

# Polyvinyl Chloride in the Environment

Subjects: **Polymer Science**

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Plastics have recently become an indispensable part of everyone's daily life due to their versatility, durability, light weight, and low production costs. The increasing production and use of plastics poses great environmental problems due to their incomplete utilization, a very long period of biodegradation, and a negative impact on living organisms. Decomposing plastics lead to the formation of microplastics, which accumulate in the environment and living organisms, becoming part of the food chain. The contamination of soils and water with poly(vinyl chloride) (PVC) seriously threatens ecosystems around the world. Their durability and low weight make microplastic particles easily transported through water or air, ending up in the soil.

poly(vinyl chloride)

PVC

pollution

aquatic environment

## 1. Introduction

Plastics are ubiquitous materials used in a wide range of human activities due to their durability, low cost, and technological versatility <sup>[1]</sup>.

In 2020, about 368 million tons of plastics were produced in the world. Moreover, almost 80% of plastic waste was discharged directly or indirectly into the environment <sup>[2][3][4]</sup>. Such uncontrolled disposal of materials can cause serious environmental damage, especially to the atmosphere, agricultural soils, and groundwater <sup>[5][6]</sup>.

Environmental factors such as wind, sunlight, and rain can cause the degradation of polymers, leading to the formation of small and durable particles: microplastics (MPs) with a size of 1–1000 µm and nanoplastics (NPs) with a size of 1–1000 nm <sup>[7][8]</sup>. It is important to detect MPs in the environment as soon as possible to avoid the biological damage they cause. The amount and type of plastics in the environment are assessed, among other things, using Fourier transform infrared spectroscopy, time-of-flight secondary ion mass spectrometry, thermogravimetric analysis technique, differential scanning calorimetry, scanning electron microscope, atomic force microscopy, water contact angle, and ion chromatography <sup>[6]</sup>.

Poly(vinyl chloride) (PVC) is one of the six commonly used plastics (which accounts for as much as 10% of global plastic production) <sup>[2]</sup>. PVC is a popular plastic due to its low price, durability, and good mechanical, chemical, electrical, and thermal properties. The global production of PVC in 2009 amounted to approximately 34 million tons. At the global level, PVC production in 2015 exceeded 35 million tons, and the annual growth was forecast at approximately 2%. At that time, the European PVC consumption was approximately 7 million tons per year <sup>[9]</sup>. In

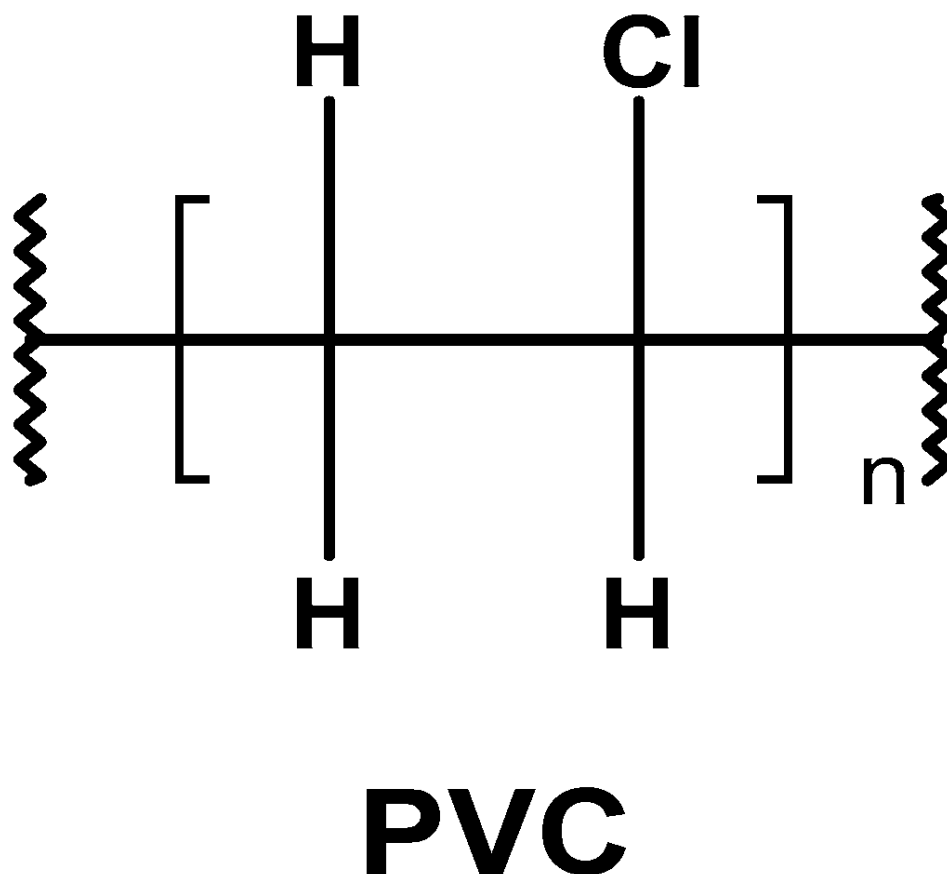
2022, PVC capacity was 59.97 million tons. The market is expected to achieve an annual growth of more than 3% during 2022–2027 [\[10\]](#).

This plastic is strong, durable, long-lasting, lightweight, and versatile, so it is widely used in many industries, such as in construction, automotive industry, pipes and cables, and household goods. The service life of PVC in construction is more than 10 years [\[11\]](#). PVC can present a number of challenges at various stages of its life cycle, particularly at the waste stage. Sound waste management and disposal are essential due to the potential emission of PVC additives (e.g., heavy metal compounds) into the air (in the case of incineration) and into the soil (in the case of landfilling) but also due to illegal dumping and incineration. Various PVC additives also have hazardous properties and, therefore, when emitted, can pose a threat to the environment and human health [\[12\]](#).

PVC is considered as the most environmentally damaging plastic and one of the most toxic substances for inhabitants of our planet. From cradle to grave, the PVC lifecycle (production, use, and disposal) results in the release of toxic, chlorine-based chemicals, and it is one of the world's largest dioxin sources. These toxins build up in water, air, and food chains. They cause severe health problems, including cancer, immune system damage, and hormone disruption. Everyone has measurable levels of chlorinated compounds (toxins) in their bodies [\[13\]](#)[\[14\]](#)[\[15\]](#)[\[16\]](#)[\[17\]](#).

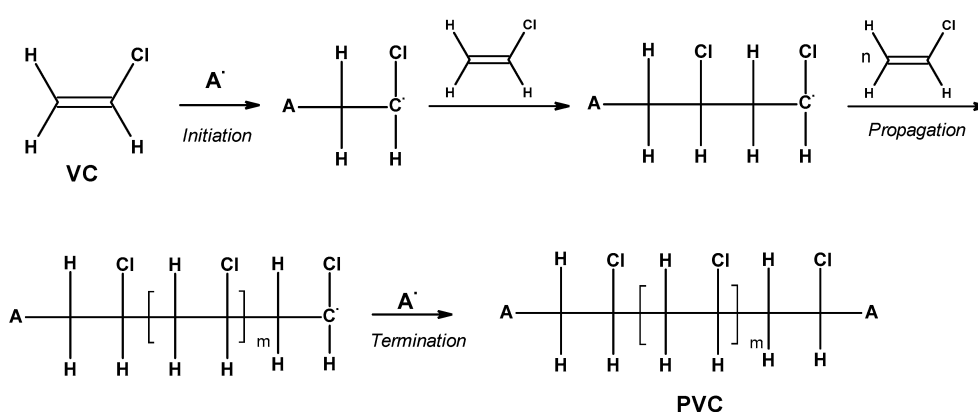
## **2. PVC Characteristics**

According to the IUPAC, the systematic name of PVC is poly(-1-chloroethylene) (**Figure 1**) [\[18\]](#)[\[19\]](#)[\[20\]](#). It presents the linear, in most atactic structure of polymer chains, with the degree of polymerization ranging from 500 to 1500, corresponding to a theoretical molecular weight range of about 31,000–94,000 g/mol (Da). Poly(vinyl chloride) is white in color and a relatively stiff plastic with a high resistance to impact, chemicals, corrosion, water, and weather conditions [\[21\]](#).



**Figure 1.** General structure of poly(vinyl chloride) (PVC).

PVC is synthesized through free-radical polymerization occurring via the head-to-tail tri-stage mechanism, depicted in **Figure 2** [22].



**Figure 2.** The free-radical polymerization of vinyl chloride (VC) ( $m = n + 1$ ).

In industrial practice developed since 1930 [23][24], vinyl chloride (VC) is polymerized in suspension processes (approximately 80% of the market), emulsions (~10–15%), bulk (~10%), and solution (~1%), respectively [20][25].

PVC production uses about 40 percent of the worldwide chlorine production, i.e., ~16 million tons of chlorine per year [26].

PVC has been one of the most widely used plastics for decades. PVC is classified into two broad categories: rigid PVC (unplasticised PVC, uPVC, rPVC, RPVC; used for automobile, health care, electronics, building and construction) and flexible PVC (fPVC; used for cables, wires, fittings, films, profiles, tubes, pipes, sheets, and bottles) [27]. Moreover, chlorinated PVC, molecularly oriented PVC, and modified PVC [28][29][30] are also produced on a smaller scale.

Pure PVC, due to its mechanical properties, requires some additives for the improvement of its processability and application needs. The most common additives used in PCV processing are, in particular, focused on the following chemical products: plasticizers, thermal stabilizers, fillers, impact modifiers, and/or pigments [31].

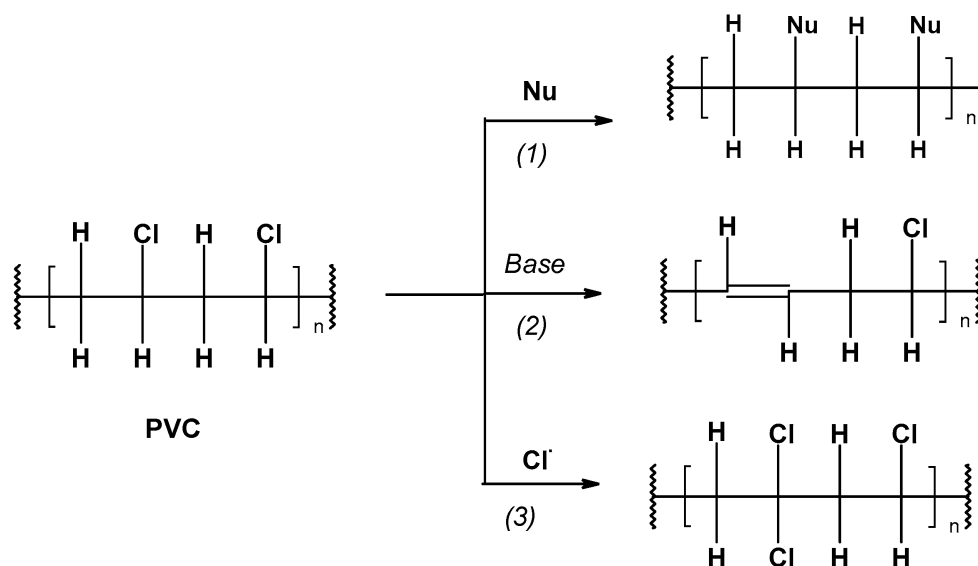
## 2.1. PVC's Physical Properties

PVC is classified as a self-extinguishing material. The limiting oxygen index (LOI) of the rigid PVC is approximately 44–49% [32].

The solubility of PVC is one of the major factors facilitating PVC leaching. Thus, the satisfactory resistance of PVC in an aqueous environment is caused by its insolubility in water [33]. Conversely, PVC is not resistant to the majority of organic solvents due to its substantial solubility, which are mostly: tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMA), and/or pyridine [34].

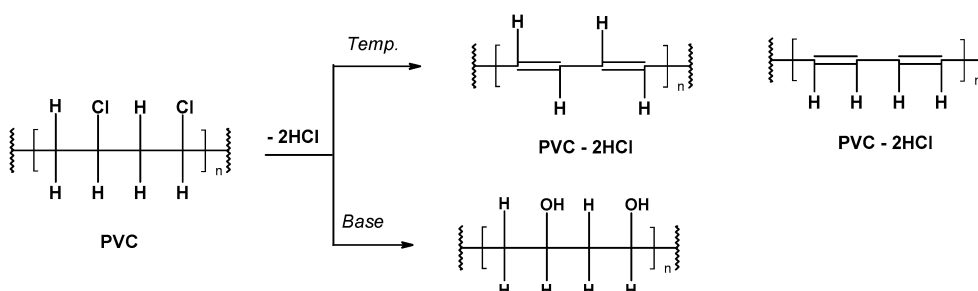
## 2.2. PVC's Chemical Properties

PVC, having a polychloroalkane structure, exhibits typical alkyl chloride reactivity, namely, it undergoes the nucleophilic substitution of chloride atom (1) [35][36], nucleophilic elimination of hydrogen chloride (2) [37], and free-radical chlorination (3) [38], which is illustrated in **Figure 3**. These reactions, due to PVC's insolubility in water [33], seem to occur on the polymer surface, facilitating its leaching.



**Figure 3.** Reaction paths of PVC: the nucleophilic substitution of chloride atom (1), nucleophilic elimination of hydrogen chloride, (2) and free-radical chlorination (3).

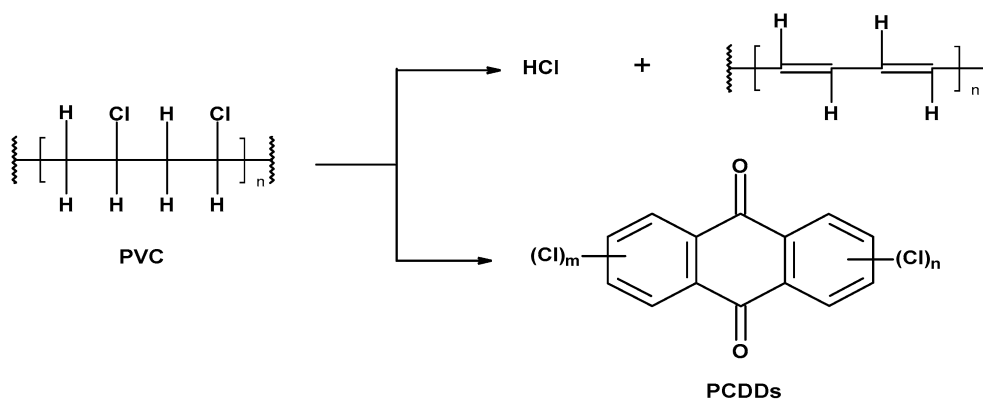
The degradation of polyvinyl chloride (PVC) is mainly caused by the thermal dehydro-chlorination reaction (**Figure 4**), leading to the formation of conjugated double bonds or chlorine substitution (hydrolytic degradation) [39][40][41].



**Figure 4.** The degradation of PVC by dehydrochlorination reactions.

PVC waste is resistant to decomposition in the environment due to its high molecular weight, highly stable covalent bonds, and hydrophobic surface properties, creating a huge environmental problem during its production and disposal [6]. PVC waste is highly resistant to decomposition in the environment but often releases harmful chlorinated compounds that negatively affect the health of organisms and the ecosystem [8]. PVC is classified as a substance with strong mutagenic and carcinogenic properties, and it is more toxic than other plastics due to the presence of chlorine atoms in it [42].

Traditional methods for the storage and incineration of PVC waste lead to the release of harmful chlorinated compounds: hydrogen chloride and chlorine-containing dioxins (**Figure 5**) [43][44].



**Figure 5.** The formation of harmful chlorinated compounds (PCDDs, where  $m$  and  $n$  can range from 0 to 4) by the decomposition of PVC.

Pure PVC can only be used in the temperature range of  $-10$  to  $+60$  °C. The stabilized softened PVC can be used in the temperature range of  $-30$  to  $+100$  °C. The greatest problems are encountered during the processing of PVC because the thermal decomposition of PVC with the release of hydrogen chloride begins visibly at the temperature of  $135$  °C. In addition, the released hydrogen chloride in the presence of oxygen from the air accelerates the polymer decomposition process to such an extent that, at the temperature of  $200$  °C, the PVC decomposes almost completely [45].

In the thermal degradation of vinyl polymers, cleavage outside the main chain or the statistical cleavage of the main chain may occur. Light-induced ageing of PVC occurs as a result of the absorbed light energy, enabling photolysis, oxidation, and cross-linking reactions. PVC-based products used under atmospheric conditions are exposed to the destructive effects of atmospheric factors, such as UV radiation, precipitation, and temperature changes leading to the physical and chemical ageing of the material. Under the influence of UV radiation, free radicals are formed, causing the cleavage of the covalent bonds in PVC's main chain, the splitting of hydrogen chloride, and the formation of new double bonds, causing the material to turn yellow. The next stage of the degradation is the photo-oxidation process leading to the whitening of the material and cross-linking due to the formation of oxygen bridges. The most characteristic changes caused by the degradation are the appearance of newly formed C=C double bonds, C=O carbonyl groups, and hydroxyl groups –OH in the chain, as well as the release of hydrogen chloride and carbon dioxide. The yellowing of the material is caused by a high temperature and low humidity. The PVC degradation process is a complex phenomenon resulting primarily from the dechlorination process, the course of which depends on the stabilizers used. PVC is the largest contributor to environmental pollution with dioxins on a global scale [45].

There are two types of the degradation of PVC [45]:

- Preliminary (occurring under the influence of temperature, called thermal) under anaerobic conditions at the molecular or ionic level,
- Secondary as a result of the increased temperature and oxygen action (thermo-oxidative degradation).

Because of the many concerns raised about PVC usage since the 1970s, PVC has become one of the most researched plastic materials from an environmental point of view. Despite all the technical and economic problems and the public discussions on the environmental dangers and hazards of chlorine chemistry, poly(vinyl chloride) (PVC) is the second most produced plastic (with a worldwide capacity of about 60 million tons in 2022 [\[10\]](#)), being behind polyolefins and before styrene polymers [\[10\]](#). But PVC also takes an important part in many environmental discussions on polymers, e.g., chlorine chemistry, toxicity of vinyl chloride, or waste and recycling problems. For a time frame of 70 years, some recent developments in the controlled polymerization of vinyl chloride, stabilization, modification of bulk properties, and chemical and material recycling of PVC are discussed.

### 2.3. Biological Activity of Poly(vinyl chloride)

Plastic products contain hundreds of potentially toxic chemical additives, which currently drive toxicity [\[46\]\[47\]](#). Micro- and nano-plastics may pose dangers of acute toxicity, (sub)chronic toxicity, carcinogenicity, genotoxicity, and developmental toxicity [\[48\]](#). This results from the polymer matrix, additives, degradation products, and adsorbed contaminants.

In contrast to its carcinogenic monomer [\[49\]\[50\]\[51\]\[52\]](#), PVC is biologically inert due to its low chemical reactivity [\[47\]](#). For instance, it is not digestible, even at the surface, for common strains (*Lactobacillus acidophilus*; *L. plantarum*, and *L. rhamnosus*) representing functional bacterial groups in the human gut microbiota. However, cytotoxicity investigations of PVC using the human cell lines Caco-2, HepG2, and HepaRG (a possible impact on intestine and liver) [\[53\]\[54\]\[55\]](#) and pulmonary cell cultures revealed the induction of cytotoxic effects [\[6\]](#). Occupational exposures at a poly(vinyl chloride) production facility are associated with significant changes to the plasma metabolome [\[56\]](#). PVC micro- and nano-particles can induce carcinogenesis to humans [\[57\]](#).

It has been reported that PVC particles produce moderate in vitro toxicity for human pulmonary cells [\[58\]\[59\]](#) and cardiometabolic toxicity [\[60\]](#). PVC induces changes in the microenvironment and secondary structure of human serum albumin (HAS) (decrease in  $\alpha$ -helix) [\[61\]](#) and bovine serum albumin (BSA) [\[62\]](#), and it causes liver injury and gut microbiota dysbiosis [\[63\]\[64\]](#). PVC dust exerts a hemolytic effect on lung fibroblast cultures [\[65\]](#), and it causes liver angiosarcoma and lung cancer [\[49\]](#).

The toxicity of water after contact with PVC materials was found to be dependent on the type of PVC composition components and temperature [\[66\]\[67\]\[68\]\[69\]](#). The aquatic toxicity of PVC microplastics towards marine organisms (microalgae, crustaceans, and echinoderms) is due to the leaching of chemical additives and not the ingestion of microplastics (MPs) [\[70\]\[71\]](#). During the ageing process of MPs, additives are released that may cause severe genotoxicity [\[72\]](#).

PVC microplastics reduce sediment catalase, polyphenol oxidase (PO), and urease activities and decrease physicochemical indicators, including total organic carbon (TOC), total nitrogen (TN), and pH value [\[73\]](#).

Studies on a combustion gas of thermoplastic poly(vinyl chloride) showed its cytotoxicity to human fetal lung tissue cell (MRC-5), African green monkey kidney cell (Vero), and Chinese hamster ovary cell (CHO), with molecular

chlorine as the major toxicant [74].

PVC composites for linoleum are equipped with antibacterial agents (e.g., 1,3-dioxanes, wollastonite, or quaternary ammonium biocides); therefore, they exhibit functions of biostatics, inhibiting the growth of microorganisms and bactericides, killing the microorganisms [75][76].

### 3. Disposal Methods of Poly(vinyl chloride) from the Environment

In the face of the increasing levels of environmental pollution from waste plastics, the development of highly efficient and environmentally friendly methods for their degradation is urgently needed. In 2000, the European Commission published a Green Paper for PVC waste [77], which assessed various environmental and health aspects and the possibility of reducing its impact on the environment. It paid particular attention to measures leading to solutions to PVC waste management problems. For example, in the Vinyl2010 Voluntary Commitment, it was suggested to reduce organochlorine emissions through the sustainable use of additives and various controlled-cycle management strategies. Its successor, VinylPlus, set an annual recycling target of 900,000 tons by 2025 and at least 1,000,000 tons by 2030 [11][78].

It seems promising to carry out complete dechlorination processes before degradation. Owing to full dechlorination, PVC can be treated in the same way as common halogen-free plastics [79]. Such methods include chemical modifications, the near-critical methanol process for PVC dechlorination and recovery of additives, and the near-critical process using an aqueous ammonia solution. Among these techniques, the well-known method is the chemical modification of PVC through the substitution of some chlorine atoms with various nucleophilic reagents. Another technique used to convert waste into energy with simple, fast reactions is hydrothermal treatment. In this technique, super- or sub-critical water is used as a solvent and reagent for the reaction of organic compounds [80].

Moreover, despite the frequent use of certain chemicals in the hydrothermal dechlorination of PVC waste, their role in this process has not been fully understood. Analyses conducted by Zhao et al. with the use of  $\text{Na}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{NH}_3\cdot\text{H}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{NaHCO}_3$  in water containing  $\text{Ni}^{2+}$  showed that the alkalinity of the additives has a significant impact on the effectiveness of the dechlorination process. The most effective additive in these studies was  $\text{Na}_2\text{CO}_3$  (concentration 0.025 M), with a maximum efficiency of 65.12% [81]. The processes carried out using subcritical water- $\text{NaOH}$  (CW- $\text{NaOH}$ ) and subcritical water- $\text{C}_2\text{H}_5\text{OH}$  (CW-  $\text{C}_2\text{H}_5\text{OH}$ ) proved that the main mechanism in the case of the dechlorination in CW- $\text{NaOH}$  is the nucleophilic substitution of hydroxyl group in PVC, while in CW- $\text{C}_2\text{H}_5\text{OH}$ —the nucleophilic substitution and direct dehydrochlorination were the equally significant processes [82]. The key parameter of the dechlorination process is temperature. As the efficiency of this process also decreases with a decrease in temperature, the above-mentioned additives were used to improve the efficiency. Unfortunately, the incorporation of the additives not only increased the costs of the dechlorination process, but also generated secondary pollution [83]. Temperature was also shown to be important in the removal of chlorine (Cl) from PVC in gas–liquid fluidized bed reactor studies where hot  $\text{N}_2$  was used as the fluidizing gas to fluidize the polymer melt [84].



Although poly(vinyl chloride) is a commercially important polymer, it is also one of the most sensitive to UV radiation. A study by Yang et al. showed that the rate of the photoaging of plastics is faster than other ageing processes; therefore, it is one of the most common methods of PVC degradation [85]. The UVA radiation in deionized water, sea sand, and air was used to photodegrade plastics. The results showed that PVC effectively absorbs the UVA radiation in air, and this is where the ageing efficiency was the greatest. The ageing process included photoinitiation, chemical bond breaking, and oxygen oxidation [72][85].

Under the influence of UV radiation (in the wavelength range of 253–310 nm) and in the presence of oxygen and moisture, PVC underwent very rapid processes of dehydro-chlorination and peroxidation to form polyenes. The irradiated material crumbled, lost its stretch, elasticity, and impact resistance, and the surface of the degraded polymer was significantly modified, i.e., loss of abrasion resistance, gloss, and interfacial free energy were observed [86][87].

The use of the photodegradation process makes it easier to dispose plastics from the environment. In order to accelerate the photodegradation of plastics, semiconductor photocatalysts such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CdS}$ , and  $\text{ZnS}$  were also used. For example, it was observed that the addition of  $\text{ZnO}$  to PVC increased the decomposition of the composite by 4.13% in the case of artificial UV radiation and by 9.7% in the case of solar radiation, respectively [88]. A photodegradable composite film was prepared by doping poly(vinyl chloride) plastic with nano-graphite (Nano-G) and a  $\text{TiO}_2$  photocatalyst. After exposure to the UV radiation (for 30 h), the weight loss rates of Nano-G/PVC,  $\text{TiO}_2$ /PVC, and Nano-G/ $\text{TiO}_2$ /PVC films were 7.68%, 8.94%, and 17.24%, respectively, while pure PVC decreased its weight by only 2.12% [89].

PVC is less biodegradable than other plastics [90][91]. Therefore, there have been many studies on the thermal decomposition and photodegradation of PVC, but there are a few reports in the literature on the biodegradation of poly(vinyl chloride) compared to other polymers [92], and microorganisms capable of decomposing it, both in the aquatic environment [93] and in the soil, are sought [94].

### 3.1. Recycling and Utilization of PVC

PVC can be recycled using various material and energy recovery methods [95].

Recycling techniques include:

mechanical methods—consisting in extruding and mixing the material with primary polymers,

chemical methods—changing the polymer structure of the material using chemical and thermal agents [96].

The mechanical recycling is the most-recommended way to recycle PVC [41]. The conventional mechanical recycling processes are based on the separation, shredding, and application of shredded material with an unchanged chemical composition to a processing equipment. In this technique, plastics are collected and sorted by hand and/or machines at recycling plants and then flaked in a high-speed mill and cleaned with a detergent and

water. Finally, the dry flakes are melted and cast into pellets from which new products can be made [97]. The limitation of the mechanical or secondary recycling is that it cannot be used in the case of the unmodified PVC waste of a known composition and origin [95].

For economic and environmental reasons, the feedstock recycling of PVC is used, including waste that cannot be mechanically recycled. This relatively simple method of PVC recycling allows for energy recovery, which consists of the gasification of fuels or direct combustion in specialized thermal utilization plants. In the case of energy recovery, a fraction of PVC is mixed with other types of waste. The thermal process consists of two steps: dechlorination and the use of the remaining hydrocarbons. Through the thermal recycling of PVC waste, hydrogen chloride is recovered, and other recovered chemicals can find various applications, especially in the chlorine industry [41]. Poly(vinyl chloride) (PVC) waste with a high chlorine content is the source of chlorine, providing hazardous chlorinated organic pollutants, which can be reused as chemicals, fuels, and feedstock [98].

Some new mechanical recycling technologies are based on selective dissolution for the recycling of PVC in an economically feasible way. However, currently, only a small amount of PVC post-consumer waste is being recycled. Incineration, in conjunction with municipal waste disposal, is a simple option that allows for the partial recovery of energy and chemical substances when state-of-the-art technology is applied [99].

One of the common chemical recycling techniques is pyrolysis, divided into hydrocracking, thermal cracking, and catalytic cracking [21]. Although pyrolysis is an effective method for converting PVC waste into energy, it yields products containing significant amounts of chlorine [100][101]. The release of harmful substances such as polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) also occurs in processes such as incineration [96]. During the thermal degradation of PVC, HCl is eliminated, leading to the formation of conjugated double bonds, and it, in turn, attacks other compounds with double bonds, leading to the production of organochlorine compounds [102]. Even if PVC is landfilled instead of incinerated, during the process, it may release, among others, phthalates and heavy metals such as lead, cadmium, and tin [79]. Therefore, these processes, including storage, pose a significant risk of releasing chlorinated organic compounds, microplastics, and pollutants into soils and waters [103]. Due to the low efficiency of the recycling and the tendency to cause secondary pollution, the traditional methods of disposal of the plastic waste—incineration and landfilling—have been banned [96]. Therefore, it has become important to develop techniques to reduce Cl migration.

### 3.2. Biodegradation of PVC Waste

The biodegradation of plastics found in the soil is a complex process. The efficiency of this process is influenced by the availability of substrates assimilable by microbial consortia, molecular weight, surface and morphological characteristics, as well as the structure of the polymers [104]. The biodegradation includes the formation of microbial biofilms on plastic surfaces, followed by the enzymatic degradation of the polymer structure, which leads to the release of oligomers and monomers [8]. The biochemical transformation of resistant polymers by microorganisms usually involves the transformation of complex compounds into simpler forms, leading to a reduction in the molecular weight, as well as the loss of the mechanical strength and surface properties of plastics. The

biochemical degradation processes of PVC consists of five stages: colonization, biodeterioration, biofragmentation, assimilation, and mineralization. The first stage of the biodegradation mechanism is the colonization of the microorganisms on the plastic surface. It involves the adhesion of living microorganisms (bacteria and fungi) to the surface of plastics and their use for microbial growth and reproduction. During colonization, the microorganisms form biofilms, which causes damage to the polymer surface [105]. The physical and chemical actions of the microorganisms lead to the biodeterioration and superficial degradation of many kinds of polymers, including PVC. They causes changes in their physical, mechanical, and chemical properties [106].

The prolonged exposure to light, high temperatures, and chemicals in the atmosphere facilitates the biodeterioration process. The microorganisms penetrate the polymers and increase pores and cracks. On the other hand, some microbial species with chemolithotrophic potential promote oxidation and reduction reactions, and chemical biodeterioration [105]. Biofragmentation is a lytic process that allows for the breakdown of polymers into monomers, dimers, or oligomers. The process involves a decrease in the molecular weight of polymers and the oxidation of the lower-weight molecules using specific enzymes (oxidoreductases and hydrolases), as well as free radicals [107]. An enzymatic depolymerization of plastics released monomers that were transported into cells, where they underwent a series of enzymatic reactions leading to complete degradation and the formation of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> [108]. The mineralization stage can be aerobic or anaerobic, and it was catalyzed by several enzymes: cutinase, laccase, esterase, peroxidase and lipase in a study [105]. PVC-MPs significantly inhibited the chemical oxygen demand (COD) removal efficiency of anaerobic granular sludge (AGS) by 13.2–35.5%, accompanied by 11.0–32.3% decreased formation of methane and 40.3–272.7% increased accumulation of short-chain fatty acids [109].

Examples of the biodegradation of PVC with different kinds of microorganisms [93][110], bacteria (*Pseudomonas*, *Mycobacterium*, *Bacillus*, and *Acinetobacter*), and fungi (*Basidiomycotina*, *Deuteromycota*, *Ascomycota*) were reported recently. Surface damage and a molecular-weight decrease were observed [111][112][113][114]. Also, an extracellular lignin peroxidase of the fungus *Phanerochaete chrysosporium* showed PVC-degrading activity [115]. Alternatively, the biodegradation of PVC occurred with bacteria isolated from the larva's gut microbiota (*Spodoptera frugiperda*). Enzymatic assays (e.g., catalase-peroxidase, dehalogenases, enolase, aldehyde dehydrogenase, and oxygenase) caused the depolymerization of PVC [116].

Enzyme specificity and temperature are of great importance in the degradation of plastics. Moreover, the use of several microbial consortia and several enzyme complexes allows for an increase in the biodegradation efficiency compared to a single enzyme or single microorganisms [8]. It is known, however, that the biodegradation of PVC involves three main reactions, including the chain depolymerization, oxidation processes, and the mineralization of the resulting intermediates [117]. An effective approach to the bioremediation of the environment from plastics is their initial thermal treatment. After the thermo-oxidative modifications of PVC, it was noticed that *Achromobacter denitrificans* bacteria isolated from compost were able to eliminate 12.3% of the plastic, which was evidenced by its weight reduction [118].

Of all higher organisms, only some insects are capable of degrading various plastics and converting them into monomeric compounds. In particular, insects in their larval stages have shown the ability to degrade plastics [119]. Insects that metabolize plastic include yellow mealworms (*Tenebrio molitor*), giant mealworms (*Zophobas atratus*), and superworms (*Z. atratus*). It is thought that this unique “plastic-eating” phenomenon may be related to the ability of some of these insects to degrade lignin [120]. The insects have also been shown to ingest polymers, with the actual ingestion being led by the microorganisms inhabiting their guts [105][120][121][122].

Some bacteria, e.g., *Pseudomonas citronellolis*, were capable of degrading PVC films. A 45-day incubation resulted in a fragmentation of the material and a decrease in its average molecular weight by 10%. The maximum weight loss during the further stages of the experiment was 19% [123]. Almost 12% weight loss of PVC was also observed in an experiment conducted in anaerobic microcosms using enriched anaerobic consortia from marine samples (waste and water). In addition, this material showed lower thermal stability after 7 months of incubation [93].

Changes in the mechanical properties of the material were also observed in the analyses carried out using isolates of marine bacteria of the genus *Vibrio*, *Altermonas* and *Cobetia*. The most effective microorganisms in the elimination of PVC turned out to be the *Altermonas* BP-4.3 strain, in which case, after 60 days of incubation, a 1.76% loss in the weight of the poly(vinyl chloride) film was observed [124]. *Micrococcus luteus* from areas heavily polluted with plastics was able to mineralize 8.87% of PVC. This level was achieved in cultures maintained for 70 days with mineral substrate [125].

The importance of microorganisms in processes such as the depolymerization of PVC was also demonstrated using the example of microorganisms living in the intestines of *Tenebrio molitor* larvae. For biodegradation tests, rigid PVC microplastic powders (MPs) were used (70–150 µm), with weight-, number-, and size-average molecular weights ( $M_w$ ,  $M_n$ , and  $M_z$ ) of 143,800, 82,200, and 244,900 g/mol, respectively, as the sole diet at 25 °C. The ingested PVC was broadly depolymerized, and the  $M_w$ ,  $M_n$ , and  $M_z$  values decreased by 33.4%, 32.8%, and 36.4%, respectively. After 5 weeks of experiments involving the incorporation of poly(vinyl chloride) into the larvae diet, their survival rate with PVC as the only component of the diet was maintained at the level of up to 80% [110]. The ability of *T. molitor* to eliminate PVC was also confirmed by Božek et al. after 21 days of the exposure of mealworm to poly(vinyl chloride) in the diet; a 3% loss in the mass of the material was observed [121]. Two bacterial strains isolated from oil-contaminated soil (*Pseudomonas aeruginosa* and *Achromobacter* sp.) showed the ability to degrade PVC containing epoxidized vegetable oil (75% by weight), resulting in a change in the material's surface topography and a decrease in its tensile strength during an incubation period of 180 days [113]. Some microorganisms are capable of degrading PVC. However, the PVC materials used in these study were largely plastics containing plasticizers. It was found that some bacterial strains acted mainly on the PVC additives, and there was a low ability to degrade PVC without the additives [123].

Apart from bacteria, microscopic filamentous fungi were also tested as organisms potentially capable of degrading PVC. Analyses carried out using *Chaetomium globosum* (ATCC 16021) have shown, for example, that this fungus was able to adhere to the surface of PVC, which was the first stage of the degradation process [111]. An exposure

of PVC fragments containing plasticizers (dioctyl phthalate and dioctyl adipate) to the atmosphere for a period of 2 years showed that between the 25th and 40th weeks, the surface of the plastic was dominated by *Aureobasidium pullulans*. After 80 weeks, the next microorganisms identified were, e.g., *Rhodotorula aurantiaca* and *Kluyveromyces* spp. All tested strains of *A. pullulans* grew in the presence of PVC, using it as a carbon source, degrading plasticizers, and producing an extracellular esterase and reducing the substrate weight during growth [126].

Biodegradation potential, through adhesion to poly(vinyl chloride) by *Lentinus tigrinus* PV2, *Aspergillus niger* PV3, and *Aspergillus sydowii* PV4, was also confirmed (Ali, 2014) [127]. For fungi of the genus *Aspergillus* (*A. Niger* Sf1 and *A. glaucus* Sf2), it was observed, among others, that there was 10% and 32% weight loss of PVC over 4 weeks of the experiment, respectively, while for *Bacillus licheniformis* Sb1 and *Achromobacter xylosoxidans* Sb2, with the same observation time, the values were 15% and 17%, respectively [128]. *Phanerochaete chrysosporium* PV1 strain showed the potential for PVC film degradation, for which Fourier transform infrared spectroscopy and nuclear magnetic resonance analysis showed significant structural changes in the material. This was confirmed by peaks corresponding to alkenes appearing, decreases in peak intensity appearing in the case of C–H stretching, and a decrease in the weight of the analyzed PVC itself [127]. The decrease in the PVC weight was also demonstrated during the experiment conducted for 12 weeks with strains isolated from the soil. The loss of 0.064 g/m<sup>2</sup> for *Mucor hiemalis*, 0.300 g/m<sup>2</sup> for *Aspergillus versicolor*, 0.341 g/m<sup>2</sup> for *Aspergillus niger*, 0.619 g/m<sup>2</sup> for *Aspergillus flavus*, 0.082 g/m<sup>2</sup> for *Penicillium* sp., 0.240 g/m<sup>2</sup> for *Chaetomium globosum*, 0.330 g/m<sup>2</sup> for *Fusarium oxysporum*, 0.240 g/m<sup>2</sup> for *Fusarium solani*, 0.364 g/m<sup>2</sup> for *Phoma* sp., and 0.145 g/m<sup>2</sup> for *Chrysionilia sitophila* was observed, respectively. The ability of *Mucor* sp. fungi to grow in the presence of poly(vinyl chloride) as the only source of carbon and energy was also demonstrated [129].

With regard to the fact that additives added to polymers may increase their physical and chemical degradation, it has also been shown that the addition of a small amount of cellulose to PVC may cause changes in its properties and facilitate its microbiological degradation [90][130][131].

Under aerobic conditions, vinyl chloride (VC) served as the sole source of carbon and energy for *Pseudomonas putida* strain AJ and *Ochrobactrum* strain TD, which were isolated from hazardous waste sites. Analyses conducted on the biodegradation of vinyl chloride, used as a monomer for PVC production, showed that alkene monooxygenase is responsible for its metabolism in AJ strains of *Pseudomonas putida* and AD *Ochrobactrum bacteria* [132]. The degradation of acetate-modified PVC (PVA) involved, among others, enzymes such as oxidases [133]. The activity of PVA oxidase was correlated with PVA dehydrogenase. The  $\beta$ -diketone group was introduced into the PVA polymer molecule through the product of the reaction carried out by the dehydrogenase. This product, through an active site of serine hydrolase, initiated the oxidation reaction by PVA oxidase. This was followed by hydrolysis to form the monomer [134]. While there is a lot of data on the enzymes involved in the degradation of modified poly(vinyl chloride), scientific reports on the mechanisms and enzymes involved in the degradation of PVC are virtually nonexistent [133]. This is due to the high chemical stability and hydrophobicity of the C-C skeleton of PVC [135]. Among the few data available, there is a mention that, in the case of genus *Cochliobolus*, in the degradation of low molecular weight PVC, laccase is involved [136].

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