الجمهورية الجزائرية الديمقراطية الشعبية

DEMOCRATIC REPUBLIC OF ALGERIA AND POPULAR

وزارة التعليم العالي والبحث العلمي

MINISTRY OF HIGHER EDUCATION

AND SCIENTIFIC RESEARCH

جامعة قاصدي مرباح ورقلة

University KASDI MERBAH-OUARGLA

Faculty of Applied Sciences

Process Engineering Department

In order to obtain

Academic master's degree in petrochemical engineering

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THEME

Polyvinyl chloride Recycling and it economic and environmental impact

Publicly defended on 12/06/2023

Thesis Defense Jury

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Promotion 2023

الملخص

تتضمن إعادة تدوير كلوريد البولي فينيل (PVC) إعادة استخدام المواد البلاستيكية ، والتي تستخدم على نطاق واسع في البناء والتعبئة..الخ .يعد (PVC) الآن أحد أكبر البوليمرات المعاد تدويرها من حيث الحجم في البلدان المتقدمة ، لأنه مناسب عمليًا لجميع طرق إعادة التدوير ، مقارنة بين الماضي والحاضر في أوروبا ، نلاحظ أن كمية (PVC)المعاد تدويرها تتزايد باستمرار لتصل كمية(PVC)المعاد تدويره إلى (640 ألف طن) في عام 2017.يوفر العمل مراجعة الأدبيات التي تركز على إعادة تدوير (PVC) من خلال طرق اعادة التدوير ميكانيكي وطرق إعادة تدوير المواد الوسيطة. توفر خيارات إعادة تدوير(PVC)الحالية والتطوير المستمر لتقنيات إعادة تدوير المواد الخام فرصًا واعدة لمعالجة نفايات (PVC) بطريقة تفيد البيئة وتوفر مزايا مالية. بحيث يختلف تأثير (PVC) المعاد تدويره عن (PVC) الأساسي على البيئة حيث لاحظنا مثلا أن نسبة الكلور أقل في (PVC) المعاد تدويره. أما من الناحية الاقتصادية ، فقد بلغ متوسط سعر الـ PVC لعام 2021 والنصف الأول من عام 2022(1216 يورو للطن)، مما يشير إلى زيادة ملحوظة بنسبة 45٪ مقارنة بفترة الخمس سنوات السابقة.

الكلمات المفتاحية: PVC (بولي فينيل كلوريد) ، إعادة تدوير **PVC** ، البيئة ، الاقتصاد.

Abstract

Polyvinyl chloride (PVC) recycling involves reusing PVC materials, which are widely used in construction, packaging ... .PVC is now one of the largest recycled polymers in terms of volume in developed countries, because it is suitable for practically all methods of recycling, compared between the past and the present in Europe, we note that the amount of recycled PVC is constantly increasing, reaching the amount of recycled PVC to 640 thousand tons in 2017. The work provides a literature review that focuses on the recycling of PVC through mechanical and feedstock recycling methods. The existing PVC recycling options and the ongoing development of feedstock recycling techniques offer promising opportunities for processing PVC waste in a manner that benefits the environment and provides financial advantages. So that the impact of recycled PVC differs from primary PVC on the environment, as we noticed that the percentage of chlorine is lower in recycled PVC. In terms of economy, the average price of PVC for the year 2021 and the first half of 2022 was 1216 euros per ton, indicating a significant increase of 45% compared to the previous five-year period.

Keywords: PVC (poly vinyl chlorid), PVC recycling, Enviroment, Economics.

Résumé

Le recyclage du chlorure de polyvinyle (PVC) implique la réutilisation des matériaux en PVC, largement utilisés dans la construction, l'emballage, etc. Le PVC est maintenant l'un des polymères les plus recyclés en termes de volume dans les pays développés, car il convient à pratiquement toutes les méthodes de recyclage. En comparant le passé et le présent en Europe, nous constatons que la quantité de PVC recyclé ne cesse d'augmenter, atteignant 640 000 tonnes en 2017. Ce travail propose une revue de littérature qui met l'accent sur le recyclage du PVC par des méthodes mécaniques et de recyclage des matières premières. Les options de recyclage du PVC existantes et le développement continu des techniques de recyclage des matières premières offrent des opportunités prometteuses pour le traitement des déchets de PVC de manière bénéfique pour l'environnement et offrant des avantages financiers. L'impact du PVC recyclé diffère du PVC vierge sur l'environnement, car nous avons remarqué que le pourcentage de chlore est plus faible dans le PVC recyclé. Sur le plan économique, le prix moyen du PVC pour l'année 2021 et la première moitié de 2022 était de 1 216 euros par tonne, ce qui indique une augmentation significative de 45 % par rapport à la période quinquennale précédente.

Mots clés : PVC (poly chlorure de vinyle), recyclage du PVC, environnement, économique.

شكر وعرفان

نشكرالله العلي القدير الذي أنعم علينا بنعمة العقل والدين :القائل في محكم التنزيل ''وفوق كل ذي علم عليم''سورة يوسف الآية 76.وقال الرسول صلى الله عليه وسلم:''من صنع اليكم معروفا فكافئوه ،فان لم تجدوا ماتكافئونه به فأدعوا له حتى تروا أنكم كافأتموه ''رواه أبو داوود...وفي ظل هذا الحديث ووفاء وتقديرا واعترافا منا بالجميل نتقدم بالشكرإلى من اوصى بهما الرحمان احسانا''والدينا الحبيبين'' الى عائلتينا و كل من ساهم في تعليمنا ولو بحرف، كما نتوجه بخالص شكرنا لأستاذنا المؤطر'' روان عزالدين'' على ماقدمه لنا من توجيهات وتعليمات أدام الله عافيته.كما لا ننسى لجنة المناقشة الأستاذ الرئيس ''طبشوش أحمد ''.والأستاذ المناقش ''باشا أسامة ''، اللذان نتشرف بمناقشتهما لأطروحتنا ونخصهما بجميل الشكر والتقدير متمنين لهم دوام الصحة والعافية والمزيد من العطاء لقسم هندسة الطرائق خاصة وجامعة ورقلة عامة .

شكرا

إهداء

اهدي ثمرة نجاحي إلى:

الذي اذا طلبت منه نجمة اتاني حامل السماء..أبي الغالي حفظه الله.

واحة الحب الفياض في صحرائي...أمي الغالية حفظها الله.

من آثرني على نفسه وعلمني علم الحياة....أخي الكبير عماد الدين حفظه الله.

النجوم الزاهرة في سماء حياتي.....اخوتي الكرام وجدتي الحبيبة رحمها الله.

الى الزهور التي عطرت حياتي بشذاها كل زهرة باسمها...صديقاتي الحبيبات.

الى رفيقة الغالية في هذا المشوار إيمان بن ساسي.

الى كل من كان ملاذي أثناء هذه الرحلة من عائلتي و اساتذتي أصدقائي في كل المراحل كل باسمه ومقامه.

إسراء

إهداء

اهدي نجاحي إلى:

إلى من شجعني على المثابرة طوال عمري إلى الرجل الأبرز في حياتي (والدي العزيز..حفظه الله)

إلى من بها أعلو وعليها أرتكز إلى القلب المعطاء(والدتي الحبيبة. حفظها الله)

إلى من بذلوا جهدا في مساعدتي وكانوا خير سند (إخواني وأخواتي...حفظهم الله)

إلى صديقاتي الوفيات.

إلى أسرتي إلى أصدقائي إلى زملائي ،أساتذتي وكل من ساهم ولو بحرف في حياتي الدراسية.

إيمان

Jjj

Abbreviations List

PVC: polyvinyl chloride

EDC: Ethylene dichloride

VCM: Vinyl chloride monomer

EVA: Ethylene acetate vinyl copolymers.

CO2: Carbon Dioxide

HCL:hydrochloric acid

EPDM: Ethylene Propylene Diene Monomer

PET: polyethylene terephthalate

AGPR: Arbeitsgemeinschaft PVC-Bodenbelag-Recycling

VEKA: Vereinigte Elastolin Kunststofftechnik GmbH & Co. KG

HDPE: High Density Polyethylene

LDPE: Low Density Polyethylene

PS :Polystyrene

PP :Polypropylene

C-Cl: carbon-chlorine

Ca-C: calcium -carbon

Cu the chemical symbol for copper

Pb: the chemical symbol for lead

SAR: Superabsorbent resin

PAANa: Sodium polyacrylate

INRS: National Institute for Research and Security

GHG: Greenhouse Gases

PRE: Plastics Recyclers Europe

DNA: deoxyribonucleic

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General Introduction

General Introduction

Plastic has found extensive use in various aspects of everyday life, ranging from the construction industry to consumer goods. Since the 1950s, the production of plastic-based products has witnessed a significant rise, with production rates increasing exponentially over time. In recent times, polyvinyl chloride (PVC) has garnered significant interest due to its extensive range of applications in various daily life uses. PVC belongs to the category of thermoplastic materials and is a prominent member of polymer-based plastics. It constitutes approximately 60% of the overall plastic consumption in major appliances across Europe. [1]

Polyvinyl chloride (PVC) is a widely utilized thermoplastic material and ranks among the most commonly consumed polymers on a global scale. With a demand surpassing 35 million tonnes annually, PVC stands as the second-largest volume leader in the plastics industry, following only polyethylene. A significant portion of society holds the belief that polymer materials, particularly poly vinyl chloride (PVC), have negative environmental impacts. The work provides a literature review that focuses on the recycling of PVC through mechanical and feedstock recycling methods. It examines the advantages and disadvantages of these recycling approaches and discusses their development prospects. [2]

One of the ecological advantages of PVC lies in its low carbon footprint, especially when considering PVC products with a long service life. Surprisingly, the carbon footprint during the manufacturing stage and throughout the entire life cycle of PVC products can be considerably lower compared to other materials, including those typically perceived as environmentally friendly.in essence, PVC exhibits an environmentally friendly characteristic as it utilizes rock salt as a raw material and offers a lower carbon footprint in both manufacturing and overall life cycle compared to alternative materials. The economic significance of PVC is attributed not only to its low production costs but also to its favorable properties. Among the key properties that contribute to its value are its high chemical resistance, advantageous mechanical properties, and resistance to water and weather conditions. [3]

The work presented in this study encompasses a comprehensive review of PVC recycling processes and their significance in terms of both the environment and the economy. The review is divided into three main parts, each focusing on different aspects.

- In the first part, we studied the basics of polyvinyl chloride, its properties and applications.
- In the second part, we studied the most important recycling processes of polyvinyl chloride.
- In the third part, we studied the importance of polyvinyl chloride and recycling to the environment and the economy.

CHAPTER I

General Information On PVC

I.1.The history of PVC

PVC is one of the most important polymers and among the most widely used plastic materials in the world. It was discovered about 1800, making it one of the first synthetic materials ever used in industry.

Henri Victor Regnault, a French chemist, was the initial inventor of PVC. Henri Regnault accidentally discovered the substance in 1835 while processing heated ethylene chloride (also known as Dutch oil).

He obtained the vinyl chloride monomer by heating the oil in an effort to breakdown it using a potassium hydroxide alcohol that had unintentionally been left outside in the sun as a gas white powder that was eventually identified as polyvinyl chloride, or PVC, appeared. However, the credit for the invention was later, in 1872, taken in Germany by Eugen Baumann.during the American economic crisis of the 1920s, Waldo Semon succeeded in increasing the plasticity of PVC and making it more elastic it was under threat of abandonment in this way, semon conceived the idea to introduce the material to the market as a textile waterproof coating layer demand accelerated again during the Second World War, PVC quickly replaced traditional materials to insulate wiring on military ships, causing demand to increase once more. During the 1950s, many more companies began to produce PVC, and global volumes increased dramatically. Throughout the decade, developers discovered additional, innovative uses and refined methods to increase durability, opening the door to applications in the building trades. By the middle of the twentieth century, five companies were producing PVC, and groundbreaking applications for PVC, or 'vinyl,' as it is also known, continued to be discovered throughout the 1960s. A vinyl-based latex was used on inflatable structures and fabric coatings, and methods for improving PVC durability were developed at the same time, allowing applications in the building industry.

PVC products quickly became essential in the construction industry; the plastic's resistance to light, chemicals, and corrosion made it the ideal choice for building applications. PVC can now transport water to thousands of homes and industries thanks to advancements in its resistance to extreme temperatures. PVC was produced by twenty companies by the 1980s. PVC is now the world's third most popular commodity plastic, after polyethylene and polypropylene. PVC's low cost, excellent durability, and processability make it the material of choice for a wide range of industries, including health care, information technology, transportation, textiles, and construction.

PVC is a polymer with a very long average life that reduces the consumption of nonrenewable resources. It is also a material that is highly recyclable, As its commercial viability grew, PVC replaced various other materials. In most cases, this occurred not only because PVC because it had technical advantages. Its properties make it a popular material among plastic processors and end users. In the1970s, the average PVC consumption per person in industrialized countries exceeded 20 pounds of PVC products per year. [4, 5]

I.2.Definition of poly vinyl chloride

PVC is a thermoplastic composite (can be used again) carbon hydrogen and chlorine that comes from petroleum. 43% carbon comes from petroleum and 57% chlorine derived from common salt. It is one of the most common types of plastic in use today its properties make it highly useful in a wide variety of applications.

According to the Vinyl Institute, vinyl polymer is special since it is only partially based on hydrocarbon materials (ethylene obtained by processing natural gas or petroleum), and the other half is based on the element chlorine found in nature (salt). At extremely high temperatures, the resultant chemical, ethylene dichloride, is transformed into vinyl chloride monomer gas. Vinyl chloride monomer is transformed into polyvinyl chloride resin, which may be used to create an unlimited variety of products, through a chemical reaction known as polymerization.[1]pvc is typically described by the following chemical structure :

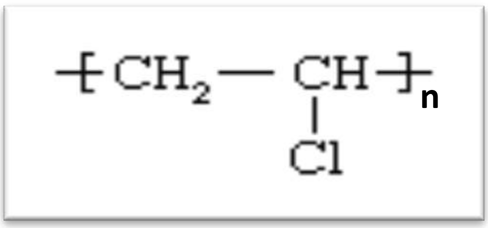

Fig I-1: PVC chemical structure. [5]

I.3.Chemical formula of poly vinyl chloride

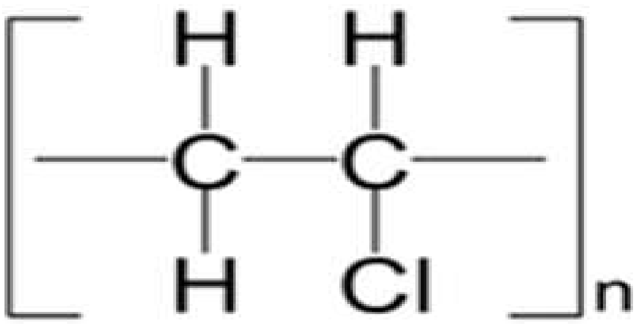

Fig I-2: General formula of PVC. [6]

I.3.1. Production of polymer

The essential raw materials for PVC are divided from salt and oil. The electrolysis of salt water produces chlorine which is combined with ethylene (obtained from oil) to form vinyl chloride monomer (VCM) molecules of VCM are polymerised to form PVC resin. the PVC production process consists 5 steps: The extraction of salt and hydrocarbon resources

1. The production of ethylene and chlorine from these resources
2. The combination of chlorine and ethylene to make ethelyene dichloride (EDC)and aftar (EDC) been cracked the vinyl chloride monomer (VCM) synthesis of vinyl chloride monomer.
3. The polymerization of VCM to make poly-vinyl-chloride (PVC).
4. The blending of PVC polymer with other materials to produce different formulations providing a wide range of physical properties.
5. The blending of PVC polymer with other materials to produce different formulations providing a wide range of physical properties.The blending of PVC polymer with other materials to produce different formulations providing a wide range of physical properties.

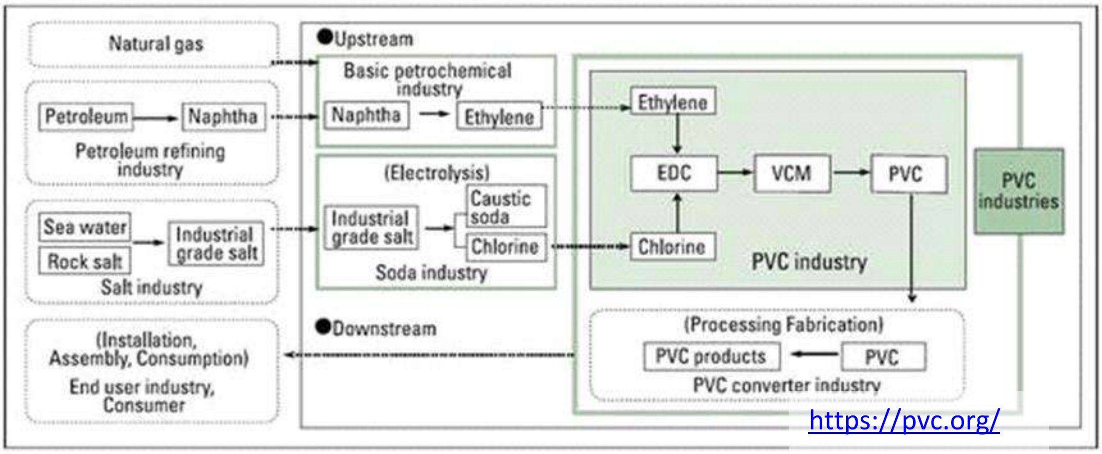

Fig I -3 : PVC production process

The petrochemical industries supply natural gas-derived ethylene. Ethylene is captured During a process known as cracking The liquid petroleum is heated and put under high pressure. As a result, the molecular weight of the chemicals found in petroleum feedstocks changes. Because of this change in molecular weight, ethylene can be identified, separated, and captured. It is then cooled to become liquefied. When the process of electrolysis occurs, chlorine, which is found in sea water extracted from salt, gains an additional electron. By passing a strong electric current through the salt water solution, chlorine is separated and extracted. The electric current will be strong enough to change the solution's molecular structure. When ethylene and chlorine combine, Ethylene dichloride (EDC) is formed. This is then subjected to another thermal cracking process, which produces the monomer vinyl chloride (VCM).

VCM is passed through a reactor containing a catalyst, where polymerization occurs. The chemicals cause the vinyl chloride monomers to react until links form between them. The joining of VCM molecules produces PVC resin, which is the starting point for all vinyl compounds. PVC has a nebulous structure and is naturally chemical resistant and fire retardant.[7]

I.3.2. polymerization of poly vinyl chloride

I.3.2.1 .polymerization major type of resins

Polymerization is the chemical reaction by which molecules add to each other to form a chain of large Length typically described by the following chemical structure :

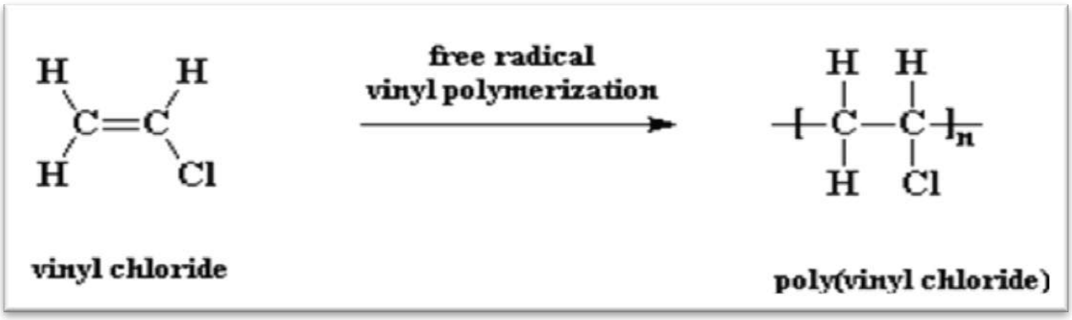

Fig I -4: vinyl chloride polymerization

The main polymerization methods include 4 different methods/techniques:

- Suspension polymerization.
- Emulsion polymerization
- Bulk or mass polymerization
- micro suspension polymerization

A. **polymerization in suspension**

is the most important method of PVC production about 80% of the total PVC produced today by the suspension The first step in the production of suspension is to feed vinyl chloride monomer into the polymerization reactor alongside water and suspension agents known as protective colloids are added to the reactor to prevent the monomer droplets coalescing and the polymer particles from agglomerating under the influence of heat and initiators and catalysts through high speed agitation, small droplets of vinyl chloride monomer are formed.

and the unreacted vinyl chloride monomer most of the water and the solid particles usually dried by centrifugation. The end result is polyvinyl chloride in form of white powder or resin, importantly all in reacted vinyl chloride monomer is recovered and recycled as a new initials.[5,8]

B. **polymerization Bulk(mass)**

bulk polymerization is carried out in the complete absence of water this method is used of liquid state monomers the important advantage of this method is the production of polymer free of impurities and the main problem is the difficulty in heat removal and this problem is solved by carrying out the polymerization in two stage Process :

In the first stage pure vinyl chloride monomer is polymerized up to 10% conversing using monomer-soluble free radical initiator this first pre-polymerization step determines the number of particles that will be formed. Heat is removed by continuously condensing the vinyl chloride vapor above the liquid reaction mixture.

In the second stage, the particles already formed grow by the formation of further polymers. The process is stopped when 70 – 90% of the monomer has been converted. In this method, no emulsifiers or additives are used. This helps to generate the purest form of PVC. [5, 8]

C. **Polymerization in emulsion**

Polyvinyl chloride is maintained in a stable emulsion in water with emulsifiers the monomer is trapped inside soap micelles that are protected by the soap. Surfactants (soaps) are used to disperse the vinyl chloride monomer in water the polymerization is activated by water soluble initiators after drying the emulsion produces polyvinyl chloride grain 15 to 200µm in diameters the product obtained are non-transparent easy to implement and tend to absorb water. This process produces finer particles and the product is mostly used in the manufacturing of plastisols.[8]

D. **polymerization micro suspension**

Micro-suspension polymerization is a technique that it is widely used on a commercial basis for the polymerization of vinyl chloride monomer into polyvinyl chloride. Like suspension use monomer soluble initiators but the polymer form as a latex of particles usually less than 2 Mm diameter Produces latex with a wide particle size polymerization take place within the dispersed vinyl chloride monomer droplets with highly soluble vinyl chloride monomer the initiator systems of this invention do not require the utilization of water

This invention reveals a vastly improved redox initiator system for use in polymerizations of this type. This invention's redox initiator systems consist of free radical generator, such as a peroxide, and a reducing agent chosen from the group consisting of ascorbic acid, is ascorbic acid, and certain ascorbic acid derivatives. This invention's initiator systems do not require the use of water-soluble metal salts. Water-soluble metal salts, on the other hand, can be used in such initiator systems in catalytic amounts where the water-soluble metal salt to free radical generator ratio is less than 0.09 mol .[9]

2. Copolymerization

Copolymers are produced when many monomers are simultaneously polymerized. The most prevalent is poly (vinyl chloride/vinyl acetate), also known as VC/VAC, which is characterized by a linear chain made of vinyl chloride and vinyl acetate molecules that randomly follow one another to form a copolymer. By using copolymerization, it is also feasible to create graft copolymers, which are made up of polymers grafted onto a different kind of molecular chain known as a "trunk."

Mention may be made of vinyl chloride copolymers that have been grafted onto ethylene acetate vinyl copolymers (EVA), polyacrylates, or acrylic core. [10]

3. Chlorinated

The chlorination process is used to change the properties of PVC, in this case clear PVC. It requires exposing PVC material to a precise and controlled amount of chlorine gas. Chlorination improves the ability of clear PVC to withstand the effects of high temperatures and chemicals. The chlorine gas reacts with the PVC material during the process, combining chlorine atoms with the polymer chain of the PVC. [5, 10]

I.3.Mixture based on polyvinyl chloride

I.3.1. formulation

Polyvinyl chloride is a thermoplastic that needs to have a variety of additives added to it in order to be used and shaped. Depending on the formulation, these additives which include plasticizers, stabilizers, pigments-lubricates, fillers, and flame retardants, can make PVC "compounds" that are rigid, flexible, transparent, or conductive. Other additives which may be used, processing aids, impact modifiers and Additives will influence or determine the mechanical properties, light and thermal stability, color, clarity and electrical properties of the product. Once the additives have been selected, they are mixed with the polymer in a process called compounding. One method uses an intensive high-speed mixer that intimately blends all the ingredients. The result is a powder, known as a ‘dry blend’, which is then fed into the processing equipment. The second method is to blend the ingredients in either a low or high-speed mixer and then transfer the powder to a melt compounder. This can either be a compounding extruder, or other special equipment for making PVC compounds.

These produce a melt which, when cool, is cut into granules ready for processing:

I.3.1.1. PVC additive

PVC requires a variety of unique additives to be added with it before it can be used to create items. A number of the product's attributes, including its mechanical characteristics, weather resistance, color and clarity, and even whether it should be used in a flexible application, can be influenced or determined by these additives. This process is called compounding. among PVC's many advantages and the reason it is such a highly adaptable polymer is that it is compatible with a wide variety of additives. PVC can be plasticized to make it flexible for usage in flooring and medical items. All PVC materials use lubricants, plasticizers, and heat stabilizers as functional additives. Flexible PVC also uses plasticizers. Optional additives include a range of substances from stabilizers, flame retardants, fillers, and pigments. In some flooring applications, the actual mass content of PVC polymer might be as low as 25%; the remaining mass is made up of additives. [5]

a. Functional additives

1. Heat stabilizers

Stabilizers are necessary in all PVC formulations to prevent the chain reaction of decomposition by heat and shear during processing. They can also enhance PVCs resistance to sunlight, and to weathering .In addition heat stabilizers have a significant impact on the physical characteristics and formulation costs.commonly used stabilizers and co-stabilizers based on:

Metals like "plead" are mostly used to create pipelines, strong construction profiles, and electrical wiring.

With other stabilizers of either mineral origin, calcium/zinc is widely used too. because of its great stability over time and very good chemical resistance to high temperatures.

The choice of heat stabilizer depends on a number of factors including the technical requirements of the PVC product.[11]

2. plasticizers

pvc becomes flexible and softer when plasticizer is added, increasing its plasticity and lowering its viscosity.

Whether a product will be used for a flooring application or a medical application, as well as the final properties required by the finished product, will influence the choice of plasticizers. There are over 300 different types of plasticizers, and only 50 to 100 of them are used commercially.

The most commonly used plasticisers are phthalates which can be divided into two distinct groups with very different applications and classifications:

- Phthalates are among the most widely utilized compounds in the field of plasticizers which can be divided into two distinct groups with very different applications and classifications:
- Low Phthalates: Low molecular weight (LMW) phthalates have a chemical backbone with eight or fewer carbon atoms.In Europe, the use of these phthalates is restricted to a few specialized applications
- Phthalates in high concentrations: High molecular weight (HMW) phthalates have 7 to 13 carbon atoms in their chemical backbone and are used in the construction industry to make electrical cables, flooring, or metal surfaces.
- Polymeric plasticizers, which are used in production tubers or that come into contact with hydrocarbons, food oil, and bitumen, have good high-temperature resistance and low volatility.
- speciality plasticizers such as Trimellitate plasticizers are employed in the manufacture of products with Special physical properties that requires the ability to resist very low temperatures or where increased flexibility is required, such as electrical circuit components, as well as in the medical and scientific fields.[11]

3. lubricants

lubricants are essential to reduce friction since friction can arise out of the separate process generally two type of lubricants may be required:

-internal: are those which reduce the friction arising out of polymer chain slippage with respect to each other (work on the PVC granules)

-external: are those witch help reduce friction between metal surface and the polymer chains in contact with it friction between the PVC and the processing equipment.[11]

b. Optional additives

These optional additives are not strictly necessary for the integrity of the plastic but are used to draw-upon other properties. Optional additives include processing aids, impact modifiers, fillers, nitrile rubbers, pigments and colorants and Flame Retardants. [11]

1.pigments/colors

pigment are insoluble organic or inorganic particles added to the polymers base to give a specific color to the plastic pigment that organic in nature are hard to disperse and tend to form clumps of pigment particles these can cause spots and speaks in the final product organic pigment metal oxides and sulfides carbon black etc..

easily dispersed in the resin but among the mall titanium dioxide is the most widely used pigment into plastic industry.[11]

2.fillers

minerals such as calcium carbonate, clay and carbon are added as fillers to polymers fillers increased rigidity, hardness and density and functional increase heat-deflection and reduce thermal expansion., depending on the role they play in PVC compounding

3. Flame retardants

Flame retardants are used in plastics to affect combustion. There are numerous flame retardants, the selection of which is primarily determined by the resin to which they are added. For example, the flame retardant could be added to keep temperatures below a certain combustion level, or to prevent combustion altogether.smother a reaction between the material and oxygen or other combustion .

flame retardants function on four basic principles: they insulate, create an endothermic cooling reaction, coat the product or actually influence combustion through reaction with materials with different physical properties.

Flame retardants can be inorganics like alumina trihydrate (ATH) or zinc borate, or organics like phosphate esters and phosphoric acid.[11]

c. Additional PVC additives

Blowing agents are additives that decompose at certain temperatures during processing to release gas, resulting in a foamed material. Processing aids are added to rigid formulations to increase melt strength and thus aid in extrusion. .Acrylic polymer resins of various molecular weights are frequently used .[7,11]

I.3.2.forms of processed PVC

I.3.2.1 .powder

PVC is produced by polymerizing vinyl chloride monomer. The raw material VCM is first pressurized and liquefied before being fed into the polymerization reactor, which is pre-loaded with water and suspending agents. The initiator is then fed into the reactor, and PVC is produced at 40 - 60°C under a few bars of pressure.

Water's role in the polymerization process is to remove and control the heat produced. PVC begins as tiny particles that grow until they reach the desired size, at which point the reaction is stopped and any unreacted vinyl chloride is distilled off and reused. The PVC is separated and dried, resulting in a white powder known as PVC resin.

To make sure that the additive in the PVC are mixed and command will two type of mixtures fast mixer the high speed of rotation of blades essures excellent dispersion of ingredients and with that the powder formed

and slow mixers their great mixing capacity and low energy consumption of agitation help get to the final product .[10,12]

I.3.2.2 .granules

The powder is directed towards a granulation unit, which generally consists of an extruder or an internal co-kneader in which the powder is gradually transformed into a viscous plastic mass under the combined effects of heat and mechanical shear a granulator equipped with a flat or perforated die and a cutting system in which the plastic mass (melted or previously cooled) is transformed into granules. [10]

I.3.2.3. viscous gel

Commonly known as plastisols, these materials are suspensions of small PVC particles (0.1 to 3 mm) made through the use of emulsion or micro suspension techniques. We can include stabilizers, fillers, pigments, colorants, and other materials in these pastes.

Plastisols are a suspension of small polymer particles in a liquid plasticizer, typically polyvinyl chloride (PVC). When heated to around 180 degrees Celsius (356 degrees Fahrenheit), the plastic particles absorb the plasticizer, causing them to swell and fuse together, forming a viscous gel Once this is cooled to below 60 °C (140 °F) it becomes a flexible, permanently plasticized solid product.[10]

I.4. poly vinyl chloride estate" properties"

I.4.1. Resins

is a white powder commonly used to produce the trrmoplastique by polemerization of vinyl chloride monomer VCM has a hight level of chemical resistance about cubic resistivity 3.5 .1013 S/ cm however it has poor resistance to aromatic and chlorinated hydrocarbons as well as retones and esters pare PVC is unstable to heat with 65 Mn heat stability and light its temperature is high between 75c and 85c with one weakness of PVC resin is ultra violet exposure the negative effect can be reduce by additives such as plasticizers in most cases however it is recommended to avoid this type of exposure.

according to its appearance and flexibility pvc is categorized into the following two categories:

- rigid pvc: use in constructions easy to process, resistant to corrosion ,chemicals and weathering
- flexible pvc: superior elasticity and tear resistant, soft and flexible ,resistant to weathering .[6]

I.4.2. transformed PVC

I.4.2.1. physical properties

is less rigid ,excellent stiffness up to near its transition temperture has high impact strength and fragile to shocks at low temperatures makes it easier to extrude or and less resistant to chemicals, and usually has lower ultimate tensile strength

The molecular structure of PVC is amorphous, . The presence of chlorine atoms and the amorphous molecular structure are inextricably linked. Although plastics appear to be very similar in everyday use, PVC has very different properties in terms of performance and functions when compared to olefin plastics, which have only carbon and hydrogen atoms in their molecular structures.[6]

I.4.2.2. Mechanical properties

PVC has great abrasion resistance, , and is fragile to impacts at low temperatures. PVC is syndiotactic and can organize itself in the crystalline phase, but the crystallinity rate never exceeds 10 to 15%. The mass volume of the PVC is 1.38 g/cm3. Amorphous PVC is transparent and relatively permeable to water vapour.

it is a chemically stable material that exhibits little change in molecular structure as well as mechanical strength. Long chain polymers, on the other hand, are viscoelastic materials that can be deformed by applying continuous external force, even if the applied force is well below their yield point. This is known as creep deformation. Despite the fact that PVC is a viscoelastic material, its creep deformation is very low when compared to other plastics due to limited molecular motion at ordinary temperature, as opposed to PE and PP, which have greater molecular motion in their amorphous sections. [6]

I.4.2.3 .Chemical properties

Plasticized PVC has better chemical resistance (up to 60° C) than plasticized PVC and resistant to acid and almost all inorganic chemicals. Although aromatic hydrocarbons, ketones, and cyclic ethers swell or dissolve PVC, it is difficult to dissolve in other organic solvents. PVC is used in exhaust gas ducts, construction sheets, bottles, tubes, and houses because of this property.Soft PVC is sensitive atmospheric agents and sunlight.Physiological-food action: vinyls may be suitable for the manufacture of objects complying with the regulations on foodstuffs and objects in contact with food.[10,13]

I.4.2.4. Thermal properties

PVC, like all thermoplastics, is very sensitive to temperature changes. The thermal properties typically determine use in low- and high temperature PVC starts to decompose when the temperature reaches 140 °C with melting temperature starting around 160 °C. The linear expansion coefficient of rigid PVC is small and has good flame retardancy, .PVC decomposes in a flame releasing gaseous hydrochloric acid but it is self-extinguishing. [10]

I.4.2.5 .Electrical proprieties

PVC has excellent electrical insulating properties, making it a primary choice for electric cables for residential buildings, vehicles… etc. but because of its higher polar nature the electrical insulating property is inferior to non-polar polymers such as polyethylene and polypropylene and generally suitable for medium or low voltage frequency insulating materials.[10]

I.5.Techniques for transforming PVC into a finished product Extrusion

Plastic extrusion is a process where granular pieces of the pvc plastics go through different components of the extruder to end up in a continuous profile with the help of heat and pressure.

Filling the hopper with smaller pvc plastic pieces that are easier to process is the first step in the plastic extrusion process. Gravity is used by the feed throat to transfer the plastic to the barrel for further processing.

When the material enters the barrel, it begins to be warmed by at least three intensity zones, with the intensity of the temperature increasing as you move away from the feed throat.

As the temperature rises, the barrel uses a continuously rotating screw to direct the molten pvc plastic to the next machine component. Because the screw and pressure generate heat, the intensity zones do not need to be as hot as the expected extrusion temperature, saving energy and facilitating the extrusion process. The liquid PVC exits the barrel via a screen held in place by the breaker plate. This screen keeps foreign substances out of the material while maintaining internal pressure. The material is fed through a feed pipe into the custom-made die, which has the same shape as the project's extrusion profile.

When the molten material is constrained through the die, it forms the same shape as the die opening, completing the extrusion process.

When the extrusion profile has passed completely through the die, it is cooled in a water shower or with a series of cooling rolls to ensure that the shape of your thermoplastic extrusion profile is permanent.

There are the 4 main types of pvc plastic extrusion processes that the industries use today:

Tubing extrusion, blow film extrusion, sheet film extrusion, over Jacket Extrusion there are also two types of extruders: witch are single screw extruder and twin screw extruders

In shortening PVC plastic extruder has the following components:

- **Hopper:** This is the first stage of the plastic extruder. Hopper stores the PVC in granulates and keeps it ready for the next stage of the process.
- **Feed Throat:** The feed throat directs the coming plastic from the hopper towards the barrel.
- **Breaker Plate:** This component acts as a filter for the barrel and helps maintain the pressure
- **Barrel:** This is a heated component that softens the plastic and takes it close to the melting point. Moreover, the rotating screw in the barrel forces the material to the feed pipe.
- **Feed pipe:** Acts as a conduit for the molten pvc coming from the barrel
- **Die:** This is the rigid metal part through which the material is pushed to get the desired profile.

Cooling System: Finally, the last stage where the extrusion profile solidifies through rapid cooling.[14,15]

I.5.1.Blow molding

With blow molding, the custom pvc plastic parts come out hollow and thin-walled when the pvc plastic part must have uniform wall thickness, this method is ideal and very similar to the glass blowing process.

The machine heats the raw pvc until it becomes liquid, then inflates it like a balloon with air. The pvc plastic is blown into a shaped mold, where it presses against the mold walls and begins to take shape. The liquid balloon is cooled after filling the mold to keep its shape

This technique is used for products like profiles, pipes, plates and sheets the choice of extruders and the operating condition of implementation depend on the form of presentation of the ready to use mixture

Also this process has a super-fast production cycle. It can produce hundreds of thousands of hollow parts within a short period of time. It can produce about 1400 pieces

(The number can significantly change depending on the product being produced) in around 12-hour work time.It’s also very versatile in terms of applications. It is often used for producing drums, plastic bottles, containers, cases, fuel tanks, etc and easy for customization, making it a lucrative option for the food and pharmaceutical industries.

Another common type of blow molding process is injection blow molding. is commonly used to make plastic bottles in one or two stages. It's especially useful for making bottle pvcplastic based preforms, which are then sold to bottling companies or used to make bottles. When discussing molding processes, the terms "blow molding" and "injection molding" are frequently used interchangeably. While they are similar, they are not necessarily the same. In both blow molding and injection molding, pvc liquid plastic is forced into a mold cavity. The distinction is that blow molding produces hollow objects, whereas injection molding produces solid objects. Only blow molding provides a quick and efficient solution for hollow objects for manufacturing companies. [14, 15, 16, 17]

I.5.2. Calendaring

Calendaring is a continuous process involving the use of a series of heated rolls that are fed with a pre-compounded paste-like mass. As this paste-like mass passes through consecutive roll nips a continuous sheet is formed to an appropriate thickness. PVC constitute the majority of calendered thermoplastic Plastic calenders are generally made in four basic configurations:

- The “I” calendar.
- The “L” calendar – offset roll is on the bottom and the take-off is from the top roll.
- The “F” calendar – offset roll is on the top and the take-off is from the middle roll, on the offset roll side.
- The “Z” calendar – the calendar has two offset rolls, and the take-off may be made either from the top or bottom offset roll, or from the backside of the stack roll. And consists of five main components Plasticating unit, Calender, Cooling Unit, Accumulator, Wind-up station. The first step in the calendering process is to melt and mix the pvc peices uniformly. This is accomplished in the plasticizing unit, where the pvc peices is melted and mixed using an internal batch mixer or a roll-mill. The paste-like mass is then fed between the nips of the first two rolls; the feeding rate is controlled by the first pair of rolls, while the sheet thickness is calibrated by subsequent rolls in the calender. As the plastic moves under high pressure between several calender rolls, the temperature of the pvc plastic material rises sharply. As it

enters the nip, the pool of material begins to rotate at high speeds and develops a vortexing action, producing a lot of frictional heat.The web widens as it exits the calendar nips The width of the sheet on the calender rolls is determined by the final product trimmed width. It is frequently desirable to cool the surface of the roll from which the web is removed. The take-off is made up of a series of rolls of varying diameters. These rolls run at a higher surface speed than the calender rolls in order to have a positive draw into the sheet.

After exiting the take-off section, the web is fed into an embossing unit. The embossing unit can be arranged vertically or horizontally. The embosser unit consists of two rolls: an engraved steel roll pressing against a rubber-covered roll. The depth of the indentations or embossing in The hardness and thickness of the rubber covering, as well as the pressure applied by the steel roll, will determine the hardness and thickness of the plastic sheet. To remove plasticizers and keep the rubber cover cool, cool water is circulated inside the steel arbor and on the outside of the rubber covering.

After exiting the embossing roll section, the web is routed through one or more series of cooling drums.

An edge slitting or trimming unit is located after the cooling drum and before the windup. This unit trims the unwanted excess sheet width from the web. A take-up system pulls the web onto the cylindrical roll for storage after it has been trimmed to the final trimmed width. [14, 15, 17, 18]

I.5.3. Injection molding:

is a manufacturing process, where a liquid pvc resin is injected into the empty cavity of a forming die, taking on the shape of the interior surface. When this resin is cooled and solidified, the forming die opens, the finished part is ejected For smaller plastic components and parts, or parts that require high levels of detail or varying thickness, we use polyvinyl chloride injection molding. This is a more intensive method of plastic manufacturing because it requires designing a double-sided mold made from steel, aluminum, or copper alloy. the PVC is melted to a liquid state and injected into the mold, creating a detailed, highly accurate finished shape that is either ready for painting or customization or to be packaged and sold It is ideal for producing large quantities of plastic products for a variety of industries and individuals.[14,15,17,19]

I.5.4 .Compression molding

Compression molding is on the earliest forms of molding it requires only on mayor piece of equipment the compression press compression molding involves shaping a measured quantity of plastic within a mold by applying pressure and heat. this method works by pouring The raw liquid pvc into a heated mold and compressed together to form the desired shape . The high temperature of the entire process ensures that the final product is strong. After that, the liquid pvc is cooled to keep its shape before being trimmed and removed from the mold. Compression molding and injection molding are very similar, but there is one significant difference between them. Molds are closed around the charge in compression molding, and the charge is injected into a closed mold cavity in injection molding.

Manufacturers nowadays frequently use compression and injection molding, but for different types of parts. Injection molding is usually a better choice for more complex parts, whereas compression molding is ideal for relatively simple designs, such as ultra-large basic shapes that cannot be produced using extrusion techniques.

The molding method is used for producing plastic parts replacing metal. The main reason behind that is the strength, lightweight, durability, and corrosion resistance of the product it can also produce parts with complex geometries if the liquid pvc is spread properly in the bottom film.

There are three parameters of importance during compression:temperature induces or reduces viscosity. Lower viscosity improves the flow and consistency of the charge, time The charge may be compressed gradually, sometimes with holding time (a period during which the charge remains compressed and heated) and pressure should be higher for a more dense charge to achieve a comparable effect Compression molding has several benefits/advantages. These advantages include: low-cost operation, good surface finish, faster than some methods, flexible design. [20, 21]

I.5.5 .Rotational molding

This method, also known as rotomoulding, involves placing the pvc resin inside the mold and then rotating it at high speeds. The pvc resin then evenly coats the entire surface of the mold, resulting in a hollowed part with uniformly thick walls. After the mold has cooled and the plastic has taken its new shape, it is removed from the mold.

This method is very material efficient, with very little waste, making it more cost effective and environmentally friendly.

The most common use for this method is for big and hollow parts. These parts include car parts, bins, road cones, pet houses and storage tanks.

The molds that are used in rotational molding are highly intricate to make products customizable and changeable. This can include things like special inserts and curves as well as logos and slots. These can be placed into the mold to change the final product.

There is no limit in terms of the size of the part being produced. That's the reason why rot molding is an ideal method for producing tanks, plastic boats, shopping cart accessories, etc.[14,15,17]

I.5.6.Thermo molding

involve the heating of thermoplastic sheet or film to a specific temperature making it flexible and soft and forcing it around the contours of a mold vacuum, air pressure or mechanical force are employed to lid in the sheet or film product by extrusion or calendaring process sheet and film can be laminated or ported to thermoforming

Very flexible to consumer needs in terms of complexity, size, and other attributes.Its excellent production efficiency can save a significant amount of time and resources, which can be utilized for other things. [14,15,17,22]

I.5.7. Finishing process

products produced by molding and forming may also require finishing to render the final products such as machining, decorating and assembling and decorative finishes

I.6.Application of PVC

Polyvinyl chloride (PVC) is one of the most used plastics in the world. Global use of polyvinyl chloride resin exceeds 40 million tonnes per year, and the demand is growing. Globally, PVC use grows by an average of 3% per year with higher growth rates in developing countries.

Due to its exceptional versatility, PVC is found in an endless array of products that, in one way or another, enhance our daily lives.

I.6.1.Constractions

Studies find that PVC building and construction products are more energy efficient to manufacture the biggest market for PVC, accounting for 76 per cent of demand PVC has been used extensively for over half a century in the construction industry About three-quarters of all vinyl produced goes into long-lasting building and construction the abrasion resistance, light weight, and strength of PVC are important technical benefits for its use in building and construction like

- Floor and
- Wall coverings
- Cladding
- Roofing membranes
- Window and door profiles

They, like all other PVC applications, can be customized with a wide range of colors and shapes it can be cut, welded and joined easily in a variety of styles PVC has been a popular building material for decades due to its physical and technical properties, as well as cost-performance advantages. and any other public building that requires a high level of hygiene and safety. Vinyl pavers are waterproof, fire resistant, and easy to clean

And wall coverings, they are designed with high thermal insulation and exceptional weathering performance, as well as good UV light resistance, and are useful even for refurbishing older homes.[23,24]

I.6.2.Healthcare

PVC possesses the largest share of the medical market, constituting 40% of all dedicated polymeric materials. It is the first choice for medical applications due to its inertness, high transparency, facility of sterilization and strength has been used for hundreds of life saving and healthcare products for almost 50 years for surgery pharmaceuticals drug delivery medical packaging due to its unrivaled performance we find it in every divers application:

• Blood bags;
• Catheters;
• All kinds of pipes and small tubes;
• Surgical gloves;
• Oxygen masks;
• Sterile packaging;
• Miscellaneous medical equipment
• Inhalation masks.[25]

I.6.3.Automotive

A modern road vehicle's average service life is now 17 years, up from 11to 12 years in the 1970s. PVC has made a significant contribution to this as the primary underbody protector (in the form of a wear-resistant coating), as humidity sealants, and in other protective profiles. PVC's durability has also made it a popular choice for cladding interior parts such as dashboards and door panels. instrument panels and associated moldings ,interior door panels , seat covering and the softness of its touch combined with its heat stability (when the vehicle is parked in direct sunlight) are unparalleled and makes cars last longer

The following characteristics will be appreciated in the automotive sector:

- Increased service life
- Lower energy consumption
- Contribution to passenger safety
- freedom of form;
- Acoustic comfort
- Reduction in the cost price
- Recyclable.[10,26]

I.6.4.Electrical

PVC (Polyvinyl chloride) is widely used in the construction of electrical cables for insulation, bedding, and sheathing in various fields: classic electric cables for power transmission at low and medium voltage for homes and offices; telephone cables; coaxial cable, TV, computer, wi-fi; cables for cars; battery cables and robotics; data transmission cables. Due to its ease of processing, PVC began to replace rubber insulated and sheathed cables in general household wiring in the 1950s. PVC is inexpensive and has excellent aging properties, with a typical service life of 25 to 30 years. PVC insulated or sheathed cable is flame retardant, which is an important consideration for most electric cables. PVC can be made chemically resistant, including oils and acids and it is tough, durable, and abrasion resistant. The addition of various additives can improve its temperature range, which is typically between -40 and 105°C, as well as its resistance to sunlight.[24]

I.6.5.Pipes

Polyvinyl Chloride Pvc pipes are the most commonly used plastic piping material collectively considered to be the largest PVC application by quantity and weight mass using PVC into water one of the fast scenarios that implemented PVC into modern society

The pipes are used to supply water in different areas like buildings, industries, facilities, and equipment and manufactured in various dimensions and sizes. pvc pipes are extensively used in sewer systems, irrigation, water service lines, drain waste vents, and various industries.whether its Pipes for Water Plumbing,Pipes for Agriculture,Industrial Use or Pipes for Chemical Handling it is currently one of the most cost-effective materials on the market. Furthermore, it is lightweight, durable, and simple to install. PVC pipes can withstand temperatures of up to 140° and pressures of up to 160 psi. Overall, it is a very tough material. It is abrasion-resistant, chemical-resistant, and resistant to a wide range of weather conditions. All of these factors combine to make PVC a long-lasting material that can be used for approximately 100 years. Furthermore, these infrequent replacements contribute to a lower environmental impact.[27]

I.6.6.Packaging

This is the second outlet for this polymer. 17% of plastic material used in packaging are PVC. Like many plastic packaging materials, and its extremely durable. on the other hand, has a higher impact tolerance and is highly reliable in terms of barrier protection

in pharmaceutical bags pvc contain possess a number of advantages wish make it a widely used material suitable for pharmaceutic packaging the main ones are

its ability to steam sterilized at 121C°its favorable cost performance

its low weight leading to low storage.

its strength resistance to breakage and transparency .

its flexibility.

in food packaging:

the use of pvc plastic is extremely common in the packaging industry.due to its rapidly gaining popularity in packaging applications in both the first- and second-level production of packaging materials because of their notable mechanical, thermal, and solvent-resistant properties pvc used in food packaging applications and replaced many traditional materials, including glass (used in bottles) and various types of card and paper. PVC food packaging has several advantages over traditional materials:

- PVC is lighter than glass, which has the added benefit of lowering transportation emissions due to the weight reduction (Association of Plastics Manufacturers in Europe, 1990)
- It is shatter resistant, which was seen as a huge benefit because it would reduce the number of glass-related accidents at home and outside.
- It has outstanding organoleptic properties:
  - PVC has no taint or taste in foodstuffs.
  - PVC can be made with high clarity and visibility of the product.
  - It has good barrier properties for ratio of performance.
- It is reasonably priced.
- It is possible to create innovative product shapes and complex designs.[29,30]

I.6.7.Sport

Every sport requires specifically designed sports equipment. In order to make sports equipment with the desired specifications, the selection of materials is extremely important. Flexible PVC is especially important in sports and can be found in a variety of applications. The combination of cost efficiency, durability, and light weight makes it ideal for roofs and flooring in permanent and temporary sports venues, as well as a wide range of sporting goods and equipment that support and enhance the performance of athletes are of prime importance in sports. Plasticisers make PVC bendable and soft, allowing it to withstand significant physical stress without breaking while also providing an infinite array of aesthetic and creative possibilities. When it comes time to replace it, flexible PVC can be reused and recycled to create new applications. Besides stadiums and large venues, flexible PVC applications are essential for a wide range of amateur and professional sports. Plasticised PVC can be found in tennis nets, in the floors of gyms and playgrounds, in balls, bags and mats, boxing gloves, clothing, footwear, etc. The list is endless. Its versatility, its unbeatable cost-efficiency ratio as well as its low maintenance requirements have made it a widespread material for decades in all kinds of sports.[30]

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CHAPTER II

PolyVinyl Chloride Recycling

II.1.Sources of PVC wastes

There are two principal sources of PVC wastes: pre-consumer and post-consumer wastes.

II.1.1.Pre-consumer wastes

Consist of both production and installation wastes .Production waste comprises compound left over from the manufacture of PVC products, such as batch remainders from extrusion mouldings and various trimmings and off-cuts from sheet and profile manufacture. This material is available in a clean condition at the point of production and consequently most is recycled internally within the manufactory process and so never enters the external waste stream.

Additional pre-consumer waste comes from trimmings left over from, for example, flooring and replacement window installation and replacement pipework. [1]

II.1.2.Post-consumer wastes

Consist of products that have been discarded at the end of their useful lives. As a result, post-consumer wastes tend to be dispersed in low abundance over a large number of users and typically require extensive cleaning to remove contaminants before they can be used for recycling. [1]

II.2.Wastes classification

All PVC waste, regardless of its origin, whether household or industrial, is classified at the French and European levels into:

in the vast Category of wastes that are neither inert nor hazardous:

- House hold waste
- Similar waste
- Non-hazardous industrial waste

Approximately 23 million tonnes of household waste are generated in France each year, equivalent to an average of 1 kilogram per person per day. Plastics make up 20% of the overall volume of household waste and 11% of its weight, with PVC accounting for less than 1% of the plastic waste.

II.2.1.Manufacturing wastes

"Manufacturing waste" refers to the leftover materials and discarded pieces produced during the processing industry's manufacturing of finished products, specifically in the case of plastics. For instance, when plastic parts are manufactured through injection molding, approximately 10 to 15% of plastic waste is generated due to the presence of excess material (referred to as the "carrot") resulting from the resin being injected into the mold. [2]. There are two industrial methods for producing vinyl chloride monomer (VCM) using different two-carbon hydrocarbons. The first method is known as the "balanced process" and utilizes ethylene, while the second method is called the "carbide" process and relies on acetylene. [3]

II.2.1.1.Balanced Process

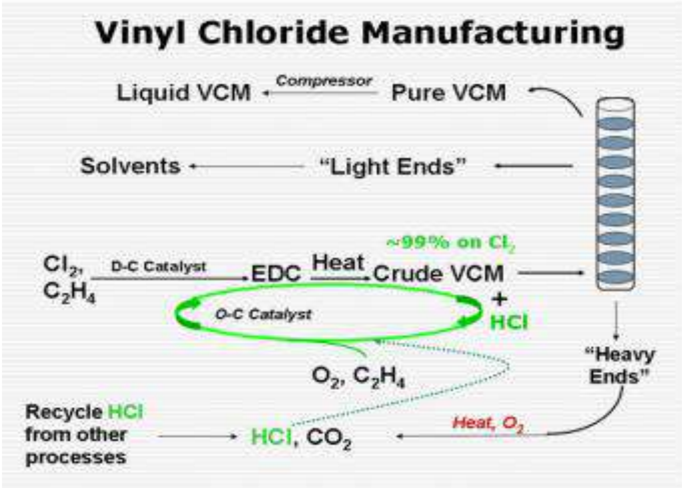

Fig II-1: Schematic representation of vinyl chlorid manufacturing. [3]

In the balanced process of VCM production using ethylene, a small portion (approximately 1-2%) of higher boiling point materials, referred to as "heavy ends," are formed. These heavy ends contain high levels of chlorination and may contain chlorinated dibenzodioxins and furans, which are considered environmental pollutants. To ensure environmental safety, the heavy ends are treated through either combustion or thermal oxidation processes. These treatments result in the generation of mainly carbon dioxide (CO2) and hydrogen chloride (HCl). The HCl can be isolated and recycled through oxychlorination or can be sold as a commercial grade aqueous solution called muriatic acid**.** . [3]

II.2.1.2.Carbide Process

The carbide process is an old method for producing small-molecule organic compounds that predates the modern petrochemical industry. The process involves synthesizing calcium carbide from limestone and coke at a temperature above 2000°C and then reacting it with water to produce acetylene. VCM is produced by directly adding HCl to acetylene over a mercury chloride/activated carbon catalyst. The resulting VCM is washed with water and base, and then distilled. However, the wash water and spent catalyst must be treated to remove and recycle mercury. [3]

II.2.2.Waste management

Four studies have been commissioned by the Commission services to assess the technical aspects of the main options for the management of PVC waste:

- Mechanical recycling.
- Chemical recycling.
- Incineration.
- Left at the dump.[4]

II.2.2.1.Mechanical recycling:

Refers to the recycling processes in which the waste is PVC is processed only mechanically, mainly by cutting and screening and grinding. The resulting recycled material can be processed (in powder form) in new products. Depending on the degree of contamination and composition from the materials collected, the quality of recycled plastic can vary widely. The quality of recycled materials determines the degree to which raw materials can be substituted Use of recycled materials: "high quality" recycled materials can be reused.

Same types of PVC applications while 'low quality' recycled materials from mixed waste fractions can only be recycled into lower value products ("down-cycling"), usually made of other materials.

II.2.2.2.Chemical recycling

Involves a number of processes by which the polymer molecules that make up plastic are broken down into smaller particles. These monomers can be directly usable to produce new polymers or other materials that can be used elsewhere as base chemicals. In the case of PVC, in addition to fragmentation of the polymer particle chain, Chain chlorine is released as hydrochloric acid (HCl). Depending on the technology used, HCl can be reused after purification or it must be neutralized to form different products that can be used or discarded. [4]

II.2.2.3.Incineration

Not all plastic waste can be recycled. Some of them will have to be burned to greatly reduce the size. In an incinerator, PVC is converted to carbon dioxide, water, hydrochloric acid (HCl), and some metal chlorides. Half of the chlorine in incinerators comes from PVC, while the other half comes from wood, paper and vegetable waste Foods that contain salt.

a)Carbon Dioxide (CO_2)

Carbon Dioxide Given the special chemical composition of polyvinyl chloride, the amount of carbon dioxide per kilogram of material generated during PVC incineration is significantly higher.

Less than the result of burning other materials such as oilor wood, charcoal, or other plastics. Thus, burning PVC waste contributes less to global warming.

b) Hydrochloric Acid (HCl)

The incineration of PVC waste produces acid Hydrochloric acid (HCl) in the flue gas, which must be neutralized, unless it is recovered. This hydrochloric acid must be removed from the flue gases

before being released into the atmosphere. To do this we use Neutralizing agents such as lime that convert hydrochloric acid into calcium or sodium chloride. [4]

c)Dioxin

Dioxin is a generic name that refers to a group of 210 substances belonging to dibenzoparadioxins and dibenzofurans.[4]

II.2.2.4.Landfilling

is increasingly restricted in many countries and it is the least preferred option in the waste management hierarchy .[5]The potential for PVC waste to be biologically and chemically inert Technically, the landfill can be recovered without any inconvenience other than visibility and loss of resources. Therefore, new regulations must be added to reduce this waste pattern it has been found from studies that rigid PVC does not degrade and that plasticized PVC degrades very slowly. A very pessimistic estimate of the time it will take to reach the onset of degradation, which corresponds to 1-2% dehydration, is several hundred years. These characteristics explain why PVC membranes, It is used to line the bottom of technical landfills to avoid contamination from waste to the ground and possibly to the groundwater table. [2]

Table II-1:The comparison of different approaches for disposing of PVC wastes. [6]

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	Small
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

II.3.Recycling of poly vinyl chloride wastes

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:[6] By comparison between the past and present situation in Europe, we note that the amount of recycled PVC is constantly increasing, reaching 194,950 tons in 2008,With the continued increase in the amount of recycled PVC, reaching 640,000 tons in 2017 (figure2).

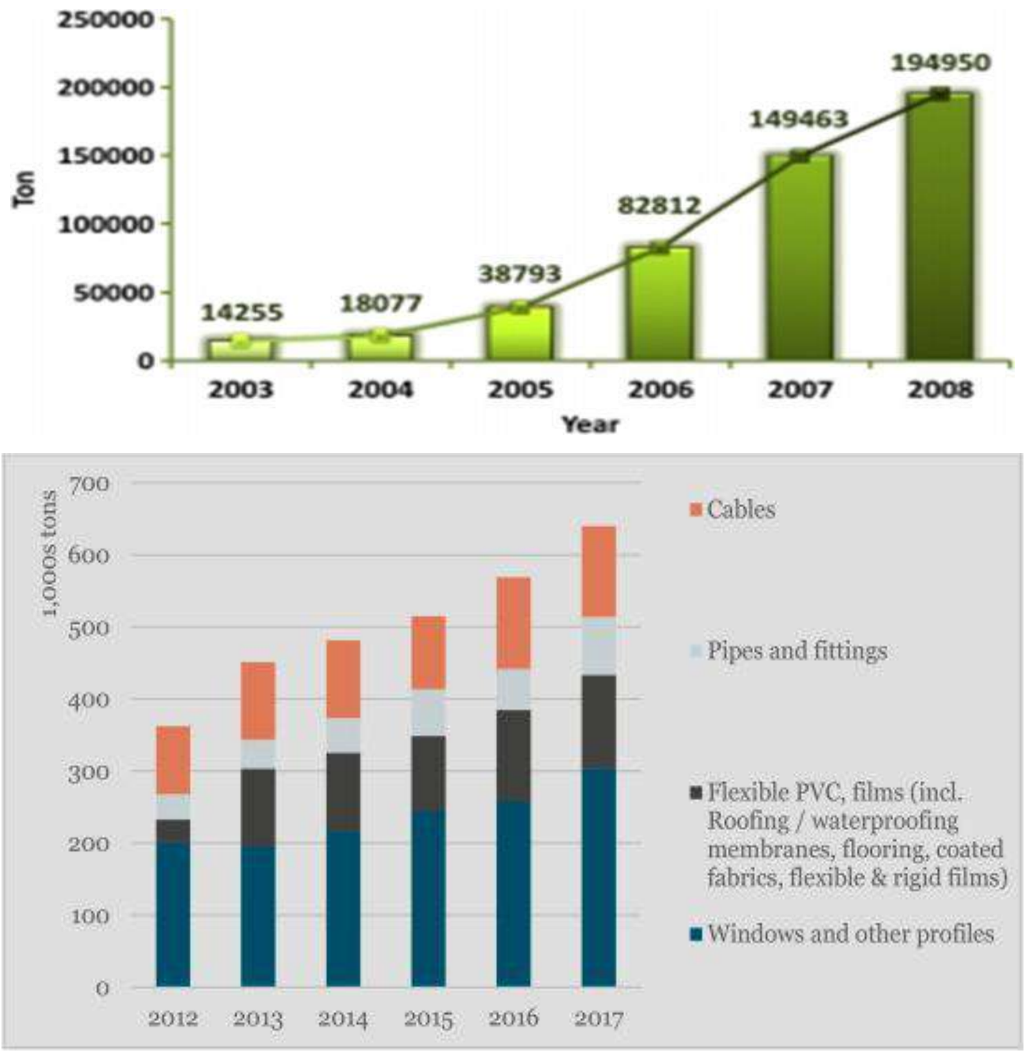

Fig II-2: the tonnage of recycled PVC Europe from 2003 till 2017. [5], [6]

II.3.1.Methods of PVC recycling

The basic PVC recycling system is schematically shown in pvc can be subject to both mechanical recycling processes and feedstock recycling:

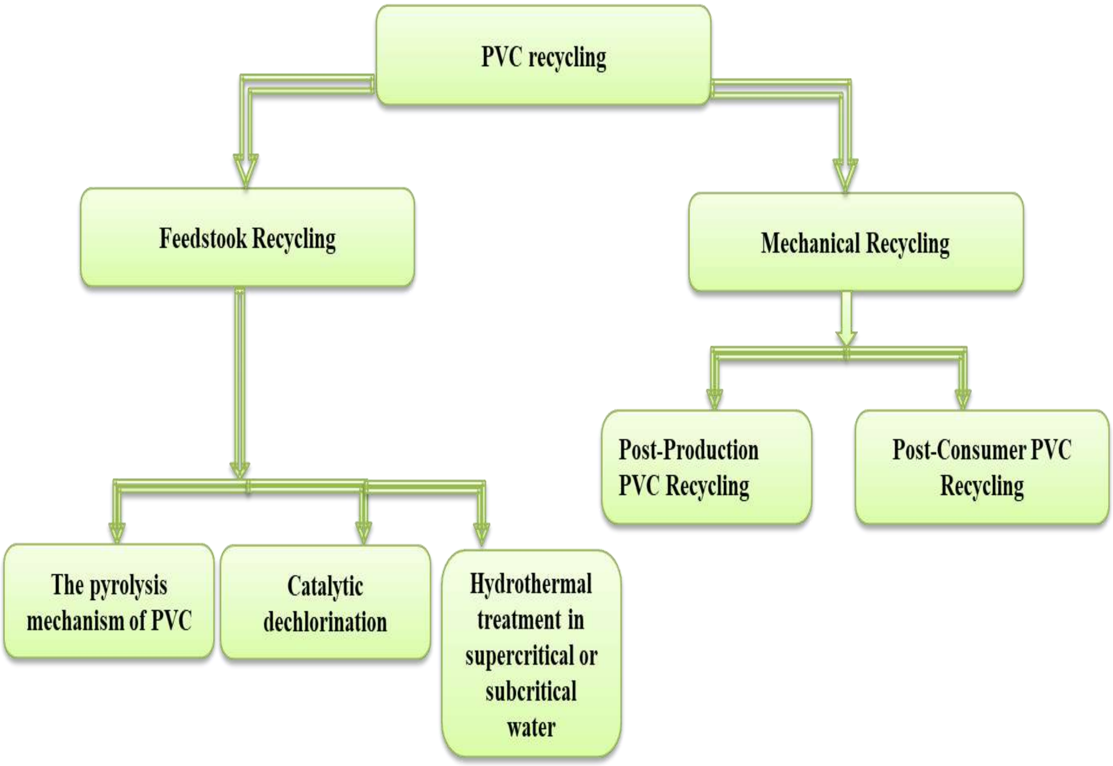

Fig II- 2: Simplified scheme of poly vinyl chloride recycling system

II.3.1.1.Pvc Mechanical Recycling

The “material recycling” or so called “mechanical recycling” is a technically relatively simple and usual recycling method in plastics industries. Mechanical recycling is a preferable method whenever sufficient quantities of homogenous and sources eparated waste stream can be made available. 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. In this approach, the plastics are collected and sorted by hand and/or by machines at reprocessing plants . 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. [6]

a) **Post-Production PVC Recycling**

It has been proven that un plasticized PVC can be processed many times without visible signs of deterioration. In addition, the number of times that the same material can be processed can be greatly increased by mixing recycling with virgin material by more than 30%, that is, waste of a certain composition, which is mainly produced in the processing plant, can be reprocessed by grinding .

Ground PVC waste can be directly processed into other products. For technical reasons, it can be made into granules, although each subsequent treatment may reduce the thermal stability of PVC.

PVC waste can be pulverised. In this process, the PVC is crushed to a particle size similar to the original PVC grain. This enables the introduction of PVC recyclate into the virgin PVC at the stage of producing dry blends.

Waste from companies producing windows made of PVC profiles is a relatively large stream of PVC recyclate, with stable properties and compositions of the blend. However, this requires the separation of protective veneers and metal waste from window fittings and plasticised PVC or EPDM, which is used as a material for seals.

Pvc recyclates have been successfully used to produce a wide range of composites, often with a high degree of filling. It has been shown that the slight contamination of PVC with incompatible polymers does not significantly affect the properties of these composites.

a) Post-Consumer PVC Recycling

Another issue is post-consumer waste management. Excellent weather resistance and aging process make PVC products, such as window profiles, building profiles, pipes and cable insulations, long lasting. The waste supply of these products can be expected to increase in the near future, as their 30-40 years of use are about to expire. Although the PVC in this waste does not decompose significantly and could constitute a valuable raw material for recycling, there may be hurdles in managing it. Over the years of using PVC products, legal regulations have changed that prohibit the use of certain chemical compounds, such as polymer additives. In the case of PVC, stabilizers containing lead (Pb) and some phthalate plasticizers are particularly problematic. Solutions are being developed to effectively separate these compounds from recycled PVC materials.

Products with a short life of less than two years make up only 15% of the total amount of PVC products. These are mainly bottles and containers. PVC has several uses, for example in the production of packaging labels made of other polymer materials, in particular PET beverage bottles, pharmacy packaging, and household chemicals made of PP and PE. Mechanical separation of PVC from this waste stream is not a problem. Sedimentation and gravimetric methods are excellent for the separation of polyolefins, since due to the large difference in density between materials. In separation from PET, high efficiency is achieved using electrostatic, flotation or differential hardness methods. For powdery materials, water snails can be used. The PVC raw materials obtained from the recovery process can be successfully processed into a number of new products, particularly polymer composites. [7]

II.3.1.1.1.Mechanical recycling for mixed plastics

Plastics Europe has extensively researched the topic of mechanical recycling for mixed plastics waste, including PVC. In situations where homogeneous plastic streams are not accessible, recycling methods tailored for mixed plastics can be employed. The presence of up to 15 percent PVC in mixed plastic waste is generally not regarded as a technical obstacle. However, it is important to note that the quality of the recycled material may be suitable for only a limited range of applications. Plastics Europe has published a technical report on this subject titled 'The mechanical recycling of mixed plastics waste.[8]

II.3.1.1.2.Description PVC recycling systems

Typically involve several steps to collect, sort, PVC recycling systems materials. Here is a description of the common processes involved:

1. **Collection**

PVC waste can be collected through various methods, such as pick-up systems or bring systems. These systems may collect waste in pure PVC fractions or mixed fractions that include PVC along with other materials.

2. **Sorting**

If PVC wastes are collected in mixed fractions, sorting plants are employed to separate different materials and obtain pure PVC materials for further treatment. These sorting plants use different techniques to separate PVC from other materials, such as size reduction, magnetic drums to separate ferrous metals, and other separation units.

3. **Mechanical Treatment**

The mechanical treatment process aims to automatically separate pure PVC fractions from other materials and produce recyclates with a defined particle size. This process typically involves shredding units to reduce the size of the materials, separation units to extract specific sizes or materials, and mills and extruders to convert the separated PVC fractions into re-granulates. Transportation, depending on the organization and location of the recycling plants, transportation may be required between each step of the recycling process to move materials efficiently.

Through specific recycling organizations or free markets and the type of financing, such as waste fees or fees incorporated into the price of related products. The overall goal is to establish an efficient and sustainable PVC recycling system that reduces waste and promotes the reuse of PVC materials. and process PVC waste materials. Here is a description of the common processes involved:

The recycling systems produce two main types of recyclates:

- **High-quality recyclates**

These recyclates have a low degree of contamination and can be reused in the production of the same PVC products. They are of high value and contribute to a circular economy.

- **Low -quality recyclates**

These recyclates are of lesser quality and are typically used as substitutes for non-PVC materials. They are commonly referred to as "downcycling" because they are used in applications other than PVC products, such as general plastic, concrete, or wood products. In addition to the material flow and technical processes, the recycling system's organization plays a crucial role. This includes the management of material.

flows through specific recycling organizations or free markets and the type of financing, such as waste fees or fees incorporated into the price of related products. The overall goal is to establish an efficient and sustainable PVC recycling system that reduces waste and promotes the reuse of PVC materials especially. To describe the various recycling systems, the following criteria have been utilized(fig 3):

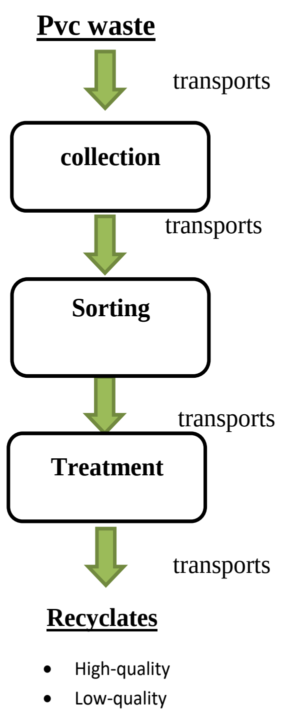

Fig II- 3: recycling system for pvc wastes)schematically(.[9]

II.3.1.1.2.1.Description of selected recycling systems

a. **mechanical recycling of pre-consumer PVC waste**

- **Methods and technologies**

1. The PVC wastes are collected by the PVC processors (production wastes) and the users of PVC intermediate products (e.g. the packaging industry using PVC films) and the handicraft enterprises installing PVC floorings, roofing membranes and other products.
2. Depending on the specific application the PVC wastes must be treated in a mechanical process (grinding) to produce regranulates of a defined size and composition. Some of the plants for the mechanical treatment of pre-consumer wastes simultaneously process PVC post-consumer wastes
3. The recycling material can be bought by compounders which often blend it with virgin PVC to produce compounds of a defined quality.

b. **mechanical recycling of pvc cable insulation**

- **Methods and technologies**

1.Collection: The cable insulation material is a byproduct of the cable recycling process**.**

2.Treatment: Typically, the cable insulation material is utilized by plastics processors for various applications such as extrusion or injection molding of plastic products.

c. **mechanical recycling of pvc window frames in Germany**

- **Methods and technologies**

1.Collection

The collection service provided by VEKA's transport services the independent container services that collect materials from these locations.

2. Sorting and Treatment

The VEKA [10] recycling plant has been constructed on the principle of maximum automatisation. The mechanical treatment process consists of the following major unit operations (Figure 4).

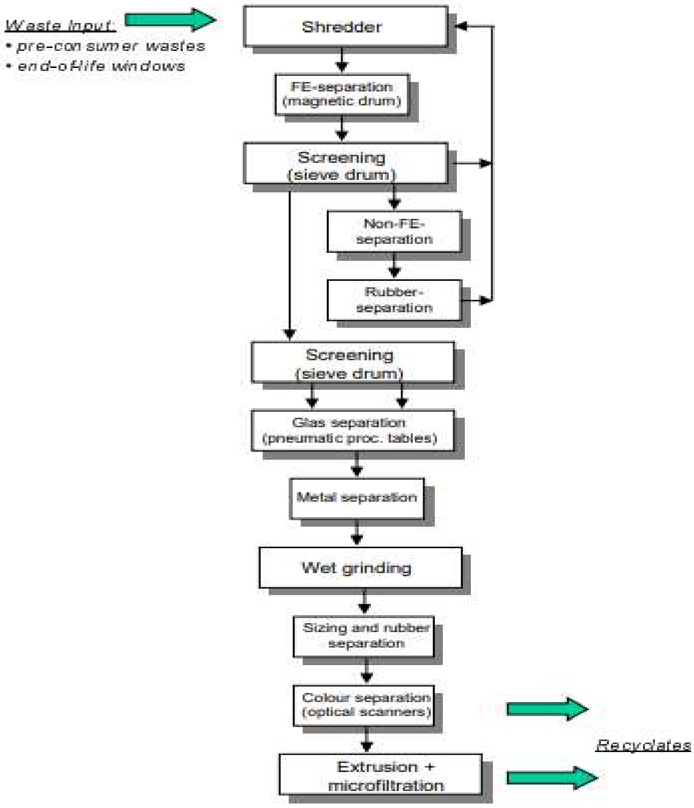

Fig II- 4: Recycling Plant for PVC Window Profiles (VEKA (. [9]

d. mechanical recycling of pvc pipe in the Netherland

- **Methods and technologies**

1. Collection

Approximately 50 collection points have been established nationwide where used pipes can be delivered at no cost. Additionally, rental containers have been installed at specific customer locations.

2. Sorting and Treatment

There exists one recycling plant at the company Wavin.(Figure 5).

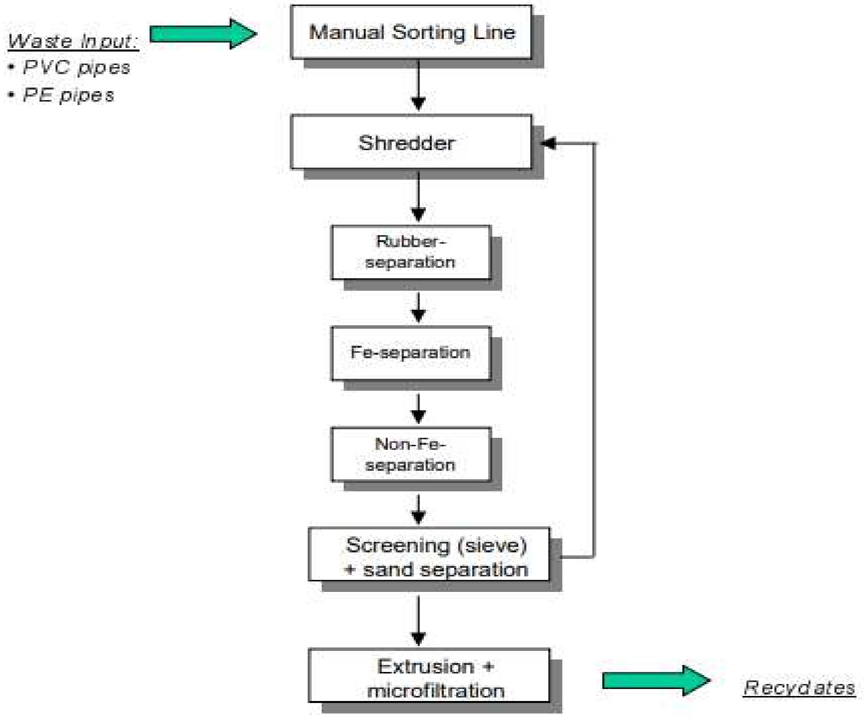

Fig II-6: Recycling Plant for Plastic Pipes (Wavin). [9]

e. mechanical recycling of pvc bottles in France

- **Methods and technologies**

1. Collection

PVC bottles are collected alongside other plastic bottles as part of the recycling process. The collection system can vary between a kerbside collection or a drop-off system, depending on the specific municipality. Once collected, the bottles are taken to a sorting station, where they undergo manual sorting into different fractions such as HDPE, PET, and PVC.

2. Sorting and Treatment

Eco-Emballages, the organization responsible for the recovery and recycling of packaging wastes, works in collaboration with Valorplast for the recycling of sorted PVC bottle fractions. Once collected, the PVC bottles are transported by Valorplast to a

Recycling plant near Paris. At the plant, the bottles undergo sorting using X-ray technology to separate any remaining PET bottles. Subsequently, the PVC bottles are processed through grinding and micronization, reducing them into fine particles for further use in recycling processes.

f. mechanical recycling of pvc floorings in Germany

- **Methods and technologies**

1.Collection

Approximately 20 central collection points have been set up for the delivery of used pipes. It is the responsibility of the "waste owner" to arrange and cover the costs of transporting the pipes to the collection points.

2.Sorting and Treatment

The mechanical treatment of the PVC material is carried out at a single recycling plant using a cryogen (low-temperature) grinding process. This process enables the grinding of flexible PVC material. The treatment process involves several major unit operations, as depicted in (Fig 6).

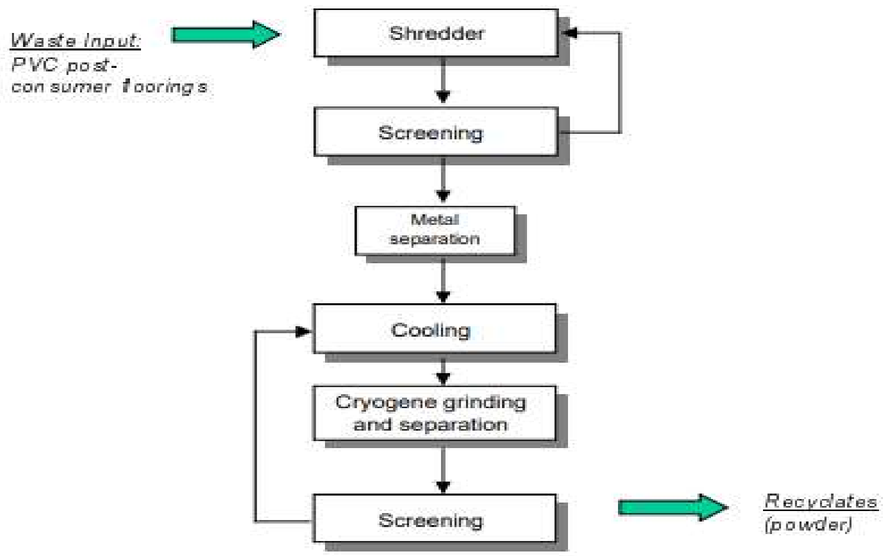

Fig II-7: Recycling Plant for PVC Floorings (AGPR). [9]

II.3.1.1.2.Factors influencing PVC recycling

Various factors influence the recycling of PVC, and it is important to understand them in order to analyze, predict, and enhance the mechanical recycling process. The total amount of PVC recycled per year can be attributed to two main factors:

• The overall annual quantity of PVC present in waste materials.
• The proportion of PVC that is successfully recycled, known as the "recycling rate."

Four major factors influence the recycling rate:

1. Technical factors, which include the quality of recyclates achievable based on the degree of contamination of collected PVC waste or relevant waste streams.
2. Legal and organizational factors, such as recycling regulations, statutory requirements, voluntary agreements or commitments of the industry, and technical standards and regulations.
3. Economic factors, particularly the overall cost of recycling, which includes the cost of collection, logistics, sorting, treatment, and
   contamination are also important factors.
4. Ecological factors, such as the potential savings of resources and emissions by substituting virgin PVC and other materials with recyclates. The savings depend on the achievable quality of the recyclates and the products or materials they can substitute, which includes both plastic and non-plastic material,

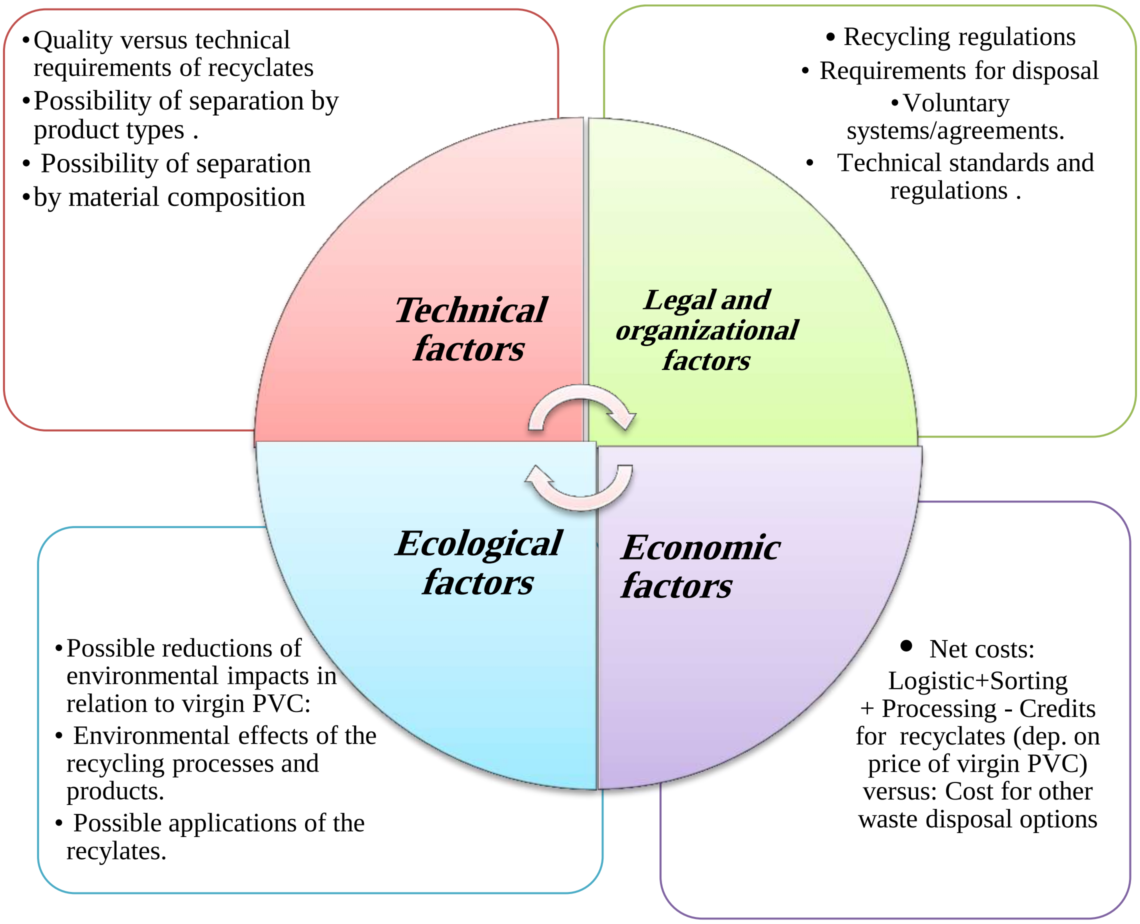

Fig II- 5: Factors influencing recycled PVC waste quantities.[9]

II.3.1.1.3.Impact of PVC on the recycling and recovery of plastics and other material

When recycling mixed plastics waste, including PVC, the initial separation process typically focuses on removing metals and stony materials to prevent damage to the shredder and grinder caused by abrasion. Following the shredding and grinding stages, the agglomerated or ground mixed plastic is melted and plasticized in an extruder. When evaluating the impact of PVC in mixed plastics recycling processes, it is necessary to differentiate between two scenarios: recycling plastics waste with a low PVC content and recycling plastics waste that is "PVC-rich."

In mixed plastics fractions, polyolefins, such as PE and PP, are the most significant materials, particularly in plastics packaging waste. The quality of the recycled products obtained from mixed plastics recycling is influenced by factors such as melting temperature, potential chemical reactions, and the rheological properties (flow characteristics) within the extruders. PVC, in particular, has a relatively low processing temperature and a narrow temperature range for optimal processing (as depicted in Figure -6). If the processing temperature of PVC exceeds its limit, it can release hydrochloric acid (HCl), leading to material degradation and an increased risk of equipment corrosion.

To prevent the detrimental effects of PVC on the recycling process and the quality of the materials, it is necessary for mixed plastics fractions with PVC content to have a minimum polyolefin content of 70%. This ensures that the PVC does not interfere with the processing and degrade the material quality. One way to mitigate the negative impacts is by absorbing the released HCl using lime or limestone. However, when the PVC content is relatively low, such as less than 5% as found in packaging waste, a dehydrogenation unit is typically installed before the extrusion process. This unit employs a thermal and chemical process to remove chlorine from the PVC.

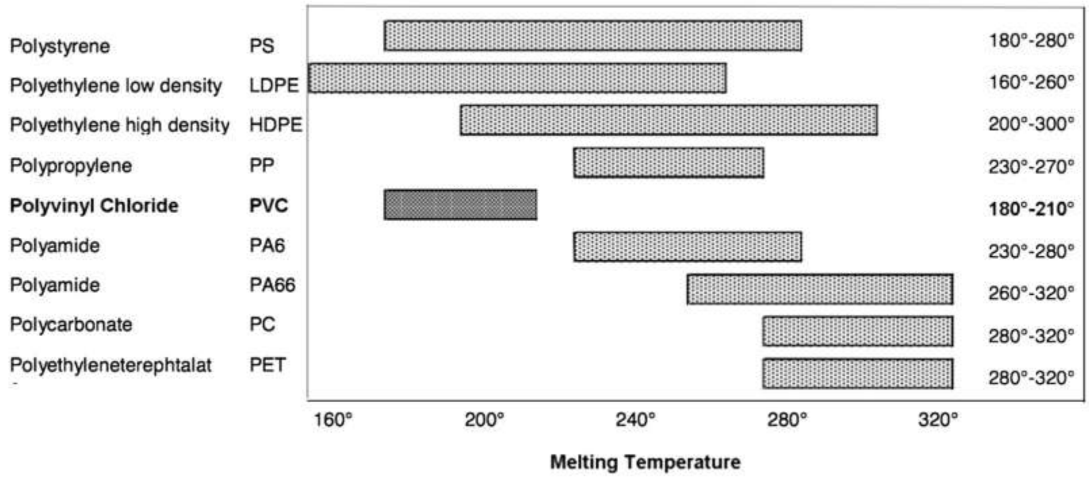

Fig II-6 : Processing temperatures of mass plastics (from Möller/Jeske). [9]

II.3.1.2 .Pvc Feedstook Recycling

In addition to the mechanical recycling of PVC, there are many more tries to prepare low molecular materials from waste PVC by chemical treatment. Recycling chemicals or raw materials is based on an idea breaking polymer waste into basic chemicals by thermoplastic, 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. [6]

The PVC industry has a feedstock recycling program that aims to assess different technologies to select the most promising ones and support commercial-scale plants. While the program mainly focuses on "PVC-rich" waste streams, it is not limited to them, as demonstrated by the industry's involvement in the Reduction of Iron Ore by Plastics project. This indicates that the program is open to considering other methods of utilizing plastics, including PVC. In order to study the practical implications of these recycling processes, trial programs encompass a broad range of "as available PVC post-consumer waste products."

These programs specifically focus on cables, flooring, and coated fabrics. (Table 2) provides a simplified overview of the characterization of these waste products.

Table II- 1: Typical weight fractions and heating values for "PVC rich" waste streams (approxim ate values). [11]

Waste stream	Chlorine wt. %	Hydrocarbons wt. %	Inorganics wt. %	Heating value MJ/kg
Flooring	18	33	49	13
Cables	21	53	26	17
Coated fabrics	27	62	11	23

Feedstock recycling should be regarded as complementary to mechanical recycling of plastics waste due to the following reasons:

- it is more effective in handling mixtures of plastics that are not economically viable to separate into individual polymer streams, which can be handled more efficiently through mechanical recycling.
- Feedstock recycling expands the overall capacity for recycling, enabling the industry to meet recycling targets set by regulatory bodies and effectively manage future waste quantities.[12]

In order to find an environmentally friendly way for treating PVC, different chemical recycling methods were summarized to understand their advantages and disadvantages.

II.3.1.2.1 .The pyrolysis mechanism of PVC

The pyrolysis mechanism of PVC involves the thermal degradation of the polymer chain, which starts at a much lower temperature than other plastics. This is due to the presence of thermally labile structural segments or defects within the PVC polymer chains, which decrease the overall stability of the material. As shown in (Fig 9).

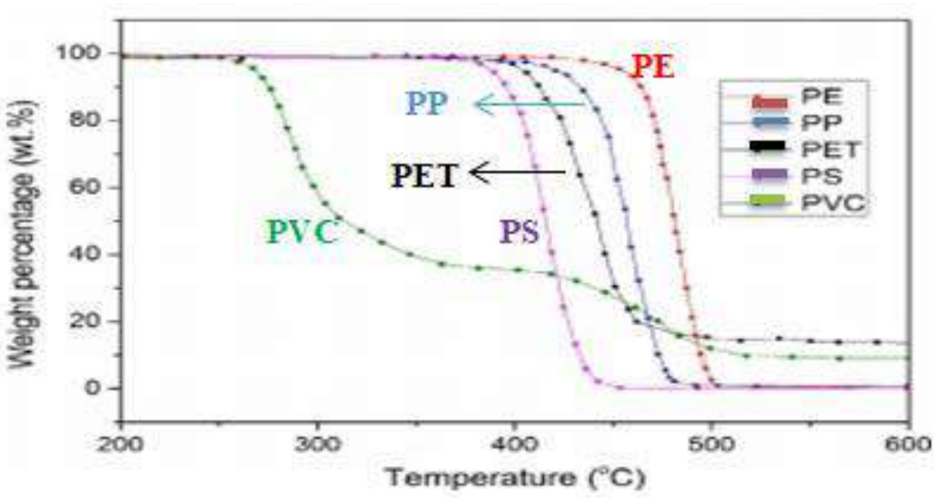

Fig II- 7: Analysis of the PE (Matsuzawa et al., 2004), PP (Matsuzawa et al., 2004), PET (Martı´ n-Gullón et al., 2001), PS (Matsuzawa et al., 2004) and PVC (Matsuzawa et al., 2004) pyrolysis at 10 K min-1.

There have been different suggestions regarding the presence of labile structural defects that contribute to the low stability of PVC.

- To explain the low stability of PVC, several labile structural defects have been proposed. According to Martínez et al., the GTTG (G = gauche, T = trans) isotactic triad conformation was suggested as a factor contributing to the thermal instability of PVC.
- Béla proposed that the initiation of PVC decomposition was attributed to the presence of random allylic chlorine atoms or branches with tertiary chlorine atoms.
- Minsker suggested that the formation of ketoallylic chlorine atoms (ACO(CH2=CH)nCHCl) (n greater or equal to 1)resulting from incidental air oxidation played a role in the low stability of PVC.

These various defects and factors collectively contribute to the reduced stability of PVC during thermal decomposition.

The instability of PVC has been attributed to various defect structures, including internal double bonds and head-to-head structures. However, there is still no consensus on the exact cause of thermal instability in PVC. Nonetheless, the presence of internal allylic and tertiary chloride segments is considered to be of primary importance Unlike HDPE, LDPE, PS, and PP, which exhibit one-stage decomposition reactions, the pyrolysis of PVC is characterized by two distinct stages. Ongoing research aims to uncover the precise mechanisms and specific defect structures responsible for the thermal instability of PVC.

the first stage

During the first stage of PVC pyrolysis, which occurs in the temperature range of approximately 250-350 °C, there is a significant weight loss of around 65%. The main reaction in this stage is the dehydrochlorination of the polymer, leading to the formation of de-HCl PVC and volatile byproducts (Jordan et al., 2001). The volatile products primarily include HCl, along with small amounts of benzene, toluene, and other hydrocarbons. As a result of this stage, a substantial portion of chlorine is removed from PVC.

The removal of chlorine at low temperatures is significant because it allows for further processing and treatment of PVC. Once the chlorine is removed, the resulting de HCl PVC can be subjected to subsequent processes or treatments for recycling, reprocessing, or other purposes.

- **The second stage**

The second phase of PVC decomposition occurs between 350 and 525 degrees Celsius, during which the de-HCl PVC undergoes cracking and decomposition.

A series reaction model proposed by a certain researcher describes the mechanism of PVC decomposition as occurring in three consecutive processes.

(1) Conversion of PVC into intermediates and HCl.

(2) Decomposition of intermediate into polyene chain and other volatiles.

(3) Decomposition of polyene into toluene (and other aromatics) and chars. [13]

II.3.1.2.2.Catalytic dechlorination

To enhance the environmental safety and maximize the retrieval of hydrocarbons from PVC waste during thermal recycling, it is essential to undertake dechlorination. Furthermore, the neutralization of hydrogen chloride (HCl) in the exhaust gas is necessary. [7]

Compared with conventional pyrolysis, catalytic cracking can inhibit the formation of chlorinated hydrocarbons, lowering the reaction temperature, shortening residence times and enhancing the selectivity of products . Catalytic dechlorination involvesthe selective cleavage of one or more C-Cl bonds, lowering toxicity and generating reusable raw materials.

The use of different carbon composites of iron oxides and calcium carbonate as catalysts/sorbents has been proposed to facilitate two distinct catalytic dehalogenation processes:

The first process is a two-step approach.

- In the first step:it involves the degradation of mixed halogenated waste plastics.
- In the second step: it focuses on the catalytic dehalogenation of organic chlorine compounds found in the oil derived from the mixed plastics.

The second process is a single-step approach where the simultaneous degradation and dehalogenation of PVC containing plastics occurs, resulting in the production of chlorine-free liquid products The single-step degradation and catalytic process was carried out using a(Ca-C) catalyst.

This passage describes three different methods for catalytic dechlorination of PVC.

- The first method involves combining thermal degradation with catalytic dechlorination of PVC to produce high-quality, chlorine-free oil.
- The second method involves catalytic hydrodechlorination of oil obtained from pyrolysis of PVCcontaining plastics to produce chlorine-free oil.

- The third method involves a non-catalytic dechlorination step at a low temperature, followed by catalytic pyrolysis at high temperature.

II.3.1.2.3.Hydrothermal treatment in supercritical or subcritical water

In a study by Kubátová et al. (2002), waste printed circuit boards and PVC were simultaneously treated using subcritical water oxidation. The results showed that the process achieved the simultaneous dechlorination of PVC, removal of brominated flame retardants, and recovery of copper (Cu) and lead (Pb) through a single-step subcritical water oxidation reaction. Dechlorination of PVC was not noticeable below 200°C. However, at 250°C, the dechlorination of PVC significantly increased to 93%, and it reached nearly 100% above 300°C. Furthermore, the chlorine present in PVC was effectively transferred to the aqueous phase during the treatment process. This study demonstrates the potential of subcritical water oxidation for the environmentally friendly and efficient dechlorination of PVC.

The experimental results indicated that the mass loss of PVC only occurred above 250°C. At temperatures of 300°C and 370°C, approximately 44% of the initial PVC remained as residue. The weight loss of approximately 56% at these temperatures corresponds precisely to the expected weight loss if all chlorine were removed from the PVC. This observation suggests that the weight loss during thermal decomposition is mainly attributed to the removal of chlorine from PVC.

Chlorinated organic compounds were not observed in the oil from PVC using subcritical and supercritical water. Nagai et al. (2007) performed degradation of PVC in supercritical water and proposed one PVC dechlorination mechanism in the presence or absence of water as shown in fig (II-11):

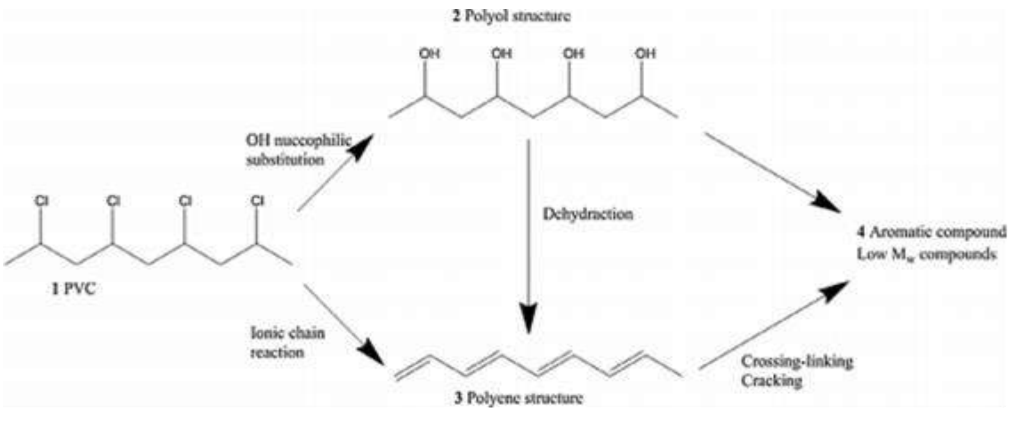

Fig II- 8 .Reaction pathway of PVC decomposition in the presence or absence of supercritical water.

Researchers have proposed that the decomposition of PVC can be categorized into three distinct stages based on temperature.

1) In the first region (T < 250 °C), PVC went through dehydrochlorination to form polyene.
2) in the second region (250 °C < T < 350 °C), polyene decomposed to low-molecular weight compounds.
3) in the third region (350 °C < T), polyene further decomposed into a large amount of low-molecular weight compounds. [13]

II. 3.1. 3. A novel process for waste polyvinyl chloride recycling: Plant growth substrate development

This study introduces a newly developed process for recycling waste PVC plastics, which are difficult to dispose of due to the production of harmful chlorinated pollutants. The process involves creating a growth substrate by combining the waste PVC with superabsorbent resin (SAR) as the main raw materials. The resulting substrate is environmentally friendly, and the SAR helps provide a sustainable water supply for the substrate. The process also enhances the physical properties of the substrate, making it useful for plant cultivation.the recycling of waste PVC was successfully achieved by utilizing surface silanization PAANa and a compression-molding foaming process to create a new growth substrate, The maximum water absorbing ratio of the product reached 62,3% with only 1.65% mass loss under optimum conditions.The study offers a highly efficient approach to recycle waste PVC for the sustainable and economically viable preparation of growth substrates. By implementing this process, waste PVC can be effectively reused, promoting sustainability, and enabling cost-effective production of growth substrates. [14]

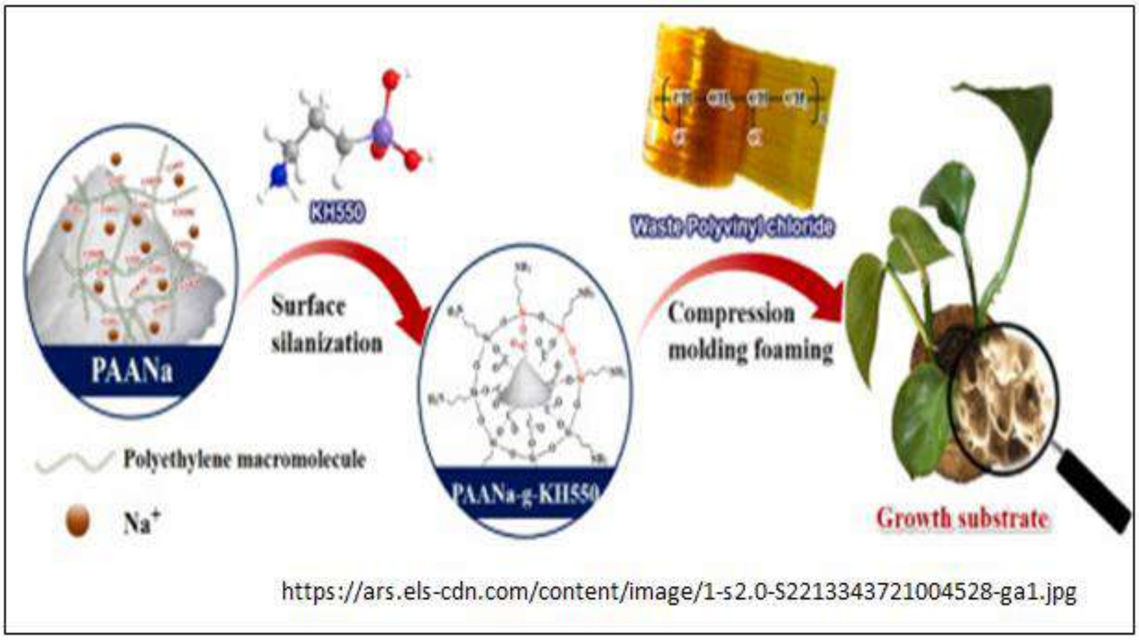

Fig II-9 : Graphical summary of the development of a plant growth substrate using waste polyvinyl chloride.[14]

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CHAPTER III

The impact of polyvinyl chloride on the environment and the economy

III.1.The impact of polyvinyl chloride on the environment and the economy

Poly vinyl chloride, despite facing some unfavorable opinions, is indeed a recyclable material. Moreover, the level of PVC recycling has been increasing steadily over the years. The existing PVC recycling options and the ongoing development of feedstock recycling techniques offer promising opportunities for processing PVC waste in a manner that benefits the environment and provides financial advantages. These advancements do not justify excluding the application of poly(vinyl) chloride in the era of sustainable development and the pursuit of a circular economy. Instead, they highlight the potential for utilizing PVC in a responsible and environmentally conscious manner.[1]

The recycling operations for plastics, specifically PVC, are experiencing notable growth, particularly in the following areas:

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. [2]

III.1.1.On environmental impact

III.1.1.1.Danger of poly vinyl chloride

Polyvinyl chloride, a thermo-resistant plastic made from polyvinyl chloride, is everywhere: in cars, houses, parks, clothes, and children's toys. It is also used in plastic tubes and bags for treating children born with health problems. The production of PVC involves the transportation and storage of many harmful substances such as ethylene dichloride, which has carcinogenic and genotoxic effects (causing DNA damage). The production of this substance also emits its fair share of atmospheric contaminants such as heavy metals and organochlorines (dioxins and furans).

At each stage of its life cycle, the numerous hazards of PVC always relate to the two same specific causes of PVC: it is made from chlorine, and large quantities of additives are necessary for it to be functional. All precursors of PVC (chlorine, dichloroethane, vinyl chloride monomer) are highly toxic, and their production generates toxic waste and emissions.

III.1.1.2.Risks related to the transformation of poly vinyl chlorid

III1.1.1.2.1. PVC Resin

PVC is not hazardous at room temperature, and the main risk associated with the resin is the inhalation of fine polymer dust. This risk applies to any product that is in powder form, and PVC does not always come in powder form during its processing. The applicable exposure limit for total dust is 10 mg/m3, and for inhalable dust, including inert dust, it is 5 mg/m3. Furthermore, there is a minimal possibility of vinyl chloride monomer being released into the atmosphere during handling, processing, and storage at room temperature, as well as during the initial hot processing.[3]

III.1.1.2.2.Additives

According to the INRS (National Institute for Research and Safety), powdered additives also carry risks of inhalation and contact during various operations, such as weighing, transferring, and mixing. Precautions should be taken to minimize exposure to these additives during handling and ensure appropriate safety measures are in place.[3]

1) Plasticizers

The quantities of plasticisers added to the PVC polymer vary depending on required properties. and the final use, plasticiser contents vary between 15 and 60%, with typical ranges for most flexible applications around 35 to 40%.

plasticisers in particular adipates, trimellitates, organophosphates and epoxidised soybean oil can also be used as softeners in PVC. These plasticizers make up a very small portion of all plasticizer usage. Since there is a lack of evidence on the effects of these plasticisers' use in PVC on the environment and human health, more information would be required to provide an accurate judgment. Therefore, the focus of this part will be on phthalates, the principal plasticizers currently evaluated in terms of their potential dangers to human health and the environment as well as their importance in terms of quantity. All of the phthalates that were extensively used in PVC applications are now found everywhere. The two main methods through which phthalates reach the environment seem to be air transport and leaching out from specific uses.

High quantities of phthalates are primarily found in sediments and sewage sludge. According to reports, certain phthalate concentrations in Denmark may surpass the national limit levels established for the use of sewage sludge in agriculture. Without waiting for the final stage of the above mentioned risk assessment process, three Member States have already started to draw up risk management strategies based on the global objective to reduce the use of phthalates.

Release of phthalates into the environment and occupational exposure to these substances is another issue in the later manufacturing stages of the vinyl lifecycle. In 1997, chemical and plastics industries in the United States reported releasing 213,621 pounds of the plasticizer diethylhexyl phthalate (DEHP) directly into the air.[4]

2) **Fillers**

Fillers are commonly found in powder form and generally do not pose specific toxicity risks. However, inhalation of fillers can lead to respiratory issues.

3) **Stabilizers**

Stabilizers play a role in resins, albeit in small quantities, and their main danger lies in their bulk handling. As mentioned by the INRS:

- Lead salts are commonly used as stabilizers. Even in low doses, they can affect the nervous system and lead to digestive and renal issues, as well as hematological abnormalities.
- Cadmium salts, known for their cumulative effects, can cause intestinal, respiratory, renal, and metabolic disorders.
- Dibutyl and dioctyl tin derivatives are moderately and slightly toxic, respectively. However, they may contain impurities that could potentially be harmful .[3]

4) Pigments

Their powdered form makes them dangerous during dry handling. Their toxicity varies depending on the specific pigment. Mineral pigments generally have similar toxicity to the metal they contain. Organic pigments can potentially contain impurities of toxic substances used in their production. [3]

5) Thermal degradation of PVC

PVC can start to break down at temperatures of 175-200°C, leading to the release of primarily hydrochloric acid vapors, which can be highly irritating to the respiratory and ocular mucous membranes. The amount of vapor increases with the temperature. In addition, residual vinyl chloride monomer (CVM) in trace amounts may be released if the polymer contains leftover monomer. Certain additives, especially plasticizers like phthalates, can volatilize and decompose at temperatures as low as 150°C, releasing irritating substances such as aldehydes and phthalic anhydride.[3]

III.1.1.3.Environmental impacts of polyvinyl chloride (PVC) production process

PVC is another significant source of halogen in waste streams because chlorine makes up around 57% of the mass of the polymer. ethylen production process consume the most energy associated to pvc manufacturins.PVC combustion produces chlorinated dioxins, which are extremely harmful to human health. Short-term exposure to dioxins can result in skin disease, while long-term exposure can result in cancer. Acidic rain is a further consequence of atmospheric chloride. Therefore, PVC dechlorination before combustion is typically necessary. The presence of PVC in the waste products during waste recycling also has a number of negative impacts. According to a study by Huang in. (2016), PVC decreased the effectiveness of tar cracking when combined with biomass and poisoned the catalysts during gasification. Additionally, was discovered co-pyrolysis with PVC and other waste materials increased carbon yield and created carbon and bio-oil that had been contaminated with chlorine.

Even landfilling is not suitable for PVC as oxidative degradation of PVC can occur under natural exposure.[4],[5]

III.1.1.3.1.Disposal of PVC Products

Most PVC products are disposed of either through landfilling or incineration. Only a small percentage is recycled 35 percent in Europe and less than 0.6 percent in the US). Because every PVC product contains different additives, only dedicated collection systems that collect a specific brand of a particular product can facilitate the recycling of PVC into products similar to the originaL Most recycling programs collect a wide range of PVC items, and it is not cost-effective and sometimes not possible to determine what additives each item contains. The mixing of PVC products that contain different, unknown additives can cause problems in the recycling process; for example, the additives can form colored compounds not present in any of the original items. Instead, PVC is usually "downcycled" into products such as plastic composite park benches, which may contain lead, cadmium, or other additives present in the original products.[6]

III.1.1.3.2.by product of PVC Products

PVC manufacture leaves behind highly hazardous, bioaccumulative, and persistent byproducts. Chlorinated dioxins are among the most dangerous and persistent pollutants present in the chemical combinations created during the manufacture of EDC and VCM. In addition, a very large portion of these mixtures consists of chemicals that have not yet been identified or tested. Many vinyl lifecycle byproducts are of major concern due to their persistent nature, which resist natural degradation and builds over time in the environment. They are also bioaccumulative and fat-soluble, which causes them to build up in living species' tissues.[4]

- **Dioxin**

  (2,3,7,8-tetrachlorodibenzo-p-dioxin) and a large number of structurally and toxicologically related compounds are among the most significant byproducts of the PVC lifecycle and are never manufactured on purpose but instead form accidentally whenever chlorine gas is used or chlorine-based organic chemicals are burned or processed under reactive conditions.

- **Phthalates**

  The main category of plasticizers used in vinyl are phthalates, a group of chemicals that pose serious health and environmental risks and are now considered to be global pollutants. Under some circumstances, phthalates are somewhat persistent and bioaccumulative. They are currently present in the air in far-off places, the deep ocean water, and inside the bodies of the majority of people. Children under the age of two are exposed to levels that are many times higher than those of a typical adult.[4]

III.1.1.4. Negative effect of PVC waste

The study reveals that the negative consequences of plastic pvc on human health and environment as a result of exposure to toxic chemicals used in the production of plastics pvc.

III.1.1.4.1.On human life

- From the moment of its production, PVC is regarded as a troublesome material due to the presence of harmful chemicals used in its manufacturing. These chemicals are highly toxic and pose a significant risk to all living organisms across various species on our planet.
- The production of PVC is associated with negative impacts, as the chemicals involved in its manufacturing process are highly toxic and pose a severe threat to all forms of life on Earth.

III.1.1.4.2. On animals

- Approximately 100,000 animals, including cows, dogs, buffalos, birds, dolphins, turtles, whales, and penguins, lose their lives annually as a result of PVC bags.
- Numerous animals perish because they consume plastic bags, mistakenly perceiving them as food, leading to their death. What's even more distressing is that the ingested plastic bag persists intact even after the animal's demise and subsequent decomposition.
- Thus, it lies around in the landscape where another victim may ingest it.

Fig III-1: Pictures of the effects of PVC on animals.[7]

III.1.1.4.3.on the landscape

1. The quantity of plastic bags littering the environment continues to rise each year, creating an escalating issue.

2. Once discarded, plastic bags have a tendency to make their way into various settings such as waterways, parks, beaches, and streets.

3. Burning plastic bags releases toxic fumes into the air, further contributing to environmental pollution and potential health hazards.[7]

Fig III-2: Pictures of plastic waste scattered in the landscape [7]

Overall, the growth of PVC recycling operations can be attributed to increased awareness about the environmental impact of plastic waste, government regulations, industry initiatives, and technological advancements in recycling processes. These factors have contributed to the expansion of PVC recycling in various regions worldwide. Where we notice a big difference between the primary PVC scenario and recycled PVC scenario in terms of Contributions of the most significant substances to key categories: a) human toxicity, terrestrial ecotoxicity, marine ecotoxicity fossil, depletion, in china(fig).[8]

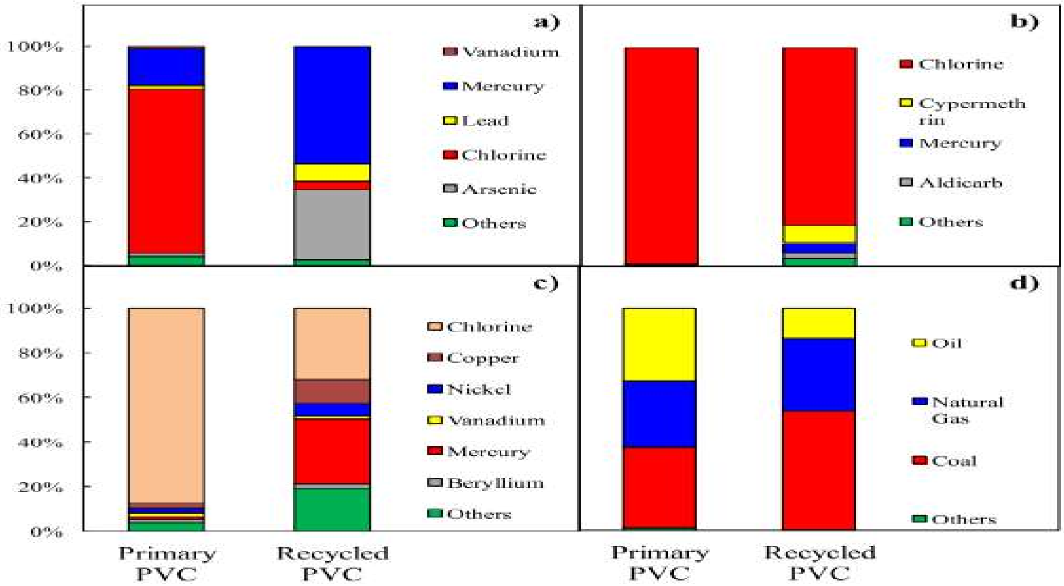

Fig III- 3: Contributions of the most significant substances to key categories: a) human toxicity; b) terrestrial ecotoxicity; c) marine ecotoxicity; d) fossil depletion.[8]

III.1.5.Emissions from recycling PVC

To mitigate global warming, it is essential to decrease greenhouse gas (GHG) emissions. The production of plastics heavily relies on carbon-based raw materials and energy sources, which currently come mainly from fossil fuels. As a result, plastic production contributes significantly to GHG emissions, primarily in the form of carbon dioxide (CO2) released from fossil fuel combustion.[9]

In the recycling step, there are two different effects which are accounted in the impact assessment:

III.1.4.1.Direct emissions from recycling

the main uncertainty in the assumptions comes from the direct GHG emissions factor of pvc for which data is not available. In the absence of data, the same factor is used (348 kg CO2e/t) from recycling plants across Europe.

III.1.4.2.Avoided emissions from recycling

The use of recycled plastic instead of virgin plastic leads to avoided greenhouse gas (GHG) emissions. GHG emission factors for the production of virgin plastics by plastic resin pvc 1900Kg/t**.** This occurs because the production process of virgin plastic and its entire life cycle, including transportation, energy consumption, and waste management, is substituted with the use of recycled plastic. By choosing recycled plastic, the need for new plastic production is reduced, resulting in a lower overall carbon footprint and GHG emissions. This highlights the environmental benefits of incorporating recycled plastic into various industries and applications.**[10]**

III.2.On an Economic impact

III.2.1.Structure and description of the PVC industry

According to recent statistics from the PVC industry, the PVC production and transformation sector in Western Europe consists of over 21,000 companies, employing more than 530,000 individuals, and generating a turnover exceeding 72 billion€. . The industry can be broadly categorized into four main segments: PVC polymer producers, stabilizer producers, plasticizer producers, and PVC transformers. More than 21,000 small and medium-sized enterprises are primarily responsible for the two or three different manufacturing processes required to transform PVC into finished products. These companies are divided into three categories based on their size: 90% of them have fewer than 100 employees, 5% have between 100 and 500 employees, and the remaining 5% have over 500 employees**. (Table III-10)** provides a summary of the information on the total number of companies, production, and employment in the entire PVC industry supply chain.[11]

TableIII-1: PVC industry: companies, production, employment. [11]

Products	Companies	Production (tonnes)	Employmen
Total PVC	21,199	7,900,000	530,000
Flexible products	10,321	3.700.000	260.000
Rigid products	10.878	4.200.000	270.000

III.2.2.PVC recycling yields

The recycling output refers to the measurement of the effectiveness or efficiency of recycling processes. In the case of PVC plastic resin recycling, data on the revenues generated by European recyclers for recycling PVC plastic resin is available from PRE (Plastics Recyclers Europe). This data provides valuable insights into the financial performance and success of PVC plastic resin recycling operations conducted by recyclers in Europe. It serves as an indicator of the economic viability and market demand for recycled PVC plastic resin within the region. European recyclers, in collaboration with PRE (Plastics Recyclers Europe), have provided data on recycling yields specifically for PVC (polyvinyl chloride). These data are based on the current recycling operations available within the EU-28 region.[10]

TableIII-2: Recycling yields by PVC plastic resin (baseline and future yields). [10]

	PVC
Baseline (2012)	**82%**
2020	**83%**
2025	**84%**

III.2.3.The prices of PVC for future purchase in the stock market

(Fig III-4) displays the average forward-purchase prices of PVC (DPVc1 indexed on Dalian Commodity Exchange) in EUR/ton, considering the conversion rate on the listing date. From 2016 to 2020, the PVC price remained stable, with an average of EUR840 per ton. However, there was a sudden surge in the price of this raw material in 2021. The average price for 2021 and the first half of 2022 reached EUR1216 per ton, indicating a significant 45% increase compared to the previous five-year period.

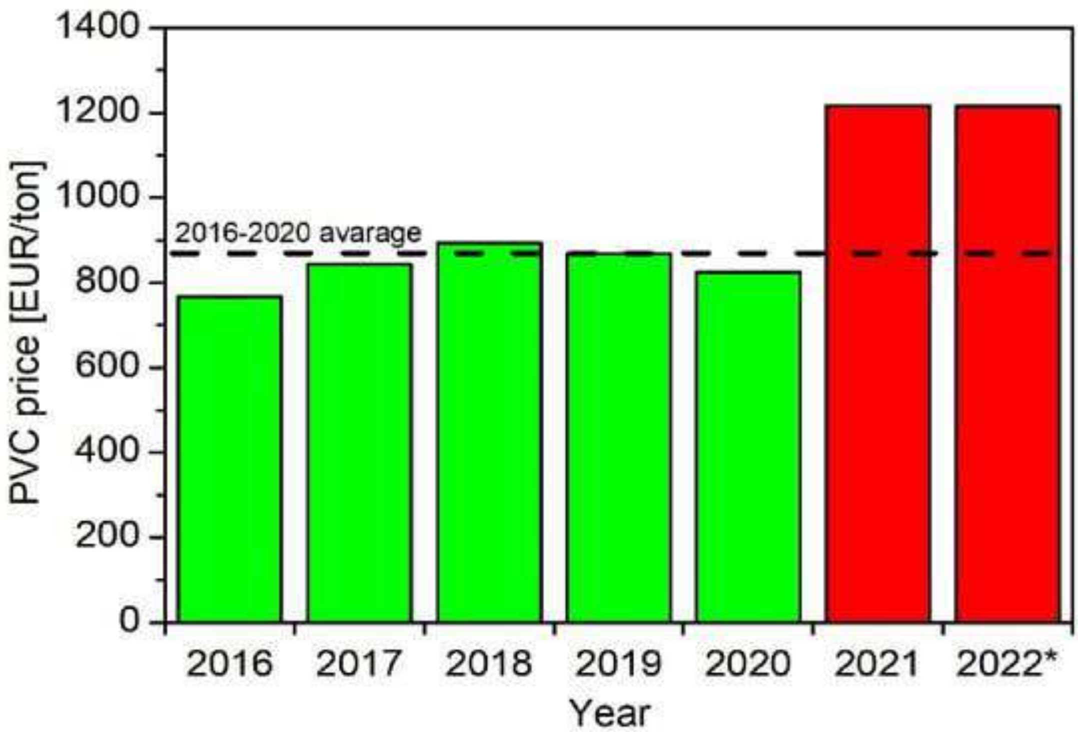

Fig III-4: PVC forward-purchase prices on the stock exchange (DPVc1 indexed on Dalian Commodity Exchange) * from January to June.[12]

Furthermore, there is a consistent and increasing demand for poly(vinyl chloride) (PVC) products, particularly in the construction and medical sectors. As a result, there is economic viability in investing and implementing organizational measures to enhance the level of material recycling. Mechanical recycling of manufacturing waste appears to be a particularly rational approach. This method is straightforward since it involves a material with a known composition and properties. Many companies can leverage their existing equipment such as extruders, mills, and agitators, making it easier to incorporate recycling into their manufacturing processes.

The advantage of PVC, which is its ease of modification, can also present a significant obstacle when it comes to recycling post-consumer waste materials. The development of appropriate technologies for separating PVC materials, which often exhibit diverse properties and compositions, or implementing simultaneous processing techniques, and producing materials with desired properties poses a challenge in this regard. When dealing with post-consumer waste, organizing waste collection systems that ensure the availability and quality of raw materials becomes a strategic task.

Another challenge arises from the fact that PVC waste may include materials produced several decades ago, some of which may contain process additives that are now prohibited. Examples of such additives include thermal stabilizers based on lead compounds and certain plasticizers. Managing and recycling PVC waste containing these outdated additives requires careful consideration and proper handling to ensure compliance with safety and environmental regulations. [12]

III.2.Limits to the PVC recycling potentials

III.2.1.Environmental limits

The general limits regarding PVC recycling have already been identified. Two significant limitations are as follows:

1. Absence of life cycle improvements: If recycling PVC products does not result in substantial environmental benefits in terms of reduced resource consumption, emissions into air and water, and waste generation compared to alternatives such as disposal, incineration, or energy recovery, there is no valid reason to promote PVC recycling, unless there are economic advantages associated with it.
2. Potential toxicological risks: The release of toxic heavy metal stabilizers like cadmium and lead from PVC during the recycling process can lead to their dispersion in products made from recycled PVC materials. Additionally, there is a possibility of cable scraps becoming contaminated with toxic polychlorinated biphenyls (PCBs). These factors pose potential risks to both human health and ecological systems.

III.2.2.Economic limits

In addition to the environmental limits, the economic viability of PVC recycling is also constrained by overall recycling costs. These costs encompass various elements, including collection costs (such as containers and transportation) and expenses related to sorting and mechanical treatment. The equation is as follows: gross recycling costs minus credits for recyclates equals net recycling costs.

The economic limit of PVC recycling lies in its profitability. If recycling operations cannot achieve profitability, the recycling potentials will not be fully utilized, unless there are legal regulations or voluntary measures in place to promote or enforce recycling. Currently, most PVC recycling is conducted under "free market" conditions, meaning it are driven by economic considerations.

The economic profitability of PVC recycling is influenced by three primary factors:

1. Gross recycling costs, which are influenced by the type of PVC waste or product groups being recycled and the available recycling and collection technologies.

2. The cost level of alternative waste management methods, such as landfilling and incineration, which compete with mechanical recycling in the waste management market.
3. The price level of virgin PVC, which determines the achievable selling price for recycled PVC materials (recyclates).To summarize, the economic limitations of PVC recycling are determined by the overall recycling costs, including collection and treatment expenses. The profitability of recycling depends on factors such as the cost of alternative waste management methods and the price of virgin PVC.[13]

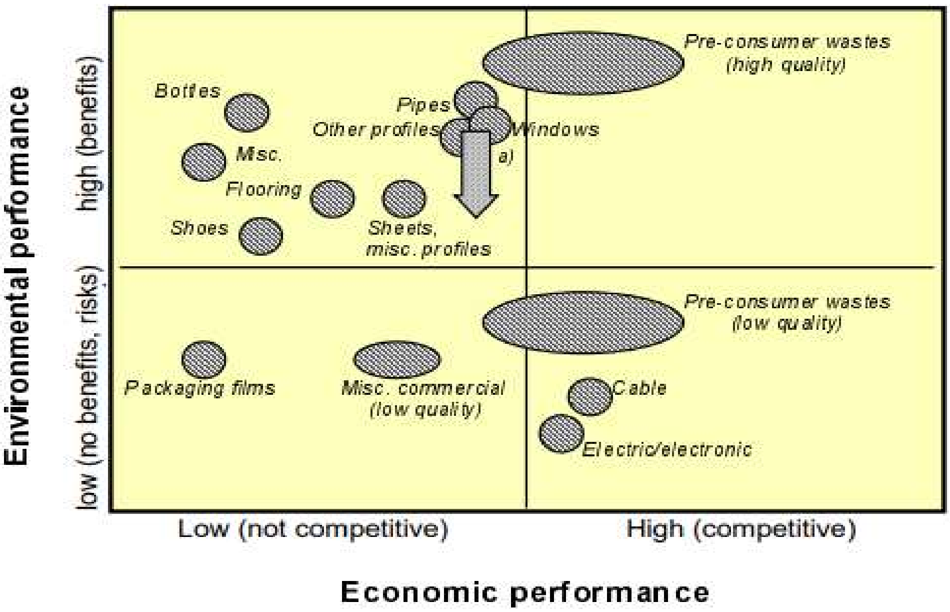

Fig III-5 :Economic and Environmental Limits to PVC Recycling .[13]

III.3.PVC recycling benefits

Recycling PVC offers several benefits due to its characteristics and the availability of recyclable waste:

1. PVC's suitability for recycling: PVC has a long history of successful recycling compared to other types of plastics. Its properties make it well suited for mechanical recycling processes.
2. Advanced mechanical recycling systems: There are well-developed and efficient mechanical recycling systems specifically designed for PVC. These systems enable the effective recovery and processing of PVC waste.

3. Abundance of recyclable PVC waste: There are significant volumes of PVC waste available for recycling. This provides ample opportunities to divert PVC from landfills and utilize it in the recycling process.
4. Resource efficiency and raw material preservation: Recycling PVC contributes to achieving resource-efficiency objectives. By using recycled PVC, the demand for virgin raw materials can be reduced, promoting the preservation of natural resources.
5. Emission and landfill reduction: Utilizing recycled PVC helps reduce emissions associated with the production of virgin PVC. Additionally, recycling PVC waste minimizes the amount of waste sent to landfills, contributing to waste management and environmental sustainability.

Overall, recycling PVC offers a way to maximize its value, reduce waste, and contribute to sustainable resource management and environmental goals. [5]

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General Conclusion

General conclusion

Despite the negative perception, PVC is a material that can definitely be recycled. Furthermore، year after year, its recycling rate increases. In the era of sustainable development and the desire to create a circular economy, the current PVC-material recycling possibilities and feedstock recycling development Perspectives, which would enable processing such waste in the future with a positive environmental and financial effect, do not constitute grounds to exclude the application of poly(vinyl) chloride our main goal with this thesis is to create awareness of how pvc recycling can help the environment by reducing pollution and greenhouse emissions which at the same time is affecting the whole world, and how we can make an impact in the world by decreasing global warming, decreasing risks related to life forms, and reducing the amount of toxic chemicals that go into the landfills .