo further reticulation to form 5–15 % of char.

5.2.2. *Pyrolysis*

5.2.2.1. Two-step degradation and dechlorination. The thermal degradation of PVC in the absence of oxygen follows a two-step mass loss, as illustrated in Fig. 10. Many works of literature, including Zhou et al. (2020), have reported similar observations in thermogravimetric analyses. This two-step thermal degradation consists of a lower temperature step (~300 °C) where dechlorination is the most prominent reaction and a higher temperature step (~500 °C) at which the remaining hydrocarbons are broken down into predominantly mono- and poly-aromatic products. The pyrolysis of PVC and PVC-containing waste is heavily influenced by the characteristic weight-loss profile of this polymer.

In the case of pure PVC resin, both one-step and two-step pyrolysis have been attempted, depending on the goal. When the objective is the dechlorination of the polymer and the production of HCl, low-temperature pyrolysis is often employed, from which about 90 % of the chlorine can be removed at temperatures of 340 °C and less (after about 2 h of reaction time) (Ma et al., 2002). At these conditions, the product gas stream mainly consists of HCl with small amounts of C_1-C_4 hydrocarbons and monoaromatics resulting from the degradation of the polymer chain. Furthermore, depending on the temperature, 4–5 wt.% of the chlorine ends up in the liquid fraction, and the rest (~1 wt.%) in the residue with higher temperatures leading to higher chlorine in the liquid fraction.

When PVC is not pure, for instance, in real-world applications, the approach towards the pyrolysis of PVC and PVC-containing feedstock changes. Low-temperature pyrolysis (i.e., first-stage degradation of PVC and dechlorination) is usually applied to dechlorinate the feedstock prior to the main pyrolysis to reduce the chlorine content in the products below the permitted levels (e.g., 10 ppm is considered the permitted Cl levels for petrochemical plants (Kaminsky, 1995)) and to mitigate

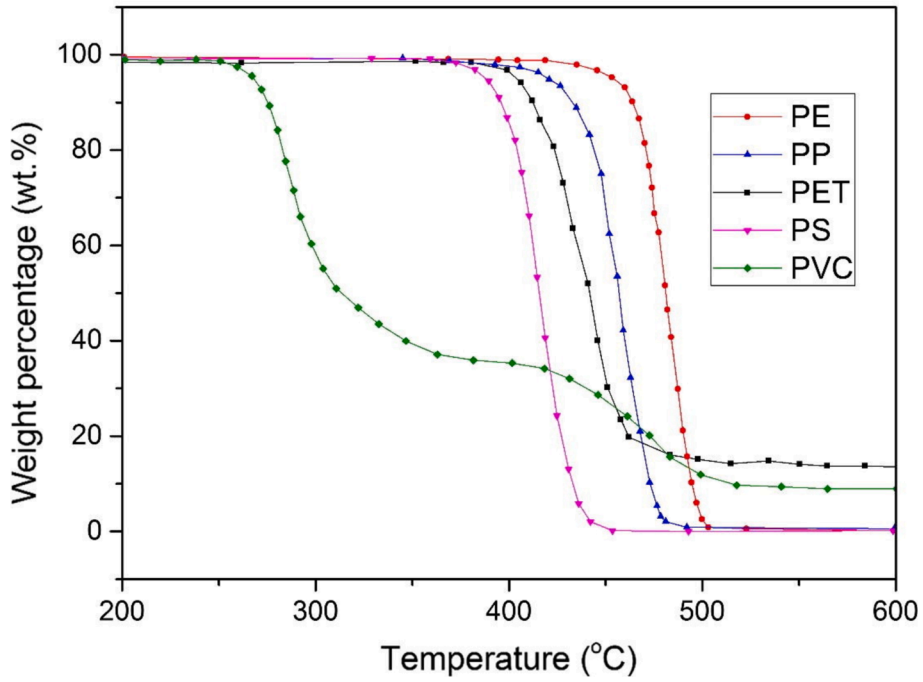

Fig. 10. Two-stage thermal degradation of PVC at 10 °C/min compared to other major polymers. Reused with permission from Elsevier (Yu et al., 2016).

corrosion in the equipment downstream (Yuan et al., 2014). López et al. (2011b) concluded that a dechlorination step at 300 °C for an hour removes more than 50 wt.% of the chlorine observed in the liquid and solid fractions after conventional pyrolysis at 500 °C. However, the additional low-temperature step increased the average carbon number in the liquid products and reduced the production of aromatics. The importance of this dechlorination step is proportional to the percentage of PVC in the feedstock. In feedstocks with less PVC share (i.e., PVC-contaminated wastes), one might deem the dechlorination operation unnecessary. The research conducted by Miskolczi et al. (2009) demonstrates the effect of the chlorine content of 0–1.15 wt.% (i.e., 0–3 wt.% PVC waste) on the presence of chlorine in different fractions of the product and the product distribution after 25 min of residence at 530 °C. Their results indicate an increase in chlorine content in all fractions up to 3.45 wt.% in gases (mainly HCl contribution) and 2129 and 2201 ppm for gasoline and light oil fractions. Furthermore, they observed approximately 5 wt.% increase in aromatic production at the highest PVC content used in the experiments.

In plasticized feeds, the plasticizers are also expected to be released at the lower temperature step of the mass loss (Apchain et al., 2022). Another aspect of plasticizer presence in the feed is the potential influence on product distribution. While the major portion of the plasticizers are released in their native form, Wang (2000) provided evidence for the partial degradation of common commercial plasticizers under pyrolysis conditions. Phthalate anhydride, oxygenated hydrocarbons, and short-chain aliphatic compounds were among the decomposition products of the plasticizers.

5.2.2.2. Process parameters. Temperature is arguably the main operating parameter of the pyrolysis process. However, pressure has also been proven to have the potential to alter the chemistry of the process. Kamo et al. (2004) followed a series of experiments focused on the effects of pressure on the pyrolytic reactions and reported interesting findings. Their results suggest that a share of liquid products is retained in the matrix of dechlorinated PVC at higher pressures, which leads to higher hydrogen content in the residue by diminishing polycondensation reactions. Moreover, the pressurized conditions gave rise to higher paraffinic content in the products and less benzene production, presumably thanks to hydrogenation reactions of the polyene in the presence of hydrogen produced by polycondensation reactions.

Heating rate is another parameter that categorizes the process into a *fast* or *slow* pyrolysis. In a comparison between fast and slow pyrolysis of PVC (i.e., heating rates of 350 and 10 °C/min, respectively), more HCl was generated in slow pyrolysis while gas, tar, and solid residue were less compared to that of the fast pyrolysis (Zhou et al., 2016). Further analysis showed higher hydrogen and C_1-C_4 yields in the fast pyrolysis. On the other hand, the yields of polyaromatic hydrocarbons (PAHs) were significantly diminished in the slower heating rate. Furthermore, in agreement with other scholars, the result showed a decreased HCl yield at higher temperatures. In contrast, based on the results from Wootthikanokkhan et al. (2003), smaller changes in heating rate (5–20 °C/min) did not affect the solid residue left, while inconsistent changes in liquid yield were observed.

Due to the problematic nature of chlorine both in the products and in the process equipment, some have entirely abandoned the idea of producing HCl as a product and instead resorted to simply capturing the chlorine using sorbents. This approach is particularly reasonable when the amount of PVC in the waste is slim (i.e., PVC-contaminated waste) and the main focus of the operation is on the other polymers present in the waste in larger quantities. For this, calcium products such as $CaCO_3$ and other minerals, including clay and iron salts, have been tested. Specifically, $CaCO_3$ is frequently cited as a cost-effective sorbent that effectively reduces chlorine content in all fractions except for the solid residue (Cho et al., 2010; Karayıldırım et al., 2005). However, results from Hubáček et al. (2022) disagree with these findings, suggesting a higher chlorine content in the liquid fraction when the sorbent is used *in-situ* for mixed samples containing 10 wt.% PVC. Instead, they recommend a stepwise approach with *ex-situ* sorbents to achieve chlorine levels of below 10 ppm (using Fe_3O_4-Si) appropriate for use in refinery applications. Although, their operational conditions suggest longer reaction and residence times compared to the works discussed previously, and thus, their finding regarding the inapplicability of *in-situ* sorbents may be due to longer contact time between the chlorine species and the reaction mixture. Bhaskar et al. (2002) also report the complete removal of halogens (Cl and Br) from their model plastic mixture containing 10 wt.% PVC and 10 wt.% HIPS-Br when a $CaCO_3$-phenol resin composite

was used as an *ex-situ* sorbent.

This approach (i.e., using a sorbent to capture HCl and promote higher dechlorination and a different profile in the products) is sometimes −debatably− referred to as catalytic pyrolysis of PVC and the sorbent in use is, therefore, the catalyst. Peng et al. (2022b) posit a three-step pyrolysis for PVC whereby HCl and intermediates are the products of the first step and the intermediates are degraded into polyenes and subsequently into aromatics and char in the second and third steps, respectively. Based on this division of degradation mechanism, they argue that the term "catalytic pyrolysis of PVC" can point to three different ideas: (1) catalytic dechlorination combined with thermal pyrolysis for chlorine-free oil, (2) catalytic upgrading of PVC oil for a chlorine-free product, and (3) thermal dechlorination and subsequent catalytic decomposition.

An example of the *combined* approach is the TGA work of de Souza et al. (2020), reflecting on PVC thermal and catalytic degradation in the presence of different ratios of ZSM-35 and MCM-41 where a 75/25 ratio of ZSM-35/MCM-41 was chosen as the most effective option in lowering the degradation temperature and increasing the conversion (i.e., transformation of PVC resin into degradation products) at lower temperatures. Peng et al. (2022a) provided more details on a number of catalysts with Py-MS experiments. All catalysts explored (i.e., HZSM-5/80 and HZSM-5/280, F20, HY5.1, and MCM-41) showed the same or lower onset temperature for the first stage of degradation, a faster rate of degradation, and in the case of F20, more overall mass loss. All catalysts showed increased production of all product categories (including HCl and aromatics) when used *in-situ* up to about 900 % in PAH yield in the case of HZSM-5/80. Although the results were less drastic when the catalysts were employed *ex-situ*, in most cases (with the notable exception of HCl) a great deal of improvement in yields was observed.

Other catalysts attempted for this purpose are mainly metal salts (Fe.AlO_x, metal oxides and chlorides, and CuAl-LDH) (Chen et al., 2018; Cheng and Liang, 2000; Ji et al., 2020; Liu et al., 2023). Although the results from Fe.AlO_x as a catalyst shows less overall mass loss and slightly increased degradation temperature for the first stage; metal oxides and CuAl layered double hydroxide promise reduced dechlorination temperatures. This is while the former reduces the temperature of the second stage and promotes complete pyrolysis in favor of aliphatics (rather than aromatics) and the latter increases char formation. The results from metal chlorides were also suggestive of less overall mass loss and a shift towards less aromatic products. Müller and Dongmann (1998), in agreement with this finding, proposed a mechanism for this observation and named Lewis acidity as the main factor. The importance of the latter finding lies in cases where the released HCl from PVC gets the chance to react with other metal salts present in the common plastic stream to produce metal chlorides potentially able to restart aromatization.

Ma et al. (2023) took a different approach and utilized different ratios of oxygen in the reaction atmosphere. Their result suggested decreased aromatization owing to the oxygen presence, which lent itself to an improved quality of the carbon nanotubes produced after pyrolysis of the oxygen-treated samples in the presence of Fe.Al_2O_3.

When the feedstock is PVC-contaminated waste with small amounts of chlorine, the main challenge of catalytic pyrolysis might change. In such scenarios, the ideal catalyst can be effectively utilized for other polymers in the stream and does not get permanently deactivated due to the presence of PVC and its degradation products (Lei et al., 2018). Thus, plants must opt for a dechlorination step (as described previously) before the main stage of pyrolysis (Lu et al., 2023). After the dechlorination pretreatment, the waste can be catalytically pyrolyzed into desired products even when small amounts of chlorine persist, though deactivation due to coke formation may remain an issue (Marino et al., 2022; Wang et al., 2023b). Nonetheless, López et al. (2011a) argued that ZSM-5 catalysts can still be de-coked and regenerated via burning in the air without any meaningful loss of quality in terms of the products. In lower chlorine concentration of 0.14 wt.%, Hwang et al. (2021) employed an iron-loaded HY catalyst directly on chlorinated wax feed and reported successful results in catalytic cracking and chlorine removal despite soft coke and chlorine deposition on the catalyst. Similar to the previous study, the catalyst exhibited comparable results after regeneration through calcination in air. The inclusion of catalyst regeneration and stability is important in PVC studies as catalyst cost plays an important role in the economy of the pyrolysis process (Ali et al., 2002).

Another variation of pyrolysis technology represented in the works of several scholars is fluidized bed configurations. Yuan et al. (2014) implemented this technology using a single molten bed liquid–gas fluidized bed reactor and achieved a very high chlorine removal efficiency of 99.5 wt.% for PVC and pipe scraps one minute after the polymer melted. Other scholars also investigated other bed materials, such as sand for different feedstocks with PVC contents of 1.2–100 wt.% with and without HCl sorbents and reported very high degrees (~100 %) of dechlorination as well (Kaminsky, 2010; Saeed et al., 2004a). Overall, studies on fluidized bed reactors for pyrolysis of PVC are yet to be methodically compared with more traditional implementations and their advantages and disadvantages are thus unclear, but a higher level of repeatability and more consistent product distribution is expected due to generally better transport phenomena inside fluidized bed reactors compared to most alternatives (Cho et al., 2010).

5.2.2.3. Product distribution. Despite the general agreement regarding the importance of chemical recycling and, in particular, pyrolysis processes, the existing body of research on PVC thermal degradation fails to clearly describe the decomposition products. Researchers have attempted a qualitative approach towards the pyrolysis of PVC, and even fewer have reported quantitative data. Although this may be due to the challenging nature of PVC and its corrosive pyrolysis products in most characterization equipment, the lack of literature on the topic is nevertheless surprising (Dadvand et al., 1999). The complex nature of pyrolysis products requires sophisticated characterization and quantification techniques. Kumagai et al. (2020) employed comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOFMS) to analyze PVC pyrolysis oil semi-quantitatively. Fig. 11 shows the GC×GC–TOFMS chromatogram of PVC resin pyrolysis products at 500 °C. Group-type analysis of products offered by this technique provides more information on the chemical nature of products. Fig. 12 summarizes the product distribution reported by other researchers divided into five categories: HCl, aliphatics, monoaromatics, polyaromatics, char, and chlorine content in the liquid sample. Other products described in the literature include CO/CO_2, (tere-)phthalates, and other oxygenated compounds, particularly in the case of plasticized PVC material (Li et al., 2023b).

O'Mara (1970) employed GC–MS to study the high-temperature pyrolysis of PVC resin and plasticized PVC (60 wt.% DOP in PVC) at 600 °C and after the complete removal of chlorine (58.3 wt.% in the resin sample) at the conditions, 3–4 wt.% of solid residue remained. In their analysis of PVC resin, more than half of the products were benzene and other monoaromatics (equivalent to ~ 24 wt.% yield) and about a quarter of the products were comprised of light aliphatic compounds (C_1-C_4). However, in the case of DOP-plasticized PVC, monoaromatic production was diminished in favor of more medium-range aliphatic compounds (C_5-C_8). The latter was likely due to the degradation products of DOP.

Chang and Salovey (1974) conducted consecutive pyrolysis experiments at several steps from 160 °C to 500 °C and analyzed the products using a GC–MS. At 340 °C, the highest HCl and benzene productions were realized at 39 and 24.5 wt.%, significantly larger than the experiment at a lower temperature at 275 °C (8 and 0 wt.%, respectively). After this step (i.e., 340 °C), 89 % of the chlorine was removed through HCl production (48.74 wt.% cumulative yield). Other notable products in their experiments were naphthalene and C_1-C_6 aliphatics and a total

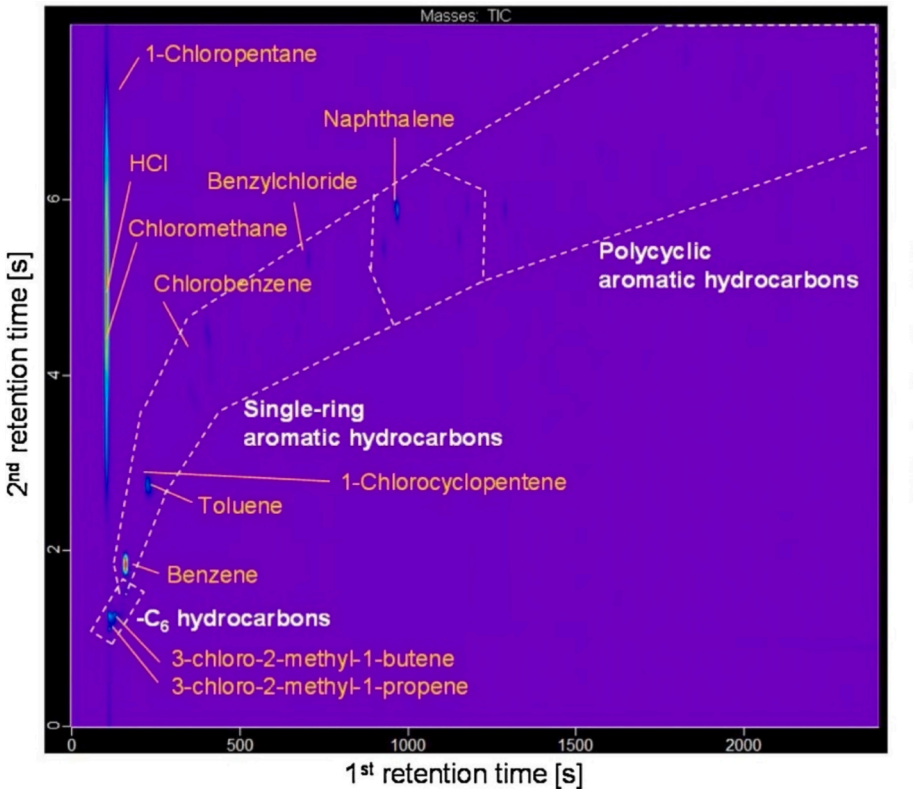

Fig. 11. GC×GC–TOFMS chromatogram of PVC pyrolysis products at 500 °C (Kumagai et al., 2020). Reused with permission from Elsevier.

of 22 wt.% solid residue was formed at the end after the last step at 500 °C. In the end, benzene and toluene with 27.6 and 5.1 wt.% were the main aromatic products.

Benzene production, as a significant fraction of the product, is accepted by and large among other researchers (Fan et al., 2022; Ma et al., 2019b; McNeill et al., 1995). Day et al. (1999) provide similar findings after pyrolysis at 700 and 900 °C with 47.5 wt.% and 46.7 wt.% HCl yield, 10.7 wt.% and 15.2 wt.% benzene and other monoaromatics, and 1.5 wt.% and 2.9 wt.% yield for polyaromatics, respectively. The experiments left behind 35.5 wt.% solid residue at 700 °C and 28.5 wt.% at 900 °C. Although the results from the two temperatures look very similar, a slight increase in poly- and substituted aromatics can be seen at higher temperatures, whereas benzene production decreases by about 20 % compared to the value at lower temperatures.

The majority of monoaromatics –and, to an extent, aromatics in general- are produced in the first stage of degradation at the same time as HCl formation. Yang et al. (2023) also report that out of the 10.55 % of monoaromatic hydrocarbons (MAHs) share in the produced volatiles, only 1.63 % is from the second stage (343–650 °C). This is contrary to the observation regarding PAHs, where their share in the first stage is mainly comprised of naphthalene, but in the second stage, they take up a slightly larger share due to the formation of heavier PAHs.

As aromatics are an unavoidable fraction of the products, deliberately promoting an aromatic-rich product mixture can be beneficial to the recycling process. Dong et al. (2023) successfully showed the effect of the dechlorination temperature on the aromaticity of the product mix. Their results suggest optimum dechlorination at 320 °C followed by fast pyrolysis (550–700 °C) results in maximal aromatic products (97.32–99.93 wt.% of the oil). The dechlorinated PVC also exhibited a slightly higher mass loss in fast pyrolysis compared to that of the PVC.

One major product of PVC pyrolysis is the solid residue. Although this fraction is often regarded as undesirable, the unavoidably considerable char quantities in PVC pyrolysis has led researchers to investigate possible applications. Ma et al. (2024) suggest halogen-based sorbents made typically from co-pyrolysis of PVC with other feed as an application. Another attractive application is nanomaterials from plastic waste pyrolysis. Yang et al. (2024) successfully synthesized carbon nanotubes from waste with 10 wt.% PVC using dechlorinating agents, despite the adverse effects of PVC on nanotube synthesis from plastic waste pyrolysis. Furthermore, Ma et al. (2023) employed oxygen to improve the characteristics of carbon nanotubes synthesized from PVC pyrolysis and reported products with higher purity and graphitization degree compared to the products obtained from PP and higher proportions than HIPS and general purpose PS.

5.2.3. *Gasification*

Compared to most plastic waste chemical recycling technologies, gasification is one of the few technologies that has achieved some maturity in the industry. It is a thermolytic process whereby a carbon-containing feed is transformed mainly into syngas ($CO + H_2$) and CO_2 using steam and oxygen (pure or in air) and high temperatures (up to 1500 °C) (Madanikashani et al., 2022). A main upside of this technology compared to pyrolysis is the more efficient use of the carbonaceous part of PVC. Compared to other recycling methods, gasification has a high feedstock flexibility, although it involves highly endothermic reactions (Dogu et al., 2021). The choice of gasifying agent results in different syngas compositions, for instance, H_2O results in higher hydrogen yields. Introducing small amounts of oxygen allows gasification to be autothermal while reducing methane yields (Zhang et al., 2011). Nevertheless, optimization of operating conditions is of paramount importance to minimize dioxin and tar formations. Compared to energy recovery pathways, the strongly reducing environment reduces the formation of dioxins, furans, and NOx. Similarly, fly ashes are collected at the bottom due to the lower temperatures compared to direct combustion systems (Arena, 2012).

On the lower end of the spectrum of PVC content in the feed, Borgianni et al. (2002) fed refuse-derived fuel with 10 wt.% PVC along with Na_2CO_3 to their gasifier and reported ~ 0.485 m^3 of H_2 and 0.079 m^3 of

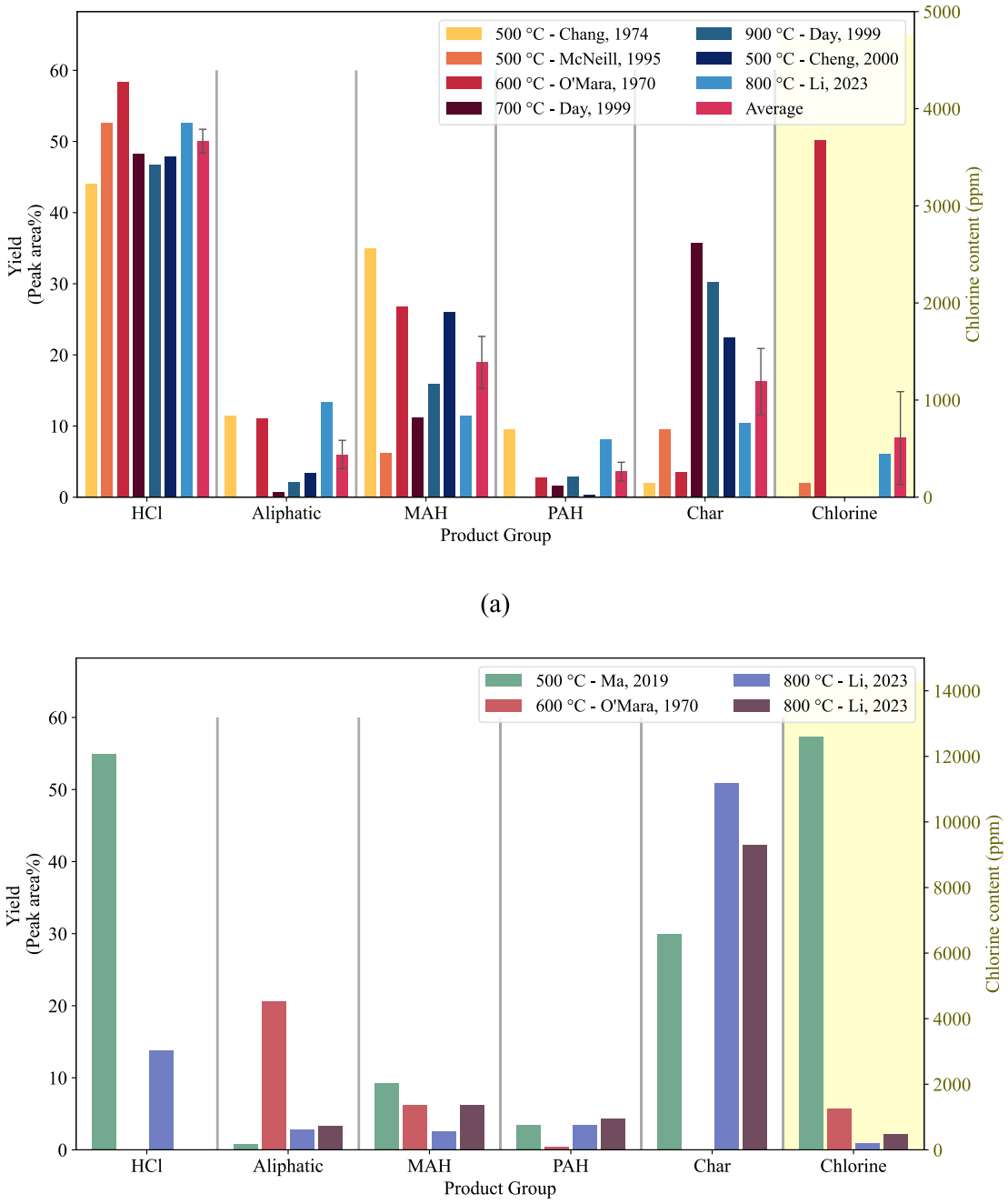

Fig. 12. Pyrolysis products of PVC (a) resin and (b) applications as described in the literature (Chang and Salovey, 1974; Day et al., 1999; Li et al., 2023b; Ma et al., 2019b; McNeill et al., 1995; O'Mara, 1970). Other products include CO_2, CO, hydrogen, and oxygenated compounds such as phthalate anhydride, esters, carboxylic acids, and alcohols.

CO per kg of feed. Despite their successful attempt at gasifying PVC-containing feed (up to 20 wt.%), their work is emblematic of the larger challenge PVC processes must cope with: HCl production.

As the PVC content in the feed decreases, so does the HCl production and, thereby, the economic importance of HCl separation as a product in the plant. In cases with smaller amounts of PVC, for instance, municipal waste streams, PVC is seen mostly as a problem, and solutions such as neutralization of HCl can be vital for the recyclability of the rest of the feed. For a PVC-contaminated mixed waste stream containing 2.2 wt.% chlorine in total, Cho et al. (2015) attempted several additives to capture HCl and reduce tar and reported successful results in the case of the Ca-additives as they pertain to HCl removal in the producer gas and the condensed liquid, as well as reduced production of CO_2 which was attributed to its absorption by the Ca-additives.

Although HCl is often seen as a challenge that needs to be eliminated, efforts have been made to consider it an opportunity to use HCl as the main product. Slapak et al. (2000) simulated a PVC waste gasification plant that produces syngas and HCl employable by a near oxy-chlorination plant. Despite their proof of the economic feasibility of the HCl product compared to incineration plants, the authors state that factors such as changes in the waste composition are neglected in their simulation. Nevertheless, using Aspen Plus, the researchers claim a 43 %

recovery of chlorine in the form of HCl (the rest in $CaCl_2$) and 14.4 MJ/kg PVC waste net energy output, assuming a waste composition of 40 % PVC, 30 % DOP, 20 % $CaCO_3$, and 10 % inorganics. The same research group later investigated the effects of additives on the gasification process and reported an increase in gas yield corresponding to the organic additives content and a decrease caused by higher inorganic additives such as calcium (Kasteren and Slapak, 2001). The presence of calcium also diminished the production of recoverable HCl thanks to the formation of $CaCl_2$.

Chemical recycling methods can also be used in combination. Gasification and pyrolysis are two processes that can easily be used in tandem. Zevenhoven et al. (1997) provide a good example of such combinations where they used gasification on the char produced from the pyrolysis of PVC. This process is particularly interesting since it utilizes one of PVC's most widely accepted challenges –char production- to its benefit. Even though PVC char did not convert as fast as wood and peat char, their results suggest an acceptable rate of PVC char conversion at 950 °C.

5.2.4. *Hydrothermal treatment*

Much like other plastics, water has been employed to decompose PVC as well. Although less popular than some of the previously mentioned methods in the literature, hydrothermal treatments have been extensively researched by scholars. While examples of supercritical treatment of PVC can be found in works as early as Sato et al.(1998), lower temperatures have also gained attention, as they are deemed to be enough for the initiation of dechlorination (Endo and Emori, 2001).

Even though radical or quasi-ionic mechanisms seem to be favored in literature when PVC degradation is discussed, ionic pathways are almost exclusively prevalent where hydrothermal methods are concerned. Supercritical water has been previously utilized for other polymers due to its low dielectric constant, high diffusivity, and other properties that promote radical reactions, especially at increased temperatures (Bai et al., 2019; Zhang et al., 2007). However, at lower temperatures (i.e., below the critical point of water), ionic pathways seem to prevail (Bühler et al., 2002). This can be explained by the fact that water exhibits its highest ion product at temperatures of about 275–300 °C and pressures above 230 bar ($[H^+] = [OH^-] = 10^{-5}$ mol/kg) and this value drops significantly once the temperature reaches 400 °C ($[H^+] = [OH^-] = 10^{-11}$ mol/kg) suggesting a very ionic environment at so-called *subcritical* conditions and less tendency to ionic species at *supercritical* conditions (Iwamura et al., 2014).

This change in the reaction pathway leads to different kinetics and products. In an ionic environment, the elimination reaction could take place as an ionic reaction, which is simultaneous with ionic nucleophilic substitution reactions where the hydroxide ions from water substitute the chlorine, thus creating C–OH bonds that can be seen in spectroscopic observations of the char (Ma et al., 2021). In specific circumstances, the hydroxyl groups undergo dehydration reactions in order to produce carbonyl groups (C = O) instead, particularly when the environment is more alkaline (Xiu et al., 2020c). Due to these pathways and the operational conditions, chain scissions and aromatization reactions are less reported for hydrothermal treatments.

Several factors, such as the presence of alkali, temperature, time, and pressure, can potentially favor or hinder possible nucleophilic substitution (S_N1/S_N2) or elimination reactions (E1/E2). While Lu et al. (2002) observed peaks associated with –OH in the residues, the same is not true for all works (Zhao et al., 2018). Zhao et al. (2018) attribute their different results to their shorter reaction times and lower pressures, which have promoted elimination reactions more than substitutions but did not provide the pressure values used in their experiments. Fig. 13 shows a proposed set of pathways for PVC dechlorination and chain cyclization in hydrothermal degradation (Tito et al., 2024).

Another difference between hydrothermal treatments and thermal degradation is the power of the water as the solvent to remove the products from the vicinity of the polymer chain and thereby reduce the auto-catalytic effect previously associated with HCl formation. Endo and Emori (2001) pointed out this observation and attributed the slower dechlorination in supercritical water temperatures (at 196 bar) compared to nitrogen to this hypothesis. Similarly, in the case of a supercritical medium, specific properties of water allowing the dilution of the immediate products promote unimolecular reactions, which, in turn, diminishes coke formation (Chen et al., 2019; Čolnik et al., 2022; Popelier et al., 2024; Thiounn and Smith, 2020).

Despite this slower reaction time, the dechlorination rates reported in hydrothermal treatments are comparable to that of the thermal processes, if not better, even at relatively lower temperatures and in the absence of catalysts or neutralizing agents (Lu et al., 2003; Soler et al., 2018; Yao and Ma, 2017). Fig. 14 shows the dechlorination efficiencies of some of the studies conducted on hydrothermal dechlorination of PVC

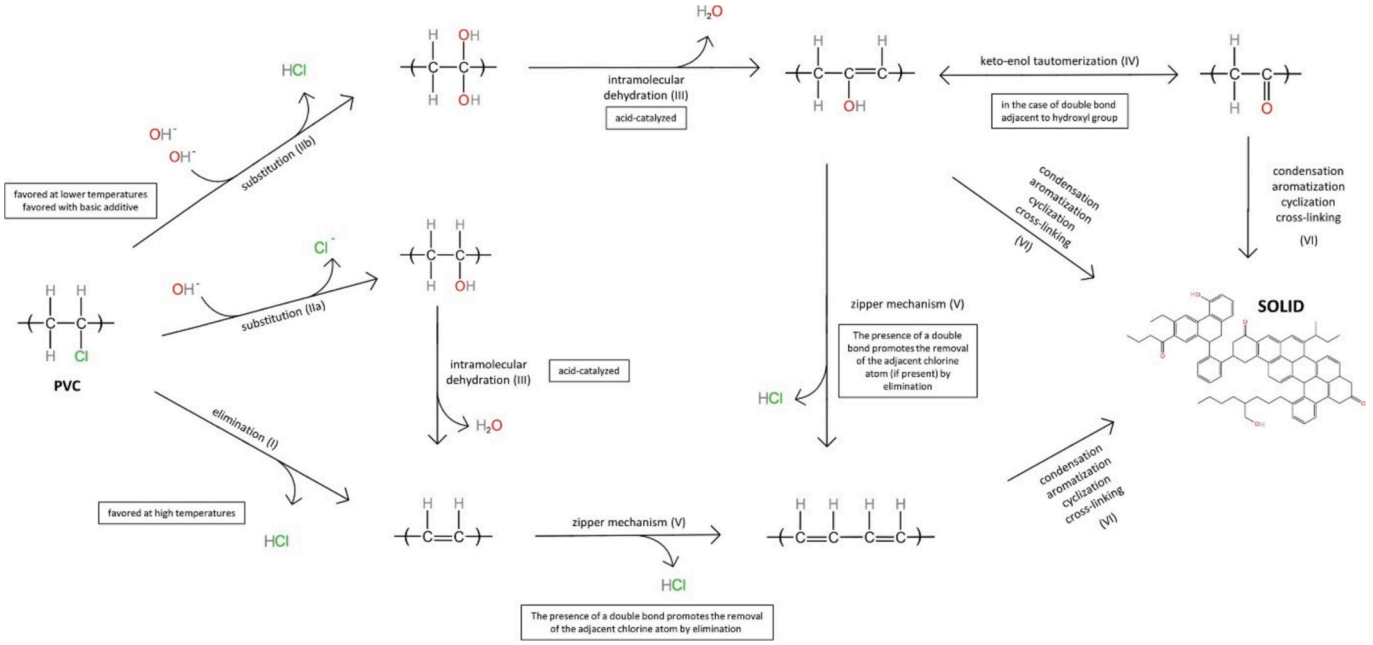

Fig. 13. Reaction pathways for hydrothermal degradation of PVC proposed by Tito et al. (2024). Reused with permission from Elsevier.

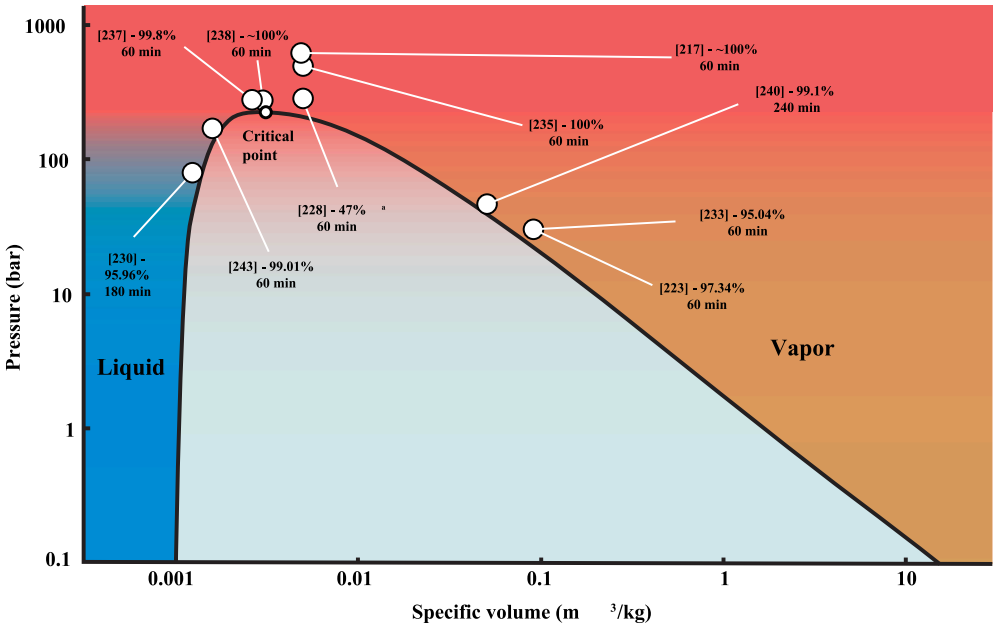

Fig. 14. Conditions used in hydrothermal treatments reported in the literature and for the maximum dechlorination level. [a] Reported as yield based on the initial mass of the feedstock.

and PVC waste with the conditions used to achieve the respective level.

One key issue in this area of research is the inconsistency in the terminology used. For instance, while the term *subcritical* is sometimes used to refer to temperatures below the critical temperature but pressures above critical pressure, sometimes (Soler et al., 2018) it refers to lower pressures and vapor environment. The importance of this distinction is in reaction pathways that would be suppressed or promoted depending on the reaction environment, whether it is superheated steam, subcooled liquid, or supercritical medium. A summary of studies performed on the hydrothermal treatment of PVC resin and PVC wastes is provided in Table 5.

While high dechlorination efficiencies have been reported across the literature, less agreement is observed regarding organic products. Polyenes of different sorts are perhaps the most agreed-upon products of PVC hydrothermal treatment (Hapipi et al., 2018; Lu et al., 2002; Ma et al., 2021; Nagai et al., 2007; Takeshita et al., 2004; Xiu et al., 2024; Xiu et al., 2020b; Xiu et al., 2023b; Xiu et al., 2020c; Zhao et al., 2018). Since water is not an inert medium, various degrees of oxidation have been reported through FTIR measurements of the hydrochar. The presence of a broad peak 3450 and 1712 cm^{-1} suggested the occurrence of –OH and C = O in the hydrochar from substitution followed by oxidation reactions in the experiments (Yao and Ma, 2017). Xiu et al. (2024) used FTIR measurements of the char to postulate that the –OH bonds are removed at elevated temperatures, particularly those above the critical point of water. This finding certainly aligns with that of Čolnik et al. (2022) in that supercritical conditions led to hydrochar that is rid of oxygen. Nagai et al. (2007), however, observed –OH bonds at supercritical temperatures, but at 500 °C, the –OH band disappeared and the C = O bond intensified, suggesting dehydrogenation reactions at high temperatures. In the same work, higher pressures at the constant temperature of 400 °C resulted in more significant –OH and C = O peaks, highlighting the importance of water properties in the reaction mechanism.

The level of hydroxylation and oxidation expectedly depends on the experiment conditions, including the state of the medium, temperature, and presence of reagents (especially those with an alkaline nature), and due to the variety of the configurations and conditions used in the literature, no clear conclusions can be drawn from the effect of each parameter on the ratio of substitution to elimination reactions and the oxygen content of the solid residue. To this point, a group of reactors has been employed for hydrothermal treatment of PVC and PVC waste from bath-type batch reactors to diamond reactors. Most of these implementations do not allow continuous monitoring of the process either visually (e.g., in diamond reactors) or via *in-situ* analysis tools, turning the process into a so-called “black box” (Ling et al., 2023).

At the moment, there are no existing industrial implementations of hydrothermal technology for PVC waste. One of the challenges with hydrothermal technology is the corrosive nature of HCl produced by PVC degradation inside the reactor, similar to the other methods of handling PVC. This is particularly concerning in hydrothermal processes given the severe conditions under which the process takes place. Salimi et al. (2023) performed extensive research on the corrosion caused by the acidic medium on a reactor made from SS316. Their results highlight a meaningful decrease in the reactor lifetime due to the leaching of metallic ions, particularly in more severe conditions. As more severe conditions were found to be needed for effective dechlorination and minimal oxygenation of the products, the importance of developing materials appropriate for such applications appears to be imperative.

In order to assess the applicability and effectiveness of this technology, more research is needed on real PVC waste, reactor materials and configurations, energy consumption, wastewater treatment, product separation, and process parameters.

5.2.5. *Non-conventional chemical recycling technologies*

Apart from discussed technologies in chemical recycling of PVC and PVC waste, a multitude of non-conventional processes has been developed to address some of the challenges in the conventional methods. In this section, a brief description of a number of these techniques is provided.

5.2.5.1. Oxidative. As an alteration of thermal pyrolysis, oxidative methods usually aim at partial oxidation of the feedstock by involving oxygen or other oxidizing agents in the reaction environment. This change changes the reaction pathways and results in different reaction mechanisms and kinetic and thermodynamic characteristics. The inclusion of oxygen in the form of pure oxygen or air has often been linked to higher dechlorination rates at lower temperatures and larger overall weight loss (100 wt.% for pure PVC resin) (Aracil et al., 2005). This

Table 5
Hydrothermal treatment of PVC and PVC waste in the literature.

Feedstock	Reagents / Catalysts	Conditions	Medium	DC_{max}[a]%	Other products	Other findings	Ref.
PVC	Coal fly ash, Coal gangue	200–250 °C, 14.7–54.9 bar	Vapor, liquid	97.34	Polyenes, polyols, polyketones	– Too long residence time decreased recoverable chlorine.	(Xiu et al., 2020c)
PVC	Concrete	200–250 °C, 13.6–46.9 bar	Vapor, liquid	95.04	Polyenes, polyols, polyketones		(Xiu et al., 2023b)
Cable	K_2CO_3	175–250 °C, 10–38 bar, 4 h	Liquid, vapor	99.1			(Gandon-Ros et al., 2020)
PVC	Cu^{2+}	200–240 °C	Unknown		Hydroxylated polyenes	– Relevant as copper is present in cable material	(Ma et al., 2021)
PVC	Na_2CO_3, KOH, NaOH, $NH_3{\cdot}H_2O$, CaO, $NaHCO_3$	220 °C, 0.5 h	Unknown	65.12	Polyenes	– Elimination was the prevalent reaction pathway due to lower pressures and residence time. – Past a certain concentration of alkali, dechlorination is reduced.	(Zhao et al., 2018)
PVC (M_w:38000)	NaOH	127–327 °C, 0.5–4 h, 30 bar (initial)	Unknown	98	Oxygenated polyenes		(Lu et al., 2002)
PVC (M_w:62000)	–	180–260 °C, 15 h	Unknown	~100		– H/C: 0.7–0.8 mol/mol	(Poerschmann et al., 2015)
PVC packaging bags	–	400–425 °C	Supercritical	47[b]	Aliphatics (7 wt.%), MAHs (5 wt.%), PAHs (4 wt.%), alcohols, naphthenes, H_2, CO_2, C_1-C_5		(Čolnik et al., 2022)
PVC (M_w:62000)	–	400–500 °C, 2–6880 bar, 600–620 s	Vapor, supercritical	NR[c]	Polyenes, polyols, polyketones		(Nagai et al., 2007)
PVC	–	200–600 °C, 16–557 bar	Vapor, liquid, supercritical	100	Polyenes, CO_2, aromatics, aliphatics, benzoic acid, benzaldehyde, phenol, hydroquinone, C_1-C_5	– Different products below and above 350 °C.	(Takeshita et al., 2004)
Cable (PVC and PE)	–	200–300 °C, 16–86 bar, 3 h	Vapor, liquid	95.96		– The solid residue was pyrolyzed at 850 °C and produced chlorinated products including Cl_2 that were substantially reduced in dechlorinated samples. – H/C: 1.32–1.68 mol/mol	(Soler et al., 2018)
PVC	–	200–260 °C, 1 h	Unknown	93	Oxygenated polyenes	– H/C_{max}:1.02 mol/mol	(Yao and Ma, 2017)
PVC	EtOH	200–240 °C, 30–150 min, 5–15 % solid/liquid, 0–80 %, ethanol/water	Unknown	96.33	MAHs, PAHs, aliphatic hydrocarbons, alicyclic hydrocarbons, oxygenated hydrocarbons, chloro-compounds	– The effect of temperature diminished past 220 °C. – Maximal dechlorination at 90 min. – Higher ethanol content increased hydrochar yield but did not alter dechlorination efficiency significantly. – Solid/liquid ratios of above 10 % decreased dechlorination and increased char yield. – H/C: 1.02–1.90 mol/mol	(Feng et al., 2023)
PVC pipe	Pd/C, Pt/C, Ru/C	300–350 °C, 0.5–4 h, 90–170 bar, 10:1 liquid:solid, 0–10 % catalyst	Vapor, liquid	99.01	Hydroxylated polyene	– The catalyst lowered the dechlorination temperature and increased its yield.	(Ghalandari et al., 2023)
PVC	MgO, CoO, NiO, ZnO, β-zeolite, NaOH, TiO_2	200–300 °C, 0.5–1.5 h	Vapor	70.3	Polyene	– The metal oxides with superheated steam lowered the pyrolysis temperature.	(Hapipi et al., 2018)
DEHP-rich flexible PVC	Ammonia	200–400 °C, 1–5 % ammonia, 0.5–1.5 h, 33–335 bar	Liquid, supercritical	99.8	2-ethyl-1-hexanol, benzaldehyde, acetophenone, polyene	– At lower temperatures (250 °C) polyene and ethyl hexanol or the main products, but at higher temperatures, the polyene degrades and aromatizes.	(Xiu et al., 2020b)
PVC		400–600 °C, 1 h, 375–608 bar	Supercritical	~100	Acetic acid, phenol, benzene, propane, butane, naphthalene	– Acetic acid only appeared at lower temperatures and naphthalene only at a higher temperature.	(Sato et al., 1998)
DEHP-rich PVC waste	Low-rank coal	350–450 °C, 165–402 bar, 0.5–2 h,	Liquid, supercritical	>98	PAHs, MAHs, oxygenates, phenols, cyclic alkanes and alkenes, heteroatom-containing hydrocarbons, paraffins and olefins, polyene	– –OH peaks disappeared after 350 °C. H/C increased as O/C decreased at elevated temperatures.	(Xiu et al., 2024)

[a] Maximum dechlorination efficiency reported as the removed chlorine divided by the total chlorine content; [b] Reported as yield (wt.%); [c] Not reported.

observation was speculated to be due to the participation of oxygen through the addition of hydroperoxide groups that enhance the dechlorination and scission reactions and lead to partially oxygenated products (alcohols and ketones) (Decker, 1976). Later Wang et al. (2021) performed a DFT study verified by experimental results to show the mechanisms of this process and explain the improved dechlorination. Their work suggested a two-faceted role for oxygen by adding more dechlorination channels and by transforming the dechlorination from an endothermic to an exothermic reaction, thereby making the dechlorination thermodynamically advantageous.

Despite the proposed upsides to oxidative pyrolysis of PVC, less is known about the role and the effect of oxygen on the organic products. Yoshioka et al. (2000) successfully converted a rigid PVC feedstock to water-soluble acids (e.g., oxalic and benzenecarboxylic acids) and CO_2. Nonetheless, oxidative thermal decomposition of PVC has been shown to produce higher amounts of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Edo Giménez et al., 2014). Considering the advantages, such as higher dechlorination and lower solid residue, more research on oxidative pyrolysis of PVC can be instrumental to its recycling.

5.2.5.2. Radiative. As chemical recycling at its core hinges upon delivering sufficient energy to break down the chemical structure of the material, other methods of energy delivery have been investigated in the literature. Radiative methods use irradiation for this purpose in an attempt to achieve more uniform heating and controllability (Yu et al., 2022). In PVC, particular properties of the polymer in adsorbing the microwave irradiation compared to other thermoplastic polymers have made microwave-assisted dechlorination an attractive process (Moriwaki et al., 2006). This receptiveness of PVC to microwave radiation is further enhanced in higher temperatures ($>T_g$), allowing an efficient process that uses a combination of a preheating step and microwave irradiation (Ito et al., 2006). Microwave-assisted dechlorination of PVC is reported to take place at a lower temperature at higher rates and better selectivity compared to conventional heating (Kobayashi et al., 2019).

The application of microwave technology has not been limited to degradation studies. Using microwave technology, Osada and Yana (Osada and Yana, 2010) were able to selectively de-plasticize and dechlorinate PVC at 150 and 235 °C in an 8 M sodium hydroxide solution. In comparison with conventional heating methods, higher temperatures of 250 and 350 °C and higher concentrations of NaOH (i.e., 16 M) were required and the extraction selectivity was still poor.

While microwaves are perhaps the main choice for radiation-induced pyrolysis of PVC, the effect of γ-irradiation has also been studied on PVC degradation. Boughattas et al. (2016a; 2016b) and Decker (1976) investigated the radio-oxidative degradation of PVC using γ-irradiation and reported similar results – higher dechlorination rates at lower temperatures as well as oxidation products. Even though their studies are not directly applicable to PVC recycling, they can shine a light on the application of electromagnetic radiation in recycling processes.

5.2.5.3. Hydrogen-assisted methods. While in oxygenated (bio-)polymers, hydrogen can be employed as a reduction agent to cleave C–O or C–C bonds, the application of hydrogen in PVC usually does not involve bond cleavages (Kratish and Marks, 2022). Hydrogen gas has been used almost exclusively by a few researchers in the catalytic hydrogenation of PVC waste. For instance, O'Rourke et al. (2023) used homogeneous Rh catalysts in an ionic liquid environment to dechlorinate and subsequently hydrogenate PVC. This tandem approach inhibits the formation of cyclic aromatic products that could otherwise create complications for the process equipment. Their method resulted in partially unsaturated polyethylene segments that were soluble in the media. In a similar work, Svadlenak et al. (2023) used a Pt/C catalyst in different alkylamines for the dechlorination of PVC resin followed by a catalytic hydrogenation/hydrogenolysis step in order to produce wax products. In their process, the competition between hydrogenolysis and hydrogenation determines the properties of the wax products.

Additionally, hydrogenation has been attempted for the phthalate ester plasticizers found in PVC waste as well. Several supported Rh catalysts were found to be effective in hydrogenating the aromatic ring in the phthalate esters, while transesterification converted BBP into safer esters in a one-pot process (Windels et al., 2022). The result was a safer alternative (cyclohexane dicarboxylates) to be used as a plasticizer. Hydrogen-assisted processes, while in the minority for PVC recycling, have proven to be an attractive technology. More research on this topic can elucidate the application and the potential of this technology as a clean process.

Chemical recycling promises the ability to handle complex feeds. However, several issues have caused this technology to remain in the research scale for PVC recycling: high energy requirements, costly equipment capable of withstanding corrosive HCl, low recovery yields, and complex product streams consisting of various chemicals requiring sophisticated downstream processing. To address these, more research on developing new corrosion-resistant materials, reactor technologies, and catalyst systems is necessary in order to increase the yields of usable fractions while reducing the overall costs of the operation. Finally, by combining chemical processes in the operation, higher conversion rates can be achieved (Zevenhoven et al., 1997).

6. Future perspective and conclusions

PVC is a versatile and widely used polymer. The wide range of formulations and characteristics make PVC a favorable choice for applications in all fields, including construction, medical applications, packaging, and electronics. PVC contains more than 50 % chlorine, and its production relies much less on fossil resources compared to other plastics. Depending on the application, PVC formulations can include high quantities of fillers and additives. Therefore, PVC products offer unparalleled qualities, such as natural flame retardation and smoke suppression, coupled with remarkable longevity at low costs.

Despite these advantages, PVC products require appropriate methods to manage their EoL. High quantities of organic and inorganic additives and the potential for HCl evolution upon heat or light degradation threatens most of the EoL options for PVC. In general PVC is not desired in mixed waste streams, as it can create issues for the recycling processes, such as corrosion, higher fouling, char formation, and catalyst poisoning. Thus, collection and sorting of the PVC waste streams must be done adequately so that it does not disturb the recycling paths of other polymers and allows the PVC itself to be recycled.

Contingent upon the waste, four types of EoL solutions have been studied. Energy recovery is the simplest choice, but is a last resort as it only recovers part of the resources used in the production of the material. Furthermore, it potentially releases several contaminants and high amounts of greenhouse gases. Mechanical recycling is currently the most used recycling approach and aims to close the loop for each product by grinding the sorted waste and converting it to PVC products. Several initiatives and schemes in Europe operate to ensure a steady and reliable flow of materials for this purpose. Solvent-based recycling focuses on using physical methods such as dissolution/precipitation to separate the polymer or the additives from the material matrix. Therefore, it is a suitable technology for producing additives and PVC resins of similar or lower properties compared to what existed in the feed. The extracted additives can be further processed and reused and the PVC resin can be used in the same or different appropriate applications. Finally, chemical recycling is the most varied method for recycling, with different implementations, such as pyrolysis, gasification, and hydrothermal treatment. All these methods attempt to recover some or all of the constituents of the polymeric chain for the production of new materials. This technology has proven effective, particularly in recovering chlorine as HCl. Chemical recycling has emerged as a promising technology

under development, particularly for complex feed containing additives (Yu et al., 2016). However, additives such as metal oxides can partially hinder the chemical degradation of PVC. The products of chemical recycling processes, such as HCl, can be used in the production of new materials, including PVC, after adequate separation and upgrading. Wherever applicable, the products stemming from the additives in the feed can also be used in new PVC articles or the synthesis of new compounds. Table 6 shows the strengths, weaknesses, opportunities, and threats (SWOT) regarding each of these methods.

Since PVC contents as low as 1 % can still affect the recycling process, it is crucial to characterize and quantify the PVC in waste and plan a recycling strategy accordingly. PVC waste can be roughly divided into two main categories:

- *PVC-contaminated* waste contains small quantities (<10 %) of PVC resin, usually characteristic of a highly complex feedstock such as MSW. Omnivorous recycling processes should tolerate PVC degradation products. However, the application of such processes has been mainly limited to the research a stage and robust omnivorous technologies for PVC recycling have yet to reach viable commercial scale (set goal of TRL7 by 2030, i.e., system prototype demonstration in operational environment (VinylPlus, 2021b)). For other processes, PVC must be either removed or neutralized. This stream and its products have the potential to be used in conventional processes while being within the range of tolerance, either with or without a pretreatment step.
- *PVC-rich* waste contains medium to high concentrations of PVC but might also contain contaminations, including high quantities of additives and other polymers. This stream is what is usually referred to as "PVC waste" and consists of construction and demolition, medical, and packaging wastes, to name a few. A PVC-focused process is advised, but depending on the contaminations, characteristics of the stream, and the recycling process, effective separation and/or extraction is crucial. Physical recycling (mechanical recycling or a combined approach) methods must be prioritized where possible due to their robustness, simplicity, and established position in the recycling industry.

Depending on the characteristics of the waste stream, products of interest, and financial incentives, one or multiple options from the technologies discussed in this review may be appropriate. Table 7 compares these technologies in terms of their suitability for different cases.

Biological methods have emerged recently as an interesting path in plastic recycling. These methods employ microorganisms or enzymes in order to degrade plastic into smaller products (Soong et al., 2022). While such processes have been attempted for other polymers (e.g., PET) often successfully, biological recycling of PVC has received little to no attention (Koshti et al., 2018; Mohanan et al., 2020). However, the environmental risk of landfilling PVC waste has compelled a number of researchers to study the biodegradation of PVC waste using a variety of biological tools (Giacomucci et al., 2019; Istamov et al., 2024; Kaczmarek and Bajer, 2007; Kırbaş et al., 1999; Peng et al., 2020; Singh Jadaun et al., 2022; Webb et al., 2000). Biodegradation of both plasticized and unplasticized PVC has been studied, but plasticized PVC has shown more susceptibility to biodegradation (Singh Jadaun et al., 2022). Biodegradation studies are, nevertheless, distinct from biological recycling. While in recycling processes the main goal is the valorization of the waste, biodegradation studies focus on mitigating the risks and costs arising from waste. Therefore, the research in this field has remained mostly limited to the destruction of PVC rather than the production of specific products. Nonetheless, several microorganisms and species (e.g., *Curvularia* sp., *Bacillus licheniformis*, *Chaetomium globosum*, and *Phanerochaete chrysosporium*) have been identified with the ability to treat PVC waste, opening new possibilities for new processes in the future (Kırbaş et al., 1999; Martins-Franchetti et al., 2010; Saeed et al., 2022; Vivi et al., 2019).

In this work, the lifecycle of PVC from raw materials and resources until its disposal, collection, sorting, and more sustainable EoL paths were discussed to provide a holistic view of PVC and its challenges. PVC is an irreplaceable polymer for its unique properties, as shown by the ever-increasing production and demand despite the challenges. However, there are several open questions concerning PVC recycling, including high contamination and corrosive products that challenge the viability of recycling and downstream upgrading plants. Economic feasibility is imperative in designing any process for recycling PVC

Table 6
SWOT analysis of different recycling technologies for PVC waste.

Method	Strengths (S)	Weaknesses (W)	Opportunities (O)	Threats (T)
Energy recovery	– Recovers energy from waste	– Environmental concerns (dioxins and other pollutants) – HCl corrosion	– More efficient modern incinerators – Employing neutralizing salts – Dechlorination pretreatment – Cleaner technologies (e.g., CLC)	– Regulations on incineration – CO_2 taxes – Public opinion
Mechanical recycling	– Simple, inexpensive, and efficient technology – Product-to-product approach (closed loop)	– Lower quality of the recycled material – Requires relatively homogeneous feed – Legacy additives will remain in the recycled material	– Improvements in extrusion technologies for less degradation – Characterization technologies for legacy additives – Better collection of single-type PVC waste	– Recyclates not suitable for all PVC applications – Heavily dependent on a consistent collection and transportation scheme
Solvent-based methods	– Separates PVC and/or additives – Reusable solvent – Higher variety of possible products from recycled material	– Limited to produce the same or lower grade of PVC – More expensive due to operations regarding the solvent – Requires multiple steps for each element in the waste – Solvent and energy consumption	– Development of better, recoverable, more efficient solvents capable of removing legacy additives as well as PVC with minimal energy requirement	– Challenge to achieve legal limits of legacy additives – Solvent consumption
Chemical recycling	– Production of HCl to obtain virgin PVC via oxychlorination – Feedstock independent	– High energy requirement – High equipment costs – Lower recovery yield compared to other techniques – Requires sophisticated separation/purification techniques for the products	– Catalytic processes for higher conversion rates, less char, and more usable organic products – New avenues for chlorine valorization such as chlorination-vaporization (Ma et al., 2024), – New reactor technologies for reducing energy requirements and improving product selectivity – Combining chemical technologies to achieve higher recoveries (Zevenhoven et al., 1997)	– Limits on chlorine and other contaminants in the pyrolysis oil by the petrochemical industry – CO_2 taxes – Demand for organic products

Table 7
Available technologies for end-of-life PVC waste compared.

	Energy recovery	Mechanical recycling	Solvent-based methods	Pyrolysis	Gasification	Hydrothermal
Feedstock	PVC-contaminated/rich	Single-type PVC-rich	PVC-rich waste	PVC-contaminated/rich	PVC-contaminated/rich	PVC-contaminated/rich
Contamination tolerance	Very high	Very low	High	High	Very high	High
Main products	Energy	PVC compound as a blend or composite with similar or lower PVC content	PVC resin or PVC compound with similar characteristics or additives	• Aromatic-rich oil • Low-hydrogen solid residue • HCl • Gaseous products	• Syngas • HCl • CO_2 • Solid residue	• Aromatic-rich oil • Low-hydrogen solid residue • Gaseous products • Aqueous solution of HCl and other water-soluble components
Additives	Incinerated alongside the feed	Remain in the mix with possible migration	Can be extracted with minimal loss	Mixed with the oil and the solid residue with partial degradation	Gasified alongside the feed	Mixed in the oil, aqueous medium, and the solid residue with partial degradation
CAPEX	Medium	Low	Medium	High for PVC-rich waste	High for PVC-rich waste	High for PVC-rich waste
Implementation	Widespread	Widespread	Commercialized	Research	Commercialized [a]	Research

[a] With limited PVC tolerance.

waste, given the relatively low cost of virgin material. The development of materials to replace PVC applications is an effective solution to tackle the problems associated with PVC waste. Nevertheless, more scientific effort in designing inexpensive and robust recycling options for PVC needs to go hand-in-hand with policymaking decisions and industrial collaborations. The question of "how much PVC will be a part of our future" must not distract us from the fact that "PVC waste will certainly be a part of our future".

CRediT authorship contribution statement

Mohammadhossein Havaei: Writing – original draft, Visualization, Conceptualization. **Oğuzhan Akin:** Writing – review & editing. **Andrea Locaspi:** Writing – review & editing. **Robin John Varghese:** Writing – review & editing. **Florent Minette:** Writing – review & editing. **Eric Romers:** Writing – review & editing. **Steven De Meester:** Writing – review & editing, Supervision. **Kevin M. Van Geem:** Writing – review & editing, Supervision.

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.

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Data availability

No data was used for the research described in the article.

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Glossary

ABS: Acrylonitrile butadiene styrene
BBP: Benzyl butyl phthalate
B-PVC: Bulk PVC
CLC: Chemical looping combustion
DBP: Dibutyl phthalate
DBT: Dibutyl terephthalate
DEHP: Bis(2-ethylhexyl) phthalate
DFT: Density functional theory
DIBP: Diisobutyl phthalate
DINP: Diisononyl phthalate
DOP: Dioctyl phthalate
ECHA: European Chemicals Agency
EMI: Electromagnetic interference
EoL: End-of-life
E-PVC: Emulsion PVC
FTIR: Fourier Transform Infrared Spectroscopy
GC×GC-TOFMS: Comprehensive two-dimensional gas chromatography-Time of flight mass spectrometry
GC-MS: Gas chromatography-Mass spectrometry
HDPE: High-density polyethylene
HIPS-Br: Brominated high-impact polystyrene
LDH: Layered double hydroxide
LDPE: Low-density polyethylene
MAH: Monoaromatic hydrocarbon
MSW: Municipal solid waste
NIR: Near infrared
PAH: Polyaromatic hydrocarbon
PCDD: Polychlorinated dibenzo-p-dioxin
PCDF: Polychlorinated dibenzofuran
PE: Polyethylene
PET: Polyethylene terephthalate
PP: Polypropylene
p-PVC: Plasticized PVC
PVC: Polyvinyl chloride
Py-MS: Pyrolysis-Mass spectrometry
REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals Regulation
SAN: Styrene acrylonitrile
SFE: Supercritical fluid extraction
S-PVC: Suspension PVC
T_g: Glass transition temperature
TGA/DTG: Thermogravimetric analysis/Differential thermogravimetry
THF: Tetrahydrofuran
U-PVC/PVC-u: Unplasticized PVC
UV: Ultraviolet
VCM: Vinyl chloride monomer