

Review article

Recycling of PVC wastes

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ABSTRACT

PVC is a universal polymer which can be processed into a wide variety of short-life or long-life products. As a result of increasing consumption of PVC-made products in recent years, the quantity of used PVC items entering the waste stream is gradually increased. Currently, there is a considerable public concern about the problem of plastic wastes, from which PVC has not escaped and the material or energy recycling may be a suitable way to overcome this problem. This review considers the various aspects of the PVC recycling such as recycling methods of PVC, special problems about some proposed processes, separation techniques, and recycling of mixed PVC wastes. In addition, an attempt is made to portray the current status of PVC recycling, the most recent technologies of recycling, and some recent scientific research in the field.

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1. Introduction

Polyvinyl chloride (PVC) is one of the most commonly used thermoplastic materials in respect to the worldwide polymer consumption. At global level, demand for PVC exceeds 35 million tonnes per year, and it is rated second only after polyethylene as volume leader in the plastics industry [1–12]. Because of the particular properties inherent in the PVC i.e., its low cost and high performance, combined with the wide range of products that can be obtained from different processing conditions and techniques, PVC has become a universal polymer [1–4]. Currently, PVC can be processed into a wide variety of short-life products, such as PVC packaging materials used in food, cleansing materials, textile, beverage packaging bottles, and medical devices, and also long-life products such as pipes, window frames, cable insulation, floors coverings, roofing sheets, etc [1,3–6,13,14].

In recent years, the question of the disposal of PVC waste has gained increasing importance in the public discussion, resulting from the rapid growth of the PVC wastes [1,9,12–15]. Moreover, although the long-life PVC products show a long service life and there is a long time-lag between PVC consumption and the amassing of PVC waste, they will finally become waste at a certain point in time [2,8,16,17]. As a result, the quantity of used PVC items entering the waste stream is gradually increased as progressively greater numbers of such PVC products approach to the end of their useful economic lives [1,9,10]. One simple route for disposing of PVC

wastes, i.e., landfilling become more expensive and in many countries this method of disposal is no longer acceptable due to the increasing consumption, decrease in available landfilling areas, and potential environmental hazards associated with the chlorine content of the polymer [1,3,18,19]. A more suitable route, which can recover the energy and/or material content of these materials, without any special environmental problems, is recycling. Recycling of the PVC and its acknowledgment has increased during recent years and now is a subject of increasing interest for several papers [7,12–14,20,21]. The terms “recycling”, “reclaiming” or “recovery” are generally taken to mean a series of processing operations carried out on plastics to produce “secondary materials or energy” [3,21–23]. Up to now, several scientists and industrialists have been funded in this field and discussed a number of examples to assess its feasibility. They suggested that PVC can be successfully recycled into a variety of products such as bottles, various pipes, pipe fittings and other profiles with good appearance and properties [3,7,17,22, 24–26]. They also claimed that the profiles properties were unaffected when virgin PVC was replaced by PVC recyclates.

Despite all advantages of the recycling, unfortunately only a very small part of PVC waste is now recycled in the world [8,12,21,27–30]. Currently, in many developing countries the current norm is to send the plastic wastes to the landfill as, for example, approximately total plastic wastes produced across Iran is dumped into the landfills and only less than 1% of total plastic wastes are recycled [12,27–30]. In the few past years, European countries and United States were faced with a similar quandary, so that a major portion of plastic waste is either landfilled or incinerated with other municipal solid waste [19,23,29]. However, recycling rates of PVC have increased steadily in the United States and European countries since the mid-1980s, as

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many new recycling programs were developed [23,31]. For example, Vinyl 2010 as a voluntary commitment was set up in Europe at 2000 to minimize the environmental impact of the PVC production, promote responsible use of additives, reduce waste, and boost collection and recycling [31]. Vinyl 2010 reported that 194,950 tonnes of PVC were recycled in 2008, a 30% increase on 2007 levels when 149,500 tonnes were recycled [31]. The amount of PVC waste which was recycled in 2008 was 2.5% of PVC consumption in Europe. It is expected that the amount of recycled PVC will nearly be 200,000 tonnes in 2010. Fig. 1 shows the tonnage of recycled PVC in Europe from 2003 till 2008 and clearly indicates the rapid increase in rate of recycling in recent decade [31]. Among the European countries, Germany is internationally regarded as the most advanced country for PVC recycling, which has the highest number of recyclers in Europe [16,17,23,31–33]. Taking the roofing materials as a representative case, the tonnage of PVC recycled in Europe can be compared in Fig. 2 by country in 2008 [31]. According to the figure, Germany has a top position in the recycling of such materials.

Simple recycling to produce secondary materials cannot by itself solve the environmental problems of plastic wastes, because of many types of plastics cannot simply be separated or processed together [3,13,29,34,35]. In fact, articles produced with the mixed recycled material would have poor mechanical properties and few possibilities of application [3,13]. Moreover, the existence of markets for recycled PVC is a key part and it does no good whatsoever to separate and process PVC waste if they do not find uses in new applications [34,36]. Currently, the recycling operation of plastics, of PVC in particular, is increasing especially in the following aspects [1,14,18,21,26,29,35–38]:

1. Development of techniques and instrumentation for separation of PVC from waste stream;
2. Improvement of current methods and/or development of new methods for recycling of PVC waste;
3. Improvement of Compatibility of recycled PVC with other polymers and virgin PVC;
4. Recycling of mixed PVC waste;
5. Development of new energy-recovery techniques;
6. Recycling of post-consumer PVC waste through specific projects;
7. Improvement of physical and mechanical properties of recycled PVC;
8. Survey on the effect of multiple recycling.

PVC is now one of the largest recycled polymers by volume in developed countries, because it is suitable for practically all recycling methods and as such it is given significant attention in the research and technology which this review reflects. PVC recycling by the following technological processes is discussed in the review:

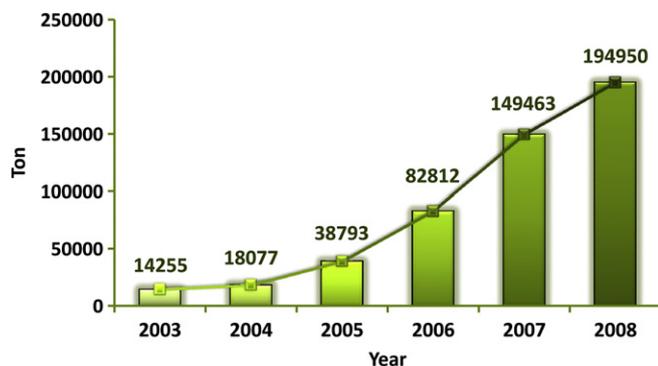


Fig. 1. The tonnage of recycled PVC in Europe from 2003 till 2008.

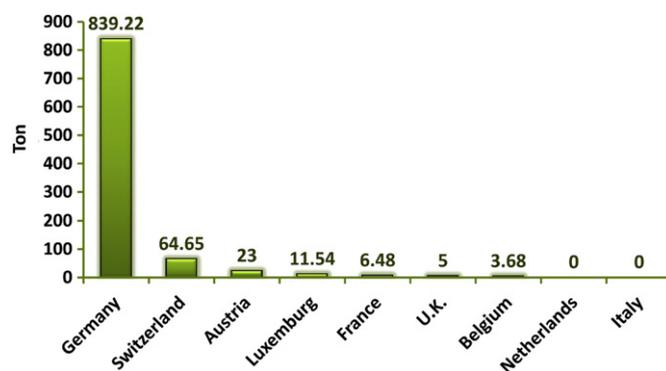


Fig. 2. The tonnage of roofing materials recycled in Europe by country in 2008.

- Energy-recovery techniques
- Mechanical recycling
- Chemical recycling

This review attempts to portray the current status of PVC recycling, the most recent technologies of recycling, and some recently published scientific research in the field. In addition, attention will be given to some other attempts for recycling which have not been thoroughly evaluated so far.

2. Methods of PVC recycling

Various material- and energy-recovery methods have been described in detail in the literatures [18,21,23,26,36,39]. However, all these recycling techniques are accompanied by degradation of PVC wastes (frequently dehydrochlorination, formation of lower molecular weight fractions, crosslinking, and/or formation of oxygenated groups), with the degree of degradation depending on the technique chosen [8,18,40,41]. In fact, due to the high chlorine content of the PVC, some of the techniques for PVC recycling are not favorable [3,34]. In particular, landfilling and composting are not suitable because of the unknown hazards associated with the oxidative degradation of PVC in the environment [1,3,18]. Incineration and pyrolysis may also be disfavoured because of the large amounts of hydrogen chloride and other toxic products that are produced [3,23,39,42]. Of the two acceptable recycling techniques, mechanical recycling and chemical recycling, the former is preferred when the provenance of PVC waste is known [2,3,8,15]. In other words, the mechanical method for recycling of PVC will be preferred if clean PVC with known composition and previous history can be available. Mechanical recycling is already practiced over many years for the post-consumer PVC wastes [2,7,9,18]. Another recycling method, chemical recycling, is based on the idea of converting plastic back into the chemicals for reuse in polymerization or other chemical processes [8,9,21,26,36,38]. Currently different process technologies are considered for chemical recycling and some of them are working in commercial-scale [3,9,10,15,21,26,36]. Table 1 shows, in brief, a comparison among the main methods of PVC waste disposing along with their strong and weak points.

2.1. Energy-recovery techniques

An approach which can be used to dispose the PVC wastes, particularly when they contain a large amount of impurities and/or combustible solids (if such is a case, it is important to keep them away from landfills), is called energy-recycling technique which consists of the energy recovery from the wastes by incineration

Table 1
The comparison of different approaches for disposing of PVC wastes.

Method of Disposing	Sensitivity to impurities	Degree of pollution generation	Costs	recycled product(s)	Properties of the recycled material	Number of plants in operation around the world	Accepting by countries (during the recent decade, especially for developed countries)
Landfilling	Non-sensitive	Very high	Low-cost	No material recycled	—	Large	Non-acceptable
Incineration	Usually non-sensitive	Very high	Usually low-cost	Energy	Usually energetically not efficient	Large	Non-acceptable
Mechanical recycling	Highly sensitive	Low	Middle-cost	PVC	It is dependent on feed material and processing variables of recycling	Fair	Highly acceptable
Chemical recycling	Relatively sensitive	Usually low	Usually high-cost	Diverse raw materials	It is dependent on feed material and processing variables of recycling	Small	Low acceptable

[3,9,12,15,21,23]. Incineration of commodity plastics increased in the last half of the 1980s, then leveled off due to the growing public resistance and finally received again special attention due to the problem of the lack of landfilling areas and also shortage of energy sources [3,18,23]. However, environmental argumentations, such as toxic emissions from inadequate equipment or inappropriate incineration conditions, are currently building up again a public resistance against this technique [1,9,29,43,44]. In fact, with incineration there is always the problem of the formation of toxic compounds and pollutants in both air emissions and solid waste residues which can be released into the environment [1,9,13,43]. In particular, PVC incineration is connected with additional problems arising from high chlorine content of this polymer which yields large amounts of hydrochloric acid (HCl) during thermal decomposition, beside the possibility of formation of persistent and toxic compounds such as toxic dioxines and furans [3,9,13,29,43,44]. HCl is believed to be linked to the formation of acid rain [15]. In addition, when PVC wastes are fired in an incinerator, HCl corrodes the boiler tubes of the incinerator and other equipments [8,33,34,39]. Therefore the steam pressure must be kept relatively low to prevent corrosion of the heat recovery boiler [33,39]. One solution to this problem may be neutralization of HCl with calcium carbonate (lime) and/or sodium hydroxide (caustic soda) to convert the released HCl to the salts [33]. However, these salts are usually contaminated and must be disposed of in special landfills, at considerable cost [33]. On the other hand, special filters can also be used to prevent problems related to atmospheric emissions during the combustion process [45]. Although the harmful effects of incineration can be alleviated by such techniques, but the most modern technologies do not prevent persistent toxic compounds from forming [3,9,13,33]. Therefore, plans to expand capacities of such installations meet with growing difficulties. Moreover, current incineration techniques need to be improved with regard to reduction of the level of pollutions. In addition, to direct firing and liquefaction, a new chemical procedure for energy recovery needs to be developed, because valuable chemicals can be produced.

Beside all above problems, net energy recovered by incineration of PVC-rich waste is not high enough to make it highly economic. As most hydrocarbon polymers, the calorific value from incineration of PVC in an ideal conditions is about 64 MJ/kg, compared to, for example, 17 MJ/kg for paper, or 16 MJ/kg for wood [15]. However, current plants of incineration for energy recovery are not fully efficient and cannot recoup the total calorific value of the waste [12,21,33]. Moreover, PVC is inherently difficult to combust, so that complete combustion of PVC-rich waste occurs at such high temperatures (>1700 K), that it is economically prohibitive [21]. Currently, mechanical and/or chemical recycling of PVC plastic wastes seems the logical solution, and therefore we will focus on this subject in the sequel of the review.

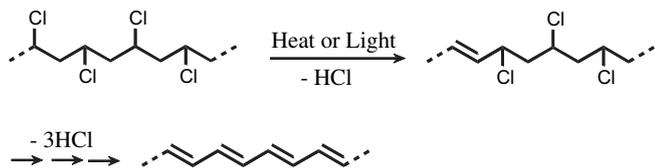
2.2. Mechanical recycling of PVC

The “material recycling” or so called “mechanical recycling” is a technically relatively simple and usual recycling method in plastics industries [1,2,5,9]. Mechanical recycling is a preferable method whenever sufficient quantities of homogenous and source-separated waste stream can be made available [46–48]. Conventional mechanical recycling processes entail separation, grinding and feeding of ground product into the conversion equipment, without any changes in the chemical composition of the material [3,15,33,46]. In this approach, the plastics are collected and sorted by hand and/or by machines at reprocessing plants [3,23,49]. The sorted plastic wastes are chopped up into the flakes in a high-speed grinder followed by cleaning with a detergent and water spray. The dry flakes are melted down and cast into pellets which can be used to make new plastic products [3,23].

The feedstock collected for mechanical recycling of PVC, includes pre-consumer PVC and suitable post-consumer PVC materials which are easy to identify and separate from the waste stream [1–3,6,9,18]. At global level, it has been estimated that the mechanical recycling of post-consumer and pre-consumer PVC wastes will be 1.4 million tonnes in 2010 [2]. However, although the mechanical recycling is a very popular method, but it cannot be achieved regardless of specific economic constraints. The available volumes of the recyclable wastes, the quality and the cost of sorting and regeneration are the most important factors that determine the final cost of the recycled material [3,15,33,46,49]. A statistical study shows that around 7.4% of the 9 million tonnes of municipal solid waste in Western Europe in 1990 are comprised of plastics materials of which PVC is estimated to account for only 10% [3,9]. This indicates a great inhomogeneity of PVC plastic wastes, resulting in a major problems in the mechanical recycling of used plastics. In fact, this inhomogeneity gives rise to a material which is very difficult to process and/or has inferior mechanical and physical properties [3,9,14,29,50].

The other difficulty of the mechanical recycling of PVC is a high sensitivity of PVC materials to environment, involving continuous changes in its morphological structures and properties during processing of PVC [7,8,18,23,40]. Because of shear stress during processing, the fusion of plastic particles progressively changes the original particle structure into a network of entanglements, affecting both physical and mechanical properties of the material [7,18]. PVC, in particular, also has a very limited thermal and photo stability which requires addition of stabilizers to prevent dehydrochlorination and discoloration, occurring during its lifetime [18,35,51–54]. Reprocessing of PVC wastes in order to obtain a recycled material aggravates this condition and leads to a reduction in properties with temperature alterations and, in particular, causes a diminution in mechanical properties [3,5,9,41]. With

respect to a great practical importance of the polymer, the thermal and photochemical degradation of PVC has been studied for a long time [3,9,39,41,51–54]. These studies can be used to develop new concepts and processes for mechanical recycling of PVC. The elimination of hydrogen chloride, at relatively low temperatures or under the influence of light is the fundamental aspect of PVC decomposition. In the first stage, this reaction starts by the formation of one double bond followed by a very fast unzipping reaction, which leads to a polyene sequences in the backbone, according to the following reactions [3,9,18,39–41,51–54]:



These polyenes, with a mean length of 5–25 conjugated double bonds, absorb visible light and cause the polymer to turn from yellow to brown, and in severe cases to completely black [3,8,9,18,51–54]. If the levels of degradation are high, secondary processes are also observed during degradation. For example, the polyene sequences can react with one another, leading to a cross-linked network [9,18,51]. Initial sites, such as allylic chlorines adjacent to internal double bonds, tertiary chlorines at branched carbons, head-to-head units, and oxygen containing structures are believed to be responsible for such instabilities [3,51–54]. The mechanisms, which occur during such degradations, are not yet fully understood and it is believed that can differ very much depending upon conditions (temperature, presence of oxygen, etc.) [41,51–54]. Moreover, some additives which may be existed in the PVC wastes such as vegetable fillers (e.g., wood fibers in wood fiber-reinforced PVC composites) can change or accelerate the dehydrochlorination process [55]. Regarding the inhomogeneity of plastic wastes, such sequential reactions can further worsen properties of the recycled material [1,40]. According to the recent evidence, the particle size, degree of residual stability, and type and amount of stabilizers are of important factors controlling the properties of the recycled material [3,7,9,18]. Ditta et al. [18] studied the ability of unplasticised PVC (U-PVC) to be processed a number of times. They investigated three different types of U-PVC: virgin lead-stabilized material; virgin calcium/zinc-stabilized material; and reground, 20-year-old, post-consumer windows. They claimed that for outdoor profiles their elongation at break does not change significantly after 20 years of service life, compared to the values when new material is used. This may be due to the high concentration of residual stabilizers and other additives in such outdoor products. However, several studies have indicated that intrinsic instability of PVC results in the worse performance and lower applicability of the recycled material [1,7,13,44,56–59]. A number of solutions to this problem have therefore been proposed, of which two approaches that are more acceptable include blending of the recycled PVC with virgin PVC and/or with other suitable thermoplastics [1,7,13,57,58]. For example, it is suggested that at least 40% and 20% virgin PVC must be incorporated into the recycled PVC pipes and recycled window frames, respectively, to produce a high quality product [60]. However, in practice this may not happened, as can be seen in the example of the German recycled window frames [60]. Sombatsompop et al. [7] have studied the possibility of recycling of PVC pipes and the effects of recycled pipes on the rheological, morphological, mechanical, and thermal properties of the PVC blends. They reported that incorporating the PVC recycle into the virgin PVC caused an increase in viscosity and a decrease in the melt flow index. According to their results, with increasing the recycled PVC loading, the hardness and density of the blends are

increased. They demonstrated that glass transition, degradation, and heat deflection temperatures were shifted with the recycled PVC loadings. Recently they also investigated the possibility of recycling of PVC bottles and cables by adding the recyclates in the various concentrations into the different virgin PVC grades [56]. According to their results, the optimum concentrations of PVC recyclates to be loaded into the virgin PVC compounds were different from one property to another. They recommended that optimum concentrations of PVC recyclates depend on the type of virgin PVC grade used and also on the properties of interest. Moreover, they claimed that some properties such as tensile strength and impact strength could be improved by incorporating recycled PVC [7,56,59]. However, as mentioned earlier, the alternative approach for improving the properties of recycled PVC is combining it with other thermoplastics [1,7,13,58,59,61,62]. For example, incorporation of acrylonitrile butadiene styrene (ABS) and/or other styrenic polymers into the recycled PVC leads to a high impact strength and high thermal stability because of the inherent properties of styrenic polymers [1,13,61,62]. Recently Garcia et al. [1,13,62] investigated such blends. They studied the compatibility of recycled PVC obtained from credit cards with virgin and recycled ABS obtained from the electrical and electronic sector. They demonstrated that partial compatibility can be obtained between the recycled PVC and the ABS, which attributed to the interaction between the polar groups of the styrene–acrylonitrile (SAN) phase and the polar groups of the PVC phase. Moreover, the use of virgin ABS offers higher compatibility than recycled ABS, because of the improved adhesion which exists between the polybutadiene phase and the SAN phase. They recommended, however, that from the economic point of view the use of blends with recycled ABS is more beneficial, although it reveals poorer results in terms of compatibility and mechanical characteristics. They also improved the performance of recycled PVC by incorporating the SAN into the blend. They demonstrated that the blending of the SAN results in an increase in the thermal stability of the recycled PVC. They also recommended that the styrenic polymers cause a strong variation in the mechanical properties, although their results showed a strong relation to the type of such polymers added, both as a result of its nature (SAN or ABS) and origin (recycled or virgin).

2.3. Chemical recycling of PVC

Besides the mechanical recycling of PVC, there are several attempts to prepare low molecular materials from PVC wastes by chemical treatment [9,21,26,36,45]. It has become apparent that mechanical recycling is limited because of down-cycling effects and difficulties in getting a clean enough raw material [8]. Accordingly, the chemical recycling (feedstock or raw material recycling) of PVC plastics, which is considered as a complementary to the mechanical recycling, is currently a growing area of research [8,9,21,26,36,45,63]. Moreover, there are a number of multiple materials, such as laminated films, which are intimately connected to each other and therefore cannot be economically sorted into a single polymer stream. The chemical recycling processes today treat these mixed plastics waste from various sources [10]. However, although the chemical recycling is less sensitive to unsorted or contaminated waste products, the energy used to produce and manufacture the product is destroyed during such process; therefore, from an energy perspective, it is less advisable than mechanical recycling [60]. Moreover, it must be emphasized that condensation polymers, such as polyethylene terephthalate (PET), are typically much more amenable to chemical recycling than addition polymers such as PVC [23].

The chemical or feedstock recycling is based on the idea of breaking up polymer waste to the basic chemicals by means of heat,

chemical agents and catalysts. The obtained products can subsequently be purified and reused in petrochemical industries to produce either the same or a related polymer [3,8–10,21,26,36,60]. One usual approach for chemical recycling of PVC wastes is currently “thermal cracking” via hydrogenation, pyrolysis or gasification [38,42,64–68]. The main intermediate product of the thermal cracking is a polyene material that continues to degrade by evolution of aromatics and converts to a products which their composition will be strongly determined by processing variables such as type of atmosphere, temperature and residence time [8]. In an inert atmosphere, the degradation products will be hydrochloric acid (HCl), gaseous and liquid hydrocarbons, and char, which among them HCl is a main product and can be reused either in vinyl chloride production, or in other chemical processes [3,8,9,64]. In the case of manufacturing process of vinyl chloride, a gas purification unit must also be added to obtain high purity hydrogen chloride gas [10]. In a steam atmosphere at high temperatures, the hydrocarbon fraction will be converted into the some other products such as carbon monoxide, carbon dioxide and hydrogen [8–10,15]. Slapak et al. [8] constructed a bench-scale bubbling fluidized bed to investigate some processing parameters on the product outcome. They showed that the choice of type of bed material is essential for the product outcome, so that the use of catalytic inactive solid quartz as bed material results in the production of large amounts of char and tar, whereas the application of catalytic active material such as porous alumina results in a high conversion of PVC into the syngas. Moreover, according to their results, temperature has a large impact on the composition of the products, so that the carbon to gas conversion improved from about 70% at 1150 K to approximately 100% by increasing the reactor temperature to 1250 K. For chemical recycling of PVC, an increase in efficiency of dehydrochlorination process is usually attributed to the successful recycling [41,69]. Therefore attempts are made to increase the HCl yield via variation of operating parameters or using new chemicals within the feed. Masuda et al. [69] have been studied thermal decomposition of mixture of PVC and various metal oxides. They demonstrated that the emission of hydrogen chloride changes significantly with the oxides used indicating the chlorine fixing ability of oxides. Wu et al. [41] recently reported that utilization of poly(ethylene glycol) (PEG) can accelerate dehydrochlorination of PVC, so that at 210 °C for 1 h the dehydrochlorination degree was as high as 74% for PVC/PEG, while for PVC only 50%. Moreover, they demonstrated that for PVC/PEG the decomposition of PVC shifted to lower temperatures compared with that of pure PVC, suggesting some interactions exist between PEG and PVC that caused the faster dehydrochlorination rate. According to their results, during this process, no waste byproducts such as KCl were produced, and satisfactory recyclability of PEG (10 cycles) can be obtained. An alternative method to thermal process of dehydrochlorination is the rather easy process of dehydrochlorination under the influence of alkaline media to recover hydrochloric acid [9]. Another possibility is the degradation of PVC by oxygen oxidation in an aqueous alkaline solution to produce various carboxylic acids [9,39]. Yoshioka et al. [39] examined such process in NaOH solutions at high temperatures. They demonstrated that dehydrochlorination of flexible-PVC occurred first and followed then by oxidation. They reported that the major products were oxalic acid, a mixture of benzenecarboxylic acids, and CO₂. However, the chlorine content could also be recovered in the form of HCl by adjusting the reaction conditions such as alkali concentration [9,39].

Among various methods of thermal cracking, pyrolysis is a more well-known procedure in the chemical recycling of PVC. The process of pyrolysis, which takes places at 500–900 °C without any oxygen, is a very suitable recycling method especially in the case of

mixed plastic wastes [60,64,65,67]. In a typical process, a PVC-rich waste can be pyrolysed to hydrocarbons (oil), soot, hydrochloric acid, chlorinated hydrocarbons, etc., which hydrochloric acid needs to be removed from the pyrolysis gas although this removal process can result in the formation of toxic dioxins in some stages [3,8,42,60,64]. The main end product of pyrolysis is, however, oil for the oil industry [60]. One main problem connected with pyrolysis of PVC and mixed plastics containing PVC materials is corrosion of the process equipment (e.g., pyrolysis reactor and piping) mainly by the formation of the acid gas (HCl). Moreover, many petrochemical specifications limit the amounts of halogens (appeared in the forms of hydrogen chloride and chloro organic compounds) to a very low range in the gas and oil derived from plastic waste. Therefore in the case of mixed plastic wastes (uneconomic to separate to a single polymer) with a low PVC content, the conventional chemical recycling is frequently used only for a waste stream in which the PVC content is less than 30% (for example, the multiple material products) [8,10,34,36,39,70]. So far, several solutions to such problems have been proposed which some of them have already been put into practical use. For example, milling of PVC with CaO can be an effective way to extract Cl from the waste [63]. An attempt has also been made to develop a process for recovering metals from alloy-wastes by using a mechanochemical reaction consisting of a co-grinding alloy and PVC waste, followed by washing with water and filtration [71]. By such co-grinding, the chlorine content of plastic waste is extracted as metal chlorides which is soluble in water and can readily be separated from the generated hydrocarbons. Currently, the NKT-Watech pyrolysis process in Europe uses another two-step pyrolysis of PVC wastes in a stirred vessel [72]. Calcium carbonate and filler are used to react with liberated HCl and produce calcium chloride. Then at the increased temperature, the polymer chains break down which produce a solid coke residue. Finally, the residual calcium chloride can be treated to make it suitable for selling [72]. Alternative approach is pre-treatment of mixed plastic waste by removing PVC and other halogenated plastics from the feed. Such pre-treatment consists of a dilution of the wastes having excessive chlorine content with less chlorine-containing or chlorine-free polymer mixture [10,60]. It is also common to dilute the chlorine-containing hydrocarbon feed with chlorine-free petroleum fractions coming from refineries [10]. Another possibility, as a less expensive and more acceptable process, is thermal dehalogenation which takes place either in a liquid or in a fluidized bed pyrolysis [10,73]. Recently, Duangchan et al. [70] have proposed a new method consisting of copyrolysis of PVC with nitrogen compounds in bio-waste to reduce the corrosive effects of the generated HCl. They studied the pyrolysis conditions between PVC and cattle manure via a statistical method and optimized conditions to provide the highest HCl reduction during PVC pyrolysis. They also applied the optimized conditions to a plastic mixture and then determined the quality of the obtained products. They concluded that the lowest heating rate, the highest reaction temperature (450 °C), and the PVC:cattle manure ratio of 1:5 are the suitable conditions which provide the highest HCl reduction. However, according to their results the presence of manure decreases the oil yield of pyrolysis by about 17%. PVC can also be chemically modified by nucleophilic substitution of chlorine atoms in its structure. Kameda et al. [26] have described reactions of rigid PVC with various nucleophiles (Nu) such as iodide, hydroxide, azide, and thiocyanate in ethylene glycol as solvent. Such reactions lead to the substitution of Cl by Nu and finally elimination of HCl, resulting in the dehydrochlorination of the rigid PVC. According to their results, the dehydrochlorination yield increased with an increasing nucleophiles concentration, resulting in a maximum substitution at high nucleophiles amounts. Moreover, when ethylene glycol was replaced by diethylene glycol,

the dehydrochlorination was found to be accelerated, which may be due to the higher compatibility of diethylene glycol with PVC, making it easier to penetrate the rigid PVC particles. Machado et al. [45] have recently described a similar process in which PVC have chemically modified to produce a sulfonated polymer with dehydrochlorinated PVC samples as intermediates.

Several different technologies based on depolymerization and repolymerization processes have been developed for chemical recycling of PVC, which unfortunately the most of them are more expensive than the mechanical recycling [3,8–10,23,39,60]. However, a few commercial-scale plants are currently working and some interesting studies relating to such techniques are available. On the other hand, although new chemical recycling technologies for PVC plastics are gaining importance, the proposed new technologies are yet expensive, polluting and energy consuming processes [3,21,23,26,36,45,60,70]. One new approach in chemical recycling is the using of PVC materials instead of coke in steel manufacturing [10]. By this recycling technology, coke which works as a reducing agent to remove oxygen from iron ore, can be partially replaced with plastic waste. From the environmental standpoint, various advantages are expected from this technology including saving coke and CO₂ reduction.

3. Separation techniques

Recycling of plastics usually requires a suitable segregation technique in which plastic materials existing in the mixed solid wastes is separated into a homogenous plastic waste. Recycling of a homogenous plastic material leads to the broader applications of the recycled products and also boosts their value [3,14,29,34,74]. Moreover, access to a sufficient, steady and reliable supply of unmixed waste materials is a main factor in the viable recycling. In the case of PVC, recycling is usually limited owing to the fact that several different polymers are present in the PVC-rich plastic mixture, which many of them are mutually incompatible making the reprocessing of them, as a whole, practically impossible [23,29,47,48,50]. In other words, although it may be possible to recycle the mixed PVC waste, the incompatibility of the different components leads to a difficult processing and inferior mechanical and physical properties of the resulting material [50,75,76]. Although, it seems that separation of PVC in mixed plastic waste is inevitable, but unfortunately a high quality and universally acceptable automatic segregation of PVC is not yet available and therefore, in most cases the recycled materials which are recovered from an incomplete separation process cannot compete with the

virgin polymer. Moreover, even if consumers can be encouraged or educated to segregate the PVC products prior to the disposal in the municipal waste stream or return used items to the collection points, there will always be small amounts of contamination in the desired plastic. Therefore, many researches, for decades, have been conducted to provide inexpensive and reliable separation methods in which PVC can simply be separated from various waste mixtures [9,14,23,29,47–50]. On the whole, such sorting methods can be classified mainly into three groups: macro, micro and molecular separation [23,34,49]. Macro sorting, which refers to the sorting of whole or nearly whole objects, involves separating plastic based on an entire product, e.g., using an optical sensing. Micro separation refers to the sorting of chipped or granulated plastics. This procedure involves the initial processing to uniform criteria, such as size or density, with subsequent separation. Molecular separation involves processing plastic by selective dissolving of various plastics in solvents and then reclaiming of dissolved materials.

As mentioned above, a number of promising methods for PVC waste separation (and therefore strategies to increase recycling of PVC plastics) have been found, which a few of them have already been put into the practical use [77–85]. Table 2 shows some of the most important methods developed for the separation of PVC from a mixed plastic wastes. One straight and primitive strategy, which is classified as a macro sorting method, is separation of PVC materials from plastic wastes using hand-sorting [23,34]. A study of PVC bottles in a mixed plastic recycling program showed that manual separation is about 80% accurate in identifying which bottles are PVC [34]. However, the manual separation of heterogeneous plastic mixtures is an expensive method which currently not economical; researches have therefore been conducted to provide suitable semi- or full-automated separation methods with minimal manual intervention.

The most recent methods for automated sorting rely on responses to differing environments such as specific gravity changes, optical recognition, and dissolution in solvents [34,49]. Each of these methods is capable of separating types of the plastic to a certain extent [14,29,47,48,77,78,85]. Selective dissolution, as a molecular separation, can be used for selective separation of PVC. Such separating, which involves selective dissolving of plastic in an organic solvent and then reclaiming of dissolved materials, can be conducted using either a single solvent at multiple temperatures or combinations of solvents at a fixed temperature [10,23,31,34,79]. The Vinyloop[®] procedure, which was founded according to such process, is a new technology that allows mechanical recycling of PVC, together with most of its additives, into a compound that can

Table 2
Separation techniques for PVC waste plastics.

Separation technique	Description	References
Manual separation	Sorting by hand	[23,34]
Selective dissolution (Vinyloop [®] procedure)	Selective dissolving of PVC in organic solvents and then reclaiming of the dissolved material	[10,31,79]
Hydrocyclone separation	Sorting according to differences in density through a centrifugal force field	[3,34]
Melt filtration	Separation by melt filtration at temperature of 204 °C through continuous screen changing equipment	[3,80]
Selective flotation process	Surface treatment of plastics having similar densities (PVC and PET), with subsequent froth flotation using nonionic surfactants	[14,74,81–83]
Liquid-fluidized bed classification	Gravimetric separation in water as a fluidizing medium through a selective thermal particle density modification induced by step changes in the fluidizing water temperature	[48]
X-ray fluorescence method	Spectroscopic separation through a characteristic backscattering from chlorine atoms in PVC	[9,23,34]
Laser-induced plasma spectroscopy method	Spectroscopic separation through analysis of the atomic emission lines generated by focusing high-energy laser radiations on plastics	[77,84]
Triboelectrostatic separation	Electrostatic separation by charging of plastics, with subsequent segregation of materials through an electric field	[29,47,85]

be easily used for production of high quality products [10,31,79]. A first Vinyloop technology was founded in Ferrara in northern Italy in 2001 [10,79]. It was the first of ten PVC recycling plants to be built across Europe with this new technology. Vinyloop is a mechanical recycling technology based on separation by the use of solvents which produces the recycled PVC compounds with superior mechanical properties. The PVC is cut into the small parts in order to maximize the surface area and then completely dissolved in an organic solvent. The stages are performed in a closed loop batch process under pressure to dissolve the PVC waste selectively and separate the PVC compound from other types of plastic waste or from the other materials in a PVC composite such as plasticizers, filler, stabilizer and pigments. After dissolution, the PVC is recovered from solution by precipitation of PVC compound and afterwards stripped with steam to recover all the solvent. The developers believe that the quality of the secondary material is same to that of virgin material. Once the PVC is recycled from the solvent, the solvent is recovered by a multi-step condensation and separation process. Moreover, all the components of the original PVC formulation are also recovered in the form of an aqueous suspension. The PVC produced by this recycling process features granulometric properties that improve the efficiency of the processing steps when it is reused. The smoothness and homogeneity of the granules improves their fluidity, and thus make them more desirable. The process is a closed loop in which (theoretically) 100% of the material is recovered. However, this does not quite happen in practice as no cycle is entirely perfect. The first Vinyloop plant is initially designed to recycle PVC from cable insulation and packaging. However, trials are going on to demonstrate the feasibility of recycling other types of initial feedstock such as pharmaceutical blister packs, floor coating, and car dashboards. In 2005, about 4000 tonnes of PVC waste, mainly cables, were recycled in the Vinyloop Ferrara plant. In 2007, the plant further improved its performance, processing 8191 tonnes of PVC waste, almost 14% over the target [10,31,79]. However, It must be emphasized that in the selective dissolution process, the solvents should be selected so that selectivity dissolves desired polymer (i.e., PVC), a feature which may be so laborious. In fact, Vinyloop-based technologies are usually restricted to pre-sorted PVC mixtures in which the contaminations of other polymers having similar solution properties are minimized. Moreover, the use of organic solvents and, consequently, the need to control emissions and to recover the solvents increase the costs of such systems.

On the other hand, several other processes commercially separate a fraction of PVC and PET from other plastics such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP) [9,14,23,34,50]. These processes are mostly based on differences in density of such polymers [3,23,34]. One example of these processes, which may be considered as a micro sorting, is separation using a hydrocyclone [3,34]. The hydrocyclone works based on the principle of sorting by a centrifugal force field. The mixed plastic wastes are first ground up and then sent through the hydrocyclone which separate various polymers according to their differences in the specific gravity [3,34]. However, the similar density of some polymers precludes the use of such simple and inexpensive method [14,50,74]. In fact, the specific gravities of PVC and PET are 1.32–1.37 g/cm³ and 1.33–1.37 g/cm³ respectively and sorting of them by a simple density-based technique are therefore impossible [9,20,74,76,81,86]. Furthermore, contamination of PVC with PET significantly limits the quality of the recycled material due to the different melting points and thermal stabilities of the polymers [9,20,76,86]. If PET is contaminated with PVC, PVC will degrade at high PET processing temperature, and conversely, PET does not melt at low processing temperatures of PVC [14]. Accordingly, special interests have been given to separate PVC from

various PVC/PET mixtures. Currently, such separations can be achieved according to difference in mechanical properties of the plastics or by full-automatic sortation devices or by new gravity-based processes in which major modifications are made to alter some physical characteristics of the plastics [14,34,80,82,83]. For example, an automatic segregation of PET from PVC can be successfully performed by melt filtration through continuous screen changing equipment at a processing temperature of 204 °C, which is below the melting point of PET and thereby allows PET and other solid contaminants to be filtered out [3,80]. Separation according to the differences in density can too be conducted by a modified method known as selective flotation process in which a spatial conditions along with a suspension medium is used to separate the desired plastic [14,74,81–83]. Already, the possibility of this technically attractive method for separation of PVC from a PVC/PET mixture has been demonstrated by Recovery Processes International, Inc. with four plants now in operation [81]. By using the flotation method, generally two fractions are obtained from the plastic wastes: a light fraction, floating on water, and a heavy fraction. The first fraction is essentially made of LDPE, HDPE, PP, and high impact polystyrene (PS); the heavy fraction is usually formed by PVC and PET [23,81,82]. However, selective flotation separation of the PET/PVC mixture cannot be achieved without changing the surface properties of these polymers [14,81,82]. In fact, the PVC and PET polymers with unmodified surface exhibit almost similar surface properties such as hydrophobicity, surface tension, and critical surface tension, which make the selective flotation impossible. Consequently, it is evident that significant change at the surface of either PVC or PET is necessary in order to obtain a selective flotation separation. This condition can be achieved using special chemical treatments such as alkaline treatment process in which the hydrophobicity of PET surface is destroyed by a strongly alkaline solution (e.g., NaOH), while the hydrophobic properties of PVC surface is remained approximately unchanged. After the surface treatment, the froth flotation separation is conducted using nonionic surfactants [14,81,83]. Recently, the most influencing factors in the selective froth flotation such as particle size, concentration of floating agents, amount of NaOH, conditioning time, and temperature have been investigated in detail [14]. It must be emphasized that, however, froth flotation has the problem of huge waste water production that must be recovered or disposed. Hu and Calo [48] have recently proposed an alternative density-based technique known as liquid-fluidized bed classification to separate waste plastic mixtures including PVC, PET, PS, HDPE, LDPE, and PP using water as the fluidization medium. They carried out their experiments in a 10 cm diameter, fluidized bed apparatus that was designed to separate fractions of plastic particles having higher or lower densities than water. Hu and Calo also suggested a new technique of separation enhancement via selective thermal particle density modification induced by step changes in the fluidizing water temperature to enhance the segregation efficiency of PVC/PET mixtures. According to their results, the liquid-fluidized bed classification is a promising separation technology for waste plastic separation.

Other separation methods considered as macro sorting are separation using physical techniques like different spectroscopic-based methods [9,23,50,77,84]. For example, x-ray fluorescence, as a well-known spectroscopic technique, can be used to detect characteristic backscattering from chlorine atoms in PVC, which has a higher absorption compared to the polyolefin plastic without chlorine [9,34]. The value of PVC absorption, electronically processed through algorithms, makes it possible to detect its presence and consequently to eject it (e.g., by a compressed air jet) [23]. However, the chlorine x-ray is weak and cannot penetrate through paper labels, which may be attached to the PVC waste. Moreover,

there is also a rapid decrease in x-ray chlorine intensity as a waste is moved away from the x-ray source and detector [34]. Therefore, in recent years, several researchers have considered other spectroscopic-based techniques which can be applied for instant and reliable identification of various plastics. For example, Gondal and Siddiqui [84] proposed laser-Induced breakdown spectroscopy (LIBS) method, which is based upon the analysis of the atomic emission lines generated by focusing high-energy laser radiations on the plastic surface, for the identification of plastic items in a waste mixture including LDPE, HDPE, PP, PS, PET, and PVC. For this, they determined the LIBS signal intensity of carbon and hydrogen for fingerprinting of the plastics and finally calculated the C/H line intensity ratio to identify the plastics. Their studies indicate that LIBS technique has excellent potential for rapid online, real-time, reproducible analysis and identification of plastics waste. Anzano et al. [77] have recently developed another spectroscopic approach based on laser-induced plasma spectrometry to classify different groups of post-consumer plastic materials using determination of their elemental ratios. In a typical process, signal ratios of C:C2:CN:H:N:O of plastics were determined under atmospheric conditions and polymeric materials are then classified according to their signal ratios as PET, polyolefins (PP and PE), PVC, and PS (the polyolefin group cannot be differentiated into individual materials; therefore they can only be identified as polyolefins). Although such spectroscopic techniques have excellent potential for online detection of PVC plastics, but sorting out the two polymers by using a spectroscopic method adds an extra cost to the recycling. A more recent physical separation, which is considered as a suitable alternative to the spectroscopic detection, is electrostatic separation that can separate the mixed plastics using a triboelectrostatic process [29,47,85]. In a typical procedure, a triboelectrostatic separation can be achieved by charging of plastics using particle/particle and particle/charger charging mechanisms, with subsequent segregation of materials through an electric field. Charging phenomenon happens when two different plastics contact or collide and charge transfer occurs until their fermi levels equalize by the work function difference between the two materials. In such process, plastics with high work function and low work function are charged positively and negatively, respectively. The final stage is separation of differently charged plastics using an electric field, in which the negatively charged plastic is moved toward a positive electrode while positively charged material is moved toward a negative electrode [29,47]. Recently, Park et al. [29] have designed a bench-scale triboelectrostatic separator for PVC removal from PVC/PET mixture. They investigated various factors such as tribo charger material (e.g., polypropylene), air velocity (the impact of collision or contact), mixture ratio of PVC:PET, and relative humidity effecting on charge efficiency. Dodbiba et al. [47] have described a similar dry method in which mixture of PP, PET, and PVC can be separated by combining air tabling and triboelectric separation process. They employed an air table to collect a PP-rich low-density fraction and a PVC/PET high-density fraction and then used a triboelectric separator to segregate the mixture of PVC/PET utilizing differences in surface charge. Hearn and Ballard [85] have proposed another electrostatic-based technique for the identification and sorting of waste packaging materials, constructing from various plastics and non-plastics. Firstly, they demonstrated that plastic packaging items can be separated from items constructed from cardboard, wood or paper by applying a controlled level of electrostatic charge and comparing the rate of charge relaxation using a non-contacting electric field meter. Subsequently, using a series of triboelectric probes they tried to segregate various plastic packaging materials constructing from PVC, PP, PS, PET, and HDPE. For such segregation, the probes are brought into contact with the packaging item to be identified, which resulted in

generation of an electrostatic charge due to the friction between the probe and the plastic materials. Due to the dependence of the magnitude and polarity of the generated charge on the type of the polymer, plastic items can be sorted into the fractions comprising PP, PET/PS, PVC, and HDPE.

4. Recycling of the unsorted PVC-rich wastes

When creation of a homogenous PVC stream is not economic, recycling of mixed plastics may be an alternative route, although the quality of the material recycled from an unsorted source is suitable only for a limited number of applications [3,35,38,50,87]. In deed, notwithstanding detailed investigations concerning various PVC separation techniques, unfortunately most of them are currently uneconomic and researches must, therefore, be still conducted to improve overall process economics. As mentioned before, one approach for recycling of mixed wastes is chemical recycling which is currently used for plastics that are intimately connected to each other (laminates or composites) [3,23,50,60,81]. However, when mechanical recycling is preferred to the chemical one, other modified processes which do not require a homogenous PVC material are required. So far, several attempts are made to develop such modified processes [3,35,50,87]. An important commercial advantage of such studies is reduction of the financial and technical difficulties in obtaining a final recycled product, using the elimination of the expensive step of separation.

Mixed plastics wastes may be defined as a mixture of products which are heterogeneous in polymer type, additives type and concentration or manufacturing technique in which plastics have been fabricated [34]. Recycling of an heterogeneous plastic waste gives a secondary material with inferior physical and mechanical properties, because of the lacking of compatibility among the various components, especially polymers existed in the waste [14,29,35,47–50,75,76]. Even at low contents of impurity, the incompatible polymer significantly worsens the mechanical properties of the PVC products [13,35,50,75]. Such recycled products can never compete with virgin plastic materials, and manufacturers must therefore find their market in areas dominated by cheap materials or must attempt to modify the critical properties of the recycle. Similar to the recycling of a homogenous PVC, a possible route for modification of secondary materials recycled from an heterogeneous source is blending of them with virgin polymer or, at least, with the recycled homopolymer [1,7,13,56]. However, it is clear that a recycled PVC material obtained from an heterogeneous waste exhibits extremely lower characteristics than that recycled from an homogenous source, even though such modifications are made. Some researchers suggest an alternative approach in which the incompatible polymers existing in recycled PVC can be miscible using a compatibilizer [3,23,34,35,75,76,87]. In such approach, the deficiencies in the properties of the resulting polymer mixture are significantly reduced and critical properties of the final blend are therefore improved. Compatibilizers are a family of additives which allow for bonding of two or more incompatible polymers when blended together [34,75,88]. Compatibilizers can be separately incorporated into the blends or generated in situ during a reactive extrusion process [23,88]. Compatibilizer migrates to the interface, acting as a bridge between the two incompatible phases, reducing the interfacial tension, improving adhesion and mechanical performance, and stabilizing the blend morphology [3,23,34,35,75,76,88]. Due to such promising effects, compatibilization of heterogeneous plastics has become a focus of interest in the field of recycling, both in industrial and academic community. According to a general rule, the properties of the resulting semi-compatible recycled blend must be intermediate between those of the two components. However, the most of such recycled materials show

properties lower than expected. Moreover, for the same blend not all properties behave in the same way [3]. Currently, compatibilizers exist for PVC/polyolefins blends, although researches for synthesis of new compatibilizers such as block or graft copolymers or functionalized polymers are still under way [23,34,87,88]. Such synthetic polymers, which have intermediate structural characteristics between PVC and desired incompatible polymer, can improve the adhesion between components much better than traditional compatibilizers. For example, Kabdi et al. [87] have studied the recycling of regenerated LDPE in the form of blends with PVC in the presence of chlorinated polyethylene as compatibilizer. They demonstrated that chlorinated polyethylene with 36% chlorine content substantially improves the properties of the binary blend, especially when weight proportion of 50:50 of compatibilizer:blend is used.

Recycling of the mixed waste containing PVC and other plastics is difficult, in particular not only because of the incompatibility of different polymers, but also due to their differences in melting point and melt flow rate [10,20,23,50,60,81]. In other words, the difference in the melting point (and therefore molding temperature) and melt flow rate for heterogeneous polymers aggravates their incompatibility and, as a consequence, for a plastics mixture containing PVC, traditional mechanical recycling may be practically impossible [15,20,50,60]. For example, laminates made of soft PVC and PP fabric cannot simply be recycled because of the inherent incompatibility and different processing conditions of PP and PVC [35]. The same condition is in the case of PVC mixed with post- or pre-consumer PP waste. The molding temperature of PVC is between 180 and 210 °C, whereas PP and all other thermoplastics can be processed within the temperatures ranging from 220 to 260 °C [3,60]. At such elevated temperatures, PVC starts to decompose, leading to a material with unacceptable mechanical and physical characteristics [3,60]. A proposed approach to overcome this problem is based on reprocessing at low temperatures in which high melting components behave as solid fillers [3]. Another useful method which is performed at elevated reprocessing temperatures, comprises the use of stabilizers in the polymer blends, which results in stabilization of PVC at high processing temperatures of other thermoplastics [1,3,23]. However, mechanical properties of the resulting recycled material obtained from such modified methods are usually still poor, and in some cases the cost of the stabilizers is also too high for a typical PVC recycling plant [3,9,13,23,35,50].

Beside traditional strategies, some new approaches are recently developed for recycling of mixed plastics. For example, organically surface-modified fillers can be incorporated into the recycled plastic waste to interact with incompatible polymers and increase the adhesion between components [35]. In fact, surface-modified fillers improve the interaction between polymers, modify the interfacial properties, enhance the thermodynamic stability of system, and reduce the phase aggregation. Moreover, with increasing filler content, the compatibilizing effects may be increased [35]. Andricic et al. [35] have recently described the preparation of composites consisting of the pre-consumer waste, which composed of PVC and PP, in the presence of nanosized surface-modified calcium carbonate (CaCO₃). The used nanoparticles of CaCO₃ were isotropic with low aspect ratio but large surface area, which resulted in a significant improvement in the mechanical and thermal properties of the recycled PVC composites. They also suggested that nanosized CaCO₃ lowers melting point of PP, which may be due to the changes in its crystalline form in the presence of CaCO₃. Another new approach for recycling of mixed PVC wastes is based on the plasticization of mixture by macromolecular compounds, especially polyurethanes. PVC is basically plasticized by low molecular mass esters such as dioctyl phthalate

(DOP) [3,40,88,89]. However, plasticizers with low molecular mass can migrate to the surface of material and finally evaporate from the surface [40,89]. This event significantly affects the stability of PVC properties. Contrary to the plasticizers with low molecular mass, the macromolecular compounds such as polyurethanes cannot leave the material surface even at a high segmental diffusion rate [40,90,91]. Moreover, polyurethanes can also modify the mechanical characteristics of the final product [40,50]. Such polyurethanes can typically be generated in the system, using either regeneration of PVC/polyurethane blends or glycolysis of polyesters like PET to produce relevant polyurethane [9,40,90,91]. Grigoryeva et al. [40] studied the possibility of the plasticization of PVC by regenerated PVC/polyurethane blends, obtained after partial thermochemical destruction of the polyurethane foam-backed PVC-sheet (soundproof materials waste). They destructed thermochemically the polyurethane foam-backed PVC-sheet using alkanolamine in a one-screw extruder. The destruction product was a thermoplastic mixture of PVC and regenerated linear polyurethanes, which are applicable for reuse without any purification and fractionation. However, polyurethanes can also be generated by a glycolysis process in which polyesters like PET convert to oligomers that are able to polycondensate with caprolactone. The obtained diols are extended with aliphatic diisocyanates, which under special conditions result in polyurethanes that are totally miscible with PVC and give blends with acceptable mechanical and physical properties [9,23,50,90,91]. It is obvious that such process can be used for mixed plastic wastes in which the PVC is only contaminated with polyesters.

5. Some strategies for recycling of the post-consumer PVC wastes

Recycling of the PVC plastic wastes is not a recent problem for plastic users and producers. The PVC goods manufacturers regularly recycle the substantial quantities of scrap materials generated in-house (i.e., pre-consumer waste) within the production cycle itself. It is, of course, important to be able to recycle the scraps which are contaminant free and have a known composition, but as mentioned before it cannot simply be applied to the post-consumer PVC wastes [18,23,34]. In fact, recycling of PVC originated from post-consumer wastes, which accounts for approximately 90% of all PVC wastes, has been considered only since recent times [2,23]. The total amount of PVC consumed globally since the early 1960's is estimated at over 400 million tonnes, of which about half is still in use in long-life products such as windows frame and pipes [3,10,92,93]. The mean lifetime of such long-life products is approximately 30 years and therefore the PVC goods, which produced 30–40 years ago, are now entering the waste stream [92,93]. Accordingly, it is estimated that the PVC waste will increase faster than the growth in consumption in the coming decades [3,92,93]. Therefore, various collection and recycling schemes relating to the PVC waste, which were created around the world in the past decades, are incrementally being grown. However, another feature which may also be important is to determine how the recycled PVC can effectively be used. It is suggested that primary recycling which is also known as closed loop method is the most effective recycling approach [3,34]. Such recycling involves converting of the plastic waste into the material which has the same application as the original product. It is a desired approach because it is not necessary to create a new market for a recycled material and also because the need for virgin material is reduced. However, for a successful closed loop recycling the secondary material must have the same physical and mechanical properties as the original product, a feature which, as mentioned before, may be so laborious.

Among the post-consumer PVC wastes, the post-consumer pipes are one of the most important PVC wastes which have a high growth perspective in the future [3,5,7]. About 40% of PVC is used for making pipes and demand of using PVC in pipes production is still increasing [5]. Collection of the PVC pipes waste is currently organized by the producers association, although the gathered materials may be a mixture of PVC and PE-pipes, with variable contamination of rubber, metals, sand, glass, stones, etc., and the separation step may therefore be inevitable [3]. On the other hand, so far several strategies by which the PVC pipes can economically be recycled to the products having defined characteristics have been proposed [3,5,7,93,94]. The most favored approach is to assess the possibility of incorporating the recycled PVC pipes into the virgin pipe grade PVC powder to make a new pipe product. Som-batsompop and Thongsang [7] have studied such possibility by investigating the effect of adding PVC pipes (with weight percentage varying from 0 to 80%) into the two commercial PVC virgin grades. Their results clearly showed an increase in the melt viscosity and no change in the die swell ratio (as an important factor in pipe production) as the concentration of the recycled PVC was increased. The mechanical and processing properties of the recycled PVC originated from post-consumer pipes and bottles in comparison with those of virgin pipe grade PVC have been investigated in another study by Wenguang and La Mantia. [5] In this study, the effects of recycled PVC on the processing and mechanical properties of recycled/virgin PVC blends in view of its use as pipe grade PVC were also evaluated. Wenguang and La Mantia demonstrated that the particle size and re-stabilization of the recycled material are the two main factors to be considered for obtaining virgin/recycled PVC blends with uniform and acceptable mechanical characteristics. According to their results, recycled material not only does not significantly reduce the modulus and tensile strength, but also improves the impact strength and processing behavior of the pipe grade virgin PVC [5]. In contrast with such investigations in which PVC pipes are recycled in a closed loop recycling process, some alternative researches have recently been conducted to assess the recycling in a non-closed loop approach. For example, Kou et al. [93] investigated the effect of replacing river sand by recycled PVC originated from scraped PVC pipes on the fresh and hardened properties of lightweight aggregate concretes. Their results showed that the as-produced concrete in which sand is optimally replaced by recycled PVC (15% by volume) has lower density, higher ductility, lower drying shrinkage, and higher resistance to chloride ion penetration. However, according to their results, such concretes have also some negative sides such as lower workability, lower compressive strength and lower tensile splitting strength. Qiao et al. [94] have proposed another non-closed loop recycling. They first recycled PVC through a solvent extraction from waste pipe to obtain additive-free PVC and then pyrolysed the extracted PVC by a two-stage process to obtain a free-chlorine PVC-based pitch. They finally did a series of process steps in which the as-prepared pitch was spun, stabilized, carbonized into carbon fibers, and further activated into the activated carbon fibers in a CO₂ atmosphere. They demonstrated that the as-prepared carbon fibers have comparable mechanical properties to similar commercial products, and the resultant activated carbon fibers exhibit a high surface area, narrow pore size distribution and low oxygen content as well. Although, such non-closed loop recycling provides a promising insight to utilize the recycled PVC pipes in various applications, but it must be emphasized here that the obtained results could also be extended to the recycled PVC materials which are originated from other products other than PVC pipes.

Over the past decades, PVC plastics (in addition to other thermoplastics such as PET and HDPE) for producing various containers have increasingly been in demand and as a consequence the higher

quantities of wastes originated from such containers have been produced [3,5,23,34,81]. It has been found that various PVC containers, especially bottles, constitute a main part of PVC wastes, and accordingly there is currently a growing awareness that specific programs are required to deal with this issue [3,20,24,25,43,56,95,96]. Although, the collection of PVC bottles is relatively simple to organize and can be an inexpensive source for recycling of large amounts of PVC materials, but there has been no infrastructure for collection and recycling of PVC bottles until a few years ago [10,24,43]. On the other hand, the presence of different polymers in the mixture of plastic containers creates difficulty in recycling and, in general, plants developed for recycling of such mixed bottles use several stages including separation of HDPE by flotation, identification of PVC and PET containers, automatic sorting, and finally washing, and micronization [3,95]. Furthermore, although many researchers have focused on the recycling of PVC packaging, or even more narrowly on PVC bottles, but some results indicate inferior mechanical and/or physical properties of the resultant recycle [20,23–25,43,56,95–97]. For example, Arnold and Maund [20] investigated the properties of recycled PVC bottle separated from the post-consumer waste stream. According to their results, the mechanical properties of the recycled flake PVC are significantly reduced compared with virgin and pure reprocessed bottle flake PVC. This reduction is mainly manifested as a change to more brittle behavior, resulting in lower tensile strength, lower ductility, lower fatigue strength, and significant scatter in results. Moreover, spectroscopic studies on heat impact at 160–180 °C temperature during the recycling process have indicated that the bottle samples are slightly and considerably affected at 160 and 180 °C heat treatments, respectively, resulting in forming the decomposition products, color change, loss of volatile components, and peroxide formation in air [43]. In contrast to other post-consumer PVC such as pipes and windows that close loop recycling is a preferred approach, there is stringent legislation relating to bottle-to-bottle recycling, mainly due to concerns of health risks [31,43]. However, the PVC recycled bottles may be suitable for the production of window frames, profiles, and pipes [3,24,25,43,96]. Other suitable option is the using of the co-extrusion process to manufacture layered products, which comprise both raw and recycled materials in different layers [3,43]. For example, it is known that recycled PVC bottles can successfully be reprocessed to form a foamed layer of co-extruded lightweight pipes. It is claimed that the characteristics of such pipes are at least as good as those achieved when foamed layer consists of the virgin PVC [3].

PVC plastics are also used in the production of window frames, and various flooring and roofing materials [2,3,18,98]. The term “post-consumer windows” arises from unplasticised window frames of PVC which were installed in houses about 20–40 years ago (according to the type of country) to replace the older timber-framed windows [18,98]. Although these products, as the first generation of unplasticised PVC windows, were not absolutely ideal, PVC windows have still achieved a substantial percentage in the marketplace because of their durability and low maintenance requirements [6,18,98]. For example, annual installation of PVC windows in Germany is about 10,000,000 units with a market share of 45% [8]. Currently, the old unplasticised windows frames are being replaced with up to date product known as second-generation frames [7,13,18,98]. The first-generation windows could be reprocessed and reused in another or the same product [3,18,34,98]. So far, several technical facilities for a fully automatic and clean recycling of post-consumer windows have been given [3,98]. Moreover, up to now many commercial projects have been conducted in this issue [3,10,31]. The other products of PVC, i.e. flooring and roofing materials are also currently being considered in recycling schemes [2,3]. For example, Yarahmadi et al. [2]

investigated old PVC flooring materials obtained from three apartment blocks built in 1964, 1971, and 1974. They studied how the important properties of PVC floorings change during their service life owing to the ageing processes, and how these can influence their suitability as the post-consumer products for recycling processes such as mechanical recycling and energy recovery. Their results showed that PVC floorings can be mechanically recycled in the form in which they were recovered without addition of any new plasticizer. Some of the floor sheets (for example, for using in interior material for railway vehicle) were layered by vulcanized surface to improve the appearance and protecting the scorch mark by fire [37]. These floor sheets which turn to a thermosetting resin may be considered as inappropriate material for recycling. In recent years, from the ecological viewpoint, reusing and recycling of such floor sheets have also been requested strongly. Ito and Nagai [37] have studied the characteristics of the recycled material made of such floor sheets to investigate their long-term stability as a necessary factor for practical application. Although, the recycled materials are generally unsuitable for outdoor use, but they have claimed that such recycled sheets may be suitable for a long-term outdoor applications.

6. Conclusion

During the recent years, the world has faced a waste crisis due to the generation of huge amounts of plastic wastes, including PVC, by industries and householders. Moreover, considering that about half of PVC is in use in long-life products and lifespan of such PVC products is about 30–40 years, a significant increase in PVC waste generation is also expected in the near future. It is suggested that material and/or chemical recycling of the PVC wastes may be a suitable solution to the problem of environmental pollutions arising from landfilling or incineration of such municipal solid wastes. The review article we presented above described in detail various aspects of PVC recycling, including diverse methods for recycling of PVC, strategies for recycling of mixed PVC wastes, and new recycling methods developed in the recent years along with the special problems relating to them. However, as it was emphasized, a simple recycling to produce a secondary material may not by itself solve the problems of disposing of PVC wastes, due to the existence of many types of incompatible polymers in a typical PVC waste stream. In fact, for a successful and economic recycling in which a recycle having an acceptable characteristic can be produced, the first step is to facilitate and improve the PVC separation methods. Therefore, the review also focused on the conventional and recent PVC separation methodologies.

Although a number of new approaches have been proposed for separation and recycling of PVC wastes, none are completely satisfactory in terms of economics and/or performance. Moreover, literature on PVC recycling has not provided detailed data in such a way that the proposed approach can practically be put to use in plastics recycling industries. Therefore, future works should be directed at extending the limited database of such recent approaches of PVC separation and recycling. Furthermore, the studies must also consider all aspects of an effective PVC waste management and calculate the costs and energy requirements for any recycling process to determine the net benefits of recycling.

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