CHARACTERIZATION AND RECYCLABILITY OF PHARMACEUTICAL BLISTERS

A Thesis Submitted to
the Graduate School of
Izmir Institute of Technology
in Partial Fulfilment of the Requirements for
the Degree of

MASTER OF SCIENCE

in Materials Science and Engineering

by
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July 2023
İZMİR

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ACKNOWLEDGEMENTS

I would like to thank my thesis advisor, Asst. Prof. Dr.-Ing Mertol GÖKELMA his constant support, fatherly patience, guidance, and encouraging approach throughout the learning and writing process of my master thesis. More, I would like to thank my colleagues Pınar YÖRÜK and Alireza HABIBZADEH for their friendship, support, and assistance throughout the life of my master's degree.

I would like to express my gratitude to my family, who deserve to better express my gratitude for their endless support and prayers. This thesis is dedicated to my dear mother, Ödül ÇAPKIN, who has always supported me and guided me to success. I would like to thank my mother Ödül ÇAPKIN, my father Mustafa ÇAPKIN, and my brother Cemal Eren ÇAPKIN, who supported me throughout my life, and whose greatest goal in their lives was to see me happy and successful.

I would also like to thank my dear boyfriend Tugay TEZCAN, who has always been by my side and guided me with his endless support.

I would like to thank my dear friend Gizem TAYLAN, who supported me in every way during my thesis, always supported me to be successful, and did not spare her love and help.

Last but not least, very special thanks go to the many others that go unmentioned but have contributed in one way or another to the successful outcome of this work.

This thesis is supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK-118C311).

ABSTRACT

CHARACTERIZATION AND RECYCLABILITY OF PHARMACEUTICAL BLISTERS

Packaging is one of the largest industries in the world. Pharmaceutical blister packages are the most preferred packaging type in the pharmaceutical industry. Especially after the COVID-19 pandemic, the use of pharmaceutical packaging has become widespread with the increasing demand for drugs. Pharmaceutical blister packages typically contain thin sheets of plastic and aluminium and generate substantial solid waste. Since these packages have a multi-layered and complex structure, they are difficult to recycle. Before recycling, plastic and aluminium need a separation process. Chemical separation or thermal processes can be used for separation. The aim of this study is to characterize different pharmaceutical blister types with SEM-EDS (Scanning electron microscopy- Energy dispersive X-ray spectroscopy), TGA (Thermogravimetric Analysis), DSC (Differential scanning calorimetry), ICP-MS (Inductively coupled plasma mass spectrometry), and FTIR (Fourier Transform Infrared Spectroscopy) and to review the different reagents used in the pharmaceutical blister layer separation process. In addition to thermal degradation, the parameters and results of the separation processes were evaluated using hydrochloric acid, formic acid, acetic acid, sulfuric acid, ethanol, acetone, and organic solvents. It also evaluates the recyclability of the separated layers (plastic and aluminium). Its recyclability was evaluated by melting the aluminium fraction under salt consisting of a mixture of NaCl-KCl-CaF_2. The plastic fraction was obtained in solid and liquid form by thermal degradation and analysed by GC-TCD (Gas Chromatography-Thermal conductivity detector).

ÖZET

BLISTER İLAÇ PAKETLERİNİN KARAKTERİZASYONU VE GERİ DÖNÜŞTÜRÜLEBİLİRLİĞİ

Ambalaj dünyanın en büyük sektörlerinden biridir. Farmasötik blister ambalajlar ilaç sektöründe en çok tercih edilen ambalaj türüdür. Özellikle COVID-19 pandemisinden sonra artan ilaç talebiyle farmasötik ambalajların kullanımı da yaygınlaşmıştır. Farmasötik blister ambalajlar, tipik olarak ince tabakalar halinde plastik ve alüminyum içeren malzemedir ve önemli miktarda katı atık üretir. Bu paketler çok katmanlı ve karmaşık bir yapıya sahip olduklarından geri dönüşümü zordur. Geri dönüşümden önce plastiğin ve alüminyumun bir ayırma işlemine ihtiyacı vardır. Ayırma için hidrometalurjik veya termal prosesler kullanılabilir. Bu çalışmanın amacı, farklı kabarcık tiplerinin karakterizasyonunu SEM-EDS (Taramalı elektron mikroskobu-Enerji dağılımlı X-ışını spektroskopisi), TGA (Termogravimetrik Analiz), DSC (Diferansiyel Taramalı Kalorimetre), ICP-MS (Endüktif Eşleşmiş Plazma Kütle Spektrometresi), FTIR (Fourier Dönüşümlü Kızılötesi Spektroskopisi) ile gerçekleştirmek ve kabarcık tabakalarının ayrılma sürecinde kullanılan farklı reaktifleri gözden geçirmektedir. Termal bozulmanın yanı sıra hidroklorik asit, formik asit, asetik asit, sülfürik asit, etanol, aseton ve organik çözücüler kullanılarak ayırma işlemlerinin parametreleri ve sonuçları değerlendirilmiştir. Ayrıca ayrılan katmanların (plastik ve alüminyum) geri dönüştürüle bilirliğini değerlendirmektedir. Alüminyum fraksiyonu NaCl-KCl-CaF_2 karışımından oluşan tuz altında ergitilerek geri dönüştürüle bilirliği değerlendirilmiştir. Plastik fraksiyonu piroliz ile katı ve sıvı formda elde edilerek GC-TCD (Gaz Kromatografisi-Termal iletkenlik dedektörü) ile analiz edilmiştir.

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CHAPTER 1

INTRODUCTION

Pharmaceutical blister packages are the most preferred packaging material in the pharmaceutical industry, as they have good protection against moisture and are inexpensive [1]. They also provide ease of use compared to other pharmaceutical packages. Pharmaceutical blister packages are a good advertising tool for pharmaceutical companies as they provide easy information about the use of drugs as well as protect the drugs [2]. It is also a more suitable packaging material for the use of solid-form drugs. Drugs in blister packages do not come into contact with each other and are airtight. Thus, it provides long and safe use [3].

According to Brooks, the pharmaceutical blister packaging market is anticipated to reach a value of US$149.3 billion by 2026, growing at a compound annual growth rate (CAGR) of 6% from 2019 to 2029 [4]. Recent growth in the use of blister packaging for drugs has resulted in a significant waste production; blister packaging now makes up 4% by weight of the daily packaging waste produced [5].

Thermoforming or cold forming is frequently used to create pharmaceutical blister packages. According to Pilchick, blisters are made up of four fundamental components: forming film, lidding material, printing ink, and heat-seal coating[3]. Plastics like polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) are typically used to make forming films [6]. Blister packaging material is used for its moisture resistance and long-term product viability [2]. Aluminium is frequently used as the lidding material because it is mechanically stable and can keep drugs away from the air. The lidding and forming films used in pharmaceutical blisters which are cold formed packaging contains aluminium. Compared to thermoforming, cold forming offers a good resistance against moisture and light. Cold forming, however, costs more to create [3].

The waste pharmaceutical blister packages are also becoming a problem due to the increasing demands of the pharmaceutical industries. Blister packaging value should be recovered in order to eliminate the negative impacts on the environment and the economy. There now three common scenarios for end-of-life blister packaging:

landfilling, incineration, and direct recycling depending on the policies and behaviour of the society [7]. The plastic and aluminium parts can acidify the soil when they are disposed. In addition, the lack of recycling increases the creation of primary aluminium, a process that uses a lot of energy[8]. Wastes that are excluded from recycling operations have a negative impact on the environment and pollute the air and water[5]. Since blister packages contain a lot of plastic and are sent to places where the metal cannot be recovered, they are increasingly seen as plastic waste. The multilayer structure of blister packaging makes recycling the trash from them difficult as well.

Pharmaceutical blisters consist of a plastic, aluminium, and a glue layer that makes them stick together. Due to their layered structure containing these different materials, it is necessary to separate (as aluminium and plastic) the layers from pharmaceutical blister packages before the recycling process. Two separation processes can be applied: wet separation (by using reagents) and thermal separation (thermal degradation). The recycling process should be applied after a separation process. Therefore, it is important to separate the layers of the samples to be recycled from each other to prevent any material losses in the recycling process. This study investigated the full characterization of pharmaceutical blister packages, the separation behaviour of their layers, and aluminium recyclability.

CHAPTER 2

STATE OF ART

2.1. Pharmaceutical Blisters Packaging Industry

Packaging plays an important role in the pharmaceutical industry because of many advantages. They protect and preserve pharmaceutical products, provide quality and safety, and ensure information to patients/healthcare providers [1,2]. There are various types of pharmaceutical packaging used in the industry such as blisters, bottles, tubes, etc. The packaging choice depends on some factors such as drug types, intended use, and regulatory requirements. For instance, liquid medicines are often stored in childproof bottles [9]. Blister packages are generally used in packaging solid-form drugs (such as tablets, and capsules) because they provide protection from light, air, and moisture [10]. Materials of pharmaceutical packaging are required to supply standards to provide safety and impact of the drugs. For instance, they should be free from contaminants, compatible with drugs' properties, and resistant to tampering [11,12].

Pharmaceutical blisters are a crucial segment in the pharmaceutical packaging industry. Blister packages are a type of packaging for pharmaceuticals in tablet form, made of aluminium and plastic via thermoplastic, and containing cavities that provide secure encapsulation[13].

Due to the increase in chronic diseases and the increasing aging population, the demand for drugs is increasing daily. For this reason, the use of blister packaging by pharmaceutical companies to protect and promote their products is increasing rapidly[14]. Therefore, the global pharmaceutical blister packaging market is expected to grow significantly in the coming years. According to a Pharmaceutical Packaging Market Size & Share report, the pharmaceutical blister packaging market is expected to achieve USD 34.1 billion by 2024, with a compound annual growth rate (CAGR) of 6.25% during the estimation period[15].

The COVID-19 pandemic has adversely affected various economies and industries. Before the pandemic, companies were aiming for sustainability. Packaging

companies were putting forward innovative technologies that are environmentally friendly and reusable. Pharmaceutical blister packages have had a positive impact during the pandemic as new trends consider the needs of customers in the pharmaceutical industry[14].

The USA has the largest pharmaceutical market in the world. Figure 2.1 shows the growth of planned drug packages. It is also important economically because the pharmaceutical industry is one of Europe's top-performing, high-tech sectors[15].

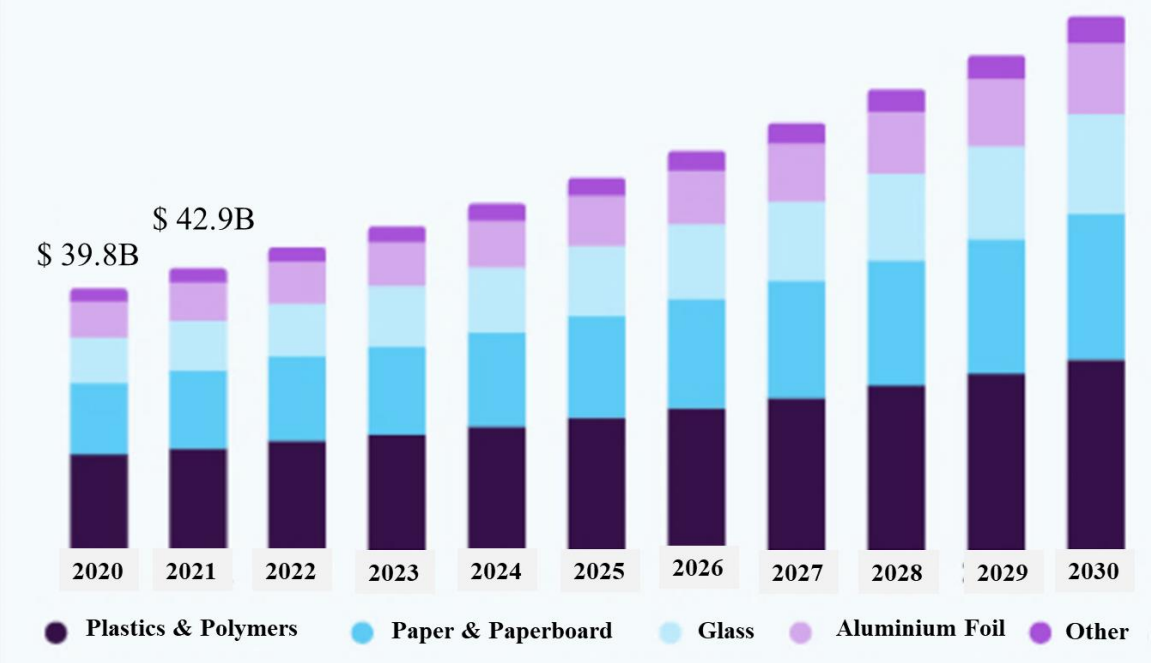

Figure 2.1. USA Pharmaceutical Packaging Market. Size, by material, 2020-2030 (USD Billion)[15].

The pharmaceutical industry is driven by increasing advances in medicine and biology. Also, the pharmaceutical industry is an important asset to the European economy as it has the best performance in Europe. For this reason, the preferred blister packages for tablets in the form of drugs have been the focus of companies. Today, companies aim for the sustainability of blister packaging. They are in search of reusing the materials in the blister packages. This pursuit of sustainability is expected to accelerate significantly in the coming years [15].

The pharmaceutical packaging market is divided into three segments based on the product: primary, secondary, and tertiary [15] (see in Figure 2.2).

Primary pharmaceutical packaging formed the largest share of the market in 2022. Tubes, bottles, and blister packages are the primary packaging and are in direct contact with the drug. They envelop the medicine and protect it from contamination. Packaging companies focus on easy-to-open lids that allow fine dosing of drugs [15].

Secondary pharmaceutical packaging is a layered coating that holds pharmaceutical packages together and protects them from external influences. Secondary packaging has an especially important role in the marketing strategy and branding of the product [15].

Tertiary pharmaceutical packaging is used to wrap or package products. Packaging ensures safe and trouble-free transportation of products. Tertiary packaging usually includes cardboard boxes, cling film, and plastic bags [15].

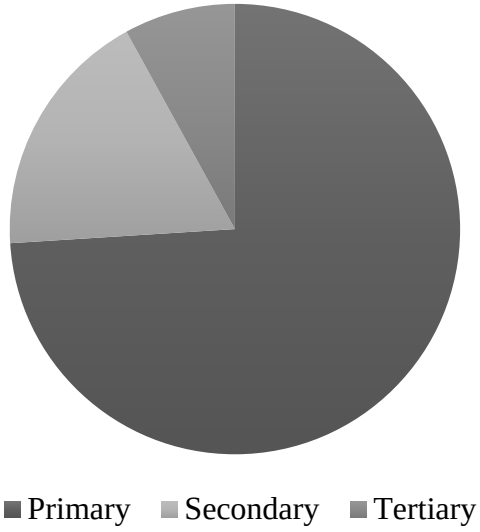

Figure 2.2. Global Pharmaceutical Packaging Market, Share by Product 2022 (%)[15].

Pharmaceutical production had the highest share in the packaging sector with 49.9% in 2022. Strong growth is expected between 2023 and 2030. Because the demand for drugs is increasing. The World Health Organization (WHO) predicts that the population over the age of 60 will almost double between 2015 and 2050, from 12% to 22%. The elderly population needs additional medical attention, which speeds up pharmaceutical production. Therefore, it is predicted that the demand for pharmaceutical packaging will increase [15].

2.1.1. Global Aluminium Foil Market for Packaging

Due to its low weight, excellent barrier qualities, cost-effectiveness, and flexibility of use, aluminium foil has become quite popular in the packaging industry (see Figure 2.3). Packaging materials made of aluminium are frequently used for goods like food, drinks, cosmetics, and pharmaceuticals. The global market for aluminium foil is expected to reach US$24.54 billion in 2021 and is projected to grow at a CAGR of 5.5% between 2022 and 2030. As a result of the global packaging industry's growth, the market is expected to grow. Additionally, it was found that the rising demand for pharmaceuticals was a contributing factor in the increased production of aluminium foil. Figure 2. depicts the development and projected development of aluminium foil utilization in blister packages over time [16].

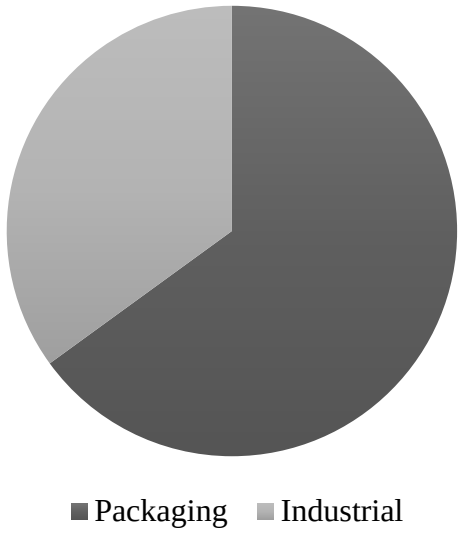

Figure 2.3. Global Aluminium Foil Market. Share by end-use, 2021 (%)[16].

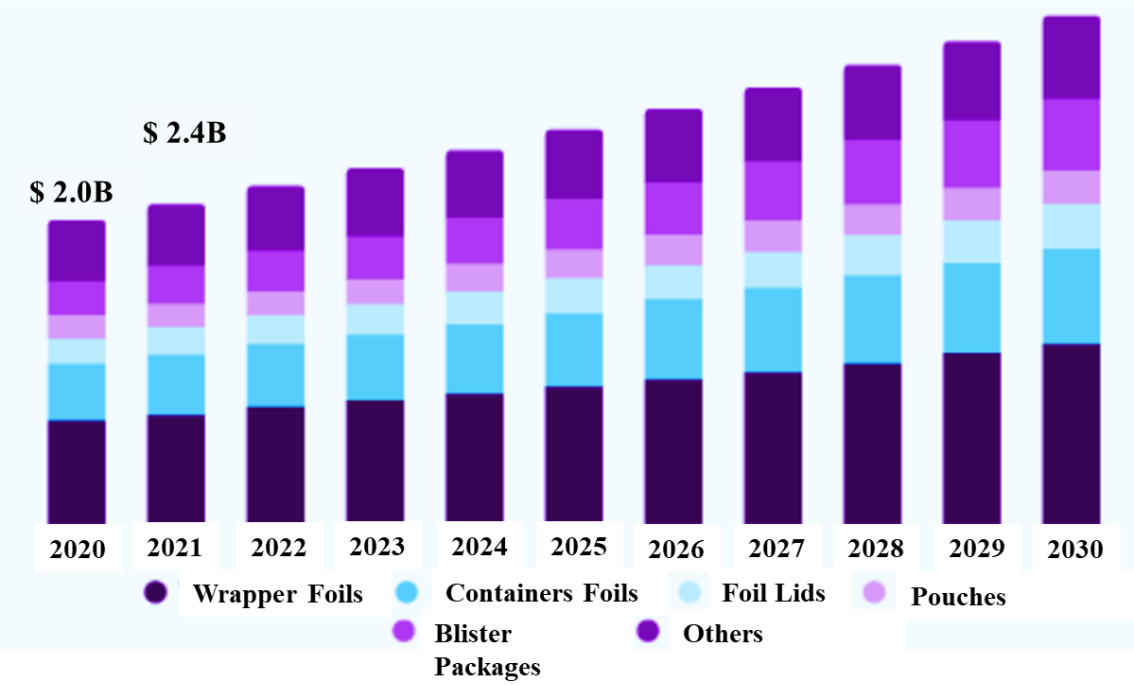

Figure 2.4. US Aluminium Foil Market. Size, by product 2020-2030 (USD Bllion)[16].

The pharmaceutical industry's investments during the projection period are expected to cause blister packages to increase significantly.

2.1.2. Global Plastic Market for Packaging

Plastic has a very common usage area and a large part of it is the packaging industry (Figure 2.). The global plastic market had a value of USD 593 billion in 2021. From 2022 to 2030, An increase of 3.7% is estimated from 2022 to 2030 (Figure 2.)[17].

More than 36% of the total demand was accounted for by the packaging end-use category in 2021, which also had the biggest revenue share. Packaging is a moderately penetrated end-use market with a considerable potential. The packaging sector has relied heavily on plastic. Additionally, the introduction of bio-based plastics has had a big impact on the food, drug, and beverage packaging industries[17].

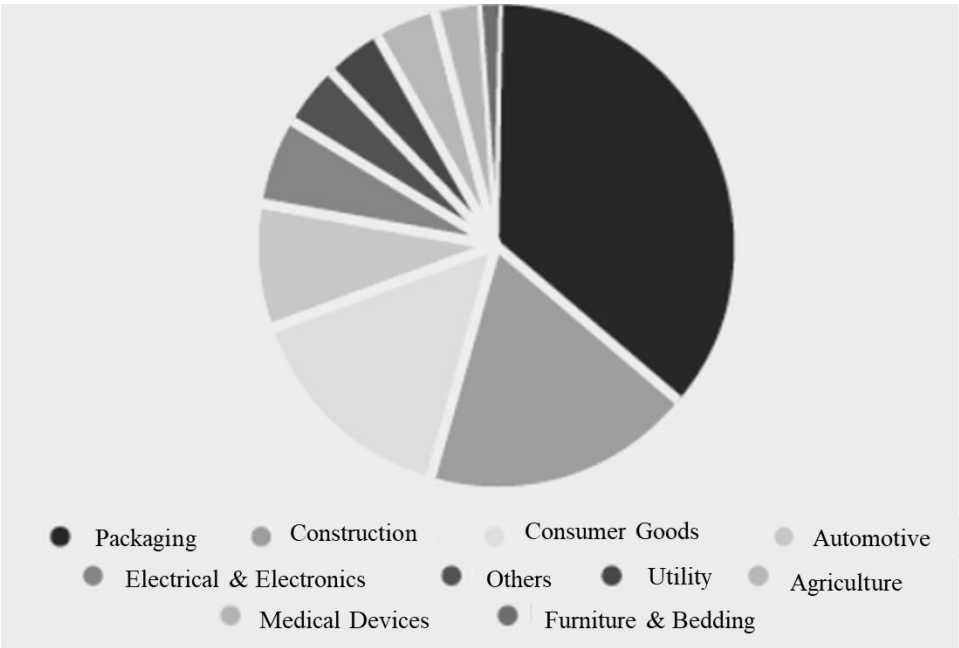

Figure 2.5. Global Plastic Market. share by end use, 2021 (%)[17].

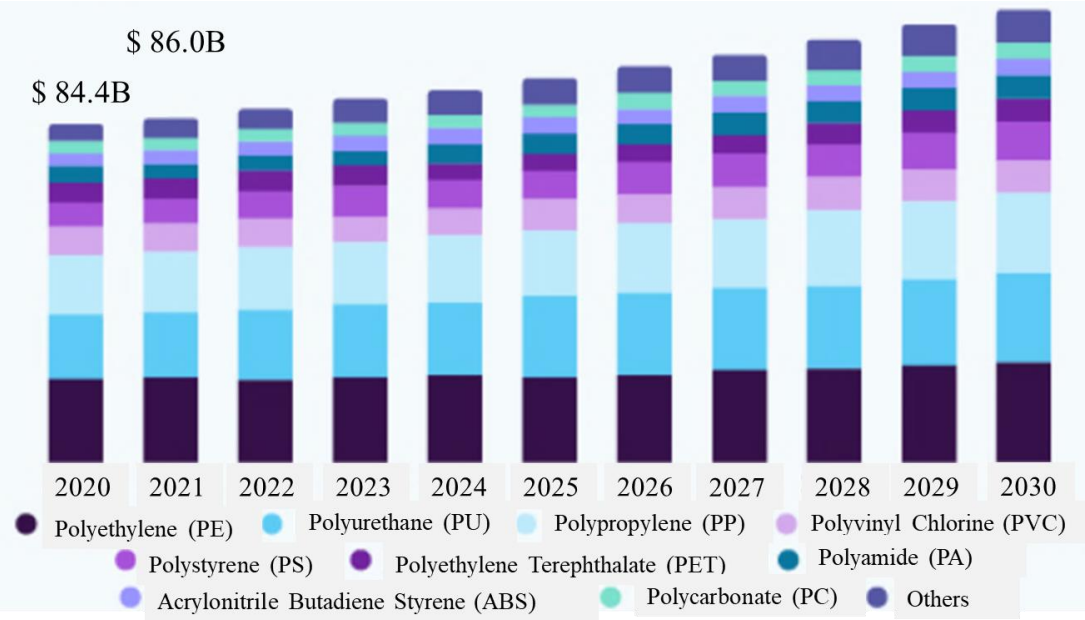

Figure 2.6. U.S. Plastic Market. size, by product 2020-2030 (USD Billion)[17].

2.2. Advantages of Pharmaceutical Blisters

Pharmaceutical blister packages provide a longer shelf life by protecting the products from moisture and gas. In addition, since it has a bubble structure, it is not affected by the negativities that may occur during transportation. Due to its structure, the products are hermetically sealed in their own cavities. Individual tablets or capsules are protected until used. Since the packages contain colourful and easily legible information, they provide easy use for patients. In addition, they are comfortable to use for the elderly as they have an easy push feature. Blister packages can be easily transported[9]. Because of these advantages, the preferability increases, and waste blister packages will be encountered after a while.

2.3. Components of Pharmaceutical Blisters

Pharmaceutical blister packages are manufactured by thermoforming and cold-forming. Pharmaceutical blister packages contain four basic components; forming film, lidding material, printing ink and heat-seal coating shown in Figure 2..

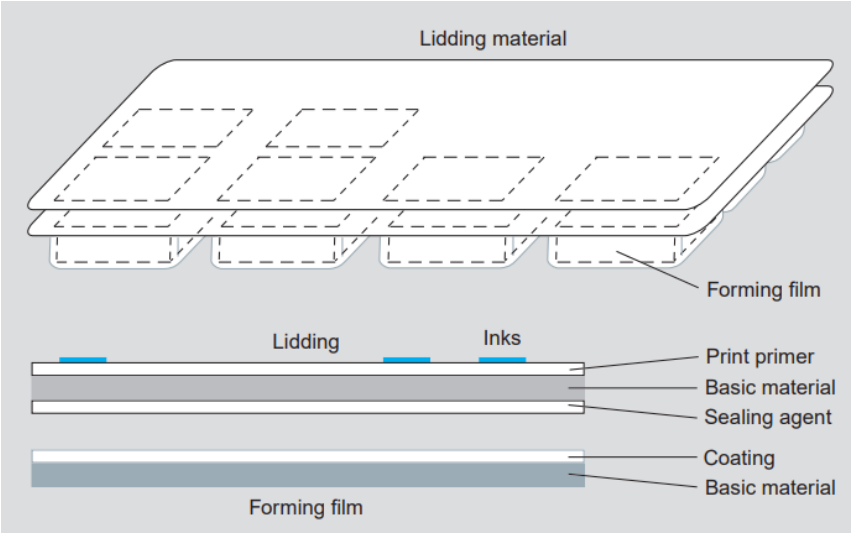

Figure 2.7. Components of Pharmaceutical Blisters Packages[3].

Pharmaceutical blisters consist of an aluminium layer and a plastic layer (Figure 2.). The forming film usually contains plastics such as polystyrene (PS), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polypropylene (PP), and polyethylene terephthalate (PET) [3].The packaging materials are selected corresponding to the resistance against the moisture of the product and durability. Lidding material generally includes aluminium as it can separate products from the air and is mechanically stable. Both the lidding and the forming film contain aluminium in cold-formed pharmaceutical packages. Cold forming provides better resistance than thermoforming. However, the production cost of cold forming is high[18].

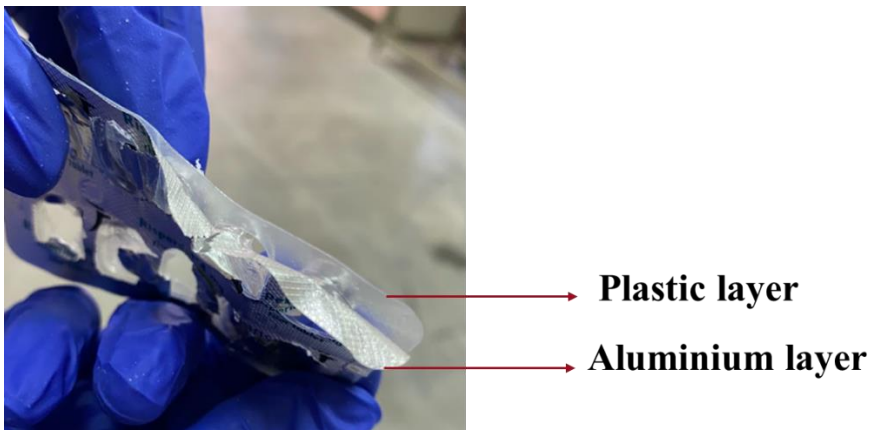

Figure 2.8. Plastic and aluminium layer of pharmaceutical blister packages.

2.3.1. Forming Film

The forming film holds the product in pockets produced with thermoformed pockets. Type, quality and thickness are the important parameters for the selection of an appropriate plastic film. These parameters are crucial for the performance of the packaging. Size and weight of the product, impact resistance, sharp or pointed edges of the packaging, ageing, migration, and cost are the requirements for selecting the best packaging materials. PP, PVC, PET and PS are the types of plastic used as forming films, and they can be thermoformed, while the substrate is aluminium cold-formed [3].

PVC is commonly used plastic for the production of blister packaging films. Because it contains almost no plasticizing components, PVC-forming film is called rigid PVC [3]. It also has a long history in pharmaceutical packaging, making it the first

choice for production in pharmaceutical companies[10]. It has high thermoformability, flexural strength, high resistance to chemical attacks, and low oil permeability. It is also easy to print and cost effective. The thermoformed PVC film is about 250 μm thick[3]. Due to the chlorine in its structure, the material is about 30% denser than PE. Because the melting and decomposition temperature of the most polymer materials are very close together, unmodified PVC is difficult to process. Stabilizers such as octyl tin compounds decrease the decomposition temperature. The decomposition of PVC creates HCl, a very strong acid. Decomposition occurs at 1008°C. PVC stabilizers make the packages suitable for food and pharmaceutical packaging. In order to enhance the oxygen and moisture barrier properties of blister packages, PVC films can be laminated with high-barrier plastics like PVDC or PCTFE (polychlorotrifluoroethylene)[10].

PVDC**,** despite its low volume, is an important component in the packaging as a lamination or coating of PVC. PVDC is applied widely as a coating for blister packaging. It decreases permeability to gas and moisture by a factor of 5 to10 compared to PVC. PVC films have a thickness of 203.2–254 μm with a 25.4–50.8 μm thick PVDC coating on one side of the PVC film [3,19,20]. The material has brilliant barrier properties to flavours, gases, odours, and moisture. In pharmaceuticals and food packaging, it provides a gas barrier against oxygen. The pure plastic material decomposes at 205°C and melts at 388°C to 401°C. PVDC forms HCl upon decomposition in the same way that PVC decomposes. In its pure form, PVDC cannot be melted. PVDC is uneconomical to use as a physical layer of the container. In order to make the container less expensive, it should be coextruded with less expensive materials[10].

PS that is a low-cost plastic is another packaging option. The polymer is atactic and cannot crystallize. PS has a density of 1.05 g/cm^3. It has a higher density than PP and PE. Since the polymer is amorph, it does not have a sharp melting point. Therefore, the material gradually softens over a wide range. The glass transition temperature (Tg) of PS is in the range of 74°C-105°C[3,10]. PS is not suitable for pharmaceutical packaging as it can soften at low temperatures[3,10].

PP has achieved preference in pharmaceutical packaging due to its good heat resistance and excellent moisture barrier. PP also has good oil resistance, a better odour barrier, and makes certain ingredients harder to absorb. It provides high heat resistance and high heat sterilization for the material[3,21]. PP that is uncoated has a lower

permeability to water vapor than PVC, but the most properties are similar to PVDC-coated PVC. The thermoforming technique uses PP films with 250-300 μm thickness. Unlike PVC, PP has good moisture-barrier properties and does not release harmful materials during cremation. However, PP is thermally unstable, slow to process, and susceptible to post-process shrinking. Its use is therefore restricted in Europe and the United States.[3].

PET is another plastic material that is used in pharmaceutical packaging. It can also alternative for PVC, but due to its higher permeability of water vapour than PVC, it is not as widely used as PVC. Even though PVDC-coated PET is a good substitute for chlorinated plastics, it lacks the water vapour barrier function of PVC[3]. When a film is manufactured with a biaxial orientation, crystallinity is induced, making it heat resistant[10].

Oriented polyamide nylon/aluminium/PVC or (OPA)/aluminium/PVC. Plastics and aluminium can be combined in layers to form films such as oriented polyamide/aluminium/PVC or nylon/aluminium/PVC. Laminates made of OPA, PVC and aluminium are of interest. It decreases permeability to water vapor owing to its laminate structure consisting of a 25 μm thick OPA, 45 μm thick aluminium and 60 μm thick PVC layer. It is also recyclable due to the high aluminium content in the laminate. Laminate of OPA/aluminium/PVC is cold formed like other laminates in company aluminium[3]. Nylon also has the advantages of high heat resistance, high strength, good chemical resistance, good toughness and good water resistance [11]. Cold forming contains more material to produce the same volume of packagings produced via thermoforming [3,11].

2.3.2. Lidding Materials

Lidding materials are crucial components of pharmaceutical blister packaging because they provide a protective seal over the induvial pockets or compartments containing the drug. The lidding materials must be compatible with the blister material and the carrier material to ensure a secure seal and effective protection of the drug. The lidding material is selected according to the size, weight of the product, and shape, weight as well as its packaging design. The lidding material. have a range of thickness from 0.36 to 0.76 mm, although the most common range falls between 0.46 and 0.61

mm. Usually, a layer of plastic that has been coated with either foil, for blisters type that can snap on, or laminations of paper/foil or paper/PET/foil are used for a child-resistant peel, as the lidding material. The lidding material is treated with clay coatings for the purpose of enhancing the printing quality. Printability and heat sealing are crucial parameters, and the lid should fulfil an effective mixture in those packages. As with the forming film, the lidding material must be suitable for the type of blister package (for example, push or peel). Figure 2.2 shows a cross-section of a peel-and-push closing material. Materials used as lidding materials are aluminium (hard/soft aluminium), paper/aluminium, and paper/PET/ aluminium [3].

Hard aluminium is mostly used as push-through lidding material in Europe. The foil generally has a 0.020 mm thickness. However, there are efforts to decrease the thickness of this foil to 0.015 mm. The aluminium hardness makes it easy to push open. Usually, just the print primer side attributes a printed design, nevertheless sometimes the side with the coating of heat-sealing also can be made. A double layer of heat-sealing coating (a heat-sealing coating and the real heat-sealing primer) has been the model for lidding materials [3].

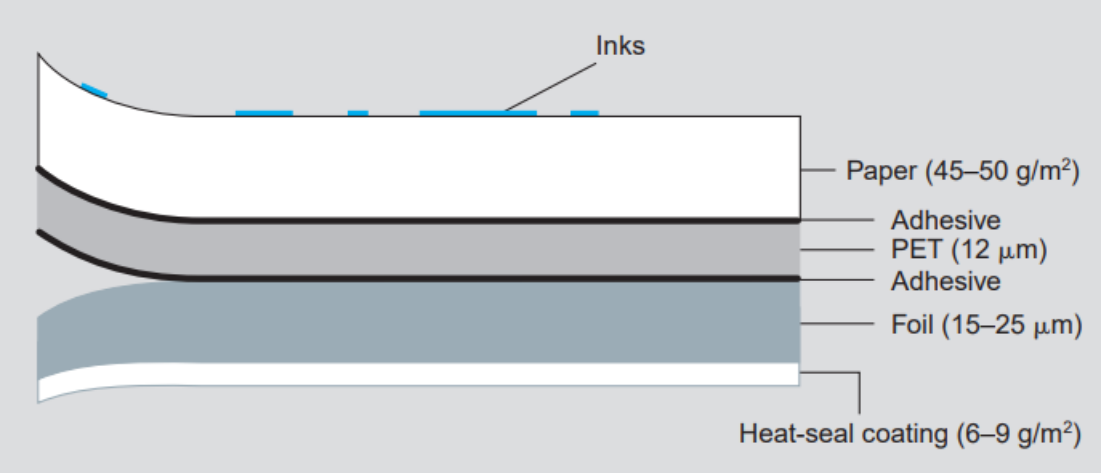

Figure 2.2. A peel-off–push-through lidding material cross-section [3].

The heat seal primer confirms good adhesion of the heat seal coating material to the aluminium foil. If the coloured heat-sealed primers are used, the primer does not allow the product to encounter the pigments. If additional printing is essential in addition to the coating, the only solution is to apply two coats of the coating. This

solution is necessary because the printing inks must be placed between the heat-seal primer and the heat-sealed coating [3].

Soft aluminium is preferred as a push cover material resistant to use by children. The aluminium type of this coating material is different, and its structure corresponds to that of hard aluminium. It usually has a thickness of 0.025 mm. The type and thickness of this aluminium prevent children from pushing the medication inside the package. In addition, this coating material has holes in the sealing joints, which ensures that it does not peel off from the formed film [3,22].

Paper/aluminium. Paper and aluminium combinations have different thicknesses in Europe and the United States. Europe uses thinner foil, while the United States prefers thicker foil. The reason for this difference is that the use of child-resistant push packaging is more common in Europe. In the United States, this material is used for peeling and so the foil needs to be thick [3,22].

Paper/PET/aluminium. The packaging consists of paper/PET/aluminium laminate is termed peel-push foil. It is widely used in the USA. Its implementation is to first peel the paper/PET laminate from the aluminium and then push the product over the aluminium layer[3,22].

2.3.3. Heat-Seal Coatings

Heat-seal coatings is an important component in the blister packages. The physical integrity and appearance of the package are dependent on the quality of the heat seal coating. Heat-seal coatings act as a bond between the plastic blister and the printed cover material. Solvent-based vinyl and water-based products are used in blister packages for heat-sealed coating. An ideal blister package heat-seal coating should have good gloss, hot-sealing, abrasion resistance, clarity, and also be able to adhere to a variation of blister films [3].

2.3.4. Print Inks

Printing inks are important components in packages which present an aesthetic look. Different methods are used to print the inks such as: letterpress, gravure, offset, flexographic, or silk-screen. Printing inks should keep their form and colour at temperatures up to 300°C. They need also be safe to use with the expected product and

be resistant against abrasion, bending, and fading. Excessive levels of hydrocarbon greases, lubricants, release agents or oils must not be present in printing inks[3].

2.4. Types of Pharmaceutical Blister Packages

There are three different pharmaceutical blister packaging types[18];

Type 1: Thermoformed package with clear plastic forming film and aluminium lidding,

Type 2: Thermoformed package with white opaque forming film and aluminium lidding,

Type 3: Cold-formed package with aluminium forming film and lidding.

Different blister package types have various component proportions. The first and second types have 80-85% by-weight plastic layer (typically PVC, PP, PET) and 10-15% by-weight metal layer (typically aluminium layer)[3,23–25]. Type 1 is the most used blister package worldwide. The third type mostly contains aluminium. It is a widely used blister package, especially in America. Type 3 blister package is preferred for moisture and light-sensitive products. Unlike types 1 and 2, they cannot be thermoformed, instead, they are formed by cold press. Type 3 blister package is designed for products requiring a high degree of protection. The use of cold-formed foils is increasing as there are moisture/photosensitive drugs on the market. Cold-formed foil is the only material that provides 100% protection against moisture, light, and oxygen, and thus the demand for this material is increasing. Type 3 blister package consists of plastic film (PVC/PE), adhesive material, foil, adhesive material, and an outer plastic film. The outer film can usually contain PET or PVC and acts as a heat-sealable layer while supporting the aluminium layer[3,26]. Plastic varieties provide better protection against external factors [3,26]. The aluminium layer, on the other hand, does not usually consist of a single thick layer but instead consists of several thin layers. In this way, the stretchability of aluminium increases and facilitate the cold stretching process [3].

Thickness is critical to ensure the barrier performance of blister packages. There are many drugs available in the market with different morphologies. Yousef et al. examined the morphologies and mass different blister packages [27]. The results are presented in Table 2.1.

Table 2.1. Dimensions and mass of different pharmaceutical blister package types[27].

Blister type	Length x Width x Thickness (mm)	Mass (g)
1	40 x 92 x 0.26	1.821
1	38 x 85 x 0.225	1.252
1	50 x 128 x 0.128	2.834
1	66 x 100 x 0.236	2.945
2	53 x 105 x 0.25	2.969
3	50 x 90 x 0.137	1.212

Shukla et al. and Laasonen et al. calculated the thickness of blister types which are between 280 and 365 μm. It was shown that the plastic layers are in the range of 260–330 μm and the aluminium layer is measured between of 25–30 μm[28,29].

Shukla et al. presented the basic composition of the layers (wt.%) for type 2 and 3 blister packages as shown in Table 2.2. The elemental analysis further showed that the metallic layer that formed after delamination in all samples was mainly aluminium. Also, the presence of significant amounts of chlorine in the plastic layers proves that the type of plastic contains PVC or PVDC[28].

Table 2.2 Elemental composition (wt.%) of the layers in type 2 and 3 pharmaceutical blisters[28].

Element	O	Na	Al	Si	P	S	Cl	Zn	Ca	Ti	Pd	Sn	Fe
Type 2													
P. layer 1	11.6	0.1	0.3	0.2	-	0.4	81.5	-	0.03	-	4.6	1.4	-
P. layer 2	16.1	1.3	0.3	0.1	0.4	0.8	76.6	0.2	-	-	4.3	-	-
Al layer	1.6	-	95.8	1.1	-	0.04	1.1	-	0.02	-	-	-	0.4
Type 3													
P. layer 1	15.8	-	0.5	0.2	-	0.4	73.0	-	0.1	4.6	4.6	0.9	-
P. layer 2	12.5	1.6	0.3	0.1	0.4	0.8	80.1	-	-	-	-	-	0.8
Al layer	1.8	-	97.3	-	0.1	-	0.1	-	-	-	-	-	0.8

2.5. Environmental Impact of Pharmaceutical Blisters

Sustainability is of great importance to researchers and industrialists, as it is critical to waste management, climate change and the rapid depletion of fossil fuels. Sustainability is important economically, environmentally, and socially. Since blister packages are preferable, some environmental problems may be encountered: waste

generation, energy consumption, resource depletion and chemical pollution. The types of packaging used for tablets affect the emissions generated during the packaging of medicines. The choice of appropriate packaging for medicines also influences the emissions that are released into the environment [30].

Waste generation. One of the most important environmental effects of pharmaceutical blister packaging is waste generation. Blister packages typically contain a combination of plastic, aluminium, and other materials that can be difficult to recycle. Most blister packages are sent to landfills without decomposing their contents. The amount of waste generated by blister packages used for single doses of medicines is significant. For example, a single blister package for a drug may contain only one or two tablets resulting in a lot of packaging waste for a small amount of medication. The use of single-dose packaging also leads to the proliferation of over-packaging, where medicines are packaged in multiple layers of blister packages to meet regulatory requirements and extend shelf life [5,8].

Energy consumption. The production of blister packages requires a large amount of energy, especially since they contain plastic and aluminium fractions. The energy consumption associated with manufacturing blister packages also contributes to greenhouse gas emissions that contribute to climate change [8].

Resource depletion. The production of blister packages requires the use of natural resources such as petroleum and metal ores. These resources are finite and can be depleted if not managed responsibly[5].

Chemical Pollution. Due to the high plastic content, chemicals can be released into the environment during the production of blister packages. These chemicals can be harmful to wildlife and ecosystems, especially once they get into waterways [5].

Primary aluminium production (molten salt electrolysis) is an energy-intensive process that uses large amounts of primary sources (ore, coke, salt) and generates large amounts of waste. Secondary aluminium production requires a significantly less energy and saves up to 95% of energy when recycled (Figure 2.3)[31].

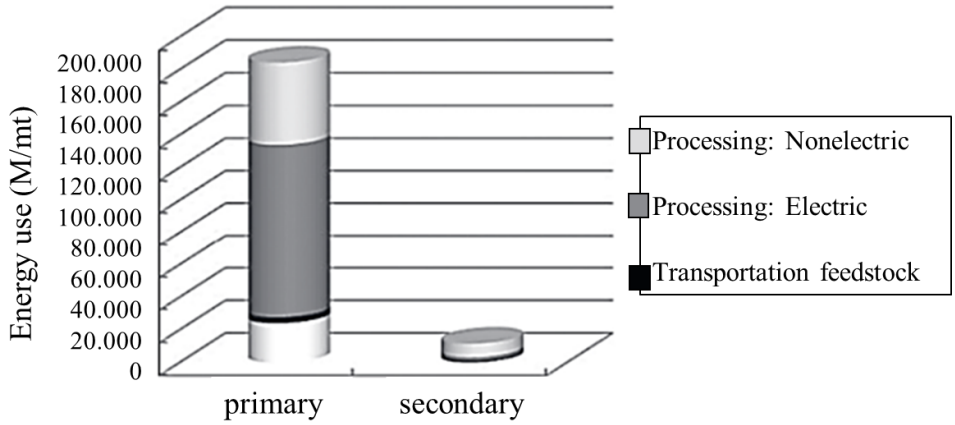

Figure 2.3. Energy uses of primary aluminium production and secondary aluminium production [31].

The use of aluminium has very high effects, especially on acidification, while PVC has significant impacts on fossil fuel depletion. PVC is the forming film with the minimal environmental affect, followed by OPA/Alu/PVC and PVC/PVDC. The impact of truck transport is more significant for larger packaging, as the amount of packaging transferred is limited by volume relatively weight. Transportation by railways and ships have a better environmental concert [32].

Raju et al. compared type 1 and 3 from environmental sustainability point of view. The analysis was conducted with four steps [30];

1. production of raw materials for blister packaging material, i.e., PVC and aluminium,
2. producing method of blister packaging material, i.e., PVC sheet and aluminium foil,
3. transportation of packaging material to the pharmaceutical plant, and
4. packaging of the tablets.

Raju et al. stated that environmental impacts are assessed using the 2001 impact judgement methodology from CML which includes intermediate categories of impacts for instance climate changes, acidification, and human toxicity. It was found that type 1 is more sustainable than the 3rd type. Production of type 3 requires 63% more energy. The impact on the climate crisis of type 3 is 70% better than type 1 packaging[30].

Bassani et al. evaluated the environmental life-cycle effects of different pharmaceutical packages. The life cycle model of the entire packaging, the models and supplies for primary packaging, secondary packaging and leaflet production are shown in Figure 2.4. It was emphasized that blister packages showed greater potential for

improving environmental performance. In addition, considering the environmental effects related to the material type, it was stated that the environmental impact of PVC-containing blister packages is low by Bassani et al [32].

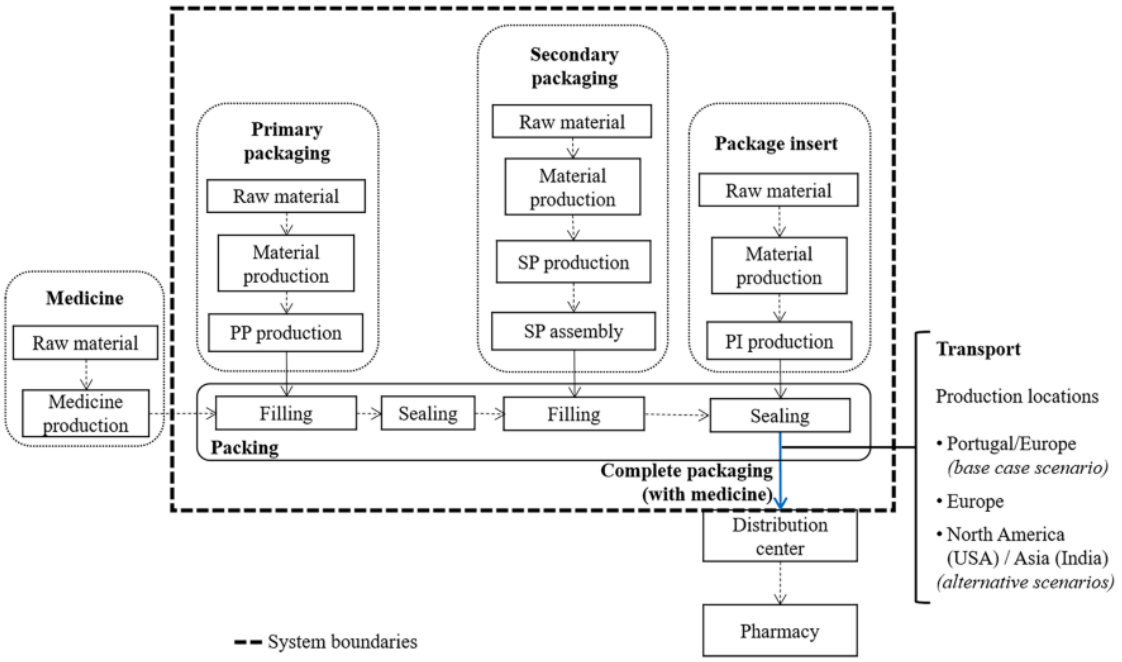

Figure 2.4. Life cycle model of pharmaceutical packaging: system boundaries and main processes [32].

2.6. Separation of the Layers in Pharmaceutical Blister Packages

Pharmaceutical blister packages have multi-layered structures that contain aluminium and plastic. Aluminium and plastic fractions must be separated from each other before recovery to increase the recycling yield. There are 3 separation methods in the literature: chemical separation methods, pyrolysis and electrohydraulic fragmentation (EHF). The chemical separation process is in which either a layer is selectively brought into solution with aluminium, or the layers is separated by dissolving only the adhesive between the layers. Another method is pyrolysis, in which the plastic part is decomposed and separated from the aluminium by the formation of composite materials. The last method is electrohydraulic fragmentation, which separates the aluminium from the plastic through a new application of EHF and reduces energy consumption.

2.6.1. Chemical Separation Methods

Chemical separation processes are commonly used to separate aluminium and plastic from pharmaceutical blisters. Hydrochloric acid (HCl) is one of the most widespread solvents for separation. Some reagents such as acetic acid ($C_2H_4O_2$), sodium hydroxide (NaOH), formic acid (CH_2O_2), organic solvent (benzene-ethanol-water) (C_6H_6 + C_2H_6O +H_2O), N, N-Dimethyl cyclohexylamine (DMCHA) ($C_8H_{17}N$), deep eutectic solvent (DES) ([$(CH_3)_3NCH_2CH_2OH$] Cl+ $C_3H_6O_3$), lactic acid ($C_3H_6O_3$), ethanol (C_2H_6O), acetone (C_3H_6O) and isopropanol (C_3H_8O) are used for the separation processes in the literature.

Reagents used in the recycling process of pharmaceutical blister packaging are among the factors affecting the environment. Reagents may contain risks to the environment. For example, reagents such as HCl (hydrochloric acid), and NaOH (sodium hydroxide) may be harmful to the environment and human health. For example, when HCl is released into the air, it causes acid rain and smoke generation, leading to air pollution. Rimšaitė et al. used formic acid, acetic acid and organic solvent in the separation process. He stated that formic acid and acetic acid adversely affect human health and the environment, but organic solvent is an acceptable reagent for the environment [23]. Nieminen et al. used DES and lactic acid to separate plastic and aluminium and reported that these reagents are environmentally friendly in their studies [18].

2.6.1.1. Reagents that Dissolve Aluminium

Wang et al. carried out experiments on the separation of layers using hydrochloric acid. The pharmaceutical blister samples were prepared for separation experiment by cutting 1 x 1 cm or 1 x 2 cm. End of the experiment, the aluminium fraction was totally dissolved in the hydrochloric acid and the plastic fraction was analysed with FTIR and the hydrochloric acid solution was analysed by spectrophotometric analysis. Temperature, time, hydrochloric acid solution concentration, liquid/solid ratio, and speed rate were investigated as an effect of experimental factors for the separation of aluminium from plastic. Increasing the temperature has been observed to increase aluminium separation. Furthermore, the dissolution rate of aluminium was shown to increase with rising hydrochloric acid

concentration, stirring speed, and leaching time. Under the following conditions, the plastic fractions are 100% separated from the aluminium fractions: 2.5 M concentration of hydrochloric acid, 25 °C, 4 h, liquid/solid ratio 15:1[24]. However, aluminium dissolves in hydrochloric acid solution so it was not recovered.

Chong-qing et al. investigated the performance of type 1 pharmaceutical blisters in sodium hydroxide solutions. Type 1 was prepared as 1 cm x 2 cm. Experiments were performed in a 1.25 M sodium hydroxide solution at 70 °C for 20 min with a solid/liquid mass ratio of 15:1. In addition, using xylenol orange as an indicator and the EDTA (ethylenediaminetetraacetic acid), the amount of Al^{3+} in the leaching solution was determined [25].

2.6.1.2. Reagents that Dissolve the Adhesive

Rimšaitė et al. used acetic acid, formic acid and organic solvent (mix with benzene-ethanol-water) as reagent and type 1 blister was used as the sample for the separation process [23]. In addition, experiments were performed under the following conditions for all three reagents trials:

- Solvent concentration: 4 M (mol/L)
- Solvent volume: 200 ml
- Sample dimensions: 1 cm x 1 cm
- Temperature 60- 100°C
- Stirring rate: 300 rpm (round per minute)

Under appropriate conditions, the reagents separated aluminium and plastic fractions allowing the recovery of both the aluminium and plastic. The solution was investigated with UV Spectrometer which confirmed that no aluminium was dissolved except in formic acid solutions. The mass loss was determined 0.02-0.08% when formic acid was used [23]. This might be due to the formation of aluminium formate, the aluminium salt of formic acid [33]. Additionally, the organic solvent (benzene-ethanol-water) confirmed enhance separation compared to the other two reagents (formic acid and acetic acid). Drug blisters reportedly contain 17% aluminium [23].

Nieminen et al. used DES for separation experiments. All three types of pharmaceutical blisters were used, and experiments were accomplished with 1 g samples. In addition, DES was prepared at 90 °C by mixing with choline chloride and lactic acid (1:9) in approximately 60 minutes until clear. Lactic acid is non-volatile and

toxic, making it suitable for separation experiments. All trials were carried out following conditions [18],

- Temperature: 80- 120 °C,
- Solvent concentration: 50- 100 wt.%,
- Solid/liquid mass ratio: 1:30- 3:30,
- Stirring rate: 0- 200 rpm.

It was observed that the separation time was shortened with increasing temperature, and the time needed for the full separation increased with decreasing solvent concentration and solid-liquid ratio. Additionally, lactic acid is an acceptable solvent for separation as it attacks the bond (glue) between plastic and aluminium layers. Furthermore, the plastic layer was analysed by FTIR (Fourier Transform Infrared Spectroscopy), and the aluminium layer was analysed by SEM-EDS (Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy). They used Table 2.3, which shows the FTIR peaks and associated layers in their study, to show that there are different plastic layers in pharmaceutical blister packages. The plastic fraction is PVC, with an acrylic adhesive between the aluminium and PVC, and three types of peaks are observed to match. In addition, Type 2 and type 3 form precisely specific peaks on the plastic fractions PCTFE (polychlorotrifluoroethylene) and nylon. The aluminium mass loss was analysed by ICP analysis (inductively coupled plasma), and the aluminium mass loss content was analysed by calculated ICP. Nieminen et al. stated that DES causes corrosion on aluminium surfaces. The lactic acid was diluted and used as is at various temperatures. It was concluded that aluminium mass loss was less than 5% when pure lactic acid was used. Regarding aluminium mass loss, using pure lactic acid is more efficient. In addition, according to the EDS results, they observed that the surface of lactic acid-treated aluminium was smoother than DES. Finally, Nieminen et al. evaluated the reusability of solvents. A total of 6 lactate and DES replicas have been prepared, and it has been reported that reuse may lead to longer separation times due to solvent colour changes. Therefore, industrial solvents must be purified before being reused [18].

Table 2.3. The FTIR peaks for the identification of polymeric layers[34–36].

Plastic	Literature (cm^{-1})	Peak Assignment
PVC	1427, 1426	C- Cl stretch
	1331, 1328	CH_2 rock
	1255, 1239	C- C stretch
	1099, 1095	C- H bend
	966, 962	C- H bend
	616, 609	CH_2 bend
PCTFE	1285, 1279	C- F stretch
	1194, 1191	CF_2 stretch
	1130, 1120	CF_2 stretch
	972, 961	C- Cl stretch
	580, 579	CF_2 wagging
Nylon (all polyamides)	3298	N-H stretch
	2932	CH stretch
	2858	CH stretch
	1634	C = O stretch
	1538	NH bend, C - N stretch
Acrylic Glue	1730	C = O bend
	1450	CH_2 bend
	1380	CH_2 bend
	1265- 1240	C- O- C stretch
	1165	C- O- C stretch

Yousef et al. used DMCHA and ethanol for the trials for layer separation in packaging. Six different types of blister packages with different properties and pill types were selected. The SEM-EDS analysis was used to analyse layers found in blister packages. Alloying elements such as Si (silicon), Fe (iron), and Ti (titanium) were mainly detected in the aluminium layer. FTIR was used to identify the plastic layer, and TGA-DSC (thermogravimetric analysis differential scanning calorimetry) were used to assess the thermal stability of the forming film and the glass transition temperature. The detection of chlorine shows that the plastic layer is PVC and PVDC. The thickness range of the blister was 130-250mm. Figure 2.5 shows the forming film, PVC, of the blister package exposed to different temperatures. A colour change was observed at 60 and 80°C, which is a sign of deterioration. Therefore, a temperature of 40°C was selected and the DMCHA ratio was set at 1:3 g/ml [27].

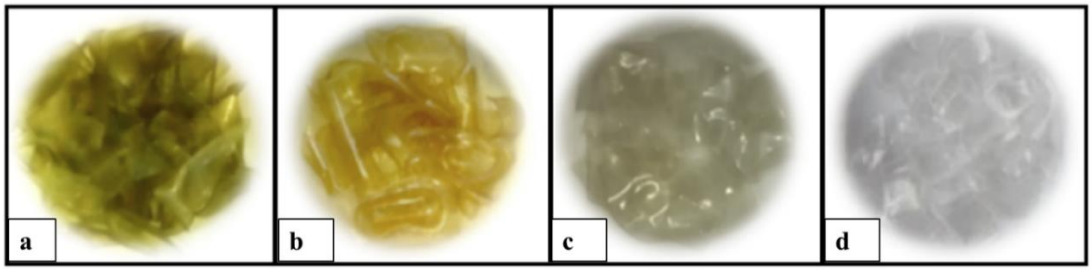

Figure 2.5. Forming films recovered at a) 80, b) 60, c) 50, and d) 40°C[27].

Shukla et al. used isopropanol and acetone for delamination experiments, diluting acetone with isopropyl alcohol. Experiments were performed at 0-100% (v/v%) at a stirring speed of 600 rpm and at 30-50°C. It has been observed for three types of blister packages that the aluminium layer is separated from the plastic layer. The purity of the aluminium was measured using ICP-OES and was > 99.4% for types 2 and 3. The plastic layer was PVC and PVDC according to FTIR analysis, and the adhesive material between the layers was polyacrylate based. The total thickness of the blisters ranged from 280 to 365 μm (260-330 μm for the plastic layer and 20-35 μm for the aluminium layer). Shukla et al. decided that the delamination process was effective for blister packages using isopropyl alcohol and acetone (50 v/v% and 200 ml) [28].

The experimental parameters for using all reagents in chemical separation methods are summarized in Table 2.4.

Table 2.4. Summary of experimental parameters used for the chemical separation of blister package layers.

Ref	Sample	Reagent	Conditions	Analysis Method
[24]	type 1	HCl (1.3-2.5M)	25-50°C 0-100 rpm up to 360 min	visible spectrophotometric analysis FTIR
[25]	type 1	NaOH (1.25M)	70°C 400 rpm 20 min 15:1 solid-liquid mass ratio	

(Cont. on next page)

Table 2.4. (cont.)

Ref	Sample	Reagent	Conditions	Analysis Method
[23]	type 1	CH_2O_2 $C_2H_4O_2$ organic solvent (C_6H_6-$C_3H_6O_3$-H_2O)	60-100°C 300 rpm 30 min	visible spectrophotometric analysis FTIR
[18]	type 1,2,3	DES $C_3H_6O_3$	80-120°C 0-200 rpm 50-100 wt.% solvent concentration 1:30-3:30 solid-liquid mass ratio	FTIR SEM-EDS ICP-MS
[27]	type 1,2,3	DMCHA+ C_2H_5OH	40-80°C 120-180 min 300 rpm 30 min	SEM-EDS FTIR TGA-DSC
[28]	type 1,2,3	C_3H_6O+ C_3H_8O	30-50°C 600 rpm 0-100% (VC_3H_6O/VC_3H_8O)	ICP-OES FTIR

2.6.2. Pyrolysis

The pyrolysis process is the most appropriate pyrometallurgical technique for the separation of plastic and aluminium in pharmaceutical blisters. Combustion procedures are not advised because of the significant amount of plastic. Pyrolysis occurs in the absence of oxygen. Solid, liquid, and gaseous fractions can be created from the process by-products. The solid fraction contains aluminium or non-pyrolyzing elements.

Basic metallurgical techniques can be used to separate the aluminium portion from the char[26,37]. Pikoń et al. and Klejnowska et al. conducted pyrolysis with pre-consumer and post-consumer pharmaceutical blisters (Figure 2.6)[26,37]. The pharmaceuticals are not in contact with pre-consumer waste materials, and transparent plastic was used for the lids. Drug-removal blisters come in a variety of forms in post-consumer waste materials. They were examined by Klejnowska et al., who reported that an examined portion of the post-consumer waste products contained: Al/Al blister, Orange plastic, Red plastic, 3.9%, 15.0%, Transparent plastic, 32.7%, and White plastic, 38.5% [26].

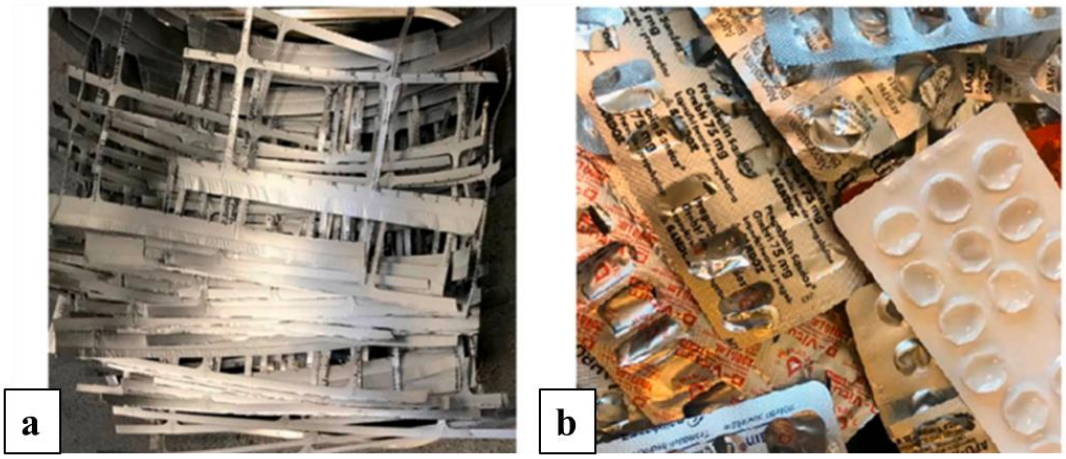

Figure 2.6. Analysed materials; a) pre-consumer waste, b) post-consumer waste[26].

Chemical analysis of pre-consumer and post-consumer materials was performed (Table 2.5). According to the results of the analysis, it was determined that the difference between the two materials was the presence of chlorine. Post-consumer waste contains less chlorine than pre-consumer waste. The reason for this is that the lidding material is presented to the consumer. The lidding material is pre-consumer only PVC but includes various types of post-consumer materials [26].

Table 2.5. Chemical analysis of the pre-consumer and post-consumer waste materials [26].

Sample	**Content (%)**				
	C	H	Cl	N	S
Pre-consumer	45.46	3.37	43.66	0.60	10.83
Post-consumer	44.27	4.47	35.03	0.35	11.33

The pyrolysis experiments were carried out at three different temperatures (400 °C, 425 °C, and 450 °C). The off gas was gathered at the beginning, middle, and end of the pyrolysis experiment. Hydrocarbons were detected using a flame ionization detector (FID), while inorganic compounds were detected using a thermal conductivity detector (TCD) [26,37].

The calorific value of the gas at 450 °C for both samples was specified by Klejnowska et al. (20.14 and 21.96 MJ/m3 for pre- and post-consumer, respectively). Additionally, Piko'n et al. reported that post-consumer waste materials had the highest calorific value of gas at 450 °C [37]. For both samples, there were no variations in the gas quality. In other words, the quality of the gas was unaffected by the contaminants present in each sample. Ultimately, 450 °C was chosen as the ideal temperature to create the gaseous fuel [26,37].

Following the pyrolysis procedure for chemical analysis, Piko'n et al. removed the char and aluminium fraction from the post-consumer waste materials (Figure 2.7). They stated that there was an average separation of 85–90% for aluminium (86.4% for pre–consumer waste and 88.5% for post–consumer waste). The pyrolysis procedure eliminated all paints and coatings. The sample created by performing the process on post-consumer material at 400 °C had the highest heat of combustion value (32,534 kJ/kg), according to calculations made by Piko'n et al [37].

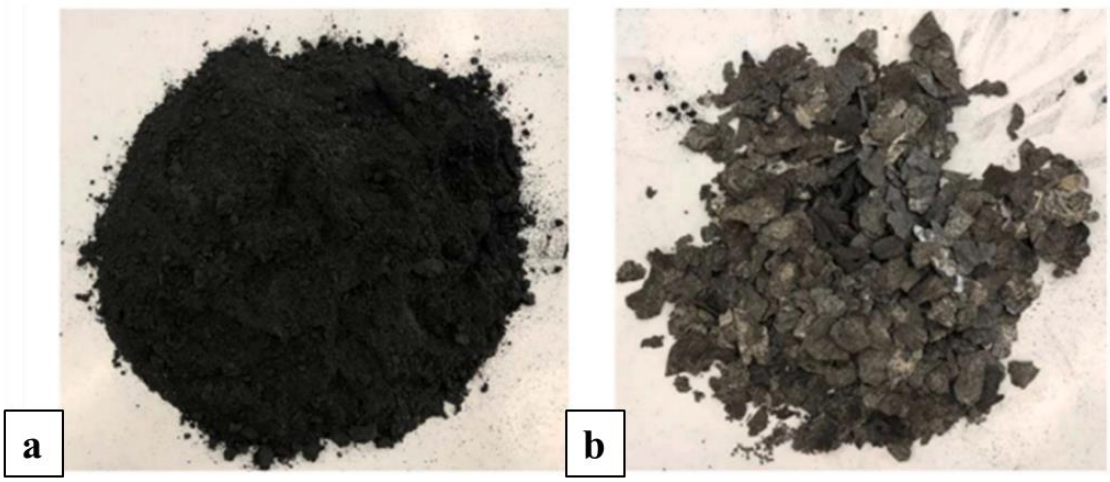

Figure 2.7. a) post-pyrolysis char obtained after the separation of the solid fraction. b) Post-pyrolysis metallic fraction obtained after the separation of the solid fraction[37].

After pyrolysis at 400, 425, and 450 °C, Table 2.6 shows the ratio of the aluminium portion to the char for both samples. Remelted aluminium that had been separated from the char. Nearly 90% of the aluminium content was recovered during the remelting procedure, which was carried out in a laboratory-scale electric furnace at 800 °C with the addition of $MgCl_2$, NaCl, and $Na_3(AlF_6)$ [37].

Table 2.6. The mass distribution of the metal and char after pyrolysis of pre and post-consumer blisters[37].

Temperature (°C)	Pre-consumer (wt%)		Post-consumer (wt%)	
	aluminium	char	aluminium	char
400	40.5	59.5	36.4	63.6
425	42.6	57.4	37.4	62.6
450	44.4	55.6	39.6	60.4

2.6.3. Electro hydrophilic Fragmentation (EHF)

For type 1 and type 2 blister packages, Agarwal et al. used the Electro hydrophilic fragmentation (EHF) method. Leaching was started by preparing a 4:1 vol ratio of phosphoric acid solution. The following experimental parameters were used: an electrode gap of 40 mm, 300 pulses, a frequency of 3 Hz, a discharge voltage of 130 kV, and ratios of 20 g/L. The blisters included 88–90 wt% plastic fraction and 10–12 wt.% aluminium, according to ICPOES analysis. The interior structure of the blisters was observed by SEM-EDS to have two layers of plastic (perhaps PVC) and an aluminium layer [38].

2.7. Recycling of Components of Pharmaceutical Blisters

As we mentioned in 2.3, the pharmaceutical blister package consists of aluminium and plastic. Developing strategies to reduce plastic and aluminium waste and increase the sustainability of these packaging is crucial. Recycling is one method for making pharmaceutical blister packaging sustainable[39].

Recycling pharmaceutical blisters and separating aluminium and plastic in them attract attention due to the cost and environmental impact of aluminium. The recycling

efforts of pharmaceutical blisters are increasing with the scope of the zero-waste strategy. Before recycling, separation methods should be applied.

2.6.4. Recycling of Aluminium

The production of dross, non-metallic impurities, and oxides must be minimized in foundries when melting and working with molten aluminium alloys. Aluminium alloy swarf and light scrap have a considerable oxidizable active surface area, which presents a problem when they are remelted. To solve these issues, fluxes are used. A material called flux is introduced to molten metal, where it combines with impurities to create skimmable dross or slag. Cleaning metal, reducing excessive oxide growth, removing non-metallic contaminants from the melt, and cleaning furnace walls are all possible using this technique[40–42].

The formation of coalescence is important in metal recycling because it allows the metal and slag to separate from each other. Coalescence has been intensively studied since the early 1900s [43] and is a crucial component of aluminium recycling yield. Aluminium oxide layer removal and coalescence in salt flux have been extensively studied [44,45]. Jordan, Milner, and Storchai provided a description of the electrochemical procedure of oxide elimination by the salt flux [46]. Al^{3+} ions weaken the oxide while salt flux penetrates it and removes it from the aluminium. According to Roy and Sahai, variations in the interfacial tension between salt, aluminium, and alumina are connected to the removal of oxide [45,47,48].

The following deoxidizing steps were presented by Jordan and Milner:

Due to the simultaneous thermal expansion of aluminium and salt element attack, oxide ruptures arise [45–47]. The oxide layer is made more susceptible to the salt attack. Al droplets' spherical form also minimizes their energy and surface area. As aluminium droplets coalesce or combine into a single large droplet, the free energy of the system is finally reduced.

The tendency of liquid surfaces to contract to a small surface area is known as surface tension. Conflicting cohesive and adhesive forces that result in equilibrium help to explain this. Cohesive forces, as compared to adhesive forces, which are stronger between liquid atoms than between liquid and gas, are what cause surface tension. The interaction between cohesive and adhesive forces is influenced by wetting, contact angle, and meniscus form. This also indicates that liquid droplets are shaped by surface

tension. The tension between two liquids, called interfacial tension, affects the shape of the aluminium droplet in the molten salt. A spherical form lowers the interfacial tension, as stated by Laplace's Law. Force per unit length or energy per unit area are the units used to describe surface tension [49].

Roy and Sahai examined the oxide layer's state and observed that when it is ruptured without being removed, it can become spherical. The oxide layer cannot be ruptured, and coalescence promoted by thermal expansion and spherical transformation of the droplets obtains the least amount of free energy. Rather, a more important factor for coalescence is the activity of surface-active components [45]. The coalescence of several fluoride additions over time is shown in Figure 2.8.

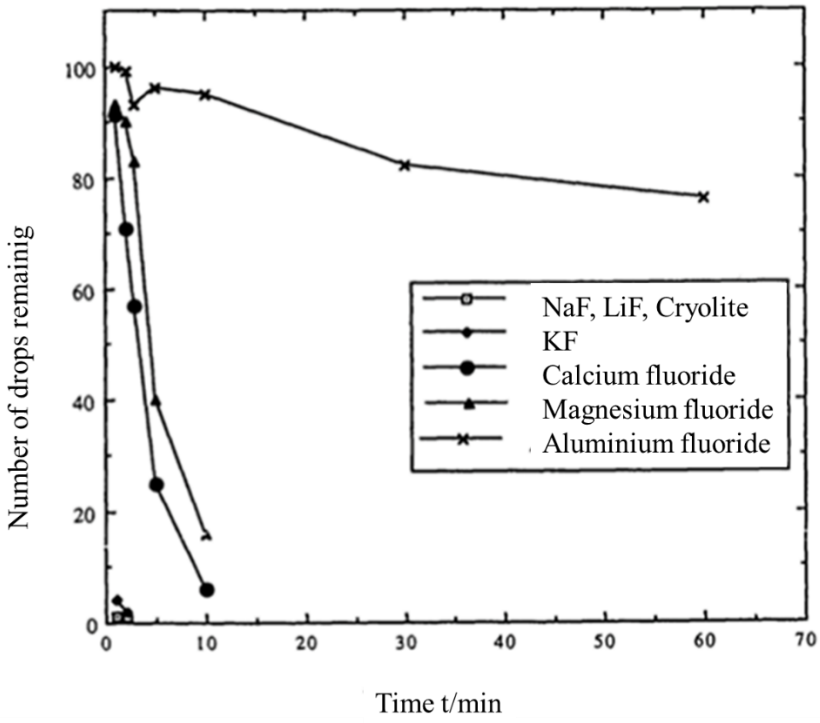

Figure 2.8. Coalescence of the amount of Al droplets over time based on different fluoride additions [45].

It is obvious that fluoride compounds enhance the coalescence of aluminium. When CaF_2 was added to equimolar NaCl-KCl, the metal loss was 0.45%, which is minimal when compared to other fluoride compounds[45]. Due to interfacial tension produced by displacement processes, other fluoride compounds with good coalescence caused additional metal loss.

Additionally, salt flux protects metal surfaces from contamination and air oxidation. The salt flux characteristics speed up the removal of oxide, which enhances coalescence. In Europe, salt fluxes with a ratio of 70/30 NaCl/KCl and trace levels of CaF_2 are frequently used for metal recovery. Figure 2.9 displays the ternary phase diagram of the salts of NaCl, KCl, and CaF_2. CaF_2 is cheap and often used in concentrations of 2 to 5 wt.% [50,51]. Figure 2.10 also includes a binary phase diagram for NaCl and KCl. The eutectic point (lowest melting point) of the binary phase diagram of NaCl KCl salts was found to be at 44 wt.% NaCl and 645 °C. The melting temperature of pure NaCl, which is 801 °C, is just 36 °C higher than the melting point of salt mixes used by European recyclers, which is 725 °C. The diagram shows how increasing the amount of NaCl raises the melting point [51].

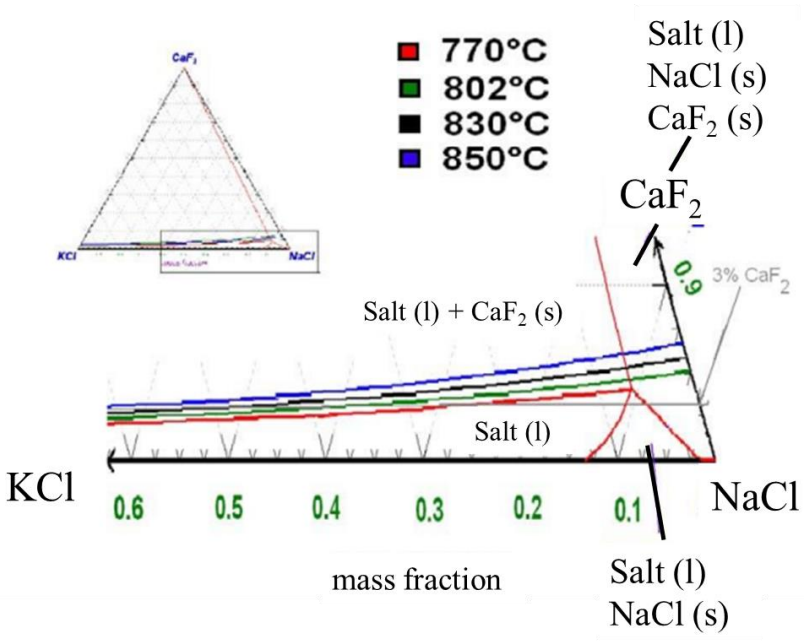

Figure 2.9. Equilibrium ternary diagram for CaF_2 -NaCl-KCl [51].

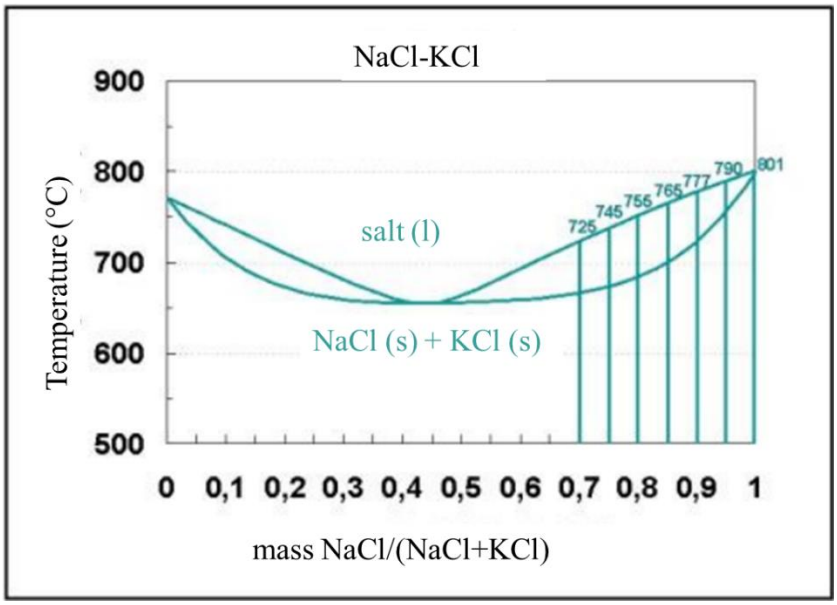

Figure 2.10. Binary phase diagram of NaCl- KCl [51].

According to Milke et al., only dissolved fluoride ions promoted oxide clearance [50]and fluorides are added to encourage coagulation by separating the oxide coating that covers the metal surface [52]. Higher concentrations reduce interfacial tension and increase salt flux viscosity, which increases melt loss. Viscosity is also increased by the dispersed oxide layers in the salt flux. The Bukhalova and Bergman phase diagram, the only one that is currently available, shows substantially reduced solubility over 730 °C. Higher aluminium/salt ratios result in increased metal loss, as shown in Figure 2.11. When there is more salt to scrap, aluminium-dispersion decreases, indicating that there is more aluminium in the salt. But when there is more salt than scrap, more aluminium is lost [51].

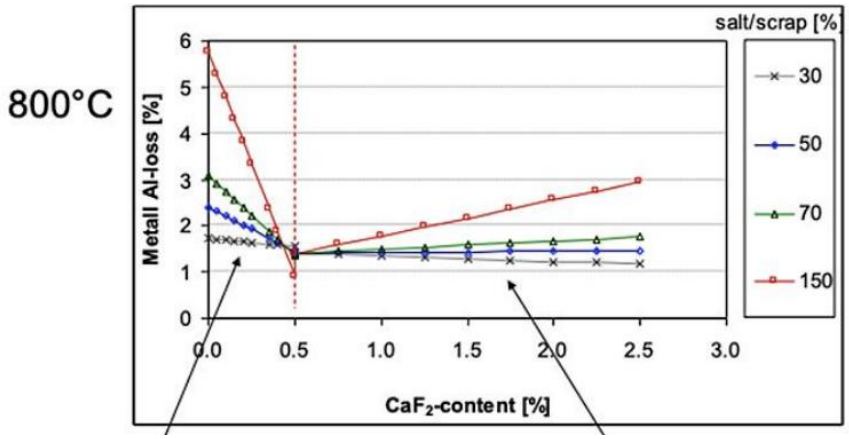

Figure 2.11. The relation between CaF_2 addition and metal loss for various aluminium/ salt ratios [51].

Influences include the fact that fluorides cannot remove the oxide layer off aluminium-pieces at low CaF_2 levels, causing them to remain in the melt and prevent combination. More CaF_2 causes the aluminium/salt surface tension to decrease, allowing more aluminium-droplets to disperse. Oxides that have been stripped increase salt slag viscosity and stop coalescence. Aluminium losses were lowest in salt/scrap ratios of 30%. A minimal amount of salt flux should be used to cover the aluminium in order to maximize recovery [50].

2.6.5. Recycling of Plastics

In addition to Section 2.6, which can be used also as a recycling method as well as a separation method. It can also be recycled by collecting plastic and directly melting it. But we are not talking about plastic recycling in this thesis, as we focus on blister delamination and aluminium recycling.

Plastics production is the process of producing plastic products from raw materials such as crude oil, natural gas, and coal. Reducing plastic production and consumption, and recycling plastic waste is important for sustainability. Recycling plastic is one of the most suitable methods to reduce the amount of plastic waste in the environment, protect natural resources, and promote sustainability. Recycling plastic saves natural resources by reducing the need for new raw materials and requires less energy than producing new plastic products from raw materials. This is because the recycling process involves fewer steps and uses less energy-intensive processes. It also

reduces greenhouse gas emissions by eliminating the need to manufacture new plastic products from fossil fuels[53–55].

Recycling of plastic is the name of the process given to recycling waste plastic products, which are shredded or simply thrown away, into different products by reprocessing, and even turning them into granules and transforming them into completely different forms. For example, plastic chairs and tables can be produced by recycling waste beverage bottles[56].

Compared to materials such as metal and glass, plastic polymer materials require much more processing. Because plastics have low charge weights and large polymer chains, they have a low mixing entropy. Because macromolecules interact with their environment, they show a higher enthalpy of mixing to organic networks of similar structure. The components sufficient to burn for the efficiency of such large units must be of the same type for the plastics to diffuse efficiently [56].

Therefore, plastics must be effectively separated before being recycled. Distinctive plastic codes (see Figure 2.) engraved on the products have been determined for the correct separation of plastics. These codes were determined by the Plastics Industry Association in 1988. Accordingly, the distinguishing code of polyethylene terephthalate, also known as PET, is "1". Consumers, who see the codes written on all products from packaging products to containers, can sort their garbage according to these. Distinguishing codes are unavailable on plastic films as their collection and recycling are impractical and uneconomical [56].

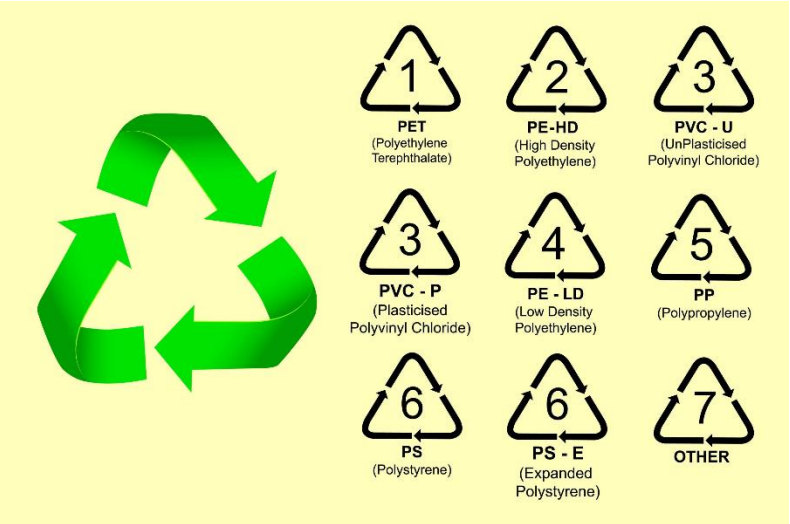

Figure 2.19. Distinctive recycling codes of plastics [57].

The sorting process, which is often based on manually sorting the materials flowing on the conveyor, is perhaps the most painful and critical step in the recycling of plastic. Separating different types of materials (paper, metal, plastic) from each other is critical. For example, in a line where the end product is granules, if the metals are not separated correctly, metal particles can cause great damage to the injection machines. Beyond that, plastics must be separated according to the above codes [56].

Another obstacle in recycling plastics is the use of additives and dyes. Since polymers are generally very fluid, it is not economical to remove additives and processes that normally separate dyes very cheaply and damage the material. For this reason, additives are used less frequently in beverage bottles and bags, allowing their effective recycling [56].[58]

The steps required to recycle plastic, including the collection, sorting and reprocessing of ready-to-use plastic in new products, are presented in Figure 2.12. In short, these steps are collection, separation and reprocessing [59].

Collection: plastic is dropped into a recycling container by users.

Separation: plants separate plastic from other materials as well as different types of plastic.

Reprocessing: the plastic is washed, ground into flakes, heated and extruded into new pellets.

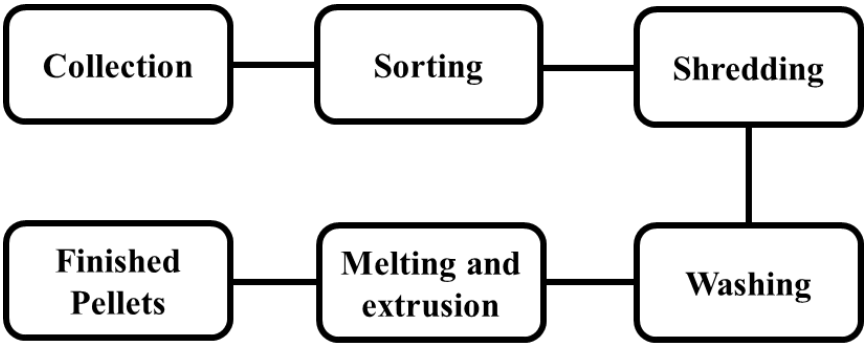

Figure 2.12. Stages of Plastic Recycling[59].

In energy recovery system, plastic waste is incinerated, and the energy is used to generate electricity with an efficiency of over 90% [58]. Flexible waste is also used as a fuel source in cement industry many developing countries such as India [53]. However, since incineration is not supported as a principle by the definition of the circular plastic

economy, which will be discussed later, energy recovery is not regarded as a beneficial use of plastic waste. Post-consumer waste and industrial waste are the two categories of flexible film waste that can exist. Both types of waste when recycled using a mechanical process can be configured as closed or open loops depending on the type of quality instream. Post-consumer flexible packaging trash is currently either burned, dumped, or has very little open-loop recycling. Due to the damaged structure of the polymer, as it undergoes a number of processing steps like shredding, washing, drying, and re-granulating before co-extrusion, the quality of recycled material from closed-loop recycling is often low. Closed-loop recycling processes often only require extrusion before being utilized to create packaging and have high-quality, homogenous input streams. The polymer has greater structural integrity as a result of the open-loop method. The input stream typically consists of homogenous plastic, but post-consumer flexible packaging has greater levels of pollutants (additives, inks, etc.) and dirt (organic waste, dust, etc.). Post-consumer plastics are the most difficult kind of plastic film waste to physically recycle because their structural layers are not uniform. Therefore, post-consumer flexible waste is usually chemically recycled or used for energy recovery. Production of sheets (43%) and composite lumber (44%) are the two primary final uses for recycled plastic films [58].

CHAPTER 3

MATERIALS AND METHODS

This chapter describes samples, experimental setup, experimental procedure, for separation and recyclability of the components in pharmaceutical blisters.

3.1. Collection of Pharmaceutical Blister Samples

1200 Pharmaceutical blisters were collected from different pharmacies in Izmir, Turkey for this study. Samples were classified according to their types. There are three different types of pharmaceutical blisters and Figure 3.1a shows type 1, Figure 3.1b shows type 2, and Figure 3.1c shows type 3. In addition, collected pharmaceutical blisters contained 63% type 1, 13% type 2, and 24% type 3 (shown in Figure 3.2). In total, type 1 blister packages containing 210 different brands from 67 pharmaceutical companies, type 2 blister packages containing 49 different brands from 30 pharmaceutical companies and type 3 blister packages containing 66 different brands from 32 pharmaceutical companies were collected.

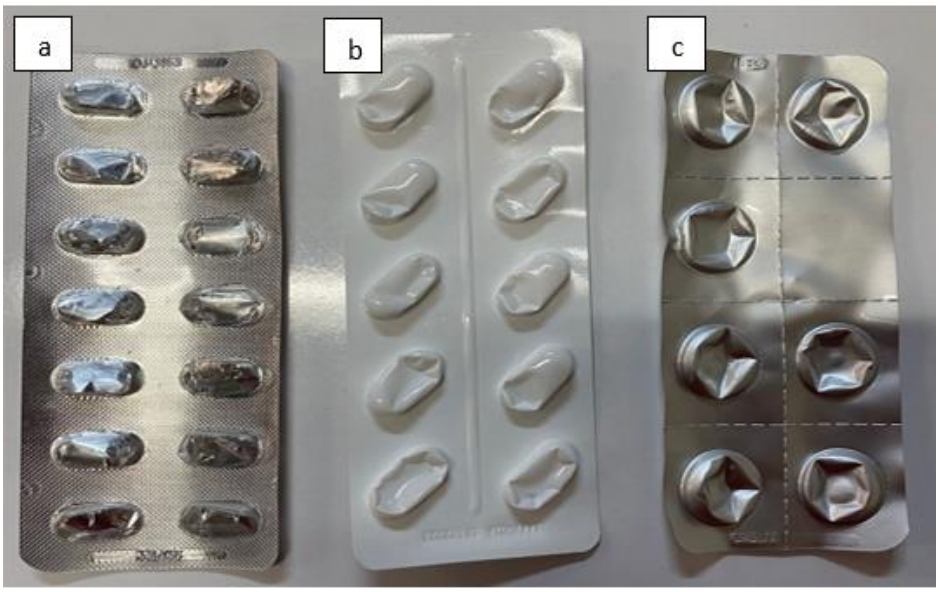

Figure 3.1. Types of pharmaceutical blister; a) type 1, b) type 2, and c) type 3.

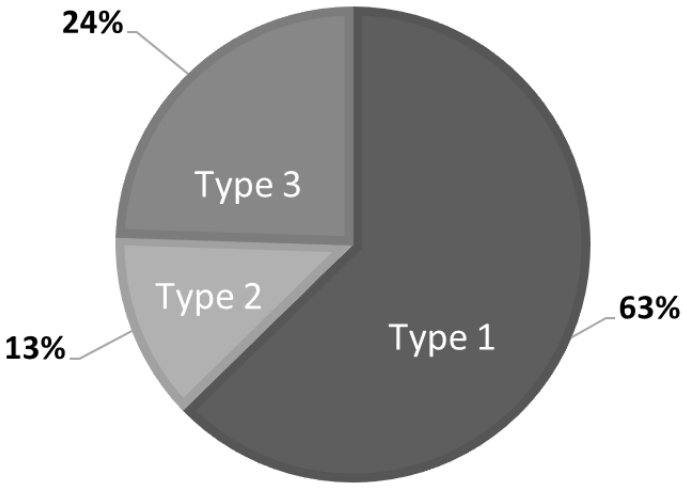

Figure 3.2. Distribution of percentages for collected 3 types of pharmaceutical blisters.

3.2. Characterization of Pharmaceutical Blisters

The structure and thickness of aluminium and plastic layers were analysed by using SEM (Scanning Electron Microscope - FEI QUANTA 250 FEG) - EDS (Energy Dispersive X-ray Spectroscopy - Oxford Aztec). The plastic part was shredded to produce the representative samples and characterization of plastic part was analysed by using FTIR (Fourier Transform Infrared Spectroscopy - Perkin Elmer BX Spectrum) with a spectral resolution of 4 cm^{-1} and 4000–500 cm^{-1} wavenumber range, TGA (Thermogravimetric Analysis - Perkin Elmer Diamond) up to 800°C with 10 K/min heating rate under N_2 atmosphere and DSC (Differential Scanning Calorimeter - Perkin Elmer Diamond). The metal content of plastic was determined by using ICP-MS (Inductively Coupled Plasma Mass Spectrometry - Agilent 7500ce Octopole) and CEM Mars 6 (Microwave Digestion System)). Microwave digestion was used to transfer metal content from the solid phase to the liquid phase by adding 10 mL of HNO_3 to 0.25 g sample at 210°C.

Randomly 20 samples were selected in type 1 and type 2, and randomly 45 samples were selected in type 3 to determine the content of aluminium and plastic. A thermal pre-treatment at 550 °C was performed using a laboratory-scale resistance chamber furnace capable of heating up to 1600 °C. (Protherm Furnaces PLF series 140-

160 max temp: 1600 °C) (shown in Figure 3.3). The plastic fraction was removed by heat and the samples were weighed before and after the thermal treatment process.

Figure 3.3. Protherm laboratory-scale electrical resistance chamber furnace.

3.3. Separation of Pharmaceutical Blister Layers

This chapter presents, two techniques for separation the layers (as plastic and aluminium) of pharmaceutical blister packages. Since the aluminium content in type 3 blister packages is higher than type 1 and type 2, separation tests were performed for type 3.

3.2.1. Chemical Separation Methods

The samples were cut in two ways (2 cm^2 and 0.5 cm^2) to compare the physical effect in separation. Figure 3.4 shows the samples and Figure 3.4a represents 2 cm^2 sample with a weight of 1g and Figure 3.4b represents 0.5 cm^2 sample with a weight of 1 g.

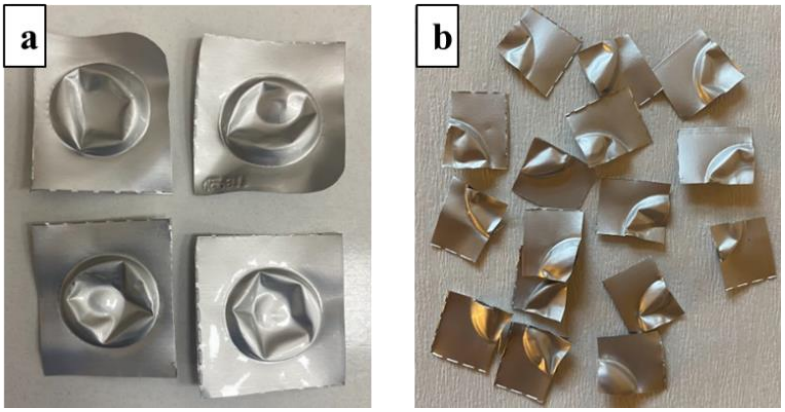

Figure 3.4. Samples for chemical separation methods; a) 2 cm^2 sample and b) 0.5 cm^2 sample.

Hydrochloric acid (HCl) (37%), formic acid (CH_2O_2) (85%), acetic acid ($C_2H_4O_2$) (99.8%), organic solvent (mixed with ethanol-benzene-water) (C_6H_6- C_2H_6O-H_2O_2) (99.7-99.9%), ethanol (C_2H_6O) (99.9%), acetone (C_3H_6O) (99.5%), and sulphuric acid (H_2SO_4) (95-97%) were used for separation. Experiments were conducted in a conical flask by using a magnetic stirrer (C-MAG HS 4 digital). Figure 3.5 presents the experimental set-up of chemical separation methods experiments. Experiments were carried out under the following conditions;

- Solution volume: 200 ml,
- Temperature: 25°C, 40°C, 60°C,
- Concentration of solution: 4 mol/L,
- Agitation speed: 200 rpm.

Each experiment was conducted until the aluminium and plastic fractions were completely separated from each other. To determine if a solution doesn't start to separate the samples were left in the solution at least for a week. After the separation part was completed, the solutions were filtered, and the separated layers were cleaned with pure ethanol and pure water. Lastly, samples were dried in memmert drying oven at 80°C and weighed. Memmert drying oven (Universal oven UN 30) is shown in Figure 3.6.

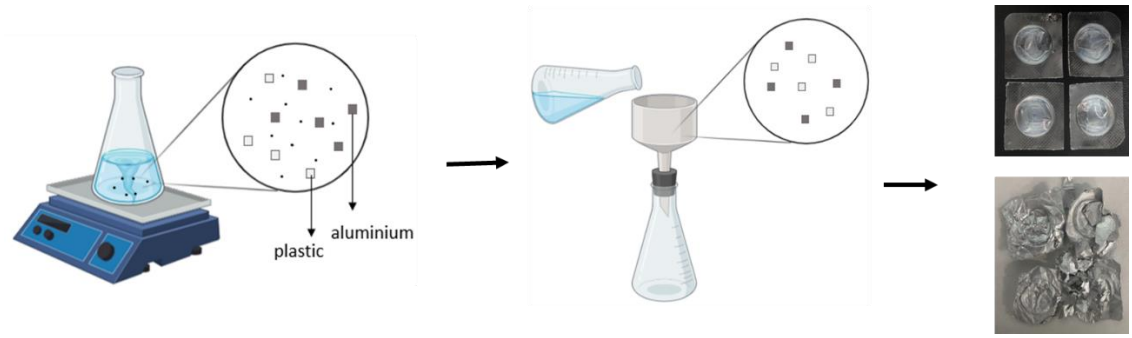

Figure 3.5. Experimental set-up for chemical separation process.

Figure 3.6. Memmert drying oven.

3.2.2. Thermal Degradation

Sample weight was about 2-3 g for thermal degradation process. Thermal degradation experiments were carried out at 450°C and 650°C by using Protherm high-temperature resistance furnace that operating temperature can be adjusted up to 1500°C (shown in Figure 3.7) and the design of the furnace provides an easy placement of the reactor. The reactor can be seen in Figure 3.8. The reactor consists of a closed steel chamber. This steel chamber has a lid. This is a sealed cap as there is an o-ring between this cap. After putting the samples into the reactor, the lid is tightened. There is a gas

inlet-outlet valve on the reactor. Thus, the desired gas can be put in and gas can be easily collected from the gas outlet. Tedlar gas sample bags (3lt.) was used to collect gas in pyrolysis experiments. Figure 3.8 presents the pyrolysis procedure scheme. Samples were placed inside the reactor. The reactor placed in the furnace was first flown with nitrogen. Then the nitrogen gas inlet was closed. A gas sample bag was connected to the gas outlet hose and gas was collected during the pyrolysis. The plastic fraction in the blisters was collected as gas and oil. The gas sample was analysed by using GC-TCD (Gas Chromatography- Thermal Conductivity Detector - Agilent 6890N). When the reactor reached the maximum temperature, it waited for a few minutes and the experiment was terminated. The reactor was left to be cooled by means of water inlets and outlets. After the pyrolysis, pure acetone, tetrahydrofuran, and pure water were used to clean the samples. After the cleaning, samples were dried by using a memmert drying oven.

Figure 3.7. High-temperature resistance furnace.

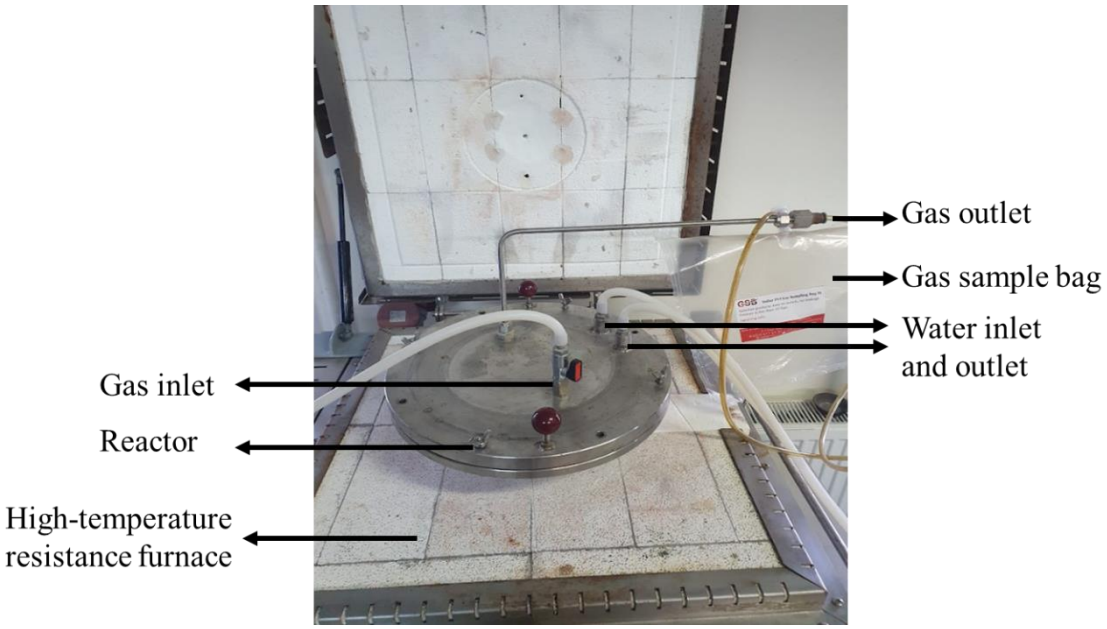

Figure 3.8. Experimental procedure for pyrolysis experiments.

3.3. Remelting the Aluminium Layers of Pharmaceutical Blisters

Remelting experiments were carried out for type 3 blister because aluminium content in type 3 blister packages is higher than other types. After the separation part, the collected aluminium fractions were remelted under a salt flux to evaluate the recycling yield. Figure 3.9 presents the set-up for remelting experiments. Experiments were performed in a clay-bonded graphite crucible (0.330lt.) at 800 °C with a 6 K/min heating rate under an open atmosphere by using an electrical resistance chamber furnace. Crucible was coated with BN (boron nitride) to remove the metal droplet from the crucible easily.

Salt flux consists of 68.6% NaCl, 29.4% KCl, and 2% CaF_2. CaF_2 was used to increase the coalescence and eliminate non-metallic inclusions [60]. The ratio of salt/sample was selected as 3 to assure that the sample is fully covered by the salt flux. At the end of the experiment, the melt was stirred with a graphite rod to obtain a better metal yield. After cooling, the solidified metal droplets were removed from the crucible by washing the salt dross.

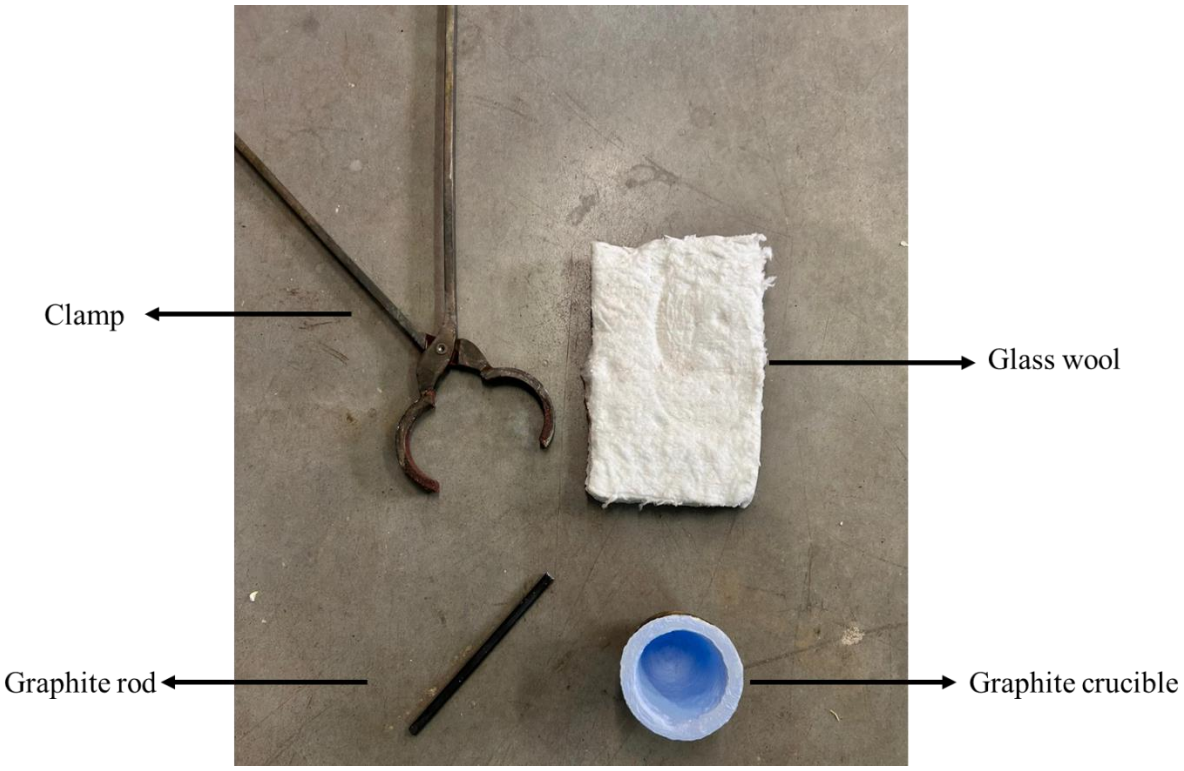

Figure 3.9. Set-up for remelting the aluminium layers of PB.

The mass ratio between the recovered mass of aluminium and the mass of scrap was used to calculate the aluminium yield (A.Y) (Equation 3). Value of $m_{Al\ in\ scrap}$ is calculated according to the decoating results. Remelting processes under salt were carried out separately for chemical separation and pyrolysis processes.

$$A.Y.\% = \frac{mAl\ recovered}{mAl\ in\ scrap} \times 100 \quad (3.1)$$

where, $m_{Al\ recovered}$ is the mass of aluminium recovered by under salt remelting, $m_{Al\ in\ scrap}$ is the mass of aluminium in the type 3.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Characterization of Pharmaceutical Blisters

Cross-section of the three types of blisters was analysed by SEM-EDS.

Figure 4.1 shows the SEM characterization and EDS mapping of type 1. Type 1 has mostly plastic layers shown in blue and one layer of aluminium between the plastic layers shown in green. The content of plastic is carbon, so was seen carbon in both layers shown in red. Ultimate analyses were applied by Klejnowska et al. They showed that the contents of C, H, Cl, and S in blisters were 38.6, 4.8, 52.9, and 3.2 wt.%, respectively [26].

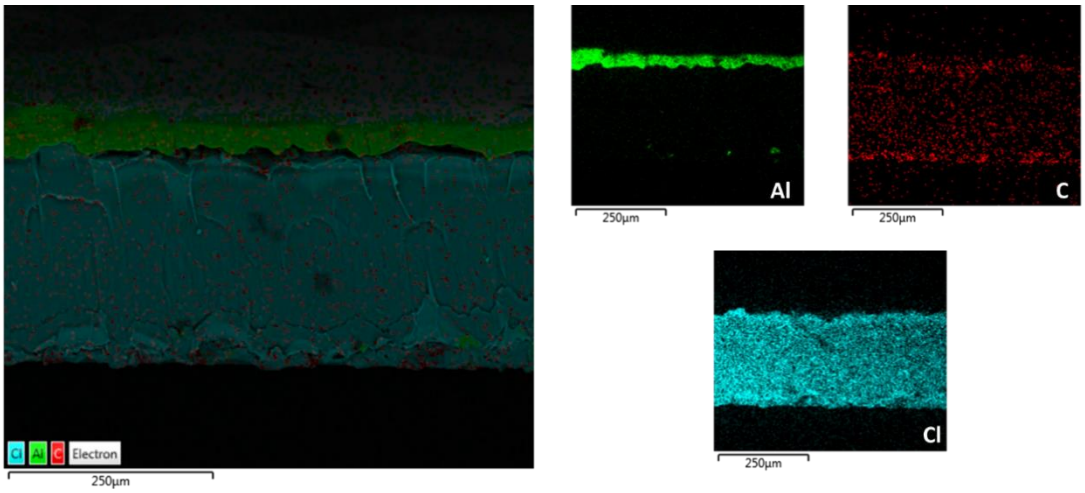

Figure 4.1. SEM morphology images and EDS mappings for type 1.

Figure 4.2 shows the SEM characterization and EDS mapping of type 2. Type 2 contains more plastic than type 1. However, unlike type 1, it was observed that Ti (shown in orange) and Ca (shown in yellow) were present in type 2. The reason for Ti was observed sample because the Ti in the plastic part of type 2 is quite high and due to the oxidation of Ti, TiO_2 is formed, which gives the sample a white colour. The white colour in type 2 can be explained by TiO_2. While the reason for Ca was observed as a filler in plastics and as a photo-stabilizer [61]. The aluminium layer appears as a thin layer

shown in blue. Since aluminium is an easily oxidized metal, aluminium always contains oxides. There is an oxide that is commonly shown in green due to the presence of aluminium.

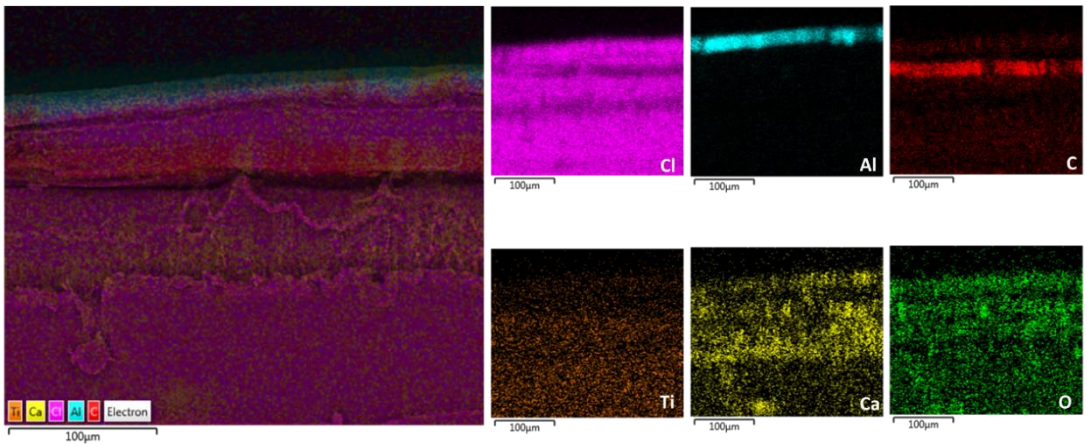

Figure 4.2. SEM morphology images and EDS mappings for type 2.

Figure 4.3 shows the SEM characterization and EDS mapping of type 3. The plastic layer appears as chlorine which is due to the PVC content and is located between the double layer of aluminium. Both aluminium layers seem oxidized partly. C is present in the polymer layers chemically in addition might be also present as contamination and dirt. The accumulated C below the aluminium layer represents PA/nylon which contains more C than PVC.

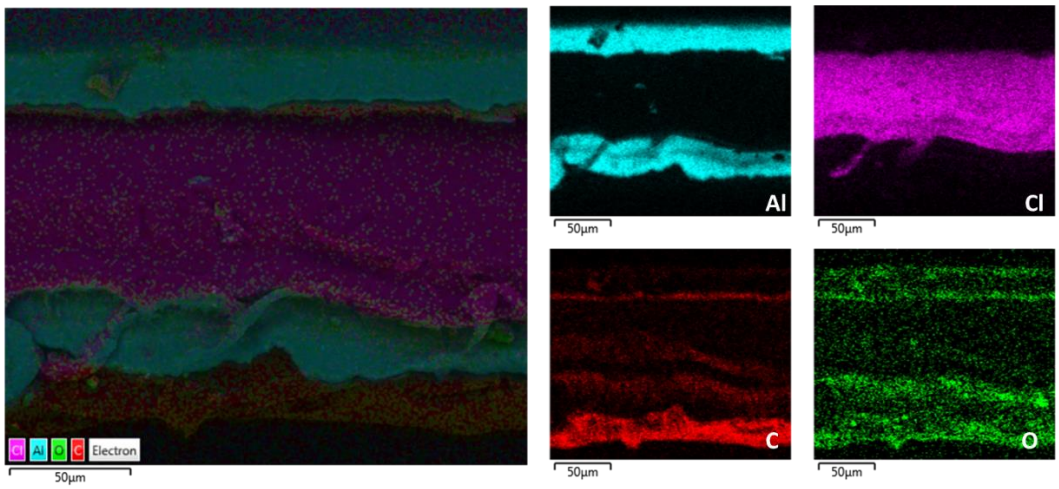

Figure 4.3. SEM morphology images and EDS mappings for type 3.

All SEM-EDS results include Cl so it can be said that Cl can come from PVC. Therefore, Cl can be interpreted as a plastic layer.

The thickness of all collected samples was measured by an electronic calliper. Table shows the average thickness and deviation for type 1, type 2 and type 3. The average thickness of type 1 was calculated as 298.56 μm with a deviation of 0.036 μm. The average thickness of type 2 samples was calculated as 400.7 μm with a deviation of 0.055 μm. The average thickness of type 3 samples was calculated as 208.04 μm with a deviation of 0.029 μm.

Table 4.1. Average thickness and deviation for three different blister packages.

Sample	Average thickness (μm)	Deviation (μm)
type 1	298.56	0.036
type 2	400.7	0.055
type 3	208.04	0.029

Thermal treatment results are present in Figure 4.4. It is observed that type 1 contains 11.52 wt.% of aluminium with a deviation of 0.594 wt.%. Type 2 contains 11.66 wt.% of aluminium with a deviation of 3.47 wt.%. Lastly, type 3 contains 59.09 with a deviation of 0.286 wt.%.

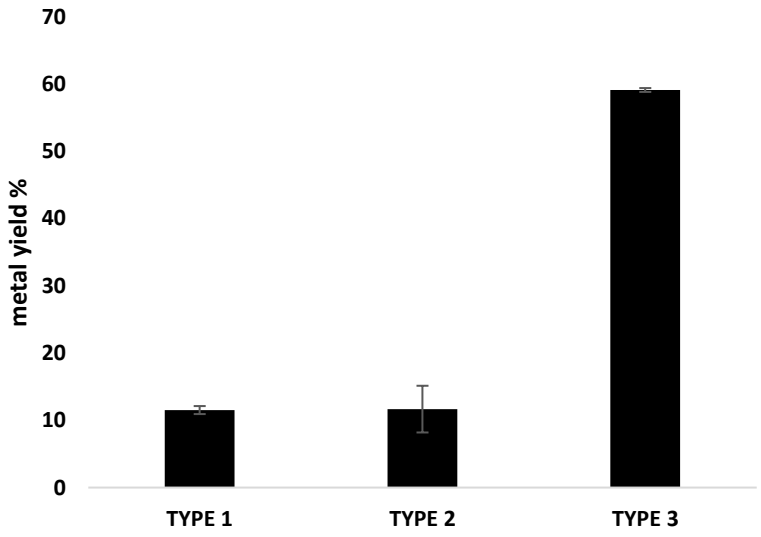

Figure 4.4. Thermal treatment results for three pharmaceutical blister samples.

4.1.1. Characterization of the Plastic Content in Blisters

The plastic fraction was removed by shredding and analysed in TGA-DSC, FTIR and ICP-MS.

Figure 4.5 shows the TGA results of the plastic fractions. The PVC curves showed no weight loss up to 250°C and degradation took place in two stages. Two degradation stages took place at 350°C and 500°C. The total mass loss of type 1 and type 2 were determined as 80 - 85 wt.% from the TGA curve for type 1 and type 2. No significant weight loss was observed in the temperature range of 500°C - 800°C, indicating that blister samples were almost completely decomposed at lower temperatures. Also, Wang et al. determined that the total mass loss of blisters was 79.0 – 85.1 wt.% and the whole decomposition can be divided into two stages, and they did not observe significant weight loss of blisters at 600°C - 900°C [62]. In the TGA curve of type 3, the polymers exhibited a three-step thermal degradation. The initial weight loss of about 200°C - 250°C is mainly due to the evaporation of moisture. The second weight loss of about 250°C.- 400°C was attributed to the dissociation of the amide bond. The final weight loss of about 400°C – 800°C was due to generalized plastic backbone degradation [63]. Type 1 and type 2 contain commonly PVC, but type 3 has PA/nylon.

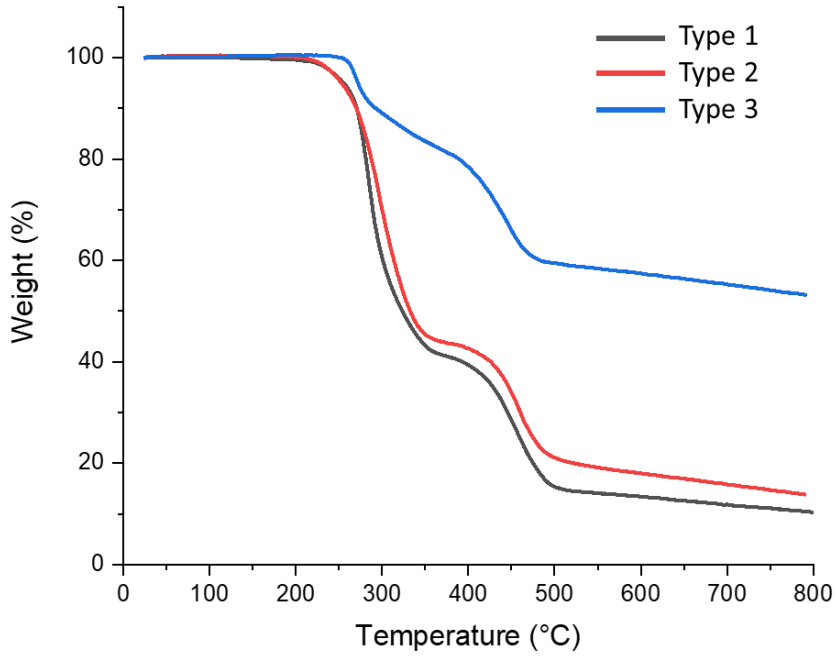

Figure 4.5. TGA results for a plastic fraction in three types of blisters.

Figure 4.6 presents the DSC curve of plastic fraction in three types of blisters. The DSC curves of type 1 and type 2 overlap with the DSC curve of PVC. The DSC curve of PVC typically has several characteristic transitions. PVC is a thermoplastic material, and the DSC curve shows the thermal behaviour of the material when heated or cooled. Since PVC is an amorphous polymer material, it does not have a clear glass transition. Instead, shows a gradual increase in heat capacity in the glass transition region, typically around 70-140 °C. This transition represents a change in the molecular mobility of the polymer. PVC tends to crystallize upon cooling. The crystallization peak appears as an exothermic peak on the DSC curve. The crystallization temperature of PVC is usually around 200-230°C. When PVC is heated above its crystallization temperature, a melting transition occurs. It has been found that the melting temperature of PVC is typically around 250-270°C. The DSC curve of type 3 corresponds to that of PA/nylon. PA/nylon is also a thermoplastic material like PVC and exhibits several characteristics transitions. The glass transition temperature (Tg) shows up as a step change in heat capacity, indicating a transition from a solid, glassy state to a more flexible, rubbery state. The Tg of nylon can vary depending on the type of nylon, with values typically ranging from 40 to 100 °C. PA/nylon undergoes a melting transition when heated above the crystal melting temperature. The melting temperature of the the PA /nylon material in type 3 is in the range of 260-280°C. PA/nylon may crystallize when cooled from the molten state. The crystallization peak appears as an exothermic peak in the DSC curve, which was observed between 290-300°C. In addition, the nylon material may thermally decompose at higher temperatures, as evidenced by a downward shift in the baseline of the DSC curve or a broad endothermic peak. The decomposition temperature varies depending on the on the nylon type and its thermal stability and has been observed after 300°C.

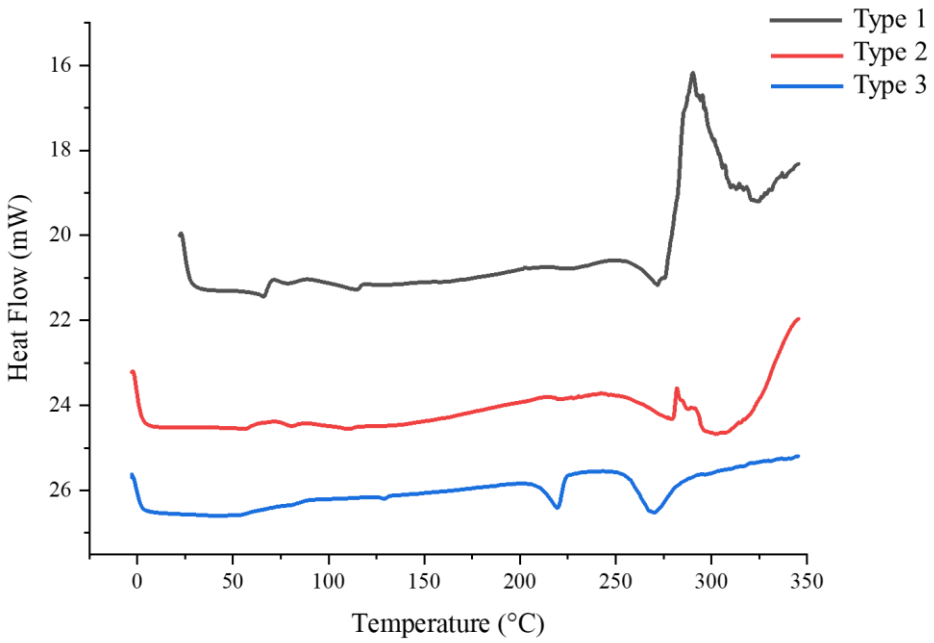

Figure 4.6. DSC results for a plastic fraction in three types of blisters.

Figure 4.7 presented FTIR results for the plastic fraction in three types of blisters. Peaks used for identification are presented with their assignments and references in Table 4.2. For all types, the noise was detected depending on the device in the range of nearly between 2000 - 2250 cm^{-1}. Type 1 and type 2 show characteristic peaks of plastic that match closely to PVC spectra measured by Higgins and Jung et al. [34,64]. The material between the aluminium and plastic layers had a spectrum that closely matched the acrylic adhesive spectrum studied by Zieba-Palus et al. in three types [36]. Therefore, it can be concluded that an acrylic–based material is responsible for the adhesion of the aluminium coating and the PVC film for all types.

Two groups of peaks located at 2600–3250 cm^{-1} were detected, which agreed with the asymmetric stretching HCl for all samples [65]. This result was matched with TGA results, where a strong mass loss specified from 300-360 ºC was observed supporting the presence of dichlorination in this stage. Zhou et al. showed strong absorption peaks between 2600 and 3100 cm^{-1} at 238 – 409 °C [18,66].

As shown in Figure 4.7, C-Cl stretching mode can be observed at 1426 cm^{-1}, CH_2 rocking mode at 1326 cm^{-1} , C- C stretching mode at 1240 cm^{-1} , C-H bending mode at 1096 cm^{-1} and 952 cm^{-1} , CH_2 bending mode at 614 cm^{-1} for all samples. FTIR is convenient with the pure PVC spectrum reported by S. Ramesh et al [67]. However, there were some different absorbance peaks were observed such as C=O stretching

mode at 1632 cm^{-1}, NH bending, and C-N stretching mode at 1540 cm^{-1} in type 3 blister packages. This result shows that type 3 also contains PA/nylon as a plastic fraction and matched the TGA curve of type 3. Moreover, minor differences in FTIR results were observed. This may be due to the different adhesive material used in the blister.

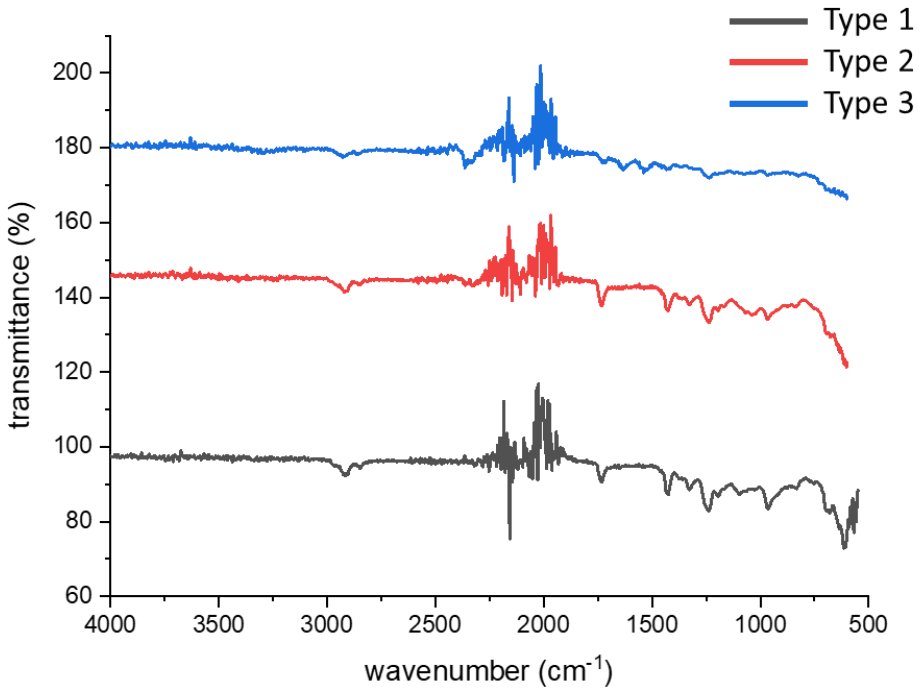

Figure 4.7. FTIR results for plastic fraction in three types of blisters.

Table 4.2. The FTIR peak assignments for the identification of polymeric layers.

Polymer	Literature (cm^{-1})	Peak Assignment	References
PVC	1427, 1426	C- Cl stretch	18
	1331, 1328	CH_2 rock	
	1255, 1239	C- C stretch	
	1099, 1095	C- H bend	
	966, 962	C- H bend	
	616, 609	CH_2 bend	
Nylon (all polyamides)	3298	N-H stretch	18
	2932	CH stretch	
	2858	CH stretch	
	1634	C = O stretch	
	1538	NH bend, C - N stretch	
Acrylic Glue	1730	C = O bend	34
	1450	CH_2 bend	
	1380	CH_2 bend	
	1265- 1240	C- O- C stretch	
	1165	C- O- C stretch	

Results from ICP-MS analysis were determined as micrograms/gram (µg/g). Table shows the ICP-MS results for 3 samples. Results vary depending on the specific plastic material, the elements analysed and the presence of any contaminants or impurities. Magnesium was observed in the plastic part of three blister packages. Magnesium is used in plastic as a flame retardant in tires. It is also used as an additive in plastics due to the mould healing properties of magnesium. Magnesium can also be used as a stabilizer, especially in PVC. They help prevent deterioration caused by heat, UV radiation and other environmental factors, thus extending the life of the plastic and preserving its physical properties. Chromium and zinc are another element that is mostly found in the plastic of three blister packages. Chromium provides colour durability and prevents the plastic from fading thanks to the pigment it contains. Chromium-based compounds can also act as UV stabilizers and heat stabilizers in plastics. Thus, it helps protect the plastic material from thermal degradation at high temperatures. Zinc-containing additives can provide antioxidant properties to plastics. They help avoid or delay the oxidative degradation of plastic that can occur due to exposure to oxygen, heat or other oxidative agents. The metals in the plastic material are used as additives to improve the durability to give colour to the plastic material.

Table 4.3. ICP-MS results for plastic part of PB.

	type 1	**type 2 (µg/g)**	**type 3**
B	1,29	1,10	1,20
Na	0,57	0,60	0,50
Mg	29,34	32,11	18,13
Al	1,89	2,30	4,50
K	0,05	0,08	0,10
Ca	0,13	0,70	1,32
Cr	28,25	25,26	24,76
Mn	1,61	1,13	0,56
Fe	0,25	0,38	4,73
Co	0,12	0,30	0,20
Ni	5,06	4,08	0,43
Zn	22,21	18,23	22,85
As	0,02	0,00	0,28
Sr	0,77	0,56	0,62
Ba	4,03	6,01	5,59
Tl	0,65	0,30	0,32
Pb	0,34	0,41	0,03

4.2. Separation of Pharmaceutical Blister Layers

Separation experiments were carried out in only type 3 blisters due to their high content of aluminium. As I mentioned before, since the aluminium content is low in type 1 and type 2, layer separation and melting under salt were not carried out. Even if the aluminium of type 1 and type 2 is desired to be recovered, this study is not feasible due to the excess energy and cost to be spent.

4.2.1. Chemical Separation Methods

The separation behaviour of the layers was evaluated according to temperature, time and sample size. The results are shown in Table .

Table 4.4. Separation behaviour according to temperature, time and sample size.

Reagents	**Temperature (°C)**	**Duration (h)**	**Surface area (cm^2)**
HCl	25	8	2
	25	6	0.5
	40	6	2
	40	4	0.5
	60	3.5	2
	60	3	0.5
CH_2O_2	25	12	2
	25	10	0.5
	40	10	2
	40	8.5	0.5
	60	8	2
	60	7	0.5

(Cont. on next page)

Table 4.4. (cont.)

Reagents	**Temperature (°C)**	**Duration (h)**	**Surface area (cm^2)**
$C_2H_4O_2$	25	20	2
	25	18	0.5
	40	16	2
	40	15	0.5
	60	12	2
	60	11	0.5
C_6H_6- C_2H_6O- H_2O	25	9	2
	25	7	0.5
	40	7.5	2
	40	5	0.5
	60	4	2
	60	3	0.5
H_2SO_4	25	48	2
	25	46	0.5
	40	12	2
	40	10	0.5
	60	8	2
	60	7	0.5
C_3H_6O	25	72	2
	25	72	0.5
C_2H_6O	25	x	2
	25	x	0.5

The results were investigated in two stages: reagents that dissolved the metal and did not dissolve the metal. A comparison of the degree of liberation of the aluminium layers for all solvents is presented in Figure 4.8.

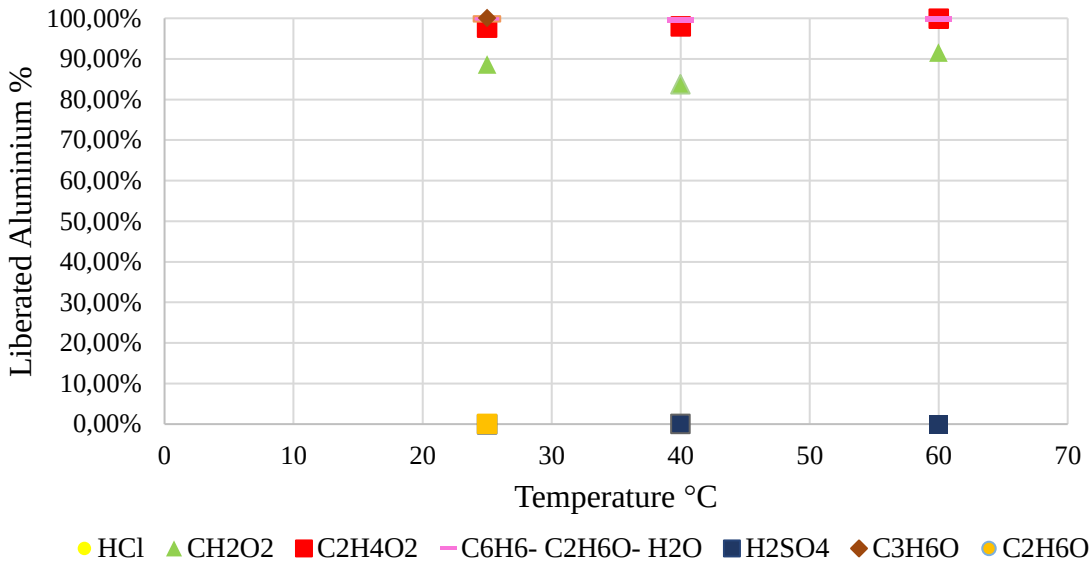

Figure 4.8. Liberated aluminium (%) for all used reagents in three different temperatures.

4.2.1.1. Reagents that dissolved the metal

The aluminium layer was not released as metal in hydrochloric acid and sulfuric acid for various reasons. In hydrochloric acid and sulfuric acid solutions, the plastic fraction was separated but since aluminium dissolves in both solutions, the metal value was lost. When aluminium was added to hydrochloric acid solution, a colour change of the solution was observed during the experiment. The hydrochloric acid solution is colourless, but after aluminium was added, it turned black within 15-20 seconds and remained yellow at the end of the experiment (shown in Figure 4.9). $AlCl_3$ has a black colour, and the black colour of the solution indicates the formation of $AlCl_3$. The iron in aluminium contaminates the solution, forming $FeCl_3$ (iron (III) chloride), and turning the solution yellow. The solution remains yellow at last. The colour changes due to the

reaction between hydrochloric acid and aluminium which forms $AlCl_3$ by the following reactions [68].

$$2Al(s)+6HCl(aq)\rightarrow 2AlCl_3(aq)+3H_2(g) \quad (4.1)$$

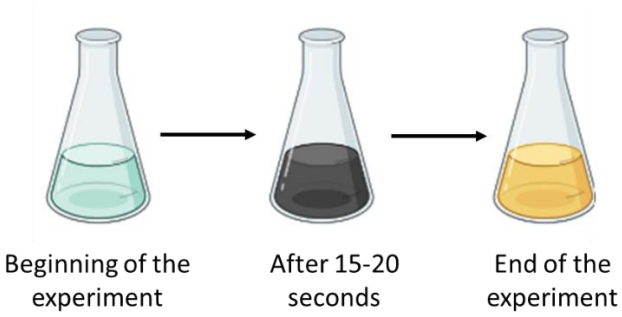

Figure 4.9. Reaction scheme between HCl and aluminium.

Although sulfuric acid is a very strong acid, the rate of dissolving aluminium is slower than hydrochloric acid. While hydrochloric acid could dissolve aluminium in 4 hours at room temperature, sulfuric acid can be preferred for plastic recovery only for materials with low metal content.

4.2.1.2. Reagents that did not dissolve the metal

No successful separation was achieved with ethanol, and no dissolution was observed. Ethanol can only be used as a solvent to remove other impurities.

Formic acid, acetic acid, acetone, and organic solvents have been successful in separating type 3 blisters without losing aluminium or plastic fractions. By dissolving the adhesive substance between the aluminium and plastic layers, the solutions successfully separated the layers. At 25°C, 40°C, and 60°C, aluminium in formic acid liberated at rates of 88.6, 83.7, and 91.5 wt.%, respectively. Aluminium mass loss was observed in formic acid solution. Also, Rimšaitė et al studied the separation of tetrapak samples and they observed mass loss of aluminium (0.8%) in separation with formic acid [23].

After the separating and drying of the samples, a white salt-like powder was observed on the aluminium surface. Aluminium formate salt ($C_3H_3AlO_6$) peaks were seen during the XRD analysis of the powder, as illustrated Figure 4.10. Formic acid and aluminium react to form aluminium formate salt, which is the primary cause of the aluminium loss [69,70].

$$2Al + 6HCOOH \rightarrow C_3H_3AlO_6 + 3H_2 \quad (4.2)$$

The reaction is exothermic and at higher temperatures, the reaction will occur faster.

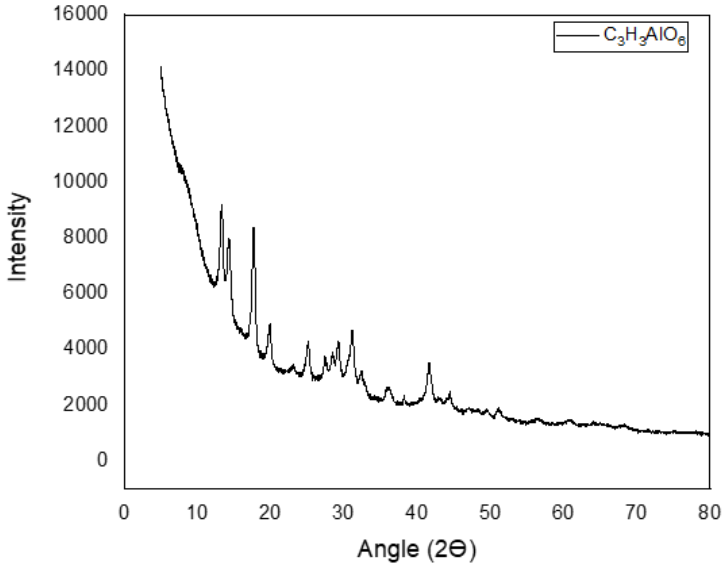

Figure 4.10. XRD results of aluminium formate.

Aluminium liberation rates in acetic acid were measured to be 97.75 wt.% at 25°C, 98.01 wt.% at 40°C, and 99.9 wt.% at 60°C, and 100 wt.% at 25°C, 99.5 wt.% at 40°C, and 100 wt.% at 60°C in organic solvent. At 25°C, the rate of aluminium liberation in acetone was measured to be 100%; higher temperatures were not investigated. At three different temperatures, it was shown that the fastest separation occurred in an organic solvent without aluminium loss. At room temperature, organic solvent separation took 7 hours, at 40 °C, 5 hours, and at 60 °C, 3 hours. At 25°C, decomposition in formic acid and acetic acid took place in roughly a day, while decomposition at 40°C and 60°C took occurred in between 6 and 8 hours. In acetone, the separation took three days. All three solvents can be used to recycle multi-layered

structures because they all achieved a significant degree of separation at room temperature without losing the metal or plastic mass.

After the separation, solutions were filtered, and samples were cleaned with ethanol and pure water. Figure 4.11 presents cleaned samples that separate layers; a) aluminium fraction that contains surface area of 2 cm^2, b) plastic fraction that contains surface area of 2 cm^2, c) aluminium fraction that contains surface area of 0.5 cm^2, and d) plastic fraction that contains surface area of 2 cm^2.

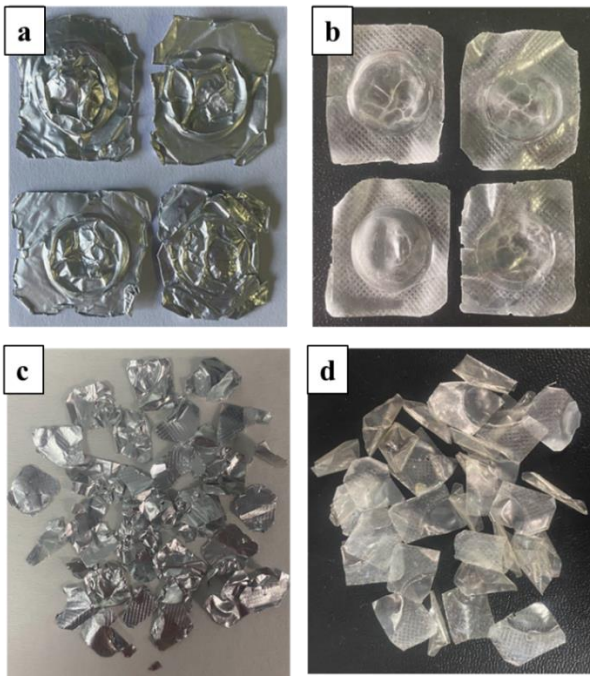

Figure 4.11. Cleaned samples after separation.

For all solutions, the fastest dissociation was observed in the samples that contains 0.5 cm^2 surface area.

4.2.2. Thermal Degradation

During thermal degradation process, plastic fraction of pharmaceutical blister was collected as an oil and gas. Aluminium fraction of pharmaceutical blister was obtained as a solid. Figure 4.12 shows the aluminium fraction samples. Oil accumulation was also observed on aluminium samples due to oil formation during pyrolysis. Oil on the aluminium samples were cleaned with acetone and tetrahydrofuran. Figure 4.12a shows the aluminium fraction with oil and Figure 4.12b

shows the cleaned aluminium fractions. Furthermore, collected oil samples presents in Figure 4.13.

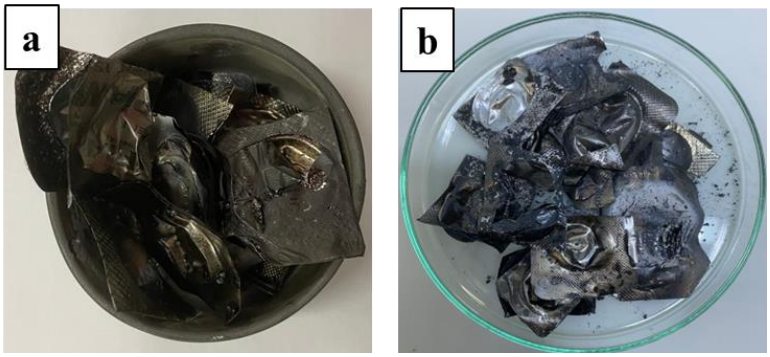

Figure 4.12. Aluminium fraction of PB after pyrolysis experiments; a) samples before cleaning and b) cleaned samples.

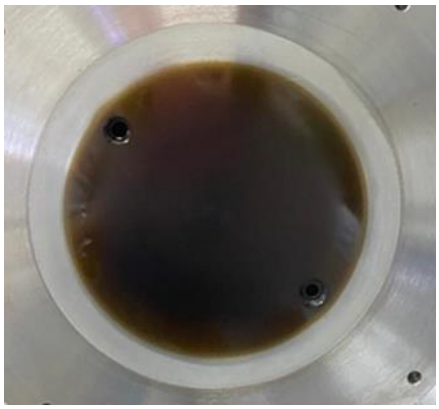

Figure 4.13. Collected oil samples during pyrolysis.

Hydrocarbons and inorganic components in gas samples analysed by using GC-TCD analysis with a using a packed column (Shincarbon ST 80/100 2m 2mm ID, serial nbr: C35240-01). Table shows the hydrocarbons and inorganic components of gas at 450°C. Table shows hydrocarbons and inorganic components of gas at 650°C. In two results, it is observed N_2 due to flowing N_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6 were observed in both results. C_3H_6 and C_3H_8 were observed at 650°C. When compared these two results, it can be said that temperature increases, formation of hydrocarbon gases increases. For instance, high content of CO was observed at higher temperature. Klejnowska et al. and Wang et al. reported that the amount of CO in the gases was

higher at higher temperatures [26,62]. Also, O_2 was observed at 650°C, this may have been caused by some O_2 may have entered into the gas cooler. Klejnowska et al. stated that the quality of the gas increased with temperature. In addition, these results match Klejnowska et al. results and it can be said that the quality of the gas is directly proportional to the temperature [26]. Piko´n et al. and Klejnowska et al. determined 450°C is suitable for the blister pyrolysis because number of carbon decreases, the calorific value increases. The quality of the gas is checked by calculating its calorific value [26,37].

Table 4.5. GC-TCD results of gas at 450°C.

#	Time	Area	Area%	Component
1	1.653	75668.4	99.782	N_2
2	2.509	35.7	0.047	CO
3	4.688	3.1	0.012	CH_4
4	7.916	86.8	0.114	CO_2
5	12.469	17.7	0.023	C_2H_4
6	13.632	7.1	0.009	C_2H_6
7	18.252	9	0.012	

Table 4.6. GC-TCD results of gas at 650°C.

#	Time	Area	Area%	Component
1	0.795	1.6	0.002	O_2
2	1.809	73333.3	98.818	N_2
3	2.554	169	0.228	CO
4	4.742	127	0.171	CH_4
5	8.018	312.4	0.421	CO_2
6	12.539	113.7	0.153	C_2H_4
7	13.706	59.7	0.080	C_2H_6
8	18.292	23.7	0.032	
9	21.833	50.2	0.068	C_3H_6
10	23.086	20	0.027	C_3H_8

4.3. Remelting the Aluminium Layers of Pharmaceutical Blisters

Figure 4.14 presents aluminium recovery yield obtained by remelting of all liberated aluminium fractions. In remelting trials, aluminium that has undergone pyrolysis has the highest recovery yield (98.27%). The second highest recovery yield (94.90%) was measured for thermal pre-treatment. This could be as a result of aluminium being easily purified during thermal pre-treatment of all contaminants. In addition, the reason for the high yield in thermal pre-treatment and thermal degradation means that the aluminium used in the blister is an aluminium of high impurity (eg. 8011 alloy). For this reason, the highest efficiency was observed in thermal degradation, since the oxidation tendency of high impurity aluminium is low. The recovery of aluminium in formic acid, acetone, acetic acid, and organic solvents was calculated to be 91.43%, 90.6%, 86.7%, and 82.99%, respectively. As a result, after separation processes, 82–95% of the aluminium's weight can be recovered by remelting the metal in a salt flux. Although thermal pre-treatment and remelting shows the highest aluminium recovery, combustion occurs during this process and completely eliminates the plastic value. Pyrolysis is a better option for such scraps to make thermal pre-treatment practical. Formic acid has the largest recovery yield of any separating agent (91%), while acetone, which recovers at a rate of 90,6% and is less harmful to the environment than acids like acetic and formic acid solutions, should also be taken into consideration. Acetone's evaporation problem needs to be fixed on an industrial scale with the right setup design. The oxidation that occurs during separation, which can take up to 7 hours to complete at room temperature, may be the cause of the low recovery yield after organic solvent separation and remelting.

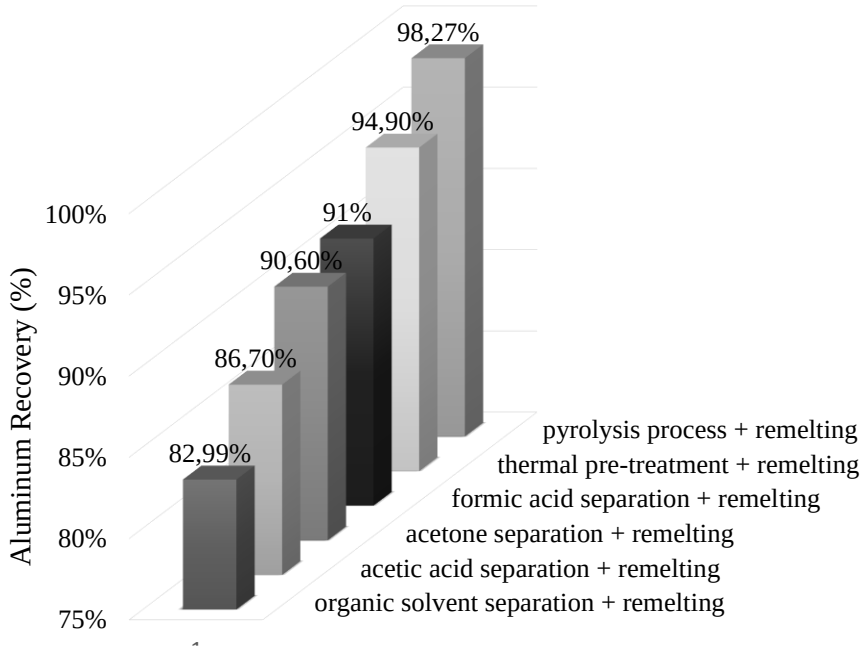

Figure 4.15. Aluminium recovery after remelting for chemical separation, pyrolysis and thermal pre-treatment processes.

Type 1 and Type 2 are more suitable for plastic recycling, type 3 is more suitable for both metal and plastic recycling. A recyclable eco-friendly design can be made into blister packages. For example, a uniform plastic material that is less harmful to the environment can be used instead of PVC as a plastic material (because it releases chlorine gas).

The following steps can be applied for feasible recycling processes;

- Choosing environmentally friendly materials in the blister packages for better recyclability, focusing on the use of type 3 blisters to increase recyclability.
- Environmentally friendly methods such as reuse of blister packs, deposit for each blister pack sold can be applied.
- Waste blister collection and recycling may become more encouraging with new legal regulations.

CHAPTER 5

CONCLUSION

Pharmaceutical blister packages have a layered structure containing aluminium and plastic. Recycling of blister packages is complicated due to their layered structure, and it is necessary to separate plastic and aluminium before recycling. This thesis investigated the characterization and recyclability of pharmaceutical blister packages. As drawn from detailed experimental research, certain conclusions can be drawn about the study performed:

- Type 1 has 11.52 wt.% of aluminium layer , Type 2 has an 11.66 wt.% aluminium layer. Type 3 has a double aluminium layer (59.0 wt.%).
- The plastic type for type 1 and type 2 mainly contains PVC and type 3 mainly consists of PA/nylon and PVC.
- Acetic acid, organic solvent, and acetone achieved almost complete separation without loss in any of the fractions.
- Better components with respect to fuel formation from plastic were observed at 450 °C.
- Type 3 blister includes an undeniable number of aluminium layers, making it a valuable material for recycling.
- The aluminium yield varies between 83-98% with pyrolysis, thermal treatment and separation of the layers by reagents before remelting.

CHAPTER 6

FUTURE WORK

- Different solvents can be tried to separate the plastic from the aluminium in the pharmaceutical blister packages.
- The environmental impact of the solvents used can be investigated.
- Aluminium, like plastics, can be prepared for ICP-MS analysis.
- Fuel production can be achieved by performing extensive recycling processes of the plastic part in the pharmaceutical blister packages.
- The kinetics of the separation should be accelerated by the process parameters.
- After the aluminium is recycled, the metal quality can be tested using the RPT (Reduced Pressure Test).

REFERENCES

1. Zadbuke, N., Shahi, S., Gulecha, B., Padalkar, A. & Patil, M. *Recent trends and future of pharmaceutical packaging technology,* **2013**, J Pharm Bioallied Sci 5, 98.

2. Das, P. S., Saha, P. & Das, R. *Pharmaceutical packaging technology: a brief outline*, **2018**, Research Journal of Pharmaceutical Dosage Forms and Technology 10, 23–28.

3. Pilchick R. *Pharmaceutical Blister Packaging*, **2000**, Part 1. 24, 68–78.

4. Brooks, K. *Pharmaceutical Packaging Market Report*, **2019** | Contract Pharma. https://www.contractpharma.com/issues/2019-06-01/view_features/pharmaceutical-packaging-market-trends/.

5. Kadam, A., Patil, S., Patil, S. & Tumkur, *A. Pharmaceutical Waste Management An Overview*, **2016**. Indian Journal of Pharmacy Practice 9, 2–8.

6. Emblem, A. *Plastics properties for packaging materials* in Packaging Technology 287–309 (Elsevier, **2012**). doi:10.1533/9780857095701.2.287.

7. Yaren Çapkın, İ. & Gökelma, M. *A review on characterization and recyclability of pharmaceutical blisters*, **2023**. Cleaner Waste Systems 4, 100082.

8. Sonyy, S. M. et al. *Waste to Energy by Incineration for a Pharmaceutical Industry*, **2022**: A Case Study. in AIP Conference Proceedings vol. 2681 (American Institute of Physics Inc.,).

9. *Pharmaceutical Blister Packaging* | Blister Packaging Supplier. https://pharmapackagingsolutions.com/blister-packaging/.

10. Bauer, E. J. *Pharmaceutical Packaging Handbook*.

11. Nasa, P., Praveen Nasa, A., Singh Mahila Vishwavidyalaya, P. & Kalan, B. A *Review on Pharmaceutical Packaging Material*, **2014**. 344 Praveen World Journal of Pharmaceutical Research vol. 3 www.wjpr.net.

12. Soroka W. *Illustrated Glossary of Packaging Terminology*. Institute of Packaging Professionals.

13. *Pharmaceutical Blister Packaging Market Size & Share Analysis - Industry ResearchReport* - Growth Trends. https://www.mordorintelligence.com/industry-reports/pharmaceutical-blister-packaging-market.

14. *Pharmaceutical Blister Packaging Market Outlook,* **2031**. https://www.transparencymarketresearch.com/blister-packaging-market-for-pharmaceutical-industry.html.

15. *Pharmaceutical Packaging Market Size*, Share & Trends Analysis Report By Material (Plastics & Polymers, Report Overview. https://www.grandviewresearch.com/industry-analysis/syringes-market.

16. *Aluminum Foil Market Size,* Share & Trends Report, **2030**.

17. Research, G. View. *Plastics Market Analysis By Product (PE, PP, PVC, PET, Polystyrene, Engineering Thermoplastics)*, **2020,** By Application (Film & Sheet, Injection Molding, Textiles, Packaging, Transportation, Construction) And Segment Forecasts. (Grand View Research, 2014).

18. Nieminen, J., Anugwom, I., Kallioinen, M. & Mänttäri, M. *Green solvents in recovery of aluminium and plastic from waste pharmaceutical blister packaging*, **2020**. Waste Management 107, 20–27.

19. Liu H. *Classification of PVC for Pharmaceutical Blister Packaging Using Pattern Recognition Techniques*, **1999.**

20. Montaudo, G. *Evolution of Aromatics in the Thermal Degradation of Poly(vinyl chloride)*, **1991**: A Mechanistic Study. Polymer Degradation and Stability vol. 33.

21. Sabee, M. M. S. M., Uyen, N. T. T., Ahmad, N. & Hamid, Z. A. A. *Plastics Packaging for Pharmaceutical Products. in Encyclopedia of Materials: Plastics and Polymers* 316–329 (Elsevier, **2022**). doi:10.1016/b978-0-12-820352-1.00088-2.

22. Pedrosa de Oliveira, D., Costa, J. S. R. & Oliveira-Nascimento, L. *Sustainability of blisters for medicines in tablet form,* **2021**. Sustainable Chemistry and Pharmacy vol. 21 Preprint at https://doi.org/10.1016/j.scp.2021.100423.

23. Rimšaitė, A., Mumladze, T. & Denafas, G. *Feasibilities of Aluminium Recovery from Combined Packaging Waste,* **2019**. International Journal of Agriculture & Environmental Science 6, 103–111.

24. Wang, C., Wang, H. & Liu, Y. *Separation of aluminum and plastic by metallurgy method for recycling waste pharmaceutical blisters,* **2015**. J Clean Prod 102, 378–383 .

25. Wang C., Wang H., Gu G., Fu J. & Liu Y. *Kinetics and leaching behaviors of aluminum from pharmaceutical blisters in sodium hydroxide solution,* **2015**. J Cent South Univ 22, 4545–4550.

26. Klejnowska, K., Pikoń, K., Ścierski, W., Skutil, K. & Bogacka, M. *Influence of temperature on the composition and calorific value of gases produced during the pyrolysis of waste pharmaceutical blisters,* **2020**. Applied Sciences (Switzerland) 10.

27. Yousef, S. et al. *Cleaner and profitable industrial technology for full recovery of metallic and non-metallic fraction of waste pharmaceutical blisters using switchable hydrophilicity solvents,* **2018**. Journal of Cleaner Production 197, 379–392.

28. Shukla, S., Halli, P., Khalid, M. K. & Lundström, M. *Waste Pharmaceutical Blister Packages as a Source of Secondary Aluminum*. **2022,** JOM 74, 612–621.

29. Laasonen, M., Harmia-Pulkkinen, T., Simard, C., Räsänen, M. & Vuorela, H. *Determination of the thickness of plastic sheets used in blister packaging by near infrared spectroscopy: Development and validation of the method,* **2004**. European Journal of Pharmaceutical Sciences 21, 493–500.

30. Raju, G., Sarkar, P., Singla, E., Singh, H. & Sharma, R. K. *Comparison of environmental sustainability of pharmaceutical packaging*. Perspect Sci (Neth) 8, 683–685 **(2016)**.

31. CHATZIKOS, N. *Influence of fluxing agent on the quality of recycled Aluminium billets*. KTH ROYAL INSTITUTE OF TECHNOLOGY SCHOOL OF INDUSTRIAL ENGINEERING AND MANAGEMENT.

32. Bassani, F., Rodrigues, C., Marques, P. & Freire, F. *Life cycle assessment of pharmaceutical packaging*, **2022**. International Journal of Life Cycle Assessment 27, 978–992.

33. Vargel, Christian. *Corrosion of aluminium* **2020**. Elsevier 748.

34. Jung, M. R. et al. *Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms*, **2018**. Mar Pollut Bull 127, 704–716.

35. Liang, C. Y. & Krimm, S. *Infrared spectra of high polymers. III. Polytetrafluoroethylene and polychlorotrifluoroethylene*, **1956**. J Chem Phys 25, 563–571.

36. Zieba-Palus, J. *The usefulness of infrared spectroscopy in examinations of adhesive tapes for forensic purposes*, **2017**. Forensic Sci. Criminol. 2, 1–9.

37. Pikoń, K. et al. *Determination of fuel properties of char obtained during the pyrolysis of waste pharmaceutical blisters*, **2021**. Energies (Basel) 14.

38. Agarwal, V., Halli, P., Helin, S., Tesfaye, F. & Lundström, M. *Electrohydraulic Fragmentation of Aluminum and Polymer Fractions from Waste Pharmaceutical Blisters*, **2020**. ACS Sustain Chem Eng 8, 4137–4145.

39. *Packaging unwrapped Sustainable food and drink packaging.*

40. Ünlü, N. & Drouet, M. G. *Comparison of salt-free aluminum dross treatment processes*, **2022**. Resour Conserv Recycl 36, 61–72.

41. Gallo, R. *Development evaluation and application of solid fluxes*, **2022**. Modern Casting 92, 30–33.

42. Gallo, R. *In Development, Evaluation, and Application of Granular and Powder Fluxes in Transfer Ladles, Crucible, and Reverberatory Furnaces*, **2001**. in s, 6th International Conference on Molten Aluminum Processing 55–69.

43. Kamp, J., Villwock, J. & Kraume, M. Drop coalescence in technical liquid/liquid applications: *A review on experimental techniques and modeling approaches,* **2017**. Reviews in Chemical Engineering 33, 1–47.

44. Van Linden, J. H. L. & Stewart, D. L. *Molten salt flux composition effects in aluminum scrap remelting,* **1988**. Light Metals 391.

45. Roy, R. R. & Sahai, Y. *Coalescence behavior of aluminum alloy drops in molten salts,* **1997**. Materials transactions, JIM 38, 995–1003.

46. Roy, R. R. & Sahai, Y. *Wetting behaviour in aluminium- alumina- salt systems,* **1997**. Materials Transactions JIM 38, 571–574 .

47. Roy, R. R. & Sahai, Y. *Interfacial tension between aluminum alloy and molten salt flux,* **1997**. Materials Transactions, JIM 38, 546–552.

48. Ye, J. & Sahai, Y. *Interaction and Interfacial Tension between Aluminum Alloys and Mplten Salts,* **1996**. Materials Transactions, JIM 37, 1479–1485.

49. Berry, M. *The molecular mechanism of surface tension,* **1971**. Phys Educ 6, 79.

50. Milke, E., Friedrich, B., Sydykov, A. & Arnold, A. *In Solubility of CaF_2 in NaCl-KCl salt flux for Al-recycling and its effect on Al-loss,* **2005**, in Proceedings of EMC 1537–1548.

51. Bolivar, R. & Friedrich, B. *The influence of increased NaCl: KCl ratios on Metal Yield in salt bath smelting processes for aluminium recycling,* **2009**. World of Metallurgy— ERZMETALL 62, 366–371.

52. Sully, A. H., Hardy, H. K. & Heal, T. J. *An Investigation of Thickening and Metal Entrapment in A Light Alloy Melting Flux,* **1953**. Journal of the Institute of Metals 82 (2).

53. Al-Salem, S. M., Lettieri, P. & Baeyens, J. *Recycling and recovery routes of plastic solid waste (PSW): A review,* **2009**. Waste Management vol. 29 2625–2643 Preprint at https://doi.org/10.1016/j.wasman.2009.06.004.

54. Lazarevic, D., Aoustin, E., Buclet, N. & Brandt, N. *Plastic waste management in the context of a European recycling society: Comparing results and uncertainties in a life cycle perspective,* **2010**. Resour Conserv Recycl 55, 246–259.

55. Ignatyev, I. A., Thielemans, W. & Vander Beke, B. *Recycling of polymers: A review,* **2014**. ChemSusChem vol. 7 1579–1593 Preprint at https://doi.org/10.1002/cssc.201300898.

56. Özkan, P. *Endüstri Ürünleri Tasarımında Kullanılan Çevre Dostu Plastik Malzemeler ve Plastiğin Geri Kazanımı,* **2009** (Marmara Üniversitesi,).

57. *Plastic identification codes. What are they and what are they for?* | SP Group. https://www.spg-pack.com/en/blog/plastic-identification-codes-what-are-they-and-what-are-they-for/.

58. Singh, S. *Recyclability by Design for Multilayer Plastic Flexible Packaging A comparative study of recyclability by design guidelines and alignment among various stakeholders*, **2020**.

59. *The Complete Plastics Recycling Process - Recycle Track Systems*. https://www.rts.com/blog/the-complete-plastics-recycling-process-rts/.

60. Peterson, R. D. *Effect of Salt Flux Additives on Aluminium Droplet Coalescence. in Second International Symposium- Recycling of Metals and Enginnered Materials*, **1990** (eds. Van Linden, J. H. L., Stewart Jr., D. L. & Sahai, Y.) (The Minerals, Metals & Materials Society).

61. Gala, A., Guerrero, M. & Serra, J. M. *Characterization of post-consumer plastic film waste from mixed MSW in Spain: A key point for the successful implementation of sustainable plastic waste management strategies*. Waste Management 111, 22–33 (*2020*).

62. Wang, B. et al. *Pyrolysis behavior, kinetics, and thermodynamics of waste pharmaceutical blisters under CO2 atmosphere*, **2023**. J Anal Appl Pyrolysis 170.

63. Zhu, T., Yang, X., He, X., Zheng, Y. & Luo, J. *Aromatic polyamides and copolyamides containing fluorene group: Synthesis, thermal stability, and gas transport properties,* **2018**. High Perform Polym 30, 821–832.

64. Higgins, F. *Pharmaceutical Packaging Materials Quality Control and USP 661.1 Compliance: Agilent Cary 630 FTIR,* **2016**. Agilent Technologies Inc.

65. Buch, V., Mohamed, F., Parrinello, M. & Devlin, J. P. *Elusive structure of HCl monohydrate,* **2007**. Journal of Chemical Physics 126.

66. Chen, Y. et al. Catalytic *Dechlorination and Charring Reaction of Polyvinyl Chloride by CuAl Layered Double Hydroxide,* **2018**. Energy and Fuels 32, 2407–2413 .

67. Ramesh, S., Leen, K. H., Kumutha, K. & Arof, A. K. *FTIR studies of PVC/PMMA blend based polymer electrolytes,* **2007**. Spectrochim Acta A Mol Biomol Spectrosc 66, 1237–1242.

68. Greenwood, N. N. & Eranshaw, A. *Chemistry of Elements*, **1984**.

69. Oskar, J. *Aluminium Formate and Process of Making the Same*, **2012**.

70. Evans, H. A., Mullangi, D. & Deng, Z. *Aluminium formate, Al(HCOO)3: An earth-abundant, scalable, and highly selective material for CO2 capture,* **2022**. Sci Adv 8.