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Chlorinated Plastics Offer Unique Opportunities and Challenges in Upcycling

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Abstract.

Chlorinated plastics are part of the everyday lives of consumers and producers alike. They can be found in buildings, automobiles, fashion, packaging, and many other places. This prevalence makes them a considerable part of the plastic waste crisis. Interest in "upcycling" (as opposed to recycling) has grown recently to augment the possibilities of managing plastic waste. The advances made in plastic upcycling have focused on polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) while chlorinated plastics, chiefly polyvinyl chloride (PVC), have received much less attention. The release of chlorine-containing molecules during treatment of chlorinated plastic greatly complicates cross-method upcycling, or even the treatment of plastic mixes containing chlorinated plastics. This review presents a case for extracting value from chlorinated plastics by highlighting appealing upcycling products made owing to, or despite, the C-Cl bond via depolymerization, carbonization and modification.

Keywords

Chlorinated Plastics, PVC, Upcycling, Depolymerization, Carbonization, Modification

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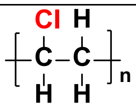
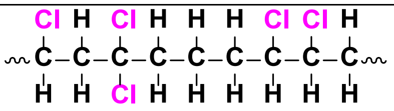
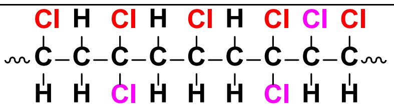
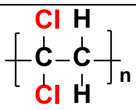
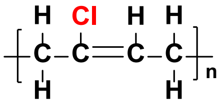
Introduction.

From industry to consumer products, chlorinated plastics (Table 1) have excelled in a variety of applications [1]. Much like other common plastics such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS), the fate of chlorinated plastic waste remains in question. Data on the fate of chlorinated plastic waste is scarce, but the case of polyvinyl chloride (PVC) offers the greatest insight into potential end-of-life outcomes for chlorinated plastics. PVC, often referred to simply as "vinyl," is the 3rd-most produced plastic annually worldwide [2], and is ubiquitous in consumer and industrial products. PVC recycling, as of 2018, is classified as "negligible" according to the U.S. EPA [3] (i.e., < 5,000 tons recycled/year). This is due to chlorine atoms in the plastic and the problems they can create downstream. During thermomechanical recycling, PVC tends to degrade through dehydrochlorination (i.e., loss of HCl) resulting in the formation of conjugated polyene segments (i.e., $-(CH=CH)_n-$) and/or crosslinks [4], reducing the value/utility of the recycled product, and exposing equipment and personnel to risk. The presence of additives in PVC furthers complicate the conventional recycling process [5]. The issues associated with conventional recycling of PVC also extend to other chlorinated plastics which include: polyvinylidene dichloride (PVDC), chlorinated polyethylene and polypropylene (CPE and CPP), chlorinated PVC (CPVC), and neoprene (polychloroprene also known as "CR").

Despite these issues, it would be a misconception to classify PVC as non-recyclable [6], especially with the fact that PVC waste sorting [7] and recycling technologies are in constant advancement. Nonetheless, the investigation of chemical recycling methods for PVC is worthwhile to pursue in parallel. Chemical recycling is divided into two types: closed-loop (to monomer) or open-loop (to new materials) [8]. Upcycling is considered an open-loop chemical recycling process that entails the production of materials of higher economic or socioeconomic value than the original plastic [9]. Due to the vague and often "all-encompassing" definition of the term "upcycling," it can be seen in literature as used interchangeably with open-loop chemical recycling.

In the case of chlorinated plastics, the same chlorine atoms that add to the challenge of conventional recycling offer opportunities for open-loop chemical recycling or upcycling via the "activation" of the polymer backbone by utilizing the C-Cl chemistry to create products of higher value than could be achieved through conventional recycling of these plastic wastes. This review focuses on upcycling (used interchangeably with chemical recycling) methods for chlorinated plastics as well as the types of products and applications. Recent reviews have covered chemical recycling of PVC specifically [10, 11], however only a single review by Huang [12] was found discussing chlorinated plastics in general. Taking inspiration from Huang's chlorinated plastic upcycling review, chlorinated plastics upcycling is categorized here by the broad areas of: depolymerization: the deconstruction of plastic into smaller fragments; carbonization: the conversion of plastic into carbonaceous materials; and modification/functionalization: the incorporation of functional group into the plastic.

Table 1. List of the most common chlorinated plastics, their structure, synthesis methods, and use.

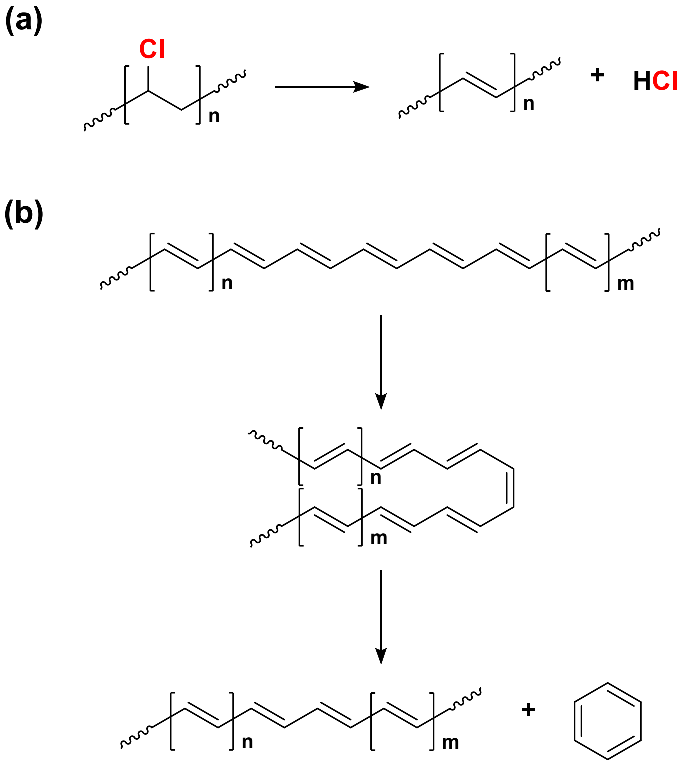
Plastic	Structure	Synthesis [13]	Applications [13]
Polyvinyl Chloride (PVC) 56.7 wt% Cl	 $\left[\overset{Cl}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \right]_n$	Free radical polymerization of the vinyl chloride monomer	Piping, packaging, window profiles, tubing, flooring, appliances.
Chlorinated Polyethylene (CPE) † 10-48 wt% Cl [13]	 $\sim \overset{Cl}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{Cl}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{H}{C}} - \overset{Cl}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} \sim$	Chlorination of polyethylene.	PVC modifier, cable jacketing, window profiles, packaging.
Chlorinated Polyvinyl Chloride (CPVC) 63-74 wt% Cl [13]	 $\sim \overset{Cl}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{Cl}{C}} - \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{Cl}{C}} - \overset{Cl}{\underset{H}{C}} - \overset{Cl}{\underset{H}{C}} \sim$	Chlorination of polyvinyl chloride.	Piping, fittings, industrial products.
Polyvinylidene Chloride (PVDC) 73.2 wt% Cl	 $\left[\overset{Cl}{\underset{Cl}{C}} - \overset{H}{\underset{H}{C}} \right]_n$	Free radical polymerization of the vinylidene chloride monomer	Plastic food wrap (i.e., original Saran Wrap), bubble wrap, etc.
Neoprene (Polychloroprene, CR) 40 wt% Cl	 $\left[\overset{H}{\underset{H}{C}} - \overset{Cl}{C} = \overset{H}{C} - \overset{H}{\underset{H}{C}} \right]_n$	Free radical polymerization of the chloroprene monomer.	Dry suits, cable jacketing, adhesives, construction, latex.

†also CPP (not shown)

Depolymerization.

Depolymerization of chlorinated plastic via diverse methods has been reported in the literature. Depolymerization methods generally aim for the production of small molecular weight fractions for use mainly as feedstock chemicals, fuels or lubricants. This entails the enhancement of liquid or gas product yields versus solid products. Among chlorinated plastics, PVC specifically was shown to be capable of photodegradation [14-16] and biodegradation via gut bacterium isolated from insect larvae [17-19] producing alcohol and fatty acid degradation intermediates. However, these two areas, and their products, are not as well investigated as pyrolysis (i.e., deconstruction of plastic through thermal decomposition).

Pyrolysis of PVC follows a two-step process where HCl is the main product of the first step (i.e., dehydrochlorination, Scheme 1a), occurring between 250 - 360 °C, and full dehydrochlorination results in a mass loss that is > 50% of the total initial PVC mass. The second step (depolymerization, Scheme 1b) occurs at higher temperatures, above 360 °C, and produces chlorinated and non-chlorinated aromatic hydrocarbon gases and liquids, but mostly char and tar residue [20]. The thermal degradation of PVC can also include a “pinch-off” mechanism that forms benzene.



Scheme 1. Mechanism of the thermal **(a)** dehydrochlorination and **(b)** depolymerization of PVC. Adapted with permission from reference [21], Copyright (2016), with permission from the American Chemical Society.

The multi-phase products of PVC pyrolysis have their own individual uses. The main product, HCl, is of low value but has many uses. The leftover carbon-containing solids can have a wide range of applications, which will be briefly summarized in the following section. Gas, liquid, and high boiling wax pyrolysis products are valued for their potential as feedstock materials for chemical processes or as fuels. However, for PVC, they are considered low-quality fuels due to their relatively low calorific value due to potential residual chlorination [22]. While those chlorinated products can be upgraded [23-25], it is important to note that chlorinated plastic pyrolysis can also produce unsafe chemicals. Pyrolysis of neoprene can produce chlorinated aromatics such as chlorobenzenes or chlorophenols [26] as well as non-chlorinated aromatics. While these have some commercial uses, this process also produces highly toxic chlorinated dioxins, which also can occur in pyrolysis of PVC [27]. The low value of the non-char depolymerization products, and the potential for release of toxic or corrosive chemicals (e.g., HCl) are a major deterrent of chlorinated plastic pyrolysis.

The desire to produce safe and high-value products motivates researchers into developing methods for the dechlorination (i.e., any reaction which liberates -Cl from the polymer backbone, including dehydrochlorination) of chlorinated plastics prior to degradation. In two-step pyrolysis, plastic mixes containing chlorinated plastics are thermally treated by first releasing HCl at lower temperatures before ramping the temperature towards degradation of the plastic mix. This method proved successful in the production of chlorine-free, or low chlorine content, oils from PVC [28] or plastic mixes containing PVC [29] or PVDC [30]. Despite success, the elevated temperatures brought interest to works in hydrothermal dechlorination [31], but it comes with the requirement of high pressures. Chemical dechlorination has seen a recent rise in interest due to the need for methods that operate under low temperatures and pressures (as low as atmospheric pressure). High degrees of dechlorination were achieved using base [32-34] or in ionic liquid (IL) media [35]. Catalytic dechlorination offers the option for either direct [36, 37], or tandem (Figure 1) [38], hydrogenation of the polymer, producing PE-like materials that can be degraded into high quality oils, similar to PE. Chlorine atoms released from PVC dechlorination can also serve the upcycling cause. HCl generated from PVC electrolysis can be used to chlorinate arenes [39]. This work showed that using PVC as a source of chlorine atoms for the chlorination of organic molecules (using electrochlorination) had a reduced global warming potential (GWP) of 71%, relative to using HCl from other sources. Further, this process can function in the presence of plasticizers commonly found in PVC (e.g., di(2-ethylhexyl)phthalate, DEHP), as well as tolerance to air and moisture.

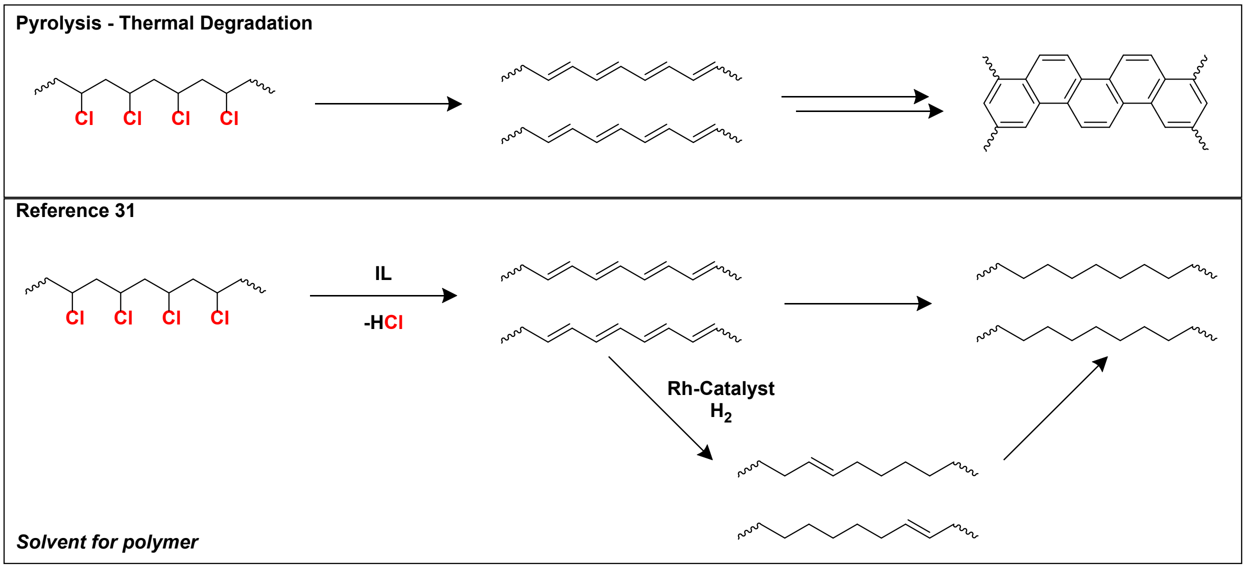


Figure 1. Production of saturated polymer from PVC through a tandem dehydrochlorination-hydrogenation method (bottom) versus thermal degradation producing polyene crosslinked polymer (top). Adapted from [38], Copyright (2023), with permission from the Royal Society of Chemistry.

Despite the advances in dechlorination chemistry, pyrolysis of chlorinated plastic is still a less than an ideal strategy, especially due to their anti-synergistic behavior in mixed plastics [40-42]. The production of pyrolysis oil from chlorinated plastics is centered around avoiding chlorine, but another method revolves around it. Chemical depolymerization utilizes the chemistry of chlorinated plastics towards the production materials of potentially higher value and a wider range of application than pyrolysis.

Chemical depolymerization usually starts with de(hydro)chlorination, either total or partial. In a recent work, mixed plastics containing up to 10% PVC were fully dechlorinated prior to hydrogenolysis [42]. This helped avoid catalyst poisoning due to chlorine impurities and produced high yields of liquid products that can be used as fuels or lubricants. A recent mechanochemical method (Figure 2) managed to depolymerize PVC into products that are water soluble, low molecular weight (only ~6% that of the starting PVC), and exhibited reasonable biocompatibility [43].

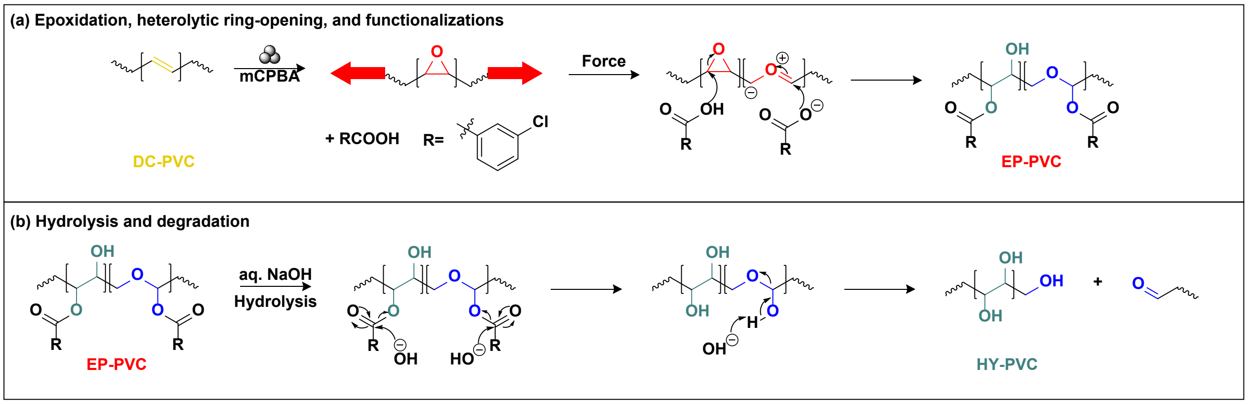
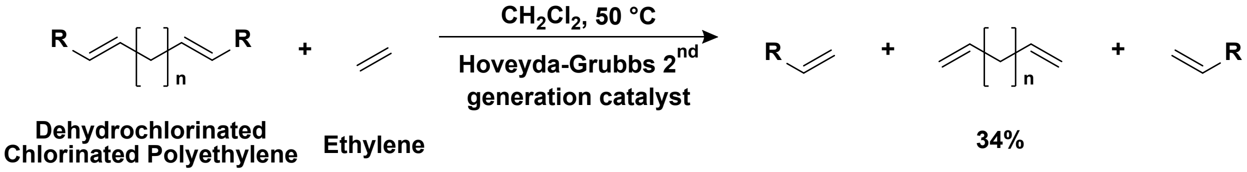


Figure 2. Mechanism of the depolymerization of dechlorinated PVC into water soluble fragments. Adapted from [43], Copyright (2023) with permission from John Wiley and Sons.

Olefin metathesis, on the other hand, utilizes partial dechlorination towards the production of low molecular weight dienes and oligomers (Scheme 2). Partially de(hydro)chlorinated CPE was depolymerized via "ethenolysis" using the Hoveyda–Grubbs 2nd generation catalyst, producing C_6 and C_7 α,ω-dienes that have known uses in polymer and chemical synthesis [35]. Success in olefin metathesis has been achieved through formation of low molecular weight oligomers (as low as 1.8 kDa) from the "cleavage" of the double bonds produced from PVC dehydrochlorination using a Grubbs catalyst and an added alkene [44].



Scheme 2. Depolymerization of dehydrochlorinated chlorinated polyethylene to produce small dienes. Reproduced from [35], Copyright (2014), with permission from John Wiley and Sons.

Research into the depolymerization of chlorinated plastics can be considered in its infancy. Compared to other plastics, not much has been reported, mainly due to the issue presented by the anti-synergistic behavior of PVC, and the biological [45] or poisonous effect of chlorine or depolymerization products on catalysts [42]. However, chemical depolymerization of chlorinated plastics may have many more opportunities for products compared to other plastics owing to the reactivity of the C-Cl bond. Yet, current chemical depolymerization strategies have not advanced much beyond 100-milligram scale, and much work is needed to understand the challenges and opportunities that occur when scaling up. For this to succeed, significant research needs to be done in analyzing and ultimately controlling product distributions, the types of separations processes needed, and design of catalysts specifically for treating chlorinated plastics. Given that PVC is intrinsically 57% Cl by mass, the ultimate depolymerization of PVC to small molecules should focus on those with the highest values.

Carbonization.

Unlike depolymerization, carbonization aims to produce solid carbonaceous materials while minimizing the amount of gas and liquid byproducts. Despite that, the leftover solid materials from pyrolysis, for example, can be considered carbonization products [46] and have their own uses. Compared to depolymerization, carbonization methods seem to be more tolerant to chlorinated plastics other than PVC [47-49]. There are similarities between carbonization and depolymerization as thermal treatment seems to be the primary current method to produce carbon-based materials from chlorinated plastics.

To further the comparison, carbonization products have a seemingly wider range of applications [50] to those of depolymerization, including as fuels which are considered the ideal pyrolysis products. Using microwave irradiation at relatively low temperatures (220 - 300 °C), PVC, PVDC, and CPE were successfully dechlorinated to produce materials that can be used as solid recovered fuel (SRF) [51]. The SRF produced had a low chlorine content and a high calorific value comparable to certain types of coal, and higher than that of traditional SRFs (i.e., those made from solid waste). Applicability of carbonization products surpass production of solid fuels. The main goal of carbonization is the production of porous carbon materials, which has applicability in fields ranging from water treatment to catalysis [52].

Porous carbons made from the chlorinated plastic carbonization are occasionally doped to expand their applicability. Manganese oxide (MnO_x) doped porous carbons were made from the carbonization of a PVC-$Mg(OH)_2$ system (Figure 3) and tested for their electrochemical performance [53]. This doped material might find use in supercapacitors as it showed high specific capacitance (up to 751.5 F/g), higher than carbon-based materials made from other plastics [54]. CPVC was used in the production of Fe_3O_4 doped carbon microfibers that showed high degradation efficiency (up to 99.9%) of Congo red (an azo dye whose use has been abandoned as it is a known carcinogen) [55].

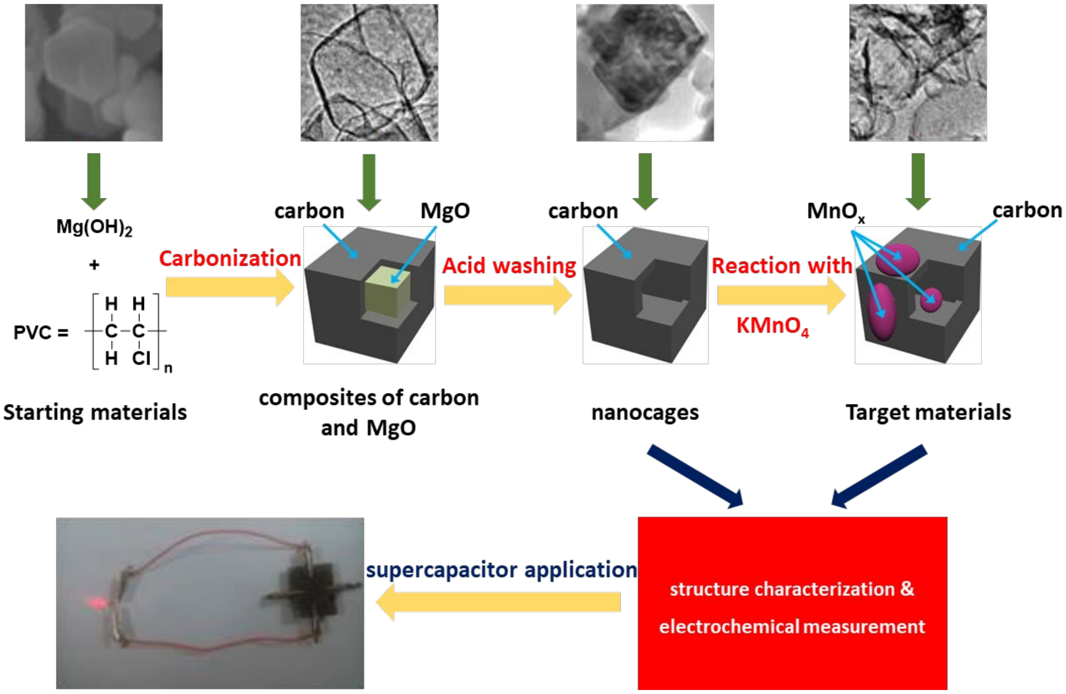


Figure 3. Synthesis process illustration for the production of doped porous carbon from PVC for supercapacitor applications. Adapted from [53], Copyright (2015), with permission from Elsevier.

Metal-free doping of carbonized chlorinated plastics was also shown to be possible. Metal-free N, O co-doped electrocatalyst was made by solvothermally dechlorinating PVC followed by carbonization [56]. The carbonized material made showed decent results in hydrogen evolution reactions. Heteroatom-doped carbon materials (with N, S, or P) were also made starting from PVDC [57].

The porosity of these carbonaceous materials allows for their use in gas adsorption. Carbonized CPVC was shown to have superior CH_4 adsorption (3.17 mmol/g) compared to other carbon adsorbents made from waste materials [58]. PVC hydrochar was used for the adsorption of CO_2, and showed remarkable success in the adsorption capacity (at 15 kPa and 100 kPa) and CO_2/N_2 (5/95, 15/85 and 30/70) selectivity compared to the competition [59]. A PVDC-based carbon material was also shown to be successful in CH_4, H_2 and CO_2 adsorption [60].

Success in the field of carbonization of chlorinated plastics brings optimism to those in the plastic upcycling field. However, it is important to consider that the current methods are energy intensive [61]. Most carbonization researchers are aware of the fact and are attempting to mitigate the energy consumption and release of toxic chemicals, yet more work and success are needed to achieve these goals.

Modification/Functionalization.

The goal of the methods discussed prior is the degradation of plastics towards new uses. Modification of chlorinated plastics aims to utilize the reactivity of the C-Cl bond to create new polymeric materials via structural changes to the plastic. Those changes usually come in the form of nucleophilic substitution (S_N2), or polymer grafting (Figure 4), alongside other methods (e.g., vulcanization [62], dehydrochlorination [63], hydrogenation [64]).

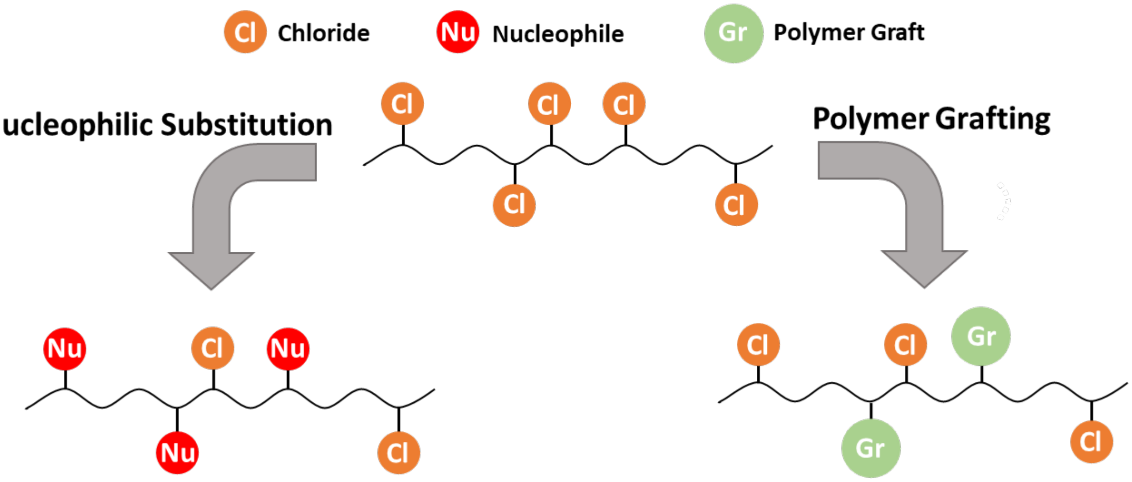


Figure 4. Illustration of the simplified change in structure of chlorinated polymers after nucleophilic substitution or polymer grafting.

The majority of works in modification of chlorinated plastics inevitably occur alongside partial dechlorination. The draw in partial modification of plastic is the potential of introducing added properties alongside maintaining some of the attractive inherent properties of the parent plastic. For example, the intrinsic antibacterial properties of PVC were enhanced by the nucleophilic substitution of isothiocyanate and thiocyanate groups [65]. The modification reduced the bacterial adhesion between 67% and 79% from the unmodified PVC. An electrochemical immunosensor was made by the nucleophilic substitution of ethylenediamine onto PVC [66]. The resultant membrane showed success in the detection of zearalenone (a mycotoxin). A copolymer made by the nucleophilic substitution of C-Cl bonds in PVC by thiols (i.e., R-SH) enhanced gas permeabilities ranging from 10-fold increase for CH_4, and 5-fold increase for O_2, N_2, CO_2 [67], albeit the performances of these materials were still at very low levels compared to state-of-the-art gas separation membranes.

An adhesive was made by the graft copolymerization of neoprene with methyl methacrylate (MMA) [68]. resulting in improved bond strength and ageing resistance compared to commercially available adhesives. CPE (which is intrinsically hydrophobic), was transformed into a hydrophilic polymer by radiation-grafting of acrylic acid as evidence by contact angle measurements [69] (Figure 5). The enhanced hydrophilicity could allow for better compatibilization of the polymer with additives and fillers.

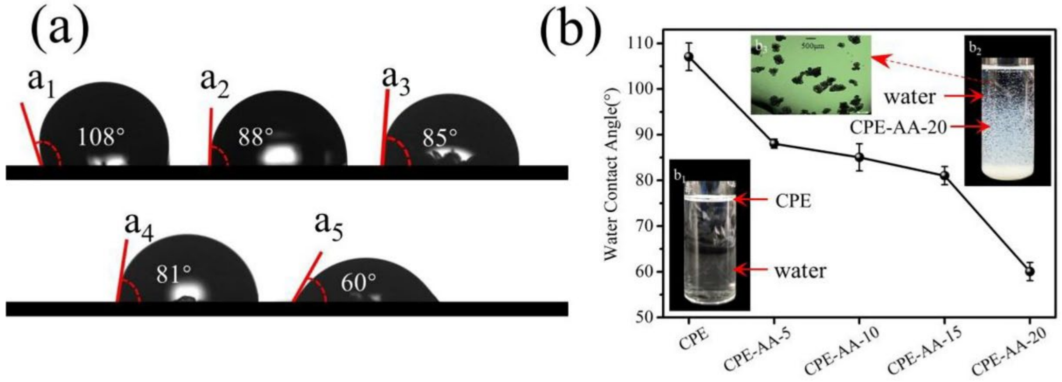


Figure 5. (a) Water contact angle of CPE (a_1) and acrylic acid grafted CPE (a_2: 5%, a_3: 10%, a_4: 15%, a_5: 20%). (b) Changes in water contact angle of CPE and acrylic acid grafted CPE; (b_1) CPE in DI water; (b_2) 20% acrylic acid grafted CPE in DI water; (b_3) microscopic image of 20% acrylic acid grafted CPE dispersed in DI water. Reprinted from [69], Copyright (2022), with permission from Elsevier.

One major hurdle of upcycling some chlorinated plastics, especially PVC, is the presence of significant quantities of plasticizers which are used to increase flexibility/processability. Unfortunately, most common plasticizers (DEHP, etc.) pose health problems due to the risk of migration [70]. To tackle this issue, covalently bonded internal plasticization became one of the most common, and fast growing, areas of PVC functionalization research. In one example, PVC that was modified with 4-aminothiophenol through nucleophilic substitution was reacted with a fatty acid- triglycidyl isocyanurate complex to produce covalently plasticized PVC [71] (Figure 6). The glass transition temperature (T_g) of PVC was reduced from 81 °C to as low as 31 °C. Further, the epoxy groups introduced into the polymer (via triglycidyl isocyanurate) improved the thermal stability of PVC by absorbing HCl released during thermal degradation. Similar works using a preceding S_N2 addition step were reported with azide as the click chemistry agent for the plasticization of PVC [72] and neoprene [73, 74].

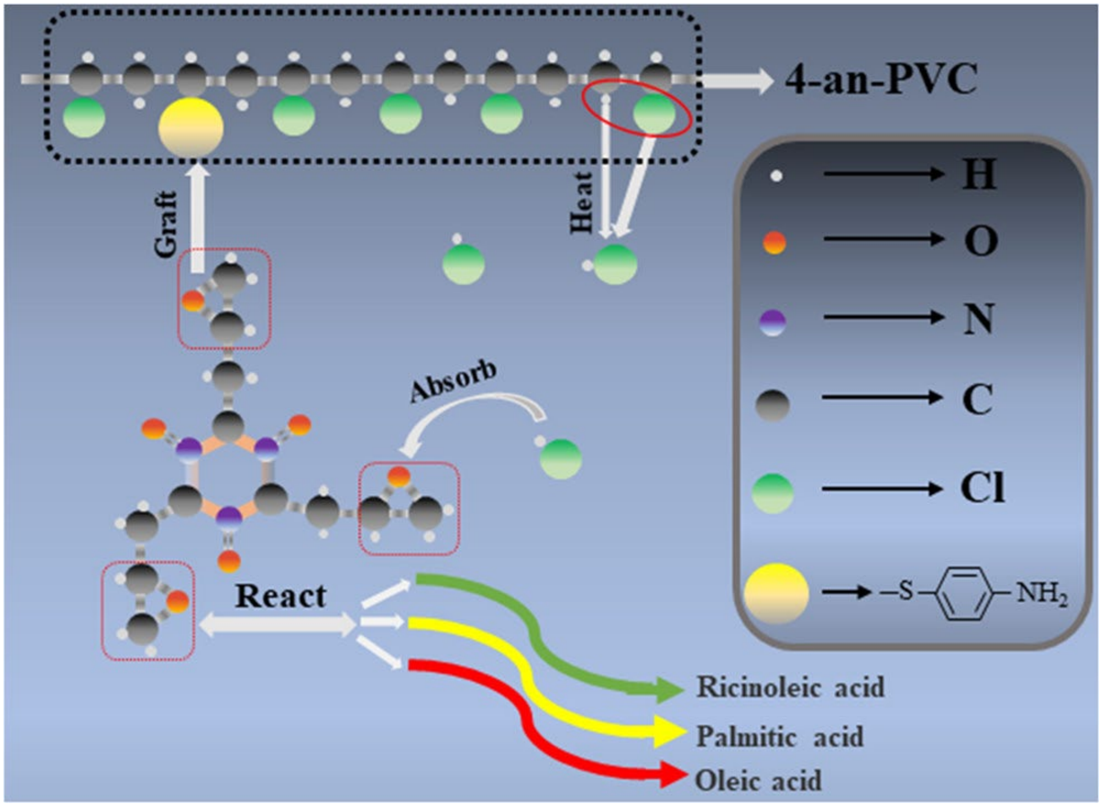


Figure 6. Illustration of the mechanism of internal plasticization of thiol-modified PVC using fatty acid-triglycidyl isocyanurate complex and the mechanism of HCl absorption by epoxy groups. Reprinted from [71], Copyright (2022), with permission from the American Chemical Society.

Modification of chlorinated plastics have shown significant progress, but they are faced with the inevitable challenge of competing elimination reactions [75, 76] that create polyenes which can become sites for crosslinking and/or further elimination reactions (Scheme 1). Thus, these polyenes introduce instability to the polymer (i.e., oxidation) and reduce solubility, which may ultimately negate the benefits achieved by functionalization. The seemingly unavoidable dehydrochlorination of chlorinated polymers, specifically PVC, during functionalization calls for more research into finding new ways that can either limit/avoid the production of polyenes, better utilization of the polyenes perhaps as sites for grafting, and possible "repair" of the polyenes to restore the PVC backbone.

Conclusions and Perspective.

Chlorinated plastics, particularly PVC, are intricately connected to the modern economy through both consumer products of varying quality/importance and industrial/construction materials (i.e., PVC pipes, which are essential to modern plumbing and access to clean water). However, once they have outlived their usefulness, all chlorinated plastics are problematic wastes if landfilled or recycled through conventional methods. This duality of chlorinated plastics is caused by what makes them special, the C-Cl bond. Attempts to recycle them via conventional thermomechanical means usually results in release of HCl and degradation of the material, reducing their value and corroding equipment. This challenge is reflected by the severe lack of PVC collection and recycling, although it is the 3rd most common plastic worldwide after PE and PP. Thus, new ways of dealing with chlorinated plastic waste are becoming of increasing interest and researchers are studying a variety of methods for the thermochemical treatment of chlorinated plastics with the goal of producing materials of higher value (i.e., upcycling).

Depolymerization is an intriguing method for the upcycling of plastics to produce small products (i .e., MW < 1000 g/mol). Pyrolysis is the most common way of depolymerization of plastics, however, chlorinated plastics present major complications for this process. As a result, de(hydro)chlorination became a growing field to remove chlorine atoms prior to pyrolysis to improve the liquid or gas yield of the process, producing more fuels, lubricants, or adhesives. Controlled chemical depolymerization (enabled by catalysis) provides opportunities to produce a wider range of materials that could be more broadly utilized, such as oligomers for chemical or polymer synthesis. While liquids and gases are the favored products for depolymerization, another upcycling method, carbonization, focuses on carbon-based solids made from the thermal treatment of plastics. The carbonaceous materials made from chlorinated plastics are attractive due to their porosity, opening the way for doping towards electrochemical or catalytic applications. In contrast to depolymerization or carbonization, the goal of modification of chlorinated plastics is to enhance the polymers' favored properties or add to them. This gives new polymers that can be used as sensors, or with enhanced gas diffusion compared to their "barrier" parent plastic. Further, chlorinated plastics can be internally plasticized, stopping the risk of plasticizer migration (leaching), which is a major and ongoing concern with the ubiquity of PVC products.

In preparing this review, it became evident that the majority of research in the area of chlorinated plastic waste upcycling has been directed towards PVC (and does not consider other chlorinated plastics). An example of which is neoprene, ubiquitous for its use in wetsuits and latex, has very little upcycling work done with it outside of fashion [77]. While PVC is the most common type of chlorinated polymer, this does not mean that methods developed for PVC upcycling/depolymerization will (fully) translate to other chlorinated polymers. But when considering the field of plastics upcycling in general, research on PVC itself is greatly underrepresented despite being the third most produced plastic [2].

Upcycling of chlorinated plastics is still in its infancy. Issues still arise from each of the methods discussed here. Depolymerization works will need to focus on ideal product yields, energy consumption, and catalyst compatibility. Given the unique chemistry of PVC among common plastic wastes, we postulate that carefully crafted depolymerization strategies for PVC might provide access to arrays of organic molecules that are either only available from natural products and/or are generally inaccessible through conventional synthetic methods. Carbonization is highly energy intensive and accompanies release of potentially harmful gases. Modification/functionalization of chlorinated plastics is a competition between substitution and elimination reactions, which could have the unintended effect of the final “upcycled” product to actually be of reduced utility and value. Compared to plastics like PET, upcycling/depolymerization of PVC (and other chlorinated plastics) has not received much attention. While some of the works discussed/cited in this review did not necessarily classify themselves as upcycling at the time of original publication (a term which has only recently come into vogue), they are still valuable examples of the upcycling concept, and provide important context for current and future works. Further, the works presented here for the upcycling of chlorinated plastics are but a sample of the total body of knowledge and are illustrative examples to consider for further research by showcasing the “power” of utilizing the chlorine chemistry inherent in these plastics.

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The reactivity of the C-Cl bond distinguishes PVC from other “unactivated” (i.e., relatively inert) commodity plastics (e.g., polyethylene [PE], polypropylene [PP]). While PVC has historically been viewed as a problematic waste for disposal and/or recycling, the C-Cl bond in PVC may also make it the most versatile plastic for upcycling.

Upcycle

Overcome Limits of Conventional Plastic Recycling

When an opponent discards a chlorinated plastic (e.g., PVC, CPVC, PVDC), negate the effect of its waste and get higher value products from depolymerization, carbonization and functionalization.

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