KAUNAS UNIVERSITY OF TECHNOLOGY

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RECOVERY OF ALUMINUM AND POLYMERS FROM COMPOSITE PACKAGING WASTE (CPW): TECHNOLOGICAL ASPECTS

Doctoral dissertation
Technological Sciences, Environmental Engineering (T 004)

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TAMARI MUMLADZE

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Abbreviations

AI	Aluminum
BOPP	Biaxially oriented polypropylene
CC	Climate change
CE	Circular economy
CP	Composite packaging
CPW	Composite packaging waste
DMCHA	N, N-dimethyl cyclohexylamine
DMF	Dimethylformamide
DSC	Differential Scanning Calorimeter
DTG	Derivative Thermogravimetry
EAA	Ethylene acrylic acid
EC	European commission
EDS	Energy-dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray analysis
EPA	United states environmental protection agency
EU	European Union
EVA	Ethylene-vinyl acetate
EVOH	Ethylene-vinyl alcohol
FTIR	Fourier transform infrared spectroscopy
GGE	Greenhouse gas emissions
GHG	Greenhouse gas
GW	Gigawatt hours
HDPE	High-density polyethylene
ISO	International organization for standardization
KW	Kilovolt
LCA	Life-cycle Assessment
LCI	Life-cycle inventory
LDPE	Low-density polyethylene
MFP	Multilayer flexible packaging
MFPW	Multilayer flexible packaging waste
MPW	Multilayer packaging waste
OPA	Oriented polyamide film
OPET	Oriented polyethylene Terephthalate
OPP	Oriented polypropylene
PC	Polycarbonate
PE	Polyethylene
PEN	Polyethylene naphthalate

PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
PVDC	Polyvinylidene chloride
RIC	Resin identification code
SED	Secondary electron detector
SEM	Scanning electron microscopy
SHS	Switchable-hydrophilicity solvents
TGA	Thermogravimetric analysis
TW	Tetra Pak waste
UV	Ultraviolet
WPB	Waste pharmaceutical blister
XRD	X-ray diffraction analysis

INTRODUCTION

Composite packaging waste (CPW), that is, multilayer packaging waste (MPW), such as food packaging and pharmaceutical blister packaging, is generally the most significant part of packaging waste which is mainly composed of multilayer laminated plastic sheets on aluminum foil [1]. According to the updated Eurostat, the most widely produced multilayer film is supported by various polymers (such as PET; PP; PE as the main component) and the aluminum layer [2, 3]. Between 2007 and 2018, the volume of packaging waste generated in the EU was estimated at 79±1.25 million tons per year, which makes this type of waste one of the most serious problems to the environment [4].

For the past fifty years, plastic has been the first material which has been selected and used as packaging materials and has become part of modern society's daily life. Today, plastics are involved in virtually all activities, and, due to their lightweight, versatility, and low price, different markets will adjust their products and incorporate them into their designs [5]. Plastics help to maintain food safety and reduce the carbon footprint caused by the movement of heavier materials in food packaging. It is commonly referred to as *multilayer flexible packaging* (MFP) and represents 17% of the totality of produced packaging films [6].

The structure of such an MFP usually includes one or more adhesives and a printable layer. MFP is widely used today to replace packages for storage and distribution of food, beverages, medicines, and consumables. Plastic packaging for this purpose accounts for 40% of all plastics [1]. With an estimated annual production growth rate of 5% to 7%, approximately 19 million tons of oil and gas will be required for plastic production [7]. In addition, MFP becomes waste when its useful life expires, which is even more important because its complex structure makes it difficult to recycle. Most of these materials are recycled, placed in landfills, incinerated, or discarded into the ocean [8].

Food packaging is characterized by high light transmission requirements, moisture resistance, water vapor and gas barrier properties. These foods must be packaged to ensure that the products are of high quality throughout their shelf life [9] and/or to be protected from the peculiar smell during the decomposition of nutrients, fat oxidation, and microbial formation [10].

The packaging industry often uses coextruded or laminated multilayer plastic films and ethylene copolymer-ethylene (EVON) to meet these requirements. On the other hand, they are also used in single-layered plastics, and recycling them into new products is easier to handle [10]. Although the permanent storage of food requires multilayer packages, the reuse of multilayer packaging is difficult because processing requires high-purity monomer materials. For this reason, the requirements for characteristics of packaging materials that maintain the characteristics of their composite structures have recently been increased [6, 11, 12].

The packaging industry annually produces high amounts of disposable consumer packaging. The packaging material varies depending on the type of product to be packaged. However, most of these packages usually feature multiple layers [15]. The increase in disposable packaging production will result in a natural increase of the amount of waste. This type of laminated packaging waste includes household and industrial waste. Therefore, the term *laminated packaging waste* refers to any waste composed of laminated packaging materials, regardless of the stage at which the waste is generated in the packaging distribution chain. Since waste contains valuable components of pure materials, such as plastic, metal (Al foil), and paper or cardboard, which represent important economic resources, it is always desirable in this field to be able to recycle as much as possible with maximum efficiency [14, 15].

In summary, today, manufacturers are facing a challenge which is reflected in the fact that they want to package their products cheaply, with quality and efficiency. As a result, the market demand for composite packaging has increased, and, over time, it has become popular among consumers. As already mentioned, composite packaging contains layers of mainly plastic, paper, and metals bonded with resins or wax. Although the packaging is getting thinner and more efficient and more durable, some issues still remain a pressing problem, such as the recycling of these packaging materials. Due to the complex structure of the packaging material, the recycling process is complicated; in addition, the recycling of this type of waste is carried out by only a few companies [13, 16]. Also, it should be noted that they are focused on recovering only one type of product. However, the available research has shown that it is possible to separate almost all components, and the quality of the recovered materials is close to the quality of the primary products, which increases their reuse in various industries. Because each material in this packaging saves significant natural resources, creating and developing a complete recycling mechanism is essential. This, in turn, will exert a positive impact on the environment and the economy.

Aim of the Doctoral Thesis

The aim of the thesis was to determine the technological feasibility and conditions for recovering aluminum and polymers from food, beverage, and medicine packaging waste by using the solvent separation method.

Objectives

1. Investigation of the problems and challenges associated with the recycling CPWs in Europe and across the globe.
2. Experimentation on separation of Al containing CPW by solvents and acids.
3. Finding the optimum separation conditions for CPWs of the selected initial condition by evaluating the effect of temperature, solid-to-liquid ratio, size, and CPWs type on separation time.
4. Investigation of the recovered recyclable materials in terms of their quality and properties

5. Assessment of the recycling rate, economic performance, environmental benefits, and environmental impacts of solvent separation of Al-containing CPWs.

Scientific novelty

1. ***Optimum process conditions for several most common CPW types have been found.*** Investigation revealed that solvent treatment can still be efficient at low temperatures (low-temperature solvent treatment of CPWs has not been reported before). Experimental data has shown that relatively large CPW samples separated at low temperatures (e.g., about 48 hours at room temperature) over a relatively short period.
2. ***The developed process allows increasing the surface area of composite packaging particles from commonly used <2cm^2 to up to 20 cm^2***. Previously reported works on solvent treatment demonstrated only separation of CPWs shredded into small pieces, while, in the present research, based on the optimized process, increased size (2 cm^2> sample size< 20 cm^2) CPWs have been delaminated.
3. ***Several types of polymers can be separated from each other and aluminum foil.*** According to the literature, CPW treatment was focused on the recovery of only one or two components. According to our study result, more than three different materials (several polymers, Al, etc.) have been recovered from food, beverage, and medicine packaging.
4. ***Increase of the recycling rate and quality of the recovered materials has been achieved.*** The materials recovered at the end of separation, namely Al (powder or foils) and polymers (PVC, PP, PE, LDPE, etc.), were denoted by good quality, e.g., the recovered Al purity was in the range of 65–97%. Also, the average recycling rate was up to 90%. The quality of the recovered materials increases the possibility of reuse in new production.

Hypotheses

Aluminum and various polymers can be successfully separated from each other by using solvent treatment (selected solvents); also, it is an environmentally friendly process which decreases the negative impact on the environment and saves natural resources.

Defended Propositions

1. The developed environmentally friendly solvent treatment method can be used to recover valuable metallic and nonmetallic materials from waste multilayer composites, such as food and medicines composite packaging waste.

2. Polymers and aluminum, recovered by solvent and chemicals treatment, can be reprocessed into high added value products in the form of the original size or powder.

Structure

This doctoral thesis consists of the following segments: Introduction, literature review, materials and methods, results and discussion, conclusions, acknowledgements, reference list, publications list, and appendix The thesis is comprised of 136 pages, 51 figures, 19 tables.

Publications

The results of the research work used to prepare the current dissertation have been published as two articles in the journals registered in the *Web of Science* database, and in two articles featured in other databases. Additionally, the research results have been presented at eight conferences.

Practical value of the work

The treatment of composite packaging waste with solvents can be considered as a favorable environmental method for recovering materials. This work aims to determine the chemical mechanism and technological conditions for the recovery of aluminum and for polymers recovering from food, beverage, and medicines packaging waste. This research corresponds to level 4 of the Technology Readiness Level.

Several laboratory experiments were performed and analyzed in the course of the research to integrate the recycling process for all the types of CP waste. In addition, a pilot plant layout for a CPW industrial recycling line was suggested on the technology's retrieved data on material flows. This includes pretreatment, separation in a specifically designed reactor, classification, and several steps to produce value-added materials.

The obtained result will be helpful for researchers working in the field of science and engineering field. Furthermore, it will help to better understand the CPW separation mechanism based on the solvent treatment approach, its efficiency and convenience. Moreover, it will promote the transfer of a recycling technology from the laboratory to the industrial scale.

Author's Contribution

The research results presented and discussed in this work were initially collected and analyzed by the author. Part of the material characterizations was handled by coauthors of the published articles from Lithuanian Energy Institute (Vidas Makarevičius, Rita Kriūkienė, and Stasė-Irena Lukošiūtė). The author prepared the published papers under the guidance of the supervisor (Gintaras Denafas) and coauthors (Samy Yousef, Maksym Tatariants) from Kaunas University of Technology. Regita Bendikienė (Kaunas University of Technology, Faculty of

Mechanical Engineering and Design) provided additional supervision for article preparation. It should be noted that all the coauthors listed above have no intention of using the published data to prepare other dissertations.

Use of Materials (Figures, tables, etc.) and Text of the published articles in the dissertation (in whole or in part)

A significant amount of the material presented in the dissertation was taken directly from the articles published by the author during their doctoral studies; the following data is given in the chapters where the text was used and the articles from which they were extracted.

Chapter 1 – Literature Review (Subsection: 1.4.2), Chapter 2 – Materials and Methods (Subsections: 2.1 and 2.2), Chapter 3 – Results and Discussions (Subsections: 3.1, 3.2, 3.4, 3.5, 3.6) is a slightly modified version of the articles: *Cleaner and profitable industrial technology for full recovery of metallic and nonmetallic fraction of waste pharmaceutical blisters using switchable hydrophilicity solvents* published in the Journal of Cleaner Production (Elsevier) [Ref. 53] and *Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents* published in the journal *Green Chemistry* (Royal Society of Chemistry) [Ref. 1].
Note: The articles have been reproduced here with the publishers' permission.

1. LITERATURE REVIEW

1.1. European recycling targets for plastic and packaging waste

The European Commission considers the consumption of plastics to be imbalanced and notes that plastics often end up in the ocean; thus, it is obvious that there is poor management and a low level of plastic waste collection. Therefore, the EU urges the states to find a solution and to take a better approach. Plastics participate in the circular economy where production, use, and destruction can become an organic part of recycling and developing new products. A continuous collection system, classification, and recycling should be the starting point for achieving social goals and environmental benefits [17].

In December 2015, the European Commission adopted the *EU Joint Action Agreement on the Circular Economy*. Plastics are of the highest priority, and there is a mandate to redefine everything in the plastics cycle. The plastics industry has ensured that all plastic packaging will be recyclable by 2030. The new recycling market will continue to grow over the next 10 years, which will help to develop new materials and technologies [5, 17, 18].

The European Commission has set itself a target for its 2018 plastics strategy of 2018: 50% of plastic packaging waste will be recyclable by 2025 and 55% by 2030. The goals set include a decrease in packaging consumption (60% by 2020, 70% by 2025, and 80% by 2030). By 2030, around 90% of recyclable packaging will consist of metals, non-metals or glass [5].

The proposal prohibits sending reusable waste to landfills by 2025, which is expected to affect fully recyclable municipal waste by 2030. This applies to the consumption of raw materials and the efficiency of the gross domestic product's efficiency up to 2030, thereby improving the resource performance. EU countries are committed to making the global climate change a priority, yet they still continue to burn natural gases and emit large amounts of carbon dioxide and other pollutants [17].

Currently, around a third of the recycled plastic packaging in the EU is recycled outside the bloc. According to the EU strategy for plastics, the average recycling rate of plastic packaging is expected to decrease from 41% to 29–32%. In the 2020, waste generation has increased (EU), and the total amount of recycled materials has also been gradually increasing. Much remains to be done in order to achieve the goal of 2018 [5]. Fig. 1 shows the statistics for packaging waste for 27 EU countries.

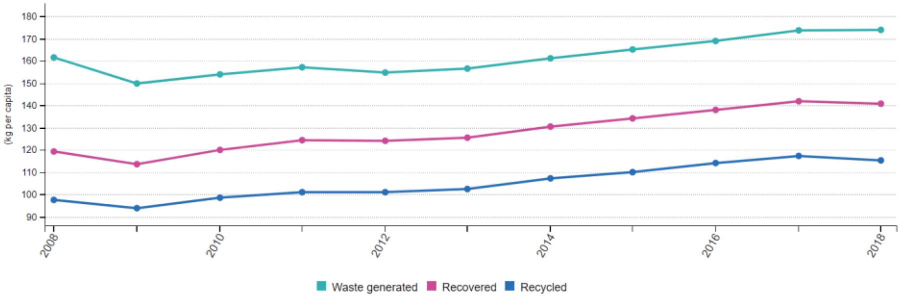

Fig. 1. Packaging waste generated, recovered, and recycled, EU, 2007–2018 [4]

Even if plastics have not yet been used in renewable raw materials, there is the need to increase the collection of recyclable materials. Collecting, sorting, and recycling understandably relates to the problem of flexible packaging removal. It is necessary to understand how to collect, sort, and recycle this type of material, as these three steps are critical and affect both the flexible packaging performance and the waste in general.

Typically, the different collection systems depend on regional and economic parameters. The idea is to analyze the general understanding of flexible packaging, integrate it into the classification system, and apply modern technologies for material collection and separation. However, it is essential to understand that they represent different waste streams due to the type of waste collection. More importantly, it is possible to identify the types of plastics and polymers that consumers use and which are recycled by consumers [19].

In addition, the recovery of basic raw materials from the packaging waste has been increasing in Europe. In 2016, 67% of the packaging waste generated in the 28 EU countries, Iceland, Liechtenstein and Norway was recycled. In 2017, the 28 EU countries recycled 55% or more, and 15 countries recycled 65% or more of their packaging waste [20]. This improvement was partly due to the EU goals for 1994 and 2008, followed by the circular economic plan (2015). The vertical line in Fig. 2 represents the 2008 target set by the Packaging and Packaging Waste Directive (94/62/EC). The countries tasked with meeting this target were Cyprus, the Czech Republic, Estonia, Hungary, Lithuania, Slovakia, and Slovenia in 2012; Bulgaria and Poland in 2014; Latvia in 2015, and so on (Fig. 2) [17].

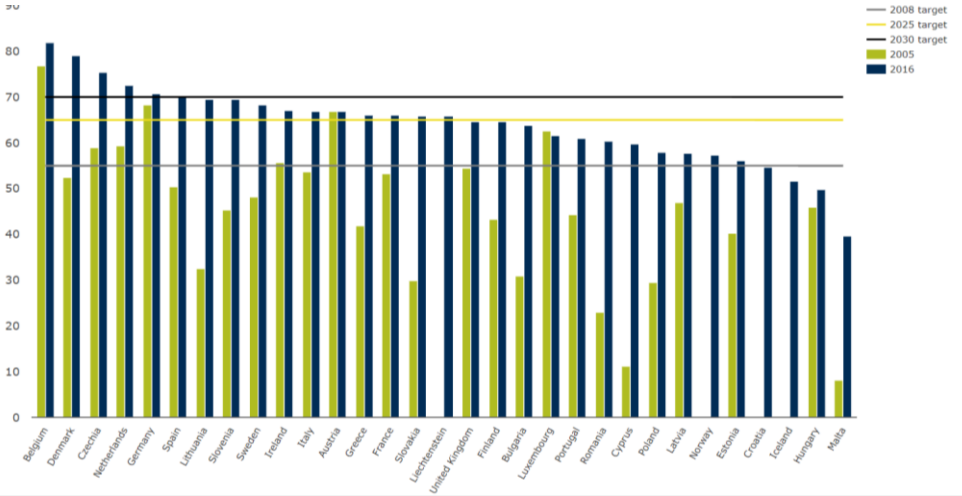

Fig. 2. Recycling rates of packaging waste in Europe by country [17]

In particular, the planning and implementation of the national and EU policies and objectives has improved in recent years. However, the regional and local governments of each country still play an important role in this process. Countries place more emphasis on recycling household waste than on packaging waste. This may be because packaging waste recycling was introduced in 1994, 2001, and 2008 [17]. In addition, countries have developed a producer liability plan for the packaging waste and introduced a mechanism to achieve this goal [17]. These waste streams overlap because municipal waste includes household packaging waste and similar sources [4, 17].

1.2. Natural recourses used in packaging production

Given the reliability of various packaging types, it is important to clarify the relationship among the natural resources used to manufacture these packaging materials, such as biomass, fossil fuels, ores, and minerals converted into completely different materials. Reliable connection of different resources and materials requires different forms of control. The focus should be on the two main packaging materials for multilayer packaging: Al and polymer [21].

According to the data of Fig. 3, around 160 million tons of bauxite are mined annually for Al production, which is extracted from the Earth’s crust, and then processed into Al [22]. This process requires a large amount of energy. Extracting 4 to 5 million tons of bauxite takes around 125 to 160 billion kWh. It also requires a great amount of water consumption, which leads to the formation of toxic sludge. Thus, the process produces large amounts of various pollutants. Furthermore, it produces GHGs, SO_2, dust, polycyclic aromatic hydrocarbons, and wastewater [23, 24].

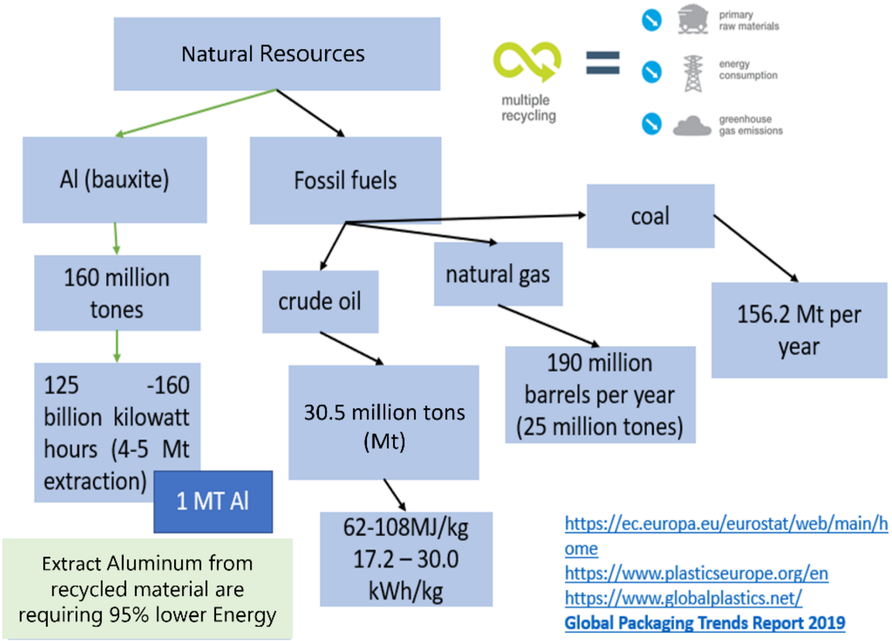

Fig. 3. Natural Resources Used in Packaging Production [4, 25–27]

For example, from November 2019 to November 2020, about 59.305 thousand metric tons of Al were produced, the first three Al producers are China, GCC countries, and Asia (excluding China) (Fig. 4), and this process required a large amount of electricity, for example, in 2020, in the entire world, for aluminum production, about 835.273 GWh of energy was consumed (this was a different power mix) (Table 1) [22].

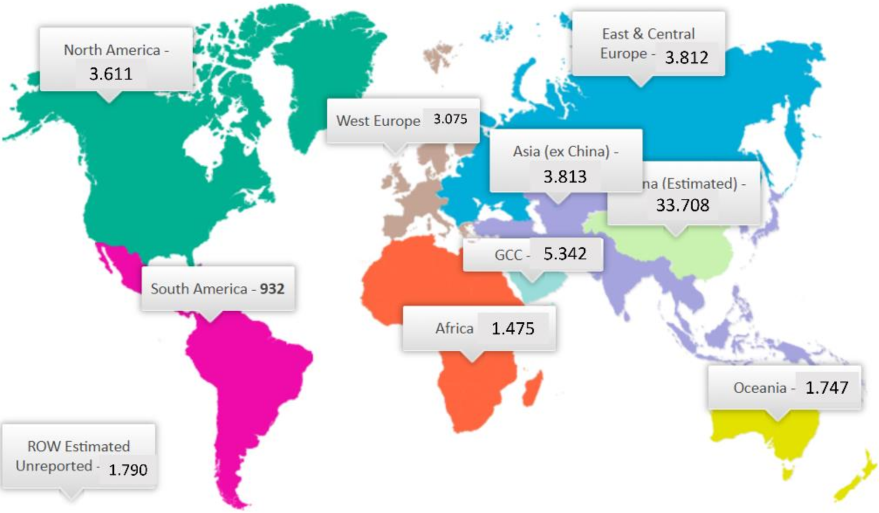

Fig. 4. Primary aluminum production – total for November 2019 to Nov 2020: 59,305 thousand metric tons of Al [28]

Period		Africa	North America	South America	Asia (ex China)	Europe	Oceania	Gulf Cooperation Council	China	World Reported	Estimated Unreported
2020	Aluminium Production (tonnes)	1,605,000	3,976,000	1,008,273	4,140,000	7,487,000	1,918,715	5,833,000	37,337,000	65,325,000	2,020,012
	Reporting Production (tonnes)	1,548,030	3,698,679	1,008,273	2,551,661	6,971,603	1,918,715	5,033,831	37,337,000	60,067,792	ND
	Power Mix										
	Hydro	11,684	48,344	12,763	1,289	96,471	8,171	0	72,231	250,953	ND
	Other Renewable	0	1,302	1,598	37	5,214	1,049	0	19,876	29,076	ND
	Other non-renewable	21	53	165	0	1,071	0	0	0	1,310	ND
	Coal	10,623	6,346	0	37,812	1,779	18,425	0	390,241	465,236	ND
	Oil	0	22	0	0	0	0	4	0	26	ND
	Natural Gas	0	1,136	2,785	0	1,240	204	76,949	0	82,314	ND
	Nuclear	0	561	0	0	3,373	0	0	2,424	6,358	ND
	Total	22,328	57,764	17,311	39,138	109,148	27,849	76,953	484,772	835,273	97,000

Table 1. Primary aluminum smelting power consumption – Global Data for 2020: Gigawatt hours (GWh) (power mix) [29]

According to the data, global plastic production was about 359 million tons in 2018, of which, around 62 million tons were produced in Europe (Fig. 5). According to the global data, China is one of the world's largest plastic manufacturers [30].

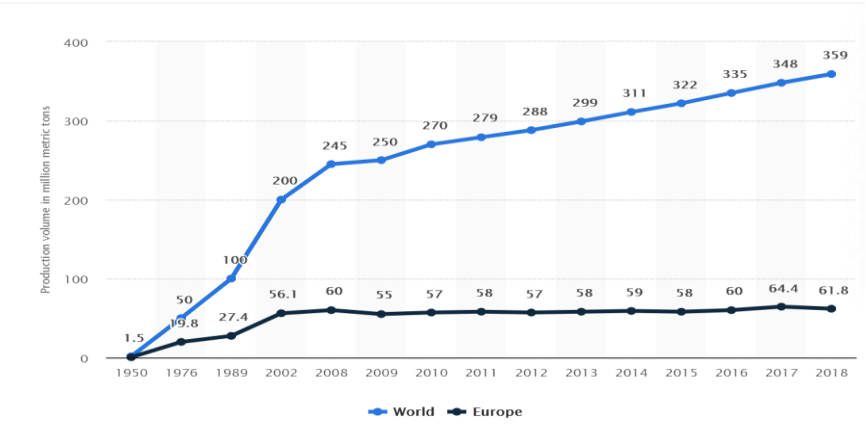

Fig. 5. Global plastic production 1950–2018 (in millions of metric tons) [29, 30]

Approximately 70% of the total plastic production is composed of seven types of plastics and polymers derived from fuels and used in food packaging [31]. Approximately 30.5 million tons of crude oil, 25 million tons of natural gas, and 152.6 million tons of coal are used to produce plastics annually and manufacture various products [32]. Plastic production is generally an energy-intensive process. According to the data, the average manufacturing process in the United States requires 62 to 108 megajoules of energy per kilogram [26].

1.3. The Function of Packaging and types of packaging and Packaging Materials

Packaging materials can be made from a variety of materials with the objective to protect the product from various adverse effects. However, the packaging made from natural materials, such as leather and leaves, only had a limited function in protecting the product. As a result, other materials, such as wood, textiles, ceramics, and glass, came onto the market. Over time, packaging materials made from these materials became known throughout the world (for example, canned tomatoes were transported in metal and glass containers at the beginning of the nineteenth century) [33].

It should be noted that one of the most common packaging materials in the mid-19th century was polyethylene. Furthermore, containers began to enter the market in the mid-20th century. This has changed and significantly improved the living standards, yet it has harmed the environment over the years [34].

1.3.1. Functions of packaging

Packaging is an essential component performing various basic functions. Different authors describe packaging functions differently; however, seven key functions have been identified when evaluating a strategic packaging decision: protection, containment, unitizing, apportion, communication, information, and convenience. Some functions may have additional functionality [35].

Below is a brief description of these features [36]:

Content: The purpose of the content is to contain the content and the safety of the environment. Many products must be sealed due to their nature. Liquids are a classic example.

Protection: The packaging protection function is intended to protect the product from external sources and vice versa. Damage can be caused by physical, chemical, climatic, etc. causes [35].

Apportion: This feature allows you to control and maintain the correct usage of a certain amount of content. The proliferation of packaging has facilitated the division of products into controlled sizes and servings and making the required quantity and size available to retail outlets and consumers.

Unitizing: In most cases, small units are divided into larger units and vice versa to improve efficiency, and it helps to make packaging suitable for different situations.

Convenience: The primary purpose of the convenience function is to make the packaging and its contents simpler and easier to use. Convenience refers to association and distribution. The primary purpose is to facilitate the handling and packaging of products in the appropriate sizes and quantities at different stages of the life cycle – convenience is concerned with all the phases of production and packaging, from distribution to the end use and recycling.

Information: Packaging is a source of information between the product and the customer. Packaging information is essential for the customer because it provides additional information about its composition, use, and manufacturing time.

Communication: A means of communication between the brand owners and consumers. This aspect of packaging is mainly considered marketing. Attracting customers and their interest in the products is done through packaging [35].

1.3.2. Types of packaging (primary, secondary, and tertiary)

Primary packaging is the type of packaging that reliably protects the product. It is also important that the packaging does not cause adverse reactions. For example, the food and beverage industry’s primary packaging would be stand-up wraps, packs for chips, candies, coffee, biscuits, etc. They should generally be non-toxic, food grade, and not cause strange colors, tastes, or other chemical reactions. In the pharmaceutical industry, the primary packaging refers to blisters used to package various tablets, capsules, and medications, in general.

Secondary packaging is used for brand promotion and product display. Usually, an outer box, box or a package containing multiple materials does not directly contact the product. It is an integral part of food packaging. For example, a box of pills containing various drugs is transported in a box displayed in the pharmacy’s aisle.

The tertiary package is used to protect and transport the product. Any company offering innovative products will use the third layer of packaging in the sales process. This package aims to protect the product and simplify its delivery process [37].

1.3.3. Types of packaging materials

Common packaging materials are paper, glass, Al, mixed materials, plastics, textiles, and steel [38].

Paper: paper is a widely used packaging material due to its light weight and low cost. Wooden boxes have been replaced with cardboard boxes, which reduces the amount of packaging materials and increases the safety of transportation. For example, for cardboard recycling, laminated cardboard containing an Al foil layer is not fully recycled due to the complexity of its structure. It should also be noted that such packaging is used for those products which require long-term storage or transportation. Laminated packaging material generally includes 70–75% paper, 20% polymer, and 4% Al foil [39].

Glass: glass is common type of packaging waste. It has some advantages such as storing food for a long time without any changes. After use, it can be sent back to the factory for recycling. At the same time, glass has disadvantages, such as heavy weight, breakage, transportation costs, etc. [40].

Aluminum: Al is attractive for packaging materials, because it is relatively light, although it requires a large amount of raw material to make. Therefore, it is essential to recycle Al packaging after the end of shelf life. Secondary Al has a high price in the market because its strength is economically recyclable [41].

Steel: Steel packaging is used for beverages, dyes, canned foods, and some other products. It should be noted that steel processing saves about 16% and reduces production costs [40].

Plastics: Plastics are the most widely used packaging material. This is due to its lightweight, long-term use, etc. Its cost is lower than that of some other materials, and it is often used to substitute other materials. About 10% of the generated waste is plastic because it remains difficult to degrade plastics in the environment for an extended period. Therefore, it is important to recycle waste plastic packaging materials [36].

Textile: Textile packaging is mainly used to transport, store, and protect products. Textile packaging is the most environmentally friendly packaging material as it can be used for an extended period. Textile packaging includes all textile packaging for industrial, agricultural and miscellaneous goods. Polyolefin-woven bags are also often used; their advantages involve lightness, low cost, environmental friendliness, and long-lasting use [42].

Mixed materials: For the manufacturing of composite packaging materials, different materials are used instead of one. This packaging material has become popular because it significantly reduces energy consumption; however, the combination of different materials reduces the recycling potential. Therefore, recycling of mixed materials is a real issue today, as it is associated with the loss of large amounts of natural resources [43, 44].

The present study mainly focuses on the primary packaging and the secondary packaging.

1.4. Composite packaging

1.4.1. Types and applications of composite packaging

Generally, composite packaging is made by combining two or more tightly bound materials, and the consumer cannot separate them. One of the essential aspects of using different materials in packaging is that it increases the product's durability, flexibility, and protection. Examples of such packaging materials include laminated or metallized polymer packaging, such as pharmaceutical blister packs, chocolate packs, and more. Table 2 shows several types of composite packaging materials and their applications [45].

Table 2. Types and applications of composite packaging [45]

CP materials	Applications	Typical Structure (outside to inside)
OPET/AI/PE Films	Pet food, coffee, and other food powders	OPET/ink/Al foil/PE
OPET Films - Metallized	Lids for yoghurt tubs	Ink/paper/Al metallization/OPET/lacquer
OPP Films - Metallized	Potato chip bags, chocolate, biscuit, wrapping films, labels	Copolymer OPP/OPP/copolymer OPP/ink/Al metallization/PE-PP copolymer/OPP/PE-PP copolymer/OPP/PE-PP copolymer
Al and Paper Wraps	Butter	Al foil/wax/paper
Multilayer Bottles	Squeezable bottles for sauces and honey	Bottle – PET/EVOH/PET Seal – OPET/Al foil/PE

Common types of composite packaging are aseptic cartons, pouches, wrappings, blisters, rigid and semi-rigid packaging, flexible packaging, blister films and foils, laminated tubes, containers, etc. [46].

Blisters, as mentioned above, are made of two or more different materials, which are different types of Al and polymer. This type of packaging is mainly used in the pharmaceutical industry, confectionery, and chewing gums. Typically, it has four components: a formable film (80–85%), lidding materials (15–20%), coating, and printing [47].

Flexible Al/plastic is usually a combination of Aluminum foil and a plastic sheet tightly bonded together. This packaging is mainly used for coffee, ice cream, sweets, chocolate, chips, and similar products. Flexible Al/plastic packaging does not split quickly, as it has combined properties of such as Al and paper combined material. Flexible Al/plastic bags are also used in laminated packaging, and are often used for beverages, animal food, etc. [48].

Food and beverage cartons (also called *Tetra-p Pack*) are one of the most sustainable packaging materials available in the market. Usually, they are made from a renewable resource, from paper as a renewable resource from well-managed forests. They are available in two types: long-term storage (or aseptic), and refrigerated:

- Shelf-stable (or aseptic) packaging comprises 74% paper, 22% plastic (polyethylene), and 4% Al. They are used for soups, water, milk, juice, beans, wine, and nutritional shakes.
- Refrigerated packaging contains approximately 80% paper and 20% polyethylene. They are used for packaging milk, juice, cream, and other beverages.

Although these are mainly composed of 60–70% cellulose and 30–40% polyethylene foils and Al, but this is not always the case. All the components are valuable raw materials for other different industrial uses. However, for recovery, there is one condition that the components must be separated entirely [45, 49].

1.4.2. General composition of multilayer packaging films

According to the literature, CP consists of several layers: coating, the outer layer, the structural layer, the bonding layer, the barrier layer, and the sealing layer, as shown in Fig. 6. Each layer performs a different function; for example, the barrier layer traps oxygen, while the coating layer covers the paint and protects the products from UV light. Thus, the structure of composite packaging may vary depending on the product and the manufacturer [50, 51].

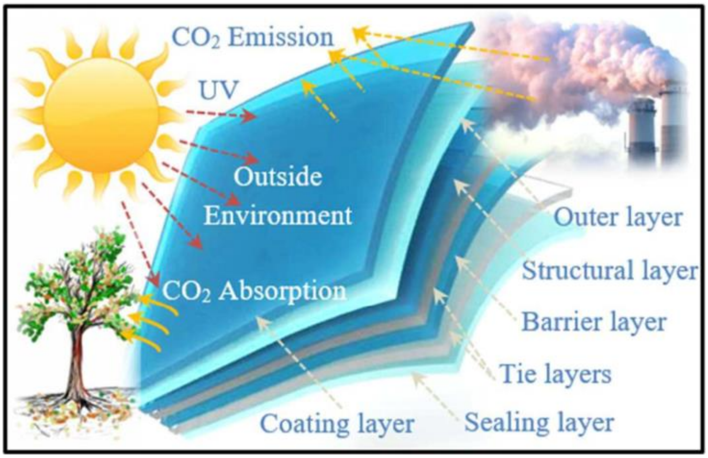

Fig. 6. Basic components of multilayer flexible packaging [1]

According to Pilchik [52], blister packaging consists of four different layers: a forming film, lidding material, heat sealing coating, and printing. The structure of pharmaceutical blisters is shown in Fig. 7 [53].

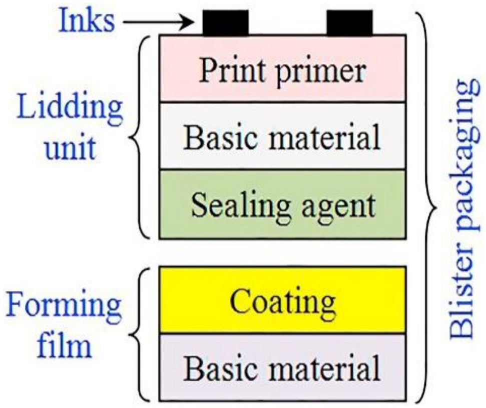

Fig. 7. Main components of blister packaging [53]

1.4.3. Description of each component of composite packaging films

As already mentioned, composite packaging films are composed of various materials with different functions and properties.

Aluminum – Al foil is the most important component in packaging materials; it is characterized by lightness and durability, corrosion, and resistance to temperature, and, most importantly, it can be recycled multiple times without compromising the quality. In addition, because Al foil packaging is relatively light, it is characterized by functionality and ecological cleanliness. Aluminum foil can also be used with uncoated metal or other materials [54]. Fig. 8 shows the Al and polymer content in several multilayer packages, where we can see that there are two main components, polymers and Al in the packages, and, in most cases, the polymer contents in packaging constitute more than 50% of the total mass [3].

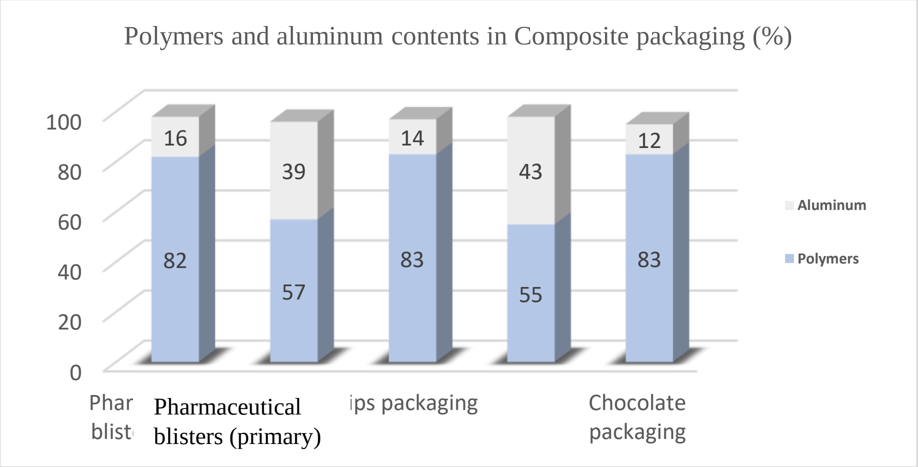

Fig. 8. Aluminum and polymer content in multilayer package foils [3]

Plastic polymers: Various types of plastic polymers, copolymers, and mixtures are used in multilayer packaging materials. The most common polymers used in producing these materials are PE, PP, PS, LDPE, HDPE, etc. Table 3 shows polymers that are commonly used in the manufacturing of multilayer packaging materials and their applications [55].

Table 3. Plastic polymers used in multilayer packaging [55]

Polymers	Functions
PE	The sealed moisture barrier for contact with food can be integrated with gas/aroma barriers
PP	This barrier can be coated with heat-sealing coatings to provide mechanical strength combined with odor/odor barriers
PA	A barrier that provides mechanical resistance to heat resistance
PS	The pressure capability of breathability can be combined with a gas/scent barrier
EVON	The oxygen barrier must protect from moisture, which is usually co-extruded between PE or PP
PVDC	The gas/odor and moisture barrier serves to protect the surface from scratches and heat abrasion [56]
EVA	Adhesion of the moisture barrier is used for coextruded layers of polar and non-polar polymers and heat-sealable contact layer with food
PVC	Mechanical strength of the gas/aroma barrier mechanical strength
EAA	It is the bonding layer of the extrusion coating between the aluminum foil and the heat-sealable food contact layer of other polymers

Bonding between layers: Multilayer films can be coextruded or laminated. Coextrusion can be carried out by blow film extrusion or forging extrusion. Composite plastic is then combined as a single product where co-extruded layers are immediately bonded together [56, 57]. Unlike coextrusion, lamination is performed by applying some adhesive type between polymers or foils (such as Al foil) to combine them into a strip. Alternatively, an adhesive is applied, such as solvent-based adhesives, water-based adhesives, solid adhesives, UV, electron beam curing adhesives, etc. [40]. The next step is to apply wax or hot glue between the two materials and then cool to bond. Table 4 shows the main adhesives used in lamination and their uses [55].

Table 4. Adhesives used for lamination [55]

Type of lamination	Adhesive
Extrusion lamination	LDPE: multilayer and multi-material packaging
	EVA: bonding between polyethylene and PVC
	EAA: used for bonding with Al foil
Dry bond lamination	Solvent-based polyurethane adhesive is used for flexible packaging
	Polyurethane dispersion is used to laminate plastic films into multi-layer flexible packaging
UV-curing	Acrylic and acrylic esters, epoxy resins, PUR, etc. are used in flexible packaging

Solventless lamination	Polyurethanes
Hot-melt lamination	EVA; EBA; LDPE

***Coatings*:** They can be applied in several ways, inside, outside or in-between layers, to change or improve the physical properties or appearance (Table 5) [55].

Table 5. Coatings used in MFP [55]

Coating	Purpose
Protective	Used to protect the surface from mechanical damage [58]
Heat-seal	Used to allow heat salability for non-salable materials [58]
Primers	Used to improve the bond between a substrate and an otherwise incompatible coating [58]
Cold seal	Its self-sealing is possible by using mixtures of acrylic resins and latex pressure; Synthetic rubber [59]
Anti-mists	Used on the food contact side to prevent condensate drops/fog
Gloss/matt	Used to change the visual perception of the design side
Gas and moisture barrier	Gas/odor/aroma and moisture barrier
UV light barrier	Barrier to UV light

Printing: Usually, two types of printing are used, such as surface printing or reverse printing, on the outer side of multilayer packaging. Reverse printing is usually printed on the inner surface; this means that the print can be better protected from various types of impact. In addition, printing coatings can be used to protect the printed surface and obtain gloss or matt effects. The composition is similar to the corresponding ink but does not contain any pigments. Table 6 shows the most standard ink systems used in packaging production [60].

Table 6. Common printing ink systems [60]

Printing ink system	Composition
Solvent-based	Pigments; PUR Solvents: alcohols, esters, and ethoxypropanol Additives: plasticizers, adhesion promoters
UV-curing	Pigment; Oligomers: epoxy acrylates, polyester acrylates Additives: waxes (PE/PTFE waxes), silicone oils, stabilizers
Water-based	Pigment; binders: styrene-acrylic copolymers, acrylic copolymers, maleic acid Solvents: water, glycol, ether Additives: wetting agents [56]

Often, due to advertising, printing is used to manufacture packaging materials directly with food. In this case, pigments based on modified cellulose are mainly used for this type of painting.

1.5. Environmental Impact of Packaging Materials

1.5.1. Importance to Control of the environment

Over time, the environment has undergone significant changes. Today, waste is one of the most pressing issues. Packaging materials serve different purposes and are associated with transportation, storage, etc. In ancient times, plant matter was used to make packaging, but it has been replaced with wood, fabric, plastic, and other stronger materials throughout the centuries. The reason for these changes was to extend the shelf life of the products and to protect them from damage and contamination [34].

Due to the growing demand for packaging, its environmental impact is rapidly increasing. The rising demand for consumer products is increasing the production of packaging materials which, in turn, increases the production of the packaging waste [61].

As we have already mentioned, the increasing demand for packaging materials harms the environment; currently, difficulties already arise in managing packaging materials worldwide, and their overuse aggravates environmental problems. Several disposal methods (e.g., landfill) continue to negatively impact the environment in recycling processes [62].

The components of the packaging material evolve daily because consumers want more robust products associated with high-quality packaging. As already mentioned, the global consumption of packaging materials is growing rapidly, and the packaging industry has become one of the main environmental pollutants. In order to solve this problem, proper and strict control of packaging waste is required [63].

1.5.2. Overview of the Environmental Impact of Packaging Materials

The fact that many packaging materials are not made of biodegradable plastics magnifies the environmental concerns. Although there are numerous technology and equipment solutions for waste processing today, billions of tons of plastic are still being sent to landfills every year, which leads to the release of harmful substances into the environment due to biased and inefficient control measures. At the same time, it causes the loss of many natural resources [64]. Although waste management is currently under development, problems related with plastic have not yet been resolved. Still, the reduction of the consumption of plastic materials will significantly contribute to solving this problem [65]. According to scholarly data, in 2008, the USA generated approximately 13 Mt of plastic packaging waste, which represents 12% of the household waste; about 23% of plastic packaging materials were recycled, and the rest was sent to landfills [66]. Due to the low share of disposal and the leakage of hazardous substances to landfills, various issues need to be discussed in order to reduce the number of plastic materials that have started to be used in various industries, although this does not reduce the demand for plastic materials. Moreover, recycled plastic can only be used under certain conditions [64]. Different countries have different recycling mechanisms; for example, only certain types of plastic are received for recycling in some countries, which causes confusion for the consumers [57]. It is also challenging to collect plastic waste because most of the population does not have individual containers, thus making it difficult to collect plastic waste separately and recycle it further [66].

Directive 94/62/EC of the European Parliament and the Council, as amended by the Packaging and Packaging Waste Directive, obliges the EU Member States to take specific measures, such as a national program, liability schemes, etc. to influence the community and reduce the impact of plastic packaging waste on the environment [67]. Additionally, EU member states have been tasked with facilitating plastic packaging materials. In some countries, the deposit system has been introduced and has already been actively used for a long time. According to this directive, countries must increase their recycling rates to a certain extent by 2025 and 2030 [68].

1.6. Lifecycle Assessment for Packaging

1.6.1. Overview of the literature on LCA

Life cycle assessment (LCA) is one of the most valuable methods in current use serving the objective of assessing the environmental impacts of products, processes, etc. The packaging sector actively uses this method to evaluate and study the possible impacts of materials on various life cycle factors [69].

In general, LCA is used to assess the environmental impact of a material's production systematically. LCA defines various parameters, such as the climate change, greenhouse gas emissions, and eutrophication; that is, parameters related to the production of a material and their impact on the life cycle.

LCA consists of four key components: purpose and scope, life cycle inventory (LCI) analysis, life cycle assessment, and life cycle interpretation [70]. Each component plays an essential role in the assessment process [71, 72].

For example, LCI analysis involves collecting and processing data at different stages of the life cycle of a product, while LCI assigns its environmental impact to some specific category [72].

In 1969, Coca-Cola was the first company to apply the LCA method to food packaging [73]. This application was made necessary by the new packaging practices of the time. Over time, the rapid development of packaging materials due to the demand for the increased shelf life has led to LCAs being applied to a wide variety of packaging materials [72]. However, all of this has had a negative impact, including the increased consumer demand for these packaging materials along with the increased packaging waste. The demand for single-use packaging has also risen. This demand has highlighted the need to use LCA so that to further assess and analyze the currently existing problems in order to improve packaging management practices. The overall environmental impact of packaging materials was 2 to 5% for food packaging and approximately 25% for beverages [26]. Many packaging materials are being produced around the world, with common examples including plastics (PET, HDPE, PP, etc.), glass, and cardboard [74].

LCA is a method for assessing the environmental impacts of a product throughout its full LC. Initially, LCA focused on the electrical balance, technology, and community attitudes [75]. Later, the LCA method was developed within the Standards ISO 14040 [76] and 14044 [77] which provided a general framework and defined the minimum standards for LCA performance. However, it is important to analyze the LC and evaluate several impact categories so that to avoid load shifts. Thus, LCA has become an instrument for decision support in the packaging design [73]. A number of LCAs for packaging have been published [78], many of which are comparative [79–82]. The comprehensive vision of LCA considers the important environmental benefits of the various waste management processes [83].

A comprehensive LCA case study was conducted on the environmental impact of various packaging systems, including the environmental impact of plastic packaging [84]. Ross [71] used life cycle assessment to examine the reuse and recycling strategy for polymer-based packaging, Zabaniotou [85] performed life cycle assessment for egg packaging made from polystyrene and recycled paper where he indicated the categories of environmental impact that exert the most prominent effect: greenhouse effect (GWP), acidification (AP), winter smog (WS), and summer smog (SS). On the basis of the result of PS eggcups LCA, more air and liquid pollutants are emitted to the environment in comparison to paper eggcups. Almeida [86] used LCA to evaluate the choice of materials for beverage packaging in Brazil. Waste management studies have been carried out for the life cycle assessment. Specifically, Banar [87] conducted a study on the life cycle assessment of waste management options in Turkey. According to the result from the study of global warming, methane had the most important impact on landfill scenarios, where up to 80% of waste is sent to the landfill. Incineration has the highest human toxicity effect due to nitrogen oxide, with a contribution of 100%. Mendes [88] did a comparative study on the environmental effects of incineration and the development of landfills through the use of life cycle assessments, where landfill scenarios had much higher acidification potential than incineration scenarios. What concerns incineration, the global warming potential was largely due to burning plastics, which creates anthropogenic CO_2 emission. Boer [89] used life cycle assessment tools for the development of integrated waste management strategies; Hong [90] used life cycle assessment to study municipal solid waste management in China, Daz [91] researched the WASTED (Waste Analysis Software Tool for Environmental Decisions) model, Ferreira [92] studied the packaging waste recycling system in Portugal, and, based on the study result, savings of 298.7 kt of CO_2 equivalent and 10.3 kt of CO_2 equivalent compared to the Incineration and Landfill standards were achieved in total. Kirkeby [93] used a computer model based on LCA to evaluate the environmental and resource impacts of waste disposal systems, Peters [94] studied an environmental comparison of biosolid management systems by using the life cycle assessment, compared to different waste scenarios, and discovered that paper recycling was more environmentally friendly than incineration, separation and landfill; moreover, landfill was the most inappropriate way of dealing with packaging. Khoo [95] determined the environmental impact of various waste conversion systems, including the global warming potential, possible acidification, terrestrial eutrophication, and photochemical ozone formation. When comparing which form of treatment is preferable (recycling, incineration, or landfill), Schmidt [96] carried out a life cycle assessment of the waste hierarchy. In Denmark, Merrild [97] performed LCA of paper waste from waste management and underscored the importance of the technical data and system limits for the evaluation of recycling and incineration. Generally, it is not easy to obtain LCA studies for packaging in the published literature. For example, Mourad [98] examined the environmental impacts due to an increase in the recycling rate from paperboard of the aseptic packaging system. Paraskevas [99] performed environmental impact analysis for primary aluminum. During the study, the result was analyzed for 29 countries around the globe. Based on the result, the researched countries produced 861M tons of CO_2 equivalent in 2012, and it also affected the natural resource extraction. Xie [100] conducted a life cycle assessment with the objective to compare composite and plastic packages for milk products in China; based on the study, composite packages showed to inflict 12 times more damage to the ecosystem than plastic packages. Also, Xie summarized that material extraction from composite packaging is more beneficial to the environment and can reduce the environmental effect of the life cycle. In another research, Xie [101] studied LCA in China for composite packaging waste. In this study, aseptic packages were treated with concentrated nitric acid. The author studied and compared four different scenarios. Based on the obtained result, the main environmental and economic benefits come from recycling, reducing energy consumption, water, resources, and land usage. Samori [102] conducted life cycle analysis for composite packaging waste and compared four waste treatment scenarios: landfill, pyrolysis, and two different ways of solvent treatment (the formic acid and SHS routes). On the basis of the obtained results, solvent treatment was more beneficial in comparison to the other two scenarios. The SHS system can decrease impact on environment (CC = 648.2 kg CO_2 eq.) and human health (HT = 562.3 kg 1.4 DB eq.) more prominently than the alternative options, also, it required less resources than formic acid treatment. Xie [103] performed life cycle assessment for Al foil and polymer composite packages made from Al foils and polymers; in this study, CPW was treated with concentrated formic acid (60%) and nitric acid. Then, LCA was done for this treatment process. The author compared three different waste treatment scenarios: landfill, incineration, and solvent treatment. The study result showed that, for incineration and recycling, the environmental impact potential was negative. Therefore, carcinogens were the main environmental impact of landfills. However, in recycling, because of the reuse of the recovered reusable materials, this treatment process had a positive effect on the environment related to fossil fuels and minerals.

According to the literature investigating life cycle assessment, primary Al production has made a significant contribution to CO_2 emissions in the production of new products. If 100% primary Al is used in new production, the amount of CO_2 emitted is seven times that of secondary aluminum. As a result, the less primary Al is used, the smaller is the impact of the produced new products on global warming [99, 104].

Bauxite and petroleum coke transportation is, presumably, commonly carried out by cargo ships, which results in high SO_2 and NO_x emissions. So far, primary Al production is the most important source of C_2H_4 emissions. A relatively large amount of SO_2 is emitted from primary aluminum production, and it involves potential for eutrophication [104]. So far, transportation is the most important source of SO_2 equivalents. This is mainly due to NO_x emissions. Therefore, when 100% primary Al is used, long-term transportation of bauxite and petroleum coke can also result in the highest emissions. Compared to extracting raw materials from natural resources, auxiliary raw materials in new production are more efficient and environmentally friendly [104].

If we summarize the above outlined literature, it can be seen that LCA is an essential tool for different types of processes, showing a big picture and giving ideas about positive and negative effects, whether it is environmentally friendly or economically favorable way. There were some objections to using the main solvent DMCHA in this life cycle assessment for the current study. This solvent cannot be found in the database at the moment. Also, it was planned to perform this assessment with another solvent, but it is not easy and not appropriate to compare the induced impact of the current technology because of the different properties of the solvents used.

1.6.2. Life cycle assessment of packaging

The European Commission recommended methods for the evaluation of the life cycle assessment of packaging as part of the pilot phase of the ecological footprint (Table 3) if the recycling rate data is not available for such parameters as the production rate, quality index, standard values determined by the European Commission [105].

Table 7. Impact Categories and assessment methods adopted by the European Commission (EU) [106, 107,]

Impact Category	**Indicators**	**Recommended LCIA Method**

Climate change	Radiative forcing as global warming potential (GWP100)	GWP100a, based on IPCC 2013
Ozone depletion	Ozone depletion potential (ODP)	Steady-state ODPs
Human toxicity, cancer	Comparative toxic unit for humans (CTUh)	USEtox model
Human toxicity, non-cancer	Comparative toxic unit for humans (CTUh)	USEtox model
Particulate matter	Impact on human health	PM method recommended by UNEP (UNEP 2016)
Photochemical ozone formation human health	The concentration of ozone concentration increase	LOTOS-EUROS
Acidification	Accumulated exceedance (AE)	Accumulated Exceedance
Eutrophication, terrestrial	Accumulated exceedance (AE)	Accumulated Exceedance
Ecotoxicity, freshwater	Comparative toxic unit for ecosystems (CTUe)	USEtox
Land use	Soil quality index[22] • Biotic production • Erosion resistance • Mechanical filtration • Groundwater replenishment	Soil quality index, LANCA
Water use	User deprivation potential	AWARE
Resource use, minerals, and metals	Abiotic resource depletion	CML 2002
Resource use, fossils	Abiotic resource depletion – fossil fuels	CML 2002

1.7. Common separation techniques for composite packaging waste

There is no suitable closed-loop system for processing high-quality laminated materials (e.g., laminated Al foil). Single-layer container recycling is easier to manage because it does not have a foil. However, the processing of multilayer flexible polyethene packaging involves a longer process. This packaging is widely used for food products and medicine pills [3]. Due to the contamination of packaging materials in the currently existing recycling system, only a small amount of them is reused [43].

As CPW is structurally complex, landfills are an easy way to dispose of this type of waste [6, 108]. However, the leakage and accumulation of Al in the soil are associated with significant environmental problems for large landfills. It is also possible that the polymer composition of CPW causes similar problems [11, 13]. A waste incinerator is the second most common treatment option for CPW because it sterilizes abnormal and anatomical waste, reduces its volume and weight, and restores energy [14]. Thermal processes can lead to gases and ash releasing large amounts of harmful substances to the environment, such as dioxins and mercury

[109]. For example, the autoclave, microwave and plasma disinfection method was developed [110]. Despite the effectiveness of this process, no restrictions have yet been developed to regulate energy consumption, recovery speed, unpleasant odor, and high costs, etc. [53]. Thus, in the recent years, chemical treatment of multilayer waste multilayer packaging materials with solvents has been developed. The focus is on recovering as much material as possible from CPW. The chemical processing approach may be summarized by separating polymers from the composite layers and breaking the adhesive bonds. Various solvents, such as benzene, ethanol, xylene, toluene, hexane, and acetone, have been used in studies to recycle composite packaging [111, 112].

The development of a recycling process is essential for CP waste, consequently, various companies and researchers have worked to address this problem.

According to literature studies, several separation methods (thermal, physical, and solvent separations) were used to separate the Al and polymer layers in the previous years, and these processes are very different from each other. These processes involve thermal, physical, and solvent separation.

1.7.1. Thermal separation

Different melting points are used; this process is carried out in a sealed container where waste is placed and then heated to reach the plastic and Al melting point. Gases produced during plastic pyrolysis can be collected from the top of the container. In the case of the substantial part, Al foil can be collected at the bottom so that to separate Al. This method has several disadvantages: firstly, there are some gas emissions associated with energy consumption, CO_2, etc., the second issue is that the processed composite materials are of relatively high cost. At the end of the process, only Al foil can be recycled, the separated plastic materials are not well recycled and can only be used only for heating, which has a low use value. Furthermore, for the plasma technology, composite packaging waste is heated at 1500° C, and, at the end of the process, plastic turns into paraffin, thereby only high purity Al is restored. This technology allows for the use of a recirculation process with minimal emissions; the reaction takes place in an oxygen-free environment; without combustion, the energy efficiency coefficient is close to 90%. However, the disadvantage of this method is that the construction and maintenance costs are too high and difficult to fund [113].

Aluminum Company of America (Alcoa), its Brazilian subsidiary Alcoa, Aluminio SA and Tetra Pak company, Klabin Company Wo mouth TSL Engenharia Ambiental companies [114] developed a plastic recovery system using an energy-generating plasma jet at 1500 °C. During this process, the composite packaging waste is heated, and plastic is recycled into low molecular weight substances, and high-purity aluminum ingot is ultimately recovered. This technology is required to produce high temperatures; also, high-quality equipment is necessary, and high investment costs are required. Simultaneously, the recovered product was converted into plastic paraffin, thereby reducing the recovery value.

Korkmaz [115] used pyrolysis at 400–600 °C to process composite packaging materials. After the recycling process, pure Al was removed; the product additionally contained unwanted gases, carbon residues, and wax [116]. Ang [117] used the hydrometallurgical process with sodium hydroxide at a temperature of 70 °C to recover Al from pharmaceutical blister residues. The duration of the process is about 80 minutes [117]. The hydrometallurgical method was also used by Wang [118]. This author used hydrochloric acid solution to separate aluminum and plastics. Wang confirmed that the processing of blisters of pharmaceutical preparations with hydrochloric acid results in a high-quality and purity product suitable for further processing [118, 135].

1.7.2. Physical separation

When applying *electrostatic physics methods,* the composite material of aluminum-polymer is made by spraying and passing through a mechanical mill of abrasive dust. Separation occurs under the influence of the friction force.. The electrostatic separation method repeatedly evaluates plastics and aluminum. In general, this method can only separate aluminum and plastic composite pipes. The disadvantage of this recycling method is that it yields powder, consumes a lot of energy, and is uneconomical. Furthermore, the separation effect is not yet acceptable, as a prerequisite for the plastic separation of plastics and the Al electric field method is that Al and plastics cannot be bonded together, whereas, for the Al polymer composite material, this method loses its effectiveness [119].

Muther [120] designed a treatment process for the dry separation process in the composite by mechanically removing a sheet made of a simple laminate product triturated to give only the usual mixture of products; the problem is that it is difficult to separate plastic and Al foil from the composite of one component. Laminated products are made by high-speed rotation so that to obtain stable single-phase composition distribution. It is the principle of the eddy current behavior when the Aluminum composite material is generated in the machine’s acceleration and and is designed to separate. According to this principle, *Austria Result Technology AG* designed the corresponding commercial processing system. For such a process, it is necessary to generate a powerful, high-speed accelerator vortex and achieve high accelerations. Therefore, with very high cost requirements, separation also increases the cost. *Enval* developed a method for mixing crushed waste with carbon, specifically, mixing shredded waste carbon, which is a highly absorbent material. This process results in 100% Al foil recovery, while oils and gases are recycled to produce electricity or the chemical materials in other technological processes [121]. *Pellenc ST* has developed a Fine Sort platform designed for flake-sized streams of 4 to 20 mm for separated layers of different materials. With *Pellenc*’s new magnetic density separation technologies, a range of apparent densities inside the ferromagnetic fluid is used to create a multifaceted process system. The process fluid contains a dilute mixture (H_2O, black oxide) and a magnetic field [122].

1.7.3. Solvent Separation

During *solvent separation*, CPW sinks into the separating agents (acids, bases, or organic solvents) by dissolving or swelling, then breaks the adhesion between the layers, and, finally, the layers are separate. However, the use of powerful acids, a lot of alkalis, and caustic soda (NaOH) during the separation process can cause the dissolution of the metallic layer in the solvent, and this strategy suffers from a low recovery rate. Waste aluminum polyaluminium chloride or aluminum sulphate was generated that cannot be obtained from aluminum foil, which reduces the recovered value as this method rarely manages to isolate the plastic composite. Acid penetrates the layer of the plastic material layer, and, consequently, the first interface (alumina) between plastic and Al is dissolved, then adding an oxidizing agent to protect the Al foil can be obtained.; there is the choice between a strongly acidic substance in the application of the process, and the options include nitric acid, sulphuric acid or phosphoric acid; in a specific study, hydrochloric acid was selected as the chosen method; since the medium was too acidic, the acid reacted with the Al foil, and the outcome is such that the rate of recovery of Al becomes very low, and it reduces the possibility of economically feasible recovery [123, 124]. Moreover, when two solvents are combined, such as a strong acid and alkali, they can cause significant corrosion of the equipment; the price of solvents itself is high, which results in higher costs when industrial production and the liquid waste from the reaction, such as stemming from improper handling, can also cause new pollution. This separation method is bound to use the organic solvent of high density, and the plastic layer is very large in terms of the adsorptive capacity of the solvent; even if it passes through the centrifugal swing dryer, it still has nearly 30% adsorptive capacity; therefore, the separation costs are too high, and, when only neat solvent is involved, the separation rate is very slow, not all organic solvents are effective[125, 127]. Therefore, in order to raise the efficiency while using an organic solvent, certain surfactants can be added, but the patent does not specify what kind of surfactant was used. The method uses a large amount of an organic solvent of high concentration, which can cause problems of environmental pollution [125].

The use of *sodium hydroxide* results in substantial economy because the organic compounds used in prior researches are relatively more expensive. At the ambient temperature, 2M sodium hydroxide solution slowly dissolves Al by etching and releases free plastics within the solution. When Al foils completely dissolve, the plastics freed from lamination come in the free-floating condition waiting for removal from the solution; fragments are then removed from the resultant, which results in a very dilute solution of sodium aluminate, and are allowed to dip with rapid stirring in the dilute nitric acid solution for about 0.5-2 minutes[126].

Then, plastics are forwarded to water baths containing sufficient water so that to wash away the adhered solvents. Fragments of recovered plastics are washed with water; the time factor varies directly with the size of shredding, and, widthwise, smaller figments will take shorter time duration. The density of sodium hydroxide/sodium aluminate solution also affects this period. Proper care should be taken for the tubes. After such frequent and specific use, the main volume of 2M sodium hydroxide solution is eventuate as Sodium aluminate solution as the primary recovery of metal Al salt.

Separation fluid was also used which was a mixture of water, acetic acid (ethanoic acid), phosphoric acid, and sodium hydroxide. The mixture of acetic acid and water attacks the bond of the multilayer material. Phosphoric acid and sodium hydroxide are added to control the side reaction of Al dissolution. The separation fluid is kept between 20–90 °C and at pH values between 2–4. In general, the low pH value favors the separation performance as a side reaction results in the dissolution of aluminum. Minimal dissolution is important for safety reasons since dissolution leads to gaseous hydrogen, which represents an explosion hazard. The pH value is therefore adjusted by adding sodium hydroxide solution to the separation fluid. Several separation fluid examples have been tested [125, 127] (Table 7.) [128].

Table 8. Examples of separation fluids [128]

Example 1	
Anionic Surfactant	12% sulfuric acid, c14-17-se-alkane, sodium salts
Co-surfactant/hydrotropic	3.3% caprylic acid
Hydrocarbon solvent	21.7% xylene (isomers)
Carbonic Acid	11.6% acetic acid
Water	51.4% H_2O
Example 2	
Anionic Surfactant	14.4% sulfuric acid, c14-17-se-alkane, NaCl
Co-surfactant/hydrotropic	1.8% phosphoric acid decyl ester, NaCl
Hydrocarbon solvent	20.0 % xylene (isomers)
Carbonic Acid	12.0% acetic acid
Water	51.8% H_2O
Example 3	
Anionic Surfactant	10.8% Sulfonic acid, c14-17-se-alkane, NaCl
Co-surfactant/hydrotropic	4.8% caprylic acid
Hydrocarbon solvent	25.0% C_8H_{10}(isomers)
Carbonic Acid	6.0% acetic acid
Water	53.4% H_2O
Temperature range 20–50 °C / PH of 1.5–4 / Time range – 30–50 minutes.	

The *CreaSolv®* process has been reported to involve complex plastics and the production of pure polymers. However, during the process, the target polymer is selected and then separated from other materials. The materials used in the *CreaSolv®* process can be of different types, for example, various composite materials, such as laminated foil, electrical and electronic waste, and mixed plastic waste [129]. The separation mechanism of the *CreaSolv®* process is shown in Fig. 9 and is discussed in Table 8 [129].

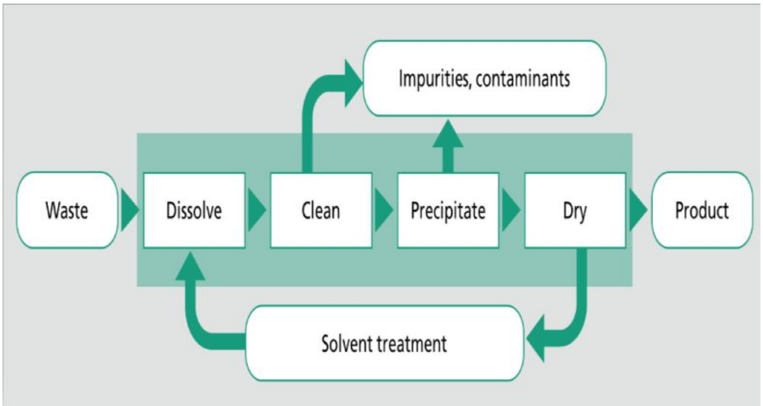

Fig. 9. *CreaSolv®* process scheme [129]

Table 9. Description of the separation mechanism given in Figure 9 [129]

Dissolve	The polymer can be selectively dissolved in the specific solvent composition. The solubility of the polymers allows them to be recovered with high purity.
Clean	Insoluble components are mechanically dissolved. Dissolved substances are removed. After washing, a macromolecular solution of the target polymer is prepared.
Precipitate	The polymer is obtained by precipitating solvents.
Dry	The polymer dries.
Solvent treatment	The distillation of the solvent is performed after the stages of purification, precipitation, and drying, and then it is returned to the recycling process.
Product	The recycled polymers were characterized by high quality; thus, they can be used as secondary raw materials in various industries.

Once the *CreaSolv®* process is complete, high-quality recycled plastic allows the remaining plastics to be used for the production of secondary products. Although this process results in the recovery of high-quality polymer, it focuses on recovering only one type [130]. The *CreaSolv®* processing is shown in Fig. 10 [131].

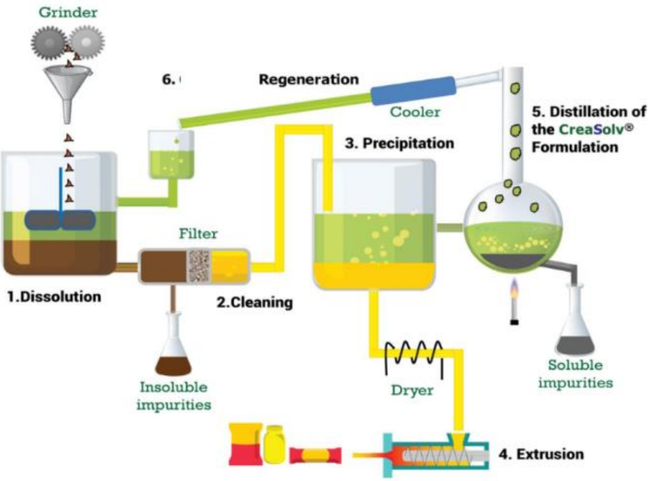

Fig. 10. Recovery process scheme – recovery of solvent base material [131]

The steps for the separation technique are defined below (Fig. 10) [131]:

1. Dissolution: After being sorted according to the type of plastic used, the plastic waste is shredded and dissolved in a 'personalized' *CreaSolv*® jar. The target polymer and some impurities dissolve.
2. Purification: Insoluble impurities are separated into a clean solution. The impurities can then be discarded or recycled if they incorporate valuable substances.
3. Precipitation: After the solubility assets are converted from the result, the best polymer is precipitated and may be restored.
4. Extrusion: The dried, reclaimed polymer is extruded into new polymer granules, and the resulting authentic materials may be used within the required application.
5. Distillation (Purification): The solution is collected and distilled by reusing the *CreaSolv*® compound. The final insoluble impurities are accumulated and disposed of as waste, or, if they incorporate valuable substances, recycled.
6. Recovered: With the aid of regeneration, *CreaSolv*® can be reused to dissolve plastic waste.

When plastics are processed, the minimal amount of solvent is used. The smallest feasible plant has a potential of 2 to 4.000 tons per year [131].

Although many studies have been conducted and many solvents have been tested, only a small fraction of these solvents are effective for the recycling process. Some chemicals involve problems that concern the polymer, causing them to decompose (e.g., toluene). The quality and purity of materials recovered after processing significantly impacts their commercial value, especially in chemical processing. According to studies, during the chemical treatment process, the materials must be recovered, the solvents evaporated or neutralized by the addition of another solvent.

Rodriguez-Gomez [132] used vegetable waste oil to separate Al and PE Tetra Pak. The main goal of this process was to produce products at a lower cost, by using less energy and fewer raw materials. Kulkarni [133] used innovative, pure and supercritical water to treat MPW. Favaro [116] used supercritical ethanol to process PET and Al composite material.

The laminated polymer separation process was carried out by using various organic solvents related to time and temperature [111]. According to Kulkarni [133], nonpolar solvents are more effective in reducing polyethylene compounds, so, polymer decomposition is an important step in the recovery strategy. The polymer recovery rate may be up to 56% under xylene reflux conditions. The good thermal properties indicate a high degree of structure [133]. Ang [117] used sodium hydroxide whereas Wang [118] used hydrochloric acid solution for the CPW separation process of CPW. Furthermore, Samori [102] used a switchable hydrophilic solvent N, N-dimethylcyclohexylamine (DMCHA) to dissolve LDPE and separate Al aseptic food from the packaging [102]. The recycling efficiency of the developed recycling method was >98% for the recovery of all multilayer composite waste layers when using various chemicals [112].

Tetra Pak is manufactured with layers of paper (75% by weight), Al (5% by weight) and LDPE (20% by weight) [134]. It was treated with acetic acid (after the initial mechanical removal of the paper layer), and the best results were achieved in studies on the separation of *Tetra Pak* (TW) wastes. The main separation products were aluminum foil (19%) and polyethylene (78%). However, this separation is incomplete because 1.19% of the Al-PE laminate remains undivided. Thus, the total separation loss of the acetic acid reagent is 1.21%. When a *Tetra* Pak is treated with formic acid, the separation products contain 20% aluminum foil, 75% polyethylene, 3.59% unseparated Al-PE laminate residues, and 0.08% dissolved Al [135]. 100% separation of *Tetra Pak* is achieved by using a mixed organic solvent reagent (benzene-ethanol) yielding separation products containing 31% aluminum foil and 69% polyethylene. Unseparated or incompletely separated remnants persist; also, the insolubility of Al in the separating agent reduces the output losses. In addition, experiments have shown that separation with this reagent is faster than separation with acidic reagents. This separation also requires a lower ratio of the reagent to the sample weight, i.e., 100 ml – 1 g of the sample; therefore, it can be argued that separation with an organic solvent is more efficient in this regard [135, 136]. Consequently, an attempt was made to separate blister packs with formic acid, acetic acid and mixed reagents based on organic solvents. However, the desired separation result, i.e., complete separation of the Al-PVC laminate layers (14% and 86%, respectively) was achieved only when using a mixed organic solvent [135].

The disadvantage of the above listed methods is that many chemicals are used in the recycling process, and this directly affects the impact on the environment.

As we can see, among packaging recycling methods, mechanical and thermal/chemical treatments are the predominant industrial technologies [130, 137].

To summarize on all the common separation methods for composite packaging waste, they are denoted by advantages as in most separation processes it was possible to recovery Al of mostly good quality; unfortunately, the polymeric fraction was not recovered or recovered at low quality. Also, other disadvantages are involved, such as high cost, low recovery rate, high energy consumption, different types of pollution, such as gas emission, water pollution, etc.

Switchable hydrophilicity solvents, N, N-dimethylcyclohexylamine. Switchable hydrophilicity solvents (SHS) can bring about significant improvements from the environmental and economical point of view in solvent separation processes which generally use large amounts of volatile, flammable, and toxic solvents. However, some of these SHSs are denoted by health and safety concerns, such as toxicity, instability, or flammability, which makes them less desirable for industrial use [138, 139]. Therefore, the number of commercially available tertiary amines suitable as ‘green and safe’ SHS systems for extraction processes is limited to a small group of compounds. Among these, N, N-dimethylcyclohexylamine (DMCHA) appears to be the best choice; DMCHA is denoted by hydrophilicity, which is why it is called SHS [139]. Jessop [140] proposed using one of the best performing SHS, DMCHA, to recover polymers, whereas Phan [141] used SHS for the extraction and separation of soybean oil, Samori [142, 143] used it for lipid extraction from algae cultures by performing the lipid extraction process of diluted *Botryococcus braunii* cultures, Samori [102] used SHS for the recycling of composite packaging and recovery materials, Fu [144] used SHS for the extraction of phenols from lignin microwave pyrolysis oil, etc. As mentioned above, DMCHA is one of the best options considering the following expected properties for a ‘good’ SHS amine that should be water-immiscible and become water-miscible when switched to CO_2. This CO_2-supported switching enables SHS separation from the extracted products at the end of the extraction process without using energy for evaporation; It has a high boiling point and low toxicity and are required to be liquid at room temperature [140, 141, 145–147].

1.8. Summary of Literature Review

Research shows that composite packaging waste (CPW) is still a serious issue these days. This is due to the shortage of recycling methods and the less-than-ideal disposal system. Landfills are a common means of disposal, but most of this kind of waste is incinerated. However, this common solution can affect human health and cause environmental problems. Therefore, an urgent task is to find and develop an appropriate processing technology for handling this type of waste.

Now that we have reviewed the current technologies for processing CPW, we can make a side-by-side comparison and indicate the most favorable research direction. When reviewing packaging recycling methods, mechanical and thermal/chemical treatments are the predominant industrial technologies. As mentioned above, several researchers are using these technologies to recycle CPW into aluminum or polymeric materials.

However, this recycling practice usually suffers from several disadvantages: recycling rate, energy consumption, CO_2 emissions, environmental pollution, generated gases, and high costs.

Taking a broad view of the currently available separation methods, we find that the separation costs are high, the recovery rate of aluminum is low, and the separation speed is slow. In addition, most separation methods ignore a significant problem which is that they do not completely separate aluminum foil from the plastic layer.

It is thus necessary to investigate a separation method that is efficient and low-cost. Taking into account all the points in the literature review, we can see that solvent treatment is a very favorable approach, denoted by many advantages over other options. However, it must be improved in the following ways so that to become more competitive, environmentally friendly, and cost-effective:

- It is necessary to investigate the conditions that provide the optimal separation efficiency for different sizes of samples. However, the process must be completed below the boiling point so that to reduce the emission of potentially hazardous gases and prevent solvent decomposition.
- Preliminary economic and environmental analysis shall be conducted to determine the additional impacts and benefits of recycling processes. The resulting materials must be carefully analyzed in order to determine their quality and potential uses and to determine whether further processing is still necessary.
- Methods of converting recovered materials into high-value products should be proposed, as certain materials may have this additional potential. It will help increase the sustainability of the approach.

Furthermore, literature analysis of the currently used and investigated practices suggested that no special pre-treatment for CPW recycling should be required. However, in most cases, the researchers were using pre-washing, crushing, removing contaminated materials, or were making suitable surfaces for separation processes to increase the efficiency and, therefore, the ‘preferability’ of their selected approach.

Therefore, it was decided to focus this thesis on developing a solvent treatment approach by using specific solvents described in the relevant literature as the studies reviewed on this topic revealed some weaknesses and yet unexplored aspects of this approach. The results of previous studies were taken into account when selecting the conditions for the experiment. The experiment was planned to be conducted under the following conditions such as, temperature range 30 to 90 °C; solid-to-liquid ratio 1:3; sample size 2–10 cm^2; solvents DMCHA, acids, acetone, etc.

2. MATERIALS AND METHODS

During the research, three experiments were performed which were focused on solvent treatment. Different types of composite packaging waste (CPW) were selected depending on the level of its popularity among the consumers, six types of waste pharmaceutical blisters (WPB) and six types of multilayer flexible packaging waste (MFPW) from Lithuanian local shops and pharmacies from Lithuania were researched. For all the experiments, consumable materials (e.g., solvents) for the main experiment were used. During the first experiment, WPB treatment was focused on DMCHA, the second experiment involved MFPW treatment by DMCHA, whereas the third experiment was for all the types of sample treatment (WPB and MFPW) with different solvents (e.g., acetone, ethyl acetate, nitric acid, etc.). For all the samples, the optimum conditions were selected, and the sample size range was 2cm^2–20cm^2; the temperature range was between 30–90 °C (the final experiment was carried out at a low temperature, specifically, 40–50 °C); the solid-to-liquid ratio was 1:3 g/ml. The relationships between the different variables were analyzed based on observational, experimental, and derived methods. After all the materials and separation conditions were chosen, solvent treatment was performed, and CPW was separated. The used solvent was regenerated. In the list, three materials were recovered after the treatment process (aluminum, polymers, ink, etc.). All the recovered materials were analyzed, and their quality and properties were studied. More information is provided in the following chapters.

2.1. Consumable Materials

Various solvents were used during the study, such as N, N-dimethylcyclohexylamine (DMCHA), ethanol, ethyl acetate, toluene, acetone, dimethylformamide (DMF), formic acid, acetic acid, and nitric acid. Table 10 shows the list of the used solvents, their formulas, molecular weight, boiling and melting points, density, solubility in water, dielectric constant, and the flash point.

Table 10. Properties of the used solvents [152]

Solvent name	*Formula*	*MW*	*BP (°C)*	*MP (°C)*	*Density (g/mL)*	*Solubility in water (g/100 g)*	*Dielectric constant*	*FP (°C)*
N, N-dimethylcyclohexylamine (DMCHA)	$C_8H_{17}N$	127.23	162-165	-60	0.85	20	2.86	42.2
Ethanol	C_2H_6O	46.07	78.5	-114.1	0.789	Miscible	24.6	13
Ethyl acetate	$C_4H_8O_2$	88.11	77	-83.6	0.895	8.7	6	-4

Acetone	C_3H_6O	58.079	56.05	-94.7	0.7845	Miscible	21.01	-20
Toluene	C_7H_8	92.14	110.6	-95	0.867	0.52	2.38	4
Dimethylformamide (DMF)	C_2H_6OS	78.13	189	18.4	1.092	25.3	47	95
Formic acid	CH_2O_2	46.03	100.8	8.3	1.22	Miscible	57.9	69
Acetic acid	$C_2H_4O_2$	60.052	118	16.6	1.0446	Miscible	6.20	39
Nitric acid	HNO_3	63	121	-41.6	1.4	Miscible	19	-

N, N-dimethylcyclohexylamine (DMCHA), a strong solvent with relatively low toxicity and volatility [145, 153], can extract materials from composite packaging waste. DMCHA is relatively hydrophobic under neutral conditions (e.g., in water) but becomes more hydrophobic when exposed to carbonated water. Therefore, DMCHA was more effective (>98%) than other solvents in the extraction process. In addition, because of its switchable polarity, the recovery rate of DMCHA is higher, and it is possible to recover it after the separation process.

Pure 96% *ethanol (CH_3CH_2OH)* was used during the separation process and served to remove any type of contamination from the surface of the prepared composite packaging waste samples prior to solvent treatment.

Ethyl acetate ($C_4H_8O_2$) was used to separate WPB and MFPW. Ethyl acetate is a slightly toxic solvent. However, if not handled properly, it can become hazardous, especially if accidentally exposed. Ethyl acetate is highly flammable and dangerous if swallowed or inhaled. This chemical can cause severe damage to internal organs through repeated or prolonged exposure. Ethyl acetate can also be irritating if it is absorbed by the eyes or skin [154].

Toluene aromatic hydrocarbons (C_7H_8) are widely used in organic synthesis. Toluene is a colorless liquid with a characteristic sweet odor. More prolonged exposure results in headache, drowsiness, etc. Meanwhile, a higher concentration can affect the heart [155, 156]. Toluene is also responsible for increasing the metabolic toxicity of the anion gap [157]. Furthermore, high-level acute exposure to toluene in rats reduces the neurogenesis of the hippocampus [158].

Acetone (CH_3COCH_3) is a simplest and smallest ketone, a colorless, volatile, and flammable liquid which is widely used in various industries. It is the least toxic industrial solvent [159]. However, one should avoid exposure to highly concentrated vapor. In addition, acetone can cause eye irritation and sometimes temporary blindness. However, in many experimental studies, acetone is non-toxic or less toxic than other alternatives [160, 161].

Dimethylformamide (DMF) is a colorless aprotic solvent with a high boiling point; it is often used as a reagent [162]. Many studies have been conducted on the toxicity of DMF [163, 164]. DMF is easily absorbed through the skin, inhaled, or ingested, and can cause abdominal pain, constipation, nausea and vomiting, headache, weakness, dizziness, skin problems, etc.

Formic acid (CH_2O_2) is denoted by low toxicity; concentrated acid is corrosive to the skin. The body metabolizes and easily removes formic acid. However, it has specific toxic effects. Formic acid and formaldehyde produced as methanol metabolites are responsible for damage to the optic nerve and cause blindness, similar to that of methanol poisoning [165]. The dangers of formic acid solutions depend on the concentration.

Acetic acid (CH_3COOH) can be a dangerous chemical if not used safely and correctly. It is highly corrosive and affects the skin and eyes and must therefore be handled carefully. Acetic acid can also damage internal organs if inhaled or ingested, or if vapor is inhaled [166].

The toxicity of *nitric acid (HNO_3)* is mainly related to its highly corrosive nature. In addition, it is an excellent oxidizer, and it instantly reacts with any tissue thus causing such effects as skin burns, eye irritation, shortness of breath, and pulmonary edema [167]. The nitric acid treatment process is successful, but it still produces a lower recovery rate in comparison to DMCHA.

2.2. Instrumental Methods for Metals and polymers analysis

Various instrumental methods were used to characterize each material during the investigation, such as FTIR, analysis and identification of the extracted polymers, chemicals, and regenerating solvents. SEM and EDS were used to study the chemical composition of the treated metal layers. Metallographic microscopy was used to study the separation of Al dye from polymer layers and to investigate other properties of waste packaging. Also, TGA was used to check the thermal stability and the glass transition temperature of the materials removed from the samples. Here follows a brief description of each instrumentation method which we used [1, 53].

Fourier transform infrared (FTIR) spectroscopy. It examines the transmitted light and shows how much energy is absorbed by each wavelength. Analysis of the properties of this absorption reveals details of the molecular structure of the sample. Samples can be solid, liquid, or gaseous, and samples of different sizes can also be analyzed [148].

Scanning electron microscopy (SEM). SEM expands a specific sample area by using a high-energy focused electron beam [149]. It is also possible to identify a specific element in the estimated area of the sample. The SEM-EDS analysis method is convenient for determining the particle size and the composition of elements [150].

Thermogravimetric Analysis (TGA). TGA is used to study the thermal stability of materials and to obtain information about their composition. By using different atmospheres within the instrument, it is possible to determine how much carbon and inorganic filler is present in the sample [151].

Metallographic method. Sometimes, in order to determine the phase diagram, one measures the volume fraction of the phases. For this, a metallographic method or the X-ray diffraction (XRD) method may be used. Therefore, metallographic analysis is an essential tool for determining phase diagrams [150].

As mentioned above, different instrumental analyzes were performed for identification of materials. It is essential to mention that, with these analyses, we were able to study the sample’s structure, to achieve identification of the materials, and also to study the amount of layers; but, in order to determine the weight of each layer, it was not possible to calculate the initial weight by using different analyzes.

2.3. Experiment 1 – Separation of composite packaging wastes by using different solvents[3]

2.3.1. Materials and waste composite packaging type selection and analysis

In this section, the separation process of several types of WPBs and MFPWs by different solvents is described. Five CPW samples (two types of WPB and three types of MFPWs), eight different solvents (ethyl acetate, ethanol, toluene, acetone, dimethylformamide (DMF), two organic acids: formic acid and acetic acid, and nitric acid (concentrated 45%, 50% and 65%)), and a mix of solvents (Benzene-ethanol-water; volume ratio of 30-20-50 respectively) are used. In this case, we indicate the sample codes for each sample. Table 11 shows the samples with the individual codes and the solvents which were used during this part of the experiment. When selecting the separation conditions (temperature, solvent content, sample size, and duration) for the experiments, previous studies were helpful, and, in some cases, it was decided to keep some primary conditions. The reason why the conditions were different is due to the different nature and characteristics of the solvent, such as the boiling point; some specific acid was chosen to clarify its effect on CPW separation if it is possible to use as alternative solvent for DMCHA. For example, as already mentioned, some solvents were effective, for example, nitric acid, but they have disadvantages, such as the production of nitrogen dioxide and quality losses after the regeneration of the solvent, etc.

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[3] References [3, 135]

Table 11. WPBs and MFPWs sample codes, sample weights, solvents used (ml)

Samples code	CPWs sample	Mass (g)	Ethyl acetate (ML)	Ethanol (ML)	Toluene (ML)	Acetone (ML)	DMF (ML)	Formic acid (ML)	Acetic acid (ML)	Nitric acid (ML)	Benzene - Ethanol-water (ML)
WPB$_a$		10	100	100	100	100	100	100	100	100	200
WPB$_b$		10	100	100	100	100	100	100	100	100	200
MFPW$_a$		2	50	50	50	50	_	100	50	50	_
MFPW$_b$		2	50	50	50	50	_	100	50	50	_
MFPW$_c$		2	50	50	50	50	_	_	50	50	_

According to the literature, the wet separation process was chosen to recover Al from CPWs by using the above mentioned solvents. The solvents were selected for their lower harmful effects on the environment. For the experiment, in order to remove contaminated particles, the samples were washed in distilled water and cut into small pieces measuring 1 cm x 1 cm [3]. In order to objectively compare the CPW separation performance with different separation media, the difference in the sample mass was determined before and after treatment.

2.3.2. Composite packaging waste separation and dissolution process

All the collected samples were washed with distilled water and then dried at room temperature (24 hours) to prepare for the separation process. The remaining samples (WPB and MFPW) (1×1 cm, 2×5 cm) were collected. Prepared CPW samples were cutted in a small peaces. The weight of each sample is different. For each experiment, we used: WPB$_a$ and WPB$_b$ (10 g); MFPW$_a$, MFPW$_b$ and MFPW$_c$ (2 g); the amount of the solvent was 50–200 ml, the time range was 15–60 minutes; the temperature was 30–90 °C; the rate of mechanical stirring was 300 rpm; the volume of the reagent depends on the weight and the size of the sample (the reagent should cover the sample) [3]. Starting from the dissolution process, after the first 5 to 10 minutes (the average of all types of solvents), the ink layers WPB$_a$, WPBb, and MFPW$_c$ start to separate. For other MFPW samples, it takes time to remove the ink. Therefore, a filtration method is used to extract ink particles from each selected sample. After the sealing layer has dissolved, the formed film (for all the samples) begins to separate from the lid. This step takes 30 minutes. The substrate and Al layer were separated and removed from the solvent. It should be noted that the results of all the samples were not the same. In some samples, Al was dissolved in the solvent, or more time was necessary for separation [1].

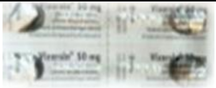
All of these steps were performed at the same time so that to reduce the overall separation time and energy consumption. The treated samples were washed with distilled water and allowed to dry for 24 hours at room temperature, while the samples treated with organic solvents were thoroughly washed with ethyl alcohol and distilled water in order to remove organic solvent residues from the resulting products. The samples were dried at room temperature. The dehydrated samples were divided into separate Al and plastic parts, and undiluted packaging layers were weighed for each fraction (products and by-products) [135].

2.4. Experiment 2 – Separation of waste pharmaceutical blisters by DMCHA[1]

2.4.1. Materials and pharmaceutical blister type waste selection

Analytical grade reagents used in the research include N, N-dimethyl cyclohexylamine (DMCHA). Six different types of WPB were collected from waste generated by local pharmacies in Lithuania. The waste diversity factor was believed to increase the precision of the results. Therefore, the WPBs chosen were the size, color and type of the pill inside. All the samples received specific codes as shown in Table 12. To prepare WPBs for separation, the samples were washed and rinsed with distilled water to remove dust, grease, chemicals, adhesives, stains, etc., and then they were dried at room temperature for 24 hours [53].

Table 12. WPB type specification and sample codes [53]

Sample code	**WPB type**	**Surface area**	**Mass (g)**	**DMA (ml)**	**Thickness (μm)**
8 **WPB1**		92mm x 40mm ($3680\ mm^2$)	1.821	60.7	260
9 **WPB2**		105mm x 53mm ($5565\ mm^2$)	2.969	98.9	250
2 **WPB3**		85mm x 38mm ($3230\ mm^2$)	1.252	41.7	225
11 **WPB4**		128mm x 50mm ($3230\ mm^2$)	2.834	32.9	128
5 **WPB5**		90mm x 50mm ($4500\ mm^2$)	1.212	40.4	137
4 **WPB6**		100mm x 66mm ($6600\ mm^2$)	2.945	98.1	236

2.4.2. Pharmaceutical waste blister analysis

SEM was used to examine the selected WPB samples and determine their thickness, number of layers, and other morphological properties. The scanning

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process was carried out on the cross-section of chipboard samples made with a sharp knife and coated with a layer of gold to avoid deformation or plasticization of the polymer surface due to heating from the high voltage used (15 kW) during scanning [53]. The scanned samples were placed between two copper clamping plates to ensure that the electron beam was perpendicular to the analyzed sample's cross-section and to avoid possible sample deflection, thereby improving the analysis accuracy. EDS was used to analyze metallic (represented by Al) and nonmetallic base composition of the samples and to determine the positions of the polymer layers and Al layers in the WPB multilayer structure. All the samples were re-examined for possible changes in chemical composition and other properties after treatment, thereby indicating possible uses for the recovered materials [53].

2.4.3. Pharmaceutical waste blister separation procedure

Chemical treatment with a hydrophilic switchable solvent (DMCHA) was used as the primary treatment method to dissolve the organic part of the above outlined structure; ultrasonic treatment was used to accelerate the separation of WPB samples [1].

Selection of dissolution conditions. To determine the best dissolution conditions in terms of the dissolution temperature, we placed the crushed WPB in a separate round bottom flask. According to the method described by Samori [102], the ratio of solid (WPB) to liquid (DMCHA) is 1:3 g/ml. The flask containing DMCHA and WPB samples was immersed in an ultrasonic bath containing a low temperature (40, 50, 60 and 80 °C) vibrating liquid (distilled water); the optimal temperature was selected based on the final state of the reduced film formation. The reason for choosing the temperature range is to avoid higher energy consumption, faster solvent degradation, and higher toxic smoke emissions [53].

Dissolution process. The dissolution process was carried out according to the selected optimal conditions; the procedure and dissolution sequence for preparing WPB samples is shown in Fig. 11. As shown in the diagram, about 120 minutes after starting the dissolution process (the average value for all samples), the ink layer began to get removed from WPB, thereby forming a DMCHA suspension. Then, the filtration method was used to extract ink particles from each sample (Fig. 11F). The molding films began to separate from the lidding assembly after the sealant layer had dissolved; this step took 180 minutes. After a further 120 minutes, the base material, the cover layer, and the printing primer layers of the molded films and the lidding unit were completely separated and removed from the solvent (Fig. 11D, E). The components of the lid assembly required additional force to achieve complete separation. Centrifugation was therefore used to free the Al foils from other plastic foils (the primer and the coating). All those steps were done simultaneously in order to reduce the overall separation time to up to 300 minutes, as proven within the Gantt table (see Fig. 12) and to decrease the overall energy consumption. To extract the sealing polymer from the solvent and regenerate DMCHA, the spent solvent was added to twice the volume of H_2O and chilled in an ice bath. Then, CO_2 was blown into the mixture for a few hours; this process was done according to Samori [102]. The sealing layer was then solidified and collected as a residue by filtration. Another important point is that the regeneration process was repeated twice because, in some samples, the coating was also dissolved in the solvent, and the solvent was initially brown. In the second stage of regeneration, it became milky white. Over night, at 40 °C, CO_2 was removed to restore the solvent to its original neutral state, and to separate it from water [53].

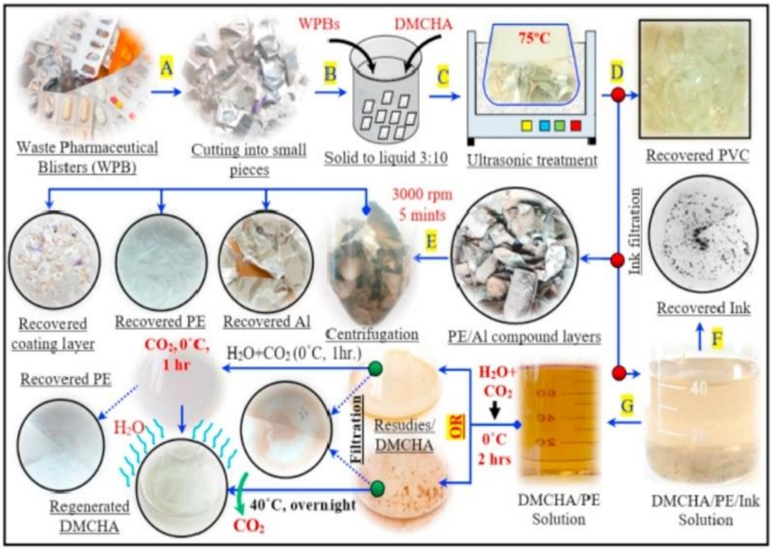
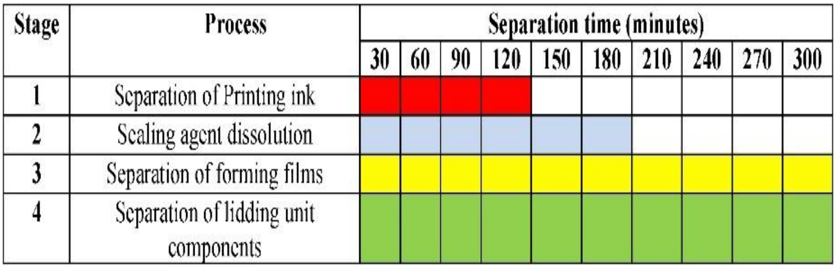


Fig. 11. Schematic flow diagram of waste blister packaging treatment



Stage	Process	Separation time (minutes)									
		30	60	90	120	150	180	210	240	270	300
1	Separation of Printing ink	🟥	🟥	🟥	🟥						
2	Sealing agent dissolution	🟦	🟦	🟦	🟦	🟦	🟦				
3	Separation of forming films	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
4	Separation of lidding unit components	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

Fig. 12. Gantt diagram of WPB separation process

2.5. Experiment 3 – Separation of multilayer flexible packaging by using DMCHA

2.5.1. Materials and waste multilayer flexible packaging type selection and analysis

Sigma-12 Aldrich Corp supplied DMCHA and other reagents. Six different types of MFPW were collected from the waste of local grocery stores in Lithuania, thus taking the waste diversity factor into account in order to increase the accuracy of the final product results. MFPWs were selected based on the food products most consumed in the EU by all generations with a specific type of packaging, mainly packagings for potato chips, chocolate bars, baked goods and ground coffee. All the samples were assigned an individual code; then, the selected samples were washed and rinsed with distilled water to remove dust, grease, chemicals, adhesives, stains, contaminants, etc., and then dried at room temperature for 24 hours. The selected MFPW samples were then examined by using SEM and their thickness, number of layers, and other morphological properties were determined at a voltage of 20 kV, magnification of 1.5 kX, and scale of 10 μm. [1].

The observation process on MFPW was performed after cutting cross-sections of the specimens with sharp cutters and coating them with gold so that to prevent deformation or plasticization of the polymer surface due to the heat generated by the high voltage (20 kV) used during the scan. Direct fixation of the samples in the vertical position of the SEM holder was problematic when testing the MFPW samples. Therefore, a simple clamp fixer was made for the MFPW samples, as shown in Fig. 13, to ensure that the electron beam was perpendicular to the tested sample's cross-section and to avoid the sample's possible deflection, consequently improving the accuracy of the analysis. As it can be seen, the tested samples were fixed between two metal corners and the corners were assembled by screw after adjusting the sample position. The corners assembled with the sample were adhered to the SEM grid holder while using a standard layer of adhesive [1].

The chemical composition of the clamped metal was analyzed by energy dispersive spectrometry (EDS) so that to avoid possible interference with the MFPW measurements. As shown in the EDS analysis, zinc (Zn) and iron (Fe) were the main elements. The fixing alloy plus a small amount of carbon (C) and oxygen (O) was used. Finally, SEM-EDS was used to analyze and determine the location and metallic and non-metallic elements in the MFPW layers [1].

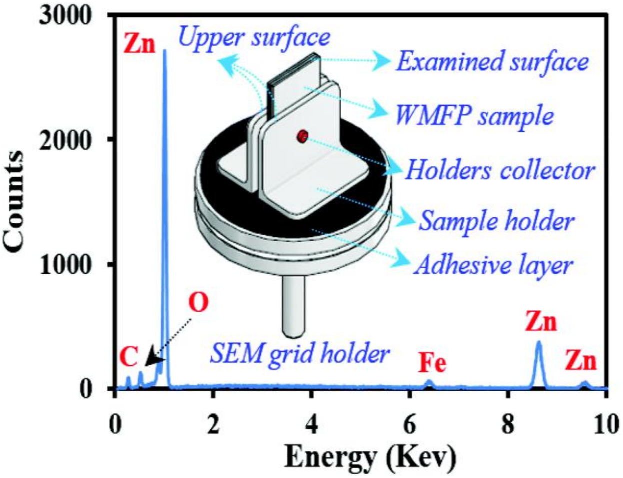


Fig. 13. Schematic drawing of the simple clamp fixator and EDS analysis of the sample surface [1]

2.5.2. Multilayer Flexible Packaging Waste Separation Procedure

In order to recover all the layers of all MFPW samples, we used chemical treatment by DMCHA to break the mechanical and chemical bonds between the MFPW layers and dissolve the adhesive polymers, and then allow all layers to separate. On the contrary, ultrasonic treatment accelerated the separation of MFPW samples [1].

Dissolution process. To overcome these problems and reduce the number of first attempts, preliminary experiments were carried out in the present study at a constant solid-liquid ratio of 1:3 g/ml – 1 (the optimal Samori result from Samori [102]), and at three different temperatures: 50 °C, 70 °C and 90 °C. Although the highest temperature (90 °C) gave the fastest separation time, the colorless appearance changed to yellow after treatment. The treated films began to degrade, thus affecting the thermal stability and the degree of crystallinity of the obtained polymers. The degradation decreased significantly with the decreasing temperature, and the obtained polymer films remained colorless, especially at lower temperatures. Therefore, the final experiments were carried out at 1:3 g/ml – 1 and 50 °C [1]. The separation time is a function of many parameters which affect the total number of the layers, the thickness of each layer, the chemical composition of each layer, etc., and the separation time is not the same for all products. Therefore, the separation time was determined regarding the optimal ratio of solids to liquid and the ultrasound bath temperature. The separation process was performed by using combined treatment over seven steps (Fig. 14).

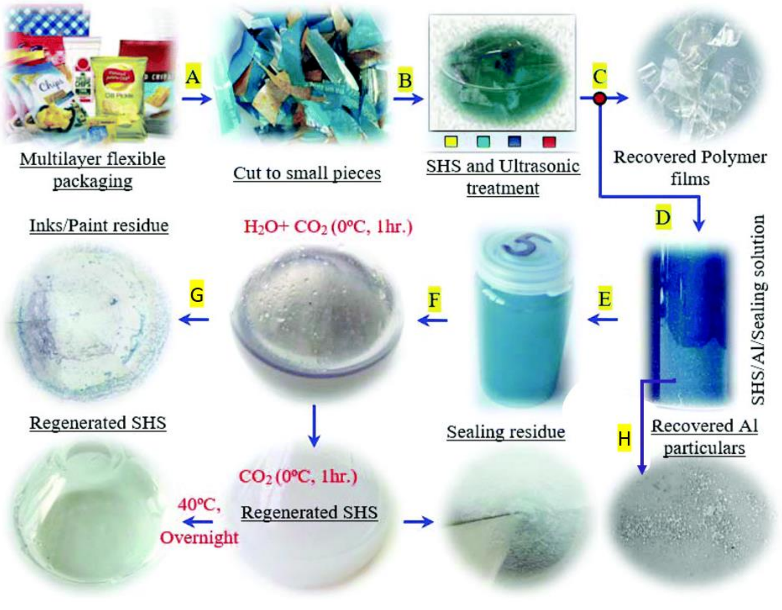


Fig. 14. Schematic flow diagram of multilayer packaging waste [1]

A. Sample preparation for the separation process cutting into small pieces.
B. The separation process begins with the dissolution of the coating layers, including the printing ink and paints in the SHS. Simultaneously, the sealing layers within the SHS begin to dissolve. Ink/paint/sealing solution was obtained after 15 to 20 minutes.
C. The barrier layer began to separate from the outer layer in the form of Al flakes and particles, while the outer layer separated 10 minutes after the passage in the form of floating polymer films (Fig. 15 A).

Fig. 15. Photographs of (A) MFPW during dissolution, (B) solutions after completion of the separation and removal of floating films, and (C) solution after CO_2 addition [1]

D. Floating polymer films were collected from the solution and centrifugation was used to precipitate aluminum flakes and particles. The ink/paint/sealing/SHS solution was then carefully removed with a pipette (Fig. 15 B).
E. The ink/paint polymer was recovered from the solution by adding the starting mixture to twice the volume of H_2O and cooling it in an ice bath with CO_2 bubbled for several hours. Solidified ink/paint particles were removed by filtration.
F. The previous step was repeated in order to extract the sealing polymer as residue from the solution.
G. Finally, the regenerated solvent was heated to 40 °C overnight to remove CO_2, recover the solvent in its original neutral state, and separate the water (Fig. 15 C).

2.6. Environmental and economic performance of the developed technique[1;2]

The performance of the recycling technology can be evaluated by the recycling rate, resource efficiency, economic benefits, and greenhouse gas emissions. The recovery rate is >99%, while the recovery rate of the standard technology is significantly lower than <66%. In terms of the resource efficiency and the mixed polymer powder, at least five different raw materials can be produced in good condition at the end of processing, which is why this technology is more desirable than raw materials produced by traditional techniques. As a result of the traditional

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[2] Reproduced from Ref. [1] with permission from the *Royal Society of Chemistry*

method, regranulated polymers are denoted by low compatibility and a high degree of thermal degradation, thereby negatively affecting the final properties of the produced materials. Moreover, granular polymers recovered by the current technology can be used in various applications with good performance, and their performance will be further improved by the additional design of the polymer sorting phase [53].

Separation was carried out at lower temperatures (50 °C) [168]. Another advantage of low temperatures is that they use less electricity during the dissolution process. Furthermore, solvent extraction of polymeric components does not require additional energy for solvent evaporation. Based on electric power and CPWs, the recovery cost of the developed system was financial and economic analysis [53].

Electricity consumption was calculated on the capacity of the ultrasonic bath, placement of 700 g of WPBs, and a proportional amount of the solvent. According to the measurements per kilowatt hour meter, the power consumption level was 73 J/s, while the total power consumption at the time of the 4-hour breakdown in the system was calculated as equations [(1), (2)]. Previous studies helped us to perform similar calculations; during the experiment, it was impossible to calculate a large amount of waste, such as 10kg or more, due to the insufficient experimental equipment in the laboratory. So, for the beginning, the calculation for the electricity consumption was done for 250 g, as for the initial data; then, this data was adapted for a large number of samples, such as 1 t of waste.

The cost of collecting WPB (from public hospitals) was estimated at $80/ton. The solvent was considered a reusable material, and the cost of the solvent cost was not considered. Consequently, its value was not considered in the economic evaluation [53].

$$\begin{aligned}&\textbf{Electric energy consumption for 250g} = 73\ \mathrm{J/s} \times 3600 \times 5 \\ &= 1314000\ \mathrm{Joules}\ (0.365\ \mathrm{KWh})\end{aligned} \tag{1}$$

$$\begin{aligned}&\textbf{Electric energy consumption per 1 ton of WPBs} = \frac{0.365\ \mathrm{X}\ 1000}{0.7} \\ &= 521\ \mathrm{KWh}\end{aligned} \tag{2}$$

$$\begin{aligned}&\textbf{Benefits per ton} = \text{Output cost} \\ &- [\text{Electric } \textbf{energy} \text{ cost} + 1\ \text{ton WPBs}] = 774\ \$/\text{ton} \\ &- [(521 \times 0.12\ \$/\mathrm{KWh}\ (\text{in EU})) + 80\ \$] = 633\ \$/\text{ton}\end{aligned} \tag{3}$$

Some studies have been conducted on solvent risk assessment in order to evaluate the environmental health and safety (EHS) properties of SHS solvents, including DMCHA [141].

Income was calculated on the average market and listed prices. The scrap price for Al, PVC (granules/recycled PVC) and PE (granules/recycled PVC) is $700/ton, $800/ton, and $850/ton, respectively (https://alibaba.com). Based on these prices, an average of ~ $800/ton for the recovered polymer components was assumed, so the benefits were estimated at $774/ton of waste. Waste packaging averaged $80 per ton. These prices were the trading prices specifically for recycled materials, but not for the original raw materials [53].

When examining greenhouse gas emissions (GGE) during SHS treatment by following Samori [102], the results showed that GGE was significantly reduced when processing materials by using novel techniques compared to the conventional techniques [102]. Turner [169] developed a scientifically sound and completely transparent approach to calculating carbon dioxide emission factors for the recycling of waste separated from source segregated waste materials by following Standard ISO 14040 in order to avoid the lack of transparency or integrity of the materials to be considered [169]. According to Turner [169], greenhouse gas emission factors for recycled materials, classified according to sources, were obtained from a series of partial LCAs performed for each test material. LCAs were performed according to ISO 14040 Standard and according to the guidelines of the *International Life Cycle Data System* [193]. LCAs were implemented by using EASETECH in order to assess the environmental technologies of the LCA model [194].

3. RESULTS AND DISCUSSION

3.1. Experiment 1 – Separation results of the waste pharmaceutical blister (WPBs) and multilayer flexible packaging waste (MFPW) by using various solvents[3]

This part describes the result for WPBs and MFPWs (five samples) when using a different solvent. It can be divided into separate sections because the obtained product was not the same for all models.

For the WPBs treatment, eight different solvents and one mixed organic solvent were used. In case MFPWs had the same solvents except for DMF and mixed organic solvent, formic acid was not used.

Separation by ethyl acetate and ethanol for the WPB and MFPW samples was partially successful. After the first few minutes, at the beginning of the separation process, some pieces removed the printed ink without heating or shaking. Then, while heating (60–90 °C) for about 5–10 minutes, the first polymer layer began to be removed, after a few additional minutes other layers started separation. Nevertheless, the separation was difficult. Some layers did not separate, and two layers had to be stacked on top of each other. During this process, from WPBs and MFPWs samples were recovered minimum three different layers: the outer polymer layers, a transparent thin polymer layer, and a polymer layer with the paint layers and Al. The separation steps and materials are shown in Fig. 16, where MFPWs were separated by ethyl acetate [3].

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[3] References [3, 135]

Fig. 16. MFPW Separation stages and separated (aluminum, transparent thin polymer layer, and polymer layer with unremoved paint) by ethyl acetate [3]

Mixed organic solvent (benzene-ethanol-water (volume ratio 30-20-50)) was used for the samples of WPBs. The separation process and steps were the same as mentioned above. The obtained result showed that the polymeric fraction and Al layers were separated (14% and the 86%, respectively), and the time was shortened (the separation times were 8–10 minutes), but the printing ink was not removed, and polymers were separated together. After the separation process, the samples were thoroughly washed with ethyl alcohol and distilled water prior to drying so that the organic solvent residues were removed. Thus, all the samples of WPBs and MFPWs were treated with acetic acid, formic acid, dimethylformamide, and toluene. The first part of the separation process was essentially similar to the previous one as, after the initial 5 minutes, the ink layer was removed. Then, it was noted that the first layer of the polymer was quickly removed; unfortunately, after the continuation of the experiment, and when heating reached the highest point, the Al layer and the polymer layer had started to dissolve into the solvents. During the separation process of $MFPW_a$ and $MFPW_b$ with toluene, from the third step of separation when the temperature increased, the rest of the polymeric fraction and Al was dissolved [3].

Furthermore, the WPB separation process of WPBs with acetic acid by heating up to 60 degrees, and the result was the same, i.e., the sample started to dissolve. In the case of formic acid separation from MFPWs, Al was dissolved in the solvent. However, the amount of Al found in solutions was relatively small – it has weight loss from 0.02% to 0.08% of Al. Therefore, by considering the possible extraction of aluminum from the corresponding type of composite packaging, it was argued that such Al mass losses could be acceptable in processing industrial packaging [135].

Separation with acetone was performed for all CPW samples. It can be mentioned that the separation time was shortened for WPBs, but, in the case of $MFPW_a$ and $MFPW_b$, the time range was increased, but, with the faster separation, we obtained a mixed polymeric fraction, and, afterwards, it was difficult to separate the constituents. For the $MFPW_c$ separation process that finished after 5–10 minutes, without heating, the difference from other CPWs is that $MFPW_c$ was simply a layered structure. So, after the initial minutes, the Ink layer and its flotation started, then, after several minutes aluminum and polymeric fractions started separation, in pharmaceutical blister production generally polypropylene are used.

An example for the process of separation of WPBs with acetone is shown in Fig. 17, where, after separation, two primary components Al (A) and mixed polymers (B) were obtained.

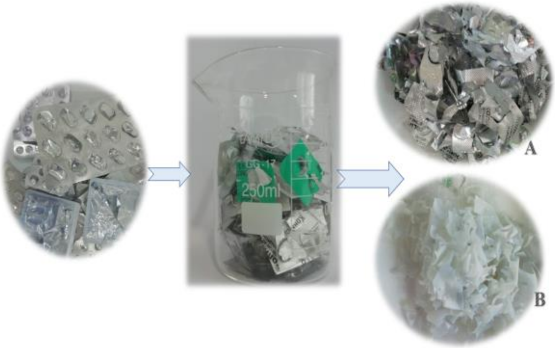

Fig. 17. Recovery components (A and B) after separation of WPBs by acetone

A different temperature was used during the treatment of WPBs by acetone, and the observations showed that the high temperatures caused the decrease of the separation time; however, high temperatures also caused polymer degradation. The empirical model that associates the treatment temperature (as an independent variable) and treatment duration (as a dependent variable) was established to be a linear function, namely TD= -t+61.25. This model explains 99% of the variation in TD (coefficient of determination R^2=0.98). The established equation is valid for the temperature range from 0 to 50 °C (as shown in Fig. 18).

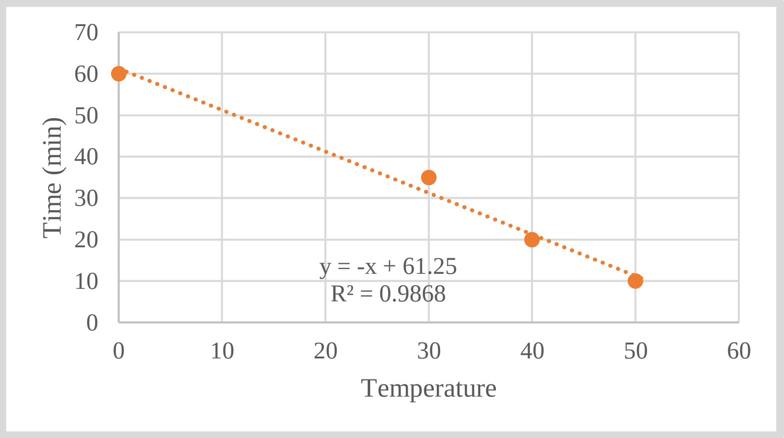

Fig. 18. Dependence of separation time on temperature for WPBs (acetone)

A different temperature was used during MFPW treatment with acetone, and the observations showed that high temperatures caused a decrease in the separation time, however, it also caused polymer degradation. The empirical model that associates the treatment temperature (as an independent variable) and the treatment duration (as a dependent variable) was established to be a linear function, namely, TD= -1.75t+123.75. This model explains 98% of the variation in TD (coefficient of determination R^2=0.97). The established equation is valid for the temperature range from 0 to 50 °C (as shown in Fig. 19).

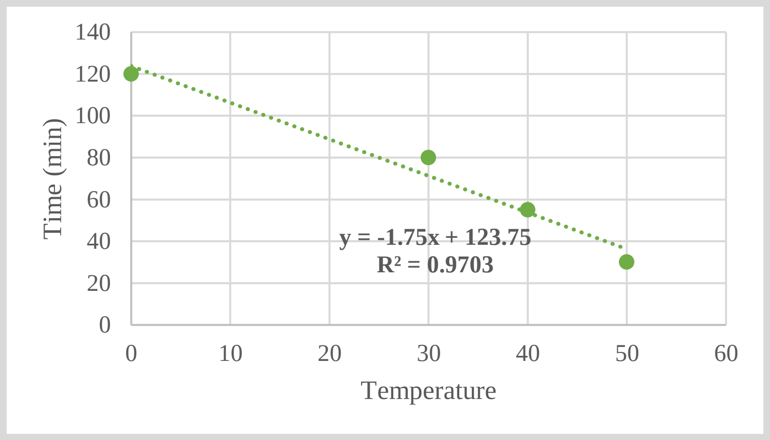

Fig. 19. Dependence of separation time on temperature for MFPWs (acetone)

One of the separation processes was performed with concentrated Nitric acid (45%, 50% and 65%) for all the WPBs and MFPWs samples. Separation by nitric acid for all the types of CPWs took too long, i.e., up to 48 hours, and did not even result in the removal of the printing ink. Also, 50% concentrated nitric acid showed a long separation, and, for MFPW samples, the time range was increased. Use of 65% concentrated Nitric acid was successful for all the types of packaging waste. The cut samples were partly or fully covered, or full of solvent, and the vessel was closed. The process was successful, and a minimum of two layers of polymer and Aluminum were obtained from WPB and MFPWs [3].

As we have seen, concentration had a significant effect on the processing time; the empirical model that associates solvent concentration (as an independent variable) and the duration of the treatment duration (as a dependent variable) has been established to be a non-linear (power) function, namely, TD=4E+08xt^-4.236. This model explains 88% of the variation in TD (coefficient of determination R^2=0.87). The established equation is valid for the concentration range from 45 to 65% (as shown in Fig. 20). There was a strong negative correlation between the solvent concentration and the separation time. Therefore, when the solvent concentration increases, the separation time decreases.

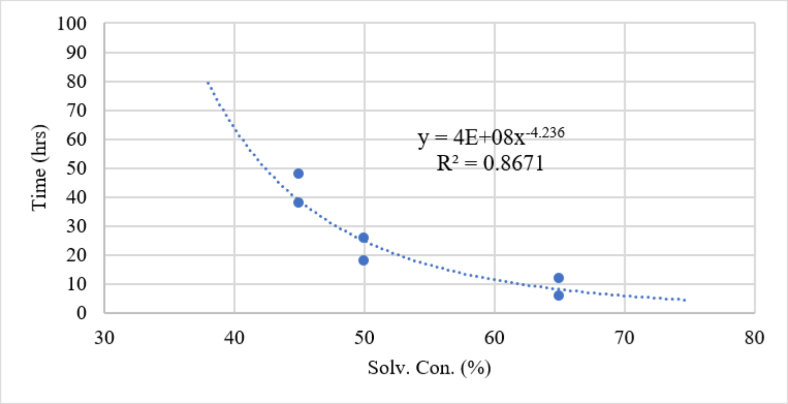

Fig. 20. Dependence of the separation time on nitric acid concentration for MFPWs

Also, during nitric acid treatment, various temperatures were used e. The empirical model that associates the treatment temperature (as an independent variable) and the treatment duration (as a dependent variable) has been established to be a nonlinear (power) function, namely, TD=1E+07xt^-3.249. This model explains 80% of the variation in TD (coefficient of determination R^2=0.89). The established equation is valid for the temperature range from 20 to 60 °C (Fig. 21).

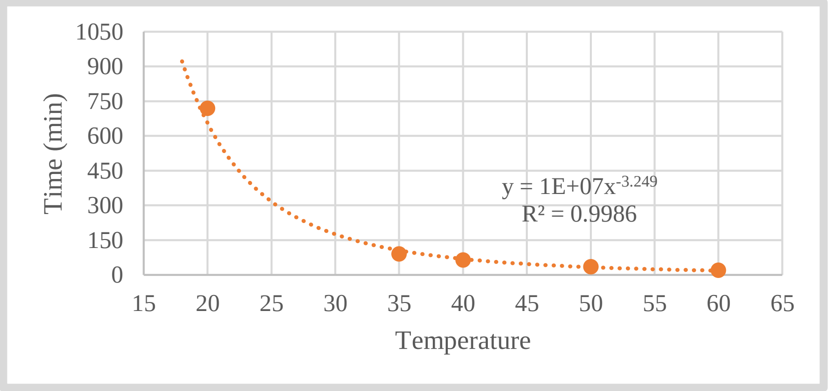

Fig. 21. Dependence of separation time on temperature for MFPWs (Nitric acid)

The separation time range was 20 minutes to 12 hours; in case of heating, the separation time was lower, but, after observation, it was also found that nitric acid was achieved without heating, i.e., at room temperature. The process was successful, and a minimum of two layers polymer and Al from WPB and MFPWs was obtained.

The separation results for $MFPW_c$ were received within a short period, and, at the end of the process, at least one layer of polymer and Al as a powder were obtained, which was extracted by filtration from the solvent and washed several times with distilled water. The separation process is presented in Fig. 22.

Fig. 22. Separation of Al and polymer from MFPW$_c$ by nitric acid

After the separation processes, the differences of the sample mass before and after treatment were determined. The collected information is presented in Table 13: mass for WPBs and MFPWs with ethyl acetate and nitric acid before and after the treatment.

Table 13. WPBs and MFPWs Sample mass before and after treatment with acetic acid and Nitric acid

Samples code	Mass Before treatment (g)	Mass after treatment **Acetic acid** (g)		Mass after treatment **Nitric acid** (g)	
		Al	Polymeric fraction	Al	Polymeric fraction
WPB$_a$	10	1.72	8.23	1.23	8.53
WPB$_b$	10	1.43	8.34	1.13	8.63
MFPW$_a$	2	-	1.38	-	1.45
MFPW$_b$	2	1.05	0.89	1.02	0.9
MFPW$_c$	2	0.21	1.57	0.33	1.6

3.2. Experiment 2 – Separation of waste pharmaceutical blisters by using DMCHA

3.2.1. Pharmaceutical waste blister structure and delamination analysis before treatment

Energy dispersion spectrometry (EDS) was used to analyze the basic metallic (represented by Al) and nonmetallic composition of the samples and to determine the polymer layers and Al layers within the WPB sandwich structure. In Fig. 23, the structure and the basic elemental composition of each type of WPB obtained by SEM-EDS is shown [53].

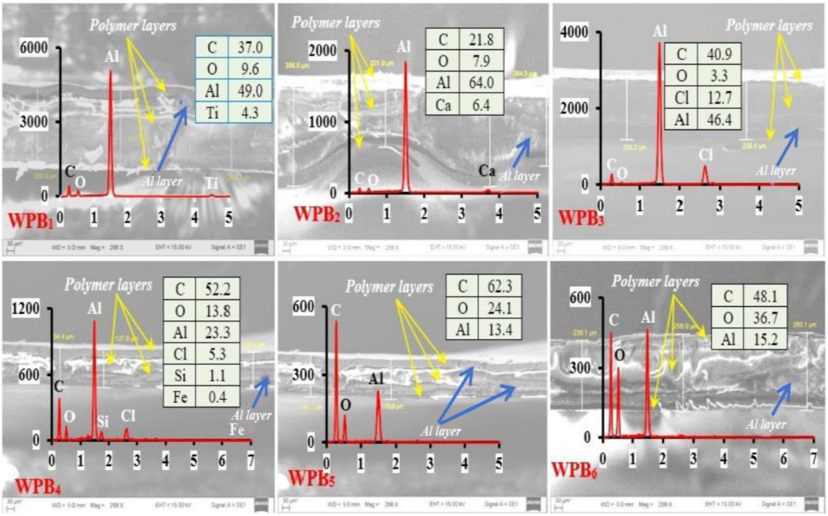

Fig. 23. SEM-ED analysis of WPB samples [53]

All the samples had several layers. It should be noted that all the samples except for WPB5 contained only one Al foil layer, while WPB5 contained a double Al layer. In addition, in all cases, the Al layer (s) was a polymer coating. Additionally, there was a significant variation in the purity of Al (13 wt.% – 64 wt.%) due to contamination with organic materials. In addition, other additives, such as titanium (Ti), silicon (Si), and iron (Fe), were found in the Al layers. The total thickness of the WPB samples ranged from 130 to 250 µm. Polyvinyl chloride (PVC) was the main polymer layer in all the samples (except for WPB2 alone) [53].

All the WPB samples featured the sandwich-type structure, as shown in Fig. 24. All WPBs consisted of two main units: the forming film and a lidding unit. The forming film unit is designed as a pocket for the product, and it should possess specific properties. In the current case, the pocket design was different for all samples: WPB$_1$ and WPB$_3$ – hemispherical shape, WPB$_2$ and WPB$_4$ – cylindrical shape, and WPB$_5$ – rectangular shape [53]. In general, the forming film should possess excellent thermoforming properties and high flexural strength. Polyvinyl chloride (PVC) is the most common plastic with such properties widely used in manufacturing, sometimes coated with PVDC or laminated [52, 170–172].

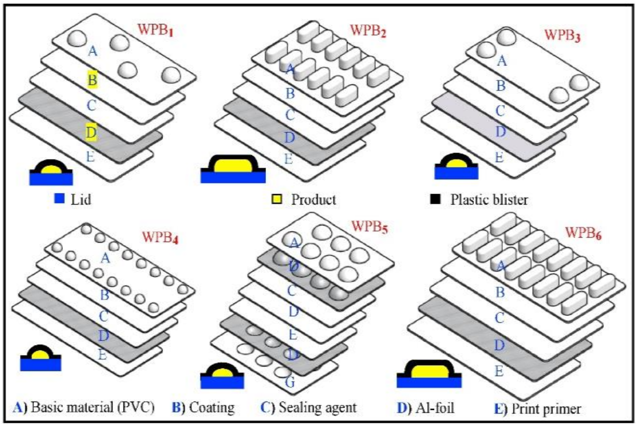

Fig. 24. Layers and components extracted from WPB [53]

The lidding unit is usually made up of a print primer, basic material (Al), coating film, heat-seal coating, and printing ink. Al foil is considered to be the main layer here, and it is used as a barrier for moisture, gases, and light. The lidding material must be selected according to the size, shape, and weight of the product. Also, the surface of the lidding unit must be compatible with the heat-sealing process.

3.2.2. Analysis of the WPB delamination mechanism after treatment.

At the end of the separation process, all PVC layers (C) and Al foil layers (B and D) of all samples were separated in similar forms or small pieces, while the coating layers were dissolved in the solvent collected as a residue. The delamination mechanism demonstrated that the printing inks were separated firstly because of the weaker adhesive bonds. After that, the PVC layers began to delaminate with an average separation time of three hours due to the similarity and intervisibility of the PVC layers and the adjacent layers (polyethylene). Meanwhile, the Al-PE layers needed more time (a further 2 h) in order to damage the adhesive bonding between them. This delay in separation can be explained by the fact that the lamination process involves extrusion of plastic materials, and Al foil is oxidized by ozone from the broad air gap at high temperatures [173]. Consequently, each film is subjected to two types of bonding in WPB: chemical and mechanical [174].

Fig. 25 shows metallographic images of WPB samples before and after treatment at a scale of 500 mm. The untreated samples were classified into two categories depending on the surface shape: corrugated and flat surface, as shown in Fig. 25 (A, B), respectively. It was clear that the surface of the corrugated samples' surfaces featured hills and concave areas which were created during the package manufacturing process for better bonding.

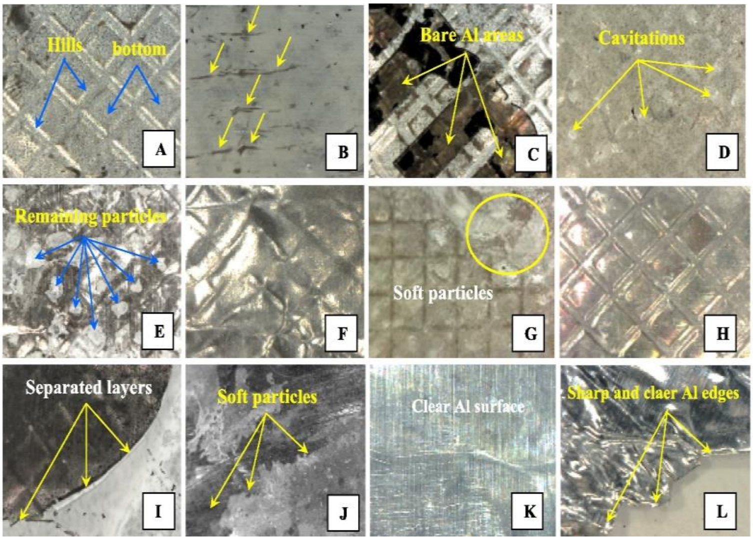

Fig. 25. Metallographic photographs of waste blisters during the treatment process [53]

It was noted that scratches were not found in corrugated samples due the hills which decrease the contact area between waste. Once the printing ink particles were separated, the Al layers became bare (Fig. 25C)); in this case, the solvent had the ability to penetrate quickly between the polymeric and Al layers of the WPB samples, thereby creating numerous cavities at the beginning in the hills and, later, at the bottoms (Fig. 25 (D, E)). Under the effect of heating and sound waves, the pressure inside the cavities increased, which led to eruption and separation of materials. Also, the opposite surface of the corrugated sample was examined, and the adhesive layer was dissolved by DMCHA; see Fig. 25 G) The attached layer was different from the layer of the other layers of the samples, as explained in the FTIR spectroscopy section. Subsequently, calcination at 550 °C for 4 h was used in order to remove any organic materials remaining on the surface of the recovered Al layers (see Fig. 25 F), and the surface became clearer, as shown in Fig. 25 H. It is worth mentioning that the coating layer in some corrugated samples separated as received because of the layer having been bonded only by mechanical bonding. Therefore, a solvent was used to weaken the friction force between the separated layers where adhesive bonding was not present (Fig. 25 I). The flat sample's separation mechanism was similar to that of the corrugated sample; the separation time was lower because the lower contact area between the Al and polymer layers made the flat sample easier to separate (see Fig. 25 G). Finally, Fig. 25 G shows the clear surface and the sharp edges of the recovered Al layer after the dissolution process and calcination [53].

3.2.3. Analysis of extracted ink particles

Fig. 26 A shows SEM-EDS images of ink particles recovered from each sample. As it can be seen in the SEM images, the surface morphology of all samples was almost identical as the samples were in the shape of fine powder. Meanwhile, EDS analysis (Fig. 26 B, C) revealed that carbon and Oxygen were the main elements in all the samples due to their organic nature. Also, some metallic elements, such as aluminum, copper, and iron, were found [53].

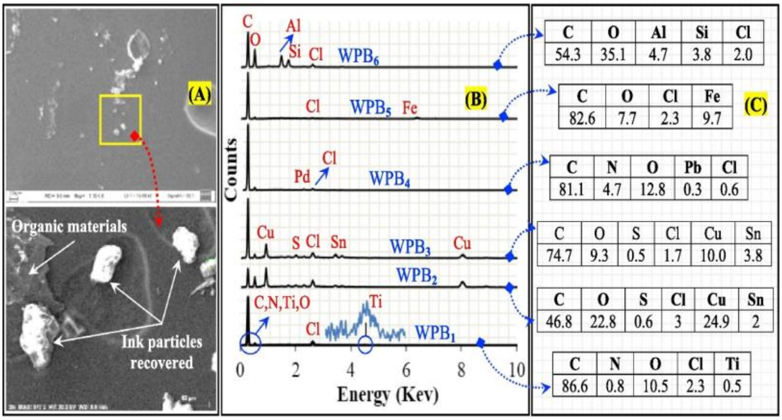

Fig. 26. SEM images and EDS analysis of recovered printing ink particles [53]

3.2.4. Analysis of recovered forming films

FTIR analysis. FTIR was used to determine the chemical structures and the functional groups of the recovered polymeric forming films, thus determining the type of the recovered polymer. Fig. 27 shows the spectra observed for each WPB sample; as a result of FTIR analysis, several functional groups were found, for instance:, C-¬H single bond stretching was observed at 2911 cm^{-1}, CH_2 groups deformation was detected at 1333 cm^{-1}, out of plane angular deformation (ρCH) at 1254 cm^{-1}, out of plane trans deformation (ωCH) at 959 cm^{-1} and C − Cl bond stretching at 836 cm^{-1}. These bands conform to the data found in the literature on PVC. On the other hand, several different absorption peaks were found in WPB1 sample, at 973 cm^{-1} rocking vibration ($-CH_2-$), 997 cm^{-1} rocking vibration ($-CH_2-$), 1167 cm^{-1} anti-symmetric deformation ($-CH_3-$), 1455 cm^{-1} symmetric deformation ($-CH_2-$), 1167 cm^{-1} symmetric deformation ($-CH_3-$), 1167 cm^{-1} anti-symmetric deformation ($-CH-$), and 2917 cm^{-1} symmetric stretching ($-CH_3-$) [53].

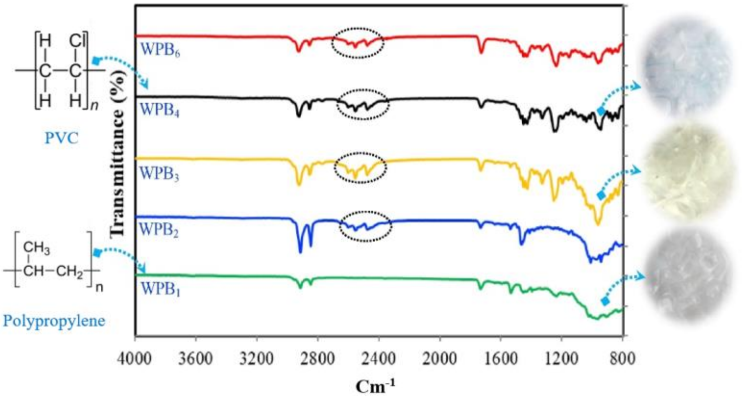

Fig. 27. A-C) FTIR spectra of recovered forming films [53]

These results are consistent with the data from the literature showing that PVC and PP are widely used as primary PBS packaging materials. The casting film is usually colorless and transparent. Consideration must be given to the product's height and weight, sharp or pointed edges of the final package, and the impact resistance, aging, migration, and cost of the film. Factors influencing the package production process must be considered as well [52].

Additional components were noted to laminate the forming film of the WPB$_2$, WPB$_4$, and WPB$_5$ samples. Based on FTIR analysis (Fig. 28), similar absorption bands were found in the WPB$_2$ and WPB$_4$ samples; symmetric stretching at 2966–3007 CH$_2$ cm^{-1}, CH$_2$ bending at 1404 cm^{-1}, CH$_2$ wagging at 1357 cm^{-1}, CH$_2$ asymmetric stretching at 1073–1038–874 cm^{-1}, C(Cl$_2$) stretching at 751–656–606 cm^{-1}, and C (Cl2) stretching at 568–446 cm^{-1}; these bands, according to Bodugöz-Sentürk [175], are PVDC. The PVDC layer in the blister pack is usually located inside the layer facing the product, and it is a good barrier against oxygen and water vapor [176]. FTIR analysis of the coated layer of the WPB$_5$ sample (double Al layers) showed that the sample had the same absorption bands as that of PVC. Table 14 shows all the materials of the extracted layers of forming films and the order of each layer in the matrix [53].

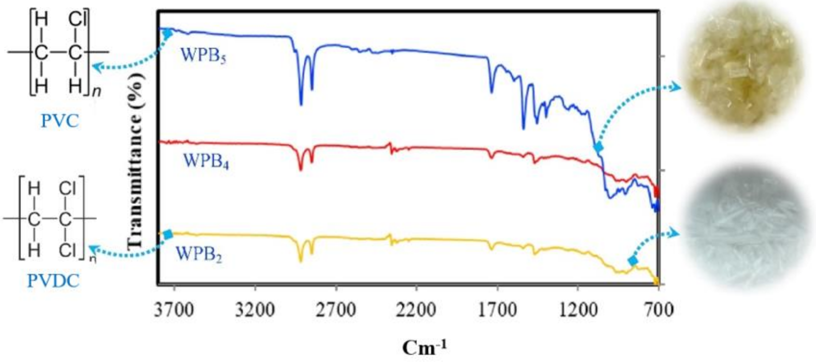

Fig. 28. FTIR of recovered coating films [53]

Table 14. Polymer types of extracted from forming films [53]

Layer name	**WPB1**	**WPB2**	**WPB3**	**WPB4**	**WPB5**	**WPB6**
Coating material	----	PVDC	----	PVDC	PVC	----
Basic material	PP	PVC	PVC	PVC	*Al	PVC

* This layer is described in detail in the analysis of recovered metals

Fig. 29 shows the separation of the forming films separated at varying temperatures. At higher temperatures, particularly, at 80 °C and 60 °C, the colorless appearance of the films changed to yellow. This means that the polymeric films started to degrade; the degradation decreased significantly with a decrease of the temperature, especially at 40 °C when the sample was of nearly original colorless appearance. Therefore, the values of 40 °C and 1:3 g/ml were selected as the optimal temperature and WPB/DMCHA ratio, respectively [53].

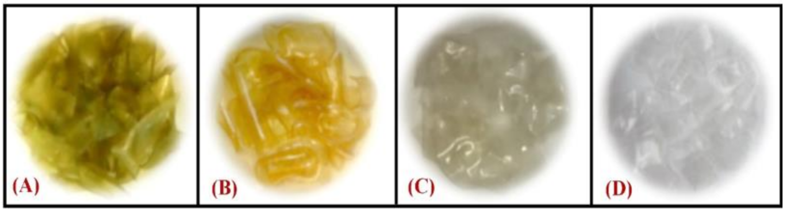

Fig. 29. Film formation recovered at A) 80, B) 60, C) 50, D) 40 °C [53]

Thermal analysis. Fig. 30 shows the results of the TGA analysis for the recovered forming films of the WPB samples. As illustrated in Fig. 30, WPB$_{2,3,4,6}$ samples (PVC films) showed the same trend and exhibited similar thermal degradation profiles which demonstrated significant weight loss in the range of 200 °C–500 °C. As shown in Fig. 30, two degradation peaks were observed at 267 °C and 452 °C, which corresponds to the initial mass losses of 53.6% and 28.8%, thereby resulting in the total mass loss of 82.4% [53].

According to Soudais [177], the first plateau is related to PVC dichlorination, polyene formation, stoichiometric elimination of HCl, and polymer crosslinking, while the second plateau is attributed to the breakage of some C–C bonds of the previously formed polyene. Thermal degradation of polyenes involved cyclization and splitting of chains. These results agree with Altenhofen [178] who reported 81.8% of the total mass loss for PVC, which means that the developed approach can be applied for PVC recovery with high performance in terms of the thermal properties of the recovered material.

Regarding the WP1 sample (PP), the thermal stability in the weight loss was >97%. These results are almost identical to the results reported in other literature by

Supan [179] for pure PP (decomposition range 380–490 °C, and a weight loss of 96%) [53].

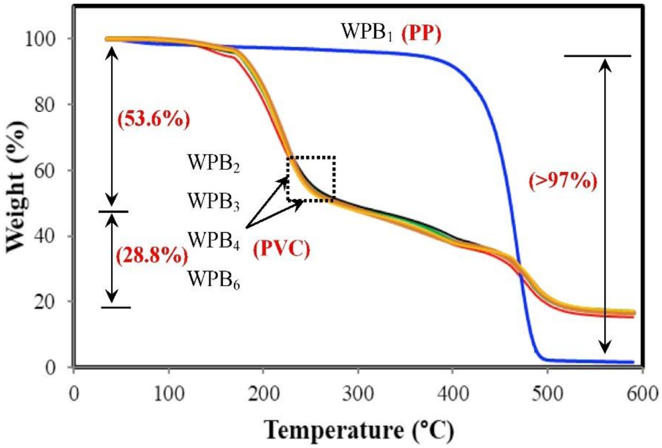

Fig. 30. Thermogravimetric curves of recovered PP and PVC forming films [53]

Differential scanning calorimetry was performed in order to determine the glass transition temperature (Tg) of the recovered forming films (PVC and PP) and thus to evaluate the effect of the developed approach on the plasticizing behavior (hump relaxation) of the recovered films. Fig. 31 shows the typical DSC curves of the recovered PVC and PP forming films. The Tg value of the PVC sample was found to be around 77 °C; in reports in the literature (80 °C) by Akhlaghi [180], the plasticizing behavior of the recovered PVC increased by ~4%. Meanwhile, the Tg of the PP sample was 166 °C [53].

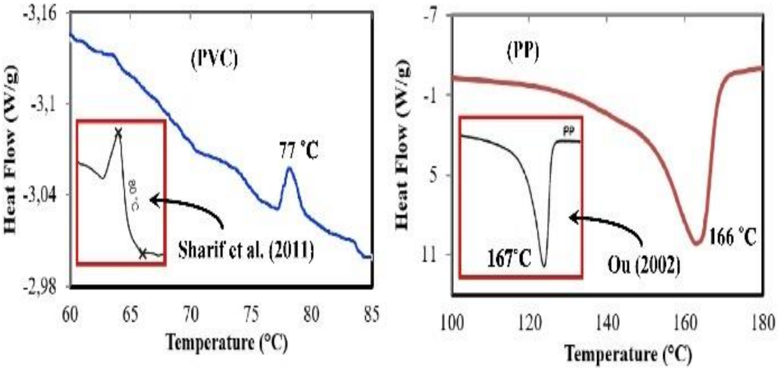

Fig. 31. DSC curves of recovered PVC and PP films [53]

3.2.5. Analysis of lidding units

Analysis of basic material layers (Al). Fig. 32 shows SEM-EDS images of recovered Al after calcination. As it can be seen, Al represented the main element in all the WPB samples with the purity being in the range of 65–97 wt.% (average

~81 wt.%). Furthermore, elemental analysis showed that the recovered Al layers contained various elements, in particular, small amounts of Ti, Fe, Silver (Ag), and Si (0.4–6.0 wt.%). Simultaneously, other elements, such as oxygen (O), were found in all the samples with a percentage of 3 to 34 wt.%, which could be a result of oxidation. In addition, the fracture surface of the recovered layers displayed smooth features. Fig. 33 shows all the elements detected in the recovered metallic foils [53].

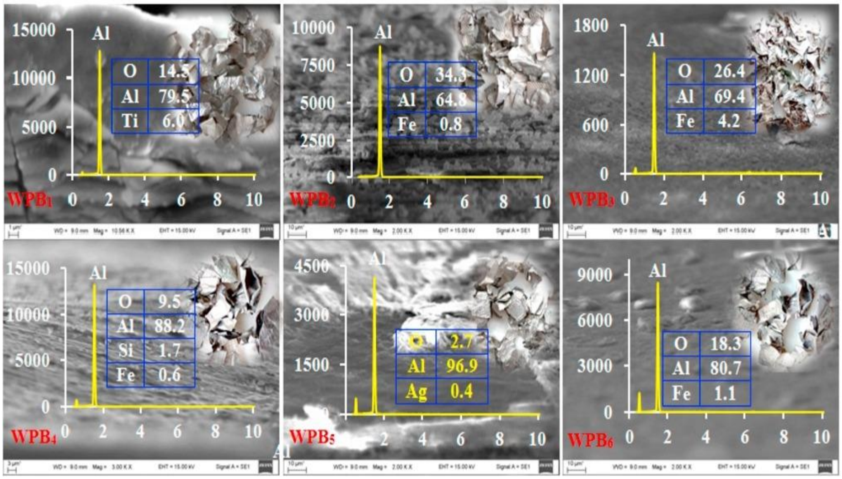

Fig. 32. SEM-EDS images and analysis of basic material layers recovered from WPB lidding units [53]

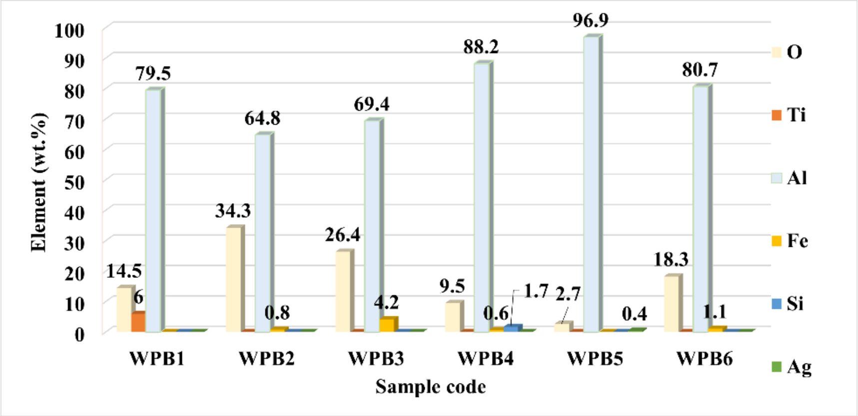

Fig. 33. Layers of basic material chemical composition recovered from lidding units of WPB [53]

Analysis of primer layers in the print. Fig. 34 shows the spectra observed for the recovered coating films for each sample. The spectral analysis of the coating samples showed vibrations corresponding to absorbed moisture (3535 cm^{-1}), O–H stretching of the end group diethylene glycol end-group (3440 cm^{-1}), Aromatic C–H stretching (3060 cm^{-1}), Aliphatic C−H stretching (2960, 2880 cm^{-1}), Aromatic summation band (1950 cm^{-1}), Carbonyl C=O stretching (1720 cm^{-1}), Aromatic skeletal stretching bands (1615, 1450, 1430, 1410 cm^{-1}), Aromatic summation band (1950 cm^{-1}), Carbonyl C=O stretching (1720 cm^{-1}), Aromatic skeletal stretching bands (1615, 1450, 1430, 1430 cm^{-1}), $-CH_2-$ deformation band (1465 cm^{-1}), C(O)−O stretching of the ester group (1270 cm^{-1}); bands in the skeletal ring region are indicative of the aromatic substitution pattern, and they indicated 1,4-substitution (1175, 1120 and 1020 cm^{-1}), O−CH_2 stretching of ethylene glycol segment in PET (980 cm^{-1}), C−H deformation of two adjacent coupled hydrogens on an aromatic ring (850 cm^{-1}) associated with the out-of-plane deformation of the two carbonyl substituents on the aromatic ring was observed at 730 cm^{-1} [53].

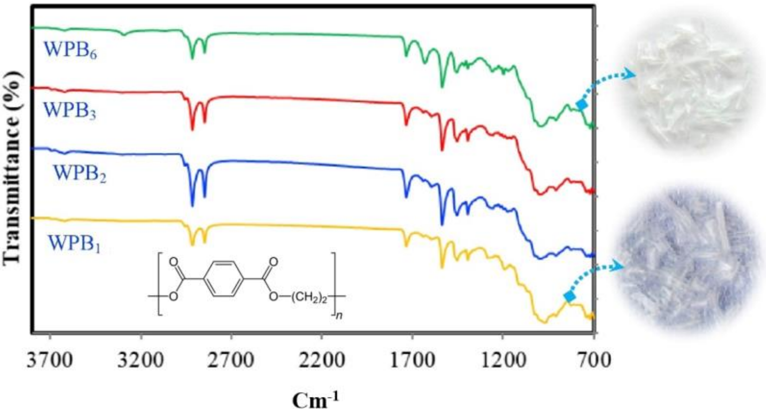

Fig. 34. FTIR spectra of print primer layers recovered from WPB [53]

Analysis of extracted residue. Fig. 35_A shows the image of the extracted particles (residue) from the solvent after adding CO_2 at 0 °C. Fig. 35_B shows the spectra observed for the recovered coating films for each sample. The spectral analysis of the coating samples showed vibrations corresponding to the characteristic peaks in the region of 1460 cm^{-1} (thereby revealing bending deformation), 2919 cm^{-1}, 2857 cm^{-1} (assignable to CH_2 as asymmetric deformation) and 719 cm^{-1} (which indicates deformation of the rocking) that is identical to the FTIR spectra of low density polyethylene (LDPE) [181]. In addition, SEM-EDS analysis was used to examine the morphology and structure of the particles (residue). As shown in Fig. 35_C, the residue had the shape of a spray of needle-like crystals free from agglomeration while still possessing a uniform structure due to regular cooling [53].

Furthermore, EDS analysis (Fig. 35_D) revealed that the residue contained carbon (C), oxygen (O), and nitrogen (N) which are considered to be the main elements in organic materials [182]. Furthermore, it is clear that a minimal amount of sulfur (S) (0.7 wt.%) was found during the EDS analysis, while the chemical structure of the PE polymer chain of PE does not contain S. The presence of a small amount of S may be a result of printing ink particles remaining in the residue, and this gives strong evidence that the dissolved LDPE was extracted with high purity.

Table 15 shows all the extracted materials and layers of the lidding unit and the order of each layer in the matrix [53].

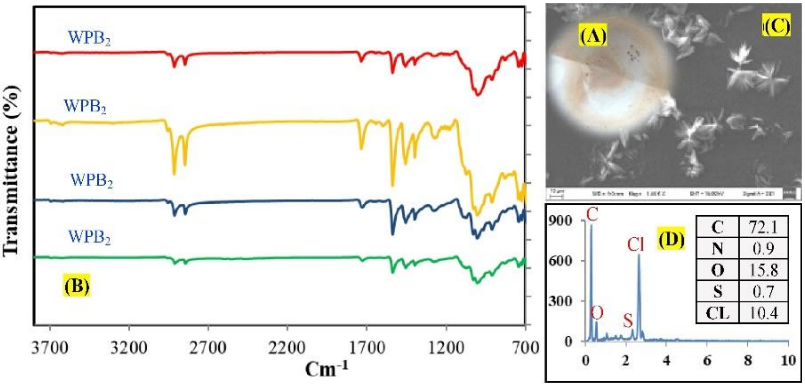

Fig. 35. A) Image of the extracted residue, B) FTIR spectra of the residues, and C, D) SEM-EDS analysis of the residues [53]

Table 15. Materials of extracted layers and lidding units [53]

Layer name	WPB1	WPB2	WPB3	WPB4	WPB5	WPB6
Print primer	PET	PET	PET	LDPE	LDPE	PET
Basic material	Al	Al	Al	Al	Al	Al
Sealing	LDPE	LDPE	LDPE	LDPE	LDPE	LDPE

3.2.6. Analysis of regenerated DMCHA

At the end of the separation process and extraction of the different organic residues, FTIR was used to determine the specific molecular components and structures of the regenerated solvent, thus verifying the sustainability of the process and the possibility of using the solvent again. This is especially important since the solvent is considered the pivotal agent in the separation process, and high solvent regeneration efficiency can bring high economic returns. Due to the technical difficulty in illustrating the FTIR results for all samples, the analysis was focused on only two samples: one sample regenerated for WPBs with a single Al layer (WPB$_2$), and another sample with a double Al layer (WPB$_5$). It was also considered that a single Al layer was exposed to the filtration process twice (as the worst case scenario) [53]. The selected samples were analyzed two times: after the extraction of residues and after the extraction of CO$_2$ extraction followed by the removal of water. The results were compared with the pure solvent in order to ensure that all residues and water and CO$_2$ were extracted. Fig. 36 shows photographic images of the regenerated DMCHA after the extraction of all residues and gases by filtration and cooling. As it is evident, the color of the recovered DMCHA ranged from yellow to colorless (i.e., the original color). Fig. 36 shows the FTIR spectra of unused and regenerated DMCHA. The spectral analysis of pure DMCHA has vibrations corresponding to the C − H stretching vibration of saturated hydrocarbon groups in the region of 2936–2776 cm^{-1}, C−H bending vibration of methyl and methyl groups at 1446 cm^{-1}. Stretching vibration of C−N at 1350–1000 cm^{-1}. After the dissolution process, the addition of CO$_2$, and water, most of these bands disappeared or became less prominently expressed. This means that the solvent became mixable with water, which is an essential characteristic of these solvents. Once the water and CO$_2$ were removed by heating at 40 °C overnight and the recovery of the subsequent separation and retrieved LDPE, the solvent restored its original structure. This means that the cooling plus CO$_2$ addition technique was useful both from the economic and the environmental points of view [53].

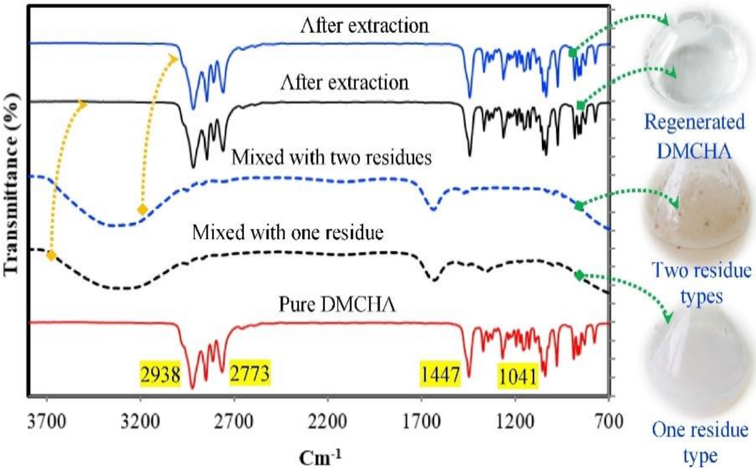

Fig. 36. FTIR spectra of unused and regenerated DMCHA [53]

3.2.7. Efficiency of the New Recycling Method

The performance of the new method was assessed on the mass balances of WPB treated by DMCHA. Table 16 shows the recycling rate of Al and polymeric layers (PVC, PP, PET, PVDC, and LDPE) for specific WPB samples and the average recycling rate; the same information is shown for the recovered DMCHA. The recovery efficiency (%) was calculated in the following way: the recovered component weight was divided by the initial weight and multiplied by 100%. As illustrated, the percentage of Al was in the range of 11–32 wt.% with the average value of 16.5 wt.%; this variation can be explained by the different WPB structure, which was single or double All layers. At the same time, the recovered polymeric components represented 81.2% of the total WPB mass. Therefore, the recycling rate of the developed approach was relatively high, being in the range of 96–99% with an average of 98% (based on the mass balance) for all WPBs. It is worth mentioning that most of the losses (~2%) occurred for the polymeric fraction during the filtration process, especially since the filtration process was repeated many times to extract printing inks and residues as outlined before. The average regeneration rate of DMCHA was >98%, which is a good value. Since the regeneration method was performed without using a heating source, the losses of DMCHA occurred mainly during filtration, and this problem can be overcome at the industrial scale by using specifically designed filtration equipment [53].

Table 16. Recycling rate of recovered WPBs and regenerated DMCHA [53]

Sample Code	**Initial weight (g)**		**Recovered components**				**Reg. DMCHA (g)**	**Recycling rate (%)**	
	WPB	DMCHA	Al		Polymeric			DMCHA	WPBs
	(g)	(g)	(g)	(%)	(g)	(%)			
WPB$_1$	1.821	60.7	0.27	15	1.51	83	58.88	97	98
WPB$_2$	2.969	98.9	0.36	12	2.56	86	96.92	98	98
WPB$_3$	1.252	41.7	0.21	17	1.01	80	40.45	99	97
WPB$_4$	2.834	32.9	0.32	11	2.46	87	32.24	99	98
WPB$_5$	1.212	40.4	0.39	32	0.79	64	38.78	98	96
WPB$_6$	2.945	98.1	0.34	12	2.58	87	97.12	99	99
Average				**16.5 %**	**81.2 %**			**98.2 %**	**97.7 %**

During the experiments for the separation of WPBs, various temperatures (40–800 °C) were used, and the faster separation time was obtained at a high temperature, but, as already mentioned above, it negatively affected the structure of the polymer and caused its degradation.

Temperature was a significant factor during the separation process. The empirical model that associates the treatment temperature (as an independent variable) and the treatment duration (as a dependent variable) has been established to be a nonlinear (power) function, namely, TD=44124xt^-1.34. This model explains 98% of the variation in TD (coefficient of determination R^2=0.98). The established equation is valid for the temperature range from 30 to 90 °C (as shown in Fig. 37). On the basis of the experiment data, faster separation times were obtained at a high temperature, so, there was a strong relationship between the temperature and the separation time when an increase of the temperature led to an increase of the separation time.

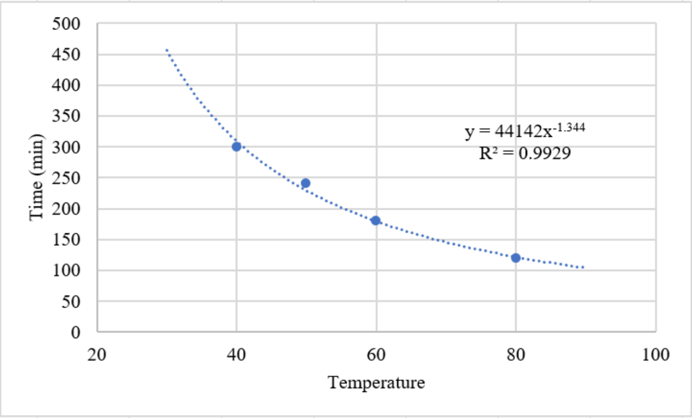

Fig. 37. Dependence of the separation time on temperature (WPBs)

The sample size was also a significant factor during separation, and the sample size range was 2cm^2–20cm^2. The empirical model that associates the treatment temperature (as an independent variable) and the treatment duration (as a dependent variable) has been established as a linear function, namely, $TD=9.1813t+9.2982$. This model explains 99% of the variation in TD (coefficient of determination $R^2=0.98$). The established equation is valid for the sample size range from 2 to 20 cm^2 (Fig. 38).

To sum up the results, a strong, positive correlation was observed between the sample size and the separation time. Thus, we can conclude that when the sample size increases, the separation time increases as well.

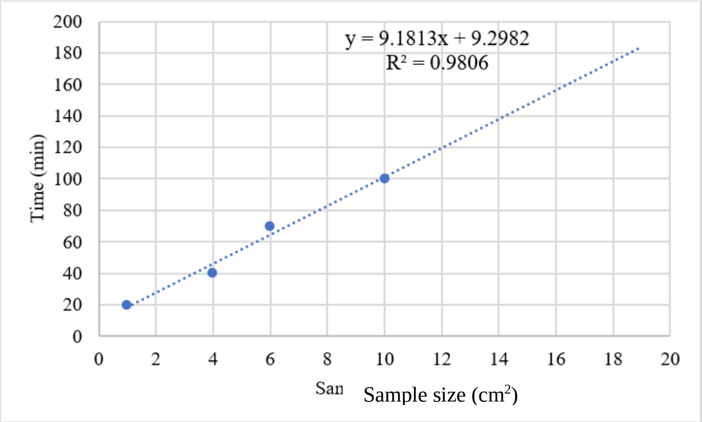

Fig. 38. Dependence of the separation time on sample size (WPBs)

There was no statistically significant correlation between these two variables with regard to the mass of the samples and the amount of the solvent. This means that increases or decreases in the mass of the samples do not significantly relate to the increases or decreases in the solvent amount.

3.3. Experiment 3 – Separation of multilayer flexible packaging by using DMCHA[2]

3.3.1. Separation Mechanism of MFPWs

All the selected samples were given specific codes, as illustrated in Fig. 39, were washed with distilled water, and later dried for 24 h at room temperature to prepare them for the separation process. Subsequently, scanning electron microscopy (SEM) was used to examine the selected MFPW samples and determine their thickness, the number of layers, and other morphological characteristics [1].

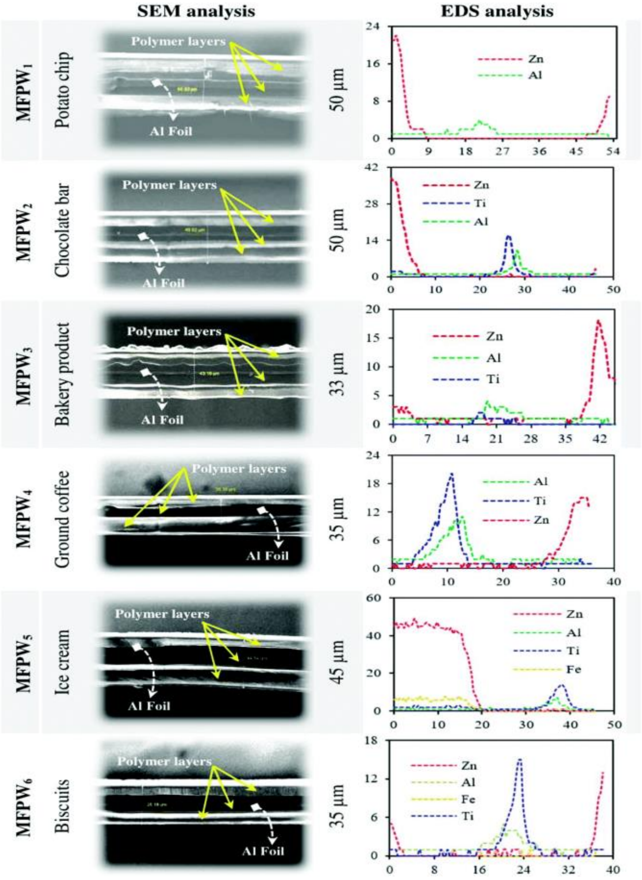

Fig. 39. MFPW sample codes, specifications, packaging type, SEM analysis, total thickness, and EDS analysis (line scanning of the cross-section) [1]

Fig. 39 shows the structure and the basic elemental composition of each MFPW type obtained by SEM-EDS (line scanning option). As it can be seen, all the

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[2] Reproduced from Ref. [1] with permission from the *Royal Society of Chemistry*

samples feature a multilayer structure (Al polymer layers) with a total thickness in the range of 35–50 µm (we note that the X-axis represents the distance or thickness). All the samples contained only one layer of Al foil, in some cases with additives, particularly with titanium (Ti); the foil layers were located mostly in the middle of the matrices. Also, two other elements, Zn and Fe, were found during the observation process. These readings were for the alloy of the clamp fixator; this presumption was supported by the fact that the two elements were detected only at the outer edges of MFPW and were not present inside the cross-section [1]. Regarding the polymer layers, all the samples contained several layers composed mainly of C and O. It should be noted that the C and O readings were excluded from the present data in order to avoid interference with the data for the other elements, particularly Al. All samples were re-examined after treatment to determine possible changes in the chemical composition and other properties which are important as an indication of the potential applications for the recovered materials. Fig. 40 shows the separation mechanism of MFPW samples when adhering to the developed approach, as observed by metallographic microscopy on a scale of 500 µm. The observation process was divided into two parts; the first part focused on examining the separation mechanism of the Al barrier layer (explained in detail in 'Analysis of the barrier layer' section), while the second part was devoted to examining the separation mechanism of polymeric components, including the ink, the paint layer, and the sealing layers [1]. As mentioned above, the barrier layer is located between two polymer layers, namely, between the coating/outer layer and the sealing layer. The barrier layer is connected to other layers by two types of bonding (chemical and mechanical) that are formed during the lamination process by an extrusion casting machine. According to the results, these connections are parallel to the transverse part of the studied samples. Other bonding was perpendicular to the cross-section of the treated samples. This bond is responsible for binding the barrier molecules together. The examination began by observing the cut samples; we intended to study the effect of the cutting on the morphology and bonds as mentioned before. As shown in the figure, pretreatment has a positive effect on perpendicular bonding where the edges of the crushed samples were accompanied by debris separated from the barrier layer in the form of flakes due to the exposure of these edges to high shearing stress. During the cutting process [183], this debris disappeared completely when the observation point was moved away from the edges of the samples, as shown in Fig. 40 A [1].

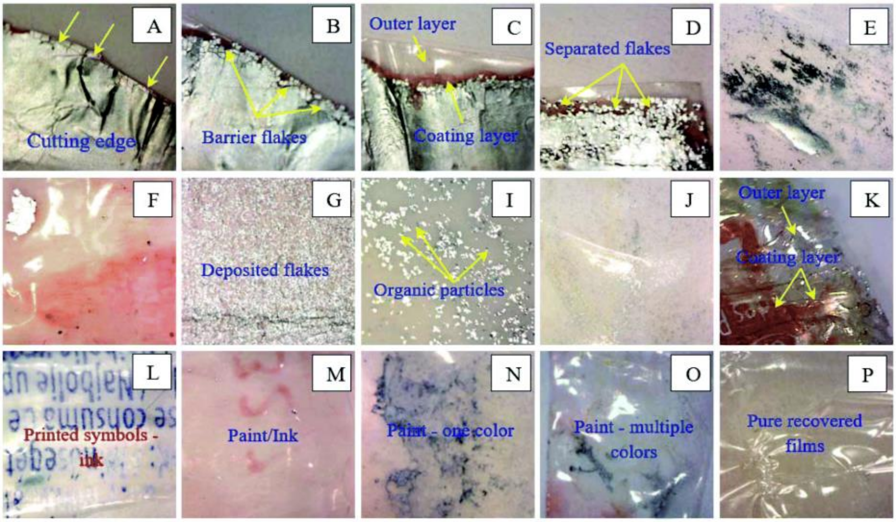

Fig. 40. Metallographic photographs of MFPW during the treatment process [1]

With the beginning of the chemical treatment, the amount of debris increased dramatically, and the rate of breakage of the vertical bonds increased due to the sound waves-induced vibration generated during the treatment as shown in Fig. 40 B and C. It is worth mentioning that the chemical treatment did not significantly impact these bonds compared to the ultrasonic treatment because the effect of the chemical treatment lies in the breakage of the bonds by dissolution, while the barrier layers offer high resistance against dissolution. However, the chemical treatment significantly impacted the parallel bonds through penetration between the layers of the MFPW samples and by breaking them by dissolution, thereby eventually liberating the barrier flakes; see Fig. 40 D. Over time, SHS penetrated more between the layers; finally, after the removal of the supporting vertical bonds, all the barrier flakes separated and formed a suspension with the SHSs; see Fig. 40 E and F. Meanwhile, Fig. 40 G shows a sediment layer formed inside the solution after leaving it for several hours. The separated barrier was aggregated in clusters composed of silver-colored barrier flakes and a red-colored liquid phase. Fig. 40 I illustrates separate flakes after filtration. As shown in the figure, the separated flakes were partially contaminated and mixed with some black particles (organic material) produced from the ink, paint, or the sealing layer (see the detailed explanation in the section ‘Analysis of the barrier layer’). Therefore, the contaminated flakes were exposed to calcination with the objective to remove any organic materials and convert them to fine power, as shown in Fig. 40 J [1]. For the second observation (the mechanism of separation of polymer components), the adhesive material was subjected to SHS, the bonds began to weaken, and the dissolution rate rapidly increased under the influence of heat and sound. The sealing layers were completely soluble in SHS, since the sealing is usually made of polyethylene which dissolves well in various solvents, inks, and paint layers. As the dissolved ink and paint had different chemical compositions, it was not easy to choose one separation mechanism. For example, some MFPW samples dissolve ink first and then the print characters, while other samples dissolve in the reverse order, and some samples even dissolve simultaneously, as shown in Fig. 40 K–O. Finally, in Fig. 40 P, pure recovered polymer films are shown [1].

3.3.2. Analysis of Barrier Layer

Figs. 41A_1, A_2, B1, and B_2 show SEM images and elemental map analysis of the recovered barrier flakes from MFPW before (A1) and after (B1) calcination. As shown in the SEM images (see Fig. 41 A1 and B1), the recovered flakes have a uniform shape with sharp edges and flat smooth surfaces with an average flake size of 100 μm. In addition, the fracture surface of the recovered layers displayed smooth features. The flakes were contaminated by some organic materials which were removed after the calcination process. The elemental map analysis showed that Al represented the main element in the recovered flakes except for a few weight percent of carbon and oxygen produced by organic materials and oxidation; the percentage of these elements decreased significantly after the calcination process. The results of the EDS elemental analysis are shown in Fig. 41 C; this analysis was used to investigate the purity of the recovered Al flakes for all the MFPW samples. Based on the result, the MFPW samples had purity in the range of 88 to 92 wt.% (average ~90 wt.%) [1]. Based on the literature information, the recovered Al flakes can be used in different applications [184, 185].

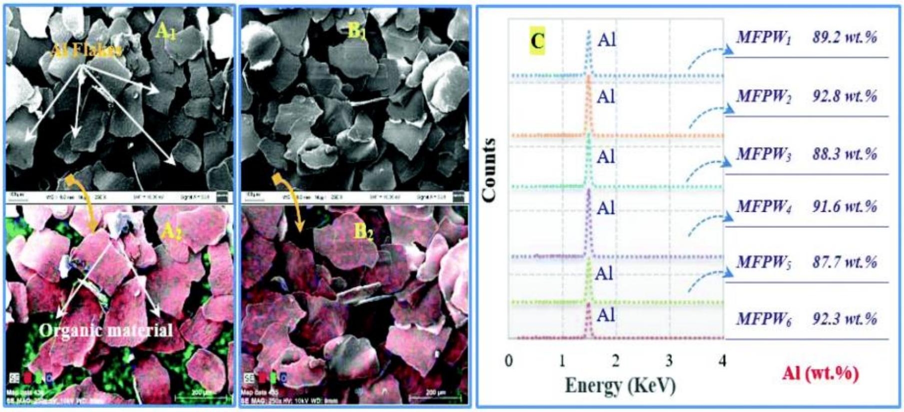

Fig. 41. SEM images ($MFPW_5$) and EDS analysis of recovered barrier flakes [1]

3.3.3. Analysis of recovered outer films

FTIR analysis. FTIR was used to determine the chemical structures and functional groups of the outer polymeric films extracted from the MFPW samples in order to determine the type of the recovered polymer. Fig. 42 shows the spectra observed for each treated sample. In the course of the analysis, similar functional groups were found in all samples, except for sample MFPW4; for example, aliphatic C–H stretch at 2750 to 3090 cm^{-1} and 1470 cm^{-1}, C=O stretch at 1745 cm^{-1}, C–O–

C stretch at 1247 and 1022 cm^{-1}. These bands are following the data found in the literature for poly(ethylene-co-vinyl acetate) (EVA), which manifests remarkable oil and grease resistance. On the other hand, several different absorption peaks were found in the WPB$_4$ sample peaks at 1709 cm^{-1} and 1237 cm^{-1} ascribed to C=O stretching vibrations and C–O–C vibrations of an ester group, respectively. Another peek at 1091 cm^{-1} was ascribed to a =C–H– a bending group of a benzene ring, whereas the peak near 722 cm^{-1} is due to the phenyl ring deformation and vibration of a CH$_2$ bending group [1]. These bands are considered the main structure of polyethylene terephthalate (PET) [186]; the results agree with the data reported in the literature discussing PET identification [195].

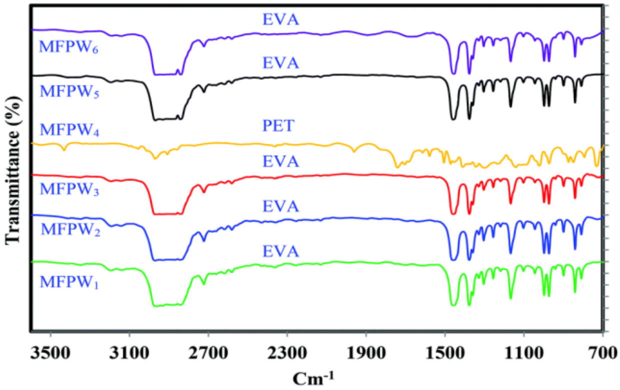

Fig. 42. FTIR spectra of recovered outer films (MFPW) [1]

Thermal analysis. Fig. 43 A shows the results of the TGA analysis for the recovered films of MFPW samples. As illustrated in this figure, the samples showed only one degradation peak, thereby indicating a single polymer type in the sample. MFPW$_{1,2,3,5,6}$ samples (EVA films) showed the same trend and exhibited similar thermal degradation profiles, thus demonstrating significant weight loss in the range of 420–500 °C. Furthermore, the thermal stability in terms of the weight loss was >98%; according to Dikobe [187], the recovered films were composed of EVA, which was indicated in the result. Similarly, the characteristic of the MFPW$_4$ sample showed the initial decomposition temperature characteristic for PET at 415 °C, and the degradation temperature was 428 °C. Furthermore, the thermal stability in terms of the weight loss was >97%. Additionally, derivative thermogravimetric (DTG) analysis further confirmed the observed trend of polymer decomposition with one degradation step, as shown in Fig. 43 B [1].

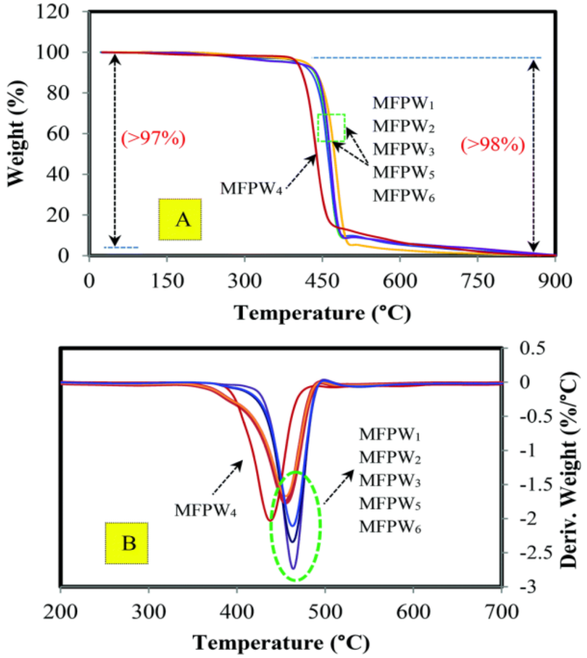

Fig. 43. (A) Thermogravimetric curves of recovered polymer films and (B) DTG analysis [1]

3.3.4. Analysis of extracted residues

First extraction. Due to the residue extracted from this step featuring a mixture composed of coating, paint, ink, etc., FTIR analysis was problematic to perform with high accuracy for all of the individual components in the mixture. In order to avoid this issue, SEM-EDS was used instead of FTIR analysis. Fig. 44 shows the photos, SEM images and EDS elemental map analysis of the first extracted residue after the filtration and drying of differenttreated MFPW samples. As shown in the SEM images (Fig. 44 A_1, B_1 and C_1), the extracted residue did not exhibit a certain shape as it showed mixed spherical particles, flakes, and conglomerates (Figs. 44 E) [1]. In order to better understand the obtained information, we used EDS and elemental map analysis to examine the chemical composition. As shown in Fig. 44 A_2, carbon (C), oxygen (O), and calcium (Ca) were the main elements in all particles [182]. C, O, and Ca that we found are typical elements for different organic materials, such as solvents, pigments, dyes, resins, lubricants, solubilizes, surfactants, particulate matter, fluorescents, and other materials which are considered the main components of inks [188]. In addition, metallic elements were found in the sample, mainly titanium (~97 wt.%) and Al (~3 wt.%) (Fig. 44 B_2 and C_2), which are widely used in the ink production as additives applied for coloring and improving the overall appearance of dry ink. On the basis of the reported composition, the extracted particles were printing inks. Hence, on the basis of the obtained result, the extracted particles were printing inks [1].

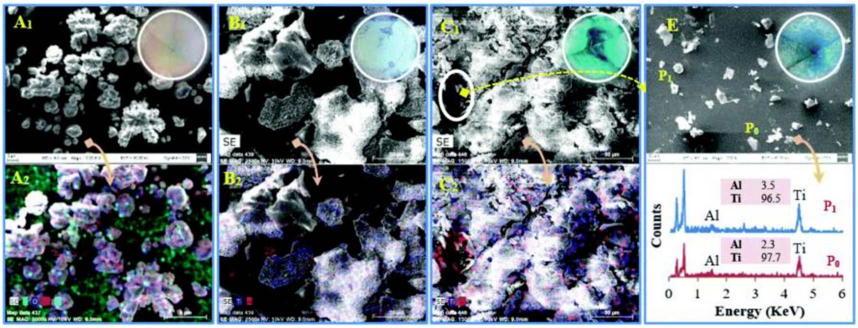

Fig. 44. SEM images and EDS analysis of the first extracted residue (MFPW5) [1]

Second extraction. All paints, inks, coating polymers, etc., were separated during the first extraction, thus leaving only one type of polymer in the solution, namely, the sealing layer. Therefore, it was easy to analyze the second extraction of residue particles after their extraction from the solvent by adding distilled water and CO_2 at 0 °C. Fig. 45 shows the spectra observed for the residue particles of all the MFPW samples. FTIR analysis of the samples gave a close view of CH stretching at 3410 cm^{-1}, CH_2 deformations at 1590 cm^{-1}, CH_2 asymmetrical bending at 1457 cm^{-1}, and symmetrical CH_2 bending at 1351 cm^{-1} with an additional peak at 1128 cm^{-1} that was identical to the FTIR spectra of low-density polyethylene (LDPE) [189]. However, detention and shifting of the functional group peaks were also observed, thus reflecting the change in the structure, and thus it can be concluded that the recovered polymer was partially degraded. This data is also supported by information in the literature where polyethene is widely discussed regarding its use for hot sealing [50, 51, 190]. Finally, after the extraction of the first and second residue, the spent solution was heated at 40 °C overnight in order to remove the mixed water as well as CO_2. Fig. 46 A and B shows the photographic images of the regenerated DMCHA after the extraction of all the residues and gases by filtration and heating, respectively [1]. As it is evident, the recovered DMCHA changed from yellow to colorless again (i.e., the original color).

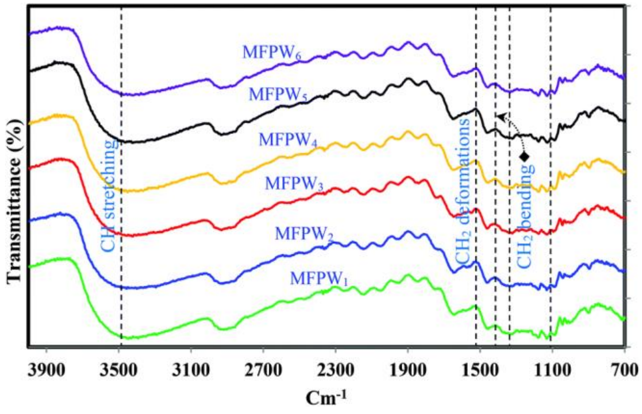

Fig. 45. FTIR spectra of the first and second (sealing layer) extracted residue [1]

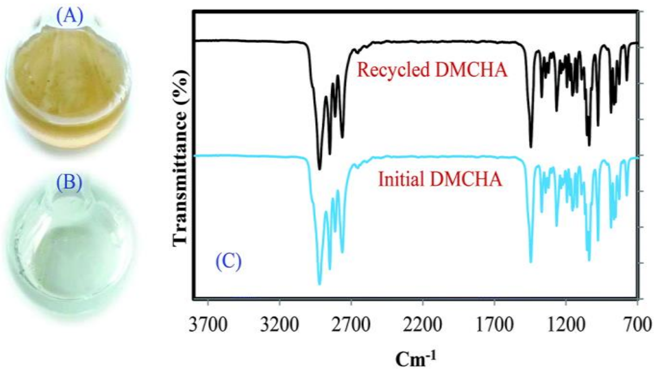

Fig. 46. Infrared spectra of recycled and original DMCHA [1]

Fig. 46 C shows the FTIR spectra of unused and regenerated DMCHA. The results indicate C–H stretching vibration of saturated hydrocarbon groups in the region of 2936–2776 cm^{-1}, C–H bending vibration of methyl groups at 1446 cm^{-1}, and stretching vibration of C–N at 1350–1000 cm^{-1}. It was clear that the properties of the initial and recovered DMCHA did not change, and the obtained readings were similar to the bands described in the literature [191]. This means that switching the solvent's polarity by CO_2 addition is useful from both the economic and environmental points of view. Finally, Table 17 shows all the materials in the residue and films extracted from the packaging and the position of each layer in the matrix [1].

Table 17. Materials and order of the recovered films, metal flakes, and residues of each MFPW sample [1]

Layer name	MFPW 1	MFPW 2	MFPW 3	MFPW 4	MFPW 5	MFPW 6
Coating (paint,inks, etc.) Residue 'A'	Ti, Al, etc.	Ti, Al, etc.	Ti, Al, etc.	Ti, Al, etc.	Ti, Al, etc.	Ti, Al, etc.
Outer layer	EVA	EVA	EVA	PET	EVA	EVA
Barrier layer	Al	Al	Al	Al	Al	Al
Sealing layer Residue 'B'	LDPE	LDPE	LDPE	LDPE	LDPE	LDPE

3.3.5. Efficiency of the New Recycling Method

Table 18 shows the recycling rate of Al and polymeric layers (EVA, PET, LDPE, etc.) for specific MFPW samples, as well as the average recycling rate. Recovery efficiency (%) was calculated in the following way: the recovered component weight was divided by the initial weight and multiplied 100%. As illustrated, the percentage of Al was in the range 12–17 wt.% with an average value of 14.2 wt.%. Simultaneously, the recovered polymeric components, including coating, the outer layer, and sealing, represented 84.3% of the total MFPW mass. Therefore, the recycling rate of the developed approach was relatively high at >99% (based on mass balance) for all MFPWs. Most of the losses occurred for the polymeric fraction during the filtration process. The developed technique showed high efficiency in DMCHA regeneration of DMCHA with a >98% recycling rate [1].

Table 18. Materials and order of the recovered films, metal flakes, and residues of each MFPW sample [1]

Sample code	**Initial weight**		**Recovered components**		**Average Recycling rate (%)**	
			Al flakes (wt.%)	Polymers (wt.%)	DMCHA	MFPW
MFPW1	One gram of MFPW	3 ml of DMCHA	14	85.7	98.7%	99.4%
MFPW2			15	84.3		
MFPW3			14	85.5		
MFPW4			17	82.1		
MFPW5			12	87.4		
MFPW6			13	86.6		
Average			14.2%	85.3%		

Various temperatures were used during the experiment, and the observations showed that high temperatures caused decreases in the separation time, however, they negatively affected the polymer structure and caused its degradation. The empirical model that associates the treatment temperature (as an independent variable) and the treatment duration (as a dependent variable) has been established as a nonlinear (power) function, namely, TD=762623xt^-2.414. This model explains 97% of the variation in TD (coefficient of determination R^2=0.98). The established equation is valid for the temperature range from 40 to 90 °C (as shown in Fig. 47). On the basis of the experiment data, faster separation times were obtained at high temperature, hence, strong relationship between the temperature and the separation time was observed when an increase of the temperature led to an increase of the separation time.

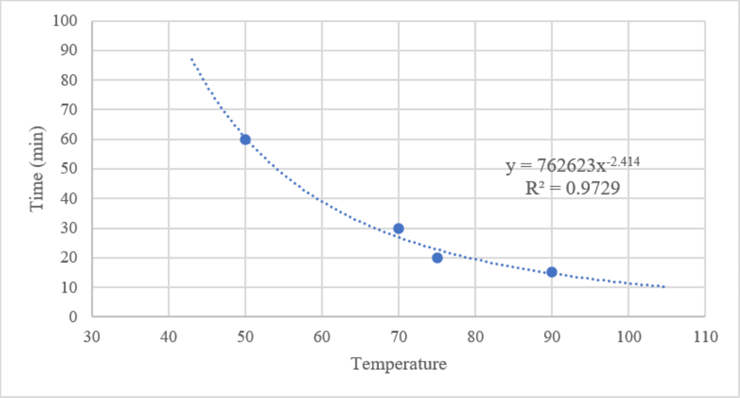

Fig. 47. Dependence of separation time on temperature (MFPWs)

The sample size was also a significant factor during the separation of MFPW. The empirical model that associates the sample size (as an independent variable) and the treatment duration (as a dependent variable) has been established as a linear function, namely, TD=5.8858t+32.559. This model explains 99% of the variation in TD (coefficient of determination R^2=0.98). The established equation validates the sample size range from 2 to 20 cm^2 (Fig. 48). To sum up, strong, positive correlation was observed between the sample size and the separation time. Thus, we can conclude that, whenever the sample size increases, the separation time increases as well.

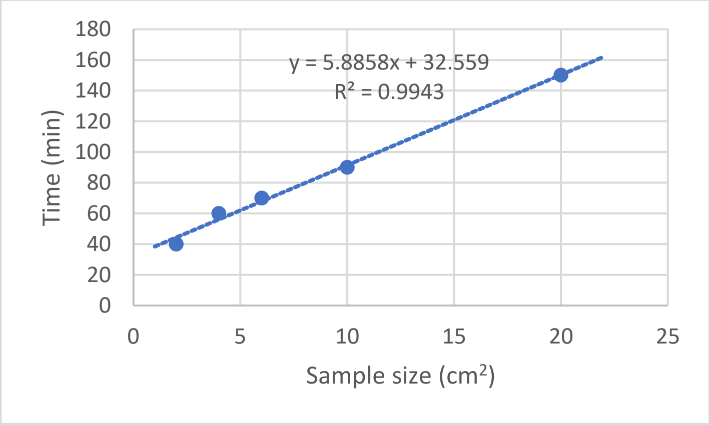

Fig. 48. Dependence of the separation time on sample size (MFPW)

3.4. Environmental and economic performance and efficiency of the developed technique[1; 2]

The economic performance of the developed technology was evaluated in order to calculate the utility of applying this technology on an industrial scale, and the evaluation is based on the raw obtained materials. As shown above, the recovered polymer components, including the coating, skins, and sealant, made up 85.3% of the total mass of MFPW (mixed polymers made up approximately 10% by weight of the recovered polymer components), while Al flakes made up 14.2% by weight of the total mass of MFPW. In comparison, Al made up 16.5% of the total mass [1].

What concerns the cost of production, Fig. 49 A shows the economic performance and the limitations of the developed WPB treatment. Al, PVC (granules/recycled PVC) and PE (granules/recycled PVC) scrap prices were believed to be USD 700/ton, USD 800/ton and USD 850/ton, respectively (www.alibaba.com, Based on this price, the benefits have been estimated at $774/ton of waste. Based on the recycling rate and on the estimated economic return, it can be concluded that the developed technique is an efficient method of recovering WPB materials, and it can be used on an industrial scale [53]. Fig. 49 B shows the economic performance of the proposed technology in terms of the condition of the granules (pure or mixed) recovered from MFPW. Energy use was measured per kilowatt hour and estimated at 264 kWh per ton (the total cost of the recovered material was estimated at $2,040 per ton, and the final benefit was estimated at $ 1,920 per ton ($2,040 per Ton minus $80 per Ton minus $40) per Ton). This is solid proof that, by applying the developed technology, the benefits of recycling can be significantly increased by reprocessing each type of polymer individually while keeping the treatment costs low due to a sustainable solvent [1].

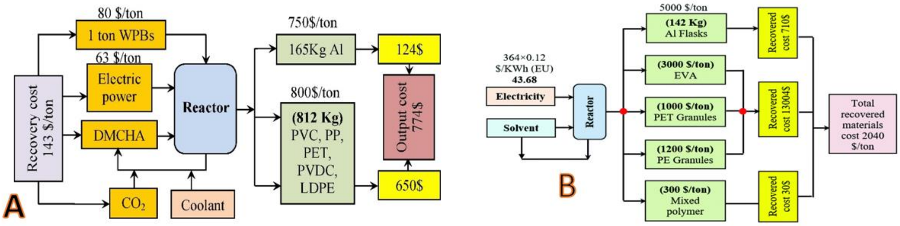

Fig. 49. Economic performance of the developed technique WPB (A) and MFPWs(B) [1, 53]

The GGE of each extract material was calculated based on the average value reported in the literature. Table 19 shows the average GGE of the recovered materials (mixed plastics, PET, HDPE, PVC, LDPE, PP and Aluminum foil) based on the Turner result; see [169]. It should be noted that the mixed plastic is 10% by weight,

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while the other polymer fraction is 75% by weight, and the Al foil is 14% by weight. Having determined the weight ratios, the GGE values were defined for each fraction. According to these calculations, the application of the modern technology on an industrial scale can reduce greenhouse gas emissions at an equivalent of 2266 kilograms of carbon dioxide per ton [1].Compared with the GGE emission reductions suggested by other literature methods, the CO_2 equivalent of the current technology has shown a significant reduction in CO_2 equivalent emissions, which is about four times better if compared to that of acidification, formic acid (-576.1 kg carbon dioxide equivalent/ton) and ten times the waste pyrolysis (-225.2 kg carbon dioxide equivalent/ton) [102].

Table 19. GHG emissions from each material

Waste material type	Average ($kgCO_2$-eq/t) [169]	Wt.%	$kgCO_2$-eq /t
Mixed plastics	-788	10%	-79
PET	-1570	75.3%	-890
HDPE	-1055		
PVC	-1259		
LDPE	-744		
PP	-1279		
Aluminum foil	-9267	14.2%	-1297
CO_2-eq reduction by the new technique ($kgCO_2$-eq/t)			-2266

As mentioned above, water is an important part of the proposed technology, and the polymer is extracted from the solution by adding two volumes of water to one volume of solvent at 0 °C. The processing of a ton of packaging waste requires 2 tons of solvent and 6 tons of water. After the extraction process, the water must be evaporated in order to recover and reuse the used solvent. This method can ensure the stability of the solvent, but it cannot guarantee the stability of the used water. Therefore, it is recommended to use a condenser to recirculate water [1]. Although the solvent system was previously used, Samori [102] focused on separating packaging waste consisting of only two materials: low-density polyethylene and Al. This research focuses on the separation of packaging waste consisting of several layers. The layer includes other components, such as paint and ink. Also, the materials obtained with advanced technology cannot be regarded as recycled materials but as products with high added value (e.g., Al microparticles). These can be used in high-tech applications and serve the objective of closing the loop waste cycle and ensuring sustainability [1].

Based on these results, the proposed approach can be seen as a cost-effective and environmentally friendly strategy by virtue of including measures that promote Europe’s transition to the circular economy, and also by promoting sustainable economic growth. Our study intended to start a new life cycle of MFPW according to the principles of circular economy [1].

3.5. Integration of the developed approach into circular economy system[1]

The high recycling rate, advanced design, proper recycling and responsible consumption are seen as the main challenges in our pursuit to close n the life cycle of waste packaging and achieve the benefits of circular economic CE), such as improving the environmental health and practicing economic recovery in EU. For this reason, a technology developed and applied on an industrial scale has been proposed, as shown in Fig. 50 [53].

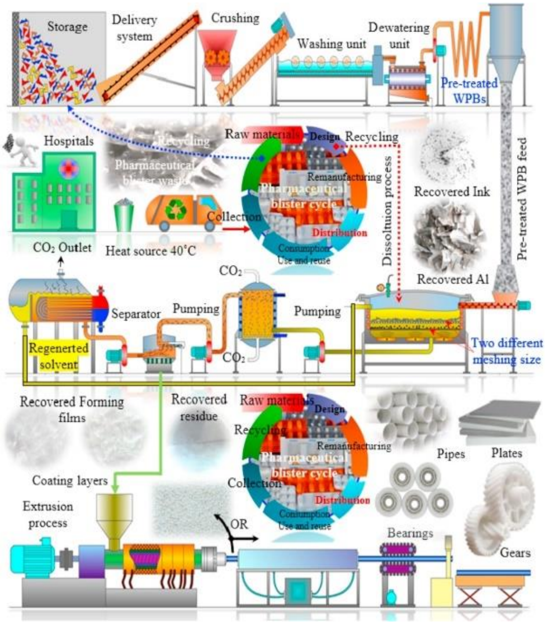

Fig. 50. Developed CPW recycling technology as part of the Circular Economy system [53]

As shown in Fig. 50, the CPW recycling/reprocessing line starts from composite packaging waste collected in hospitals and local markets according to the international standards and then sent to the factory for processing. This technology requires prior treatment. The treated CPW is placed in a chemical reactor in order to separate the ink, form a lidding, coat, and to dissolve the remaining polymeric elements. Various filtering methods are used. When designing particle extraction (ink, Al, etc.), the polymer solidification unit is used in order to extract the dissolved organic material from the solvent by cooling and adding CO_2. A filter device separates the hardened polymer, and CO_2 is removed by removing the solvent. In the last part of the technology design, i.e., when heating in a heat exchanger, a polymer extrusion line scheme for processing recycled polymers into a new product was presented. The proposed plan aims to maximize the use of recyclable materials/products by making full use of all materials, as well as raw materials,

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products, and waste, thereby disrupting the operation of the system, saving energy, and reducing gas emissions. Effective and environmentally sound strategies include promoting Europe's transition to a circular economy, international competitiveness, increasing sustainability, and creating new jobs [53].

3.6. Feasibility of a green pilot plant for CPWs recycling[2]

During the adoption of new recycling technology, equipment replacement and production readjustment usually result in the loss of a significant amount of resources used previously. In order to avoid this problem and maximize the benefits of old recycling lines and avoid the need to dispose of the older generation equipment, recycling technologies and separation stages currently in use in the EU serving the function of reusing some parts of these phases have been explored. The construction of a new facility will reduce the cost of natural resources[1]. Overall, literature research determined that all standard recycling technologies start with the collection process due to the transfer of waste to a warehouse where waste is converted into new raw material. Various mechanical processing methods that have already become standard practice are being used in many EU countries, e.g., Lithuania, Belgium, Estonia, Latvia [192].

Our study proposes an environmentally friendly recycling technology based on an innovative design for solvent-based recycling technology for composite packaging waste (CPW). The proposed plan is based on the results of laboratory experiments aimed to determine the chemical composition and the optimal separation conditions for various types of CPW [1].

3.6.1. Layout of the green pilot plant for CPW recycling

As mentioned above, based on the research and the obtained results, it has been proposed to build a new facility based on the total amount of raw material recovered at the end of the treatment process. In total, five types of these raw materials can be obtained: Mixed polymer powder, EVA film, PET film, PE powder, and Al flake. The number of materials recovered after using the proposed approach may be higher, depending on the structure and the total number of layers in the processed packaging. In this case, minor adjustments to the basic design are required. Fig. 51 shows the proposed design of the new system [1]. As it can be seen, the distribution starts with the pretreatment process (indicated by the purple rectangle). The four initial steps (sorting, grinding, washing the rotating drum, and friction water washing) are identical to the initial steps involved in the traditional mechanical processing systems. The SHS basic phase treatment follows this and begins to separate the coating layers (including ink and paint) from Al flakes and other polymers and adhesives. This step involves the regeneration of solvents with a separate unit.Then, three types of separation units are used to achieve complete separation of alum and ink/dye from the polymer fraction, starting with the separation by centrifugation and

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filtration. Different infrared sorting units are used to sort different polymers, and then each type of polymer is processed for granulation [1].

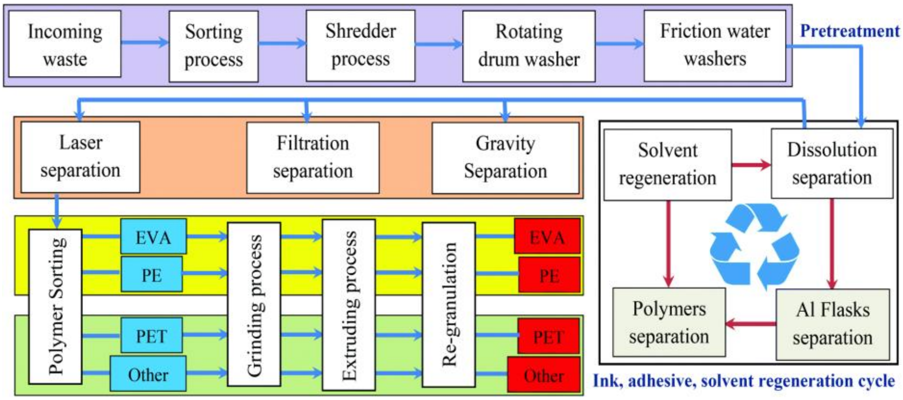


Fig. 51. Suggested layout of new green plant [1]

CONCLUSIONS

The work was performed within the scope of this thesis pursuing to determine the chemical mechanism and the technological conditions for Al and polymers recovering from food, beverage, and pharmaceutical packaging waste. From the above outlined results, the following points can be summarized:

1. Various types of CPW, including WPB and MPFW, have been treated with acidic and organic solvents. Separation with this method was found to be possible to carry out at a high recovery rate (>98%). At the end of the process, under optimal conditions, more than five different raw materials, such as Al and various types of polymers, can be obtained. During the study of the separation process, it was noticed that the first layer which is separated from the sample was the ink layer because it features weak bonding; then, other layers of polymers and Al started to separate from each other. After the ink layers, the outer polymer layer was separated, and the average separation time was 3 hours. Also, in some cases, additional forces were necessary for separation in order to damage the adhesive bonding between some layers which are quite strongly bonded and require extra time for separation. For example, during MFPW treatment, centrifugation was used to separate Al flakes and other particles.
2. The effects of temperature, solvent concentration, sample volume, separation time, and the solid-liquid ratio were studied, and complete separation was achieved under all research conditions. For all samples, the optimum conditions were selected, and the sample size range was 2cm^2–20cm^2; the temperature range was between 30–90 °C (the final experiment was carried out at a low temperature, specifically, at 40–50 °C); the solid-to-liquid ratio was 1:3 g/ml. The temperature and the sample size were significant factors during the separation process, and, when the temperature was increased, the separation time s decreased, whereas, for the sample size, it was the opposite: when the sample size was increased, the separation time also increased. Also, what regards the temperature, faster separation times were obtained at a high temperature, but then polymer degradation started. Hence, all the experiments were carried out at a low temperature. With respect to the solid-to-liquid ratio and concentration, it had no strong effect on the separation time.
3. With CPW processing, the recovered materials can be used in various industries. A high level of efficiency characterizes this process compared to the traditional process. It is possible to extract at least two types of raw materials, e.g., Al and mixed plastics (with limitations in terms of thermal degradation compatibility). The recovered component can be used in powder metallurgical applications. At the same time, polymeric components have been represented by mixed polymers (ink, paint, glue, etc.), EVA films, PE powder, PET films, etc.; they could be used for light applications together. Polyvinyl chloride was a significant fraction of polymer in WPB. Quality of recovered polymers was like virgin polymer with a low degradation rate.

The purity of the Al foil ranged from 65 to 97% by weight (on average, 81% by weight). Also, elemental analysis showed that Al layers contained several elements, including small amounts of Ti, Fe, Ag, and Si (0.4–6.0% by weight), which were used to improve quality. Therefore, it can be said that recycled Al can be used in a variety of industries. The thermal stability of the recovered forming films was almost like that of a virgin polymer with a low degradation rate.

4. All the components of CPW were successfully recovered during the laboratory experiment. In WPB recycling, the recovered metal constituted 16.5% by weight. Al was the main element, whereas nonmetals constituted 81.2% by weight. Therefore, the recovery rate was relatively high, specifically, in the range of 96 to 99% with an average of 98% (based on the mass balance) for all WPBs. Furthermore, most of the losses (~2%) occurred for the polymeric fraction during the filtration process. MFPW, respectively, contained 14.2% by weight of Al, and the polymer fraction made up 85.3% by weight. Therefore, the recovery rate was relatively high at >99% (based on the mass balance) for all MFPWs. It had high efficiency in DMCHA regeneration of DMCHA with an >98% recovery rate. Compared to the use of the primary raw materials in production, secondary raw materials are more acceptable. The total cost of the recovered material from MFPW was estimated at $2,040 per ton, and the final benefit was estimated to be $1,920 per ton.

As outlined above, the results show that CPW separation when using various chemicals can be seen as a new and viable alternative to separating plastics and Al. Repetition of the use of solvents, simple or without purification, improves the presented method from the economic and environmental points of view. Thus, we can conclude that the introduction of the proposed technology can promote adherence to the principles of sustainability and the circular economy while at the same time pursuing and implementing the EU vision of developing new technologies.

RECOMMENDATIONS

As there is some limitation in terms of performing complete LCA for this suggested recycling method (e.g., DMCHA is not available in the LCA inventory database), it will be helpful for performing future studies and for implementing the Life cycle assessment method for Composite Packaging Waste recycling with the solvent of DMCHA so that to study and investigate its effect(s) on the environment and human health.

SANTRAUKA

ĮŽANGA

Sudėtinių pakuočių atliekos (SPA), t. y. maisto produktų pakuotės ir lizdinės vaistų pakuotės, paprastai sudaro didžiąją dalį pakuočių atliekų, daugiausia susidedančių iš daugiasluoksnių plastikinių lakštų laminuotų ant aliuminio folijos [1]. Apskaičiuota, kad 2007–2017 m. ES susidarė 79±1,25 mln. tonų pakuočių atliekų per metus, todėl šios rūšies atliekos aplinkosauginiu požiūriu tampa vienos iš svarbiausių [4].

Šiais laikais gamintojai susiduria su iššūkiu, siekdami pigiai, kokybiškai ir efektyviai supakuoti savo gaminius. Rinkoje išaugo sudėtinių pakuočių (SP) paklausa, o laikui bėgant jos tapo populiarios tarp vartotojų. Kaip jau minėta, SP sudaro daugiausia plastiko, popieriaus ir metalo sluoksniai, sujungti dervomis arba vašku. Nors pakuotės yra plonesnės, efektyvesnės ir patvaresnės, kai kurie klausimai išlieka opia problema, pavyzdžiui, šių pakavimo medžiagų perdirbimas. Dėl sudėtingos pakuotės medžiagos struktūros perdirbimo procesas yra sudėtingas. Be to, šios rūšies atliekas perdirba tik kelios įmonės. Pažymėtina ir tai, kad šios įmonės dažniausiai perdirba tik vienos rūšies produktus. Tačiau esami tyrimai rodo, kad įmanoma atskirti beveik visas sudedamąsias dalis, o gautų medžiagų kokybė yra artima pirminių produktų kokybei. Tai padidina jų pakartotinį panaudojimą įvairiose pramonės šakose. Kadangi kiekviena šios pakuotės medžiaga padeda sutaupyti daug gamtos išteklių, būtina sukurti ir plėtoti visapusišką perdirbimo mechanizmą, kuris savo ruožtu turės teigiamą poveikį aplinkai ir ekonomikai.

Daktaro disertacijos tikslas

Disertacijos tikslas – įvertinti aliuminio ir polimerų atgavimo iš maisto, gėrimų ir vaistų pakuočių technologines galimybes ir sąlygas atskyrimo tirpikliais metodu.

Uždaviniai

1. nustatyti problemas ir iššūkius, susijusius su SPA perdirbimu Europoje ir visame pasaulyje;
2. atlikti eksperimentinį aliuminio turinčių SPA perskyrimą tirpikliais ir rūgštimis;
3. nustatyti optimalias atskyrimo sąlygas pasirinktos pradinės būklės SPA, įvertinant temperatūros, kietosios medžiagos ir skysčio santykio, dydžio ir SPA tipo įtaką atskyrimo laikui;
4. ištirti gautų antrinių žaliavų kokybę ir savybes;
5. įvertinti aliuminio turinčių SPA perskyrimo tirpikliais įtaką šių atliekų perdirbamumui, ekonominius rodiklius, aplinkosauginę naudą ir poveikį aplinkai.

Mokslinis naujumas

1. ***Nustatytos optimalios perskyrimo tirpikliais proceso sąlygos kelioms labiausiai paplitusioms SPA rūšims.*** Tyrimas atskleidė, kad apdorojimas tirpikliais gali būti veiksmingas ir esant žemai temperatūrai (SPA apdorojimas žemoje temperatūroje tirpikliais anksčiau nebuvo tirtas). Eksperimento duomenys parodė, kad sąlyginai dideli SPA mėginiai per palyginti trumpą laiką buvo perskirti žemesnės temperatūros sąlygomis (pvz., apie 48 val. kambario temperatūroje).
2. ***Nustatytos didesnių SPA mėginių apdorojimo galimybės.*** Anksčiau aprašytuose tyrimuose, susijusiuose su SPA apdorojimu tirpikliais, buvo įrodyta, kad įmanoma perskirti tik į smulkius gabalėlius susmulkintas SPA, o šiame tyrime, remiantis optimizuotu procesu, pavyko perskirti didesnio dydžio (2 cm^2> mėginio dydis< 20 cm^2) SPA.
3. ***Kelių rūšių polimerai gali būti atskirti vienas nuo kito ir aliuminio folijos.*** Remiantis literatūros duomenimis, SPA apdorojimas buvo nukreiptas tik į vieno ar dviejų komponentų atskyrimą. Remiantis šio tyrimo rezultatais, iš maisto, gėrimų ir vaistų pakuočių buvo išskirtos daugiau nei trys skirtingos medžiagos (keli polimerai, aliuminis ir kt.).
4. ***Geresnis perskirtų medžiagų perdirbamumas ir kokybė.*** Perskyrimo proceso pabaigoje gautos medžiagos, t. y. aliuminis (milteliai arba folija) ir polimerai (PVC, PP, PE, LDPE ir kt.), buvo geros kokybės, pavyzdžiui, atgauto aliuminio grynumas siekė 65–97 %. Be to, vidutinis perdirbamumo lygis siekė iki 90 %. Atgautų medžiagų kokybė padidina pakartotinio jų naudojimo naujoje gamyboje galimybę.

Hipotezės

Aliuminį ir įvairius polimerus galima sėkmingai atskirti vienas nuo kito apdorojant tirpikliais (atrinktais tirpikliais), šis procesas sumažintų poveikį aplinkai ir tausotų gamtos išteklius.

Apgintas pasiūlymas

1. Aplinkai nekenksmingas apdorojimo tirpikliu metodas gali būti naudojamas vertingoms metalinėms ir nemetalinėms medžiagoms atgauti iš daugiasluoksnių atliekų, pavyzdžiui, maisto ir vaistų pakuočių atliekų.

2. Polimerai ir aliuminis, gauti apdorojant tirpikliais ir cheminėmis medžiagomis, gali būti perdirbami į didelės pridėtinės vertės produktus originalaus dydžio arba miltelių pavidalu.

Disertacijos struktūra

Daktaro disertacija susideda iš šių dalių: įvadas, literatūros apžvalga, medžiagos ir metodai, rezultatai ir diskusija, išvados, padėka, literatūros sąrašas, straipsnių sąrašas ir priedai. Daktaro disertacijos apimtis – 136 psl., 51 pav., 19 lentelių.

Straipsniai ir konferencijos

Tyrimo rezultatai, panaudoti rengiant šią disertaciją, paskelbti 2 straipsniuose žurnaluose, registruotuose *Web of Science* duomenų bazėje, ir 2 straipsniuose kitose duomenų bazėse. Tyrimų rezultatai buvo pristatyti 8 konferencijose.

Praktinė reikšmė

Nagrinėjant šią temą ir siekiant integruoti visų tipų SPA perdirbimo procesus, buvo atlikti ir išanalizuoti keli laboratoriniai eksperimentai. Buvo apžvelgtos visų medžiagų, gaunamų iš SPA, pavyzdžiui, aliuminio ir polimerų, taikymo sritys ir rekomenduota bent keletas kiekvienos medžiagos taikymo sričių. Remiantis gautais duomenimis apie medžiagų srautus šioje technologijoje buvo pasiūlytas ekologiškas bandomosios gamyklos, skirtos pramoninei SPA perdirbimo linijai, planas, į kurį įeina pirminis apdorojimas, atskyrimui specialiai suprojektuotas reaktorius, klasifikavimas ir keli pridėtinės vertės medžiagų gamybos etapai. Gautas rezultatas bus naudingas mokslininkams, dirbantiems mokslo ir inžinerijos srityje. Tai padės geriau suprasti SPA perskyrimo tirpikliais mechanizmą, šio metodo privalumą ir patogumą. Be to, tai paskatins perdirbimo technologijos perkėlimą iš laboratorinio lygio į pramoninį.

Autoriaus indėlis

Šiame darbe pateiktus ir aptartus tyrimo rezultatus surinko ir išanalizavo šios disertacijos autorius. Dalį medžiagų charakteristikų nustatė publikuotų straipsnių bendraautoriai iš Lietuvos energetikos instituto. Paskelbtus straipsnius autorius parengė vadovaujamas darbo vadovo (Gintaro Denafo) ir bendraautorių (Samy Yousef, Maksym Tatariants) iš Kauno technologijos universiteto. Papildomai straipsnių rengimui vadovavo Regita Bendikienė (KTU Mechanikos inžinerijos ir dizaino fakultetas). Svarbu pažymėti, kad visi pirmiau išvardyti bendraautoriai neketina naudoti paskelbtų duomenų rengiant kitas disertacijas.

Pastaba: Visi publikuoti moksliniai straipsniai naudojami šioje disertacijoje, gavus leidėjų leidimą.

SANTRUMPOS

Al	Aliuminis
DLPA	Daugiasluoksnės lanksčių pakuočių atliekos
DMCHA	N,N-dimetil-cikloheksilaminas
DMF	Dimetilformamidas
DTP	Didelio tankio polietilenas
EIRS	Energiją išsklaidanti rentgeno spektroskopija
EVA	Etileno-vinilacetatas
LVPA	Lizdinių vaistų pakuočių atliekos
FTIR	Furjė transformacinė infraraudonųjų spindulių spektroskopija
GCA	Gyvavimo ciklo analizė
IŠESDK	Išmetamas šiltnamio efektą sukeliančių dujų kiekis
KHT	Kintančio hidrofiliškumo tirpiklis
KV	Kilovoltas
MTP	Mažo tankio polietilenas
PE	Polietilenas
PET	Polietileno tereftalatas
PP	Polipropilenas
PVC	Polivinilchloridas
PVDC	Polivinilideno chloridas
SEM	Skenuojanti elektroninė mikroskopija
SP	Sudėtinė pakuotė
SPA	Sudėtinių pakuočių atliekos
TGA	Termogravimetrinė analizė
ŽE	Žiedinė ekonomika

1. LITERATŪROS APŽVALGA

1.1. Europos plastiko ir pakuočių atliekų perdirbimo tikslai

Europos Komisija traktuoja, kad plastiko vartojimas yra nesubalansuotas. Pažymima, kad plastikas dažnai patenka į vandenyną. Taigi akivaizdu, kad plastikas prastai tvarkomas, o jo atliekos menkai surenkamos. Todėl EK ragina valstybes rasti sprendimą ir laikytis tvaresnio požiūrio. Plastikas yra žiedinės ekonomikos dalis, kur gamyba, naudojimas ir šalinimas gali tapti organiška perdirbimo ir naujų produktų kūrimo dalimi. Nuolatinė atliekų surinkimo, rūšiavimo ir perdirbimo sistema turėtų būti atspirties taškas, siekiant socialinių tikslų ir aplinkosauginės naudos [17].

Pagal ES plastikų strategiją tikimasi, kad vidutinis plastikinių pakuočių perdirbimo lygis sumažės nuo 41 proc. iki 29–32 proc. Pastaraisiais metais atliekų susidarymas padidėjo (ES), taip pat palaipsniui didėjo ir perdirbamų medžiagų skaičius. Tačiau norint pasiekti šį 2018 m. iškeltą tikslą, dar reikia daug nuveikti [5].

1.2. Pakuočių gamyboje naudojami gamtiniai ištekliai

Atsižvelgiant į įvairių rūšių pakuočių patikimumą, svarbu išsiaiškinti ryšį tarp gamtinių išteklių, naudojamų šioms pakuočių medžiagoms gaminti, pavyzdžiui, biomasės, iškastinio kuro, elementų ir mineralų, paverstų visiškai kitomis medžiagomis. Remiantis duomenimis, aliuminio gamybai kasmet iškasama apie 160 mln. tonų boksito, kuris išgaunamas iš Žemės plutos ir vėliau perdirbamas į aliuminį [22]. Šiam procesui reikia daug energijos. Norint išgauti 4–5 mln. tonų boksito, reikia apie 125–160 mlrd. kVh energijos. 2018 metais pasaulyje plastiko buvo pagaminta apie 359 mln. tonų, iš kurių apie 62 mln. tonų pagaminta Europoje [30].

Per metus plastiko gamybai sunaudojama apie 30,5 mln. tonų žalios naftos, 25 mln. tonų gamtinių dujų ir 152,6 mln. tonų anglies. Plastikas plačiai naudojamas įvairių produktų gamyboje [32].

1.3. Pakuočių paskirtis ir pakuočių bei pakavimo medžiagų rūšys

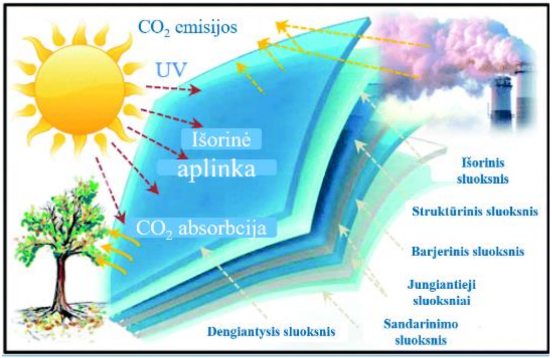
Pakuočių medžiagos gali būti pagamintos iš įvairių medžiagų, siekiant apsaugoti produktą nuo įvairių neigiamų poveikių [33]. Tai esminis įvairių pagrindinių funkcijų komponentas. Iš viso, nustatytos septynios pagrindinės pakuočių funkcijos: apsauga, izoliavimas, unifikavimas, paskirstymas, komunikacija, informavimas ir patogumas [35]. Pakuotės tipą galima skirstyti į pirminį, antrinį ir tretinį [37]. Pakuotėms gaminti dažniausiai naudojami popierius, stiklas, aliuminis, mišrios medžiagos, plastikas, tekstilė ir plienas. Paprastai SP gamybai naudojamos mišrios medžiagos, kurios tampa populiarios, nes gerokai sumažina energijos sąnaudas [43, 44].

1.4. Sudėtinės pakuotės

Paprastai sudėtinė pakuotė gaminama sujungiant dvi ar daugiau skirtingų medžiagų, kurios tarpusavyje glaudžiai susietos ir vartotojas negali jų atskirti.

Vienas iš esminių skirtingų medžiagų naudojimo aspektų yra tai, kad padidėja pakuotės medžiagos patvarumas, lankstumas ir produkto apsauga. Tokių pakavimo medžiagų pavyzdžiai yra laminuotos arba metalizuotos polimerinės pakuotės, pavyzdžiui, lizdinės vaistų pakuotės, šokolado pakuotės ir kt. [45].

1-ame paveikslėlyje pavaizduotas bendras SP sluoksnių išdėstymas. Kiekvienas sluoksnis atlieka skirtingą funkciją. SP struktūra gali skirtis priklausomai nuo gaminio ir gamintojo [50, 51].



1 pav. Pagrindiniai daugiasluoksnių lanksčiųjų pakuočių komponentai

1.5. Pakavimo medžiagų poveikis aplinkai

Dėl didėjančios pakuočių paklausos sparčiai didėja jų poveikis aplinkai. Didėjanti vartojimo produktų paklausa skatina pakuočių medžiagų gamybą, o tai savo ruožtu didina pakuočių atliekų susidarymą [61].

Nors šiandien yra daugybė atliekų apdorojimo technologijų ir įrangos, kasmet sąvartynuose išmetama milijardai tonų plastiko, o tai savo ruožtu dėl neobjektyvių kontrolės priemonių lemia kenksmingų medžiagų patekimą į aplinką. Kita vertus, dėl to prarandama daug gamtinių išteklių [64].

1.6. Gyvavimo ciklo vertinimas pakuočių pramonėje

Pakuočių sektoriuje aktyviai taikomas gyvavimo ciklo analizės (GCA) metodas, kuriuo siekiama įvertinti galimą pakuočių medžiagų poveikį aplinkai per visą gyvavimo ciklo laikotarpį [59]. Buvo atliktas išsamus įvairių pakuočių sistemų poveikio aplinkai, įskaitant plastikinių pakuočių poveikį aplinkai, GCA tyrimas [84]. Bendroje pakuočių medžiagų poveikio aplinkai dalyje 2–5 proc. sudaro maisto pakuočių ir apie 25 proc. gėrimų pakuočių atliekos [26].

1.7. Bendrieji sudėtinių pakuočių atliekų rūšiavimo būdai

Remiantis literatūros duomenimis, ankstesniais metais aliuminio ir polimero sluoksniams atskirti buvo naudojami keli perskyrimo metodai (terminis, fizikinis ir perskyrimas tirpikliais).

Korkmaz [115] naudojo pirolizės būdą, skirtą 400–600 °C temperatūroje apdoroti sudėtines pakuočių medžiagas. Po perdirbimo proceso būdavo pašalinamas grynas aliuminis. Produkte taip pat buvo nepageidaujamų dujų, anglies likučių ir dervos [116]. Ang [23] naudojo hidrometalurgijos procesą su natrio hidroksidu 70°C temperatūroje aliuminio atgavimui iš lizdinių vaistų pakuočių atliekų nuosėdų. Procesas truko apie 1 valandą 20 minučių [117]. *Pellenc ST* įmonė sukūrė smulkiojo rūšiavimo platformą, skirtą skirtingų medžiagų sluoksnelių (nuo 4 iki 20 mm dydžio) perskyrimui. Taikant naujas *Pellenc* magnetinio tankio perskyrimo technologijas, daugialypės proceso sistemos feromagnetinio skysčio viduje kūrimui yra naudojamas įvairaus piltinio tankio diapazonas. Proceso srautą sudaro praskiestas mišinys (H_2O, juodasis oksidas) ir magnetinis laukas [122]. Rodriguezas-Gomezas [132] aliuminio ir PE atskyrimui iš tetrapakų naudojo panaudotą augalinį aliejų. Šio proceso pagrindinis tikslas buvo gaminti produktus mažesnėmis sąnaudomis, naudojant mažiau energijos ir mažiau žaliavų. Kulkarni [133] naudojo naujovišką, gryną ir superkritinį vandenį, S. Favaro [116] naudojo superkritinį etanolį PET ir aliuminio kompozitų medžiagai apdoroti.

Apibendrinant visus įprastus sudėtinių pakuočių atliekų atskyrimo metodus, galima teigti, kad daugumoje atskyrimo procesų galima išgauti daugiausiai geros kokybės aliuminio. Deja, polimerinė frakcija nebuvo išgauta arba buvo išgauta prastos kokybės. Kiti trūkumai – tai, pavyzdžiui, didelė kaina, mažas išgaunamų medžiagų kiekis, didelės energijos sąnaudos, įvairi tarša (dujų išmetimas, vandens tarša ir kt.).

1.8. Literatūros apžvalgos santrauka

Tyrimai rodo, kad sudėtinių pakuočių atliekos (SPA) vis dar yra rimta šių dienų problema. Taip yra dėl to, kad trūksta perdirbimo metodų, o atliekų šalinimo sistema nėra ideali. Sąvartynai yra įprastas atliekų šalinimo būdas, ir didžioji dalis sudėtinių pakuočių atliekų yra deginamos. Šis būdas gali turėti įtakos žmonių sveikatai ir sukelti aplinkosaugos problemų. Todėl neatidėliotinas uždavinys – rasti ir sukurti tinkamą atliekų apdorojimo technologiją šios rūšies atliekoms tvarkyti.

Apibendrinant esamus atskyrimo metodus, galima teigti, kad šiuo metu atskyrimo sąnaudos yra didelės, aliuminio atgaunama nedaug, o perskyrimo greitis yra mažas. Be to, taikant daugumą perskyrimo metodų, neatsižvelgiama į svarbią problemą, t. y. aliuminio folija visiškai neatskiriama nuo plastiko sluoksnio.

Todėl šioje disertacijoje nusprendžiau daugiausia dėmesio skirti apdorojimo tirpikliais metodo plėtojimui, naudojant konkrečius literatūroje aprašytus tirpiklius, nes apžvelgti šios temos tyrimai atskleidė kai kuriuos šio metodo trūkumus ir iki šiol neištirtus aspektus.

2. MEDŽIAGOS IR METODAI

Tyrimo metu buvo atlikti trys eksperimentai, kurių metu daugiausia dėmesio skirta atliekų apdorojimui tirpikliais. Buvo atrinktos skirtingos sudėtinių pakuočių atliekos (SPA), atsižvelgiant į jų populiarumo tarp vartotojų lygį: šešių rūšių lizdinių vaistų pakuočių atliekos (LVPA) ir šešių rūšių daugiasluoksnių lanksčių pakuočių atliekos (DLPA). Visiems bandiniams buvo parinktos optimalios sąlygos: bandinio dydis nuo 2 cm^2 iki 10 cm^2, temperatūra nuo 30 iki 90 °C (galutinis eksperimentas atliktas žemesnėje 40–50 °C temperatūroje), kietos medžiagos ir skysčio santykis 1:3 g/ml.

2.1. Naudojamos medžiagos

Tyrimo metu buvo naudojami įvairūs tirpikliai: N,N-dimetilcikloheksilaminas (DMCHA), etanolis, etilacetatas, toluenas, acetonas, dimetilformamidas (DMF), skruzdžių rūgštis, acto rūgštis, azoto rūgštis.

2.2. Metalų ir polimerų analizės instrumentiniai metodai

FTIR buvo naudojama išskirtiems polimerams, cheminėms medžiagoms ir regeneruojantiems tirpikliams analizuoti ir identifikuoti. Apdorotų metalo sluoksnių cheminei sudėčiai tirti naudota skenuojanti elektroninė mikroskopija (SEM) ir energiją išsklaidanti rentgeno spektroskopija (EIRS). Metalografinis mikroskopas buvo naudojamas aliuminio dažiklio atskyrimui nuo polimerinių sluoksnių ir kitoms pakuočių atliekų savybėms tirti. TGA naudota atgautų polimerų terminiam stabilumui ir stiklėjimo temperatūrai patikrinti.

2.3. 1-ias eksperimentas. Sudėtinių pakuočių atliekų atskyrimas naudojant įvairius tirpiklius[3]

Buvo naudojami penki SPA bandiniai (LVPA ir DLPA), tirpikliai (etilacetatas, etanolis, toluenas, acetonas, DMF; rūgštys: CH_2O_2, acto rūgštis ir HNO_3 (45 %, 50 % ir 65 %)), taip pat naudotas tirpiklių mišinys (benzenas-etanolis-H_2O (30:20:50).

Perskyrimo tirpikliais procesas buvo vykdomas pagal pasirinktas optimalias sąlygas. Visų bandinių sluoksniai pradėjo atsiskirti vienas nuo kito po to, kai buvo ištirpintas sandariklio sluoksnis. Pagrindinė medžiaga, dangos ir kiti sluoksniai buvo perskirti ir išskirti iš tirpiklio. Galiausiai, filtruojant iš tirpiklio buvo išskirtos likusios sudedamosios dalys.

2.4. 2-as eksperimentas. Lizdinių vaistų pakuočių atliekų perskyrimas DMCHA[1]

Tyrimams naudojami analitinės klasės reagentai yra DMCHA.. Šešios skirtingos LVPA rūšys buvo surinktos iš Lietuvos vietinių vaistinių atliekų. Siekiant paruošti FLPA atskyrimui, bandiniai buvo nuplauti ir nuskalauti distiliuotu vandeniu, kad būtų pašalinti bet kokie priedai, ir po to 24 val. džiovinti kambario temperatūroje.

Remiantis Samorì [102] aprašytu metodu, kietosios medžiagos ir skysčio santykis buvo 1:3 g/ml. Kolba su DMCHA ir LVPA bandiniais buvo panardinta į ultragarso vonią su žemesnės temperatūros (40, 50, 60 ir 80 °C) vibruojančiu skysčiu (distiliuotu vandeniu); optimali temperatūra pasirinkta atsižvelgiant į galutinę atskirtos plėvelės susidarymo būklę; FLPA bandinių paruošimo procedūra ir tirpinimo seka parodyta 2 pav. Centrifugavimo būdu atskirtos aliuminio plėvelės nuo kitų plastikinių plėvelių. Polimerų išskyrimui ir DMCHA regeneravimui panaudotas tirpiklis buvo supiltas į dvigubai didesnį H_2O tūrį ir atšaldytas ledo vonelėje. Tada į mišinį kelias valandas buvo leidžiamas CO_2. Tai buvo atlikta pagal Samorì [102]. Po to sandarinimo sluoksnis sukietėjo ir filtruojant buvo surinktas kaip nuosėdos; regeneracijos procesas buvo pakartotas du kartus.

2 pav. Lizdinių vaistų pakuočių atliekų apdorojimo schema

2.5. 3-as eksperimentas. Daugiasluoksnių lanksčių pakuočių perskyrimas naudojant DMCHA[2]

Eksperimentui buvo naudojamas DMCHA. DLPA buvo atrinktos atsižvelgiant į daugiausiai ES vartojamus maisto produktus tam tikro tipo pakuotėse: bulvių traškučių, šokolado batonėlių, kepinių, maltos kavos, ledų ir sausainių.

Šiame tyrime buvo atliekami preliminarūs eksperimentai, esant pastoviam kietosios medžiagos ir skysčio santykiui 1:3 g/ml - 1 [102] ir trims skirtingoms temperatūroms: 50 °C, 70 °C ir 90 °C. Nors aukščiausia temperatūra leido pasiekti greičiausią atskyrimo laiką, po apdorojimo bespalvių plėvelių išvaizda pasikeitė į geltoną (apdorotos plėvelės pradėjo irti). Sumažinus temperatūrą, gautos polimerinės plėvelės išliko bespalvės. Todėl paskutiniai eksperimentai buvo atlikti esant 1:3 g/ml santykiui ir 1 °C ir 50 °C temperatūrai. Atskyrimo procesas buvo atliekamas taikant kombinuotą apdorojimą per septynis etapus (3 pav.).

3 pav. Daugiasluoksnių lanksčių pakuočių atliekų atskyrimo schema

A. bandinių paruošimas perskyrimo procesui, t. y. bandinių supjaustymas mažais gabalėliais;
B. dangos sluoksnių, įskaitant spausdinimo rašalą ir dažus, tirpinimas;
C. barjerinis sluoksnis pradėjo atsiskirti nuo išorinio sluoksnio; (3A pav.);
D. iš tirpalo buvo surinktos plūduriuojančios polimero plėvelės, o dribsnių formos aliuminis ir dalelės nusodinti panaudojus centrifugavimą; (3B pav.);
E. iš tirpalo buvo surinktas rašalo ir dažų polimeras; sukietėjusios rašalo ir dažų dalelės išskirtos filtruojant;
F. ankstesnis etapas buvo pakartotas, kad būtų išskirtas sandarinimo polimeras;
G. galiausiai regeneruotas tirpiklis (3C pav.).

2.6. Sukurtos technologijos aplinkosauginiai ir ekonominiai rodikliai[1;2]

Perdirbimo technologijos efektyvumą galima įvertinti pagal perdirbimo lygį, išteklių naudojimo efektyvumą, ekonominę naudą ir išmetamų šiltnamio efektą sukeliančių dujų kiekį. Remiantis laboratoriniais eksperimentais, sukurtos technologijos lygis medžiagų atgavimo ir perdirbamumo požiūriu yra >99 %, o atitinkamai standartinės technologijos lygis yra gerokai mažesnis nei <66 %. Vertinant išteklių naudojimo efektyvumą, proceso pabaigoje galima atgauti bent penkias skirtingas geros būklės žaliavas ir jas naudoti įvairiose srityse. Pagal kilovatvalandės metrui matavimus energijos sąnaudos buvo 73 J/k s; tirpiklis laikytas pakartotinai naudotina medžiaga ir į tirpiklio sąnaudas neatsižvelgta; pajamos apskaičiuotos remiantis vidutinėmis rinkos ir literatūroje pateikiamomis vertėmis.

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[1] Atkurta iš [53] nuorodos, gavus Elsevier leidimą.

[2] Atkurta iš [1] nuorodos, gavus Royal Society of Chemistry leidimą.

Kalbant apie IŠESDK apdorojant KHT, Samorì [102] ištyrė sukurtos sistemos IŠESDK ir rezultatai parodė, kad IŠESDK, palyginti su tradiciniais metodais, gerokai sumažėjo. Šiame darbe kiekvienos išgaunamos medžiagos IŠESDK buvo apskaičiuotas, atsižvelgiant į vidutines literatūroje pateiktas vertes.

3. REZULTATAI IR DISKUSIJA

3.1. 1-ias eksperimentas. Lizdinių vaistų pakuočių atliekų (LVPA) ir daugiasluoksnių lanksčių pakuočių atliekų (DLPA) perskyrimo rezultatai naudojant įvairius tirpiklius[3]

LVPA apdorojimui buvo naudojami aštuoni skirtingi tirpikliai ir vienas mišrus organinis tirpiklis. DLPA buvo naudojami tie patys tirpikliai, išskyrus DMF, mišrus organinis tirpiklis ir skruzdžių rūgštis.

LVPA ir DLPA bandinių perskyrimas *etilacetatu* ir *etanoliu* buvo sėkmingas iš dalies. Kai kurie sluoksniai neatsiskyrė, o du sluoksnius reikėjo sudėti vieną ant kito. Šio proceso metu atgauti mažiausiai trys sluoksniai: išoriniai polimero sluoksniai, plonas skaidrus polimero sluoksnis ir polimero sluoksnis su dažais ir aliuminiu.

LVPA bandiniams naudotas *mišrus organinis tirpiklis* (benzenas, etanolis ir vanduo (30:20:50)). Gauti rezultatai parodė, kad polimerinė frakcija ir aliuminio sluoksniai buvo atskirti, tačiau spausdinimo dažai nebuvo pašalinti, o polimerai buvo atskirti kartu.

Visi LVPA ir DLPA bandiniai buvo apdoroti *acto rūgštimi, skruzdžių rūgštimi, DMF ir toluenu*. Pirmoji atskyrimo proceso dalis buvo panaši, tačiau pratęsus eksperimentą, aukštesnėje temperatūroje aliuminio ir polimerų sluoksniai pradėjo tirpti visuose naudotuose tirpikliuose. Tačiau aliuminio nuostoliai buvo nedideli, todėl galim teigti, kad tokie aliuminio masės nuostoliai gali būti priimtini apdorojant pramonines pakuotes.

Visi SPA bandiniai buvo atskirti *acetonu*. Galima paminėti, kad LVPA atskyrimo laikas sutrumpėjo, o DLPAa ir DLPAb atveju laiko intervalas šiek tiek pailgėjo, tačiau dėl greitesnio atskyrimo buvo gauta mišri polimerinė frakcija, kurią buvo sunku atskirti.

Koncentruota azoto rūgštis (45 %, 50 % ir 65 %) buvo naudojama visiems LVPA ir DLPA bandiniams. Atskyrimas naudojant 45 % ir 50 % azoto rūgštį vyko ilgai. 65% koncentracijos azoto rūgštis buvo sėkmingai panaudota visų rūšių pakuočių atliekoms perskirti. Supjaustyti bandiniai buvo iš dalies arba visiškai užpilami tirpikliu ir uždaromi talpoje. Šis procesas buvo sėkmingas. Iš LVPA ir DLPA mažiausiai buvo atgauti dviejų sluoksnių polimeras ir aliuminis.

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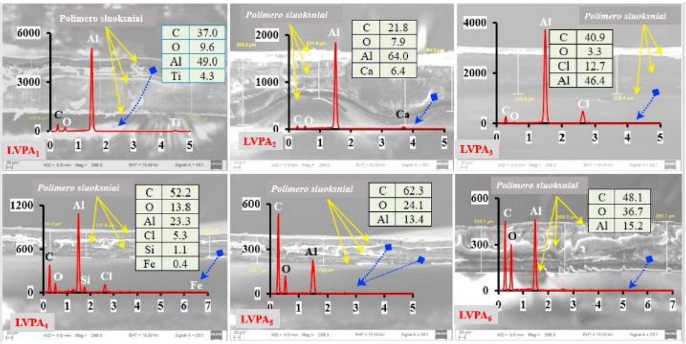
[3] [3, 135] nuorodos

3.2. 2-as eksperimentas. Farmacinių lizdinių plokštelių atliekų atskyrimas naudojant DMCHA[1]

4-ame paveikslėlyje pavaizduota kiekvienos rūšies LVPA struktūra ir pagrindinė elementinė sudėtis, gauta SEM-EIRS metodu.



4 pav. LVPA bandinių SEM-EIRS analizė.

Visuose bandiniuose buvo keli sluoksniai. Visuose bandiniuose buvo tik vienas aliuminio folijos sluoksnis, išskyrus LVPA5, kuriame buvo dvigubas aliuminio sluoksnis. Be to, visais atvejais aliuminio sluoksnį(-ius) gaubė polimerinė danga; dėl užterštumo organinėmis medžiagomis, taip pat dėl rastų priedų (Ti, Si, Fe) labai skyrėsi aliuminio grynumas (13–64 % masės). Bendras LVPA bandinių storis svyravo nuo 130 iki 250 µm.

Atskyrimo proceso pabaigoje visi visų bandinių PVC sluoksniai ir aliuminio folijos sluoksniai buvo atskirti panašiomis formomis arba mažais gabalėliais, o dangos sluoksniai buvo ištirpinti tirpiklyje ir surinkti kaip nuosėdos. Delaminavimo mechanizme pastebėta, kad pirmiausia dėl silpnesnių adhezinių ryšių atsiskyrė spausdinimo rašalas.

Metalografiniu mikroskopu buvo tiriamas ištirpinimo procesas, spausdinimo dažų ir aliuminio plėvelių atskyrimas nuo polimerinių komponentų ir gautų aliuminio sluoksnių morfologija. 5-ame paveikslėlyje parodyta, kad visuose bandiniuose dėl jų organinės prigimties pagrindiniai elementai buvo C ir O, taip pat rasta kai kurių metalinių elementų, pavyzdžiui, Al, Cu ir Fe.

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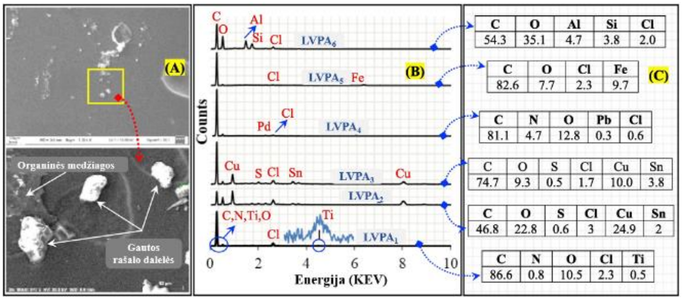
[1] Atkurta iš [53] nuorodos, gavus Elsevier leidimą.



C	O	Al	Si	Cl
54.3	35.1	4.7	3.8	2.0

C	O	Cl	Fe
82.6	7.7	2.3	9.7

C	N	O	Pb	Cl
81.1	4.7	12.8	0.3	0.6

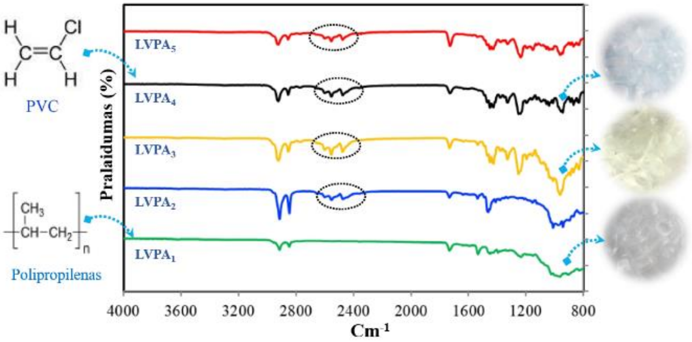
C	O	S	Cl	Cu	Sn
74.7	9.3	0.5	1.7	10.0	3.8

C	O	S	Cl	Cu	Sn
46.8	22.8	0.6	3	24.9	2

C	N	O	Cl	Ti
86.6	0.8	10.5	2.3	0.5

5 pav. Gautų spausdinimo dažų dalelių SEM vaizdai ir EIRS analizė

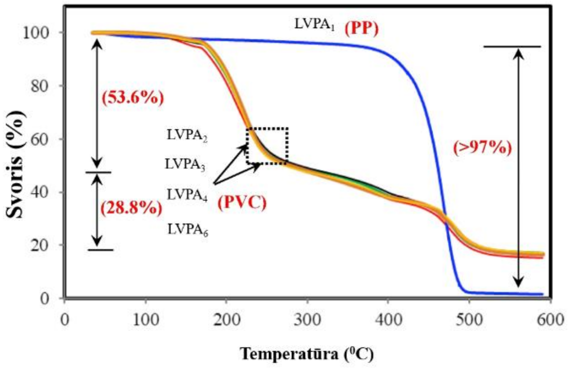
FTIR buvo naudojama polimerų cheminei struktūrai, funkcinėms grupėms ir gautoms polimerinių formavimo plėvelių rūšims nustatyti, taip nustatant gauto polimero rūšį. 6-ame paveikslėlyje pateikti kiekvieno LVPA bandinio spektrai.



6 pav. Gautų formavimo plėvelių (A-C) FTIR spektrai

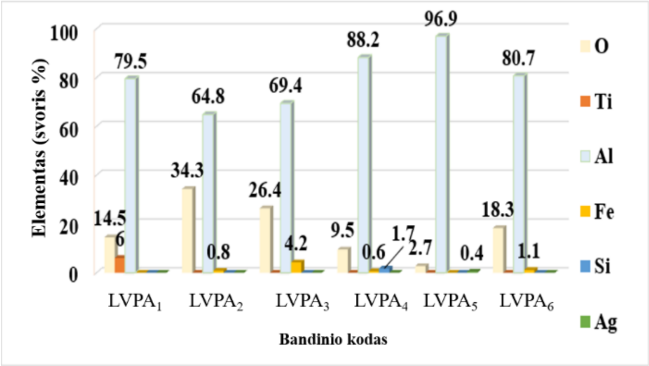
Šie rezultatai atitinka literatūros duomenis, iš kurių matyti, kad PVC ir PP plačiai naudojami kaip pagrindinės LVPA pakavimo medžiagos. Liejimo plėvelė paprastai yra bespalvė ir skaidri. Atsižvelgiama į gaminio dydį ir svorį, senėjimą, migraciją, kainą ir kt. Taip pat būtina atsižvelgti į pakuotės gamybos procesui įtaką darančius veiksnius [52].

7-ame paveikslėlyje pateikti atgautų LVPA bandinių formavimo plėvelių TGA analizės rezultatai. Pastebėtos dvi skilimo smailės (LVPA$_{2,3,4,6}$) 267 °C ir 452 °C temperatūroje, atitinkančios pradinius 53,6 % ir 28,8 % masės nuostolius, todėl bendras masės nuostolis yra 82,4 %. LVPA1 bandinio terminio stabilumo masės nuostolis buvo >97 %.



Pav. 7. Gautų PP ir PVC formavimo plėvelių termogravimetrinės kreivės

Po kalcinavimo išgauto aliuminio SEM ir EIRS analizės parodė, kad aliuminis yra pagrindinis elementas visuose LVPA bandiniuose, o jo grynumas svyruoja nuo 65 % iki 97 % masės (vidutiniškai ~81 % masės). Analizė taip pat parodė, kad atgauto aliuminio sluoksniuose yra įvairių elementų (Ti, Fe, Ag, Si). 8-ame paveikslėlyje pavaizduoti visi elementai, aptikti išgautose metalinėse plėvelėse.

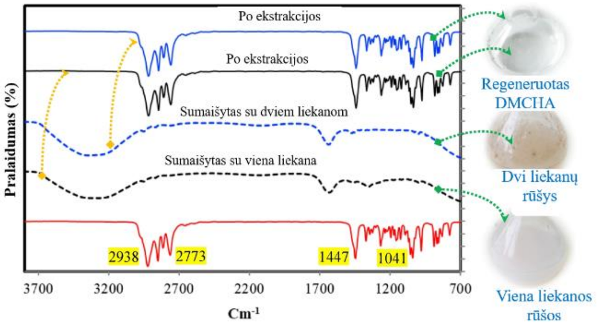


8 pav. Pagrindinių medžiagų sluoksnių, išgautų iš LVPA dengiančių sluoksnių, cheminė sudėtis

Be to, gautų dalelių (nuosėdų) morfologijai ir struktūrai ištirti naudotos SEM ir EIRS analizės; nuosėdos buvo adatinių kristalų formos (be aglomeracijos) ir vienodos struktūros, nes buvo reguliariai aušinamos. EIRS analizė parodė, kad nuosėdų sudėtyje yra C, O ir N, laikomų pagrindiniais organinių medžiagų elementais 182].

Pasibaigus atskyrimo procesui ir įvairių organinių nuosėdų ekstrakcijai, FTIR metodu buvo nustatyti regeneruoto tirpiklio specifiniai molekuliniai komponentai ir struktūros, taip patikrinant proceso tvarumą ir galimybę vėl naudoti tirpiklį. Kadangi sunku pavaizduoti visų bandinių FTIR rezultatus, analizuoti tik du bandiniai: viengubas aliuminio sluoksnis (LVPA2) ir dvigubas aliuminio sluoksnis (LVPA5);

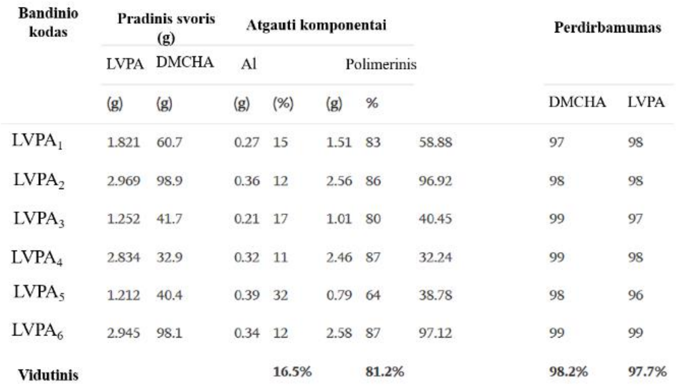
bandiniai buvo analizuoti du kartus: po nuosėdų ekstrakcijos ir po CO_2 ekstrakcijos, po kurios buvo pašalintas vanduo. 32-ame paveikslėlyje pateiktos regeneruoto DMCHA fotonuotraukos ir nenaudoto bei regeneruoto DMCHA FTIR spektrai.



Pav. 9. Nepanaudoto ir regeneruoto DMCHA FTIR spektrai

Naujojo metodo veiksmingumas buvo įvertintas remiantis DMCHA apdorotų LVPA masės balansais. 4-oje lentelėje pateiktas konkrečių LVPA bandinių aliuminio ir polimerinių sluoksnių perdirbamumo laipsnis ir vidutinis perdirbamumo laipsnis; aliuminio procentinė dalis sudarė 11–32 % masės (vid. 16,5 % masės); atgauti polimeriniai komponentai sudarė 81,2 % visos FLPA masės; perdirbimo laipsnis buvo 96–99 % (vid. 98 %). Daugiausia (~2 %) polimerinės frakcijos nuostolių patirta filtravimo proceso metu; DMCHA regeneracijos vidutinė norma buvo > 98 %.

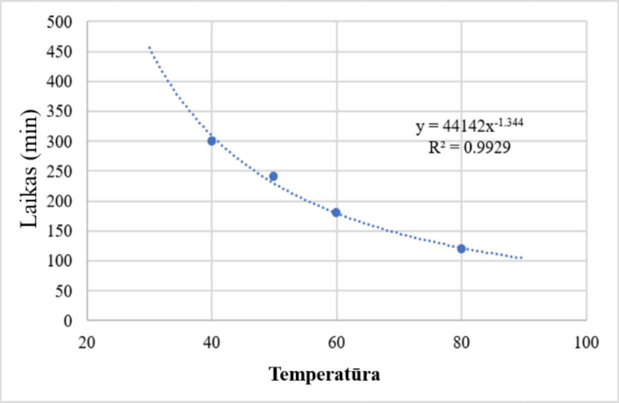
4 lentelė. Iš LVPA atgautų medžiagų ir regeneruoto DMCHA perdirbamumo lygis



Bandinio kodas	Pradinis svoris (g)		Atgauti komponentai					Perdirbamumas	
	LVPA	DMCHA	Al		Polimerinis				
	(g)	(g)	(g)	(%)	(g)	%		DMCHA	LVPA
$LVPA_1$	1.821	60.7	0.27	15	1.51	83	58.88	97	98
$LVPA_2$	2.969	98.9	0.36	12	2.56	86	96.92	98	98
$LVPA_3$	1.252	41.7	0.21	17	1.01	80	40.45	99	97
$LVPA_4$	2.834	32.9	0.32	11	2.46	87	32.24	99	98
$LVPA_5$	1.212	40.4	0.39	32	0.79	64	38.78	98	96
$LVPA_6$	2.945	98.1	0.34	12	2.58	87	97.12	99	99
Vidutinis				**16.5%**		**81.2%**		**98.2%**	**97.7%**

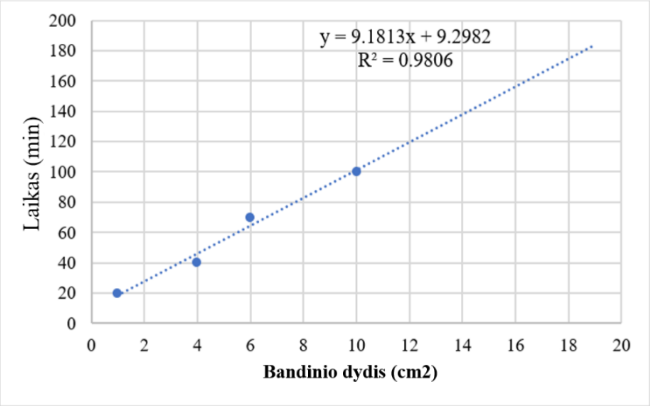
Eksperimentų metu FLPA atskyrimui buvo naudojama skirtinga temperatūra (40–80 °C); greitesnis atskyrimo laikas buvo pasiektas aukštoje temperatūroje, tačiau, kaip jau minėta, tai neigiamai paveikė polimero struktūrą ir sukėlė jo degradaciją.

Temperatūra buvo svarbus veiksnys atskyrimo procese.—(kaip parodyta 10 pav.). Remiantis eksperimento duomenimis, greitesnis perskyrimo laikas buvo gautas esant aukštesnei temperatūrai, todėl tarp temperatūros ir atskyrimo laiko buvo stipri priklausomybė, kai didėjant temperatūrai, didėjo perskyrimo laikas.



10 pav. LVPA perskyrimo laiko priklausomybė nuo temperatūros

Perskyrimo metu reikšmingas veiksnys buvo ir bandinio dydis. Ryšiui tarp kintamųjų įvertinti buvo apskaičiuotas Pirsono koreliacijos koeficientas (11 pav.); Empirinis modelis, susiejantis gydymo temperatūrą ir gydymo trukmę, buvo sukurtas kaip linijinė (galios) funkcija, ty TD = 9,1813xt ^ + 9,2982. Šis modelis paaiškina 99 % TD kitimo (determinacijos koeficientas R2 = 0,98). Nustatyta lygtis galioja imties dydžio diapazonui nuo 2 iki 20 cm^2.

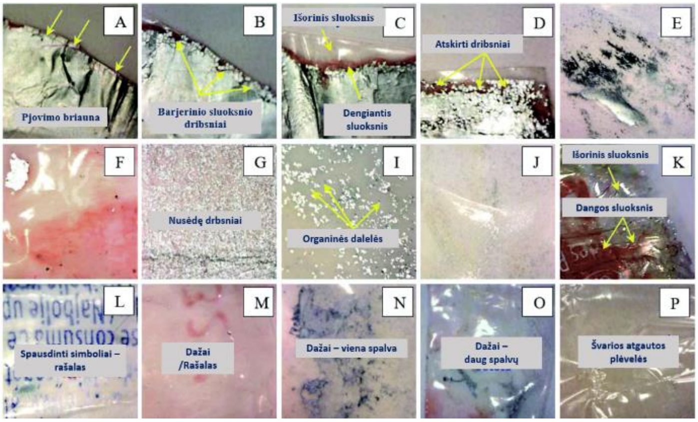


11 pav. LVPA perskyrimo laiko priklausomybė nuo bandinio dydžio

Koreliacija tarp šių dviejų kintamųjų nebuvo statistiškai reikšminga bandinių masės ir tirpiklio kiekio atžvilgiu.

3.3. 3-as eksperimentas. Daugiasluoksnių lanksčių pakuočių atskyrimas naudojant DMCHA [2]

Remiantis SEM analize, visi DLPA bandiniai yra daugiasluoksnės struktūros (aliuminio ir polimerų sluoksniai) (35–50 μm); juose yra tik vienas aliuminio folijos sluoksnis ir keli polimerų sluoksniai. Siekiant nustatyti galimus cheminės sudėties ir kitų savybių pokyčius, bandiniai buvo tiriami du kartus, t y. prieš apdorojimą ir po jo. 37-ame paveikslėlyje parodytas DLPA bandinių atskyrimo mechanizmas pagal sukurtą metodą, stebėtas metalografiniu mikroskopu 500 μm masteliu.



12 pav. DLPA metalografinės nuotraukos apdorojimo proceso metu

Iš DLPA atgautų barjerinių dribsnių formos prieš ir po kalcinavimo SEM vaizdai ir elementų žemėlapių analizė rodo, kad dribsniai buvo užteršti keliomis organinėmis medžiagomis, kurios buvo pašalintos po kalcinavimo proceso. Pagrindinis elementas atgautuose dribsniuose buvo aliuminis. EIRS elementų analizė rodo, kad iš visų DLPA bandinių atgauto aliuminio dribsnių grynumas buvo 88–92 % masės (vid. ~90 % masės).

FTIR analizė (13 pav.) rodo kiekvieno apdoroto bandinio spektrus; visuose bandiniuose rasta panašių funkcinių grupių, išskyrus DLPA4 bandinį; LVPA4 bandinyje rasta kelios skirtingos absorbcijos smailės 1709 cm-1 ir 1237 cm-1 smailės, priskiriamos atitinkamai esterio grupės C=O tempimo virpesiams ir C–O–C virpesiams.

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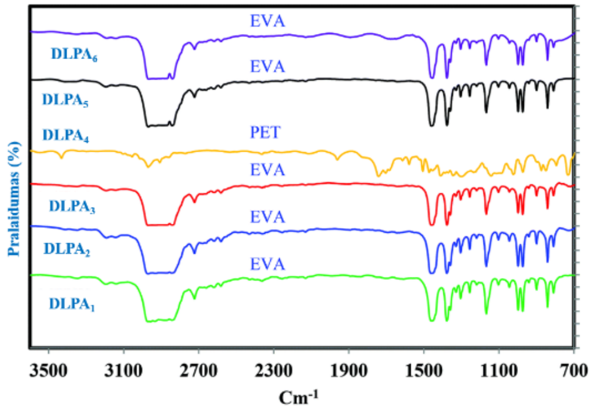
[2] Atkurta iš [1] nuorodos, gavus *Royal Society of Chemistry* leidimą.



13 pav. Atgautų išorinių DLPA sluoksnių FTIR spektrai

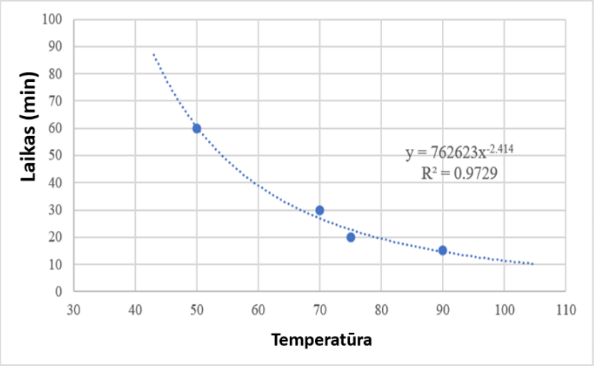
Iš DLPA bandinių atgautų plėvelių TGA analizė parodė tik vieną skilimo smailę, rodančią, kad bandinyje yra vieno tipo polimeras; DLPA4 bandinio pradinė skilimo temperatūra, būdinga PET, buvo 415 °C, o skilimo temperatūra buvo 428 °C. Be to, terminis stabilumas, išreikštas svorio nuostoliais, buvo >97 %.

Išskirtos nuosėdos neturėjo specifinės formos, t. y buvo sferinių dalelių, dribsnių formos plokštelių ir konglomeratų. Elementų žemėlapio analizė rodo, kad visoms dalelėms C, O ir Ca buvo pagrindiniai elementai. Be to, bandinyje buvo rasta metalinių elementų, daugiausiai titano (~97 % masės) ir aliuminio (~3 % masės).

Pirmojo perskyrimo metu buvo atskirti visi dažai, rašalas, dangos polimerai ir t. t., todėl tirpale liko tik vienos rūšies polimeras, t. y. sandarinimo sluoksnis. Galiausiai, po pirmojo ir antrojo perskyrimo nuosėdų panaudotas tirpalas per naktį buvo kaitinamas 40 °C temperatūroje, kad būtų pašalintas susimaišęs vanduo ir CO_2; atgautas DMCHA iš geltono vėl tapo bespalvis (pradinė spalva).

Konkrečių DLPA bandinių aliuminio ir polimerinių sluoksnių atgavimo lygis aliuminiui buvo 12–17 % masės (vid. 14,2 % masės), o polimerinių komponentų – 84,3 % masės. Daugiausia polimerinės frakcijos nuostolių patirta filtravimo proceso metu. Sukurtas metodas pasižymėjo dideliu DMCHA regeneracijos efektyvumu, o perdirbamumo lygis siekė > 98 %.

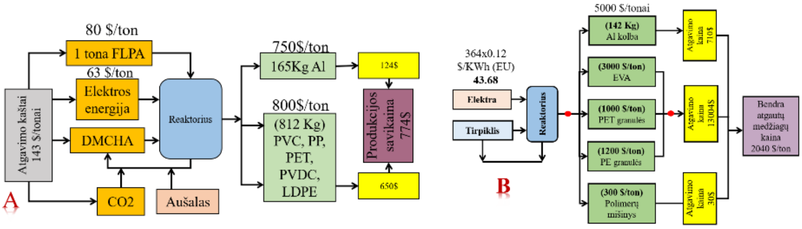
Eksperimento metu buvo naudojamos skirtingos temperatūros. (kaip parodyta 14 pav.). Empirinis modelis, susiejantis apdorojimo temperatūrą (kaip nepriklausomą kintamąjį) ir apdorojimo laiką (kaip priklausomą kintamąjį), buvo sukurtas kaip nelinijinė (galios) funkcija, ty TD = 762623xt ^ -2,414. Šis modelis paaiškina 97 % TD kitimo (determinacijos koeficientas R2 = 0,98). Nustatyta lygtis galioja temperatūros diapazonui nuo 40 iki 90^0C.



14 pav. DLPA perskyrimo laiko priklausomybė nuo temperatūros

3.4. Sukurtos technologijos aplinkosauginis ir ekonominis veiksmingumas ir efektyvumas[1,2]

Siekiant apskaičiuoti šios technologijos taikymo pramoniniu mastu naudingumą, buvo įvertintas sukurtos technologijos ekonominis efektyvumas, o vertinimas pagrįstas atgautomis žaliavomis. Kalbant apie gamybos sąnaudas, 15-ame paveikslėlyje parodytas sukurto FLPA ir DLPA apdorojimo ekonominis efektyvumas ir apribojimai. Taikant šią technologiją, galima gerokai padidinti perdirbimo naudą, jei kiekviena polimero rūšis būtų perdirbama atskirai, o apdorojimo sąnaudos gali būti sumažinamos, naudojant tvarų tirpiklį.



15 pav. Sukurtos technologijos FLPA (A) ir DLPA (B) ekonominiai rodikliai

Kiekvienos gautos medžiagos IŠESDK buvo apskaičiuotas remiantis vidutine literatūroje nurodyta verte. Mišraus plastiko dalis sudaro 10 % masės, kitos polimerų frakcijos – 75 % masės, o aliuminio folijos – 14 % masės. Remiantis šiais skaičiavimais, taikant šiuolaikines technologijas pramoniniu mastu galima sumažinti šiltnamio efektą sukeliančių dujų išmetimą iki 2266 kg CO_2 ekvivalento.

Vanduo yra esminis siūlomos technologijos elementas, naudojamas polimerams iš tirpalo išgauti. Šis metodas gali užtikrinti tirpiklio stabilumą, tačiau negali užtikrinti naudojamo vandens stabilumo. Vandeniui recirkuliuoti

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[1] Reproduced from Ref. [53] with permission from the Elsevier.

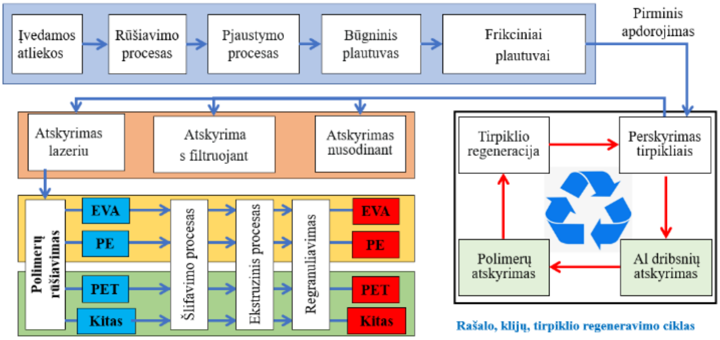
[2] Reproduced from Ref. [1] with permission from the Royal Society of Chemistry

rekomenduojama naudoti kondensatorių. Siūlomas metodas gali būti laikomas ekonomiškai efektyvia ir aplinkai nekenksminga strategija, įskaitant priemones, kuriomis skatinamas Europos perėjimas prie žiedinės ekonomikos, bei skatinamas tvarus ekonomikos augimas.

3.5. Sukurto metodo integravimas į žiedinės ekonomikos sistemą[1]

Didelis perdirbamumo lygis, pažangus dizainas, tinkamas perdirbimas ir atsakingas vartojimas laikomi pagrindiniais uždaviniais siekiant sutrumpinti pakuočių atliekų gyvavimo ciklą ir įgyvendinti ekonominio pranešimo (ES) naudą, pavyzdžiui, pagerinti aplinkos sveikatą ir ekonominį atsigavimą. Dėl šios priežasties buvo pasiūlyta technologija, sukurta ir taikoma pramoniniu mastu. Siūlomu planu siekiama maksimaliai padidinti perdirbamų medžiagų ir (arba) produktų naudojimą, visapusiškai panaudojant visas medžiagas ir žaliavas, produktus ir atliekas, taip sutrikdant sistemos veikimą, taupant energiją ir mažinant išmetamų dujų kiekį.

Pasiūlyta ekologiška bandomoji SPA perdirbimo gamykla. Remiantis šiuo tyrimu ir gautais rezultatais, buvo pasiūlyta statyti naują įrenginį, pagrįstą bendru perdirbimo proceso pabaigoje išgaunamų žaliavų kiekiu. Iš viso, galima gauti penkių rūšių žaliavų: mišrių polimerų miltelių, EVA plėvelės, PET plėvelės, PE miltelių ir dribsnių formos aliuminio. Panaudojus siūlomą metodą, gaunamų medžiagų skaičius gali būti didesnis. Tai priklauso nuo apdorojamos pakuotės struktūros ir bendro sluoksnių skaičiaus. Tokiu atveju reikia nežymiai pakoreguoti pagrindinę konstrukciją. 16-ame paveikslėlyje pavaizduota siūloma naujosios sistemos konstrukcija.



Pav. 16 Siūlomas naujos ekologiškos gamyklos planas

3.6. Siūlomas ekologiškos bandomosios SPA perdirbimo gamyklos planas[2]

Tyrime pasiūlyta aplinkai nekenksminga perdirbimo technologija, pagrįsta naujovišku dizainu. Tai sudėtinių pakuočių atliekų (SPA) perdirbimas tirpikliais. Siūlomas planas grindžiamas laboratorinių eksperimentų rezultatais, kurie siekiant nustatyti įvairių rūšių SPA cheminę sudėtį ir optimalias atskyrimo sąlygas [1].

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[2] Atkurta iš [1] nuorodos, gavus Royal Society of Chemistry leidimą.

IŠVADOS

Šis tyrimas buvo atliktas, remiantis darbo tikslu nustatyti aliuminio ir polimerų regeneravimo iš maisto, gėrimų ir vaistų pakuočių atliekų cheminį mechanizmą ir technologines sąlygas. Iš minėtų rezultatų galima apibendrinti šiuos aspektus:

1. Įvairūs SPA tipai, įskaitant LVPA ir DLPA, buvo apdoroti rūgštiniais ir organiniais tirpikliais. Nustatyta, kad atskyrimas šiuo metodu buvo atliktas su didele atgavimo norma. Proceso pabaigoje, esant optimalioms sąlygoms, galima atgauti daugiau kaip penkias skirtingas žaliavas, pavyzdžiui, aliuminį ir įvairių rūšių polimerus. Tiriant perskyrimo procesą, buvo pastebėta, kad pirmasis sluoksnis, atskirtas nuo bandinio, buvo rašalo sluoksnis, nes jis turi silpną jungtį. Vėliau vienas nuo kito atsiskyrė kiti sluoksniai, t. y. polimerai ir aliuminis. Po rašalo sluoksnių buvo atskirtas išorinis polimerų sluoksnis; vidutinė atskyrimo trukmė – 3 valandos. Be to, kai kuriais atvejais perskyrimui reikėjo papildomų jėgų, kad būtų pažeistas lipnus kitų sluoksnių ryšys, kuris yra gana stiprus ir kuriam atskirti reikėjo papildomo laiko. Pavyzdžiui, apdorojant DLPA, buvo naudojamas centrifugavimas, siekiant atskirti aliuminio dribsnius ir kitas daleles.
2. Buvo tiriamas temperatūros, tirpiklio koncentracijos, bandinio tūrio, atskyrimo laiko ir kietojo bei skystojo medžiagų santykio poveikis. Visiškas perskyrimas buvo pasiektas visomis tyrimo sąlygomis. Visiems bandiniams buvo pasirinktos optimalios sąlygos; bandinio dydis buvo nuo 2 cm^2 iki 20 cm^2; temperatūra buvo nuo 30 °C iki 900 °C (galutinis eksperimentas atliktas žemoje 40–500 °C temperatūroje); kietųjų medžiagų ir skysčio santykis buvo 1:3 g/ml. Temperatūra ir bandinio dydis buvo svarbūs veiksniai atskyrimo proceso metu. Kai temperatūra didėjo, perskyrimo laikas trumpėjo. Tačiau kai bandinio dydis didėjo, atskyrimo laikas taip pat ilgėjo. Be to, esant aukštai temperatūrai, perskyrimo laikas buvo greitesnis, tačiau polimeras pradėdavo irti. Taigi visi eksperimentai buvo atliekami žemoje temperatūroje. Kietųjų medžiagų ir skysčių santykis bei koncentracija neturi didelės įtakos perskyrimo laikui.
3. Apdorojant SPA, gautas medžiagas galima naudoti įvairiose pramonės šakose. Šiam procesui būdingas aukštas efektyvumo lygis, palyginus su tradiciniu procesu. Galima atgauti bent dviejų rūšių žaliavas, pavyzdžiui, aliuminį ir mišrius plastikus (su terminio skilimo suderinamumo apribojimais). Atgautas komponentas gali būti naudojamas miltelinėje metalurgijoje. Taip pat polimeriniai komponentai buvo atstovaujami mišrių polimerų (rašalo, dažų, klijų ir kt.), EVA plėvelių, PE miltelių, PET plėvelių ir t. t. Jie kartu galėtų būti naudojami lengvoms reikmėms. Polivinilchloridas buvo reikšminga polimero dalis FLPA. Jo kokybė buvo kaip ir pirminio polimero, mažai suyrančio. Aliuminio plėvelės grynumas buvo nuo 65 iki 97 % masės (vidutiniškai 81 % masės). Be to, elementinė analizė parodė, kad gautuose aliuminio sluoksniuose yra keletas elementų: nedideli kiekiai Ti, Fe, sidabro (Ag) ir Si (0,4–6,0 % masės), naudojamų kokybei pagerinti. Todėl galima teigti, kad perdirbtas

aliuminis gali būti naudojamas įvairiose pramonės šakose. Gautų formuojančių plėvelių terminis stabilumas buvo beveik toks pat kaip ir pirminio polimero, o degradacijos greitis buvo nedidelis.

4. Laboratorinių eksperimentų metu sėkmingai atgauti visi SPA komponentai. Perdirbant LVPA, atgautas metalas sudarė 16,5 % masės. Aliuminis buvo pagrindinis elementas iš visų elementų, nemetalai sudarė 81,2 % masės. Todėl atgavimo lygis buvo gana aukštas – 96–99 %, o vidutiniškai 98 % (remiantis masės balansu) visose FLPA. Be to, daugiausia nuostolių (~2 %) filtravimo proceso metu patyrė polimerinė frakcija. DLPA sudėtyje atitinkamai buvo 14,2 % masės aliuminio ir 85,3 % masės polimerų frakcijos. Todėl visų DLPA regeneravimo lygis buvo palyginti aukštas, t. y. >99 % (remiantis masės balansu). DMCHA regeneravimas buvo labai efektyvus; jo regeneravimo lygis siekė > 98 %. Palyginus su pirminių žaliavų naudojimu gamyboje, antrinės žaliavos yra priimtinesnės. Apskaičiuota, kad bendra iš DLPA gautų medžiagų kaina buvo 2 040 USD už toną, o apskaičiuota finansinė nauda – 1 920 USD už toną.

Kaip minėta anksčiau, rezultatai rodo, kad SPA perskyrimas, naudojant įvairias chemines medžiagas, gali būti laikomas nauja ir perspektyvia alternatyva plastikams ir aliuminiui atskirti. Pakartotinis tirpiklių naudojimas (paprastų tirpiklių arba nevalytų tirpiklių), pagerina darbe pristatytą metodą ekonominiu ir aplinkosauginiu požiūriu. Taigi galima daryti išvadą, kad siūlomos technologijos įdiegimas gali paskatinti tvarumo ir žiedinės ekonomikos principų laikymąsi ir kartu įgyvendinti ES viziją kurti naujas technologijas.

REKOMENDACIJOS

Kadangi šiame siūlomame perdirbimo metode yra tam tikrų apribojimų atliekant išsamią GCA (pvz., DMCHA nėra GCA inventoriaus duomenų bazėje), būsimuose tyrimuose būtų naudinga atlikti ir išanalizuoti sudėtinių pakuočių atliekų perdirbimo su DMCHA tirpikliu gyvavimo ciklo vertinimo metodą bei ištirti ir nustatyti jo poveikį aplinkai ir žmonių sveikatai.

References

1. MUMLADZE, T., YOUSEF, S., TATARIANTS, M., KRIUKIENE, R., et al. Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents. *Green Chemistry*. 30 July 2018. Vol. 20, no. 15, p. 3604–3618. DOI 10.1039/c8gc01062e. https://pubs.rsc.org/en/content/articlehtml/2018/gc/c8gc01062e
2. MIETH, A. and SIMONEAU, C. *Report of an inter-laboratory comparison from the European Reference Laboratory for Food Contact Materials - Publications Office of the EU*. 2015. https://op.europa.eu/en/publication-detail/-/publication/25bad27e-e344-4b97-a8a6-007c6e27b1e9/language-en/format-PDF/source-search
3. MUMLADZE, T., TATARIANTS, M., RIMSAITE, A., YOUSEF, S., et al. Recycling of multilayer packaging foils by using different organic solvent. - Kauno technologijos universitetas. . 2019. https://vb.ktu.edu
4. EUROSTAT.EU. Packaging waste statistics - Statistics Explained. . October 2020. https://ec.europa.eu/eurostat/statistics-explained/index.php/Packaging_waste_statistics#Recycling_and_recovery_rates
5. EUROPEAN COMMISION. A European Strategy for Plastics in a Circular Economy COM/2018/028 final. . 2018. https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1516265440535&uri=COM:2018:28:FIN
6. WAGNER, J.R. and MARKS, S.B. Multilayer Flexible Packaging (Second Edition). In : *Multilayer Flexible Packaging: Second Edition*. Elsevier Inc., 2016. p. 3–13. ISBN 9780323371001.
7. *Plastics-the Facts 2019 An analysis of European plastics production, demand and waste data*. 2019. https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf
8. CLARK, S., JUNG, S. and LAMSAL, B. Food Processing: Principles and Applications: Second Edition. Wiley Blackwell, 2014. ISBN 9781118846315.
9. KARKHANIS, S.S., STARK, N.M., SABO, R.C. and MATUANA, L.M. Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films. *Composites Part A: Applied Science and Manufacturing*. 1 November 2018. Vol. 114, p. 204–211. DOI 10.1016/j.compositesa.2018.08.025.
10. SCHMID, M., DALLMANN, K., BUGNICOURT, E., CORDONI, D., et al. Properties of whey-protein-coated films and laminates as novel recyclable food packaging materials with excellent barrier properties. *International Journal of Polymer Science*. 2012. Vol. 2012. DOI 10.1155/2012/562381. https://www.hindawi.com/journals/ijps/2012/562381/
11. BORG, M.A. Clinical waste disposal-getting the facts right. *Journal of Hospital Infection*. 1 February 2007. Vol. 65, no. 2, p. 178–180. DOI 10.1016/j.jhin.2006.09.017.
12. BUGNICOURT, E., SCHMID, M., NERNEY, O.M., WILDNER, J., et al. Processing and validation of whey-protein-coated films and laminates at semi-industrial scale as novel recyclable food packaging materials with excellent barrier properties. *Advances in Materials Science and Engineering*. 2013. Vol. 2013. DOI 10.1155/2013/496207.
13. KOMILIS, D.P. Issues on medical waste management research. *Waste Management*.

1 February 2016. Vol. 48, p. 1–2. DOI 10.1016/j.wasman.2015.12.020.

14. SIRACUSA, V., INGRAO, C., LO GIUDICE, A., MBOHWA, C., et al. Environmental assessment of a multilayer polymer bag for food packaging and preservation: An LCA approach. *Food Research International*. 1 August 2014. Vol. 62, p. 151–161. DOI 10.1016/j.foodres.2014.02.010.
15. CHRISTENSSON, I. and CARLSSON, B. Packaging container laminate possessing fat resistance properties - Tetra Laval Holdings & Finance S.A. 1996. https://www.freepatentsonline.com/5520970.html
16. GENTE, V., LA MARCA, F., LUCCI, F. and MASSACCI, P. Electrical separation of plastics coming from special waste. *Waste Management*. 1 January 2003. Vol. 23, no. 10, p. 951–958. DOI 10.1016/S0956-053X(03)00088-6.
17. EEA. Waste recycling — European Environment Agency. . 2018. https://www.eea.europa.eu/data-and-maps/indicators/waste-recycling-1/assessment-1
18. European Environment Information and Observation Network — Eionet Portal. . https://www.eionet.europa.eu/
19. AMERICAN CHEMISTRY. *2015 United States National Postconsumer Plastic Bottle Recycling Report*. 2016. www.plasticsrecycling.orgwww.americanchemistry.com
20. Waste recycling — European Environment Agency. . https://www.eea.europa.eu/data-and-maps/indicators/waste-recycling-1/assessment-1
21. THE INTERNATIONAL ALUMINIUM INSTITUTE. Aluminium in Packaging – Life Cycle Data. . https://packaging.world-aluminium.org/facts/life-cycle-data/
22. WORLD ALUMINIUM-STATISTICS. World Aluminium — Primary Aluminium Production. . https://www.world-aluminium.org/statistics/primary-aluminium-production/#linegraph
23. EPA and US ENVIRONMENTAL PROTECTION AGENCY. *"Final Air Toxics Standards for Clay Ceramics Manufacturing, Glass Manufacturing, And Secondary Nonferrous Metals Processing Area Sources: Fact Sheet." EPA*. 2019. https://www.epa.gov/technical-air-pollution-resources
24. POPPENHEIMER, L. Aluminum Beverage Cans – Environmental Impact | Green Groundswell. . 2019. https://greengroundswell.com/aluminum-beverage-cans-environmental-impact/2014/07/17/
25. LUTTENBERGER, D., PUNCHARD, B. and MAISEVIČIŪTĖ-HAYDON, R. *Global Packaging Trends 2019*. 2019. https://www.mintel.com/global-packaging-trends-2019
26. Plastics - the Facts. *PlasticsEurope*. 2018. https://www.plasticseurope.org/en/resources/publications/619-plastics-facts-2018
27. Global Plastics, LLC – The Green Plastics Company. . https://www.globalplastics.net/
28. Recap 2020: Slowdown in production activities due to COVID19 let down primary aluminium demand & prices; Recovery began in H2; Aluminium Extrusion, Profiles, Price, Scrap, Recycling, Section. . https://www.alcircle.com/news/recap-2020-slowdown-in-production-activities-due-to-covid19-let-down-primary-aluminium-demand-prices-recovery-began-in-h2-62063
29. TISEO, I. Plastic Waste Worldwide - Statistics & Facts | Statista. . 2020. https://www.statista.com/topics/5401/global-plastic-waste/

30. TISEO, I. *Plastic waste in Europe - Statistics & Facts | Statista*. 2020. https://www.statista.com/topics/5141/plastic-waste-in-europe/
31. The Environmental Impact of Food Packaging | FoodPrint. . https://foodprint.org/issues/the-environmental-impact-of-food-packaging/
32. THOMPSON, R.C., MOORE, C.J., VOM SAAL, F.S. and SWAN, S.H. Plastics, the environment and human health: current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences*. 27 July 2009. Vol. 364, no. 1526, p. 2153–2166. DOI 10.1098/rstb.2009.0053. https://royalsocietypublishing.org/doi/10.1098/rstb.2009.0053
33. GONZÁLEZ-GARCÍA, S., SANYE-MENGUAL, E., LLORACH-MASANA, P., FEIJOO, G., et al. Sustainable Design of Packaging Materials. In : *Environmental Footprints and Eco-Design of Products and Processes*. Springer, 2016. p. 23–46.
34. VARUN, SHARMA, A. and NAUTIYAL, H. Environmental Impacts of Packaging Materials. In : *Environmental Footprints and Eco-Design of Products and Processes*. Springer, 2016. p. 115–137.
35. HELLSTRÖM, D., OLSSON, A. and NILSSON, F. Introduction to packaging. In : *Managing Packaging Design for Sustainable Development*. John Wiley & Sons, Ltd, 2016. p. 3–15.
36. HELLSTRÖM, D., OLSSON, A. and NILSSON, F. Fundamentals of Packaging Design. In : *Managing Packaging Design for Sustainable Development*. John Wiley & Sons, Ltd, 2016. p. 1–2. https://onlinelibrary.wiley.com/doi/full/10.1002/9781119151036.part1
37. LOCKAMY, A. A concejtlual framework for assessing strategic packaging decisions. *The International Journal of Logistics Management*. 1 January 1995. Vol. 6, no. 1, p. 51–60. DOI 10.1108/09574099510805251.
38. VARŽINSKAS, V. and MILČIUS, E. Sustainable Packaging: Concept, Materials, and Tools for Design. In : . Springer, Cham, 2020. p. 760–772. https://doi.org/10.1007/978-3-319-95726-5
39. LEWIS, H. Helen Lewis Research. . 2016. http://helenlewisresearch.com.au/
40. MARSH, K. and BUGUSU, B. Food packaging - Roles, materials, and environmental issues: Scientific status summary. *Journal of Food Science*. 1 April 2007. Vol. 72, no. 3, p. R39–R55. DOI 10.1111/j.1750-3841.2007.00301.x. https://onlinelibrary.wiley.com/doi/full/10.1111/j.1750-3841.2007.00301.x
41. POTTER, N.N. and HOTCHKISS, J.H. Food Science: Fifth Edition - Norman N. Potter, Joseph H. Hotchkiss - Google Books. . 2012. https://books.google.lt/books?id=GRQJAgAAQBAJ&redir_esc=y
42. DIRGAR, E. and ORAL, O. *PACKING TEXTILES AND THEIR APPLICATION AREAS*. [no date].
43. HELLSTRÖM, D. and OLSSON, A. Managing Packaging Design for Sustainable Development: A Compass for Strategic Directions | Wiley. 2017. ISBN 978-1-119-15093-0.
44. LINDH, H., WILLIAMS, H., OLSSON, A. and WIKSTRÖM, F. Elucidating the Indirect Contributions of Packaging to Sustainable Development: A Terminology of Packaging Functions and Features. *Packaging Technology and Science*. 1 April 2016. Vol. 29, no. 4–5, p. 225–246. DOI 10.1002/pts.2197. https://onlinelibrary.wiley.com/doi/full/10.1002/pts.2197
45. LEWIS, H. *The business case for packaging sustainability*. 2014. http://helenlewisresearch.com.au/category/publications/selected-reports-handbooks-

and-guidelines/

46. Packaging & the Environment - EUROPEN. . https://europen-packaging.eu/sustainability/packaging-environment.html
47. DIXON, J. *Packaging Materials 9. Multilayer Packaging for food and Beverages ILSI Europe Report Series RepoRt Commissioned by the ilsi Europe Packaging Materials Task Force*. 2011.
48. PIERGIOVANNI, L. and LIMBO, S. *Food Packaging Materials*. 2016. http://www.springer.com/series/11853
49. KLAIMAN, K., ORTEGA, D.L. and GARNACHE, C. Consumer preferences and demand for packaging material and recyclability. *Resources, Conservation and Recycling*. 1 December 2016. Vol. 115, p. 1–8. DOI 10.1016/j.resconrec.2016.08.021.
50. ALEXANDER H. TULLO. The cost of plastic packaging. *C&EN Global Enterprise*. 17 October 2016. Vol. 94, no. 41, p. 32–37. DOI 10.1021/cen-09441-cover. https://pubs.acs.org/doi/10.1021/cen-09441-cover
51. CINELLI, P., SCHMID, M., BUGNICOURT, E., COLTELLI, M.B., et al. Recyclability of PET/WPI/PE multilayer films by removal of whey protein isolate-based coatings with enzymatic detergents. *Materials*. 14 June 2016. Vol. 9, no. 6. DOI 10.3390/ma9060473. /pmc/articles/PMC5456749/?report=abstract
52. PILCHIK, R. Pharmaceutical Blister Packaging, Part I. . November 2000. http://pharmanet.com.br/pdf/blister.pdf
53. YOUSEF, S., MUMLADZE, T., TATARIANTS, M., KRIUKIENE, R., et al. Cleaner and profitable industrial technology for full recovery of metallic and non-metallic fraction of waste pharmaceutical blisters using switchable hydrophilicity solvents. *Journal of Cleaner Production*. 1 October 2018. Vol. 197, p. 379–392. DOI 10.1016/j.jclepro.2018.06.154.
54. LAMBERTI, M. and ESCHER, F. Aluminium Foil as a Food Packaging Material in Comparison with Other Materials. *Food Reviews International*. 28 September 2007. Vol. 23, no. 4, p. 407–433. DOI 10.1080/87559120701593830. http://www.tandfonline.com/doi/abs/10.1080/87559120701593830
55. MIETH, A., HOEKSTRA, E. and SIMONEAU, C. *JRC Publications Repository - Guidance for the identification of polymers in multilayer films used in food contact materials: User guide of selected practices to determine the nature of layers*. 2016. https://publications.jrc.ec.europa.eu/repository/handle/JRC100835
56. GOTRO, J. Recycle and Disposal of Plastic Food Packaging Waste 9: Some of the Challenges Facing the Business of Municipal Waste Sorting - Polymer Innovation Blog. . 2017. https://polymerinnovationblog.com/recycle-disposal-plastic-food-packaging-waste-9-challenges-facing-business-municipal-waste-sorting/
57. CULTER, J., KROHN, J. and TODD, W. Optimizing barrier performance of multi-layer PE films. *Packaging Technology and Engineering*. 2014. Vol. 8, no. 6, p. 30–32. http://www.pkg-guru.com/pdfiles/HDPE-tappi.pdf
58. GOTRO, J. Recycle and Disposal of Plastic Food Packaging Waste 8: More About Waste Plastic Sorting Technologies - Polymer Innovation Blog. . 2017. https://polymerinnovationblog.com/recycle-disposal-plastic-food-packaging-waste-8-waste-plastic-sorting-technologies/
59. NIAOUNAKIS, M. Polymers Used in Flexible Packaging. In : *Recycling of Flexible Plastic Packaging*. 1st Edition. 2019. p. 57–96. ISBN 9780128163351. https://www.elsevier.com/books/recycling-of-flexible-plastic-packaging/niaounakis/978-0-12-816335-1

60. MIETH, A. and SIMONEAU, C. *JRC Publications Repository - Report of an inter-laboratory comparison from the European Union Reference Laboratory for Food Contact Materials: ILC 02 2014 – Identifying the composition of multilayer plastic packaging films*. [no date]. https://publications.jrc.ec.europa.eu/repository/handle/JRC95333
61. RESTUCCIA, D., SPIZZIRRI, U.G., PARISI, O.I., CIRILLO, G., et al. New EU regulation aspects and global market of active and intelligent packaging for food industry applications. *Food Control*. 1 November 2010. Vol. 21, no. 11, p. 1425–1435. DOI 10.1016/j.foodcont.2010.04.028.
62. RADHAKRISHNAN, S. Environmental Implications of Reuse and Recycling of Packaging. In : *Environmental Footprints and Eco-Design of Products and Processes*. Springer, 2016. p. 165–192.
63. BERNARDIN, F.E. and RUTLEDGE, G.C. Simulation of mechanical properties of oriented glassy polystyrene. *Polymer*. 16 November 2007. Vol. 48, no. 24, p. 7211–7220. DOI 10.1016/j.polymer.2007.09.034.
64. KERRY, J.P., O'GRADY, M.N. and HOGAN, S.A. Past, current and potential utilisation of active and intelligent packaging systems for meat and muscle-based products: A review. *Meat Science*. 1 September 2006. Vol. 74, no. 1, p. 113–130. DOI 10.1016/j.meatsci.2006.04.024.
65. COLES, R. and KIRWAN, M. Food and Beverage Packaging Technology. Oxford, UK : Wiley-Blackwell, 2011. ISBN 9781444392180. http://doi.wiley.com/10.1002/9781444392180
66. CHIN, A.W. *Polymers for Innovative Food Packaging An Interactive Qualifying Project Report Submitted to the Faculty of Worcester Polytechnic Institute*. 2010. https://digital.wpi.edu/concern/student_works/ff365564x?locale=en
67. ARFIN, T. and SONAWANE, K. Bio-based materials: Past to future. In : *Bio-based Materials for Food Packaging: Green and Sustainable Advanced Packaging Materials*. Springer Singapore, 2018. p. 1–32. ISBN 9789811319099.
68. DIRECTIVE 94/62/EC. Directive 94/62/EC on packaging and packaging waste. . https://eur-lex.europa.eu/eli/dir/1994/62/oj
69. NIAOUNAKIS, M. Recycling of Flexible Plastic Packaging - 1st Edition. 2019. ISBN 9780128166031. https://www.elsevier.com/books/recycling-of-flexible-plastic-packaging/niaounakis/978-0-12-816335-1
70. GARCIA-GARCIA, G., RAHIMIFARD, S., MATHARU, A.S. and DUGMORE, T.I.J. Life-Cycle Assessment of Microwave-Assisted Pectin Extraction at Pilot Scale. *ACS Sustainable Chemistry and Engineering*. 4 March 2019. Vol. 7, no. 5, p. 5167–5175. DOI 10.1021/acssuschemeng.8b06052.
71. ROSS, S. and EVANS, D. The environmental effect of reusing and recycling a plastic-based packaging system. *Journal of Cleaner Production*. August 2003. Vol. 11, no. 5, p. 561–571. DOI 10.1016/S0959-6526(02)00089-6.
72. VIGNALI, G. Life-Cycle Assessment of Food-Packaging Systems. In : *Environmental Footprints and Eco-Design of Products and Processes*. Springer, 2016. p. 1–22. https://www.springer.com/gp/book/9789812879110
73. HUNT, R.G. and FRANKLIN, W.E. LCA - How it Came about - Personal Reflections on the Origin and the Development of LCA in the USA. *International Journal of Life Cycle Assessment*. 1996. Vol. 1, no. 1, p. 4–7. DOI 10.1007/BF02978624. https://link.springer.com/article/10.1007/BF02978624
74. HUANG, C.C. and MA, H.W. A multidimensional environmental evaluation of

packaging materials. *Science of the Total Environment*. 25 May 2004. Vol. 324, no. 1–3, p. 161–172. DOI 10.1016/j.scitotenv.2003.10.039.

75. WERNET, G., BAUER, C., STEUBING, B., REINHARD, J., et al. The ecoinvent database version 3 (part I): overview and methodology. *International Journal of Life Cycle Assessment*. 1 September 2016. Vol. 21, no. 9, p. 1218–1230. DOI 10.1007/s11367-016-1087-8. https://link.springer.com/article/10.1007/s11367-016-1087-8
76. ISO - ISO 14040:2006/Amd 1:2020 - Environmental management — Life cycle assessment — Principles and framework — Amendment 1. . https://www.iso.org/standard/76121.html
77. ISO - ISO 14044:2006/Amd 2:2020 - Environmental management — Life cycle assessment — Requirements and guidelines — Amendment 2. . https://www.iso.org/standard/76122.html
78. FLANIGAN, L. An AnAlysis of life CyCle Assessment in PACkAging for food & BeverAge APPliCAtions. . 2013.
79. VON FALKENSTEIN, E., WELLENREUTHER, F. and DETZEL, A. LCA studies comparing beverage cartons and alternative packaging: Can overall conclusions be drawn?. *International Journal of Life Cycle Assessment*. 27 November 2010. Vol. 15, no. 9, p. 938–945. DOI 10.1007/s11367-010-0218-x. www.ace.be/index.jsp?nodeId=10073&isoCode=de.
80. HUMBERT, S., ROSSI, V., MARGNI, M., JOLLIET, O., et al. Life cycle assessment of two baby food packaging alternatives: Glass jars vs. plastic pots. *International Journal of Life Cycle Assessment*. 20 March 2009. Vol. 14, no. 2, p. 95–106. DOI 10.1007/s11367-008-0052-6. https://link.springer.com/article/10.1007/s11367-008-0052-6
81. BRANDER, M., BURRITT, R.L. and CHRIST, K.L. Coupling attributional and consequential life cycle assessment: A matter of social responsibility. *Journal of Cleaner Production*. 1 April 2019. Vol. 215, p. 514–521. DOI 10.1016/j.jclepro.2019.01.066.
82. ASSOCIATES, F. *PEER REVIEWED FINAL REPORT LCI SUMMARY FOR EIGHT COFFEE PACKAGING SYSTEMS Prepared for THE PLASTICS DIVISION OF THE AMERICAN CHEMISTRY COUNCIL*. 2008.
83. VIGNALI, G. Life-Cycle Assessment of Food-Packaging Systems. In : *Environmental Footprints and Eco-Design of Products and Processes*. Springer, 2016. p. 1–22. https://link.springer.com/chapter/10.1007/978-981-287-913-4_1
84. MADIVAL, S., AURAS, R., SINGH, S.P. and NARAYAN, R. Assessment of the environmental profile of PLA, PET and PS clamshell containers using LCA methodology. *Journal of Cleaner Production*. 1 September 2009. Vol. 17, no. 13, p. 1183–1194. DOI 10.1016/j.jclepro.2009.03.015.
85. ZABANIOTOU, A. and KASSIDI, E. Life cycle assessment applied to egg packaging made from polystyrene and recycled paper. *Journal of Cleaner Production*. 1 August 2003. Vol. 11, no. 5, p. 549–559. DOI 10.1016/S0959-6526(02)00076-8.
86. ALMEIDA, C.M.V.B., RODRIGUES, A.J.M., BONILLA, S.H. and GIANNETTI, B.F. Emergy as a tool for Ecodesign: evaluating materials selection for beverage packages in Brazil. *Journal of Cleaner Production*. 1 January 2010. Vol. 18, no. 1, p. 32–43. DOI 10.1016/j.jclepro.2009.03.019.
87. BANAR, M., COKAYGIL, Z. and OZKAN, A. Life cycle assessment of solid waste management options for Eskisehir, Turkey. *Waste Management*. 1 January 2009.

Vol. 29, no. 1, p. 54–62. DOI 10.1016/j.wasman.2007.12.006.

88. MENDES, M.R., ARAMAKI, T. and HANAKI, K. Comparison of the environmental impact of incineration and landfilling in São Paulo City as determined by LCA. *Resources, Conservation and Recycling*. 1 April 2004. Vol. 41, no. 1, p. 47–63. DOI 10.1016/j.resconrec.2003.08.003.

89. DEN BOER, J., DEN BOER, E. and JAGER, J. LCA-IWM: A decision support tool for sustainability assessment of waste management systems. *Waste Management*. 1 January 2007. Vol. 27, no. 8, p. 1032–1045. DOI 10.1016/j.wasman.2007.02.022.

90. HONG, J., LI, X. and ZHAOJIE, C. Life cycle assessment of four municipal solid waste management scenarios in China. *Waste Management*. 1 November 2010. Vol. 30, no. 11, p. 2362–2369. DOI 10.1016/j.wasman.2010.03.038.

91. DIAZ, R. and WARITH, M. Life-cycle assessment of municipal solid wastes: Development of the WASTED model. *Waste Management*. 1 January 2006. Vol. 26, no. 8, p. 886–901. DOI 10.1016/j.wasman.2005.05.007.

92. FERREIRA, S., CABRAL, M., DA CRUZ, N.F., SIMÕES, P., et al. Life cycle assessment of a packaging waste recycling system in Portugal. *Waste Management*. 1 September 2014. Vol. 34, no. 9, p. 1725–1735. DOI 10.1016/j.wasman.2014.05.007.

93. KIRKEBY, J.T., BIRGISDOTTIR, H., BHANDER, G.S., HAUSCHILD, M., et al. Modelling of environmental impacts of solid waste landfilling within the life-cycle analysis program EASEWASTE. *Waste Management*. 1 January 2007. Vol. 27, no. 7, p. 961–970. DOI 10.1016/j.wasman.2006.06.017.

94. PETERS, G.M. and ROWLEY, H. V. Environmental comparison of biosolids management systems using life cycle assessment. *Environmental Science and Technology*. 15 April 2009. Vol. 43, no. 8, p. 2674–2679. DOI 10.1021/es802677t. https://pubs.acs.org/sharingguidelines

95. KHOO, H.H. Life cycle impact assessment of various waste conversion technologies. *Waste Management*. 1 June 2009. Vol. 29, no. 6, p. 1892–1900. DOI 10.1016/j.wasman.2008.12.020.

96. SCHMIDT, J.H., HOLM, P., MERRILD, A. and CHRISTENSEN, P. Life cycle assessment of the waste hierarchy - A Danish case study on waste paper. *Waste Management*. 1 January 2007. Vol. 27, no. 11, p. 1519–1530. DOI 10.1016/j.wasman.2006.09.004.

97. MERRILD, H., DAMGAARD, A. and CHRISTENSEN, T.H. Life cycle assessment of waste paper management: The importance of technology data and system boundaries in assessing recycling and incineration. *Resources, Conservation and Recycling*. 1 October 2008. Vol. 52, no. 12, p. 1391–1398. DOI 10.1016/j.resconrec.2008.08.004.

98. MOURAD, A.L., GARCIA, E.E.C., VILELA, G.B. and VON ZUBEN, F. Environmental effects from a recycling rate increase of cardboard of aseptic packaging system for milk using life cycle approach. *International Journal of Life Cycle Assessment*. 10 March 2008. Vol. 13, no. 2, p. 140–146. DOI 10.1065/lca2007.06.340. http://dx.doi.org/10.1065/lca2007.06.340

99. PARASKEVAS, D., KELLENS, K., VAN DE VOORDE, A., DEWULF, W., et al. Environmental Impact Analysis of Primary Aluminium Production at Country Level. In : *Procedia CIRP*. Elsevier B.V., 1 January 2016. p. 209–213.

100. XIE, M., LI, L., QIAO, Q., SUN, Q., et al. A comparative study on milk packaging using life cycle assessment: From PA-PE-Al laminate and polyethylene in China.

Journal of Cleaner Production. 1 November 2011. Vol. 19, no. 17–18, p. 2100–2106. DOI 10.1016/j.jclepro.2011.06.022.

101. XIE, M., QIAO, Q., SUN, Q. and ZHANG, L. Life cycle assessment of composite packaging waste management - A Chinese case study on aseptic packaging. *International Journal of Life Cycle Assessment*. 1 March 2013. Vol. 18, no. 3, p. 626–635. DOI 10.1007/s11367-012-0516-6. https://link.springer.com/article/10.1007/s11367-012-0516-6
102. SAMORÌ, C., CESPI, D., BLAIR, P., GALLETTI, P., et al. Application of switchable hydrophilicity solvents for recycling multilayer packaging materials. *Green Chemistry*. 3 April 2017. Vol. 19, no. 7, p. 1714–1720. DOI 10.1039/c6gc03535c. https://pubs.rsc.org/en/content/articlehtml/2017/gc/c6gc03535c
103. XIE, M., BAI, W., BAI, L., SUN, X., et al. Life cycle assessment of the recycling of Al-PE (a laminated foil made from polyethylene and aluminum foil) composite packaging waste. *Journal of Cleaner Production*. 20 January 2016. Vol. 112, p. 4430–4434. DOI 10.1016/j.jclepro.2015.08.067.
104. ARGERICH, J. and HOLMBERG, P. *Life Cycle Assessment A Comparison Between a New Produced and a Remanufactured Rear Subframe*. [no date]. http://www.teknat.uu.se/student
105. SALA, S. and CERUTTI, A.K. Development of a weighting approach for the Environmental Footprint. . 2018. DOI 10.2760/446145. https://ec.europa.eu/jrc
106. *Product Environmental Footprint Category*. [no date]. https://ec.europa.eu/environment/eussd/smgp/pdf/PEFCR_guidance_v6.3.pdf
107. FAZIO, S., CASTELLANI, V., SALA, S., SCHAU, E., et al. *JRC Publications Repository - Supporting information to the characterisation factors of recommended EF Life Cycle Impact Assessment methods: New methods and differences with ILCD*. [no date]. https://publications.jrc.ec.europa.eu/repository/handle/JRC109369
108. GUILLARD, V., GAUCEL, S., FORNACIARI, C., ANGELLIER-COUSSY, H., et al. The Next Generation of Sustainable Food Packaging to Preserve Our Environment in a Circular Economy Context. *Frontiers in Nutrition*. 4 December 2018. Vol. 5, p. 121. DOI 10.3389/fnut.2018.00121. https://www.frontiersin.org/article/10.3389/fnut.2018.00121/full
109. ZHAO, W., VAN DER VOET, E., HUPPES, G. and ZHANG, Y. Comparative life cycle assessments of incineration and non-incineration treatments for medical waste. *International Journal of Life Cycle Assessment*. 16 March 2009. Vol. 14, no. 2, p. 114–121. DOI 10.1007/s11367-008-0049-1. https://link.springer.com/article/10.1007/s11367-008-0049-1
110. NEMA, K.S. and GANESHPRASAD, K.S. Plasma pyrolysis of medical waste. *Current science* . 2002. Vol. 83, no. 3. https://www.researchgate.net/publication/240636751_Plasma_pyrolysis_of_medical_waste
111. CERVANTES-REYES, A., NÚÑEZ-PINEDA, A., BARRERA-DÍAZ, C., VARELA-GUERRERO, V., et al. Solvent effect in the polyethylene recovery from multilayer postconsumer aseptic packaging. *Waste Management*. 1 April 2015. Vol. 38, no. 1, p. 61–64. DOI 10.1016/j.wasman.2015.01.034.
112. ZHANG, S., LUO, K., ZHANG, L., MEI, X., et al. Interfacial separation and characterization of Al-PE composites during delamination of post-consumer Tetra Pak materials. *Journal of Chemical Technology & Biotechnology*. 1 June 2015. Vol. 90, no. 6, p. 1152–1159. DOI 10.1002/jctb.4573.

http://doi.wiley.com/10.1002/jctb.4573

113. LI, L., WANG, Q., YAN, D., LIU, Y., et al. Method for separating paper plastic-aluminum composite packing waste - CN101891903A. 2009. https://patents.google.com/patent/CN101891903A/en

114. Plastics Recyclers Europe. . https://www.plasticsrecyclers.eu/

115. KORKMAZ, A., YANIK, J., BREBU, M. and VASILE, C. Pyrolysis of the tetra pak. *Waste Management*. 1 November 2009. Vol. 29, no. 11, p. 2836–2841. DOI 10.1016/j.wasman.2009.07.008.

116. FÁVARO, S.L., FREITAS, A.R., GANZERLI, T.A., PEREIRA, A.G.B., et al. PET and aluminum recycling from multilayer food packaging using supercritical ethanol. *Journal of Supercritical Fluids*. 1 March 2013. Vol. 75, p. 138–143. DOI 10.1016/j.supflu.2012.12.015.

117. ANG, C. qing, ANG, H., U, G. hua, U, J. gang, et al. Kinetics and leaching behaviors of aluminum from pharmaceutical blisters in sodium hydroxide solution. *Journal of Central South University*. 1 December 2015. Vol. 22, no. 12, p. 4545–4550. DOI 10.1007/s11771-015-3004-x. https://link.springer.com/article/10.1007/s11771-015-3004-x

118. WANG, C., WANG, H. and LIU, Y. Separation of aluminum and plastic by metallurgy method for recycling waste pharmaceutical blisters. *Journal of Cleaner Production*. 1 September 2015. Vol. 102, p. 378–383. DOI 10.1016/j.jclepro.2015.04.067.

119. MYERS, T. Alcoa Participates in the World’s First Carton Packaging Recycling Plant Using Innovative Plasma Technology; The Plasma Process Separates Aluminum and Plastic, Components of the Aseptic Package | Business Wire. . 13 May 2005. https://www.businesswire.com/news/home/20050513005361/en/Alcoa-Participates-in-the-Worlds-First-Carton-Packaging-Recycling-Plant-Using-Innovative-Plasma-Technology-The-Plasma-Process-Separates-Aluminum-and-Plastic-Components-of-the-Aseptic-Package

120. AMI. *Polyethylene Film extruders in Europe*. 2017. https://www.ami.international/pubs/prod.aspx?catalog=Publishing&product=p374

121. ENVAL. THE ENVAL PROCESS - pyrolysis . . https://www.enval.com/process/

122. FLEXIBLE PACKAGING EUROPE. Recycling & Recovery of Flexible Packaging. . https://www.flexpack-europe.org/en/sustainability/recycling-recovery.html

123. LI, X., ZHANG, W. and (李雪辉张文超). Method of recovery and utilization of aluminium plastic composite film - CN1718408A. 27 July 2005. https://patents.google.com/patent/CN1718408A/en?oq=CN1718408A

124. TONG, Y.(童亚林). Environmental protection fast separating agent for aluminium plastic aluminium and separation production technology - CN1559704A. 11 March 2004. https://patents.google.com/patent/CN1559704A/en?oq=CN1559704A

125. LEI, H., LI, Z., CHEN, L., JIAN, D., et al. Method for fast stripping plastic-aluminum composite material by force chemistry - CN101475702A. 16 January 2009. https://patents.google.com/patent/CN101475702A/en

126. NIAOUNAKIS, M. Solvent- and/or Chemical Agent-Based Separation. In : *Recycling of Flexible Plastic Packaging*. Elsevier, 2020. p. 211–264.

127. GAO, L., WANG, W. and (高磊红王未肖). Aluminum-plastic composite packing separating agent and method of separating and reclaiming the same -

CN101054446A. 30 April 2007. https://patents.google.com/patent/CN101054446A/en?oq=CN101054446A+

128. KERNBAUM, S. and SEIBT, H. Separating Fluid, Method And System For Separating Multilayer Systems - US20130319618A1. https://patents.google.com/patent/US20130319618A1/en

129. CREASOLV® PROCESS. Recycling plastics - The CreaSolv® Process - Fraunhofer IVV. . https://www.ivv.fraunhofer.de/en/recycling-environment/recycling-plastics.html

130. SCHLUMMER M., FELL T., MÄURER A. and ALTNAU G. he Role of Chemistry in Plastics Recycling. *A Comparison of Physical and Chemical Plastics Recycling. Kunststoffe international 5,.* 2020. https://www.ivv.fraunhofer.de/content/dam/ivv/en/documents/Leistungsangebot/Recycling_Environment/The-Role-of-Chemistry-in-Plastics-Recycling.pdf

131. CREACYCLE. Creacycle - The Process. . https://www.creacycle.de/en/the-process.html

132. RODRÍGUEZ-GÓMEZ, J.E., SILVA-REYNOSO, Y.Q., VARELA-GUERRERO, V., NÚÑEZ-PINEDA, A., et al. Development of a process using waste vegetable oil for separation of aluminum and polyethylene from Tetra Pak. *Fuel*. 1 June 2015. Vol. 149, p. 90–94. DOI 10.1016/j.fuel.2014.09.032.

133. KULKARNI, A.K., DANESHVARHOSSEINI, S. and YOSHIDA, H. Effective recovery of pure aluminum from waste composite laminates by sub- and super-critical water. *Journal of Supercritical Fluids*. 1 January 2011. Vol. 55, no. 3, p. 992–997. DOI 10.1016/j.supflu.2010.09.007.

134. TETRA PAK. Packaging material for Tetra Pak. . https://www.tetrapak.com/packaging/materials

135. RIMŠAITĖ, A., MUMLADZE, T. and DENAFAS, G. Feasibilities of Aluminium Recovery from Combined Packaging Waste. *International Journal of Agriculture & Environmental Science*. 25 November 2019. Vol. 6, no. 6, p. 103–111. DOI 10.14445/23942568/ijaes-v6i6p114.

136. ZHANG, S.F., ZHANG, L.L., LUO, K., SUN, Z.X., et al. Separation properties of aluminium-plastic laminates in post-consumer Tetra Pak with mixed organic solvent. *Waste Management and Research*. 12 April 2014. Vol. 32, no. 4, p. 317–322. DOI 10.1177/0734242X14525823. http://journals.sagepub.com/doi/10.1177/0734242X14525823

137. KAISER, K., SCHMID, M. and SCHLUMMER, M. Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling*. 22 December 2017. Vol. 3, no. 1, p. 1. DOI 10.3390/recycling3010001. http://www.mdpi.com/2313-4321/3/1/1

138. BORSODCHEM. *SAFETY DATA SHEET N,N-DIMETHYLCYCLOHEXYLAMINE*. [no date]. www.poison.org

139. VANDERVEEN, J.R., DURELLE, J. and JESSOP, P.G. Design and evaluation of switchable-hydrophilicity solvents. *Green Chemistry*. 25 February 2014. Vol. 16, no. 3, p. 1187–1197. DOI 10.1039/c3gc42164c. www.rsc.org/greenchem

140. JESSOP, P.G., KOZYCZ, L., RAHAMI, Z.G., SCHOENMAKERS, D., et al. Tertiary amine solvents having switchable hydrophilicity. *Green Chemistry*. 8 March 2011. Vol. 13, no. 3, p. 619–623. DOI 10.1039/c0gc00806k. https://pubs.rsc.org/en/content/articlehtml/2011/gc/c0gc00806k

141. JESSOP, P.G., PHAN, L., CARRIER, A., ROBINSON, S., et al. A solvent having switchable hydrophilicity. *Green Chemistry*. 11 May 2010. Vol. 12, no. 5, p. 809–81. DOI 10.1039/b926885e. www.rsc.org/greenchem

142. SAMORÌ, C., LÓPEZ BARREIRO, D., VET, R., PEZZOLESI, L., et al. Effective lipid extraction from algae cultures using switchable solvents. *Green Chemistry*. 28 January 2013. Vol. 15, no. 2, p. 353–356. DOI 10.1039/c2gc36730k. https://pubs.rsc.org/en/content/articlehtml/2013/gc/c2gc36730k

143. SAMORÌ, C., TORRI, C., SAMORÌ, G., FABBRI, D., et al. Extraction of hydrocarbons from microalga Botryococcus braunii with switchable solvents. *Bioresource Technology*. 1 May 2010. Vol. 101, no. 9, p. 3274–3279. DOI 10.1016/j.biortech.2009.12.068.

144. FU, D., FARAG, S., CHAOUKI, J. and JESSOP, P.G. Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent. *Bioresource Technology*. 1 February 2014. Vol. 154, p. 101–108. DOI 10.1016/j.biortech.2013.11.091.

145. CHURAMAN, A. and JANSEN VAN VUUREN, R. Chemical Recycling of Polystyrene with Tertiary Amine Switchable Hydrophilicity Solvents. *Inquiry@Queen's Undergraduate Research Conference Proceedings*. 25 March 2019. DOI 10.24908/iqurcp.13381. https://ojs.library.queensu.ca/index.php/inquiryatqueens/article/view/13381

146. BOYD, A.R., CHAMPAGNE, P., MCGINN, P.J., MACDOUGALL, K.M., et al. Switchable hydrophilicity solvents for lipid extraction from microalgae for biofuel production. *Bioresource Technology*. 1 August 2012. Vol. 118, p. 628–632. DOI 10.1016/j.biortech.2012.05.084.

147. SAMORÌ, C., PEZZOLESI, L., BARREIRO, D.L., GALLETTI, P., et al. Synthesis of new polyethoxylated tertiary amines and their use as Switchable Hydrophilicity Solvents. *RSC Advances*. 8 January 2014. Vol. 4, no. 12, p. 5999–6008. DOI 10.1039/c3ra47144f. https://pubs.rsc.org/en/content/articlehtml/2014/ra/c3ra47144f

148. BIRKNER, N. and WANG, Q. How an FTIR Spectrometer Operates . . https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/How_an_FTIR_Spectrometer_Operates

149. ERDMAN, N., BELL, D.C. and REICHELT, R. Scanning electron microscopy. In : *Springer Handbooks*. Springer, 2019. p. 229–318. https://doi.org/10.1007/978-3-030-00069-1_5

150. ZHAO, J.C. Methods for Phase Diagram Determination. Elsevier Ltd, 2007. ISBN 9780080446295.

151. EBNESAJJAD, S. Surface and Material Characterization Techniques. In : *Surface Treatment of Materials for Adhesive Bonding*. Elsevier, 2014. p. 39–75.

152. Common Solvents Used in Organic Chemistry: Table of Properties. . https://organicchemistrydata.org/solvents/

153. MERCHAN-ARENAS, D.R. and VILLABONA-DELGADO, C.C. Chemical-Enhanced Oil Recovery Using N, N -Dimethylcyclohexylamine on a Colombian Crude Oil. *International Journal of Chemical Engineering*. 2019. Vol. 2019. DOI 10.1155/2019/5241419.

154. *Occupational health guidelines for chemical hazards.* 1981. https://www.cdc.gov/niosh/docs/81-123/

155. TORMOEHLEN, L.M., TEKULVE, K.J. and NAÑAGAS, K.A. *Hydrocarbon toxicity: A review*. 2014. Informa Healthcare.

156. DHARMARAJAN, L. and AMMAR, H. Expanding the differential: Toluene-induced toxicity. *BMJ Case Reports*. 31 July 2017. Vol. 2017, p. bcr-2017-220986. DOI 10.1136/bcr-2017-220986. https://casereports.bmj.com/content/2017/bcr-2017-220986
157. BROWN, J.H., HADDEN, D.R. and HADDEN, D.S.M. Solvent abuse, toluene acidosis and diabetic ketoacidosis. *Archives of Emergency Medicine*. 1991. Vol. 8, no. 1, p. 65–67. DOI 10.1136/emj.8.1.65.
158. YOON, J.-H., SEO, H.-S., LEE, J., MOON, C., et al. Acute high-level toluene exposure decreases hippocampal neurogenesis in rats. *Toxicology and industrial health*. 1 November 2016. Vol. 32, no. 11, p. 1910–1920. DOI 10.1177/0748233715599087. http://www.ncbi.nlm.nih.gov/pubmed/26475279
159. WEBER, M., POMPETZKI, W., BONMANN, R. and WEBER, M. Acetone. In : *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2014. p. 1–19. http://doi.wiley.com/10.1002/14356007.a01_079.pub4
160. BOWEN, S.E., HANNIGAN, J.H., DAVIDSON, C.J. and CALLAN, S.P. Abstinence following toluene exposure increases anxiety-like behavior in mice. *Neurotoxicology and Teratology*. 1 January 2018. Vol. 65, p. 42–50. DOI 10.1016/j.ntt.2017.12.010.
161. DUMAS, O., DESPREAUX, T., PERROS, F., LAU, E., et al. Respiratory effects of trichloroethylene. *Respiratory Medicine*. 1 January 2018. Vol. 134, p. 47–53. DOI 10.1016/j.rmed.2017.11.021.
162. JONES, G. and STANFORTH, S.P. The Vilsmeier Reaction of Fully Conjugated Carbocycles and Heterocycles. In : *Organic Reactions*. John Wiley & Sons, Inc., 1996. p. 1–330. https://onlinelibrary.wiley.com/doi/full/10.1002/0471264180.or049.01
163. KILO, S., GÖEN, T. and DREXLER, H. Cross-sectional study on N,N-dimethylformamide (DMF); effects on liver and alcohol intolerance. *International Archives of Occupational and Environmental Health*. 1 November 2016. Vol. 89, no. 8, p. 1309–1320. DOI 10.1007/s00420-016-1164-0. https://link.springer.com/article/10.1007/s00420-016-1164-0
164. HURTT, M. 13-Week inhalation toxicity study of dimethylformamide (DMF) in cynomolgus monkeys. *Fundamental and Applied Toxicology*. 1 May 1992. Vol. 18, no. 4, p. 596–601. DOI 10.1016/0272-0590(92)90119-3.
165. Formic acid. . https://fscimage.fishersci.com/msds/45433.htm
166. Acetic acid. . https://fscimage.fishersci.com/msds/00120.htm
167. TOXICANTS, N.R.C. (US) S. on R.-E. ACUTE TOXICITY OF NITRIC ACID. . 1998. https://www.ncbi.nlm.nih.gov/books/NBK230433/
168. DA CRUZ, N.F., SIMÕES, P. and MARQUES, R.C. Economic cost recovery in the recycling of packaging waste: The case of Portugal. *Journal of Cleaner Production*. 1 December 2012. Vol. 37, p. 8–18. DOI 10.1016/j.jclepro.2012.05.043.
169. TURNER, D.A., WILLIAMS, I.D. and KEMP, S. Greenhouse gas emission factors for recycling of source-segregated waste materials. *Resources, Conservation and Recycling*. 1 December 2015. Vol. 105, p. 186–197. DOI 10.1016/j.resconrec.2015.10.026.
170. FLORIAN, L. Method and apparatus for recycling packaging material - GB2557682A. 15 December 2016. https://patents.google.com/patent/GB2557682A/en
171. LOVIS, F., SEIBT, H. and KERNBAURN, S. Method and apparatus for recycling

packaging material - GB2525858A. 5 May 2014. https://patents.google.com/patent/GB2525858A/es

172. PILCHIK, R. Pharmaceutical blister packaging, part II: Machinery and assembly. *Pharmaceutical Technology*. January 2000. https://www.researchgate.net/publication/287699910_Pharmaceutical_blister_packaging_part_II_Machinery_and_assembly

173. OLAFSSON, G. and HILDINGSSON, I. Sorption of Fatty Acids into Low-Density Polyethylene and Its Effect on Adhesion with Aluminum Foil in Laminated Packaging Material. *Journal of Agricultural and Food Chemistry*. 1 February 1995. Vol. 43, no. 2, p. 306–312. DOI 10.1021/jf00050a008. https://pubs.acs.org/doi/abs/10.1021/jf00050a008

174. LIU, Y., TAO, Y., LV, X., ZHANG, Y., et al. Study on the surface properties of wood/polyethylene composites treated under plasma. *Applied Surface Science*. 15 November 2010. Vol. 257, no. 3, p. 1112–1118. DOI 10.1016/j.apsusc.2010.08.032.

175. BODUGÖZ-SENTÜRK, H. and GÜVEN, O. Enhancement of conductivity in polyaniline-[poly(vinylidene chloride)-co-(vinyl acetate)] blends by irradiation. *Radiation Physics and Chemistry*. 1 February 2011. Vol. 80, no. 2, p. 153–158. DOI 10.1016/j.radphyschem.2010.07.025.

176. HIGGINS, F. Pharmaceutical Packaging Materials Quality Control and USP 661 . 1 Compliance : Agilent Cary 630 FTIR Application Note. *Agilent Technologies*. 2016. https://www.agilent.com/cs/library/applications/5991-6978EN.pdf

177. SOUDAIS, Y., MOGA, L., BLAZEK, J. and LEMORT, F. Coupled DTA-TGA-FT-IR investigation of pyrolytic decomposition of EVA, PVC and cellulose. *Journal of Analytical and Applied Pyrolysis*. 1 January 2007. Vol. 78, no. 1, p. 46–57. DOI 10.1016/j.jaap.2006.04.005.

178. ALTENHOFEN DA SILVA, M., ADEODATO VIEIRA, M.G., GOMES MAUMOTO, A.C. and BEPPU, M.M. Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid. *Polymer Testing*. 1 August 2011. Vol. 30, no. 5, p. 478–484. DOI 10.1016/j.polymertesting.2011.03.008.

179. SUPAN, K.E., ROBERT, C., MILLER, M.J., WARRENDER, J.M., et al. Thermal degradation of MWCNT/polypropylene nanocomposites: A comparison of TGA and laser pulse heating. *Polymer Degradation and Stability*. 1 July 2017. Vol. 141, p. 41–44. DOI 10.1016/j.polymdegradstab.2017.05.006.

180. AKHLAGHI, S., SHARIF, A., KALAEE, M. and MANAFI, M. Miscibility and thermal behavior of poly(vinyl chloride)/feather keratin blends. *Journal of Applied Polymer Science*. 15 September 2011. Vol. 121, no. 6, p. 3252–3261. DOI 10.1002/app.33869. http://doi.wiley.com/10.1002/app.33869

181. MEHMOOD, C.T., QAZI, I.A., HASHMI, I., BHARGAVA, S., et al. Biodegradation of low density polyethylene (LDPE) modified with dye sensitized titania and starch blend using Stenotrophomonas pavanii. *International Biodeterioration and Biodegradation*. 1 September 2016. Vol. 113, p. 276–286. DOI 10.1016/j.ibiod.2016.01.025.

182. ACHILIAS, D.S., ROUPAKIAS, C., MEGALOKONOMOS, P., LAPPAS, A.A., et al. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *Journal of Hazardous Materials*. 19 November 2007. Vol. 149, no. 3, p. 536–542. DOI 10.1016/j.jhazmat.2007.06.076.

183. ELÇI, H. Utilisation of crushed floor and wall tile wastes as aggregate in concrete

production. *Journal of Cleaner Production*. 20 January 2016. Vol. 112, p. 742–752. DOI 10.1016/j.jclepro.2015.07.003.

184. FAN, G., JIANG, Y., TAN, Z., GUO, Q., et al. Enhanced interfacial bonding and mechanical properties in CNT/Al composites fabricated by flake powder metallurgy. *Carbon*. 1 April 2018. Vol. 130, p. 333–339. DOI 10.1016/j.carbon.2018.01.037.
185. TRINH, P. Van, LUAN, N. Van, PHUONG, D.D., MINH, P.N., et al. Microstructure, microhardness and thermal expansion of CNT/Al composites prepared by flake powder metallurgy. *Composites Part A: Applied Science and Manufacturing*. 1 February 2018. Vol. 105, p. 126–137. DOI 10.1016/j.compositesa.2017.11.022.
186. JOO, E., CHANG, Y., CHOI, I., LEE, S.B., et al. Whey protein-coated high oxygen barrier multilayer films using surface pretreated PET substrate. *Food Hydrocolloids*. 1 July 2018. Vol. 80, p. 1–7. DOI 10.1016/j.foodhyd.2018.01.027.
187. DIKOBE, D.G. and LUYT, A.S. Morphology and properties of polypropylene/ethylene vinyl acetate copolymer/wood powder blend composites. *Express Polymer Letters*. 2009. Vol. 3, no. 3, p. 190–199. DOI 10.3144/expresspolymlett.2009.24.
188. CORZO, R., SUBEDI, K., TREJOS, T. and ALMIRALL, J.R. Evaluation of the Forensic Utility of Scanning Electron Microscopy-Energy Dispersive Spectroscopy and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry for Printing Ink Examinations. *Journal of Forensic Sciences*. 1 May 2016. Vol. 61, no. 3, p. 725–734. DOI 10.1111/1556-4029.13110. http://doi.wiley.com/10.1111/1556-4029.13110
189. ACHILIAS, D.S., GIANNOULIS, A. and PAPAGEORGIOU, G.Z. Recycling of polymers from plastic packaging materials using the dissolution-reprecipitation technique. *Polymer Bulletin*. 13 September 2009. Vol. 63, no. 3, p. 449–465. DOI 10.1007/s00289-009-0104-5. https://link.springer.com/article/10.1007/s00289-009-0104-5
190. BHATIA, M., GIRDHAR, A., TIWARI, A. and NAYARISSERI, A. Implications of a novel Pseudomonas species on low density polyethylene biodegradation: an in vitro to in silico approach. *SpringerPlus*. 1 December 2014. Vol. 3, no. 1, p. 1–10. DOI 10.1186/2193-1801-3-497. https://link.springer.com/articles/10.1186/2193-1801-3-497
191. WANG, S., ZHENG, C., ZHAO, J., LI, X., et al. Extracting and recovering diesel from oil-based drill cuttings using switchable hydrophilic solvents. *Chemical Engineering Research and Design*. 1 December 2017. Vol. 128, p. 27–36. DOI 10.1016/j.cherd.2017.09.036.
192. RAGAERT, K., DELVA, L. and VAN GEEM, K. Mechanical and chemical recycling of solid plastic waste. *Waste Management*. 1 November 2017. Vol. 69, p. 24–58. DOI 10.1016/j.wasman.2017.07.044.
193. Clavreul, J., Baumeister, H., Christensen, T. H., & Damgaard, A. (2014). An environmental assessment system for environmental technologies. Environmental Modelling & Software, 60, 18–30. doi:10.1016/j.envsoft.2014.06.007
194. European Union ; International Reference Life Cycle Data System (ILCD) Handbook - General guide for Life Cycle Assessment - Provisions and Action Steps; https://eplca.jrc.ec.europa.eu/
195. https://www.azom.com/article.aspx?ArticleID=12384 “Characterizing the Composition of Polymer Laminates Using IR Microscopy”.

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LIST OF ARTICLES AND SCIENTIFIC CONFERENCES

Publications in journals included into the list of the *Web of Science* database

1. Mumladze, Tamari; Yousef, Samy; Tatariants, Maksym; Kriūkienė, Rita; Makarevičius, Vidas; Lukošiūtė, Stasė Irena; Bendikienė, Regita; Denafas, Gintaras. Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents // Green chemistry. Cambridge: Royal Society Chemistry. ISSN 1463-9262. 2018, vol. 20, iss. 15, p. 3604-3618. DOI: 10.1039/C8GC01062E [Appendix 1].
2. Yousef, Samy; Mumladze, Tamari; Tatariants, Maksym; Kriūkienė, Rita; Makarevičius, Vidas; Bendikienė, Regita; Denafas, Gintaras. Cleaner and profitable industrial technology for full recovery of metallic and non-metallic fraction of waste pharmaceutical blisters using switchable hydrophilicity solvents // Journal of Cleaner Production. Oxford: Elsevier. ISSN 0959-6526. 2018, Vol. 197, pt. 1, p. 379-392. DOI: 10.1016/j.jclepro.2018.06.154 [Appendix 2].

Other publications

1. Mumladze, T.; Tatariants, M.; Rimšaitė, A.; Yousef, S.; Denafas, G. Recycling of multilayer packaging foils by using different organic solvent // Iranian journal of energy and environment. Babol, Mazandaran: Babol Noshirvani University of Technology. ISSN 2079-2115. eISSN 2079-2123. 2019, vol. 10, iss. 1, p. 38-42. Access online: [seen June 19, 2019] [Appendix 3].
2. Rimšaitė, Asta; Mumladze, Tamari; Denafas, Gintaras. Feasibilities of aluminium recovery from combined packaging waste // International journal of agriculture & environmental science. Thennur: Seventh Sense Research Group®. ISSN 2394-2568. 2019, vol. 6, iss. 6, p. 103-111. DOI: 10.14445/23942568/IJAES-V6I6P114 [Appendix 4].
3. Mumladze, T.; Šleiniūtė, A.; Denafas, G. The possibility of recycling of multilayer packaging waste: reducing environmental impacts // CEST 2019: 16th international conference on environmental science and technology: empowering science to deliver change, 4–7 September 2019, Rhodes, Greece. [S.l.] : [CEST]. 2019, A55, p. 1-2. Internet access: [seen Nov 28, 2019].

Conference Materials

Posters & Oral presentations

1. Mumladze, T.; Denafas, G. Separation of composite packaging waste and reuse of recovered materials, economic and environmental efficiency: review // International online conference "Compounds and materials with specific

properties”, July 10–11, 2020, Tbilisi, Georgia: book of abstracts / editors: N. Lekishvili, I. Chikvaidze. Tbilisi: Tbilisi University Press, 2020. ISBN 9789941139390. p. 79-80.

2. Mumladze, Tamari; Denafas, Gintaras. Blister packaging waste and their recallability by using chemicals // International conference on recycling and waste management (ICRWM-19), Edinburgh, Scotland, September 9, 2019 / Institute for Scientific and Engineering Research. Edinburgh: ISER Explore. 2019, p. 44-46.
3. Mumladze, Tamari; Šleiniūtė, Agnė; Samuel, Nizy Sara; Denafas, Gintaras. Aluminum recovering from food and medicines packaging waste: chemical and technological aspects // Respublikinės studentų mokslinės konferencijos “Chemija ir cheminė technologija 2019” pranešimų medžiaga = Proceedings of the national scientific students’ conference “Chemistry and chemical technology 2019.” Vilnius: Vilniaus universiteto leidykla, 2019. ISBN 9786090701768. p. 218. Internet access: [seen June 03, 2019].
4. Mumladze, T.; Šleiniūtė, A.; Denafas, G. Environmental problems related to multilayered packaging waste // Actual environmental problems: proceedings of the IX international scientific conference of young scientists, graduates, master and PhD students, November 21–22, 2019, Minsk, Republic of Belarus. Minsk: International Sakharov Environmental Institute of Belarusian State University, 2019. ISBN 9789857224890. p. 190-191. Internet access: [seen Feb 26, 2021].
5. Mumladze, T.; Šleiniūtė, A.; Denafas, G. Recycling possibilities of multilayer packaging foils: a review // Матеріали XX Міжнародної науково-практичної конференції "Екологія. Людина. Суспільство", (23 травня 2019 р., м. Київ). Київ : НТУУ "КПІ ім. Ігоря Сікорського". 2019, p. 63.
6. Šleiniūtė, A.; Mumladze, T.; Denafas, G. Chemical aspects of recovered aluminum from food and blister packaging waste // CEI2019: Current environmental issues, September 24–26, 2019; Białystok, Poland: conference program [and abstracts]. Białystok: University of Białystok. 2019, P19, p. 72. Internet access: [seen Nov 14, 2019].
7. Mumladze, Tamari; Tatariants, Maksym; Yousef, Samy; Rimšaitė, Asta; Denafas, Gintaras. Recycling of multilayer packaging foils: using different organic solvent // Linnaeus Eco-Tech 2018: The 11th International conference on the establishment of cooperation between companies and institutions in the Nordic countries, the Baltic Sea region and the world: Kalmar, Sweden, November 19–21, 2018: book of abstracts. Kalmar: Linnaeus University, 2018. ISBN 9789188898289. ISSN 2002-8008. p. 69. Internet access: [seen Feb 23, 2021].

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