

Review

# Recycling of Polymer-Based Multilayer Packaging: A Review

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**Abstract:** Polymer-based multilayer packaging materials are commonly used in order to combine the respective performance of different polymers. By this approach, the tailored functionality of packaging concepts is created to sufficiently protect sensitive food products and thus obtain extended shelf life. However, because of their poor recyclability, most multilayers are usually incinerated or landfilled, counteracting the efforts towards a circular economy and crude oil independency. This review depicts the current state of the European multilayer packaging market and sketches the current end-of-life situation of postconsumer multilayer packaging waste in Germany. In the main section, a general overview of the state of research about material recycling of different multilayer packaging systems is provided. It is divided into two subsections, whereby one describes methods to achieve a separation of the different components, either by delamination or the selective dissolution–reprecipitation technique, and the other describes methods to achieve recycling by compatibilization of nonmiscible polymer types. While compatibilization methods and the technique of dissolution–reprecipitation are already extensively studied, the delamination of packaging has not been investigated systematically. All the presented options are able to recycle multilayer packaging, but also have drawbacks like a limited scope or a high expenditure of energy.

**Keywords:** multilayer packaging; recycling; delamination; selective dissolution; compatibilization

## 1. Introduction

Because of the considerably high amounts of packaging waste produced in their daily lives, most consumers perceive plastic packaging in a negative way by. This negative judgement, however, disregards the positive impact of packaging on sustainability by protection of the packaged goods. The resources contained in those goods and the amount of water, farmland, and energy that were necessary for their production makes them valuable products, worthy of protection. Protection can be provided directly by preventing the good from contamination and indirectly by extending its shelf life. In addition to the protection, transportability and storage capability are also primary functions of packaging. Secondary functions, like the communication of information and the promotion of the article, are also important aspects. Since the demand of both primary and secondary functions is growing, the complexity of packaging is increasing [1,2].

Initially, packaging consisted of a single material. In many cases, this concept works fine, such as for glass jars, polyethylene terephthalate (PET) soda bottles, or metal cans. However, each of these materials has a limitation that inhibits its broader utilization: glass is heavy and fragile, PET does not provide a sufficient oxygen barrier for many products, and metal is not transparent. By combining different materials, ideal packaging concepts for most packaging requirements can be tailored [3]. While for some kinds of multilayer packaging, like LPBs (liquid packaging boards), an end-of-life

recycling option is already established on the market [4], for polymer–polymer multilayer materials no industry solution has been available until now. For the recycling of multilayer postindustrial waste [4,5], a delamination process has been proposed.

In a previous review from 1996, Hensaw et al. [6] reviewed the general recycling options for polymer composite materials, comprising pyrolysis, hydrolysis, energy recovery, and compression–injection molding. In 2011, Jesmy et al. [7] gave an overview of the recycling of polymer blends with the exclusive description of recycling by extrusion and compatibilizer-aided blending, with only one small abstract dealing with packaging materials. Hamad et al. [8] described methods to recycle polymeric materials by reprocessing and compounding, as well as by polymer degradation. The advantages and limitations of the dissolution–reprecipitation technique were discussed in a conference abstract by Achilias et al. [9]. In 2017, Ragaert et al. [10] published a review that provides a detailed description of the current pathways for the recycling of solid plastic waste, via both mechanical and chemical recycling. As a promising option for multilayer packaging recycling, pyrolytic decomposition was mentioned. In the eyes of the authors, the complexity of the packaging systems is an argument against mechanical recycling.

Nonetheless, several approaches to the mechanical recycling of multilayers are described in the literature. In this study, an overview of those solutions, approaches, and ideas concerning the recycling of multilayered packaging systems is provided. Consideration was hereby given to multilayer systems with at least two materials, of which at least one is made of plastic. Other materials can be metals like aluminum or a fibrous material like cardboard. Those strategies, in general, can be divided into two categories. The first category includes methods according to which recycling is performed by the separation of the different components of the multilayer, either by the dissolution–reprecipitation technique or the delamination of the multilayer. The delamination can be performed physically (e.g., by selective dissolution), chemically (e.g., by the reactive removal of an interlayer), or mechanically. The second strategy comprises the joint processing of the constituents of the multilayer packaging, whereby the use of additives is often necessary. Additionally, an overview of the packaging market and the state of the art of the end-of-life treatment of multilayer packaging waste is given. This review is the first article that provides an overview and detailed description of the different techniques of multilayer packaging recycling. Additionally, these techniques are discussed and evaluated critically.

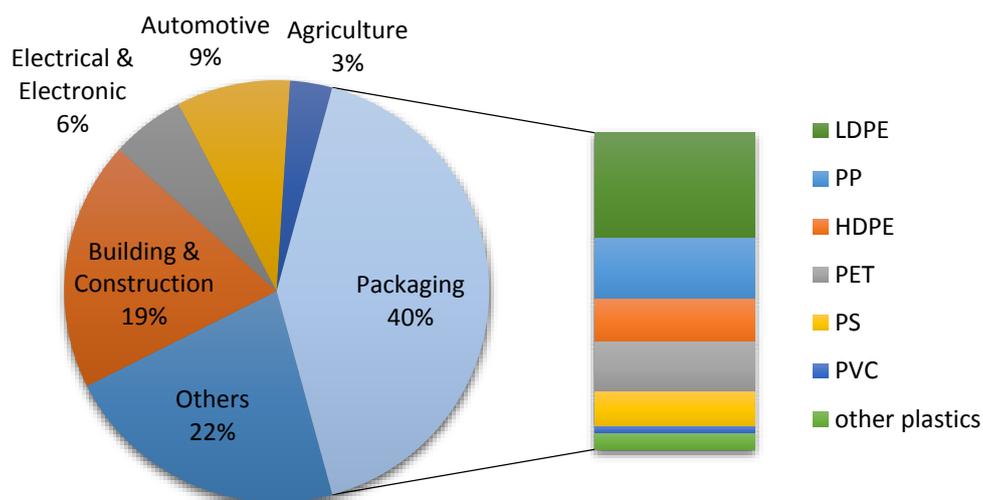
## 2. Packaging and Current End-of-Life Situation

### 2.1. Packaging

#### 2.1.1. Plastic Market and Applications

In Europe, 49 million tons of oil and gas were used for the production of plastic in 2015, constituting 4 to 6% of the total amount. About 40% thereof was used for packaging [11]. Polyolefins (PO) make up the biggest share thereof, with low-density polyethylene (LDPE) being the most prominent, followed by polypropene (PP), high-density polyethylene (HDPE), and polyethylene terephthalate (PET). Smaller shares are contributed by polyvinyl chloride (PVC), polystyrene (PS), polyamide (PA), and other plastics (cf. Figure 1) [11,12].

For multilayer packaging, the typical polymers listed in Figure 1 as well as more special polymers with useful functions are generally used [13]. One reason for the growing number of multilayer packaging is that costs can be reduced by adding an additional number of layers and thus decreasing the amount of material, in comparison to what would be needed to make a single layer perform the same function. More often, however, the multilayer structure allows the package to perform a combination of functions that is not possible with a single layer [1,14].



**Figure 1.** Fields of application of plastic materials and polymer types predominately used in packaging. The respective share of the different polymers is derived from a graphic illustration of the polymeric composition of plastic packaging in Europe [11]. Abbreviations used: LDPE (low-density polyethylene), PP (polypropene), HDPE (high-density polyethylene), PET (polyethylene terephthalate), PVC (polyvinyl chloride), PS (polystyrene), PA (polyamide).

### 2.1.2. Flexible Plastic Packaging Market

A two-layer packaging obviously consists of an inner side, facing the product, and an outer layer. Usually, in this case, the inner layer provides sealability, and the outer layer resistance against abrasion, printability, or barrier. Common sealant layers provide low-temperature sealability for fast packing line speeds and may also contribute to barrier performance. Ethylene-vinyl acetate (EVA), LDPE, linear-low-density polyethylene (LLDPE), PE plastomers, and ionomers are standardly used, among which ionomers additionally provide exceptional oil and grease resistance [3].

Because those sealants often lack stiffness, structural integrity, and abrasion resistance, an outer layer, which also may bring an additional functionality, is used. HDPE provides a moisture barrier and is often used in packaging dry foods such as cereal and crackers. PA may be used where exceptional mechanical resistance is needed, such as in brick packages for cheese. Oriented PET films provide an excellent surface for printing. Paper is a low-cost substrate often used in pouches and bags [3].

A three-layer packaging provides even greater flexibility in packaging design. Sealability is still the primary function of the inner layer, whereas the outer layer is supposed to provide abrasion resistance, heat resistance (during sealing), stiffness, structural integrity, a surface for printing, and in some cases, a moisture barrier. The additional center layer can provide a variety of functions. An oxygen barrier may be provided, e.g., by EVOH or a metallization layer. In some cases, an adhesive may be needed in the center layer to allow for the lamination of two dissimilar materials. In many cases, reverse printing is applied, which means that films are printed and laminated to a sealant layer with the print side facing inward to ensure protection from the outside by the film layer. In food packaging, also a layer of recycled material is allowed to be incorporated into the center layer for some applications [3,14,15] As specified in Regulation (EU) No 10/2011, recycled plastics from commingled postconsumer waste should not be in direct contact with food. Nonetheless, they can be integrated in an inner layer of the packaging if they are separated by a functional barrier that avoids the transfer of non-authorized substances from the recycled layer to the foodstuff. To avoid set-off migration effects through the nonfood contact side of the packaging to the food contact side of other packaging during the storage of stackable packaging, symmetrical multilayer structures with functional barriers at both sides of the recycled layer can also be developed. For nonfood packaging, no restriction concerning the contact with the filling material exists [16,17]).

In extended concepts like five-layered films, the centered layer is often surrounded by two adhesive layers that enable adhesion to the outer and inner layer. For example, this structure is common for barrier films with PA-6 or EVOH, since these polymers do not adhere to most sealants and outer layers [3]. An overview of commonly used materials and their respective functions is shown in Table 1.

**Table 1.** Overview of common functional layers [3,14,18]. Abbreviations used: BOPA (biaxially oriented polyamide), EVA (polyethylene-vinyl acetate), OPA (oriented polyamide), OPET (oriented polyethylene terephthalate), OPP (oriented polypropene), PVDC (polyvinylidene chloride), PVOH (polyvinyl alcohol), PE (polyethene), LD (low-density), LLD (linear low-density), HD (high-density).

Mechanical Stability	Oxygen Barrier	Moisture Barrier	Light Barrier	Tie Layers	Sealant
HDPE	EVOH	PE (LD, LLD, HD)	aluminum	polyurethanes	LLDPE
PP, OPP	PVDC	PP, OPP	TiO <sub>2</sub> filled polymers	Acid/anhydride grafted polyolefins	LDPE
OPET	polyamides (nylon, BOPA)	EVA			EVA
PS	polyesters, OPET	ionomers			ionomers
Paper	coatings (SiO <sub>x</sub> , Al <sub>2</sub> O <sub>3</sub> , PVOH, nano particles)	PVDC			PP, OPP
	aluminum				PA, OPA
					PET, OPET

The GVM (Association of Packaging Market Research) [13] divides multilayer packaging films into five categories, whereby only multilayered packaging with a polymer content higher than 50%, and packaging without paper are considered:

- flexible plastic and plastic composites without barrier layer (“simple multilayers”)
- flexible plastic and plastic composites with an organic barrier layer
- flexible metallized plastic and plastic composites films with coatings based on AlO<sub>x</sub> or SiO<sub>x</sub>, respectively
- thermoformed plastic and plastic composites
- plastic and plastic composites with Al foil.

These five categories made up 17.7 billion m<sup>2</sup> (approximately 1.89 Mt; the number of ~1.89 Mt was derived by calculation of the ratio of the amount of multilayer packaging in Germany in 2009 to the area of multilayer packaging in Germany in 2009 [1]. By using this ratio, the mass of multilayer packaging was derived from the area of multilayer packaging in 2016 in Europe [13]. Thus, the number of 1.89 Mt is an approximation based on the assumption that the composition of multilayer packaging was the same in Germany in 2009 as in Europe in 2016. The respective shares of the different categories are given in Table 2, along with the use of one example of the corresponding category [13].

The sum of the five most important material combinations in each of the five categories given in Table 2 makes up 56.3 % m<sup>2</sup> of plastic-based flexible packaging. The remaining 43.7 % m<sup>2</sup> consists of a large number of material combinations, whereof simple PET–PO multilayers and thermoformed PET–PO multilayers still represent an important larger proportion [13].

**Table 2.** Quantities of the five flexible plastic-based multilayer packaging categories and, in each case, the most important example is given in millions (mio.) m<sup>2</sup> and in percent m<sup>2</sup>. The percentage refers to the sum of packaging used in these categories in Europe in 2016 [13]. PET-BO is the abbreviation for biaxially-oriented PET.

Group	Materials	Mio. m <sup>2</sup> Film	Share in m <sup>2</sup> -%
Simple multilayers	total	<b>6565.6</b>	<b>37.1</b>
	Thereof: PA/polyolefin	2710.2	15.3
Packaging with organic barriers	total	<b>4499.9</b>	<b>25.4</b>
	Thereof: EVOH	4304.7	24.3
Thermoformed packaging	total	<b>2482.1</b>	<b>14.0</b>
	Thereof: PA/polyolefin	756,3	4.27
Packaging with inorganic barriers	total	<b>2996.1</b>	<b>16.9</b>
	Thereof: PET-BO/layer/polyolefin	1362.9	7.7
Packaging with Al-foil	total	<b>1153.1</b>	<b>6.5</b>
	Thereof: PET/Al/plastic	829.1	4.7
		<b>17,696.9</b>	<b>100</b>

### 2.1.3. Composite Packaging Containing Paper and Plastic

LPBs (liquid packaging board) consists of about 21% PE, 4% aluminum, and about 75% cardboard. The cardboard layer is supposed to provide stability, the PE layers provide protection against moisture from the outer and the inner side of the packaging, while the aluminum acts as a gas barrier. In 2016, 178 kt of LPBs were used in Germany [19,20].

### 2.1.4. Trend towards Avoidance of Multilayer Packaging

Currently, an opposite trend towards the broader use of multilayers can be observed. Because of the more environmentally friendly image of monomaterial packaging, ambitions towards the substitution of multilayer packaging by monolayers can be observed. For example, the RecycleReady Technology of DOW<sup>®</sup> (Midland, MI, USA) allows for the substitution of heterogeneous multilayer packaging, e.g., containing PET and PE, by an all-polyolefine packaging containing a barrier adhesive [21]. Based on a combination of the proprietary Borstar<sup>®</sup>-Technology for bimodal PE and the machine direction-oriented (MDO) processing technology, Borealis developed a full PE laminate as an alternative to multilayered structures [22]. In general, however, the substitution of multilayer packaging systems should only be carried out if the protection of the product can be equally assured.

## 2.2. End-of-Life Treatment of Multilayer Packaging

The end-of-life treatment of postconsumer packaging waste comprises three steps:

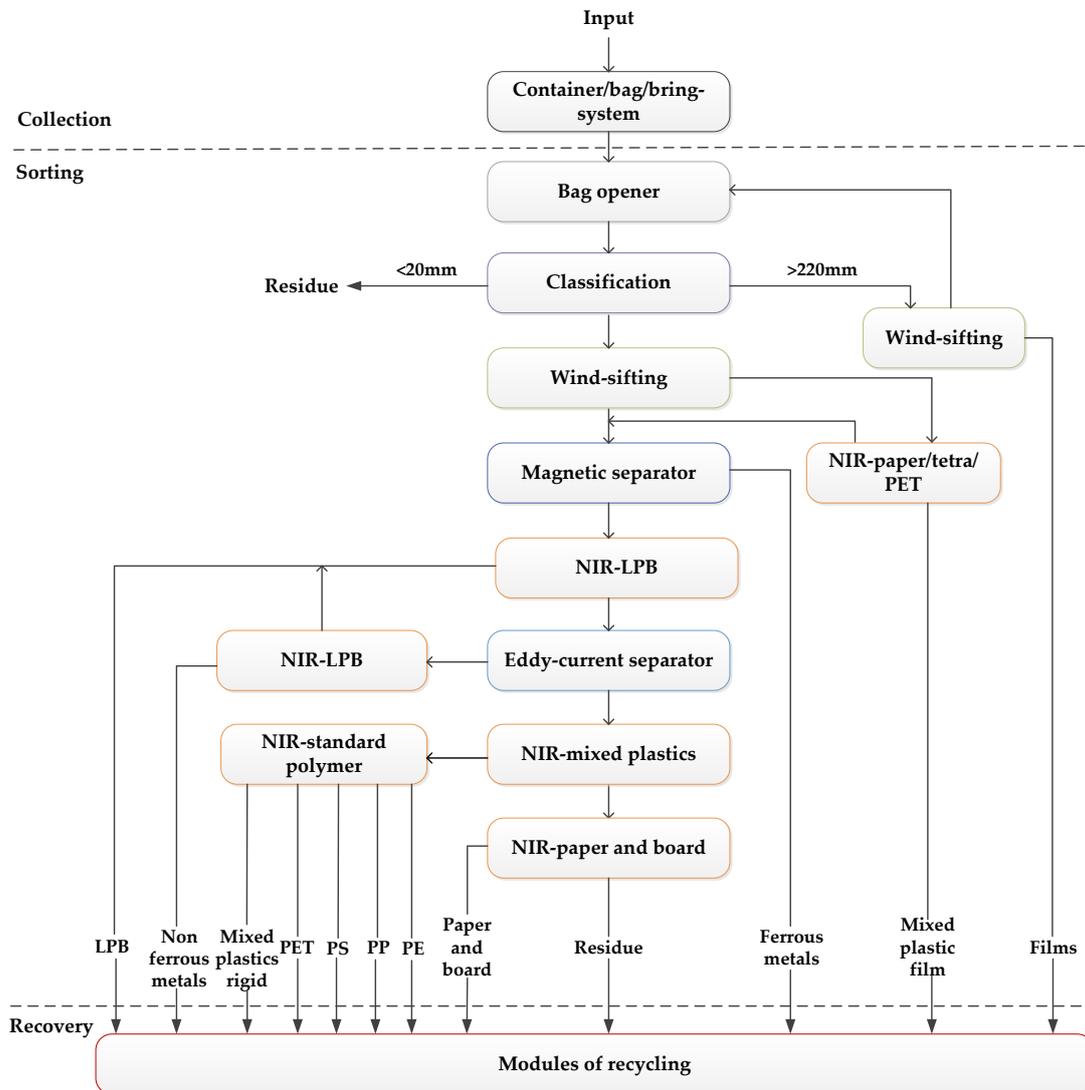
- collection
- sorting
- reprocessing

A proper collection is a prerequisite for an effective sorting and collection. However, since it is a question of logistics and not a technical problem, it does not lie within the scope of this review. An overview of the different collection systems is given in [23].

In this section, the state of the art of multilayer packaging sorting and reprocessing is summarized. Subsequently, in the next section, the state of science of multilayer reprocessing is described in detail.

The sorting process of postconsumer waste is essential to generate a decent amount and quality of recycling material. In Figure 2, a sorting scheme of the lightweight packaging fraction is shown. It is a simplified example of the structure of a sorting plant intended to sort the “yellow sack” produced within the “Duales System” in Germany. The input contains postconsumer packaging made of plastic,

metals, and composite packaging. Material recovery facilities in other European countries like Belgium or the Netherlands follow similar standards [24].



**Figure 2.** Scheme of a standard state-of-the-art sorting plant. Adapted from [20]. NIR is the abbreviation for near infrared.

Thin-walled, flexible packaging items enter the film fraction and the mixed plastic films by classification and wind sifting. Since the film fraction should only contain films bigger than DIN A4, the amount of multilayer packaging contained in this fraction is not expected to be significantly high. The mixed plastic films, instead, contain flexible packaging sized smaller than DIN A4 [25]. Here, a higher amount of multilayer packaging is expected to be contained.

Downstream in the process, LPBs and plastic-coated cardboard packaging are identified by NIR reflection measurements by means of a specific spectrum and separated from the other materials by using pulses of compressed air. LPB is the only kind of multilayered packaging that is assigned to its own sorting fraction [24].

Downstream, aluminum is removed from the main material flow by an eddy current separator which sorts by electric conductivity. In Germany, unlike other European countries, polymer-based packaging coated with aluminum is assigned to this aluminum fraction. Depending on the structure

of the multilayer, this separation step works more or less efficiently. Relatively low aluminum content in combination with high polymer content can prevent aluminum from being separated [24].

Dimensionally stable plastics can be sorted by an NIR separator. Stable multilayer packaging should be sorted into the rigid mixed plastics or remain in the residue.

Following sorting, the presorted polymers have to be recycled. This reprocessing of the sorted polymers can be done in three ways:

1. energetic utilization is the recovery process of energy contained in the polymers by converting it into thermal or electrical energy by incineration. Since this type of recycling does not deliver a material product, it will not be considered as recycling in the following text [26];
2. mechanical recycling, which describes the production of new products while the polymer chains stay preserved. This is done by processing the polymer waste with physical methods like shredding, solving, or melting [26,27].
3. chemical recycling, whereby polymer waste is turned back into its oil/hydrocarbon component in the cases of polyolefins and into monomers in the case of polyesters and polyamides. These can be used as raw materials for the production of new polymers [26].

The fractions containing multilayer packaging are partially incinerated and partially recycled mechanically.

The presorted aluminum fraction, in which aluminum-containing multilayer packaging can also be contained, usually undergoes a pyrolysis step that removes the plastic components as well as the lacquers or residual contents, before the aluminum is remelted. In the case of a packaging in which the aluminum foil constitutes 19% and the plastic components make up the remaining 81%, the overall recycling rate is 17%, whereby the loss of aluminum can be attributed to the formation of aluminum oxide [24].

The presorted LPB fraction is shredded and fed into a special paper treatment in which the fibers are dissolved and separated from the plastics and the aluminum, to be added to the fiber preparation. In some cases, the LDPE–Al reject is separated by selective dissolution, and the output can be utilized to replace primary raw materials in high-quality applications. In most cases though, the utilization of the reject takes place in the rotary kilns of cement plants, where the plastic functions as fuel, and the aluminum replaces the aluminum ore Bauxite [24].

The sorting residue is incinerated completely, while mixed plastic fractions can either be recovered by material recycling or by incineration, depending on the quality and on economic issues.

In the cases of the mechanical recycling of fractions in which multilayers are contained, the presorted material has to undergo a second sorting step. Here, material that is not polyolefin-based has to be removed. Therefore, the material is first shredded and washed, and afterwards it is treated by sink-float separation. Since polyolefins are usually the target polymer, only the components with a density lower than 1 are processed in the following extrusion, while the components with a density higher than 1 are incinerated. If a multilayered packaging has a high polyolefin content, it is possible that its density is low enough for the multilayer to enter the polyolefin recycling flow. The non-polyolefinic material contained in those multilayers can be largely removed by melt filtration [24].

In 2015, only 1.74% of the 2870 kt packaging waste produced in Germany was recovered by chemical recycling, which shows that this kind of waste recovery only plays a subordinate role in the current market. Mechanical recycling (39.4%) and energy recovery (58.8%), however, are at competitive levels (cf. Table 3) [11].

In the waste hierarchy (a set of priorities for the efficient use of resources) mechanical recycling is number three, after waste avoidance and reuse. However, mechanical recycling should be favored over energy recovery and disposal. This hierarchy is quantified in several studies, as reported below.

**Table 3.** Treatment of packaging waste in Germany, 2015 [11].

Total	Recovery			Removal in kt/%		
	Mechanical	Chemical	Energetic	Total	Disposal	Incineration Without Energy Recovery
2867 kt	1130 kt	50 kt	1687 kt	3 kt	3 kt	0 kt
100%	39.4%	1.7%	58.8%	0.1%	0.1%	0.0%

One of the key benefits of recycling plastics is the reduction of the requirement of plastics production [28]. Incineration has the potential to recover the chemical energy bound in the polymer, corresponding to the caloric value. Since most polymers have a caloric value in the same range as that of crude oil (~40 MJ/kg) [29], plastic waste can be regarded as a crude oil substituent. However, it should be noted that the processing energy that is required to produce plastic items cannot be recovered by incineration. Mechanical recycling has the potential to save this processing energy as well as the chemical energy. Depending on the type of polymer, the processing energy of polymers ranges from 27 MJ/kg (PE) to 53 MJ/kg (PET) [29]. The ecologic benefit of mechanical recycling results from the savings of processing energy minus the energy used to collect, transport, and reprocess the plastic (~9 MJ/kg) [28,30–32].

Additionally, it must be taken into account that efficiencies of about 40% are considered to be the industry standard of energetic recovery. While a prospective increase of the efficiency of incineration plants would reduce the energetic advantage of mechanical recycling, the growing proportion of renewable energies in the energy mix, reduces the ecological benefit of the energetical utilization of plastic waste [31,33–35].

In Germany, a new packaging law will enter into force in 2019, which sets new quotas concerning the recycling of plastic packaging. The amount of recycled postconsumer plastic packaging waste has to be increased from ~40% to 63% by 2022 [36]. In order to achieve this target, innovations concerning new recycling and sorting technologies, as well as new strategies concerning packaging development are necessary.

Since multilayer packaging makes up a large percentage of the packaging market and is currently mostly treated by incineration, it is an option to try reaching the quotas by pursuing a solution for the recyclability dilemma of multilayer packaging. As described in Section 2.1.4, the replacement of multilayer packaging by monomaterials can be an option for some multilayer systems. However, it is expected that not all kinds of multilayer packaging can be substituted by monomaterials, and functionality, costs, and marketing are still the main drivers of the packaging market. Thus, it may be worthwhile having a closer look at the recycling strategies of multilayered packaging.

### 3. Recycling Methods

#### 3.1. Theoretical Background of Polymer Blends and Solutions

In general, it can be said that there are two ways to recycle multilayered packaging items: the first option is to separate the different components and make them available for recycling in separated recycling streams, the second option is to process the used components together in one compatibilization step. For the separation of the different components, two methods are applied: a separation can be performed either by delamination of the system or by selective dissolution–precipitation of the different components.

While the delamination methods can be based on the chemical decomposition of an inter- or adhesive layer, methods based on selective dissolution and methods based on the combined processing of the different constituents can be described by the thermodynamics of polymer solutions.

In order to enable the spontaneous solubility of polymers in solvents or other polymers, the Gibbs free energy of mixing  $\Delta G_{mix}$  has to be zero or negative.  $\Delta G_{mix}$  for the solution process is given by the Gibbs–Helmholtz equation (Equation (1)) [37,38]:

$$\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}, \quad (1)$$

Since the gain in entropy  $\Delta S_{mix}$  is negligible because of the high molecular weight of the polymer chains, the enthalpy difference  $\Delta H_{mix}$  of the blending process has to be negative, which means that the process has to be exothermic (c.f. Equation (1)) [37–39].

Flory and Huggins described  $\Delta G_{mix}$  by the determination of the entropy of the mixing of an assembly of polymer chains and solvent. This is done by counting the number of ways solvent molecules and polymer segments, or two different polymer segments can be accommodated on a lattice. According to the Flory–Huggins theory,  $\Delta G_{mix}$  is generally defined as [40]:

$$\Delta G_{mix} = RT \left[ \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \phi_1 \phi_2 \chi_{12} \right], \quad (2)$$

where  $N_i$  stands for the degree of polymerization of the polymer ( $i$  is the number of monomers per chain),  $\phi_{1,2}$  is the volume fraction of the molecules,  $\chi_{12}$  is the Flory–Huggins interaction parameter,  $R$  is the gas constant, and  $T$  is the absolute temperature.

The first two logarithmic terms of the Flory–Huggins-Equation give the combinatorial entropy of mixing, which, by definition of  $\Phi$ , is negative and always promotes mixing, while the third term is the enthalpy of mixing [40,41].

For polymer blends,  $N_i$  is large in both cases and, so, the combinatorial entropy becomes vanishingly small. Therefore, the miscibility behavior of the system is determined by the value of the last term, i.e., the enthalpy of mixing. An exothermic heat of mixing may be caused by specific interactions between the components of the blend, like covalent and ionic bonds. Weak, nonbonding interactions such as hydrogen bonding, ion–dipole-, dipole–dipole- or donor–acceptor interactions or Van der Waals interactions often do not lead to polymer miscibility. This is why polymer miscibility is more an exception rather than the rule [30].

In the case of  $N_1 = 1$ , the general equation transforms into the equation for polymer solutions:

$$\Delta G_{mix} = RT \left[ \phi_1 \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \phi_1 \phi_2 \chi_{12} \right], \quad (3)$$

Additionally, for polymer solutions, the combinatorial entropy promotes the solubility of the system. In the case of a solvent–solvent mixture, all three terms of the Flory–Huggins equation contribute to solubility. This explains why many miscible solvents systems exist and why the solubility of polymers, in general, is lower than the solubility of molecules with a low molecular weight [42].

As described in the following subsections, the formation of polymer solutions in both solvents and other polymers plays an important role for the recycling of multilayered polymer-based packaging.

### 3.2. Separation of Multilayer Components

This section is dedicated to methods that enable the separation of the different components in a multilayer packaging. A distinction is made between methods in which the target polymers are recycled by dissolution and precipitation, and those that perform a separation of the different layers by delamination.

#### 3.2.1. Recycling of a Target Polymer by Selective Dissolution–Reprecipitation

Pioneer work concerning the recycling of polymer mixtures by selective dissolution was done by Nauman et al. [43] in 1992. Here, the different polymers of the mixture are dissolved at a certain temperature one after another, eventually even in the same solvent. The solution of the first polymer is

separated from the residue by filtration and eventually additivated, before the polymer is recovered by conventional techniques for extracting a polymer from a solvent. The solvents used in the study were, among others, tetrahydrofuran, xylene, or toluene. This scheme was also explicitly tested for multilayer structures. As expected, the selective dissolution process worked for bilayer materials, since both polymers were in contact with the solvent. Surprisingly, it also worked on multicomponent materials where the inner polymer was well shielded from the solvent by an outer polymer with a solution temperature higher than that of the inner polymer. Instead of codissolving at the higher temperature, the inner layers were not well shielded from the solvent, and selective dissolution could occur even when the ordering of the individual polymers was incorrect based on the criterion that the outermost layers must dissolve at the lowest temperatures. It appears that the diffusion of the solvent through the undissolved outer layers causes delamination at the internal polymer-to-polymer interfaces, exposing the entire structure to the solvent. Delamination has also been observed at polymer–metal interfaces. The multilayer structures tested were PP/Maleated-PP, Tie Layer/EVOH/Maleated-PP, Tie Layer/PP, and PA-6/Tie/EVOH/EVA/Surlin<sup>®</sup> [43].

In 1995, a patent specification was published that reports on the extraction of polyolefins from composite packaging containing one or several synthetic polymers as well as metals or natural polymers. As solvent cycloalkanes, *n*-alkanes or *iso*-alkanes, and mixtures thereof can be used. After removal of the nonsoluble components, the solution is dispersed in an aqueous tenside solution. In this way, a dispersion consisting of the precipitated polymer, an aqueous phase, and an organic phase are produced. The precipitation of the polyolefin is nearly quantitative, and the size of the polyolefin particles can vary between 0.01 and 8.00 mm, with the particles having a very smooth surface. A further advantage is that the number of washing steps and also the costs and time expenditure can be reduced by this precipitation method [44].

In 2001, a method was introduced by Mäurer et al. [45] for the treatment of polymer-containing waste, which was also specified for packaging recycling [46]. In the case of packaging recycling, the method aims to recover PE, the polymer component that has the highest value-adding potential, because of its big mass fraction. PE can be recovered in a quality close to that of the virgin material, while the undissolved components remain as a residue of little value. Unlike Nauman's and other earlier patents, solvents applied by Mäurer et al. are not classified as hazardous materials and therefore do not require special labelling. Additionally, a better recovery of the solvent is achieved. In 2017, it was announced that the method was going to be realized in pilot scale in Indonesia to recycle plastic sachet waste from landfills [47]. Aside from packaging recycling, this method is also applied to the waste of electrical and electronic equipment, end-of-life vehicles, and construction materials [48–51].

In the literature, several more patents describing the dissolution–reprecipitation method for commingled postconsumer packaging waste can be found, even though multilayered packaging is not mentioned directly [52–54].

Lindner et al. [52] described a method to obtain LDPE from presorted plastic films, consisting of four steps for the removal of inks, removal of low-molecular-weight components, solution of the film components, precipitation and removal of undesirable polymers, and finally recovering of LDPE from the solution [52]. In WO 2000077082 A1 [53], a patent specification from 2000, the polyolefinic components were dissolved from commingled postconsumer plastic packaging and separated from the undissolved residue by common mechanical separation technologies. Afterwards, the different polyolefins HDPE, PP, and LDPE were successively precipitated from the solution by crystallization, by applying shear forces at different temperatures, while oligomers, inks, and additives were intended to remain in the solution [53]. WO2005118691A2 [54], a patent specification from 2006, described the recycling of PA-6 and PA-6,6 from commingled polyolefin polymer waste. By admixing the waste with an ester solvent and heating the admixture to a temperature above the melting temperature of the contained polymer, an ester solvent composition with dissolved polyamide and a separate immiscible liquid polyolefin phase was formed. The separation of the discrete molten polyolefin phase from the

ester solvent composition could be performed by skimming, decantation, filtration, centrifugation, or combinations thereof [54].

Additionally, different descriptions of the recovery of packaging-relevant polymers from different polymer mixtures, not explicitly originating from packaging waste, exist [55–57].

One advantage of the dissolution–precipitation method is that the input does not have to run through a complex sorting scheme. The input, thus, can consist of a heterogeneous mixture of different multilayer and non-multilayer packaging systems. Additionally, the precipitated polymer can be expected to be of very high-quality, even competing with the virgin polymer. The biggest drawbacks of this method are the energy-intensive drying of the polymer and the fact that all polymer components that do not dissolve remain as a residue of little value.

### 3.2.2. Delamination of Multilayer Packaging

The mechanism of multilayer delamination can be induced physically by the dissolution of macromolecules, and mechanically or chemically by the decomposition of an interlayer or by reactions at the interface.

In the literature, several methods of physical delamination by dissolution of interlayers are presented. The TetraPak patent of 1996 described a multilayer packing comprising PVOH or other water-soluble, thermoplastic resin layers disposed on both sides of a paperboard base material layer, and other thermoplastic synthetic resin layers laminated thereon. An aluminum foil layer may also be contained over a polyolefin adhesive resin layer. The advantage of this composition is that, in hot water, the polyvinyl alcohol or another water-soluble, thermoplastic resin promptly dissolve on both sides of the paperboard base material layer. Thus, a fast separation of the components and a low fiber content in the resins can be achieved [58].

A similar method was described by DE 4328016 A1 [59], a patent specification from 1994, that described a multilayer structure which contains at least three layers, whereof two layers (that are insoluble in a non-neutral aqueous medium) have to be separated by one layer of a polymer that is soluble in non-neutral aqueous solution. This separation layer can consist of at least one acrylate, one aminoacrylate, and, optionally, one neutral vinyl monomer [60]. Such polymers are insoluble in basic solutions, but soluble in acidic solutions. An example of a polymer suitable to be a separation layer is a copolymer of ethyl acrylate and methacrylic acid [61]. To facilitate the separation of the delaminated components of a multilayer with, for instance, five layers, different separation layers can be installed [62].

In 2004, Mukhopadhyay [63] introduced a method in which the components of an aluminum–plastic packaging could be recovered by delamination induced by 50–70% nitric acid. In this medium, neither aluminum nor the plastic component were affected, but the binder adhesive was dissolved. The delaminated constituents were separated by their specific gravity in a series of baths. The time needed for the delamination process depends on the size of the film fragments and the concentration of nitric acid. Stripes of a width of 0.25 cm and a length of preferably less than one meter take about four to seven hours to completely delaminate the structure. In contrast to hydrochloric acid and sulfuric acid, nitric acid does not dissolve aluminum, because a passivating  $\text{Al}_2\text{O}_3$ -layer is formed [63].

Alkali-soluble polymers can also be used for water-resistant labels that can easily be removed in alkaline milieus [61].

A patent specification of Kernbaum and Seibt [64] from 2013 described another method for the removal of the bonding agent between the different layers. As separating fluids, nanoscaled dispersions or precursors of these nanoscaled dispersions were used that contained an organic solvent, a watery component, and at least one stabilizing amphiphilic surfactant. With the help of this separating fluid, the separation of adhesions and coatings is possible by reducing interfacial tensions between the phases of glued and coated materials, thus causing separation. The solid, delaminated components of the multilayer system are usually separated by a swim-sink method, but also by using the differences of the magnetic or electrical properties of the materials [64].

Delamination by mechanical impact is an exception, since adhesion between the different layers in a multilayer packaging usually is too strong.

In 2016 Perick et al. [65], however, published a packaging that comprised a transparent outer layer and an inner layer that usually consists of a material different from the outer layer. A special characteristic of the packaging is that the inner and outer layer were not connected together for at least 30% and preferentially even over 70%. Shredding of the multilayer provided separated particles, at least at the areas where both layers were not connected by an adhesive. Those single-material particles can be separated by common techniques. The printed layer is exposed after the shredding of the multilayer and can be washed off with water [65].

In the following, an overview of the recycling methods is given in which the delamination, and thus the separation of the components, is obtained by the chemical or biochemical degradation of one (inter)layer of the multilayer or by reactions at the interface.

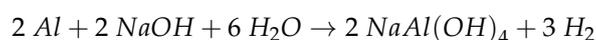
A method introduced by Patel et al. [66] in 2016 addressed a multilayer packaging consisting of PET and PE. Here, sulphuric acid with concentrations ranging from 68 to 98% was used to degrade the PET component. The PE film was not affected and could be reused after several washing steps. Since no information was given on the utilization of the decomposition products of PET, probably no noteworthy reuse is possible [66].

In 2011, Kulkarni et al. [67] proposed the recovery of aluminum from multilayered plastic–aluminum packaging structures by decomposition of the polymeric components in a sub- and supercritical water process. In comparison to polyolefins, condensation polymerization polymers such as PET or PA can be depolymerized into their monomers comparatively easy at subcritical conditions. This method leaves pure aluminum [67].

Another method to chemically delaminate multilayer packaging structures is by enzymatic decomposition of a bio-based interlayer. Multilayer films were produced that were composed of PE and PET films with an interim barrier layer based on a whey protein isolate that also achieves valuable barrier properties suitable for modified atmosphere packaging [68,69]. Whey proteins can be degraded by enzymatic hydrolysis. Because of this biochemical treatment, the coating layer can be washed off from the plastic substrate layer. The washing of samples based on PET–whey and PET–whey–PE was efficient when performed with an enzymatic detergent containing protease enzymes. Different types of commercial enzymatic detergents presented positive results in removing the protein layer from the PET substrate and from the sandwich films, achieving detachment from the PET and PE films. This allowed for further separation of the different polymer films by density separation. The mechanical properties of the plastic substrate, such as stress at yield and stress and elongation at break, were evaluated by tensile testing on films before and after cleaning. Hereby, no significant affection from washing with enzymatic detergents could be observed [68,70].

Additionally, some delamination strategies based on the decomposition of an aluminum layer in non-neutral watery solutions are described in the literature.

Le et al. [71] and Benzing et al. [72] both offered an option to recycle multilayer packaging containing aluminum films. One aspect of the method was the separation of the components by selective dissolution of the intermediate aluminum layer. Aluminum was reacted with an alkali or acid aqueous solution to be dissolved in an aqueous solution phase. Generally, the reaction rate of aluminum with an alkali is higher than that of aluminum with an acid. The reaction rate depends on the concentration and temperature of the alkali or acid aqueous solution and on the rate of diffusion caused by agitation. A reaction equation of the alkali aqueous solution, which is exemplified by sodium hydroxide (NaOH) aqueous solution and aluminum, is as follows [71,72].



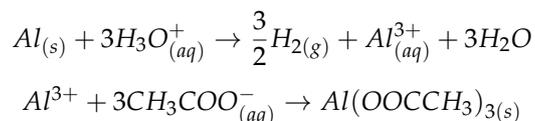
In other words, aluminum is dissolved in a sodium aluminate state in the aqueous solution, and hydrogen gas is generated as a result of the reaction. The soluble sodium aluminate can be

precipitated as poorly soluble aluminum hydroxide. According to the Bayer process, aluminum hydroxide can be converted to  $Al_2O_3$  and subsequently reduced to elemental aluminum.

According to Le's [71] invention, the other layers include PET, PP, and PE. The polyolefin layers can be separated from the PET film by using different gravities, and in order to ensure a complete removal of PET and PO from the respective other fraction, an extraction step can be installed downstream. According to Benzing et al. [72], a paperboard layer can also be contained in the multilayer. Mukhopadhyay et al. [73], however, also described a recovering method of aluminum, paperboard, and polymer-containing multilayer structures by a basic solution. Again, the aluminum was recovered as a water-soluble salt, while the cardboard and plastic component could be separated by their differences in density [73].

Another method to induce delamination of multilayer packaging, can be by a chemical reaction at the interface between two layers. Several publications describe the separation of polymer–aluminum multilayer packaging by the use of acids. Polymer–aluminum multilayers, for example, are used in the case of LPBs. Here, at first, the cardboard component has to be removed in a watery medium.

Fowkes et al. [74,75] described the delamination mechanism of a PE–Al film through fatty acids in 1982. In this case, acid and water molecules diffused through the LDPE layer to the interface. Adhesion at the interface consisted mainly of ionic bonds, hydrogen bonds, and Van der Waals forces between aluminum oxide and oxygen-containing groups of the adhesive polymer like alcohols, ketones, aldehydes, or carboxylic acid on the surface of the polymer [74–76]. Thus, the adhesion between the Al foil and LDPE was mainly due to ionic and hydrogen bonds and Van der Waals forces between their oxidized species. Since the aluminum oxide layer can be dissolved at  $pH = 4$ , elementary aluminum is laid open and is able to react with the aqueous acid under formation of hydrogen and aluminum acetate [77].



The sorption of the acids to the polymer and aluminum surface can induce delamination by reducing interlayer adhesion.

The sorption and the solubility in the polymer were affected by the degree of saturation of the fatty acids. Since the sorption increases with the amount of double bonds but the rate of diffusion decreases with increasing numbers of double bonds because of the increasing rigidity, monosaturated or nonsaturated acids are to be preferred to induce delamination [77]. Nonetheless, this diffusive delamination mechanism requires long reaction times and has a low separation efficiency, which is why further measures have to be taken for recycling applications [76].

Early patents already described the separation of the different layers of laminated packaging with acidic solvent mixtures [78,79]. The waste was treated with an organic acid or a mixture of organic acids e.g., acetic acid. In 1995 Johansson et al. [78] introduced a method that was carried out at a high temperature (80 °C), close to the flash point of acetic acid, which not only required a large amount of energy, but also added a safety risk. The mixture used is highly aggressive because of the high concentration (80%) of acetic acid. This mixture will attack the aluminum components and lead to the formation of hydrogen, as well as to a loss of the amount of aluminum recovered in the process [78].

Kersting et al. [79] published a method for separating an aluminum foil from plastic films, such as PE films, in 1992. The laminates were placed in a 20% solution of low fatty acids (e.g., acetic acid, propionic acid, formic acid, butanoic acid) and heated to 100 °C for 10–20 min. An important aspect of the invention is also that the cooling process was carried out in a closed vessel, whereby a reduced pressure of about 200 hPa could form. Air and solvent traces between the plastic and the aluminum foil expanded because of the decrease of pressure and thus promoted a separation of the components [79].

In a more recent patent from 2012 of Bing et al. [80], a similar delamination method utilizing organic acids (e.g., acetic or formic acid) was described. As a difference, an additional organic solvent (e.g., acetone, chloroform) that works as a swelling agent to accelerate diffusion, and a surfactant

(e.g., polyoxyethylene sorbitan monolaurate) to decrease the surface tension and thus increase the wettability, were used here. Plastic–aluminum composites like toothpaste housings, can be separated by using a mixed separating agent consisting of 40–70% organic acid, 10–20% surfactant, and 20–40% organic solvent [80].

In 2015, Lovis et al. [81] introduced a method that is based on the usage of a microemulsion comprising swelling agents, carboxylic acids, water, and surfactants. These microemulsions had interfacial tensions low enough to penetrate the interphase and counteract adhesion [81].

Delamination of aluminum-containing packaging was also reported in a case of damage caused by the ingredients of cosmetic products. Here, compounds comprising a phenyl and a hydroxyl group caused delamination by diffusion to the aluminum–polymer interface [82,83].

The methods that provide the delaminated multilayer components have in common that different materials have to be separated from each other to be recycled in single-material streams. This can easily be performed by electrostatic separation if one component is aluminum and the second one is a polymer. The separation of the different components proves to be rather difficult if a polymer/polymer mixture is present. For the conventional NIR-separation technique, a ballistic trajectory has to be calculated. This is difficult for the delaminated components, since delaminated layers can be very thin (layers in multilayer packaging often have a thickness of 5 to 30  $\mu\text{m}$ ) and often are cut into small pieces to make intermediate layers and interfaces accessible for delamination treatment. Separation by density also proves to be difficult. Using the float–sink technique, pieces may be undesirably separated. For example, if air bubbles are attached to a surface of the PET layer with a density of 1.38  $\text{g}/\text{cm}^3$ , or if the PET layer is positioned on a plurality of PP or PE ( $\delta = 0.9\text{--}0.97 \text{ g}/\text{cm}^3$ ) films, it will float on water. If a polyolefinic layer is positioned under a plurality of PET layers, it will sink in water. These mistakes can be reduced through the addition of a surfactant or through the repetition of the separation process using the specific gravity differences.

If incorrectly incorporated material has a melting point higher than the melting point of the actual material flow, it can be caught in a melt filtration step by a screen or mesh provided on a breaker plate between a screw and a die. The entry of the component with the highest melting point occurs in dependence upon the size of the mesh.

The share of low-density plastics contained in the sink fraction is usually constituted by polyolefins if water is used as a separation medium. Since those have a melting point lower than PE and PA, they cannot be removed by melt filtration. Instead, the polyolefins can be dissolved selectively using an organic solvent to extract them from the sink fraction. As an alternative to the removal of the impurities, a compatibilization step is also conceivable.

The costly and time-consuming separation step is in competition with the quality of the recycled material.

For multilayers that are delaminated into more than two different polymer types, and mixtures of multilayers containing more than one type of multilayers, the purification becomes even more complex. Eventually, new flake-sorting technologies could also be applied here.

The scenario of commingled postconsumer multilayer packaging by delamination would require a separate sorting path for multilayers and thus a marker that makes them sortable.

### 3.3. Combined Processing

The blending of polymers is an approach to recycling polymer-based multilayers without separating the components. However, because of insufficient solubility, most blends have poor mechanical properties and unstable morphologies, which is why the addition of additives is necessary (cf. 3.1).

In contrast to miscible polymers, immiscible blends do not involve thermodynamic solubility and cannot be characterized by the presence of one phase and one single glass transition temperature. Their overall behavior depends upon the properties of the single components and their ratio, as well

as the morphology of the blend and the properties of the interface. Those factors complicate the prediction of blend properties.

Compatibilization is a process and technique for improving a blend performance by making blend components less immiscible through the addition or in situ generation of a macromolecular species that exhibits interfacial activity in heterogeneous polymer blends. Those compatibilized blends consist of one component finely dispersed in the other, with good adhesion of the phases and strong resistance to coalescence. Therefore, the material can be considered macroscopically homogeneous.

As compatibilizers, macromolecular chains with a blocky structure, such as block or graft copolymers, are often used. One of the blocks is miscible with one blend component, and a second block is miscible with the other blend component. Polyolefins grafted or copolymerized with molecules containing anhydridic, acidic, or ionic groups are often used as well.

The theory and mechanism of compatibilizing is described in the literature in detail [37,84], and recycling-related compatibilization is discussed [38].

Ragaert et al. [10] provided a summary of typical compatibilizers used to process nonmiscible polymers to produce a blended material. In the following, concrete examples of multilayer packaging recycling are presented.

### 3.3.1. Recycling of Multilayers Containing PE/PA

As can be seen in Table 2, laminates containing PA and polyolefins play an important role. The blending of polyolefins with PA produces thermodynamically immiscible two-phased systems [85–87]. In literature, several techniques for the compatibilization of those blends can be found.

A method commonly used to induce the compatibility between PA and polyolefins is by addition of the polyolefin component grafted with maleic anhydride (PE/PP-g-AH). This concept was employed by Choudhury et al. [88] in 2005 to recycle a postconsumer oil pouch material consisting of a coextruded film made of LDPE, LLDPE, and PA-6. During the melt extrusion of the pouch components together with the compatibilizer, intermolecular interactions between the primary amine end group of PA-6 and the anhydride groups can take place. The polyethen backbone of the PE-g-AH copolymer is able to form a Van der Waals interaction with the polyolefinic contents of the pouch (cf. Figure 3). During the formation of the imide, one equivalent of water is formed as a by-product. In order to shift the equilibrium to the side of the imide, the removal of water is necessary. This requires an extruder with venting capabilities.

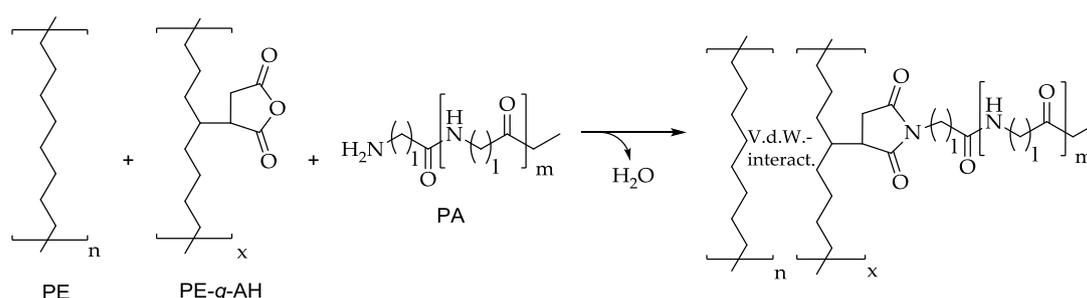
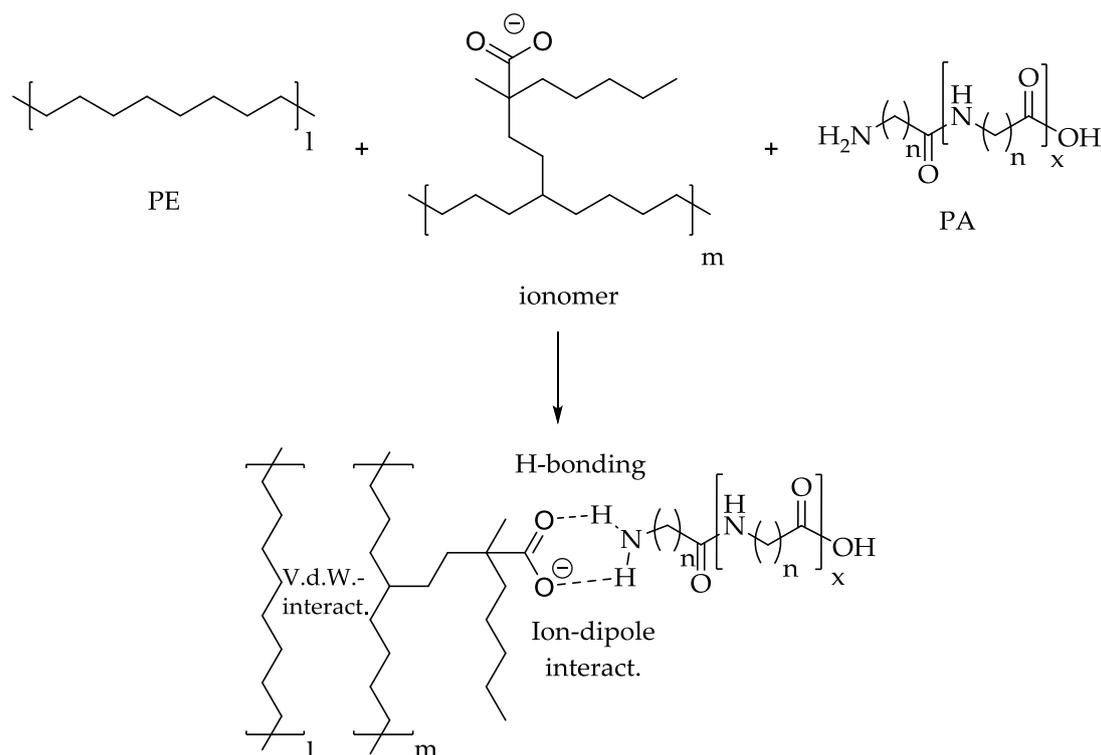


Figure 3. Compatibilization mechanism of PE and PA using PE-g-MA. Adapted from [89].

With this method, tensile strength, hardness, and percent elongation-at-break of the compatibilized blend could clearly be improved by the increased interfacial adhesion.

Dagli et al. [90] used the same technique and recycled PP/PA blends by using PP-g-AH copolymer as a compatibilizer in 1994.

Another compatibilizer tested for the LLDPE/LDPE/PA oil pouch was an ionomer of an ethylene–methacrylic acid copolymer. The intermolecular interactions expected to cause the decrease of interfacial tension between the different phases in this case are depicted in Figure 4 [88].



**Figure 4.** Compatibilization mechanism of PE and PA using an ionomer. Adapted from [88].

Blends compatibilized by the ionomer exhibit a higher degree of crystallinity, which causes even better tensile properties than the blends compatibilized by PE-*g*-AH.

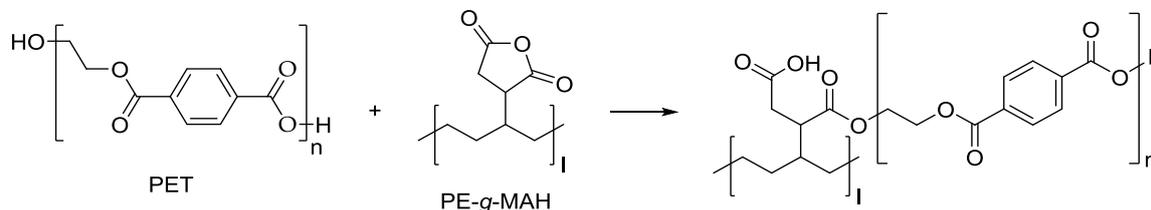
Additionally, several patents describing the recycling of multilayered films based on polyolefins and polyamide can be found in the literature. In DE 3938552, a patent specification from 1991 compatibilization was induced by radical cross-linking between the different polymer types by using peroxides and coagents like 2-butyne-1,4-diol. The diol reacts with the secondary amide of the polyamide, and the triple bond promotes radical cross-linking with the polyolefin. The polyethylene/polyamide blend was diluted with polypropylene to adjust the mechanical properties and the melt viscosity [91]. In DE 4223864 A1, multilayers consisting of PA and PE (0.5–50%) were mixed to PA (40–98%) together with 1–50% compatibilizer. An additional 0–60% could be filler materials. The compatibilizers used were polyethenes of different molecular weights, which were fitted either by the grafting of PE or by the copolymerization of ethene with other monomers reactive with respect to PA (anhydrides, amino, acid, epoxide, ester groups, and salts of carboxylic acids). The products obtained could be used as a replacement material for PA [92].

In EP 0575855A1 [93], a patent specification published in 1993, washed and unsorted plastic household waste, and the swimming fraction of the plastic waste treatment were treated. The processing was performed in a polymer melt in the presence of unsaturated monomers and radical initiators. Initiated by the peroxide, the monomers grafted onto the different polymer components. Thus, different graft copolymers with different graft matrices but the same sidechains resulted. Hence, the incompatibility of the different polymers could be reduced and an improvement of strength and toughness could be achieved [93].

### 3.3.2. Recycling of Multilayers Containing PE/PET

Like PA, PET is often used in packaging applications in combination with polyolefins but does not exhibit miscibility. Again, polyolefins grafted with maleic anhydride (PE/PP-*g*-MA) can be used to compatibilize PET and PO. The anhydride groups of the compatibilizer can react with the PET

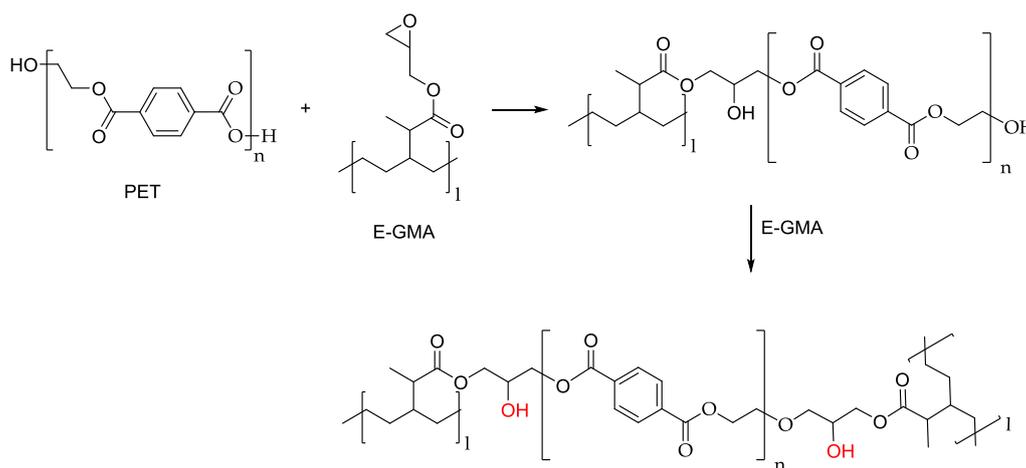
hydroxyl end group in an esterification, promoting a chemical anchoring between the polyester and the compatibilizer (cf. Figure 5). The polyolefin phase of PE/PP-g-MA is miscible with the PO component, allowing for physical anchoring [94].



**Figure 5.** Chemical reaction between the terminal hydroxyl groups of PET with maleic anhydride groups of PE-g-MA [95].

In 2001, Uehara et al. [94] recycled postindustrial plastic films containing 70% of PE, 10% of PET, 10% of PA-6, and 10% adhesives and ink by using PE-g-MA. Because the reaction of the succinic ring of the maleic anhydride with the terminal secondary amine PA is very fast [96,97], PE-g-MA first compatibilizes the PA component and, subsequently, the PET component. This causes poor mechanical properties at low PE-g-MA contents (3–5%), where the PET component stays uncompatibilized, and a sudden increase to 5 to 10%.

Additionally, the compatibilization effect of a copolymer of ethylene-glycidyl methacrylate (E-GMA) was investigated. In the case of E-GMA, the preferred reaction of the glycidyl groups involves the COOH end group of PET [98]. By increasing the concentration of E-GMA, however, the competition among the reactions between PA and both PET terminal groups can be overcome. Even though an increase of the concentration of E-GMA to 15% overcomes this competition between the reactions, the mechanical properties of the material compatibilized by 15% E-GMA are not competitive with the properties of the material compatibilized with 15% PE-g-MA. This is due to a cross-linking effect of E-GMA that has to be taken into account at higher E-GMA concentrations. The reactions depicted in Figure 6 give rise to a complex macromolecular structure that has a direct impact on the viscosity and the mechanical properties of the blend [94].



**Figure 6.** Cross-linking mechanism of E-GMA with PET. The hydroxyl groups marked in red show possible reaction sites for further cross-linking reactions. Adapted from [94].

In contrast to E-GMA, PE-g-MA cannot induce cross-linking, since it can only react with the terminal hydroxyl group of PET. Thus, for the recycling of scraps containing polyolefins and PET,

the usage of PO-*g*-MA seems to be a good method, especially if higher amounts of compatibilizer are needed [94].

In 2000, Wyser et al. [99] investigated the recycling of a multilayer packaging material consisting of PP–PET–SiO<sub>x</sub> by using a maleic acid-grafted polyolefin component, in which the polyolefin component was PP. The compatibilization mechanism is already depicted in Figure 5. While the unmodified recycled PP–PET–SiO<sub>x</sub> blend exhibited a coarse morphology and was brittle because of a lack of adhesion between the two polymer phases, the compatibilized material showed a fine blend morphology, with PET domains smaller than 7 nm at concentrations of 5 and 10%. Since, however, at concentrations above 5% of PP-*g*-MAH, a brittle interphase started forming between the PP and the PET, with a corresponding drop in the ductility, the best results with a fine morphology and excellent ductility were obtained with a high content of PP-*g*-MAH [100].

According to this study, the size of the SiO<sub>x</sub> inclusions, resulting from the fragmentation of the oxide coating during reprocessing, did not influence the mechanical properties of the blend, as long as the concentration was below  $2 \times 10^{-3}$  [99,100].

Like for polyamides, ionomers can also be used for compatibilization. Choudhury et al. [100] investigated the recyclability of LDPE/LLDPE/PET-based postconsumer laminated oil pouches by the addition of a zinc salt of ethylene methacrylic acid copolymer (Surlyn<sup>®</sup> ionomer) in comparison to PE-*g*-MAH (Fusabond<sup>®</sup>). Again, because of its higher crystallinity, the blend compatibilized by the ionomer exhibited better tensile properties compared to blends implemented by the anhydride grafted additive. Also, the increase of the impact strength and hardness was more effective with the Surlyn<sup>®</sup> ionomer than with Fusabond<sup>®</sup> for the system studied [100].

The technique of compatibilization is uncomplicated in application, since it can be performed in a melt-processing step like extrusion. One disadvantage of this method is that, in order to add the optimal amount of compatibilizer, the composition of the input has to be known. While the addition of too little compatibilizer provides unsatisfactory product properties, the addition of an excess amount results in unnecessary costs due to high-priced compatibilizers. In order to get a consistent product quality that is usually desired by the purchaser, the composition of the input material has to be consistent. Thus, in multilayer recycling, this method, above all, is suitable for postindustrial waste, like edge trim and start up waste, that accounts for about 10–15% of the input. Here, the proportion of the components is known and constant in composition. Additionally, compatibilization only adds one additional life cycle to the polymer and thus it does not promote a circular economy in the proper meaning of the word. The end-of-life treatment of material recycled by compatibilization is incineration, since it cannot be assigned to a sorting stream.

The direct incorporation of compatibilizers into multilayer structures, however, allows for the utilization of this method for postconsumer waste. In 2016, Dow introduced a self-recyclable multilayer structure packaging that already contains a compatibilizer and even claimed to show improved compatibilization, when compared to adding a compatibilizer component as a separate stream in a recycling process. In the multilayer structure, at least one polyolefin component, at least one layer consisting of a polar polymer (e.g. PA, PET), and at least one tie layer consisting of a maleic anhydride-grafted polymer had to be present. The compatibilizer, which can be an anhydride and/or carboxylic acid-functionalized ethylene- $\alpha$ -olefin copolymer, was present in the range of 1% to 35% in the polyolefin layer. Examples are Retain 3000, a maleic anhydride-grafted ethylene-octene plastomer, or Amplify<sup>TM</sup> TY, a MAH-grafted polymer [101].

### 3.3.3. Others

In the literature, several further descriptions of polymer packaging recycling containing several polymer types can be found that are not explicitly meant for multilayered packaging. Nonetheless, the strategies described are similar to the methods mentioned before, and mostly polyolefin-based compatibilizers grafted with anhydrides or acids can be found [102–105].

Additionally, other different descriptions of the blend recycling of non-packaging material can be found. Here again, acid or anhydride-grafted polyolefins [106,107], polyolefins grafted with glycidyl methacrylate [107–109], or ionomers are used in the literature [110,111].

Also, the compatibilization of packaging plastics other than polyolefins, PET, and PA is described in the literature [111–115].

Additionally, a method is described in which PP and PET were processed together without a compatibilizer. Microfibrillar composites were instead produced, which means that, in a mixture of two immiscible polymers, the polymer with the highest melting point is used as a natural reinforcement element in the one with the lower melting point. Therefore, a special thermal–mechanical treatment consisting of three steps has to be performed: first, the immiscible polymers are melt-blended to create a dispersion of the polymers; in a second step, the filaments are continuously drawn at a certain temperature; in the third step, the isotropization is conducted. In the case of PET and PP, PET forms microfibrils in the PP matrix, whereby improved mechanical properties result. This processing method can be seen as an option to utilize PP waste streams containing small amounts of PET [116,117].

#### 4. Summary & Conclusions

Decent sorting is a basic prerequisite for the production of high-quality recycled polymers. According to the current state of the art, plastic and plastic multilayer packaging is not assigned to a special sorting stream. Instead, plastic and plastic multilayer packaging can be found in different recycling pathways like films, mixed plastics, or the residue.

The residue and, in some cases, the mixed plastics are utilized directly by incineration. In the cases of mechanical recycling, as it is performed with films and, in some instances, also with mixed plastics, multilayers are usually an impurity and have to be separated from the presorted input in a second separation step.

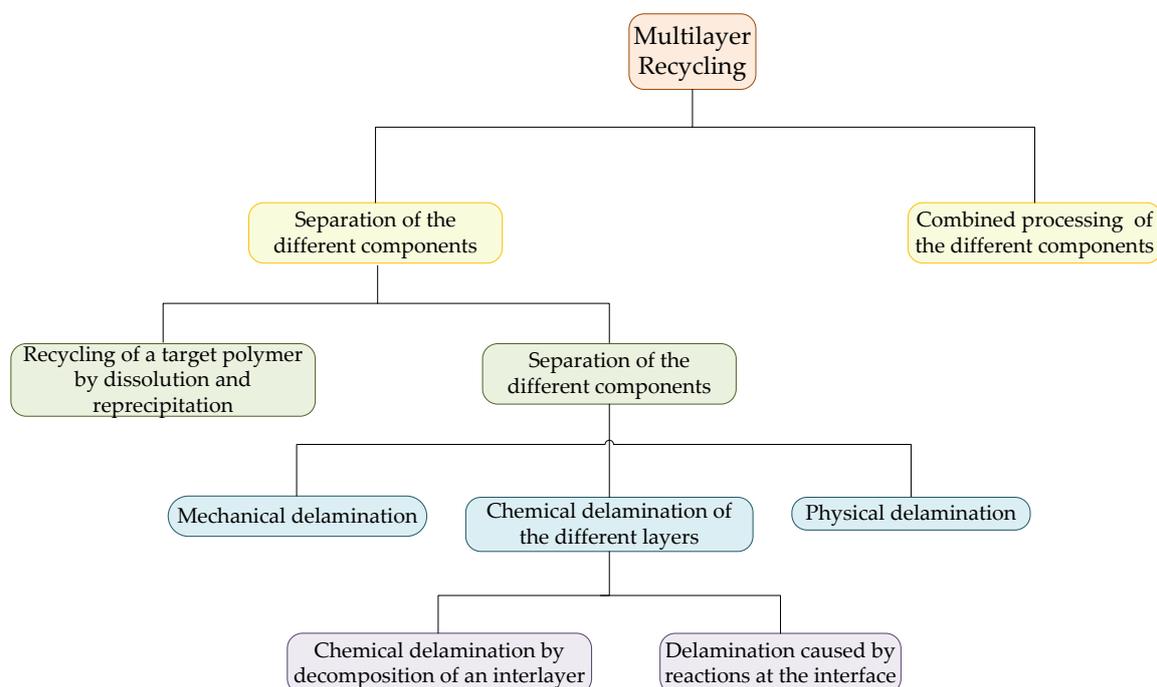
The current state of research, in general, describes two general ways to recycle multilayered packaging items: the first option is to separate the different multilayer components and make them available for recycling in separated recycling streams; the second option is to process the used components together in one compatibilization step.

Compatibilization is achieved by the addition or generation of suitable molecules that act as compatibilizers. The methods, which are based on the separation of the different materials of a multilayer, can be subdivided into two strategies: either the determined target polymers are separated only by the selective dissolution–reprecipitation method, or the multilayer is delaminated by physical, chemical, or mechanical means (cf. Figure 7). Physical delamination methods in general are based on the dissolution of either an adhesive or an interlayer to induce delamination and thus the separation of the different layers. As solvents, organic solvents, water and aqueous solutions with a pH value different from seven were mentioned. Mechanical delamination remains an exception, since, usually, a strong adhesion between the different layers is given. Only one case is known in which weak adhesion allows for the mechanical separation of a multilayered packaging by shredding. The methods in which the separation of the different layers is induced by a chemical reaction can be subdivided into methods in which delamination is induced by a reaction at the interphase, and those in which delamination is induced by decomposition of an interlayer (e.g., Al, whey-protein, PET).

The technique of compatibilization has the big advantage that it is uncomplicated in performance. However, with regard to both the quality and the costs, the optimal amount of compatibilizer has to be added, since neither a shortage of compatibilizer, nor an excess amount of compatibilizer is desirable. This means that the composition of the input should be known. Postindustrial waste has a constant and known composition and thus can be recycled by compatibilization.

In the case of commingled postconsumer multilayer packaging waste, a very high degree of sorting would be necessary to provide a consistent product quality that is usually desired by the purchaser. However, the composition of postconsumer waste is subject to fluctuations, and no ideal

sorting can be guaranteed. Thus, the scenario of commingled postconsumer multilayer packaging waste by compatibilization does not seem to be realistic.



**Figure 7.** Schematic overview of the introduced recycling methods of multilayer packaging.

Additionally, compatibilization only adds one additional life cycle to the polymer, and the end of life treatment of material recycled by compatibilization is incineration.

It is the only method that is successfully established on the market today, e.g., to improve the quality of slightly contaminated polymers or the recycling of postindustrial packaging waste. Thus, compatibilization is used, for instance, to handle poorly sorted PE or PP fractions recycled from packaging waste. Its scope, however, is limited by the described issues.

The method of the selective dissolution and recovery of one target polymer from a mixture of different packaging and polymer types does not require a high degree of sorting. Here, neither the input nor the output has to run through a complex sorting process, and the input can thus contain different multilayer and nonmultilayer packaging systems. The quality of the obtained polymer can be high enough to compete with the virgin material and free of additives or other contaminants. In general, however, the recycling of the sorting fractions that are, according to the current situation, utilized by incineration is quite conceivable with this method.

However, one big drawback is that the solvent has to be removed from the polymer solutions under expenditure of energy and time. This method is the most efficient if only few polymers make up major parts of the total amount. The economic efficiency decides on the number of polymers separated from the polymer mixtures. Thus, one further disadvantage is that, usually, not all components of more complex multilayers or mixtures of different multilayer structures are recovered.

Until today, extensive research has been done on the polymer recovery by the dissolution–reprecipitation technique. First industrial pilot plants exist or are currently installed, however, the feasibility in industrial practice and sustainable economic efficiency has not been proven yet.

In contrast to the dissolution–reprecipitation technique, recycling by delamination only dissolves a minor, if any, component. For this reason, the amount of polymer that will be regained and dried is much lower, and, hence, the delamination processes could be more energy-efficient and cost-effective. Additionally, not only the main component, but all components could be regained.

The methods that provide the delaminated multilayer components have in common the feature that the different materials must be separated from each other to be recycled in single material streams.

This separation step is essential for the quality of the recycled polymer. What has to be taken into account is that, with increasing heterogeneity of the mixture, the complexity of the separation grows. Therefore, the input should be as defined as possible, since a defined input is a prerequisite for a successful separation process later on. This means that a separate recycling stream for delaminable multilayers has to be established. This scenario would require the application of new marker-based sorting technologies.

Currently, however, only delamination methods suitable for particular types of multilayer exist. Waste fractions containing only one multilayer occur at specific production sites with low amounts, maybe too low to justify an investment in a sophisticated recycling technology. A more general method to delaminate a broader range of multilayer structures would be desirable, as it would be applicable for real packaging waste.

In order to shape a future with higher recycling rates and more efficient recycling procedures, innovative techniques and methods have to be established. In addition to the substitution of multilayered packaging by monomaterial solutions, innovative recycling methods can be considered.

Common compatibilization does not seem to be a feasible technique for postconsumer packaging waste, since fluctuations in the composition of the input can be unpredictable and no constant product quality can be guaranteed. The direct addition of compatibilizer into the packaging system, however, might be a strategy to avoid these problems.

Because of its advanced stage of development, the dissolution–reprecipitation method could be available for the recycling of existing recycling streams in the near future. It could be an attractive alternative to incineration or to the production of low-quality recycled materials. In the long term, the recycling of multilayer packaging by delamination might also be an attractive option. Here, in contrast to the dissolution–reprecipitation method, a lower amount of energy has to be expended for polymer drying. Thus, a systematical delamination procedure could be an ecologically and economically more sustainable solution if the separation of the delaminated polymer layers as well as a selective sorting of recyclable multilayer packaging items are possible.

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