Technische Universität München

TUM School of Life Sciences

Development of a reversible-crosslinking polyurethane-based Diels-Alder adhesive for multilayer packaging and a corresponding solvent-based recycling process

Katharina Maria Anna Kaiser

Vollständiger Abdruck der von der TUM School of Life Sciences der Technischen Universität München zur Erlangung des akademischen Grades einer

Doktorin der Naturwissenschaften

genehmigten Dissertation.

Vorsitzender:	apl. Prof. Dr. Petra Först
Prüfer der Dissertation:	1. Prof. Dr. Horst-Christian Langowski
	2. Prof. Dr. Cordt Zollfrank
	3. Prof. Dr. Bernd Mayer

Die Dissertation wurde am 01.02.2022 bei der Technischen Universität München eingereicht und durch die TUM School of Life Sciences am 02.06.2022 angenommen.

“If you have built castles in the air, your work need not be lost; that is where they should be. Now put the foundations under them.”

Henry David Thoreau (1817-1862)

Acknowledgments

Ganz besonderer Dank gilt meinem Doktorvater Prof. Dr. Horst-Christian Langowski, der sich dazu bereit erklärt hat, diese Arbeit zu betreuen und mit seiner ganzheitlichen Sicht auf das Thema und seinem umfangreichen Fachwissen immer wieder geholfen hat, Probleme aus anderen Blickwinkeln zu betrachten.

Prof. Petra Först danke ich herzlich für die Übernahme des Prüfungsvorsitzes und bei Prof. Dr. Cordt Zollfrank und Prof. Bernd Mayer möchte ich mich herzlich dafür bedanken, dass sie sich dazu bereit erklärt haben das Amt des Zweit- bzw. Drittprüfers zu übernehmen.

Dr. Andreas Mäurer möchte ich aufrichtig dafür danken, dass ich die Möglichkeit hatte, diese Arbeit in der Abteilung Verfahrensentwicklung Polymerrecycling anfertigen zu können. Außerdem danke ich ihm für die vielen Freiheiten, die er mir bei der Themenfindung und der Umsetzung meiner Arbeit gelassen hat und für die menschliche Art, mit der er seine Funktion als Abteilungsleiter und Betreuer ausübt.

Meiner Mentorin Dr. Cornelia Stramm danke ich für ihre herzliche Art mit der sie sich als Beratungsperson und Korrekturleserin zur Verfügung gestellt hat.

Meinen Studenten Daniel Bauer, Gerrit Stöbener und Dominik Putz danke ich für ihre tatkräftige Unterstützung im Labor.

Bei Kerstin Müller, meiner Mitstreiterin im „Projekt Promotion“, möchte ich mich von Herzen für den fachlichen Austausch, die vielen bereichernden Gespräche Abseits der Arbeit und ihren Besuch in Barcelona bedanken.

Allen Kollegen der VR danke ich für das familiäre Verhältnis und die herzliche Atmosphäre. Vor allem danke ich Tanja Ginzinger dafür, dass sie die Extrusionen in dieser Arbeit organisiert hat, und dem Technikumsteam für die Unterstützung beim Upscaling.

Mein Dank richtet sich auch an Norbert Rodler, Markus Pummer und Brigitte Seifert, die immer ein offenes Ohr für meine Fragen und Probleme rund um die Laminierung bzw. optische Analytik hatten, mir mit Rat und Tat zur Seite gestanden sind und mir mit lustigen und aufmunternden Gesprächen neue Motivation verschafft haben.

Mein größter Dank gilt meiner Familie für das entgegengebrachte Vertrauen, die Ermöglichung meines Studiums und die liebevolle Unterstützung in all den Jahren. Bei Max möchte ich mich für die Paperbelohnung bedanken und dafür, dass er mich so liebevoll durch die letzte Phase meiner Promotion begleitet hat.

List of Abbreviations

Remark: The abbreviations used in the individual publications have not been included in this list and are instead explained individually in the respective publication.

CMR	Carcinogenic, mutagenic or toxic to reproduction
DMSO	Dimethyl sulfoxide
EVOH	Ethylene vinyl alcohol, thermoplastic copolymer
FTIR	Fourier-transform infrared spectroscopy
HDI	Hexamethylene diisocyanate
HOMO	Highest occupied molecular orbital
IPDI	Isophorone diisocyanate
LUMO	Lowest unoccupied molecular orbital
MDI	Methylene diphenyl diisocyanate
MEK	Methyl ethyl ketone or butanone
MO	Molecular orbital
NIR	Near-infrared
NMR	Nuclear magnetic resonance
PE	Polyethene, here used for PE-LD and PE-LD as an umbrella term
PE-LD	Polyethene of low density
PE-HD	Polyethene of high denisty
PET	Poly(ethylene terephthalate)
PP	Poly(propene)
PVC	Polyvinyl chloride/poly(1-chloroethylene)
TDI	Toluene diisocyanate
UV	Ultraviolet

Preliminary Remarks

The work presented in this publication-based thesis has been published in international peer-reviewed journals. The individual publications are listed below and correspond to the individual chapters of the thesis. All of these publications were published under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in this thesis without any further permission.

Articles

- Katharina M. A. Kaiser, Recycling of multilayer packaging using a reversible cross-linking adhesive. *J. Appl. Polym. Sci.* **2020**, *137*(40), 49230.

  https://doi.org/10.1002/app.49230

- Katharina M. A. Kaiser, Johann Ewender, Frank Welle, Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law. *Polymers* **2020**, *12*(12), 2988.

  https://doi.org/10.3390/polym12122988

- Katharina M. A. Kaiser, Tanja Ginzinger, Production of a PET//PE-LD laminate using a reversibly cross-linking packaging adhesive and recycling on a small-scale technical plant. *Recycling* **2021**,*6*(3), 47.

  https://doi.org/10.3390/recycling6030047

Review

- Katharina M. A. Kaiser, Markus Schmid, Martin Schlummer, Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling* **2018**, *3*(1), 1.

  https://doi.org/10.3390/recycling3010001

Table of Contents

Acknowledgments V

List of Abbreviations VI

Preliminary Remarks VII

Table of Contents VIII

1. Introduction 1

2. Background 3

    2.1. Production of Multilayer-Packaging 3

        2.1.1. Extrusion 3

        2.1.2. Lamination 4

    2.2. Recycling of Post-Consumer Packaging 5

        2.2.1. Solvent-based recycling 6

        2.2.2. Mechanical recycling 7

3. Recycling of Polymer-Based Multilayer Packaging: A Review [23] 9

4. Theoretical Background on Adhesion and Debonding 36

    4.2. The Chemistry of Polyurethane Adhesives 37

    4.4. Debonding on Demand 45

    4.5. The Diels-Alder Reaction 46

5. Objective of the thesis 48

6. Recycling of multilayer packaging using a reversible crosslinking adhesive [46] 50

7. Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law [47] 63

8. Production of a PET//PE-LD laminate using a reversibly cross-linking packaging adhesive and recycling on a small-scale technical plant 65

9. Discussion 109

    9.1. Conclusion 112

10. Outlook 114

11. Summary 117

12. Zusammenfassung 119

13. References 121

Curriculum vitae...**Fehler! Textmarke nicht definiert.**

1. Introduction

In prehistoric times, those materials were used and shaped as tools, which were found in the immediate environment of humans. Even naturally occurring polymers such as natural resins were used as adhesives early in human history. However, it took until the 19th century before the naturally occurring polymers natural rubber, casein and cellulose could be transformed into the first predecessors of plastics through chemical modification. At the beginning of the 20th century bakelite was produced, the first fully synthetic material, and soon after that numerous other synthetic products such as polyvinyl chloride, polystyrene and polyolefins followed. [1,2]

Since then, plastics have in many cases replaced other materials and also created a multitude of new applications. The possible areas of application for plastics seem to be limitless, and so the amount of plastic produced has increased more than twenty-fold between 1964 and 2020 [2–4] Around 367 million tonnes of plastic are produced annually, the majority of which is made up of the polyolefins polyethene (PE) and poly(propene) (PP), ahead of polyvinyl chloride (PVC) and poly(ethylene terephthalate) (PET). [3,4]

Depending on the application, however, different plastics dominate. In the third largest application area of plastics, the automotive sector, polyurethanes, polyamides, acrylonitrile butadiene styrene, polyolefins and others are used in a wide range of different plastics. The second largest field of application is the building & construction sector with around 20 wt.%. PVC, polystyrenes and polyolefins are mainly used in this field. At around 40 wt.%, most plastics are used in packaging, where polyolefins and PET clearly dominate. Polystyrene, PVC, polyamide and other plastics are used in smaller quantities. [5,6]

The reasons for the great importance of plastics in the packaging market is that, compared to rigid materials such as glass, steel and aluminum, plastics offer clear advantages because they are light-weight, transparent and break-proof. The different types of plastic allow a wide range of possible applications, but as mono-materials they often do not fully meet many packaging specific requirements. Multilayer packaging, which are usually composed of two or more material layers, overcome this problem. [7]

Multilayer structures combine the properties of the individual materials, which are selected on the basis of their individual properties and combined in the packaging to meet all the necessary requirements for the particular application. [8] However, there is often not just one, but many different material combinations that can meet the requirements of an application. If this is the case, selection is based on other criteria such as price or availability of multiple suppliers.

The packaging-relevant properties that are influenced by the polymer choices include barrier properties, abuse-resistance, sealability, machinability, and consumer impact. Barrier effects of packaging are necessary to prevent oxygen, water, light, taste or fat from entering or leaving the packaging. Permeation through polymer films is a three-step process that leads to an interaction of the contents with the environment. For this, molecules must first dissolve in the film structure, diffuse through the material and desorb on the other side. The driving force for this are concentration or pressure gradients. Cosmetics, medicines and perishable foods carry odors, active ingredients and flavors and are also susceptible to atmospheric oxygen. An organic or inorganic barrier layer with low gas permeability prevents an exchange of substances with the environment. Ethylene-vinyl alcohol is frequently used as an organic barrier material, while inorganic barriers include aluminum foils or e.g. aluminum oxide in the form of a thin vapor deposited layer. [7,8] On their own, thin layers of these barrier-materials would not have abuse resistance, which is why they are combined with more stable, tear and impact strength and puncture-resistant packaging materials, such as polyethylene, polypropylene or polyethylene terephthalate. To make the packaging sealable at high speeds, thermal resistance and relatively low melting temperatures are required. Therefore, an PE-LD layer, for example, is often found on the product side of sealed packaging. In order to appeal to potential buyers, shine is often desirable, which can be achieved with an outer PET layer.

The heterogeneity of the packaging market, which has evolved in recent years due to the many possible combinations of a large number of different materials, is a challenge for the sorting and recycling of post-consumer packaging. Since the recycling system was designed from the beginning to recycle monomaterials, multilayer packaging is often simply not recycled or can also contribute to foreign materials being introduced into the monomaterial recycling streams.

Since according to the European Plastics Strategy all packaging should be recyclable by 2030 [9] and Germany aims to increase recycling rates for plastic packaging to 63% by 2022, [10] it is necessary to develop and establish new strategies for the recyclable design of packaging and also new recycling technologies. In this work, the approach is to develop a polyurethane adhesive containing thermally labile Diels-Alder adducts for packaging purposes and a corresponding recycling process that allows separation of the bonded layers and thus their recycling.

2. Background

In order to be able to modify established packaging designs and the recycling system accordingly, it is first necessary to understand how packaging is currently produced and recycled. The relevant processes are described in the chapters 2.1 and 2.2.

2.1. Production of Multilayer-Packaging

In order to convert polymer raw materials into a functional packaging, usually first a mechanical-physical modification of the polymer to granulate and then the desired products is carried out. This modification also includes the addition of additives such as antistatics, stabilizers, lubricants or fillers, which can be used, for example, to adjust the chemical resistance, mechanical properties or processability. [11] Further processing of the additivated and granulated material can be carried out by various techniques, with co-extrusion or extrusion and subsequent lamination being particularly relevant with regard to multilayer packaging. These two technologies will be discussed in the following.

2.1.1. Extrusion

In the extrusion of plastics, the plastic is first melted and then pressed through a profiled die which determines the shape and cross-section of the extruded material. Continuous extrusion is usually achieved here by screw extrusion, whereby the material is continuously conveyed by one or more screws, but also compacted and homogenized.

In a standard 3-zone extrusion, the screw is divided into three sections: feed zone, transition zone and metering zone. In the feed zone, the pellets are first preheated and compacted without melting. This then takes place in the transition zone, which is sometimes also referred to as the compaction zone, since the granules have significantly more volume than the melt. In the last zone, the metering or discharge zone, the pressure necessary to overcome the resistance of the forming die. [11,12]

The extrusion through the die theoretically results in an endless molded piece that can take the form of a strand, pipe, tube or film, for example. In addition to the extruder and the forming die, the complete extruder line contains downstream components such as cooling, haul-off and winding or size reduction equipment.

Different extruders are used depending on requirements. While a twin-screw extruder is used for compounding, such as granulation with incorporation of the additives, for the production of semi-finished products, such as films, single-screw extruders are used. [12]

For packaging production, on the one hand, wide-slot dies with a coat-hanger-shaped distribution channel ensure uniform distribution of the melt, with the film thickness resulting from the discharge thickness and the haul-off speed. In this way, cast films from a few millimeters to approx. 100 µm can be produced. After leaving the slot die, the film produced is usually stretched in the extrusion direction, making it oriented and thinner. [12]

With the aid of an annular die outlet and supporting air, the melt can be blown into a tube in the blown film process. This also allows the production of very thin films with a thickness of 10 µm. [12]

To produce multilayer films by extrusion, the coextrusion process is used. This is possible using both blown film and cast film manufacturing principles and allows the coextrusion of three, five, seven, nine or more layers. [8] Each plastic to be incorporated into a composite must first be melted in its own extruder, and the output of a single extruder can be split to create multiple layers of the same material in the laminate. [13] The individual melt streams can be combined in different ways. In so-called feed block coextrusion, the individual melt streams are combined into a single laminar melt stream in the feed block located just upstream of the die. Die coextrusion, on the other hand, requires a complex die that combines the melt streams at the die exit. [13,14] It is important that the materials do not mix so that each layer retains its individual identity and thus characteristic properties. [15]

The advantage of coextrusion over lamination is that no intermediate steps are required. In addition, with coextrusion, the individual layers can be extremely thin; since the structure is handled only as a unit, it is not necessary for the individual layers to be mechanically robust. [8]

2.1.2. Lamination

In the manufacture of multilayer packaging by lamination, substrate films are bonded together through a controlled roll-to-roll process using an adhesive. [7] There are different methods for this.

In dry-bond lamination, a solvent- or water-based adhesive is first coated onto the primary film, which is then passed through a vented oven to remove the solvent or water. Upon exiting the oven, the adhesive is warm and tacky, but dry because the solvent has been removed. The secondary film is then introduced through a heated roller to produce a laminate that is then wound up under pressure. Since the primary film runs the longer distance during lamination, it is usually chosen to be the more heat-resistant and less stretchable material. [16]

Solvent-free laminations differ from dry-bond lamination in that the adhesive consists of a solid, which must be melted for use in order to be applied to the primary web with a roller system. In wet-bonding, the solvent, usually water, is not evaporated prior to lamination and must therefore escape through one of the substrates. Therefore, wet bonding is only suitable for laminates where one of the substrates is paper-based. [16]

Some substrates, such as polyolefins, must be treated with ozone or plasma prior to lamination to clean the surface and increase surface energy by applying functional groups. This allows uniform application of the liquid over the entire surface in a uniform wet layer and better adhesion of the adhesive. [16]

Lamination processes are particularly suitable when the materials to be bonded are already available as films, which is the case, for example, with aluminium foils or oriented film. Lamination can also be used to protect ink and create a particularly glossy finish when the ink can be placed between two films. [7,8]

2.2. Recycling of Post-Consumer Packaging

Various recycling technologies are available for the recovery of plastics, whereby a general distinction can be made between physical and chemical recycling (Figure 1). The main difference between these two methods is that in physical recycling the polymer chains are preserved, since only physical processes such as melting or dissolving are carried out, whereas in chemical recycling the polymer chains are degraded into fragments or monomers by chemical reactions.

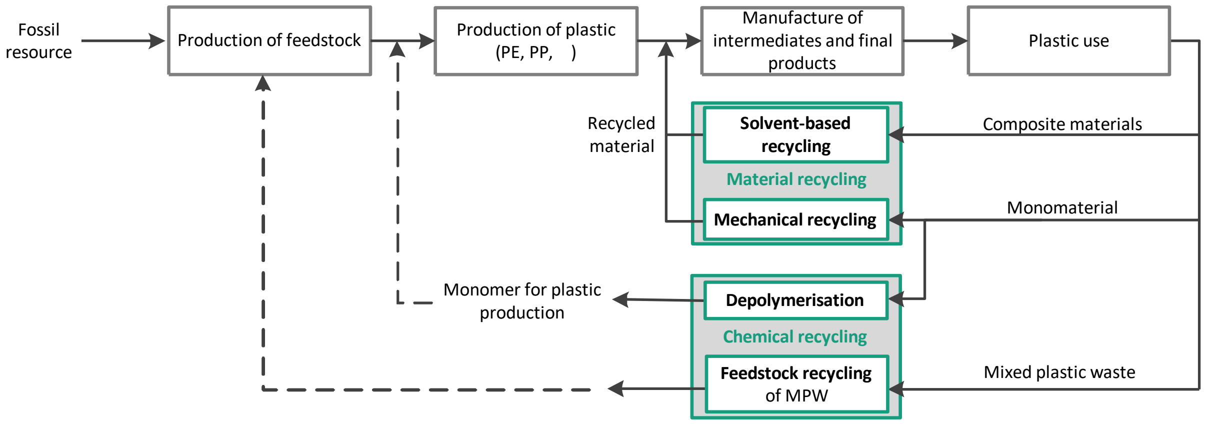


Figure 1. Overview of the different recycling technologies and how they are integrated into the process chain. Adapted from [17]

The term chemical recycling covers a wide range of methods. The products of these processes can be monomers, gases or oils and require further processing to become a new polymer. Depolymerization methods generally have higher requirements for the purity of the input material than feedstock recycling methods. However, since the plastic is not preserved in chemical recycling, it does not fall under the definition of the recycling quota from the point of view of the German Federal Environment Agency and the Packaging Act. Thus, these methods will not be discussed further. [10,18]

In physical recycling, a distinction can be made between classical mechanical recycling and solvent-based recycling. These two methods will be discussed in more detail below.

2.2.1. Solvent-based recycling

Solvent-based recycling is based on dissolving polymers from waste streams and subsequently purifying and recovering them by precipitation and/or drying.

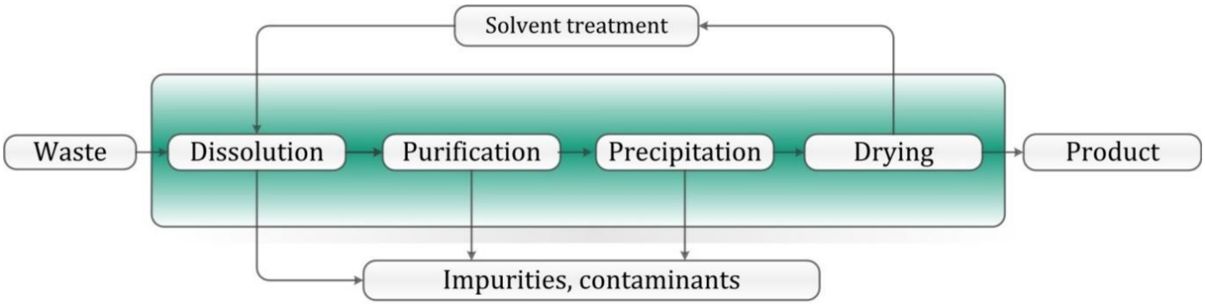


Figure 2: CreaSolv® process as an example of solvent-based recycling methods. [19]

Figure 2 shows the general process scheme of the solvent-based CreaSolv® process, which is an example of solvent-based recycling. [19] The process uses selective solvent formulations with high boiling points that allow safe plant operation. These are used to extract the target polymer, while the insoluble components are removed from the polymer solution by filtration or centrifugation. The target polymer is dried and solvent and precipitant are recovered and reused. [19]

Solvent-based recycling is a suitable method to recover plastics from material streams that cannot be recycled in a high-quality way by mechanical recycling. These material streams include sorting residues, multi-component packaging and unsorted plastic waste.

2.2.2. Mechanical recycling

Mechanical recycling describes the processing of plastic waste through the steps of washing, melting & cleaning into new plastic products, leaving the polymer chains and chemical structure largely unchanged.

In order to obtain recycled polymers of decent quality, mechanical recycling of post-consumer plastic waste usually requires pretreatment in form of sorting and washing steps. Pre-sorting takes place in sorting plants, where sorting fractions are generated, each of which is treated separately in further processing. Figure 3 shows the individual steps of the presorting process.

Figure 3. Overview of the individual process steps involved in sorting post-consumer plastic packaging. Adapted from [20]

In the sorting process, after the input has been spread on a sorting belt, the materials must be classified according to size. This means that materials larger than DIN A4 are sorted out by means of a drum screen, as these would hinder the downstream sorting steps. The films among the large-sized materials are sorted into a plastic film fraction using a suitable air classifier. In addition, materials smaller than 20 to 50 mm are sorted out into a residual fraction to ensure that the downstream sorting units can work efficiently. Flexible packaging smaller than DIN A4 but is sorted into the soft mixed plastic fraction. In the downstream process, liquid packaging board and plastic-coated cardboard packaging are identified by near-infrared technology and separated from the other materials by compressed air pulses. Aluminum is removed from the main material stream by an eddy current separator that sorts according to electrical conductivity, while dimensionally stable plastics can be separated by near infrared sorting and sorted by polymer type. [20,21]

This sorting process produces various material fractions, which are then further processed individually, provided they can be recycled. This further treatment usually involves shredding, water washing to remove the majority paper labels and other impurities. Density separation is also performed at the same time to separate polyolefins from other plastics. Finally, the extrusion of the plastic for the production of regranulate under melt filtration and degassing. [20]

From this process of pretreatment and actual recycling, requirements result that a packaging must meet in order to be considered recyclable. [20–22]

One basic prerequisite for the recycling of packaging is the existence of sorting and processing infrastructure for the high-quality recycling of this packaging. Additionally, it must be possible to sort the packaging item into the fraction intended for it. This means that the packaging has to have the minimum size for sorting and, in the case of plastic packaging, that the surface properties of the packaging has to allow the target material to be identified. During further processing, it is important that the packaging does not introduce any impurities into the recycled product, since high-quality recycled materials cannot be produced if incompatible composite materials or undesired additives are present. [22]

In many cases, multilayer packaging does not meet these requirements for recyclability. This is partly because sortability is complicated by the presence of different materials and also because, in many cases, the different materials cause recycling incompatibilities, which lead to an evaluation as non-recyclable and to the fact that the packaging cannot be assigned to any sorting fraction.

The following chapter therefore discusses the approaches that could be considered suitable for the recycling of multilayer packaging.

3. Recycling of Polymer-Based Multilayer Packaging: A Review [23]

Katharina Kaiser, Markus Schmid and Martin Schlummer

Basically, there are two possible approaches for recycling multilayer packaging. Either the components can be separated for recycling or the components can be processed together to give a blended material.

Combined processing into recyclates with good mechanical properties is often only possible by adding compatibilizers, since most polymers are thermodynamically immiscible due to their different chemical structures. When recycling multilayers of PE and PET, for example, PE grafted with maleic anhydride or ethylene glycidyl methacrylate can be used as compatibilizers to obtain a macroscopically homogeneous material.

The separation of the materials from each other, can either be done by the dissolution–reprecipitation process by dissolving a target polymer by using selective solvents (compare chapter 2.2.1), or by delamination of the different layers. Delamination of multilayer packaging can occur physically by solvating polymers from plastic interlayers, mechanically or chemically by decomposition of an interlayer, or by reactions at the interface. While mechanical delamination remains an exception, since there is usually strong adhesion between the layers, there are some approaches for physical delamination, but these are only suitable for selected composites, such as aluminum-containing composites. For chemical delamination, this is achieved by decomposition of an intermediate layer, which can be PET, whey or aluminum.

Since the compatibilization for heterogeneous post-consumer multilayer waste would only allow downcycling to blends and delamination is only possible for selected structures and the dissolution-precipitation method requires energy-intensive drying, a systematic extension of the delamination method to a wider range of multilayer strategies would be a promising research approach.

Recycling **2018**, *3*, 1, DOI:10.3390/recycling3010001

Author Contributions: Katharina Kaiser wrote the manuscript and was involved in the revision and finalization of the paper. Markus Schmid and Martin Schlummer helped design the overall outline and contributed to selected sections and to the revision and editing of the manuscript.

recycling

MDPI

Review

Recycling of Polymer-Based Multilayer Packaging: A Review

Katharina Kaiser [1,2,*], Markus Schmid [1,2] and Martin Schlummer [2]

[1] Technical University of Munich, TUM School of Life Sciences Weihenstephan, Weihenstephaner Steig 22, 85354 Freising, Germany; markus.schmid@ivv.fraunhofer.de
[2] Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Strasse 35, 85354 Freising, Germany; martin.schlummer@ivv.fraunhofer.de
* Correspondence: katharina.kaiser@ivv.fraunhofer.de; Tel.: +49-8161-491-466

Received: 27 October 2017; Accepted: 19 December 2017; Published: 22 December 2017

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 polyethene (LDPE) being the most prominent, followed by polypropene (PP), high-density polyethene (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].

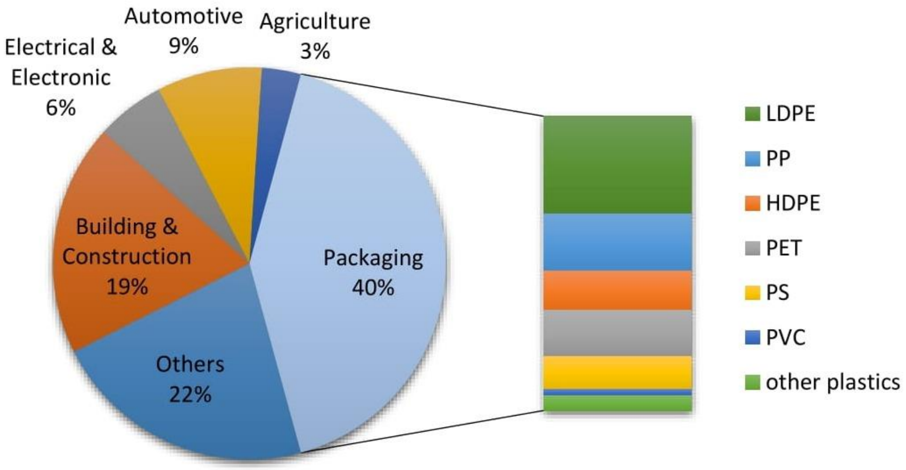


Figure 1. Fields of application of plastic materials and polymer types predominately used in packaging. The respective share of the different polymers is derived from a graphic illustration of the polymeric composition of plastic packaging in Europe [11]. Abbreviations used: LDPE (low-density polyethene), PP (polypropene), HDPE (high-density polyethene), 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 polyethene (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_2 filled polymers	Acid/anhydride grafted polyolefins	LDPE
OPET	polyamides (nylon, BOPA)	EVA			EVA
PS	polyesters, OPET	ionomers			ionomers
Paper	coatings (SiOx, Al_2O_3, 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_x or SiO_x, respectively
- thermoformed plastic and plastic composites
- plastic and plastic composites with Al foil.

These five categories made up 17.7 billion m^2 (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^2 of plastic-based flexible packaging. The remaining 43.7 % m^2 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^2 and in percent m^2. 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^2 Film	Share in m^2-%
Simple multilayers	total	**6565.6**	**37.1**
	Thereof: PA/polyolefin	2710.2	15.3
Packaging with organic barriers	total	**4499.9**	**25.4**
	Thereof: EVOH	4304.7	24.3
Thermoformed packaging	total	**2482.1**	**14.0**
	Thereof: PA/polyolefin	756,3	4.27
Packaging with inorganic barriers	total	**2996.1**	**16.9**
	Thereof: PET-BO/layer/polyolefin	1362.9	7.7
Packaging with Al-foil	total	**1153.1**	**6.5**
	Thereof: PET/Al/plastic	829.1	4.7
		17,696.9	**100**

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® (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®-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].

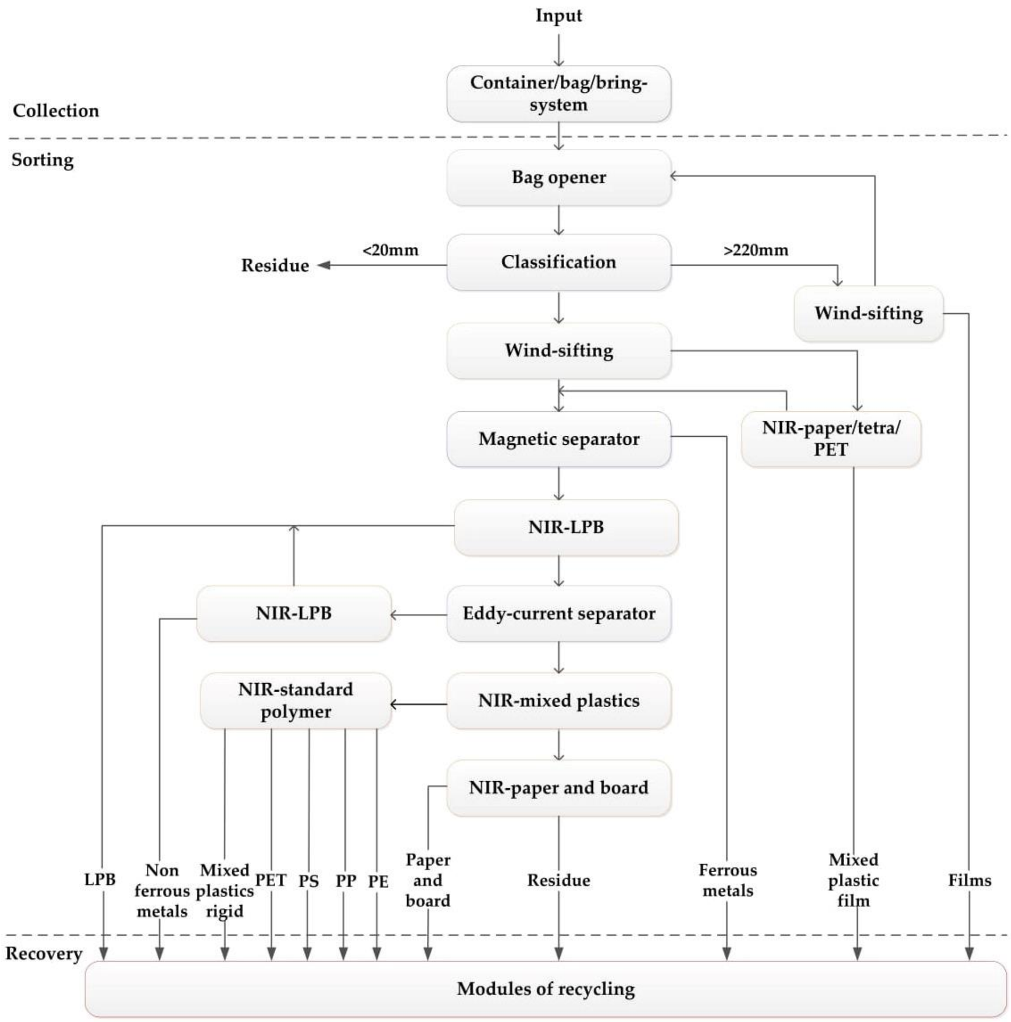


Figure 2. Scheme of a standard state-of-the-art sorting plant. Adapted from [20]. NIR is the abbreviation for near infrared.

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].

Recovery				**Removal in kt/%**		
Total	**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 ΔG_{mix} has to be zero or negative. ΔG_{mix} for the solution process is given by the Gibbs–Helmholtz equation (Equation (1)) [37,38]:

$$\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix}, \tag{1}$$

Since the gain in entropy ΔS_{mix} is negligible because of the high molecular weight of the polymer chains, the enthalpy difference ΔH_{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 ΔG_{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, ΔG_{mix} is generally defined as [40]:

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

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, χ_{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 Φ, 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:

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

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 where PP/Maleated-PP, Tie Layer/EVOH/Maleated-PP, Tie Layer/PP, and PA-6/Tie/EVOH/EVA/Surlyn® [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 Al_2O_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].

$$2\ Al + 2\ NaOH + 6\ H_2O \rightarrow 2\ NaAl(OH)_4 + 3\ H_2$$

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].

$$Al_{(s)} + 3H_3O^+_{(aq)} \rightarrow \frac{3}{2}H_{2(g)} + Al^{3+}_{(aq)} + 3H_2O$$

$$Al^{3+} + 3CH_3COO^-_{(aq)} \rightarrow Al(OOCCH_3)_{3(s)}$$

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 rigidness, monosatured 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, butonoic 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 μm) 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 g/cm^3, or if the PET layer is positioned on a plurality of PP or PE (δ = 0.9–0.97 g/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 copoylmer 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.

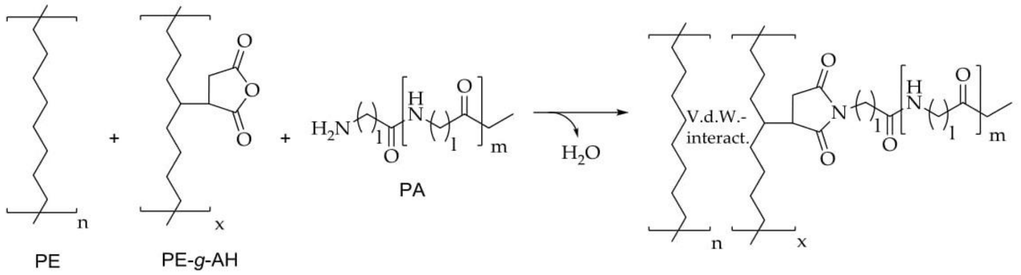


Figure 3. Compatibilization mechanism of PE and PA using PE-*g*-MA. Adapted from [89].

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].

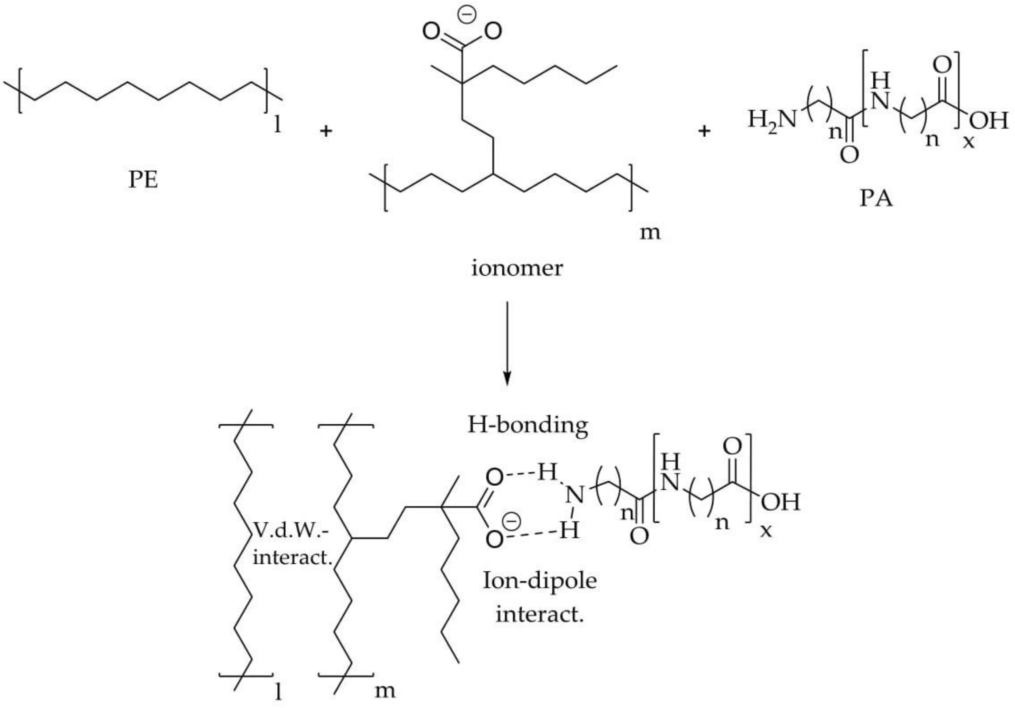


Figure 4. Compatibilization mechanism of PE and PA using an ionomer. Adapted from [88].

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 polypropene 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].

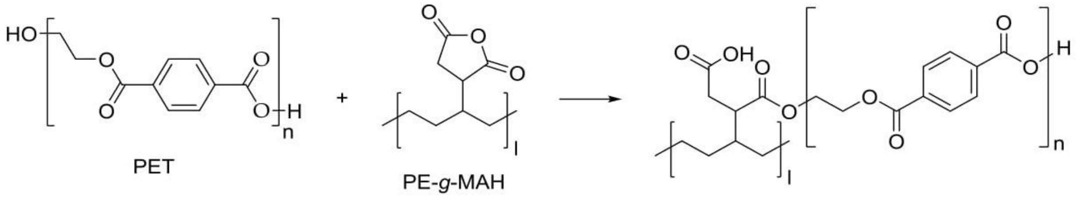


Figure 5. Chemical reaction between the terminal hydroxyl groups of PET with maleic anhydride groups of PE-*g*-MA [95].

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].

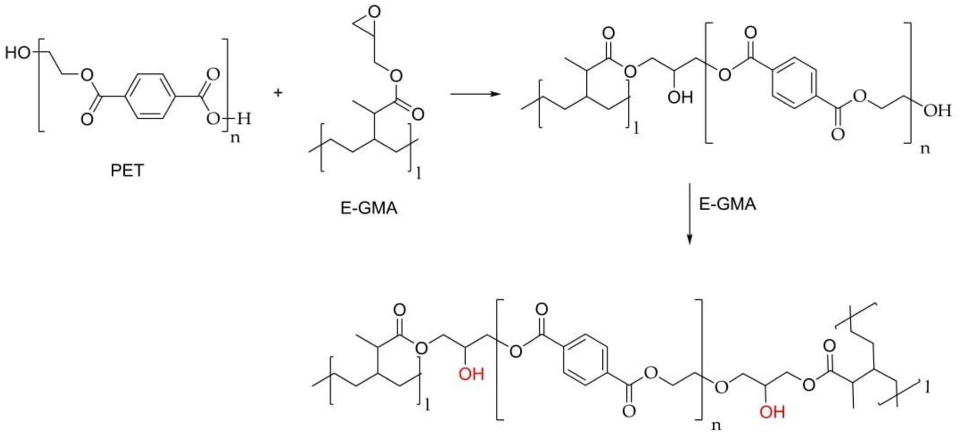


Figure 6. Cross-linking mechanism of E-GMA with PET. The hydroxyl groups marked in red show possible reaction sites for further cross-linking reactions. Adapted from [94].

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_x 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–SiOx 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 mm 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 SiOx 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 2×10^{-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® ionomer) in comparison to PE-*g*-MAH (Fusabond®). 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® ionomer than with Fusabond® 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 containes 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^{TM} 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.

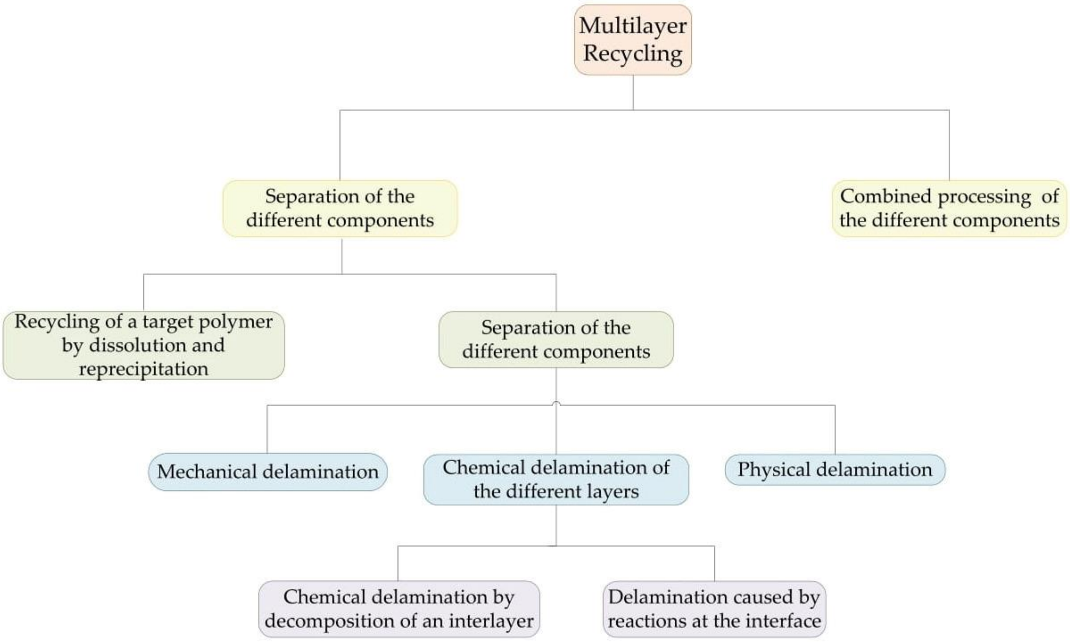


Figure 7. Schematic overview of the introduced recycling methods of multilayer packaging.

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 productions 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.

Acknowledgments: This work was supported by the Industry Association for Food Technology and Packaging (IVLV).

Author Contributions: Katharina Kaiser wrote the manuscript and was involved in the revision and completion of the work. Markus Schmid and Martin Schlummer were responsible for the overall outline and contributed to selected sections as well as to the revision and editing of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References and Note

1. Gesellschaft für Verpackungsmarktforschung (GVM). *Entwicklung des Verpackungsverbrauchs Flexibler Kunststoffe nach Branchen—Auswertung des Deutschen Marktes 2009, Prognose 2014*; GVM—Gesellschaft für Verpackungsmarktforschung: Mainz, Germany, 2010.
2. PlasticsEurope. *Plastic Packaging: Born to Protect*; PlasticsEurope—Association of Plastics Manufacturers: Brussels, Belgium, 2012.
3. Morris, B.A. *The Science and Technology of Flexible Packaging. Multilayer Films from Resin and Process to End Use*; Elsevier: Amsterdam, The Netherlands, 2016; ISBN 9780323243254.
4. APK AG. Available online: https://www.apk-ag.de/de/ (accessed on 22 December 2016).
5. Saperatec AG. Available online: http://www.saperatec.de/technology/#technologie_top (accessed on 19 December 2016).
6. Henshaw, J.M.; Owens, A.D. An overview of recycling issues for composite materials. *J. Thermoplast. Compos. Mater.* **1996**, *9*, 4–20. [CrossRef]

7. Jesmy, J.; Jyotishkumar, P.; Sajeev, M.; Thomas, G.; Thomas, S. Recycling of polymer blends. In *Recent Developments in Polymer Recycling*; Fainleib, A., Grigoryeva, O., Eds.; Transworld Research Network: Kerala, India, 2011; pp. 187–214, ISBN 978-81-7895-524-7.
8. Hamad, K.; Kaseem, M.; Deri, F. Recycling of waste from polymer materials: An overview of the recent works. *Polym. Degrad. Stab.* **2013**, *98*, 2801–2812. [CrossRef]
9. Achilias, D.S.; Giannoulis, A.; Papageorgiou, G.Z. Recycling of polymers from packaging materials using the dissolution-reprecipitation technique: Advantages and limitations. In Proceedings of the Conference on Environmental Science and Technology, Kos Island, Greece, 5–7 September 2007.
10. Ragaert, K.; Delva, L.; Geemb, K.V. Mechanical and chemical recycling of solid plastic waste. *Waste Manag.* **2017**, *69*, 24–58. [CrossRef] [PubMed]
11. PlasticsEurope. *Plastics—The Facts 2016*; PlasticsEurope—Association of Plastics Manufacturers: Brussels, Belgium, 2016.
12. Consultic. *Produktion, Verarbeitung und Verwertung von Kunststoffen in Deutschland 2015*; Consultic Marketing & Industrieberatung GmbH: Rückersdorf, Germany, 2016.
13. Gesellschaft für Verpackungsmarktforschung (GVM). *Flexible Plastic Packaging Market in Germany and in Europe*; GVM—Gesellschaft für Verpackungsmarktforschung: Mainz, Germany, 2017.
14. Ebnesajjad, S. *Plastic Films in Food Packaging—Materials, Technology and Applications*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2013; ISBN 9781455731152.
15. Wagner, J.R. *Multilayer Flexible Packaging*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2000; ISBN 9780323477185.
16. PlasticsEurope. *Funktionsal Barriers for the Use of Recycled Plastics in Multi-Layer Food Packaging*; Packaging Europe: Brussels, Belgium, 2017.
17. European Parliament and Council Directive (EC) No 1935/2004: Of 27 October 2004: On materials and articles intended to come into contact with food and repealing directives 80/590/eec and 89/109/eec. *Official Journal of the European Union*. 2004.
18. Dixon, J. *Packaging Materials: 9. Multilayer Pacjaging for Food and Beverages*; ILSI Europe: Brussels, Belgium, 2011; ISBN 9789078637264.
19. Markwardt, S.; Wellenreuther, F.; Drescher, A.; Harth, J.; Busch, M. *Comparative Life Cycle Assessment of Tetra Pak Carton Packages and Alternative Packaging Systems for Liquid Food on the Nordic Market*; ifeu—Institut für Energie- und Umweltforschung Heidelberg: Heidelberg, Germany, 2017.
20. Gesellschaft für Verpackungsmarktforschung (GVM). *Recycling-Bilanz für Verpackungen—Berichtsjahr 2016*; GVM—Gesellschaft für Verpackungsmarktforschung: Mainz, Germany, 2017.
21. Corey, N.; Blodgett, S. *Breakthrough DOW Technology Enables Recyclable Flexible Plastic Packaging*; The Dow Chemical Company: Midland, MI, USA, 2016.
22. Borstar®-Based Full PE Laminate Solution Improves Recyclability of Flexible Packaging Materials. Available online: https://www.borealisgroup.com/news/borstar-based-full-PE-laminate-solution-improves-recyclability-of-flexible-packaging-materials (accessed on 19 September 2017).
23. Cimpan, C.; Maul, A.; Jansen, M.; Pretz, T.; Wenzel, H. Central sorting and recovery of MSW recyclable materials: A review of technological state-of-the-art, cases, practice and implications for materials recycling. *J. Environ. Manag.* **2015**, *156*, 181–199. [CrossRef] [PubMed]
24. Christiani, J. *Prüfung und Testierung der Recyclingfähigkeit*; Cyclos-HTP: Aachen, Germany, 2017.
25. Der grüne Punkt. *Product Specification 08/2014 Fraction-No. 310-1*; Der grüne Punkt: Cologne, Germany, 2014.
26. Hopewell, J.; Dvorak, R.; Kosior, E. Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B* **2009**, *364*, 2115–2126. [CrossRef] [PubMed]
27. BIO Intelligence Service. *Studie über ein Erhöhtes (Werkstoffliches) Recyclingziel für Kunststoffe*; Plastics Recyclers Europe: Brussels, Belgium, 2013.
28. Morris, J. Recycling versus incineration: An energy conservation analysis. *J. Hazard. Mater.* **1995**, *47*, 277–293. [CrossRef]
29. Kindler, H.; Nikles, A. Energiebedarf bei der Herstellung und Verarbeitung von Kunststoffen. *Chem. Ingeneur Tech.* **1997**, *51*, 1125–1127. [CrossRef]
30. Jesson, J.K.; Pocock, R.; Stone, I. *Barriers to Recycling: A Review of Evidence Since 2008*; The Waste & Resources Action Programme: Banbury, UK, 2014.

31. Fricke, K.; Bahr, T.; Thiel, T.; Kugelstadt, O. *Stoffliche oder Energetische Verwertung—Ressourceneffizientes Handeln in der Abfallwirtschaft*; GGSC-Infoseminar: Berlin, Germany, 2009.
32. Bund für Umwelt und Naturschutz. *Wege zu einer Nachhaltigen Abfallwirtschaft*; Bund für Umwelt und Naturschutz: Berlin, Germany, 2010.
33. Christiani, J.; Griepentrog, U.; Weber, H.; Giegrich, J.; Detzel, A.; Breuer, L. *Grundlagen für eine ökologisch und ökonomisch Sinnvolle Verwertung von Verkaufsverpackungen*; ifeu—Institut für Energie- und Umweltforschung Heidelberg GmbH, HTP Ingenieurgesellschaft für Aufbereitungstechnik und Umweltverfahrenstechnik Prof. Hoberg und Partner: Heidelberg, Germany, 2001.
34. Kreibe, S. *Recyclingfreundliche Verpackungen—Eine Einordnung aus ökologischer Sicht*; Interseroh Fachtagung Future Resources 2017; Verpackung ist Rohstoff: Frankfurt, Germany, 2017.
35. Alwast, H.; Birnstengel, B. *Resource Savings and CO_2 Reduction Potentials in Waste Management in Europe and the Possible Contribution to the CO_2 Reduction Target in 2020*; Prognos AG, Ifeu—Institzt für Energie- und Umweltforschung, INFU—Institut für Umweltforschung: Heidelberg, Germany, 2008.
36. Landbell AG. Verpackungsgesetz-info.de. Available online: verpackungsgesetz-info.de/ (accessed on 25 Novermber 2017).
37. Liu, N.; Baker, C. Reactive polymers for blend compatibilization. *Adv. Polym. Technol.* **1992**, *11*, 249–262. [CrossRef]
38. Feldman, D. Polyblend compatibilization. *J. Macromol. Sci.* **2005**, *42*, 587–605. [CrossRef]
39. Koning, C.; van Duin, M.; Pagnoulle, C.; Jérôme, R. Stragegies for compatibilization of polymer blends. *Prog. Polym. Sci.* **1998**, *23*, 707–757. [CrossRef]
40. Manias, E.; Utracki, L.A. Thermodynamics of polymer blends. In *Polymer Blends Handbook*; Utracki, L.A., Wilkie, C.A., Eds.; Springer: Berlin, Germany, 2014; Volume 1, ISBN 978-94-007-6065-3.
41. Hansen, C.M. *Hansen Solubility Parameters—A User's Handbook*; CRC Press: London, UK, 1998; Volume 2, ISBN 9780849372483.
42. Dill, K.A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Chemistry and Biology*; Garland Science: New York, NY, USA, 2002.
43. Nauman, E.; Lynch, J. Polymer Recycling by Selective Dissolution. US005278282A, 11 January 1994.
44. Thome, R.; Kraus, S.; Schubert, J. Process for Treating or Working Up Composite and Plastic Materials. EP0644230 A1, 22 July 1995.
45. Mäurer, A.; Wolz, G.; Schlummer, M.; Luck, T.; Knauf, U.; Kippenhahn, R. Method for Separating and Recovering Target Polymers and Their Additives from a Material Containing Polymers. EP1311599 A1, 21 May 2003.
46. Mäurer, A.; Schlummer, M. Good as new. Recycling plastics from weee and packaging waste. *Waste Manag. World WMW* **2004**, *4*, 33–34.
47. Unilever. Unilever Develops New Technology to Tackle the Global Issue of Plastic Sachet Waste. Available online: https://www.unilever.com/news/Press-releases/2017/Unilever-develops-new-technology-to-tackle-the-global-issue-of-plastic-sachet-waste.html (accessed on 30 June 2017).
48. Mäurer, A.; Schlummer, M. Method for Treating Waste Containing Plastic. WO11082802 A1, 14 July 2011.
49. Mäurer, A.; Schlummer, M.; Beck, O. Method for Recycling Plastic Materials and Use Thereof. US8138232 B2, 20 March 2012.
50. Knappich, F.; Hartl, F.; Schlummer, M.; Mäurer, A. Complete recycling of composite material comprising polybutylene terephthalate and copper. *Recycling* **2017**, *2*, 9. [CrossRef]
51. Fraunhofer Institute for Process Engineering and Packaging IVV—Process Development for Polymer Recycling. Available online: https://www.ivv.fraunhofer.de/de/forschung/verfahrensentwicklung-polymer-recycling.html (accessed on 30 June 2017).
52. Lindner, W.; Thiele, A.; Gorski, G. Method for Obtaining LDPE from Used Plastic Films. EP1392766A1, 3 March 2004.
53. Lindner, W. Method of Separating Polyolefinic Synthetic Mixtures. WO2000077082 A1, 21 December 2000.
54. Mauldin, L.B.; Cook, J.A. Separation of Polyolefins from Polyamides. WO2005118691 A2, 2 February 2006.
55. Bosewitz, S.; Seifert, D.; Kaeufer, H.; Seefeldt, H.; Klein, F. Recovery of Pure Olefins from Solution and Separation of Plastics with Close Precipitation Temperatures. DE19822234 A1, 18 November 1999.

56. Arlt, W.; Sadowski, G.; Seiler, M.; Behme, S. Mixed Polyolefin Separation Used for Low Density Polyethylene and High Density Polyethylene in Waste Involves Using Lower Alkane as Solvent and Different Lower Alkane as Separation Aid. DE19905029 A1, 16 November 2000.
57. Feick, E.; Heller, B.; Kaiser, T.; Ruf, S.; Schleich, R.; Bungert, B.; Thiele, A.; Gorski, G. Method for Separating at Least One Selected Polymer from a Mixture of Polymers. US20040116563 A1, 17 June 2002.
58. Bergerioux, C. Easy-to-Recycle Laminated Material for Packaging Use. US5506036 A, 9 April 1996.
59. Bentmar, M.; Berlin, M.; Leth, I.; Lundgren, B. A Delaminable Packaging Laminate and a Method of Producing the Same. EP0934160 A1, 11 August 1999.
60. Deibig, H.; Dinkelaker, A. Aminogruppen Enthaltendes Polymerisat, Verfahren zu Seiner Herstellung und Verwendung. EP0320757 A2, 21 June 1989.
61. Deibig, H.; Dinkelaker, A.; Rossmann, K. Soluble Adhesive Films. US5094912 A, 10 March 1992.
62. Gerber, M. Packaging Material Which Can Be Delaminated for Recycling—Contains Layers of Plastic, Metal Foil and/or Cellulosic Material, Sepd. by Layer(s) of Polymer Which Is Soluble in Non-Neutral aq. Medium. DE4328016 A1, 3 March 1994.
63. Mukhopadhyay, A. Process of Delamination of Multi-Layer Laminated Packaging Industrial Refuse. US20040054018 A1, 18 March 2004.
64. Kernbaum, S.; Seibt, H. Separating Fluid, Method and System for Separating Multilayer Systems. US20130319618 A1, 5 December 2013.
65. Perick, M. Method for Recycling Plastics from a Film Packaging Bag, Film Packaging Bag and Film Composite Sheet for Manufacturing a Film Packaging Bag. EP3059061 A1, 24 August 2016.
66. Patel, K.M.; Vaviya, M.M.; Patel, M.H. Process for Recovering Low-Density Polyethylene from Flexible Packaging Material. WO15159301 A3, 21 January 2016.
67. Kulkarni, A.K.; Daneshvarhosseini, S.; Yoshida, H. Effective recovery of pure aluminum from waste composite laminates by sub- and super-critical water. *J. Supercrit. Fluids* **2011**, *55*, 992–997. [CrossRef]
68. Cinelli, P.; Schmid, M.; Bugnicourt, E.; Coltelli, M.; Lazzeri, A. Recyclability of PET/WPI/PE multilayer films by removal of whey protein isolate-based coatings with enzymatic detergents. *Materials* **2016**, *9*, 473. [CrossRef] [PubMed]
69. Schmid, M.; Held, M.; Noller, K. Innovative concepts for food packaging. *Packag. Films* **2011**, *2*, 4–8.
70. Schmid, M.; Dallmann, K.; Bugnicourt, E.; Cordoni, D.; Wild, F.; Lazzeri, A.; Noller, K. Properties of whey-protein-coated films and laminates as novel recyclable food packaging materials with excellent barrier properties. *J. Polym. Sci. A Polym. Chem.* **2012**, *2012*, 562381. [CrossRef]
71. Lee, Y.C.; Kim, M.J.; Lee, H.C. A Recycling Method of Multilayer Packaging Film Waste. EP1683829 A1, 26 July 2006.
72. Benzing, K.; Fleig, J.; Feiss, D.; Rott, H. Separating Aluminum-Containing Composites, E.g. For Recycling Packaging Materials, Involves Treatment with Alkali Solution to Dissolve Aluminum and Precipitate Other Materials. DE10102554 A1, 25 July 2002.
73. Mukhopadhyay, A. Process for Delamination of Laminated Packaging. EP2516526 A2, 31 October 2012.
74. Allen, K.W. A review of contemporary views of theories of adhesion. *J. Adhes.* **1987**, *21*, 261–277. [CrossRef]
75. Fowkes, F.M. Acid-base interaction in polymer adhesion. In *Microscopic Aspects of Adhesion and Lubrication*; Georges, J.M., Ed.; Elsevier: Amsterdam, Netherlands, 1981; Volume 7, pp. 119–134, ISBN 978-0-444-42071-8.
76. Olafsson, G.; Jägerstad, M.; Öste, R.; Wesslin, B. Delamination of polyethylene and aluminum foil layers of laminated packaging material by acetic acid. *J. Food Sci.* **1993**, *58*, 215–219. [CrossRef]
77. Olafsson, G.; Hildingsson, I. Sorption of fatty acids into low-density polyethylene and its effect on adhesion with aluminum foil in laminated packaging material. *J. Agric. Food Chem.* **1995**, *43*, 306–312. [CrossRef]
78. Johansson, H.; Ackermann, P.W. Method of Recovering Individual Component Parts from Packaging Material Waste. US5421526 A, 6 June 1995.
79. Kersting, J. Process for Separating Aluminium Foils from Plastic Foils, in particular PE-Foils. EP0543302 B1, 30 October 1996.
80. Bing, C. Method for Separating and Recycling Aluminum and Plastics. CN101797574 B, 23 May 2012.
81. Lovis, F.; Seibt, H.; Kernbaum, S. Method and Apparatus for Recycling Packaging Material. WO2015169801 A1, 12 November 2015.

82. Garrido-López, Á.; Santa-Cruz, A.; Moreno, E.; Cornago, J.; Cañas, M.C.; Tena, M.T. Determination of cosmetic ingredients causing extrusion-coated and adhesive joint multilayer packaging delamination. *Packag. Technol. Sci.* **2009**, *22*, 415–429. [CrossRef]
83. Ortiz, G.; Garrido-López, Á.; Tena, M.T. Delamination of multilayer packaging caused by exfoliating cream ingredients. *Packag. Technol. Sci.* **2007**, *20*, 173–182. [CrossRef]
84. Ajji, A.; Utracki, L.A. Interphase and compatibilization of polymer blends. *Polym. Eng. Sci.* **1996**, *36*, 1574–1585. [CrossRef]
85. Curto, D.; Valenza, A.; La Mantia, F.P. Blends of nylon-6 with a polyethylene functionalized by photooxidation. *J. Appl. Polym. Sci.* **1990**, *39*, 865–873. [CrossRef]
86. Nir, M.M.; Ram, A. Performance of reprocessed multilayer LDPE/nylon-6 film. *Polym. Eng. Sci.* **1995**, *35*, 1878–1883. [CrossRef]
87. Utracki, L.A.; Dumoulin, M.M.; Toma, P. Melt rheology of high density polyethylene/polyamide-6 blends. *Polym. Eng. Sci.* **1986**, *26*, 34–44. [CrossRef]
88. Choudhoury, A. Recycling of nylon-6/polyethylene waste oil pouchwes using compatibilizers. *Indian J. Chem. Technol.* **2006**, *13*, 233–241.
89. Shashidhara, G.M.; Biswas, D.; Shubhalaksmi Pai, B.; Kadiyala, A.K.; Wasim Feroze, G.S.; Ganesh, M. Effect of PP-*g*-MAH compatibilizer content in polypropylene/nylon-6 blends. *Polym. Bull.* **2009**, *63*, 147–157. [CrossRef]
90. Dagli, S.; Xanthos, M.; Biesenberger, J.A. Kinetic studies and process analysis of the reactive compatibilization of nylon-6/polypropylene blends. *Polym. Eng. Sci.* **1994**, *34*, 1720–1730. [CrossRef]
91. Diesen, H. Crosslinking Polyethylene and Polyamide by Organic Peroxide—Esp. Re-Use of Composite Packaging Material. DE3938552 A1, 23 May 1991.
92. Timmermann, R.D.; Dujardin, R.D.; Orth, P.D.; Ostlinning, E.D.; Schulte, H.D.I.; Dhein, R.D.; Grigat, E.D. Impact Resistant, Optionally Filled Polyamide Mixtures with Polyamide-Polyethylene Laminated Film Wastes. EP0583595 B1, 22 May 1996.
93. Buhler, K.; Gebauer, M. Process of Recycling Scrap Polymers. EP0575855 A1, 29 December 1993.
94. Uehara, G.A.; França, M.P.; Canevarolo, S.V. Recycling assessment of multilayer flexible packaging films using design of experiments. *Polímeros* **2015**, *25*, 371–381. [CrossRef]
95. Rätsch, M.; Wohlfahrt, B. Untersuchung zur Umsetzung von Maleinsaureanhydrid-Copolymeren mit Alkoholen. *Acta Polym.* **1986**, *37*, 708–712. [CrossRef]
96. Macoskoa, C.W.; Jeona, H.K.; Hoyeb, T.R. Reactions at polymer/polymer interfaces for blend compatibilization. *Prog. Polym. Sci.* **2005**, *30*, 939–947. [CrossRef]
97. Becker, D.; Porcel, F.; Hage, E., Jr.; Pessan, L.A. The influence of the compatibilizer characteristics on the interfacial characteristics and phase morphology of a PA/SAN blends. *Polym. Bull.* **2008**, *61*, 353–362. [CrossRef]
98. Orr, C.A.; Cernohous, J.J.; Guegan, P.; Hirao, A.; Jeon, H.K.; Macosko, C.W. Homogeneous reactive coupling of terminally functional polymers. *Polymer* **2001**, *42*, 8171–8178. [CrossRef]
99. Wyser, Y.; Leterrier, Y.; Manson, J.-A. Effect of inclusions and blending on the mechanical performance of recycled multilayer PP/PET/SiOx films. *J. Appl. Polym. Sci.* **2000**, *78*, 910–918. [CrossRef]
100. Choudhury, A.; Mukherjee, M.; Adhikari, B. Recycling of polyethylene/poly(ethylene terephthalate) post-consumer oil pouches using compatibiliser. *Polym. Polym. Compos.* **2006**, *14*, 635–646.
101. Parkinson, S.; Oner-Deliormanli, D.; Chirinos, C.; Walther, B.W. Self-Recyclable Barrier Packaging. WO2016109023 A1, 7 July 2016.
102. Pracella, M.; Chionna, D.; Ishak, R.; Galeski, A. Recycling of PET and polyolefin based packaging materials by reactive blending. *Polym. Plast. Technol. Eng.* **2004**, *43*, 1711–1722. [CrossRef]
103. Pracella, M.; Rolla, L.; Chionna, D.; Galeski, A. Compatibilization and properties of poly(ethylene terephthalate)-polyethylene blends based on recycled materials. *Macromol. Chem. Phys.* **2002**, *203*, 1473–1485. [CrossRef]
104. Lopes, C.M.; Gonçalves, M.D.C.; Felisberti, M.I. Blends of poly(ethylene terephthalate) and low density polyethylene containing aluminium: A material obtained from packaging recycling. *J. Appl. Polym. Sci.* **2007**, *106*, 2524–2535. [CrossRef]

105. Pawlak, A.; Morawiec, J.; Pazzagli, F.; Pracella, M.; Galeski, A. Recycling of postconsumer poly(ethylene terephthalate) and high-density polyethylene by compatibilized blending. *J. Appl. Polym. Sci.* **2002**, *86*, 1473–1485. [CrossRef]
106. Ebadi, H.; Yousefi, A.A.; Ouroumiehei, A.A. Morphology and reological, thermal and thermochechanical properties of PP/PET blends. *Iran. J. Polym. Sci. Technol. (Sci.)* **2004**, *16*, 381–390.
107. Lei, Y.; Wu, Q.; Clemons, C.M.; Guo, W. Phase structure and properties of poly(ethylene terephthalate)/high-density polyethylene based on recycled materials. *J. Appl. Polym. Sci.* **2008**, *113*, 1710–1719. [CrossRef]
108. Torres, N.; Robin, J.J.; Boutevin, B. Study of compatibilization of HDPE/PET blends by adding grafted or statistical copolymers. *J. Appl. Polym. Sci.* **2001**, *81*, 2377–2386. [CrossRef]
109. Chen, R.S.; Ab Ghani, M.H.; Salleh, M.N.; Ahmad, S.; Gan, S. Influence of blend composition and compatibilizer on mechanical and morphological properties of recycled HDPE/PET blends. *Mater. Sci. Appl.* **2014**, *5*, 943–952. [CrossRef]
110. Fetolaza, A.; Egijlazhal, J.I.; Nazheal, J. A lithium ionomer of poly(ethylene-co-methacrylic acid) copolymer as compatibilizer for blends of poly(ethylene terephthalate) and high density polyethylene. *Polym. Eng. Sci.* **2002**, *42*, 2072–2083. [CrossRef]
111. Razavi, S.; Shojaei, A.; Bagheri, R. Binary and ternary blends of high-density polyethylene with poly(ethylene terephthalate) and polystyrene based on recycled materials. *Polym. Adv. Technol.* **2011**, *22*, 690–702. [CrossRef]
112. Kim, J.K.; Kim, S.; Park, C.E. Compatibilization mechanism of polymer blends with an in-situ compatibilizer. *Polymer* **1997**, *38*, 2155–2164. [CrossRef]
113. Kallel, T.; Massardier-Nageotte, V.; Jaziri, M.; Gerard, J.-F.; Elleuch, B. Compatibilization of PE/PS and PE/PP blends. I. Effect of precessing conditions and formulation. *J. Appl. Polym. Sci.* **2003**, *90*, 2475–2484. [CrossRef]
114. Mamoor, G.M.; Shahid, W.; Mushtaq, A.; Amjad, U.; Mehmood, U. Recycling of mixed plastics waste containing polyethylene, polyvinylchloride and polyethylene therephtalat. *Chem. Eng. Res. Bull.* **2013**, *16*, 25–32. [CrossRef]
115. Pionteck, J.; Pötschke, P.; Proske, N.; Zhao, H.; Malz, H.; Beyerlein, D.; Schulze, U.; Voit, B. Morphology of reactive PP/PS blends with hyperbranched polymers. *Macromol. Symp.* **2003**, *198*, 209–220. [CrossRef]
116. Delva, L.; Ragaert, K.; Cardon, L. The upcycling of post-industrial PP/PET waste streams through in-situ microfibrillar preparation. *AIP Conf. Proc.* **2015**, *1695*, 020019.
117. Kuzmanovic, M.; Delva, L.; Cardon, L.; Ragaert, K. The effect of injection molding temperature on the morphology and mechanical properties of PP/PET blends and microfibrillar composites. *Polymers* **2016**, *8*, 355. [CrossRef]

4. Theoretical Background on Adhesion and Debonding

Since multilayer packaging includes a variety of different heterogeneously assembled structures, the selection of a specific interlayer to induce delamination usually leads to the fact that only some specific multilayer structures can be delaminated and recycled.

However, since an approach is sought that allows the recycling of the widest possible range of multilayer structures, it makes sense to take a closer look at laminating adhesives, since they can be found in a large variety of different multilayer structures. However, laminating adhesives are also a heterogeneous class with different molecular compositions and designed to provide high cohesion and adhesion to substrates. Therefore, if one wants to modify laminating adhesives so that they also allow separation of the substrates again, one must first understand the theory of adhesives. This will be discussed in the following.

4.1. Theories of adhesion

Lamination is the process of bonding two surfaces together with a layer of a third substance. Essential for bonding by an adhesive are the two processes of adhesion and cohesion. Adhesion describes the bonding of two different substances, the adhesive and the substrate, to each other. Cohesion, on the other hand, describes the internal strength of the adhesive. Cohesion is created by the covalent bonds within the adhesive polymers, the bonds created by cross-linking the adhesive, the intermolecular interactions between the adhesive molecules and the mechanical entanglements of different adhesive molecules. [21]

The mechanisms involved in the formation of adhesion depend on the type of substrate and adhesive. Altogether, there are four different mechanisms to describe adhesion, whereby several theories are often necessary at the same time to describe the corresponding mechanism.

With mechanical adhesion, the liquid adhesive penetrates the surface irregularities and bonds the substrates by curing. Thus, for mechanical adhesion, the porosity/roughness and absorbency of the substrates play an important role. An obvious example from the packaging sector where mechanical adhesion plays an important role is the bonding of paper and cardboard. As long as the cohesion of the adhesive is sufficiently strong, a substrate failure of the paper rather than an adhesion failure is to be expected in this case. [12,22]

While the theory of mechanical adhesion explains the bonding of rough and absorbent surfaces, it does not explain adhesion to smooth, surfaces such as metals or also to the poorly penetrable plastic films, relevant for packaging. [22]

In these cases, other theories can be applied. The most famous of all is probably the adsorption theory, which is based on the assumption that there is intensive contact between the two materials on molecular level at the interface. This can lead to the formation of intermolecular forces such as Van der Waals forces or hydrogen bonds but also primary interactions such as covalent or ionic bonds. The Van-der-Waals forces, which are said to play an important role in adsorption theory, can be divided into London, Debye and Keesom forces, depending on whether none, one or both of the binding molecules have dipole character. These forces decrease with the sixth power of the distance. Although considerable adhesion can already be achieved by van der Waals forces alone, the presence of primary bonds can improve the values even more. A comparable effect to that achieved through covalent bonds can be achieved through the so-called diffusion theory and the resulting entanglements. [23,24]

Diffusion and entanglement play an important role when using polymer substrates and adhesives. Polymers are in a constant state of motion called reptation. If the adhesive polymer is soluble in the substrate polymer, this allows the polymer chain of the adhesives to cross the interface with the substrate and thus penetrate it, forming an interphase. This diffusion becomes more likely, when the polymer is above its glass transition temperature and is also influenced by the crystallinity of the polymer, the molecular weight and the distribution [22,23]

After inter-diffusion, entanglement between the polymers of the different materials can take place. During entanglement, a polymer interlocks in such a way that the polymer chain crosses other polymer chains at three places. This makes it impossible to detach the polymers from each other by simply pulling on the chain, as this will trap another polymer chain at a different place. [23]

The prerequisite for this is that the polymer has the necessary length for the three crossovers which is called the critical entanglement mass Mc and depends on the stiffness of the polymer chains. [23]

For the sake of completeness, the electrostatic theory should be mentioned here, which, however, has no relevance for the bonding of packaging materials.

4.2. The Chemistry of Polyurethane Adhesives

4.2.1. General Considerations on polyurethanes

Polyurethanes were discovered in 1937 by Otto Bayer, [24] who thus added polyaddition to the previously known polymerisation mechanisms of polycondensation and anionic polymerization.

The term "polyurethanes" is generally understood to mean the polymers produced by the diisocyanate-polyaddition process. Accordingly, it is a comprehensive category of polymers with different starting materials, compositions and properties: [25]

Due to the large number of starting materials, the diverse reaction patterns and the possibility of controlled polymerisation via intermediate prepolymers, polyurethanes fulfil the most diverse product requirements and appear in the form of soft and firm foams, of coatings, sealants, elastomers or of adhesives. [25,26]

In general, these polymers contain the urethane group (**1**) as a characteristic structural unit, which is formed by the addition of isocyanates to alcohols - even if the urethane group often only plays a subordinate role compared to ether, esters and sometimes also urea groups. [25]

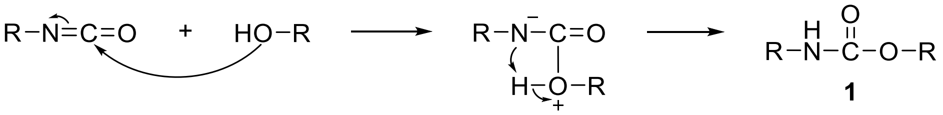


Figure 4. The name-giving reaction of polyurethanes: mechanism of urethane formation from isocyanate and alcohol.

4.2.2. Reactivity of isocyanates

The fundament of polyurethane chemistry lies in the high reactivity of the isocyanates, more specifically in the electrophilicity of the carbon atom. This can be explained by looking at their resonance structures.

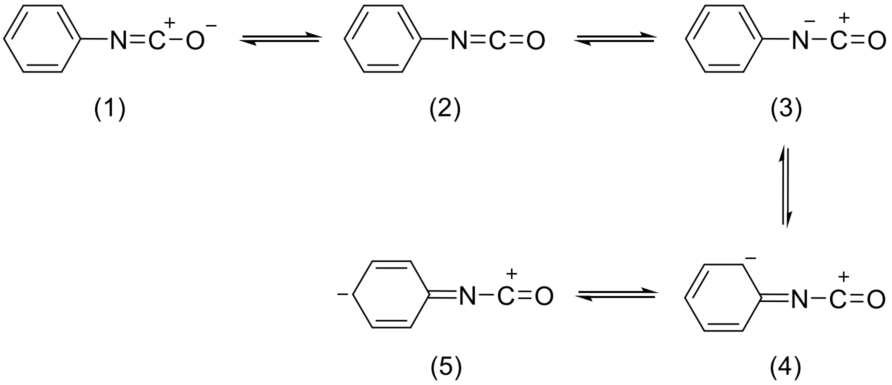


Figure 5. Resonance structures of the NCO group considering an aromatic substituent.

The strongly pronounced positively polarized character of the C-atom in the cumulated double bond system of the N=C=O-group, which is evident in the resonance structures, explains the clearly prominent reactivity towards nucleophiles. This effect is enhanced by electron-withdrawing substituents that further increase the positive charge on the C-atom of the isocyanate group, accelerating the electron transfer from nucleophiles to the C-atom.

If R is aromatic, resonance structures (4) and (5) becomes important. In this case, the negative charge is delocalized in the π-electron system of the benzene ring. Especially when electron-withdrawing substituents are in ortho- or para-position, the negative charge in the ring system can be stabilized and thus further reduce the charge on the carbon atom of the isocyanate group. [25,27] If a second isocyanate group is in the ortho or para position on the aromatic ring, the reactivity of the first group is increased. In ortho-position, however, a steric hindrance can simultaneously lead to a lower reactivity again. Especially sterically demanding substituents in ortho-position reduce the reactivity of the isocyanate group. [28]

4.2.3. Reactions of isocyanates with nucleophiles

A crucial reactivity of isocyanates is the addition of α-H-acid nucleophiles to the electrophilic C-atom of the isocyanate group. Figure 6 gives an overview of the most common addition reactions of nucleophiles to isocyanates.

By far the most important and name-giving reaction in polyurethane chemistry is the addition of alcohols to isocyanates, which takes place under relatively mild conditions and forms carbamic acid esters, trivially also called urethanes (**1**), as reaction products. [25] Hereby, aliphatic primary alcohols react faster than secondary and tertiary alcohols due to their low steric hindrance. In the case of phenols, the reaction is even slower and forms urethane adducts that readily cleave.

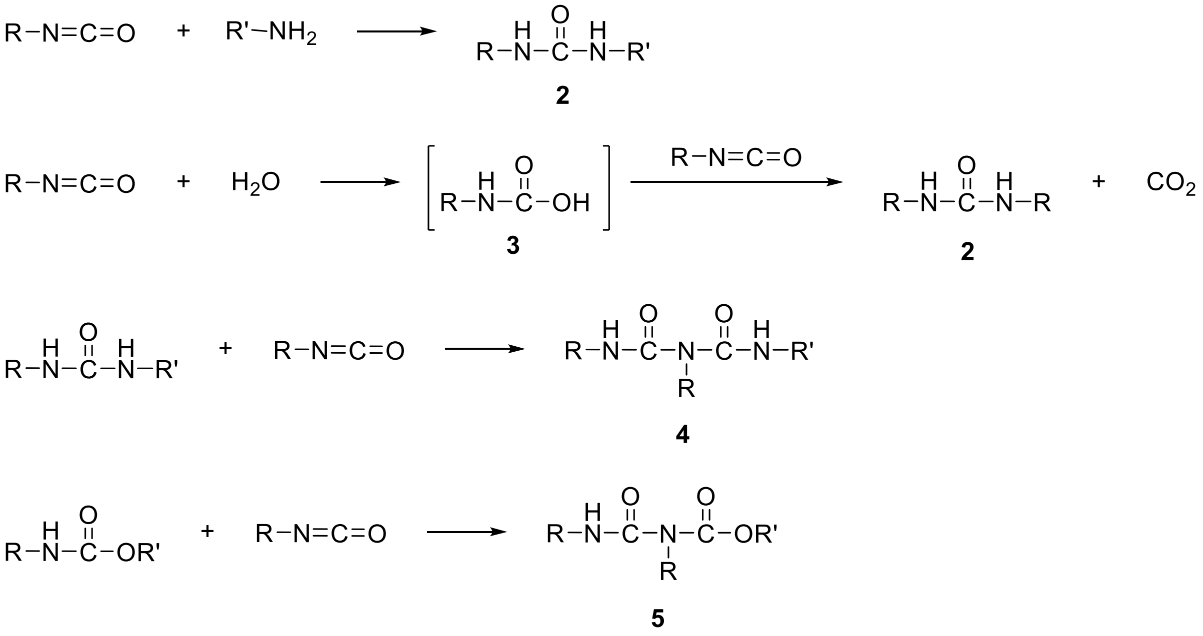


Figure 6. Reactions of isocyanates with nucleophiles.

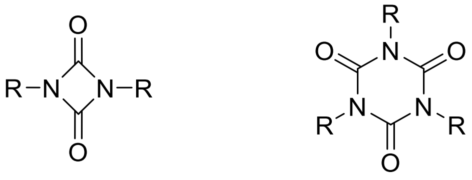
In adhesives, the urea (**2**) formation reaction plays a role in addition to the urethane reaction. This takes place between isocyanates and amines and is much faster than the reaction of isocyanates and OH-groups, although there are also major differences in the amines due to electronic and steric differences, and the more basic aliphatic amines react faster than aromatic amines. [25] In polyol formulations can this high reactivity be used, for example, to act as reactive thickeners. [27]

Since the reaction of isocyanates with atmospheric moisture always plays a role in the curing of PU adhesives and this also results in urea formation, the presence of a certain proportion of urea groups can be assumed. Specifically, when an isocyanate reacts with water, the unstable carbamic acid (**3**) is formed first, which decomposes to form a primary amine with CO_2 splitting off. The resulting amine then reacts with another isocyanate as described above to form urea (**2**). [25] Due to the gas release, the reaction of isocyanates with water can be used to form foam in the production of PU foams. To avoid the reaction with water in the production of adhesive prepolymers, syntheses must be carried out in the absence of moisture. [27]

Isocyanates can also react with the reaction products of the addition of isocyanates and alcohols or amines, the urethanes and urea groups. However, their acidic H atoms are no longer as active as those of the respective starting materials, but under correspondingly energetic conditions, the reaction with isocyanates can still form allophanates (**5**) or biurets (**4**). The formation of biuret-groups is significantly faster than the formation of allophanates. These types of reaction can be used to create cross-linking in the polymer system and thus alter the properties of the polymer. [25]

4.2.4. Reactions of isocyanates with isocyanates

Isocyanates can also react with each other to form dimers, trimers, polymers, carbodiimides and uretonimines, either under special conditions or using specific catalysts. Figure 7 gives an overview of the reaction mechanisms that isocyanates can enter into with each other.



6 **7**

Figure 7. Products of isocyanate dimerization (6) and trimerisation (7).

Trimerization of multifunctional isocyanates to form a stable isocyanurate ring (**7**) can be used to build rigid foams.

Dimerization to the uretdione (**6**) occurs at low temperatures and can be reversed at higher temperatures. This allows isocyanate groups to be selectively capped and made accessible again at higher temperatures.

For the production of polyurethane adhesives, however, these reactions are usually not important, but quality control should ensure that the isocyanates used are not dimerized, as this would change the chemical structure and properties of the adhesive.

4.2.5. Starting materials for polyurethane production

The main components of polyurethane adhesives are usually molecules with at least two OH-groups, known as diols, and diisocyanates. The respective chemical structure of different polyol and diisocyanates leads to different adhesive tendencies, resistance and health aspects. To circumvent the high volatility and toxicity of many typical starting materials, prepolymers are usually prepared for adhesive formulations. These represent reactive oligomers that, unlike the final product, are still soluble or meltable but easier and safer to handle than the pure starting materials. The polyol component in two-component polyurethane adhesives can consist of one or several different polyols of low to high molecular weight and also hydroxyl-terminated prepolymers or mixtures of both. The isocyanate component often consists of low to medium molecular weight diisocyanate prepolymers. [29]

The broad field of urethane chemistry offers the flexible packaging industry a wide choice of different adhesives. Classically, packaging adhesives are applied in dissolved form, i.e. solvent-based. However, solvent-free adhesives are on the rise, as they do not cause solvent vapors and can save costs. [29]

4.2.6. Isocyanates in polyurethane chemistry

Polyisocyanates with two or more functional groups are necessary for polyurethanes. In terms of quantity, aromatic isocyanates account for the largest share, although aliphatic and cycloaliphatic isocyanates also play an important role. The reasons for the predominance of aromatic isocyanates are their higher reactivity and economic reasons. Aliphatic isocyanates play a role mainly when specific reactivities or when special property requirements for the end products, such as UV light resistance or the prevention of the formation of aromatic amines in food contact materials, are to be achieved. Due to the generally higher reactivity of aromatic isocyanates, these only require the use of catalysts under certain conditions, which usually consist of metal compounds or amines. [29]

However, there are also differences within the various isocyanate categories.

The most important representatives of the aromatic diisocyanates are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). Since it is produced via the condensation of aniline with formaldehyde and subsequent phosgenation, in addition to the diphenylmethane-4,4′-diisocyanate (**9**), the 2,4'- (**10**) and 2,2'- (**8**) isomers and also 3- and higher-nucleated products are obtained. Mixtures with a proportion of trinuclear or multinuclear products are commonly called "polymeric MDI" (**13**). The different products can be separated from each other by distillation.

MDI has a relatively low vapour pressure compared to the other diisocyanates. Nevertheless, due to its suspected carcinogenic effect, high precautionary measures must be taken during handling.

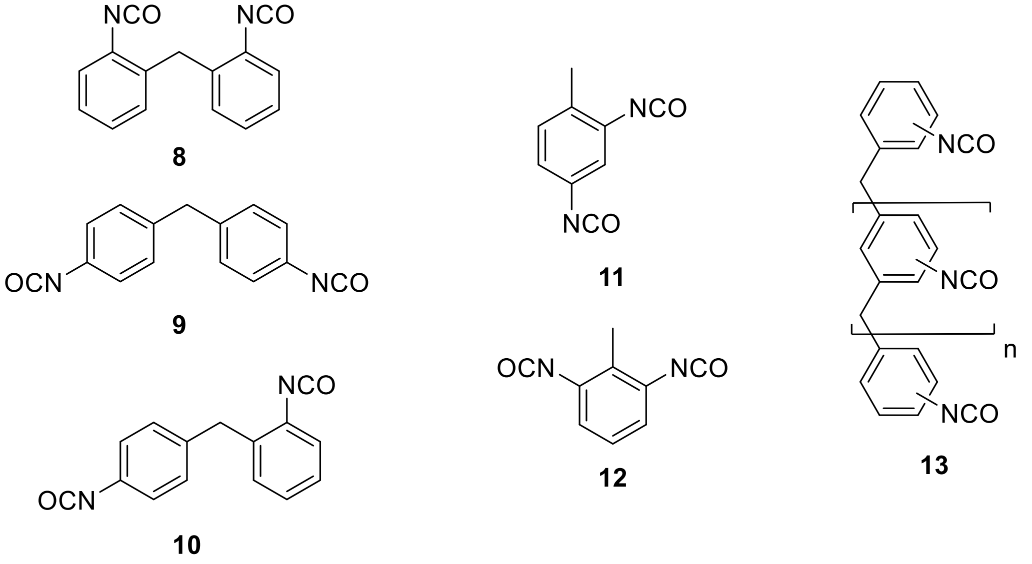


Figure 8. The main aromatic diisocyanates: MDI and its isomers (10-12), TDI and its isomers (13, 14) and Polymeric MDI (15).

TDI is also obtained as a mixture of isomers. The isomers in this case are 2,4- (**11**) and 2,6-TDI (**12**), with mixtures of the two compounds available in various ratios and also pure 2,4-TDI. Due to the different reactivities of the two isocyanate groups, pure 2,4-TDI is well suited for the production of low-monomer prepolymers. [25,27]

Aliphatic isocyanates have the advantage that, unlike aromatic isocyanates, they do not change their color with time. This makes them suitable starting materials for applications with high optical demands. However, their use is limited by the lower reactivities and higher prices. Aliphatic isocyanates are therefore only used if this cannot be avoided. This is the case, for example, in food packaging, wound plasters or aqueous PU adhesive dispersions. [25,27]

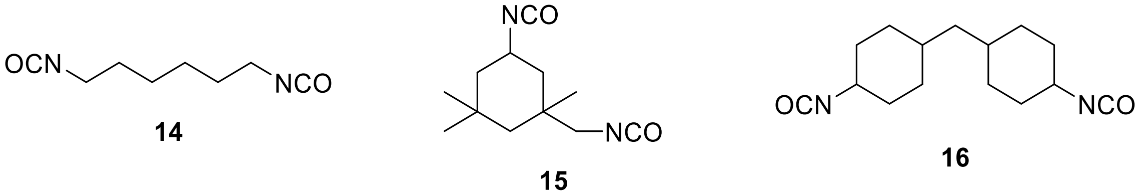


Figure 9. Structural formulas of the most relevant aliphatic diisocyanates: hexamethylene diisocyanate (HDI) (16), Isophorone diisocyanate (IPDI) (17) and Bis(4-isocyanatocyclohexyl)methane (H_{12}MDI) (18).

The most commonly produced aliphatic isocyanate is hexamethylene diisocyanate (HDI) (**14**). It is a linear, symmetrical molecule obtained by reacting the polyamide raw material hexamethylene diamine with phosgene. [27]

Bis(4-isocyanatocyclohexyl)methane, whose systematic name is usually replaced by H_{12}MDI (**16**), is, as the trivial name suggests, the aliphatic derivative of 4,4’-MDI (**9**). In contrast to MDI, in this case the starting material 4,4'-Methylenedianiline is first hydrogenated before phosgenation is carried out. [27]

Isophorone diisocyanate (IPDI) (**15**) is a methyl- and isocyanate/isocyanate methyl group-substituted cyclohexane derivative and is also produced by phosgenation and, due to its differently reactive isocyanate groups, does not provide polymer distributions according to Schulz-Flory, which is why it is well suited for the production of very uniform prepolymers.

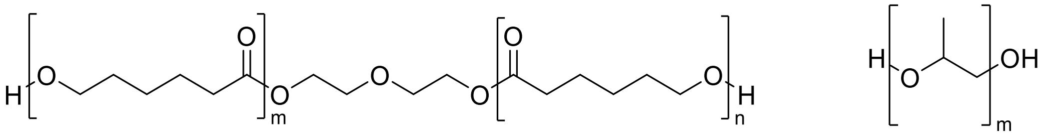
As a rule, aliphatic isocyanates are only used within the chemical industry, as they are not only highly toxic but also very volatile. [25]

4.2.7. Polyols in polyurethane chemistry

Besides isocyanates, polyols are an essential component for polyurethanes. Smaller di- and triols such as glycol, butanediol, glycerol or trimethylolpropane are often used as chain extenders or crosslinkers. Diols with higher molecular weights of up to 8000 g/mol, on the other hand, are used to produce the actual backbone when building up the polyurethane. Polyester or polyether diols are usually used for this purpose. [25]

Since the diols are not hazardous substances, the formulation of polyurethane adhesives is usually preferably adapted via modification of the polyol. [27]

Due to their intermolecular interactions, polyester polyols have a higher viscosity and greater stiffness. In addition, the polar ester groups cause a relatively high polarity of the polyester polyols, which can lead to good adhesion to polar substrates. However, the ester groups tend to hydrolytic cleavage. The production can be done via ring-opening polymerisation e.g. of caprolactone with a glycol as a starter molecule or polycondensation between dicarboxylic acids and glycols. [25,27]



17 **18**

Figure 10. Polycaprolactone (17) as an example of a polyester diol and polypropylene glycol (18) as an example of a polyether diol.

Polyether polyols have good stability with regard to hydrolysis, but are more susceptible to oxidation. Since polyether polyols usually have a lower viscosity than most polyester polyols, they are often used to reduce the viscosity of formulations. Due to their fairly low polarity, they improve wetting of low-energy surfaces. [26]

Typically, the preparation proceeds via the catalyzed ring-opening polymerisation of propylene oxide or ethylene oxide, starting from a low molecular weight diol or triol as the starter molecule. If the catalysis is carried out using KOH as catalyst, only relatively low molecular weights are achieved due to chain termination reactions. Catalysis by dimetal complexes yields higher molar masses. [27]

4.2.8. Amines

Diamines are well suited as crosslinkers and chain extenders due to their increased reactivity with isocyanates compared to alcohols. To some extent, the reaction of isocyanates with atmospheric moisture during the application of the adhesive or coatings produces amines that form urea groups as described in section 4.2.3. The formation of urea can also be used specifically for this purpose, as they can enable the formation of biuret groups and thus the generation of crosslinking. Polyamines are also used as reaction partners for isocyanates in the production of elastomers and in reaction injection molding. [25]

4.3. Use of Isocyanate-Based Adhesives in Packaging Laminates

As described in chapter 4.2.6 polyurethane adhesives used for packaging may contain either aromatic or aliphatic isocyanates. In the case of aromatic isocyanates, the formation of primary aromatic compounds can occur, which are of toxicological concern.

During the curing process, the aromatic isocyanates also react with water molecules, whereby primary aromatic amines are formed. These subsequently react with further isocyanate groups and the amines are thus removed from the adhesive system. If the packaging laminate comes into contact with food before the adhesive has fully cured, both unreacted isocyanates and primary aromatic amines can migrate into the food. However, it is also possible that an adhesive is not formulated correctly, e.g. because the reactivity of the alcohol component is too low, or the proportion of monomeric isocyanate is still too high. [26,29,30]

According to Commission Regulation (EU) no. 10/2011 [31], primary aromatic amines must not pass into the food. A detection limit of 0.01 mg/kg applies to the sum of all primary aromatic amines released. The packaging structure and also the composition of the food are decisive for how much migrant can pass into a food. Dry foods typically absorb fewer migrant than liquid or acidic foods. [30]

For retorting packages, the prolonged exposure to temperature causes thermal degradation of the adhesive. In the case of adhesives based on aromatic isocyanates, monomeric isocyanate can be formed as a result. To prevent migration into the food, a suitable barrier would have to be used. [30]

4.4. Debonding on Demand

One disadvantage of bonding by the use of adhesives is that the created connection usually cannot be undone without damaging the connected parts. This disadvantage can be overcome by using debondable adhesives. These are based on different technologies, which are presented below. The strategies on which these are based are the use of reactive fillers, the electrical induction of debonding, or the use of reversible/reworkable adhesive systems. [32]

Reactive fillers can be activated by external energy sources and thus induce delamination by different mechanisms.

If magnetic nanoparticles are contained in an adhesive or primer, by applying alternating electromagnetic fields, the particles are heated and can cause thermoplastic primers or adhesives to melt, allowing the bonded materials to be separated by low mechanical force. [33,34]

Core-shell particles are another category of reactive fillers. Their principle is usually based on the fact that the particles expand under the influence of temperature and thus induce mechanical separation. In this process, the outer shell softens while the interior of the particle expands at the same time. In this process, gases can also be released, which additionally contribute to debonding. [32,35,36]

In order to break bonding by applying an electrical voltage to the electrically conductive substrates, electrolytes must be added to the adhesive for ion transport. [32,37,38]

Another way to modify the chemical structure of adhesives for debonding is through the incorporation of labile functional groups that can reverse the cross-linking of the adhesive. Although various reaction mechanisms are possible, [39] the Diels-Alder system is the best researched and most widespread.

When it comes to debonding packaging, the approach of separating via electrical discharge is not promising because electrically conductive substrates are not always present and, in general, applying voltage to post-consumer packaging is difficult to imagine. The method of heating magnetic particles to soften a primer or adhesive is also not very promising in the case of packaging, as another mechanical force would have to be applied for separation of the materials. Even with separation using core-shell particles, it cannot be assumed that the substrates will not simply fall apart after the particles have expanded. In addition, it would have to be assumed that with all these methods, the adhesive would still be left on at least one of the two substrates after separation and could thus hinder recycling. Also, for the adhesives containing labile functional groups, the mere reversion of the crosslinking does not automatically cause the substrates to fall apart. However, the reversion of the crosslinking allows the adhesive to be dissolved with solvent and thus the substrates should be able to be separated from each other and the adhesive removed without leaving any residue. Therefore, the Diels-Alder reaction, which plays a particularly prominent position in reversible-crosslinking adhesives, will be discussed in more detail below.

4.5. The Diels-Alder Reaction

In 1928, Otto Diels and Kurt Alder discovered the Diels-Alder reaction, for which they were awarded the Nobel Prize in Chemistry in 1950. [40] The Diels-Alder reaction is a reversible pericyclic [π4s+π2s] cycloaddition. The reaction proceeds in a single step, in which a diene reacts with an alkene, usually called a dienophile. Two new σ-bonds are formed via an aromatic transition state and thus form a cyclohexene system. [40,41]

A prerequisite for the dienes to undergo a Diels-Alder reaction is that they are present in the s-cis conformation. In the case of open-chain dienes, there is an equilibrium between the trans and cis conformation, which, however, is on the side of the trans product for steric reasons. With most cyclic dienes, the cis conformation is normally always present, which is why they are very well suited for the Diels-Alder reaction. [40]

The dienophiles used for the Diels-Alder reaction usually have electron-withdrawing substituents conjugated to the alkene. The reason for this lies in the molecular orbital (MO) theory: donor substituents D increase the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) while acceptor substituents A decrease the energy of both frontier orbitals (compare Figure 11).

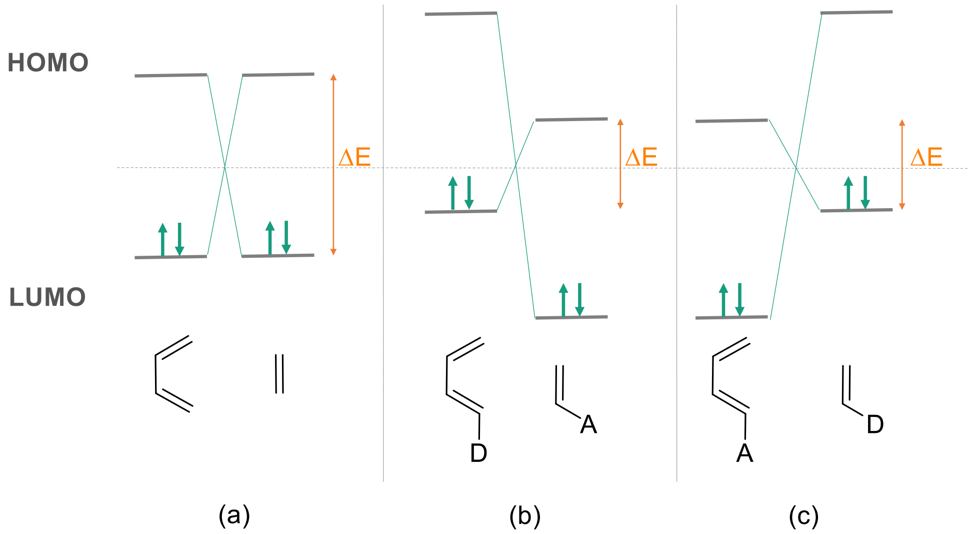


Figure 11. MO scheme for the reaction between butadiene and ethylene and between their donor/acceptor substituted derivatives. Adapted from [42].

A binding interaction can only take place between occupied orbitals of one component and unoccupied orbitals of the other component, i.e. between $\mathrm{HOMO_{diene}}$ – $\mathrm{LUMO_{ene}}$ (Figure 11b) or $\mathrm{HOMO_{ene}}$ – $\mathrm{LUMO_{diene}}$ (Figure 11a). If $\Delta E_{\mathrm{HOMO\text{-}LUMO}}$ is minimized by suitable substitution, the strength of the interaction increases and the reaction rate increases.

The product of the Diels-Alder reaction can be in the form of two diastereomers: The so-called endo- and exo-products. According to the endo- also called Alder rule, the transition state of the endo-product is stabilized due to secondary orbital interactions. This results in an energetically favorable transition state in which the endo-product emerges preferentially under kinetic control. Under thermodynamic product control, however, the thermodynamically more stable exo-product is formed preferentially. [40,41,43]

The Diels-Alder reaction is interesting for polymer chemistry because some of the adducts formed can be partially reopened in the corresponding retro-reaction. This is possible since a strong increase in entropy occurs when the Diels-Alder adduct is opened and so the positive value of the reaction enthalpy ΔH of the retro-reaction can be overcome when the temperature is increased so that a spontaneous course of the reaction can take place. [41] When the Diels-Alder adducts are incorporated into polymer networks, their retro-reaction therefore allows the networks to split under the effect of temperature. This can be utilized, for example, in self-healing polymers or reversible cross-linking plastics. [44,45]

5. Objective of the thesis

As described in Chapter 2.2.2, the recycling of multilayer packaging by means of classical mechanical recycling is usually not possible, as it is only suitable for monomaterial fractions or materials that are compatible. Solvent-based recycling, on the other hand, also allows the recycling of composite materials, but has not yet become established on the market and is more energy-intensive than mechanical recycling due to the polymer drying process. The aim of this work was therefore to combine the advantages of solvent-based recycling with those of mechanical recycling by using solvents to separate multilayer packaging into its individual components and thus make them accessible for mechanical recycling.

In order to realize this, suitable interlayers in the typical structures of multilayer packaging must be identified and dissolved so that the packaging is delaminated. Since the structures of multilayer packaging are very versatile, but laminated packaging plays an important role in the packaging market, the laminating adhesives could be a suitable layer for delamination. However, packaging adhesives are usually cross-linked and therefore not soluble. This could be changed by using reversibly crosslinking adhesives as described in Chapter 4. The objective of this work therefore was to develop a reversibly crosslinking Diels-Alder adhesives for the production of packaging laminates and thus produce multilayer laminates that can be delaminated by means of solvent and temperature exposure to subsequently mechanically recycle the individual components of the laminate.

In order to meet this task, three questions were scientifically investigated.

1. **Is it possible to formulate Diels-Alder adhesives so that they can be used to make packaging laminates and then delaminate them with a solvent treatment? How is the behavior of the adhesive influenced by the length of the prepoylmer, the curing temperature and the substrates of the laminate?**

To answer this question, functionalized polyurethane prepolymers were synthesized on a laboratory scale, and different laminate structures were prepared and delaminated. This work is described in Chapter 6.

2. **Is it possible to implement this principle while taking food law requirements into account?**

Since the adhesive formulation must not contain any carcinogenic, mutagenic or reprotoxic substances according to food regulations, it must be adapted accordingly. However, for chemicals that are not listed in the Annex of Commission Regulation (EU) no. 10/2011, [31] it must be ensured that the legally specified maximum level of 0.01 mg/kg food is not reached. Migration experiments were necessary in order to check under which conditions this specification could be complied with. This work is described in Chapter 7.

3. **Is it possible to transfer the principle from laboratory scale to pilot scale in such a way that the recyclates could be reused in a packaging application?**

In order to verify how realistic, it is to actually implement recycling of laminates bonded with Diels-Alder adhesives by delamination, it was necessary to upscale both laminate production and recycling. (Chapter 0)

These three questions are answered and discussed in the following chapters 7-8 and are and recapitulated in chapter 9.

6. Recycling of multilayer packaging using a reversible crosslinking adhesive [46]

Katharina M. A. Kaiser[1,2*]

To prepare a Diels-Alder adhesive for multilayer packaging, linear NCO prepolymers of different lengths were first prepared from 4,4'-MDI and a polyester diol and functionalized with furfuryl alcohol and *N*-(2-hydroxyethyl)maleimide. In addition, a molecule with three furan groups was prepared, which is used to crosslink the adhesive.

Based on these starting materials, PET//PE, PET//aluminum and PE//aluminum laminates were prepared by hand lamination and cured at room temperature and 60 °C, whereby the time, for complete curing was monitored by the decrease of ring deformation mode of maleimide at 696 cm^{-1} in the FTIR spectrum. Using ^1H NMR spectroscopy, it was found that the adhesive cured at room temperature had an exo/endo ratio of Diels-Alder diastereomers of 1:1.8 and that cured at 60 °C had a ratio of 1:0.2.

The results of the T-peel tests of the different laminates indicate that the increased curing temperature has a positive influence on the bond adhesion and the adhesion to aluminum. For the aluminum composites, a decrease in adhesive strength with increasing length of the adhesive molecules can be observed, while for the polymer//polymer composites such an effect is not noticeable.

When heated in dimethyl sulfoxide to 105 °C, the Retro-Diels-Alder reaction takes place to allow the adhesive polymers to dissolve and thus be removed from the laminate. As a result, the laminate disconnects and the clean PE, PET and aluminum films can be recovered separately. Here it can be observed that the type of composite has an influence on the speed at which delamination proceeds, since the different materials have different barrier effects against the solvent, but the influence of the solvent over the cut edge predominates. There is also a tendency for the delamination time of the composites cured at 60 °C to exceed that of the composites cured at room temperature, which is as expected based on the different exo/endo ratios.

IR spectroscopy demonstrated that no adhesive residues remained on the surfaces of the films.

J Appl Polym Sci **2020**, *137*, 49230, DOI:10.1002/app.49230

Received: 7 January 2020 | Revised: 25 February 2020 | Accepted: 27 February 2020

DOI: 10.1002/app.49230

ARTICLE

Journal of Applied Polymer Science WILEY

Recycling of multilayer packaging using a reversible cross-linking adhesive

Katharina M. A. Kaiser[1,2]

[1]TUM School of Life Sciences Weihenstephan, Technical University of Munich, Freising, Germany

[2]Process Development for Polymer Recycling, Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany

Correspondence
Katharina M. A. Kaiser, TUM School of Life Sciences Weihenstephan, Technical University of Munich, Weihenstephaner Steig 22, 85354 Freising, Germany.
Email: katharina.kaiser@ivv.fraunhofer.de

Abstract

Plastic-based multilayer packaging has an important function on the packaging market, but is currently not recyclable as the polymer layers used are usually thermodynamically immiscible. This work therefore follows the approach to prepare separable multilayer packaging using a packaging adhesive modified with thermally unstable adducts, and proposes a corresponding recycling process. For this purpose, typical multilayer structures (polyethylene (PE)// polyethylene terephtalate (PET), PET//aluminum, and PE//aluminum) were prepared by curing furan-/maleimide-functionalized polyurethane (PU)-prepolymers with a three-functional cross-linking agent. Adhesions of up to over 3N per 15 mm test specimen were measured or substrate failures of PET films were observed. However, heating in dimethylsulfoxide, the retro-Diels–Alder reaction takes place and the cross-linked adhesive turns thermoplastic and dissolves in the solvent. Thus, the laminate separates and the pure PE, PET, and aluminum foils can be recovered without any PU residue.

KEYWORDS

addition polymerization, adhesives, packaging, polyurethane

1 | INTRODUCTION

According to the European Plastics Strategy, all packaging used should be reusable or recyclable by 2030.[1] At present, multilayer packaging, in which different materials are combined in a layered structure, represents the largest proportion of nonrecyclable packaging, accounting for around 20% of all flexible packaging.[2] The reason for the high proportion of multilayer packaging is that the combination of different materials allows tailor-made property profiles to be created with low material consumption.[3] Defined barrier properties against oxygen, water vapor, light, or loss of aroma enable long shelf lives and thus enable the current form of food trade and also reduce food losses.[4] Since in many cases the different polymers/materials are immiscible, these packagings usually cannot be recycled. Additionally, the current recycling systems aims at the recycling of monomaterials and multilayer packaging is sorted out and sent to incineration.[5]

Accordingly, in order to increase the recycling rates for polyethylene (PE), polypropylene (PP), polyethylene terephtalate (PET), and aluminum, new recycling strategies are required to handle multilayer materials and other composites. To address this problem from the packaging design side, it is one option to replace heterogeneous multilayer packaging with packaging consisting of different PE and/or PP types and thus to produce a type of monomaterial packaging. In this way, however, it is often not possible to generate the material properties that are usually achieved with conventional multilayers, which can also have negative effects on the contents.[4,6] Another approach would be to connect the components of the multilayer packaging in such a way that the different materials can be separated again after their lifetime. The individual components could thus be recycled separately.[5]

Such "disjoinable" multilayer packaging can be achieved by using a thermoreversible cross-linked adhesive systems, which allows the separation of the laminates under defined conditions. After selective sorting of the multilayer packaging from postconsumer packaging waste, which is possible using new technologies,[7] the recycling rate could be increased in this way.

Reversible cross-linking can be achieved for example, by exposure to ultrasound, UV light, or heat.[8–15] An important example of such a thermo-responsive system is the Diels–Alder/retro-Diels–Alder (DA) equilibrium between furan and maleimide derivatives.[16–22] The major advantage of this system is the expedient temperature range of the [4 + 2] cycloaddition and the cycloreversion: the formation of the adduct starts at room temperature, but the reverse reaction requires temperatures of 90–130°C. The back reaction therefore takes place in a temperature range in which most conventional polymers are dimensionally stable. However, in the case of PE, for example, the retro-DA reaction would have to take place in a correspondingly low temperature range.[20]

Here, it is shown that multilayer packaging can be produced using laminating adhesives with reversible cross-links. Since cross-linked polyurethanes (PU) based on 4,4′-Methylene diphenyl diisocyanate (MDI) and polyester diols are frequently used for packaging adhesives,[23] the adhesive in this paper comprises PU prepolymers of different molecular weights functionalized with maleimide/furan derivatives and a cross-linking agent. Using these components PET//PE, PET//aluminum, and PE//aluminum laminates were produced; characterized; and the film materials PET, PE, and aluminum were recycled by temperature treatment in a solvent.

2 | EXPERIMENTAL

The method presented in this paper comprises the production of the laminates, the production of the individual adhesive components, and the recovery of the composite materials via a recycling process.

The adhesive polymers are linear polyester–PU prepolymers, functionalized with maleimide/furan moieties. In addition, a cross-linking molecule, containing three furan groups was synthesized using furfuryl glycidyl ether and a trithiol. Based on this, laminates are produced and cured. For recycling, the laminates are reduced in size (1 × 1 cm) and treated with a heated solvent (dimethylsulfoxide [DMSO], 105°C) under moderate stirring. This process allows opening of the DA adducts and subsequent solvation of the adhesive components. After this, the delaminated materials of the laminates can be sorted diversely, for example, by density separation, while the DMSO can be reused several times before it has to be distilled and the adhesive is discarded. An overview of the individual steps of the process is given in Figure 1. The exact procedure of these steps and a description of the syntheses are given in the following.

2.1 | Preparation of the adhesive

MDI (98%) was obtained from Alfa Aesar (Ward Hill, MA) and used as received. Furfuryl alcohol (FFA) (98%, Sigma–Aldrich, MO) was distilled prior to use, the diol Capa 2054 (Perstorp, Malmö, Sweden) is dried prior to use at reduced pressure at 50°C. The maleimide functional group, *N*-(2-hydroxyethyl)-maleimide (*N*-HEMI), is prepared with DA and retro-DA cycloaddition through a three steps process as described by Heo et al.[24] and Duan et al.[25] Ethyl acetate (≥ 99.5%) was purchased from TH Geyer and, if necessary, dried with molecular sieve (4 Å) to a H_2O content < 50 ppm and stored under nitrogen ($H_2O \leq 50$ ppm). Reactions involving the use of MDI were carried out under a nitrogen atmosphere.

To produce the prepolymers, MDI was heated to 50°C to give a clear, colorless liquid to which Capa 2054 was added all at once. After the exothermic reaction subsided, the mixture was heated to 70°C until reaction control with Fourier transform infrared spectrometer (FTIR) showed no further decrease of the NCO-signal at 2260 cm^{-1}. For the preparation of furan-functionalized prepolymers, furfuryl alcohol, and eventually some ethyl acetate to ensure homogeneous mixing, was then added and the mixture was stirred at 70°C until the NCO-signal vanished. Possible residues of ethyl acetate were removed under reduced pressure. For the preparation of maleimide-functionalized prepolymers, *N*-HEMI was dissolved in ethyl acetate and then added to the mixture. The reaction was kept at 70°C until the NCO-signal vanished. Residues of ethyl acetate were removed under reduced pressure.

2.1.1 | Maleimide-functionalized prepolymers (1M–6M)

Infrared spectroskopy (IR) $\tilde{\nu}$ = 3,329 (br), 2,941 (m), 2,864 (m), 1,702 (s), 1,736 (s), 1,528 (s), 1,217 (s), 1,068 (s), 695 (intensity depends on molecular weight) cm^{-1}.

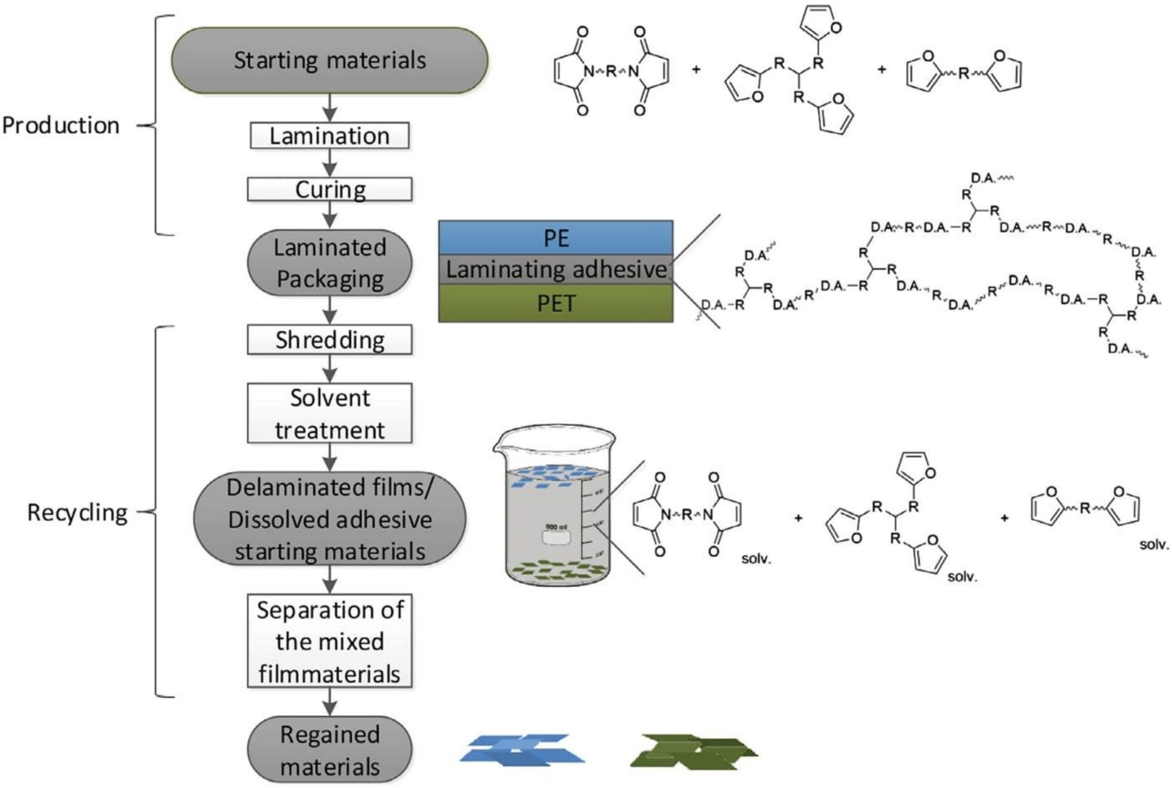


FIGURE 1 Overview of the complete laminate production and recycling process: PET//PE, PET//aluminum, PE//aluminum, and PET//PET laminates are produced starting from maleimide/furan-functionalized PU prepolymers of different molecular weights and a cross-linking molecule. For subsequent recycling, the laminates are shredded and treated with a heated solvent to induce the retro-Diels–Alder reaction and, subsequently, the dissolution of the adhesive components. Due to its low density, PE can be collected from the surface and thus be separated from PET or aluminum. R stands for the PU backbone of different chain lengths, formed from MDI and a polyester diol. D.A., Diels–Alder adduct [Color figure can be viewed at wileyonlinelibrary.com]

^{1}H nuclear magnetic resonance (NMR) (300 MHz, DMSO-d_6) δ 9.74–9.38 (m; N*H*), 7.38–7.31 (m; Ar), 7.09–7.07 (m; Ar), 7.02 (4H; s; C*H* [*N*-HEMI]), 4.24–4.16 (m; CH_2 [polyester]), 4.15–4.08 (8H; m; CH_2 [*N*-HEMI]), 4.06–3.96 (m; CH_2 [polyester]), 3.78 (s; CH_2; [MDI]), 3.73–3.56 (m; CH_2 [polyester]), 2.31–2.24 (m; CH_2 [polyester]), 1.66–1.46 (m; CH_2 [polyester]), 1.37–1.27 (m; CH_2 [polyester]) (for details, see Appendix).

2.1.2 | Furan-functionalized prepolymers (1F–6F)

IR $\tilde{\nu}$ = 3,329 (br), 2,941 (m), 2,864 (m), 1,702 (s), 1,736 (s), 1,528 (s), 1,217 (s), 1,068 (s), 740 (intensity depends on molecular weight) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.71–9.40 (m; N*H*), 7.68 (2H; s; C*H* [FFA]), 7.37–7.33 (m; Ar), 7.17–7.01 (m; Ar), 6.50 (4H; dd; C*H* [FFA]), 5.09 (4H; s; CH_2 [FFA]), 4.18–4.09 (m; CH_2 [polyester]), 4.05–3.95 (m; CH_2 [polyester]), 3.78 (s; CH_2 [MDI]), 3.65–3.57 (m; CH_2 [polyester]), 2.30–2.23 (m; CH_2 [polyester]), 1.64–1.49 (m; CH_2 [polyester]), 1.39–1.23 (m; CH_2 [polyester]) (for details, see Appendix).

The cross-linker was made from furfuryl glycidyl ether (produced according to a prescription of Rostami et al.[21]) and trimethylolpropane tris(3-mercaptopropionate) according to a prescription of Habibi et al.[26] (see Appendix).

FTIR

For IR measurements, a Fourier transform infrared spectrometer (L1280034) with the software Spectrum One by Perkin Elmer (Shelton, CT) was used. The instrument used in this study was the ATR (Golden Gate, Perkin Elmer, Shelton, CT) device. For one spectrum, 10 scans were recorded. The wavenumbers in the mid-infrared region range from 4,000 to 600 cm^{-1}.

^{1}H NMR

^{1}H NMR spectra were recorded on Bruker AV-300C spectrometers at ambient temperature (300 K). ^{1}H spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. δ (^{1}H) were referenced internally to the relevant residual solvent resonances. For furan-functionalized polymers, Mn was calculated by setting the integral of the two β-hydrogen atoms of the bound furfuryl-moiety (6.50 ppm) to 4, because in the functionalized linear polymers there are two furfuryl-groups bound. For maleimide-functionalized polymers, the signal of the hydrogen atoms of the maleimide-ring was set to 4. The integral of the NH signals of the urethane groups could be used to calculate the repeating units and the molar mass.

Gel permeation chromatography (GPC)

To perform size exclusion chromatography, an amount of 50 mg of each sample was dissolved in 10 ml of tetrahydrofuran. Thereof, 40 μl was injected with an ASI-100 Automate Sample Injector of Dionex Corporation (Sunnyvale, CA). A narrow molecular weight distribution polystyrene standard (PSS Polymer Standards Service; Mainz, Germany) was used as calibration. The measurements were performed with a flow rate of 1 ml/min (Bischoff HPLC Compact Pump) at 40°C. Detection was performed with the Shimadzu (Kyoto, Japan) Refractive Index Detector RID-6A. The separation column used was the GPC/SEC-column SDV, linear M, 300 × 8 mm, 5 μm, 100 Å of PSS. The curves were examined with the PL Cirrus GPC/SEC Software (Version 1.2).

Rheological determination of the critical molecular weight (Mw [crit.])

Rheological measurements were performed using an Anton Paar (Graz, Austria) Rheometer with TruGap cone-plate geometry (1°–25 mm, $d = 0.049$ mm) and a peltier temperature control system at 85°C. The evaluation was carried out with the Rheoplus software 3.40. If necessary, the zero shear viscosity was determined after smoothing of the curve by Carreau–Yasuda simulation.

2.2 | Production of laminates

All adhesives were coated on corona treated (PET: 600 W m^{-5} min^{-1}, PE: 1,000 W m^{-5} min^{-1}; surface tension > 38 mN/m) DIN A4 films using the coating unit CUF 5 (Sumet Messtechnik, Denklingen, Germany) with 40 mm/s speed of application, and the integrated convective dryer was set to a temperature of 70°C and a drying time of 60 s. The adhesives were applied in the form of an ethyl acetate solution with a 30% solid content. For the target dry film thickness of 3.6 μm, a wired rod with 12.0 μm wet film thickness was used. The film materials used are PET (23 μm, Hostaphan), PE (45 μm, Hanita), and aluminum foil (20 μm).

The coating weight in g/cm^2 was determined by measuring the weight difference of a square 100 cm^2 coated film and the film after the removal of the adhesive and division through 100.

Subsequently to coating, a second film sheet (PET, PE, and aluminum) was laminated on the adhesive, using a hand-held roller. Each sample was cured both at room temperature and in an oven set at 60°C, under the pressure of a 5 kg weight.

Additional thickness measurements were performed with a precision thickness gauge FT3 with 0.1 μm resolution (Rhopoint Instruments, Beyhill on Sea, UK) at five random positions around the film testing area with a repetition accuracy of 0.5 μm. The values were averaged for further analyses.

2.2.1 | Differential scanning calorimetry (DSC)

DSC was performed on a DSC 821e instrument of Mettler-Toledo GmbH (Gießen, Germany) following the DIN EN ISO 11357-1 method. Specimens were heated from 23 to 200°C at a heating rate of 10 K min^{-1}. Two heating runs were performed with 6–10 mg of sample.

2.2.2 | Determination of curing time

The curing of the adhesives was tracked by infrared spectroscopy from the decrease of the maleimide signal at 696 cm^{-1}. The quantification of the reaction rate was done with the software Spectrum One by Perkin Elmer by correlating the intensity of the signal at 696 cm^{-1} with the intensity of the signal at 817 cm^{-1}. The intensity of the maleimide signal was divided by the intensity of the signal at 817 cm^{-1}. The time course over the curing time is shown in Table 5S.

2.2.3 | T-peel test

A Schenk-Trebel universal testing machine type RM 50 from Bischoff Prüftechnik GmbH (Solingen, Germany) was used for tensile testing. Before the measurement, the laminates were stored for at least 24 hr at 23°C and 50% relative humidity and cut into 15 mm wide strips. The test direction was perpendicular to the laminating direction of the laminates. The angle between the nonseparated part and the machine direction was kept at 90°; test speed was adjusted to 50 mm/min. Five test specimens were used for each measurement. Since the measurement results were sometimes influenced by air bubbles and were therefore subject to fluctuations, constant ranges for determining the measurement values were selected if necessary with the aid of the Test&Motion program from Doli Elektronik GmbH (Münsingen, Germany).

2.2.4 | Statistical hypothesis testing

The five bond strength values obtained per laminate were subjected to a statistical analysis to evaluate significant differences in bond strength between the different laminates. Therefore, the Program Visual-XSel 12.0 Multivar (CRGRAPH, Munich, Germany) was used. For each laminate, the five values are first examined for normal distribution using the Anderson–Darling normality test, with a significance value of 0.05. A *t*-test was used to compare two laminates (e.g., to compare storage at room temperature and 60°C), provided that a normal distribution of the five samples was present in both cases. In cases where there was no normal distribution, the Wilcoxon *U* test was performed. For the simultaneous comparison of $n > 2$ laminates, the multi-*t* test was applied in the case of normal distributions, in the presence of a nonnormally distributed laminate the Mood's-Median Test. The significance level was set to .05 in each case.

2.3 | Recovery of the materials

The laminates were each cut into 20 square samples with dimensions of 1×1 cm. The samples were then placed in 100 ml DMSO, heated to 105°C and stirred with a 400 rpm stirring bar. The delamination process was followed by observation as well as by occasional sampling.

2.3.1 | FTIR

For IR measurements, a Fourier transform infrared spectrometer (L1280034) with the software Spectrum One by Perkin Elmer (Shelton, CT) was used. The instrument used in this study was the ATR (Golden Gate, Perkin Elmer, Shelton, CT) device. For one spectrum, ten scans were recorded. The wavenumbers in the mid-infrared region range from 4,000 to 600 cm^{-1}.

2.3.2 | Determination of the absorbed solvent by Headspace-GC

The experiments were performed on a CLARUS-500-TRAP with FID detector. The initial temperature was 50°C for 4 min and the sample was then heated to 320°C at 20°C/min and held for 5 min.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of the functionalized prepolymers of different chain lengths and determination of the Mw (crit.)

First, the PU prepolymers of different lengths with maleimide/furan functionalization, which is necessary for the production of the DA adhesives, were prepared and analyzed. They were synthesized from the long-chain polyester diol Capa 2045, methylene diphenyl diisocyanate and furfuryl alcohol or *N*-HEMI in a procedure slightly modified to literature procedures.[24–27] By adjusting the ratio of the starting materials, the prepolymer was obtained in different chain lengths. In Table 1, an overview of the different compositions and the experimentally and theoretically determined molecular weight in each case are given. The experimental values were determined via GPC and ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra, the molar mass was determined by normalizing the signals of the bound furans. The molecular masses resulted from the integrals of the N─H protons of the urethane groups. In this respect, it should be noted that polyester-PUs can form several hydrogen bonds in concentrated DMSO-d_6 solution and thus give several NH peaks in the ^{1}H NMR.[28] In the present case the NH in the urethane can form three hydrogen bonds (between NH and S═O if DMSO-d_6, NH and C═O-group of the Polyester-softsegment and NH and the C═O groups of the hardsegment.) This explains the two to three NH signals in the range of 9.6–9.4 ppm. The ^{1}H NMR spectra also show that no side reactions have occurred. Urea groups would be expected to appear in the high field shifted range, allophanate groups in the low field shifted range.[29,30]

The theoretical value was calculated using the Carothers equation,[31] assuming a conversion of $p = .99$. In addition, a theoretical molar mass was calculated from the equivalents of the individual adhesive components (Table 1).

The value determined by GPC tends to be slightly higher than the value determined by ^{1}H NMR. However, considering the results of the GPC measurement and that the measurement was performed with a polystyrene standard, the molecular weight seems to be overestimated due

TABLE 1 Overview of the compositions of the prepolymers produced and the molar masses determined by GPC, ^{1}H NMR or theoretical methods

Name	FFA	Capa	MDI	Mn from equivalents (g/mol)	Mn (theo)[31] ($p = .99$) (g/mol)	Mn_{GPC} (g/mol)	M_{NMR} (g/mol)
	2.0	n	1+n	$=2 \cdot M_{FFA} + n \cdot M_{Capa} + (1+n) \cdot M_{MDI}$	$= \left(\frac{1+\frac{n}{n+1}}{1+\frac{n}{n+1}-2\cdot\frac{n}{n+1}p} \right) \cdot M_0 + 2 \cdot M_{FFA}$	--	--
	2	1	2				
1F	2.0	2.0	3.0	2,047	4,044	3,193	2,136
2F	2.0	4.0	5.0.	3,648	5,481	5,656	3,963
3F	2.0	6.0	7.0	5,248	9,485	7,183	5,756
4F	2.0	8.0	9.0	6,849	11,924	9,050	8,009
5F	2.0	10.0	11.0	8,449	14,201	11,294	10,086
6F	2.0	13.0	14.0	10,850	17,344	16,958	13,629

Note: The theoretical molar mass was calculated using the Carothers equation and an assumed turnover of $p = .99$. Furthermore, it was calculated from the equivalents of the materials used.

to the deviating spatial behavior in the solution. The ratio between the ^{1}H NMR and GPC value is approximately 0.89 for the longer prepolymers. For the two shorter prepolymers, however, the GPC measurement provides significantly higher values deviating from the ratio of 0.89. This can be explained by the fact that short-chain polymers are at the end of the GPC calibration curve and, consequently, the values have relatively high uncertainty. In addition, the elution curves (compare Figure S15) show that the synthesis of the shortest polymer, 1F, produced a relatively high oligomer content. The oligomer content decreases with increasing molecular weight, which is explained by more isocyanate groups' ability to react due to the higher diol content.

The molecular masses determined by the Carothers equation slightly overestimated the molecular masses determined by ^{1}H NMR. This may be due to the fact that the assumed turnover of 0.99 for the calculation was not completely achieved. For the shorter polymers, the molar masses determined by ^{1}H NMR correspond almost exactly to the molar masses calculated from the ratio of the monomers used.

Based on the molecular weights determined by ^{1}H NMR, the critical molecular mass (M_c) was determined to ensure that the prepolymers had a molar mass that enabled entanglement and thus fulfilled a basic requirement for adhesion.[32] For this purpose, the zero shear viscosities of the furan-functionalized prepolymers were measured and applied double-logarithmically against the molar mass. Figure 2 shows that a slope of 3.13 is present for the prepolymers with a higher molecular mass than 3F. This slope is close to 3.4, the typical slope for molar masses above M_c. The slope between 0F and 1F is approximately 1.0, which is a typical slope for values below the critical molar mass. Thus, the Mw (crit.) is between 1F and 2F.[33]

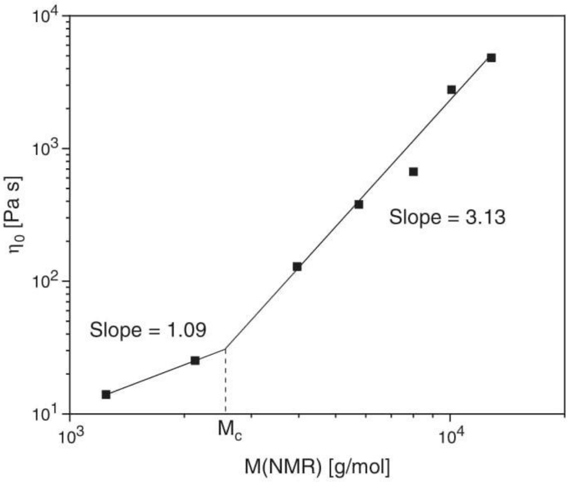


FIGURE 2 Estimation of the critical molar mass by double logarithmic application of the molar mass (determined by ^{1}H NMR spectroscopy) of the different prepolymers against the respective zero shear viscosity

For the laminate production, a chain length with a molar mass slight below the Mw (crit.) (1F) was selected and compared with the polymers above the Mw (crit.) (3F, 5F, and 6F). These prepolymers were each reacted with their corresponding maleimide-functionalized prepolymer (1M, 3M, 5M, and 6M) and a molecule carrying three-functional groups for cross-linking. The adhesives were formulated in such a way that equimolar amounts of furan and maleimide groups are present. In each formulation, about 50% of the furan groups are provided by the cross-linker molecule, the other half by the linear furan-functionalized prepolymer. Table 2 gives an overview of the formulations and their names.

TABLE 2 Overview of the adhesive formulations

Name	Furan-functionalized prepolymer		Maleimide-functionalized prepolymer		Crosslinking agent	
	Name (FX)	Eq.	Name (MX)	Eq.	Name	Eq.
Adhesive 1	F1	0.51	M1	1.00		0.33
Adhesive 2	F3	0.51	M2	1.00		0.33
Adhesive 3	F5	0.51	M3	1.00		0.33
Adhesive 4	F6	0.51	M4	1.00		0.33

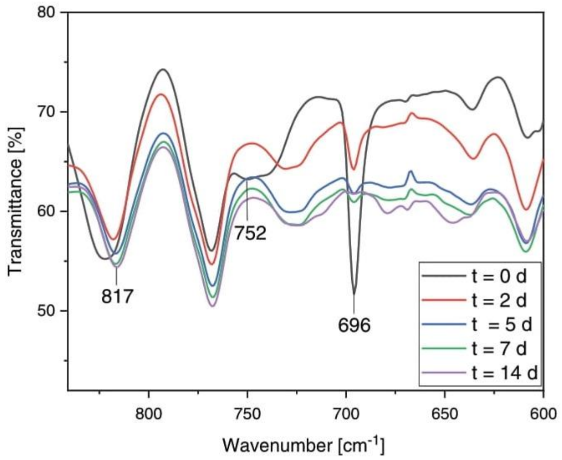


FIGURE 3 Monitoring of curing at various temperatures (IR) and determination of the exo/endo ratio (^{1}H NMR) [Color figure can be viewed at wileyonlinelibrary.com]

However, because shorter polymers have a relatively higher solubility compared with polymers with higher molecular weights,[34] faster laminate separation and thus a more efficient recycling process can be expected. In the special case of the use of 1F/1M, polymers above the critical molar mass are present in the adhesive due to the reaction between the two polymers. In the recycling process, however, the DA adducts open, which again results in polymers below the critical molar mass. This will further accelerate the delamination of the laminate.

The packaging relevant laminates PET//PE, PET//aluminum, and PE//aluminum and the additional laminate PET//PET, each with an adhesive layer thickness of 3–3.5 μm, were produced.

The curing of the adhesives was tracked by infrared spectroscopy from the decrease of the ring deformation mode of the maleimide at 696 cm^{-1} and the decrease of the absorption band of the furfuryl moiety at 752 cm^{-1}.[27] The curing process of Adhesive 1 at room temperature over 14 days is shown in Figure 3.

The relative height of the maleimide absorption band at 696 cm^{-1} to the constantly high absorption band at 817 cm^{-1} was used to estimate the rate of decrease of the maleimide groups and thus the curing rate. At 60°C and after 2 days, approximately 89% of all groups were converted, and at room temperature, approximately 70% of all groups were converted. The adhesive was completely cured after 3 days at 60°C and 14 days at room temperature. After this time, no further change in the maleimide absorption band was noticed.

A little residual signal could be noticed in some cases, which could be due to inaccuracies in the calculations caused by uncertainties in the estimation of molar masses. As expected, no difference in the curing time between the different prepolymer lengths could be observed.

However, curing at different temperatures changes the ratio between endo and exo adducts. To quantify this ratio, 1F and 1M were reacted without cross-linking agents and cured at both room temperature and 60°C. As expected, the samples cured at 60°C had a higher proportion of the thermodynamically more stable exo adduct (DA_{exo}:DA_{endo}; 5:1) (Figure 4b), whereas the sample stored at room temperature had a considerably higher proportion of the kinetically preferred endo adduct (DA_{exo}:DA_{endo}; 5:9) (Figure 4a).[16,35]

This finding is consistent with the results of the DSC measurements (see Figure S19). Furthermore, the evaluation of the DSC curves showed that the onset for the opening of the endo adduct takes place at around 80°C and at 115°C for the exo adducts. Due to the melting point of PE, the temperature in the recycling process should not exceed 105°C. Therefore, an excess of endo adducts would be beneficial for recycling.

3.2 | Adhesion

Before the laminates were recycled, adhesion measurements of the cured laminates were carried out using a T-peel test to validate the bonding.

In an ideal peel test, the peeling force increases to a certain extent depending on the adhesive strength of the

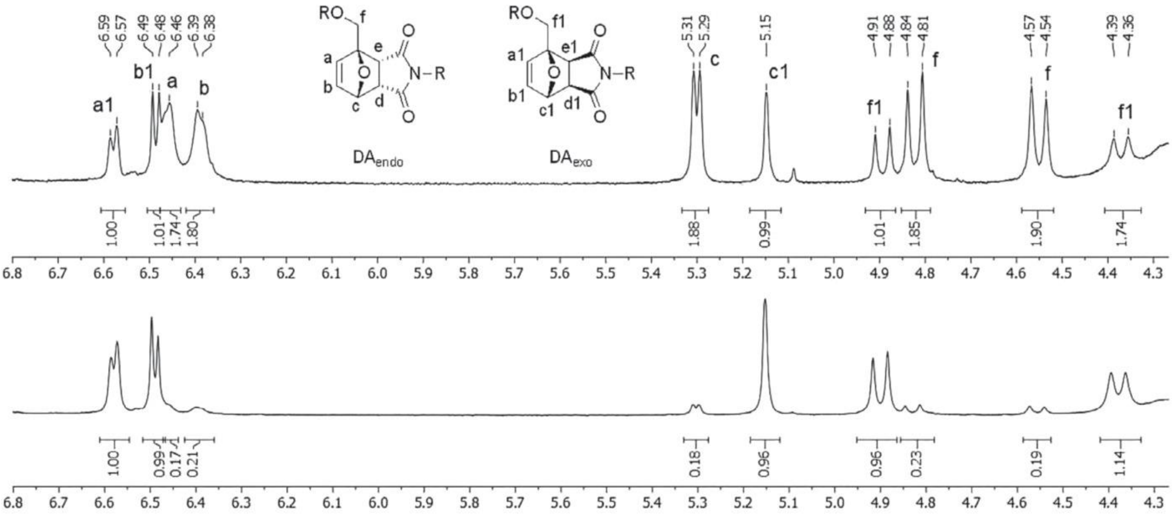


FIGURE 4 Excerpts of the ^{1}H NMR spectra of Adhesive 1 to estimate the exo/endo ratios: (a) shows that curing at room temperature provides an exo/endo ratio of about 1:1.8 and (b) shows that the exo/endo ratio obtained at 60°C is about 1:0.2

sample and then remains at a constant value. Figure 5 shows a typical force versus measurement distance curve obtained for a representative test specimen. Due to small inhomogeneities in the adhesive layer, such as air bubbles or small variations in the application thickness of the adhesive, which are often unavoidable during hand lamination, fluctuations in the determined force can be seen in many of the bond strength measurements. All measurement curves can be found in the Appendix. The mean values of the measurements (five samples each) are found in Table 2. In cases where material tearing in one of the substrate films (usually PET) occurred during measurement, no representative force was reported as the films often do not completely tear immediately, and therefore the values determined before the total tear are too low. In these cases, the bonding is stronger than the cohesion of the PET film.

To determine whether there were significant differences between the mean values given in Table 3, significant tests were carried out.

In the case of aluminum laminates, a significant decrease in adhesive strength was observed for longer prepolymers, whereas no significant differences were observed for pure plastic laminates. The reason for this is the viscosity of the 30% ethyl acetate solution in which the adhesive is applied, increases with increasing molecular weight. As a result, the adhesive is less able to penetrate surface irregularities of the aluminum foil and thus causes poorer adhesion.[36,37] The fact that longer polymers are theoretically capable of stronger entanglement is of no importance on metal surfaces. Contrarily, with polymer substrates, entanglement plays an important role in adhesion. This could explain why the measured bond strengths of the PET//PET and PET//PE composites increase with an increasing chain length or remain comparable despite increasing viscosity.

Furthermore, the use of prepolymers of different lengths changes the degree of cross-linking and the ratio between flexible and rigid structures in the adhesive.

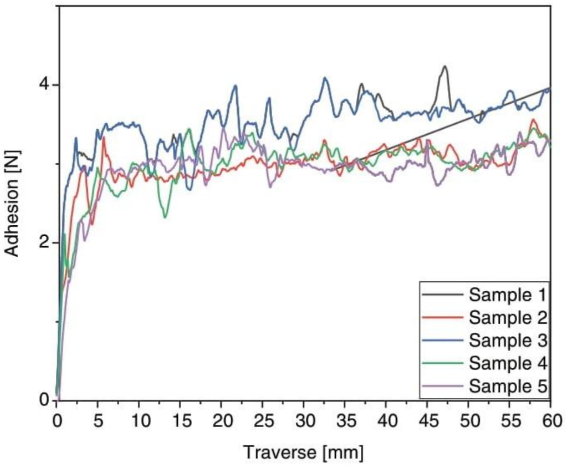


FIGURE 5 Typical curves of an adhesion measurement (5 samples/laminate) (in that case: Adhe. 2 PE/Alu, 60°C) without substrate failure. Fluctuations are due to inhomogeneities in the application (e.g., air bubbles) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Mean values and standard deviations of the bond strength measurements related to the 15 mm width of the test strips

	PET//PET		PET//PE		PET//Alu		PE//Alu	
	rt	60°C	rt	60°C	rt	60°C	rt	60°C
1M/1F	Tear of PET	Tear of PET	2.10 ± 0.08 N	3.00 ± 0.14 N	2.05 ± 0.06 N	1.95 ± 0.27 N	2.3 1 ± 0.01 N	3.15 ± 0.14 N
3M/3F	Tear of PET	Tear of PET	3.26 ± 0.09 N	Tear of PET	2.16 ± 0.11 N	2.25 ± 0.21 N	2.38 ± 0.13 N	3.18 ± 0.28 N
5M/5F	1.52 ± 0.12 N	1.56 ± 0.15 N	2.12 ± 0.07 N	Tear of PET	0.39 ± 0.05 N	0.79 ± 0.08 N	0.89 ± 0.11 N	1.57 ± 0.02 N
6M/6F	3.17 ± 0.39 N	3.08 ± 0.16 N	2.58 ± 0.18 N	Tear of PET	0.79 ± 0.08 N	0.66 ± 0.05 N	1.04 ± 0.20 N	1.65 ± 0.12 N

Note: The numerical values indicate the mean value from five measurements. All measurement curves can be found in the Supporting Information.

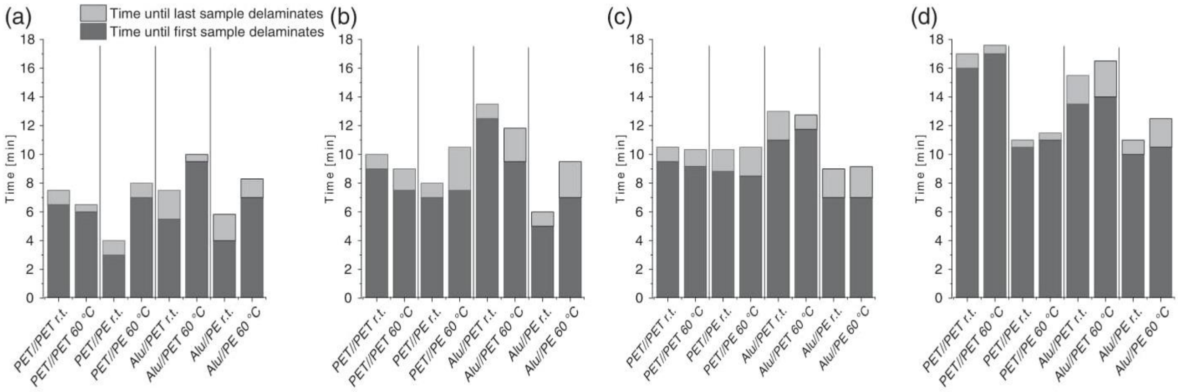


FIGURE 6 Schematic representation of the delamination process. The filled arrows symbolize the dissolution process of the adhesive components over the cutting edge of the laminate pieces. The unfilled arrows symbolize the permeation of the solvent through the PE film, which also causes an early start of the dissolution process in the middle of the sample pieces

In some cases, laminates cured at 60°C showed significantly higher adhesive strength than those cured at room temperature. This could be due to the improved surface contact of the adhesive during the curing process as polymers are less viscous at 60°C and can therefore form more intermolecular interactions with the surface of the substrates.[36,38] The higher mobility of polymer chains at elevated temperatures could contribute to a stronger entanglement with the polymers of the substrates and thus to a stronger adhesion.[36] In the case of a PU adhesive containing polyester, it is expected that PET laminates would exhibit greater adhesion than PE laminates due to the greater structural similarity and the resulting stronger intermolecular interactions. In the present experiments, this could not be determined. Instead, the adhesion of PET and PE laminates appears to be comparable, or even stronger, for PE laminates.

3.3 | Delamination

After the T-peel test had confirmed the adhesion of the laminates, the films were made available for recycling by delamination. The delamination of the laminates was performed with 1 cm^2 flakes at 105°C in DMSO under moderate shearing. The temperature was chosen so that the temperature would be as high as possible to allow a retro-DA reaction to take place, but the PE should still be dimensionally stable. DMSO was chosen because of its satisfactory solubility of the prepolymers and its high boiling point, which allows the retro-DA reaction to be carried out.

To determine the minimum dissolution time of the polymers, delamination experiments were first carried out with laminates, which were only prepared with furan-functionalized prepolymers (1F–6F). For practical reasons, PET//PET laminates were used. As expected, the delamination times of the composites increased with increasing chain length (1F 5:30 min, 2F 6:30 min, 3F 7:20 min, 4F 8:00 min, 5F 9:30 min, and 6F 11:00 min).

This trend is also evident in the cross-linked adhesives (Figure 6), although some PE laminates have lower dissolution times than pure, noncross-linked prepolymers in PET//PET laminates. In general, the type of laminate also influences the delamination duration. Composites that do not contain PE tend to have longer dissolution times.

FIGURE 7 Graphical representation of the delamination times of the various composites. The bars with the close-meshed pattern symbolize the time until the delamination of the first samples can be observed. The bars with the wide-meshed pattern symbolize the time until the delamination of the last sample can be observed: (a) shows the results of Adhesive 1, (b) Adhesive 2, (c) Adhesive 3, and (d) Adhesive 4 [Color figure can be viewed at wileyonlinelibrary.com]

In PET-containing laminates, it can be observed that the adhesive is removed from the outside cutting edges. The samples can only be moved mechanically against each other shortly before complete delamination because the adhesive is hardly influenced in the middle of the laminate nips before. Especially with PET//aluminum laminates, the adhesion in the middle of the laminate slice is maintained for a relatively long time. With PE//aluminum composites, the two films can be shifted more quickly against each other and the adhesion in the middle decreases more quickly.

These observations can be explained by the barrier properties of PET and PE. The diffusion coefficient of organic solvents for PE is significantly higher than for PET,[39] especially because the test temperature of 105°C is almost in the melting range of PE. Thus, in the case of PET, the solvent primarily penetrates the adhesive via the cut edges, whereas in the case of PE, the solvent can also permeate through the film (Figure 7).

As was to be expected, samples cured at 60°C tend to have a longer delamination time than samples stored at room temperature. The effect, however, was less significant than expected. Generally, the significantly higher proportion of exo adduct would lead to a longer delamination time due to the higher activation energy for the retro-DA reaction. However, in both cases, enough adducts seem to be opened at 105°C to allow dissolution of the adhesive by DMSO. By means of DSC, an onset for the retro reaction of the endo adduct of 80°C and the exo adduct of 115°C was determined. However, according to Froidevaux et al.,[16] the temperature of the retro-DA reaction of the endo adduct is lower and the DSC analysis is not an appropriate analytical tool to precisely detect the onset of the retro-DA reaction. Moreover, in the retro-DA reaction of the exo adduct, the onset may not be accurately determined due to signal overlaps.

However, in all cases, it must be taken into account that the determined delamination times are subject to a certain degree of uncertainty as it is sometimes visually difficult to determine the exact delamination time.

3.4 | Recovery of monomaterials and characterization

After complete delamination, the monomaterial films (PET, PE, and aluminum) were suspended separately. As

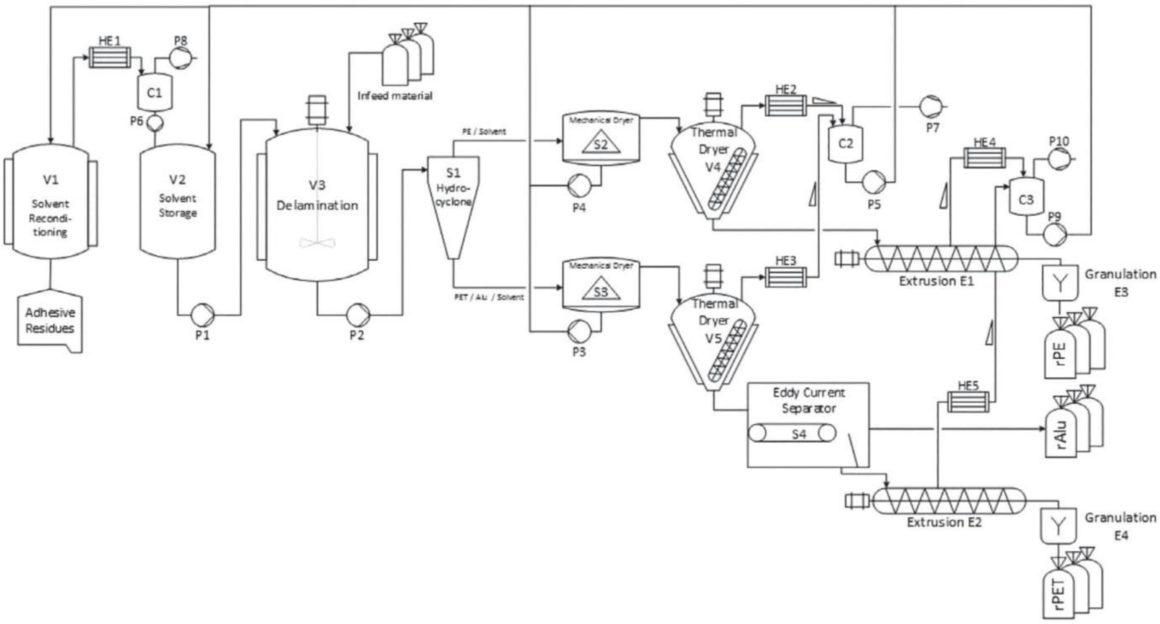


FIGURE 8 Possible process flow diagram for implementation. C, catchpot; E, extrusion incl. Granulation; H, heat exchanger; P, pump; S, separator; and V, vessel

PE has a density of lower than 1 g/cm^3, it floats on the surface of DMSO and can be easily separated from the sinking materials PET and aluminum. The adhesive components were solvated and could no longer be detected by IR spectroscopy on the surface of the films (see Supporting Information Figure S22 and Figure S23). Headspace-GC was used to determine the amount of solvent absorbed by the PE/PET films. The results of 4.5 ppm for PE and 2.1 ppm for PET show that extrusion degassing would be necessary for further processing of the two monomaterial polymer streams. The following chapter describes a possible process flow diagram of the upscaled recycling process (Figure 8).

3.5 | Process flow diagram

The delamination process is carried out in a heated vessel, connected to a solvent reservoir and an infeed for the material to be treated. A hydrocyclone is suitable for density separation of the flakes obtained after delamination, in which PE can be separated from PET and aluminum. A predrying of the respective three material fractions can be achieved mechanically by a decanter centrifuge. The subsequent thermal drying can be carried out via a vacuum dryer that ensures a low residual solvent content of down to 1%.

The aluminum can then be removed from the PET// aluminum fraction by an eddy current separator or electrostatic separation. Reextrusion of the PET and PE-fraction is then carried out under degassing.

The solvent recovered by mechanical/thermal drying and degassing can, due to the low concentration of monomers in solution, be used again directly for delamination for $n > 10$ rounds before a distillation of the solvent would become necessary.

An additional recovery of the adhesive is not aimed at, as this would be difficult to achieve on the one hand and impurities such as printing inks would be contained in the distillation sump under real conditions.

4 | CONCLUSIONS

Multilayer packaging is an effective way to protect food items, but it remains under criticism as it is not recyclable. New technologies, such as debondable adhesives, are an option to address this problem. This research article has shown that producing typical packaging laminates with PU adhesives containing DA adducts is possible. Subsequently, these laminates can be delaminated into individual materials by treating the size-reduced composite material with a heated solvent. Although there are different ratios between endo and exo adduct in the adhesives due to different curing temperatures, no significant difference in delamination times could be observed. Instead, differences in the barrier properties of the respective film materials and longer prepolymers have an influence on delamination times. However, as the difference between the dissolution times is in the minute range, the longer dissolution times do not hinder the feasibility.

The materials obtained after delamination no longer exhibited adhesive residues and can be made accessible for recycling as a pure material through density separation or eddy current separation.

With regard to the material characterization of the laminates, a future scale-up to machine lamination will be advantageous because defects and the standard deviation of the bond strength measurements can be reduced. To use this method for the production of recyclable multilayer packaging, it is necessary to use only raw materials that are harmless from a food law point of view. Further research that includes this aspect will be published.

ACKNOWLEDGMENTS

Special thanks go to Kerstin Müller, Stefan Schießl, Dominik Reiter, and Dr. Cornelia Stramm for proofreading. Additional thanks go to the technical team members of the Materials Development department for corona treatment and advice concerning lamination and the laboratory team of the Materials Development department for providing laboratory equipment. Further thanks go to Daniel Bauer for his assistance with the syntheses and Perstorp Holding AB for providing Capa 2054.

CONFLICT OF INTEREST

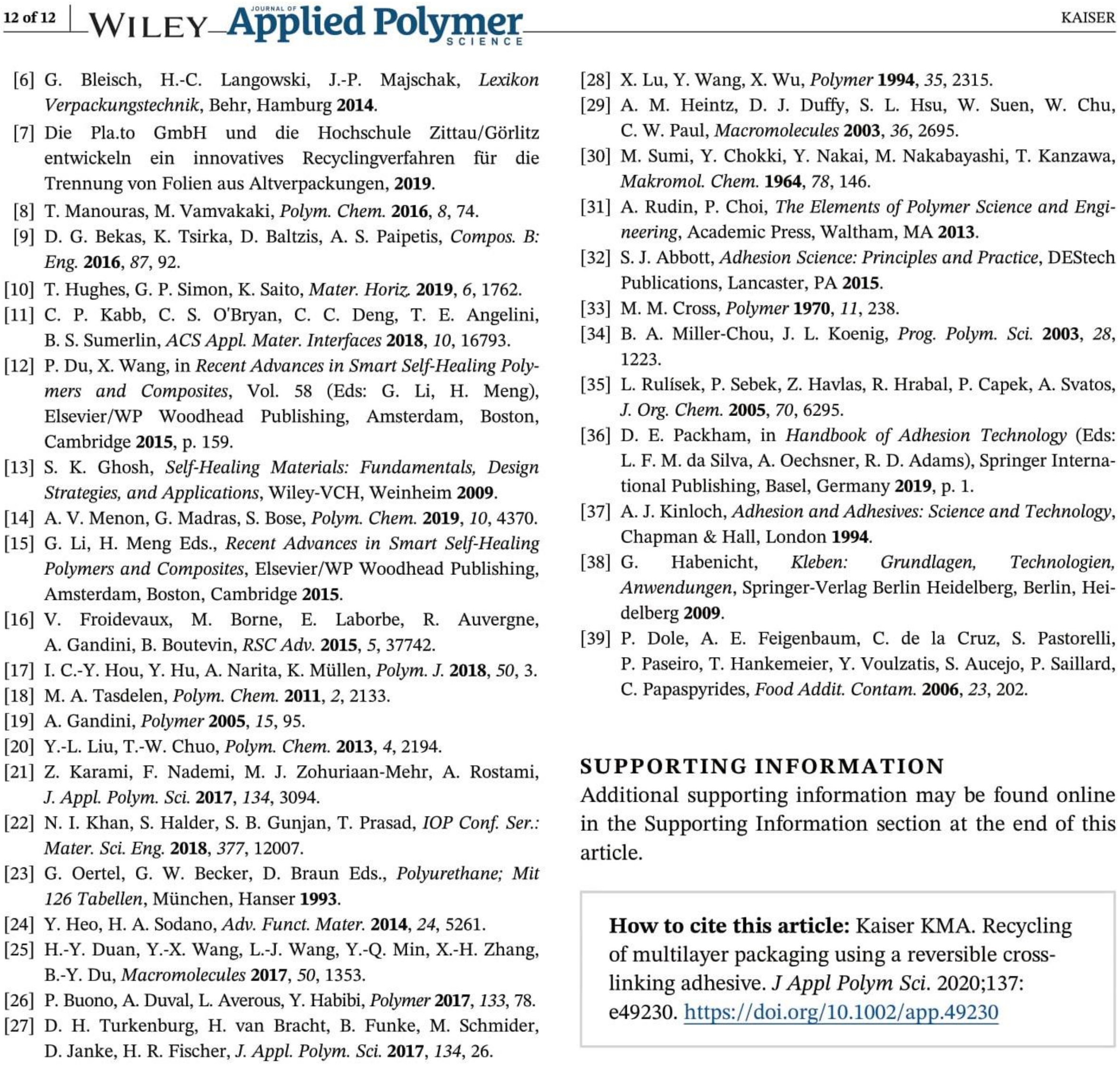
The authors declare no potential conflicts of interest.

ORCID

Katharina M. A. Kaiser https://orcid.org/0000-0002-9810-3416

REFERENCES

[1] *European Comission, A European Strategy for Plastics in a Circular Economy*, **2018**.
[2] A. Nonclercq, *Mapping Flexible Packaging in a Circular Economy [F.I.A.C.E]: Final report*, **2016**.
[3] J. Dixon, Packaging materials: 9. in *Multilayer Packaging for Food and Beverages*, International Life Sciences Institute, Washington D.C. **2011**.
[4] P. Singh, A. A. Wani, H.-C. Langowski Eds., *Food Packaging Materials: Testing & Quality Assurance*, CRC Press Tayöpr & Francis Group, Boca Raton, London, NY **2017**.
[5] K. Kaiser, M. Schmid, M. Schlummer, *Recycling* **2018**, *3*, 1.



[6] G. Bleisch, H.-C. Langowski, J.-P. Majschak, *Lexikon Verpackungstechnik*, Behr, Hamburg **2014**.

[7] Die Pla.to GmbH und die Hochschule Zittau/Görlitz entwickeln ein innovatives Recyclingverfahren für die Trennung von Folien aus Altverpackungen, **2019**.

[8] T. Manouras, M. Vamvakaki, *Polym. Chem.* **2016**, *8*, 74.

[9] D. G. Bekas, K. Tsirka, D. Baltzis, A. S. Paipetis, *Compos. B: Eng.* **2016**, *87*, 92.

[10] T. Hughes, G. P. Simon, K. Saito, *Mater. Horiz.* **2019**, *6*, 1762.

[11] C. P. Kabb, C. S. O'Bryan, C. C. Deng, T. E. Angelini, B. S. Sumerlin, *ACS Appl. Mater. Interfaces* **2018**, *10*, 16793.

[12] P. Du, X. Wang, in *Recent Advances in Smart Self-Healing Polymers and Composites*, Vol. 58 (Eds: G. Li, H. Meng), Elsevier/WP Woodhead Publishing, Amsterdam, Boston, Cambridge **2015**, p. 159.

[13] S. K. Ghosh, *Self-Healing Materials: Fundamentals, Design Strategies, and Applications*, Wiley-VCH, Weinheim **2009**.

[14] A. V. Menon, G. Madras, S. Bose, *Polym. Chem.* **2019**, *10*, 4370.

[15] G. Li, H. Meng Eds., *Recent Advances in Smart Self-Healing Polymers and Composites*, Elsevier/WP Woodhead Publishing, Amsterdam, Boston, Cambridge **2015**.

[16] V. Froidevaux, M. Borne, E. Laborbe, R. Auvergne, A. Gandini, B. Boutevin, *RSC Adv.* **2015**, *5*, 37742.

[17] I. C.-Y. Hou, Y. Hu, A. Narita, K. Müllen, *Polym. J.* **2018**, *50*, 3.

[18] M. A. Tasdelen, *Polym. Chem.* **2011**, *2*, 2133.

[19] A. Gandini, *Polymer* **2005**, *15*, 95.

[20] Y.-L. Liu, T.-W. Chuo, *Polym. Chem.* **2013**, *4*, 2194.

[21] Z. Karami, F. Nademi, M. J. Zohuriaan-Mehr, A. Rostami, *J. Appl. Polym. Sci.* **2017**, *134*, 3094.

[22] N. I. Khan, S. Halder, S. B. Gunjan, T. Prasad, *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, *377*, 12007.

[23] G. Oertel, G. W. Becker, D. Braun Eds., *Polyurethane; Mit 126 Tabellen*, München, Hanser **1993**.

[24] Y. Heo, H. A. Sodano, *Adv. Funct. Mater.* **2014**, *24*, 5261.

[25] H.-Y. Duan, Y.-X. Wang, L.-J. Wang, Y.-Q. Min, X.-H. Zhang, B.-Y. Du, *Macromolecules* **2017**, *50*, 1353.

[26] P. Buono, A. Duval, L. Averous, Y. Habibi, *Polymer* **2017**, *133*, 78.

[27] D. H. Turkenburg, H. van Bracht, B. Funke, M. Schmider, D. Janke, H. R. Fischer, *J. Appl. Polym. Sci.* **2017**, *134*, 26.

[28] X. Lu, Y. Wang, X. Wu, *Polymer* **1994**, *35*, 2315.

[29] A. M. Heintz, D. J. Duffy, S. L. Hsu, W. Suen, W. Chu, C. W. Paul, *Macromolecules* **2003**, *36*, 2695.

[30] M. Sumi, Y. Chokki, Y. Nakai, M. Nakabayashi, T. Kanzawa, *Makromol. Chem.* **1964**, *78*, 146.

[31] A. Rudin, P. Choi, *The Elements of Polymer Science and Engineering*, Academic Press, Waltham, MA **2013**.

[32] S. J. Abbott, *Adhesion Science: Principles and Practice*, DEStech Publications, Lancaster, PA **2015**.

[33] M. M. Cross, *Polymer* **1970**, *11*, 238.

[34] B. A. Miller-Chou, J. L. Koenig, *Prog. Polym. Sci.* **2003**, *28*, 1223.

[35] L. Rulísek, P. Sebek, Z. Havlas, R. Hrabal, P. Capek, A. Svatos, *J. Org. Chem.* **2005**, *70*, 6295.

[36] D. E. Packham, in *Handbook of Adhesion Technology* (Eds: L. F. M. da Silva, A. Oechsner, R. D. Adams), Springer International Publishing, Basel, Germany **2019**, p. 1.

[37] A. J. Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman & Hall, London **1994**.

[38] G. Habenicht, *Kleben: Grundlagen, Technologien, Anwendungen*, Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg **2009**.

[39] P. Dole, A. E. Feigenbaum, C. de la Cruz, S. Pastorelli, P. Paseiro, T. Hankemeier, Y. Voulzatis, S. Aucejo, P. Saillard, C. Papaspyrides, *Food Addit. Contam.* **2006**, *23*, 202.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Kaiser KMA. Recycling of multilayer packaging using a reversible cross-linking adhesive. *J Appl Polym Sci*. 2020;137:e49230. https://doi.org/10.1002/app.49230

7. Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law [47]

by Katharina M. A. Kaiser, Johann Ewender and Frank Welle

In order to comply with food law requirements, a Diels-Alder adhesive formulation was developed that does not contain CMR chemicals. The necessary furan groups were incorporated via furfurylamine, which also makes it possible to avoid the use of a crosslinking molecule, since the urea groups formed by the reaction of isocyanate with furfurylamine enable the production of linear furan prepolymers with furan side chains. This means that *N*-(2-hydroxyethyl)maleimide and furfurylamine are the only two chemicals contained in the adhesive formulation that are not listed in the Annex to EU Regulation 10/2011. In order to comply with the legal requirements, it must be ensured that these two substances do not exceed the prescribed maximum level of 0.01 mg/kg food.

In the T-Peel test, the adapted adhesive formulation showed a laminate adhesion appropriate for packaging purposes of 3.07±0.11 N/15 mm in the case of the PET//PE laminate and 2.30±0.41 N/15 mm and 2.39±0.33 N/15 mm for PET//aluminum and PE//aluminum, respectively. The slightly higher laminate adhesion in the case of the PET//PE laminate seems to be due to the possibility of delamination of the adhesive polymers with the substrate polymers, which is not possible for the bond to aluminum. Delamination of the laminates in solution with the modified formulation is possible in 30 minutes without leaving residues of the adhesive polymers on the substrates.

By means of migration modeling it was shown that furfurylamine and *N*-(2-hydroxyethyl)maleimide have a lag time of only a few minutes with a 45 µm thick PE-LD layer at room temperature which means that PE-LD cannot be regarded as a barrier against the two substances under these conditions. However, if the residual content of the two substances is below 30 mg/kg, the saturation concentration in the food will also be below the legal limit, provided that a PET//PE (23 µm//45 µm) composite is used.

To verify how the use of an ethylene-vinyl alcohol copolymer (EVOH) barrier between the adhesive and the food affects the passage of the two chemicals into the food, the activation energies and diffusion coefficients for diffusion through EVOH were determined. By using these, it was possible to determine through migration modeling that the lag-time of the migrants extends to at least 9 years just by using a 3 µm thick layer of EVOH.

From a food law point of view, the use of the described adhesive is possible, provided that the residual concentrations of the two substances in the adhesive are below 3 µg/kg, or a thin EVOH barrier is used.

Polymers **2020**, *12*, DOI:10.3390/polym12122988

Author Contributions: K. Kaiser planned and carried out the experiments necessary to produce the laminates and for recycling and performed the migration modeling and wrote the corresponding parts of the manuscript. F. Welle determined the diffusion coefficients and the activation energies for diffusion and wrote the corresponding chapters in the manuscript. J. Ewender performed the experiments necessary to determine the diffusion coefficients.

Note to 2.9 *Statistical Hypothesis Testing*:

In this publication the Anderson-Darling test was performed with a sample size of n = 5 which is to small to guarantee that no false positive results were obtained for the normal distribution. The consequence of this could be that a Student T-test was incorrectly used instead of a Wilcoxon U test, over- or underestimating differences in significance. However, strictly speaking, the laminate adhesion of different laminate structures measured by the T-Peel test cannot be compared with each other anyway, since different materials can absorb different amounts of energy. Therefore, a direct comparison of the values measured for composite adhesion is only of limited use anyway.

Note to 3.4 *Activation Energys of Diffusion*:

The correlation coefficient on page 79, it must be added that the coefficient of determination was determined according to Pearson and that the coefficient of determination R^2 is not legitimate in the Figure 10, since a nonlinear relationship is shown here.

polymers MDPI

Article

Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law

Katharina M. A. Kaiser [1,2,*], Johann Ewender [2] and Frank Welle [2]

[1] TUM School of Life Sciences Weihenstephan, Technical University of Munich, Weihenstephaner Steig 22, 85354 Freising, Germany
[2] Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Strasse 35, 85354 Freising, Germany; johann.ewender@ivv.fraunhofer.de (J.E.); frank.welle@ivv.fraunhofer.de (F.W.)
* Correspondence: katharina.kaiser@ivv.fraunhofer.de

Received: 21 November 2020; Accepted: 11 December 2020; Published: 15 December 2020

Abstract: Lacking recyclability of multilayer packaging can be overcome by using a thermoreversible crosslinking adhesive consisting of maleimide- and furan-functionalized polyurethane-(PU-) prepolymers, reacting in a Diels–Alder-reaction. Here, the furan-functionalized PU-prepolymer carries furan-side-chains to avoid the usage of an additional crosslinking agent. Thus, *N*-(2-hydroxyethyl)maleimide and furfurylamine are the only two chemicals contained in the adhesive that are not listed in the appendix of EU Regulation 10/2011. Using migration modelling, it could be shown that, at 23 °C, both chemicals have lag-times of only a few minutes if 45 μm PE is used as a barrier. However, if the residual content is below 30 mg/kg, the legally specified maximum amount of 0.01 mg/kg food is not reached. After determining the diffusion coefficients and the activation energy of diffusion through ethylene-vinyl alcohol copolymer (EVOH), it could be determined that the lag-time of the migrants can be extended to at least 9 years by the use of 3 μm EVOH. From a food law point of view, the use of the described adhesive is possible if the above-mentioned measures are complied.

Keywords: multilayer packaging; recycling; adhesive; Diels-Alder; EVOH; barrier testing; migration; diffusion coefficient; activation energy

1. Introduction

In multilayer packaging, different materials are combined with each other in a layered structure, which enables the creation of customized property profiles. By combining the materials, defined barriers against oxygen, water vapor, light, or aroma can be created, thereby enabling extended shelf lives. Additionally, material combination provides the possibility to produce sealable packaging, achieve certain optical effects, and obtain desired mechanical properties with low material consumption. Because of these advantages, multilayer packaging is an important part of the packaging market [1–4].

However, these multilayered films are usually not recyclable, as many different materials are incompatible and thus cannot be processed together [5–7]. According to the European Plastics Strategy, all packaging should be reusable or recyclable by 2030 [8]. To achieve this goal, innovations in design-for-recycling and recycling methods must therefore be promoted.

In a previously published article [9], the approach of producing multilayer packaging with thermoreversibly crosslinking adhesives and recycling them with a corresponding solvent-based recycling process was presented. PET-PE, PE-aluminum, and PET-aluminum laminates were produced using an adhesive containing Diels–Alder adducts. Under the influence of temperature in DMSO, the laminates can be delaminated by inducing the retro-Diels-Alder reaction. The individual film materials (PE, PET, aluminum) can be recovered without adhesive residues and thus made accessible for recycling [9,10]. In post-consumer recycling, such packaging could therefore be recovered after it has been sorted out of the post-consumer packaging stream using appropriate technologies. The technologies that can be envisaged for such sorting include built-in marcers based on fluorescence, photoluminescence, or digital watermarks, which enable identification and sorting. [11–15]. One option for sorting multilayer packaging without markers is based on the fact that multilayer films usually curl up when exposed to temperature and can therefore be separated by wind sifting [16].

The problem with the adhesive system described in the previous paper is that the carcinogenic chemical furfuryl alcohol [17] and a toxicologically unevaluated cross-linker, a molecule with three furan groups, were used. However, in food packaging, it is also important that all substances contained in the adhesive system are safe and that all requirements under food law are met. According to EU Regulation 10/2011, chemicals included in the Union list of authorized substances may be used in food contact materials without further regulation [18]. Non-listed chemicals that are carcinogenic, mutagenic, or toxic to reproduction may not be used without prior authorization. However, non-listed chemicals that are not carcinogenic, mutagenic, or toxic to reproduction may be used behind a functional barrier, provided that a maximum migration limit of 0.01 mg/kg into the food is respected [18].

According to the method described in the previous paper, *N*-(2-hydroxyethyl)maleimide, furfuryl alcohol, and a crosslinker molecule with three furan groups were used in addition to common packaging adhesive components [9,19]. While *N*-(2-hydroxyethyl)maleimide is allowed to be used as a non-cancerogenic/reprotoxic/mutagenic (CRM) chemical behind a functional barrier, furfuryl alcohol is potentially carcinogenic and the cross-linker molecule is not toxicologically evaluated because it is not commercially available. These two chemicals should therefore not be used in food packaging without prior testing and approval by the European Food Safety Authority.

Accordingly, the adhesive formulation in this paper contains, in addition to common components of packaging adhesives, only furfurylamine and *N*-(2-hydroxyethyl)maleimide. These two chemicals may both be used behind functional barriers, provided the maximum migration limit of non-listed substances behind a functional barrier is respected [20,21]. Since crosslinking of the adhesive is ensured by furfuryl side chains on the furfuryl-prepolymer, the use of an additional crosslinking molecule is unnecessary.

The aim of the study is to discuss the modified adhesive formulation with regard to its suitability for packaging and recycling purposes, which on the one hand means that sufficient adhesive strength and good separability of the packaging has to be achieved. Additionally, for food law evaluation, the migration behavior of furfurylamine and *N*-(2-hydroxyethyl)maleimide through PE, PE/EVOH/PE, PET has to be assessed. For this purpose, the diffusion coefficients of the migrants through PET, ethylene–vinyl alcohol copolymer (EVOH) and activation energies of diffusion have to be determined. Based on the experimentally determined activation energies of diffusion and the residue contents of free furfurylamine and *N*-(2-hydroxyethyl)maleimide it can be determined how much of the migrants can migrate into the packaged food at the end of shelf life.

On this basis it will be discussed under which conditions the adhesive could be used for food packaging from a food law perspective.

2. Materials and Methods

2.1. Characterization by Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectrometer from Perkin Elmer (Shelton, CT, USA) and the corresponding software Spektrum One were used to measure and process IR spectra. The measurements were performed with an ATR (Golden Gate, Perkin Elmer, Shelton, CT, USA) measurement unit, whereby ten scans were carried out for each spectrum. The measured wavelength range was 4000 to 600 cm^{-1}.

2.2. Determination of the Molecular Weight

The size exclusion chromatography was performed in THF. For this purpose, 50 mg of each sample was dissolved in 10 mL THF and 40 µL of this solution was then injected using an ASI-100 Automate Sample Injector Unit from Dionex Corporation (Sunnyvale, CA, USA). For calibration, a narrow molecular weight distribution polystyrene standard (PSS Polymer Standards Service, Mainz, Germany) was used. The measurements were performed with a flow rate of 1 $mL \cdot min^{-1}$ (Bischoff HPLC Compact Pump) at 40 °C. The refractive index detector RID-6A from Shimadzu (Kyoto, Japan) was selected as the detector. The separation column used was the GPC/SEC-column SDV, linear M, 300 × 8 mm, 5 µm, 100 Å of PSS. Evaluation of the elution curves was performed with the PL Cirrus GPC/SEC Software (Version 1.2).

2.3. Preparation of the Adhesive

4,4′-Methylene diphenyl diisocyanate (MDI) (98%) was obtained from Alfa Aesar (Ward Hill, MA, USA) and used as received, if a dimer formation could be excluded. Furfurylamine (≥99%, Merck, Darmstadt, Germany), the polyesterdiol Capa™ 2054 (Perstorp, Malmö, Sweden) was dried prior to use at reduced pressure and under a slightly elevated temperature. In addition, an isocyanate prepolymer from Morchem SA (Les Franqueses del Vallès, Spain) was used for the preparation of the furan-functionalized prepolymer.

The maleimide functional group, *N*-(2-hydroxyethyl)maleimide, was prepared via a Diels–Alder and retro-Diels–Alder reaction in a three-step process [22,23]. Methyl ethyl ketone (≥99.5%) was purchased from TH Geyer and, if necessary, dried with molecular sieve (4 Å) to an H_2O content <50 mg/kg and stored under nitrogen ($H_2O \leq 50$ mg/kg). Reactions involving the use of isocyanate compounds were carried out under a nitrogen atmosphere.

2.4. Furan-Functionalized Prepolymer

To produce the furan-functionalized prepolymer (see Figure 1, Figure S1), the isocyanate prepolymer (152 g, solids content 106 g, 43.2 mmol, 3.00 equiv.) was added to a three-necked flask, which was set under nitrogen and equipped with a mechanical stirrer. Afterwards, 2.80 g (28.8 mmol, 2.67 mL, 1.00 equiv.) furfurylamine were diluted with methyl ethyl ketone (MEK) and were slowly added to the stirred prepolymer so that the temperature inside the flask would not exceed 30 °C. The reaction mixture was then stirred for 30 min at room temperature, before heating the oil bath to 110 °C. It could be observed that the reaction mixture initially became clear and then turned yellowish with time. The mixture was stirred at this temperature until the isocyanate signal at 2264 cm^{-1} in the IR did not decrease any further. It can therefore be assumed that all urea groups have reacted with isocyanate groups. Then, the mixture was cooled to about 70 °C and 20 mL MEK were added to keep the polymer stirrable. To finish the reaction, 2.80 g (28.8 mmol, 2.67 mL, 1.00 equiv.) furfurylamine in 10 mL MEK was then added to this viscous polymer solution to functionalize the remaining NCO-groups.

The product was obtained as a clear, yellowish viscous polymer solution with a solids content of 83%.

Details on material characterization can be found in the Supporting Information.

This polymerization was carried out similarly to the method of Du et al. [24].

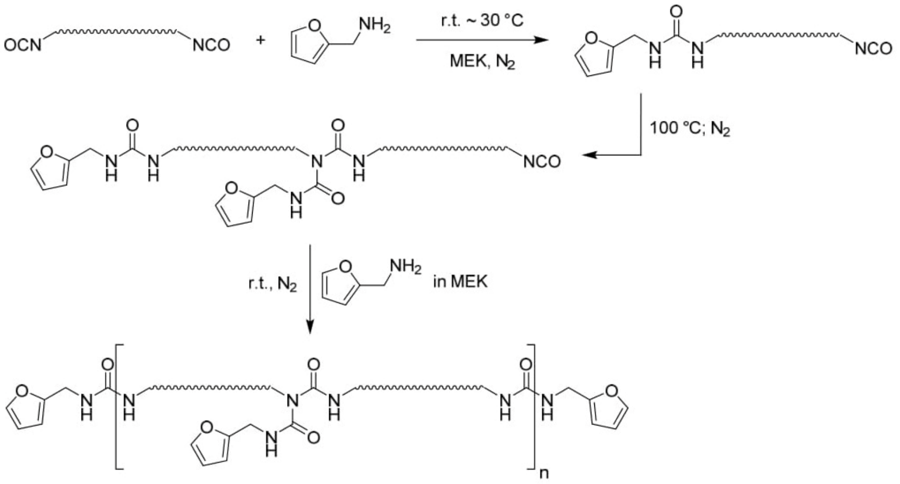


Figure 1. Reaction scheme for the preparation of the furan prepolymer with side groups.

2.5. Maleimide-Functionalized Prepolymer

To produce the maleimide-functionalized prepolymer (see Figure 2, Figure S2), MDI (4.50 g, 18 mmol, 3.00 equiv.) was heated to 50 °C to give a clear, colorless liquid to which 12.0 g (12 mmol, 2.00 equiv.) polypropylene glycol 1000 was added all at once. After the exothermic reaction subsided, the mixture was heated to 80 °C until reaction control with FTIR showed no further decrease of the NCO-signal. Subsequently, 1.69 g (12 mmol, 2.00 equiv.) *N*-(2-hydroxyethyl)maleimide was added to the mixture. The reaction was kept at 80 °C until the NCO-signal vanished.

The polymer was obtained as a clear, yellow viscous and tacky polymer.

Details on material characterization can be found in the Supporting Information.

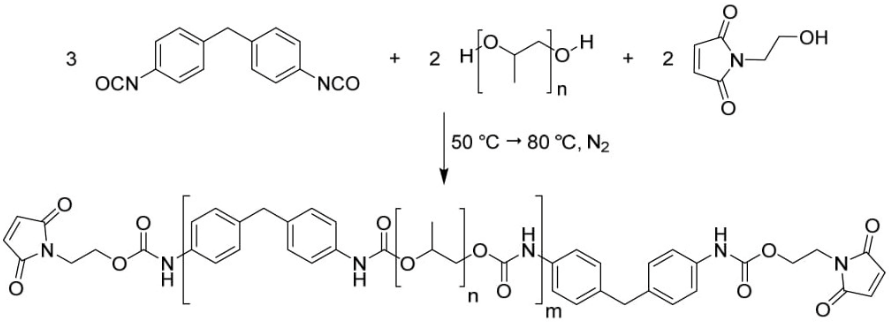


Figure 2. Reaction scheme for the preparation of the maleimide-prepolymer.

2.6. Preparation of the Adhesive Mixture

To prepare the adhesive (see Figure 3), total of 0.78 g (52.0 mmol of maleimide-groups, 1.00 equiv.) of the maleimide-prepolymer was weighed into a vial together with 1.20 g (52.0 mmol of furan-groups, solids content 1.00 g) of the furan polymer and dissolved in 4.15 g MEK by shaking. In this way, a low-viscous, pale yellow solution with 30% solids content was obtained.

Details of the infrared spectrum can be found in the Supporting Information.

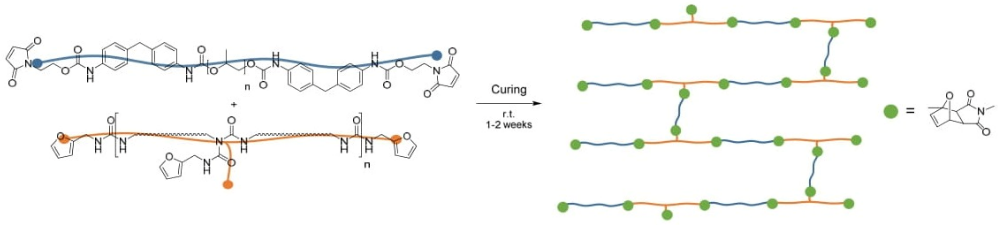


Figure 3. Cross-linking reaction of the two adhesive components during the curing process.

2.7. Production of Laminates

Before use, the polymer films were treated with corona (PET: 600 Watt/5 m/min, PE: 1000 Watt/5 m/min, surface tension >38 mN/m) and then cut into pieces in DIN A4 format. The coating was applied by means of the CUF 5 (Sumet Messtechnik, Denklingen, Germany) coating unit at an application speed of 40 mm/s, a drying temperature of 70 °C, and a drying time of 60 s. To achieve the target dry film thickness of 8 µm, a wired rod with 27 µm wet film application was used. The films used were PET (23 µm, Hostaphan), PE (45 µm, Hanita), and aluminum foil (20 µm). For curing, the samples were stored at room temperature under the pressure of a 5 kg weight.

The thickness of the coating was checked using a precision thickness gauge FT3 (Rhopoint Instruments, Beyhill on Sea, UK) with an accuracy of 0.1 µm at five randomly selected positions on the film with a repeatability accuracy of 0.5 µm. The values were averaged for closer examination. However, since the film thicknesses of PE, PET, and aluminum foils also appeared to fluctuate, the adhesive thickness was also partially checked by microtome sections. Microtome sections were prepared using the device Jung Autocut 2055 of Leica Microsystems GmbH (Wetzlar, Germany). The samples were each cut into microtomes with thickness of 20 µm and analyzed using an optical microscope with objectives of 40- and 200-times magnification.

2.8. T-Peel Test

A Schenk-Trebel universal testing machine type RM 50 from Bischoff Prüftechnik GmbH (Solingen, Germany) was used for tensile testing. Before the measurement, the laminates were stored for at least 24 h at 23 °C and 50% relative humidity and cut into 15-mm wide strips. The laminates were tested perpendicular to the direction of lamination. During the entire measurement, there was an angle of 90° between the measuring direction and the non-separated part of the sample. The measuring speed was 50 mm/min in all cases and the measuring range was 60 mm, while the measuring range between 5 and 60 mm was used for the analysis. The Test & Motion program from Doli Elektronik GmbH (Münsingen, Germany) was used for evaluation.

2.9. Statistical Hypothesis Testing

Five bond strength values were determined per laminate and then subjected to statistical analysis to determine the significant differences in bond strength between laminate types, using Visual-XSel 12.0 Multivar (CRGRAPH, Munich, Germany). For this purpose, the five values for each laminate were first examined for normal distribution using the Anderson-Darling normality test, with a significance value of 0.05. A *t*-test was used to compare two laminates since a normal distribution of the five samples was present in all laminates.

2.10. Recovery of the Materials

With scissors, the laminates were each cut into 20 square pieces with dimensions of 1 × 1 cm and then added to 50 mL DMSO. Resulting mixture was then heated to 105 °C and stirred with a stirring fish at a speed of 400 rpm (compare Figure 4). The delamination process was monitored both by observation and by occasional sampling.

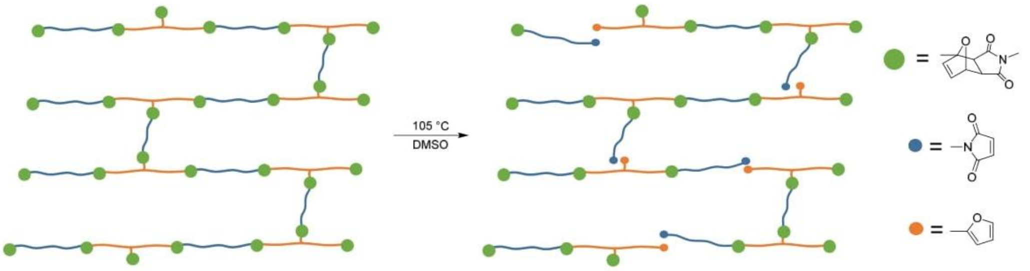


Figure 4. The retro-Diels–Alder reaction opens the polymer network sufficiently to solvate the polymer fragments.

2.11. Determination of Residual N-(2-hydroxyethyl)maleimide and Furfurylamine

The unreacted amount of furfurylamine and *N*-(2-hydroxyethyl)maleimide was determined using gas chromatography–mass spectrometry (GC-MS). Since a slightly different residual content of maleimide or furan is expected in each polymerization batch, two batches per prepolymer were analyzed. This allows an estimation of how well the residual amount of furfurylamine and *N*-(2-hydroxyethyl)maleimide can be controlled.

The analyses were carried out using a Trace GC 1310 unit from Thermo Fisher Scientific Inc. (Waltham, MA, USA) with a liquid autosampler and mass spectrometry coupling. The separation column used was an Rxi-624 Sil-MS, with a length of 30 m, an inner diameter of 0.25 mm, and a layer thickness of 1.4 µm. After an isothermal time of 2 min at 50 °C, the temperature was raised up to 320 °C at a rate of 10 °C/min and kept at this temperature for 15 min. A Thermo DSQII, quadrupole MS unit in electronic ionization mode was used as the MS-unit. The measuring method was selective ion monitoring and the measured fragment masses for furfurylamine were *m*/*z* 69, 77, 80, 86 and for *N*-(2-hydroxyethyl)maleimide m/z 82, 98, 110, 111. The quantification was performed for each substance using an external standard series. The detection limit determined for *N*-(2-hydroxyethyl)maleimide was 10–15 mg/kg, for furfurylamine of 10 mg/kg.

In this way, it was determined that the residual content of furfurylamine in both furan-functionalized prepolymers was approximately 15.0 mg/kg (compare Table 1). The residual content of maleimide in the two maleimide-functionalized prepolymers was quite different, which can be attributed to slightly different amounts weighed during synthesis. Therefore, calculations were performed for both maleimide concentrations in the following discussion.

Table 1. Residual content of furfurylamine and *N*-(2-hydroxyethyl)maleimide determined via GC-MS.

		Measurement 1	**Measurement 2**
Residue of furfurylamine			
Furan-functionalized prepolymer 1	mg/kg	15.9	15.0
Furan-functionalized prepolymer 2	mg/kg	15.3	13.5
Residue of *N*-(2-hydroxyethyl)maleimide			
Maleimide-functionalized prepolymer 1	mg/kg	36.0	35.5
Maleimide-functionalized prepolymer 2	mg/kg	120.6	122.0

2.12. Determination of the Ethylene Content in the Measured EVOH Barrier

DSC was performed on a DSC 821e instrument of Mettler-Toledo GmbH (Gießen, Germany) following the DIN EN ISO 11357-1 method. Samples were heated from 23 °C to 200 °C at a heating rate of 10 K·min^{-1}. Two heating runs were performed with 6–10 mg of sample. The program used for evaluation was Mettler-Toledo's STARe software, whereas the second heating run was used for evaluation.

The analysis showed that the EVOH used has a melting point of 183 °C, implying that the ethylene content is 32%.

2.13. *Determination of Diffusion Coefficients in EVOH*

Diffusion coefficients of organic substances in EVOH were determined from the lag times of the permeants through a PE/EVOH/PE film, with an EVOH thickness of 3 µm and PE layers of 25 µm and 30 µm respectively. For this purpose, the EVOH films were clamped in a permeation steal cell between two sealant rings. The surface area of the tested films was 191 cm^2. The permeation cell was placed in a climate chamber, that has a lower and an upper space separated by the film, while the lower space of the permeation cell had a volume of 7667 cm^3. The permeants of different polarities and functional groups (overall 38, listed in Tables S7–S11) are injected as a liquid mixture into the lower space of the permeation cell through a septum by use of a syringe. After injection, the liquid mixture of permeants evaporated immediately at the high temperatures (65 °C to 80 °C) applied in the permeation tests. The upper space of the permeation cell was permanently rinsed with a pure stream of nitrogen (20 mL/min) which moved the permeated substances out of the cell. The nitrogen stream went through a connected enrichment unit and the permeants were trapped on this unit over a period of 20 min. The enrichment unit was connected to a gas chromatograph with flame ionization detection (GC/FID). The permeants were directly desorbed into the gas chromatograph and the amount of permeants was determined quantitatively. During the GC run, the next sample was trapped on the enrichment unit and subsequently injected into the GC. By use of this method, one kinetic point was measured every 45 min. Gas chromatographic conditions: column: Rxi 624, length: 60 m, internal diameter: 0.32 mm, film thickness: 1.8 µm, carrier gas: 100 kPa helium. Temperature program: 40 °C (2 min), rate 10 °C/min to 200 °C, rate 20 °C/min to 260 °C hold for 5 min. Pre-trap: substances collected on 20 mm length by 5 mm diameter of Carbopack B, desorbed at 300 °C. Main trap: substances focused at −46 °C on 20 mm length by 1.4 mm diameter of Carbopack B, desorbed at 320 °C. Calibration was performed with injections of known amounts of the applied permeants. The diffusion coefficients (D_P) were determined according to the lag time method [25–27] (Equation (1)) and the activation energies of diffusion (E_A) were calculated from the D_P at various temperatures according to the Arrhenius Equation (Equation (2)).

$$lag\ time = \frac{l^2}{6D_P} \tag{1}$$

D_P is the diffusion coefficient of the permeant in the barrier film, l is the thickness of the film.

$$D_P = D_0\, e^{-\frac{E_A}{RT}} \tag{2}$$

D_0 is the pre-exponential factor, R is the gas constant and T is the temperature in Kelvin.

2.14. *Diffusion Modelling*

For diffusion modelling, the AKTS SML software version 4.54 (AKTS AG Siders, Sierre, Switzerland) using finite element analysis was used. The mathematical principles on which the program is based were published by Rodiut et al. [28].

The packaging geometry for which the calculations were carried out was chosen in accordance with the commission regulation (EU) No 10/2011 with a contact surface between package and food of 6 dm^2 and a food volume of 1 kg.

Since the furan- and maleimide-functionalized prepolymers are mixed in a two-component adhesive, the concentrations of furfurylamine and *N*-(2-hydroxyethyl)maleimide contained in the adhesive are reduced. With the ratio of the two polymers used in the present case, 9 mg/kg residual content of furfurylamine and 14 mg/kg/47 mg/kg residual content of *N*-(2-hydroxyethyl)maleimide were obtained in the adhesive used. These values were used for the migration modeling as initial concentrations of the migrants in the adhesive.

Material-specific settings that have been selected to model the migration for the PET-PE/EVOH/PE laminate are given in Table 2 and for PET-PE/EVOH/PE laminate in Table 3. The diffusion coefficients used can be found in Table 4 and reflect the scenario at 23 °C.

Table 2. Material-specific settings used for the PET-PE-laminate.

		Air	**PET**	**Adhesive**	**PE**
Thickness	µm	100	23.0	8.00	45.0
Density	g/cm^3	1.20×10^{-3}	1.38	1.10	0.97
Partition coefficient		1.00	1.00	1.00	1.00

Table 3. Material-specific settings used for the PET-PE/EVOH/PE-laminate.

		Air	**PET**	**Adhesive**	**PE**	**EVOH**	**PE**
Thickness	µm	100	23.0	8.00	28.0	3.00	28.0
Density	g/cm^3	1.20×10^{-3}	1.38	1.10	0.97	1.16	0.97
Partition coefficient		1.00	1.00	1.00	1.00	1.00	1.00

Since the density of the PU adhesive is not known, a density of 1.10 g/cm^3 was assumed, which is about an average value for unfoamed PU materials. [29] For the medium air, the very high diffusion coefficient of 0.02 cm^2/s was assumed since this value reflects that the volatile migration substances are directly transported away from the surface. For PE, the diffusion coefficient according to Piringer at 23 °C was selected, since determination according to Piringer was found sufficient [30]. The modelling parameters for PU were not given in the scientific literature. Therefore, the diffusion coefficients valid for PE were also selected for the PU adhesive, which can be considered as the worst case for PU. In this way, a fast diffusion of the migrant out of the adhesive was assumed and thus, a worst-case scenario is represented. Also, to represent a worst-case scenario, the distribution coefficients were chosen as 1 in all cases.

Table 4. Diffusion coefficients used for diffusion modelling, if not stated otherwise.

Migrant	**Layer**	**Scenario**	**Diffusion Coefficient 23 °C**	**Source**
Furfurylamine	Air	/	0.02 cm^2/s (assumed as worst case)	
	Adhesive	/	3.55×10^{-8} cm^2/s	Diffusion coefficient assumed as for PE
	PE	/	3.55×10^{-8} cm^2/s	Piringer [30]
	PET	real	2.78×10^{-15} cm^2/s	[31]
		worst case	2.39×10^{-14} cm^2/s	[31]
	EVOH	real	9.26×10^{-19} cm^2/s	this study
		worst case	5.21×10^{-17} cm^2/s	this study
***N*-(2-Hydroxyethyl) maleimide**	Adhesive	/	1.81×10^{-8} cm^2/s	Diffusion coefficient assumed as for PE
	PE	/	1.81×10^{-8} cm^2/s	Piringer [30]
	PET	real	2.25×10^{-16} cm^2/s	[31]
		worst case	1.94×10^{-15} cm^2/s	[31]
	EVOH	real	1.79×10^{-20} cm^2/s	this study
		worst case	1.00×10^{-18} cm^2/s	this study

3. Results and Discussion

3.1. Adhesion and Recyclability

An overview of the entire process, which consists of laminate production using Diels-Alders adhesive and the subsequent recycling of the laminate, is shown in Figure 5.

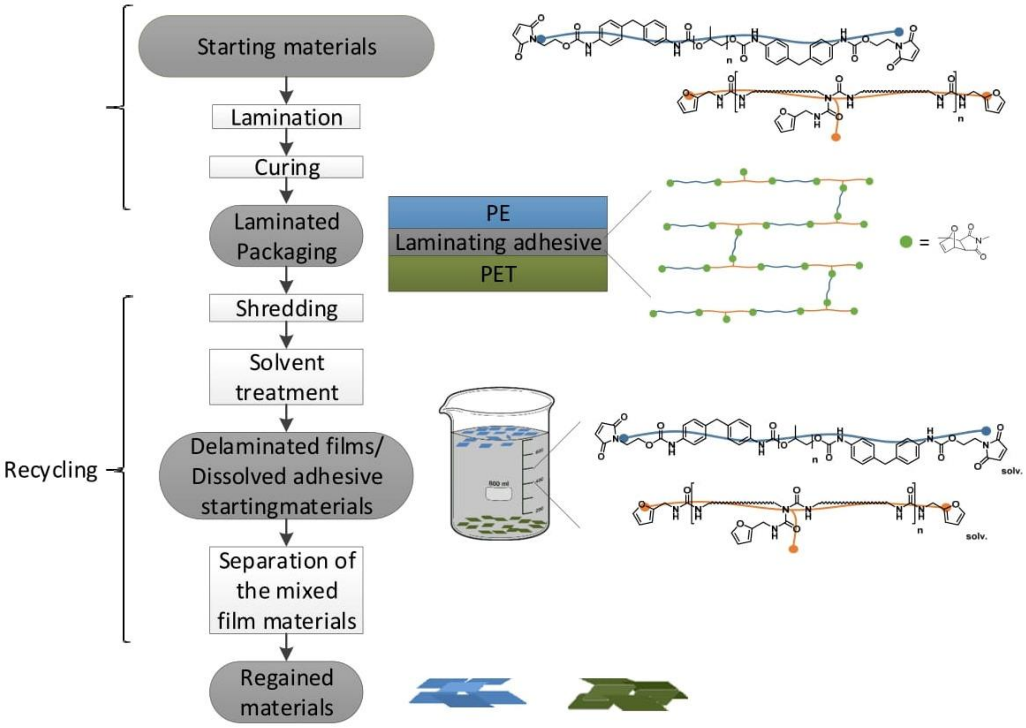


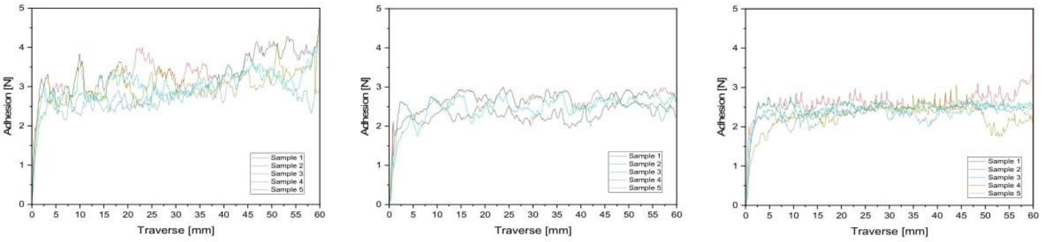
Figure 5. Schematic presentation of the complete laminate production and recycling process: PET-PE, PET-aluminum, and PE-aluminum laminates were produced with an adhesive made of maleimide/furan-functionalized PU prepolymers, with the furan prepolymer carrying furan side chains for crosslinking. For subsequent recycling, the laminates must first be shredded and then treated with a heated solvent to cause the retro-Diels–Alder reaction and then the dissolution of the adhesive components. The separation of PE from PET and aluminum was achieved by skimming the PE from the surface of the solvent. Adapted from [9].

The formulation of the adhesive was chosen in such a way that crosslinking of the adhesive is achieved without the need for an additional crosslinking molecule, since the furan-functionalized prepolymer contains furan-functionalized side chains. The ratio between the starting materials of the furan-functionalized prepolymer was chosen such that on average three functional groups are contained in the polymer (see material & methods). In many formulations, functionalization with *N*-(2-hydroxyethyl)maleimide results in the presence of solid prepolymers. This is not necessarily an obstacle to successful bonding, but it does prevent the adhesive from being tacky during the lamination process, which can cause problems because of the stresses that are applied to the laminates in the laminating machine and during winding. Therefore, polypropylene glycol was used in the maleimide-functionalized prepolymer as a diol, as it ensures that this prepolymer is a viscous liquid at room temperature, thereby creating tack in the lamination process and allowing the adhesive to flow better onto the surface of the laminated film.

Furthermore, the formulation was designed to allow dissolution of furan- and maleimide-prepolymers in MEK. This was especially important for the furan-functionalized prepolymer, as the urea and biuret groups contained in the prepolymer provided a low solubility, probably due to hard segment phases formed by the urea-groups [32]. MEK is suitable as a solvent for solvent-based adhesives for packaging purposes because it is non-toxic and has a low boiling point, making it a common solvent for these purposes [33].

The bond strength results achieved with this adhesive system on PE-PET, PE-aluminum, and PET-aluminum laminates are between 2 and 3 N/15 mm and are shown in Figure 6 and Table 5.

Details on the measurements are given in Tables S1–S6. The significance test showed that the bond strength in the PET-PE laminate was significantly different than in the PET-aluminum and PE-aluminum laminates. The two aluminum laminates, however, did not differ significantly in their bond strength. On closer inspection of the laminates separated by performing the T-Peel Test, it can be seen that in the case of the aluminum laminates, an adhesion failure occurred, whereas in both cases, the adhesive adhered to the plastic film and no residues on the aluminum film can be detected. In the case of the PET-PE laminates, however, a cohesive failure was observed. As the adhesion to aluminum seems to be weaker than to PET and PE, the lower forces in the case of the PET-aluminum and PE-aluminum laminates can be explained. One possible explanation for the lower adhesion to aluminum could be, that typically no entanglement is possible between adhesive and metal surfaces. [34,35] The measured bond strengths were supposed to be sufficient for packaging in most cases.



(a) **(b)** **(c)**

Figure 6. Results of the T-Peel test of the three laminate types (**a**) PET-PE, (**b**) PET-aluminum, and (**c**) PE-aluminum.

Table 5. Mean values and standard deviations of the bond strength measurements related to the 15 mm width of the test strips. The numerical values indicated the mean value from five measurements. The corresponding measurement curves can be found in Figure 6.

Laminate		Mean Value
PET-PE	N/15 mm	3.07 ± 0.11
PET-aluminum	N/15 mm	2.30 ± 0.41
PE-aluminum	N/15 mm	2.39 ± 0.33

After the bonding of the laminates could be proven by T-Peel test, the laminates were recycled in a laboratory scale. The laminate flakes cut to 1 cm^2 were treated at 105 °C in DMSO. The times determined for delamination of the laminates, without further mechanical impact, are shown in Table 6.

Table 6. Delamination times of the laminates. Since not all flakes delaminate at the same time, the start time of the delamination and the end of the delamination are given.

Laminate	PET-PE	PE-Aluminum	PET-Aluminum
Start of delamination	27 min	29 min	35 min
End of delamination	33 min	36 min	40 min

Within 40 min, which is still a reasonable time for recycling processes, all laminates were separated from each other. However, the delamination speed could be influenced by a smaller film piece size, as this increases the surface area of the cut edges through which the solvent can penetrate the adhesive. Similarly in the previous work, [9] the PE-containing laminates PE-PET and PE-aluminum are separated faster than the PET-aluminum laminate, since the diffusion coefficient of PET is significantly higher than that of PE [36], especially since the melting point of PE is almost reached at 105 °C.

In the case of the two PE laminates PET-PE and PE-aluminum, the PE can be skimmed off the surface of the solvent because of density differences, while PET and aluminum, on the other hand, sink to the ground. An eddy current separator would be necessary to separate PET and aluminum in a mixed fraction. After removal of the solvent adhering to the surface of the flakes by exposure to temperature at reduced pressure, HS-GC was used to determine 17 mg/kg solvent in PE and 9224 mg/kg in PET. These would need to be removed by a solvent degassing during re-extrusion if the process were to be carried out on a larger scale. A more detailed description of the proposed upscaled version of the process can be found in the previous publication [9]. Furthermore, no residues of the adhesive polymers can be detected on the films by means of infrared spectrometry (see Figures S3 and S4).

3.2. Migration Modelling of N-(2-hydroxyethyl)maleimide and Furfurylamine through PE According to Piringer

With the exception of *N*-(2-hydroxyethyl)maleimide and furfurylamine, all chemicals used in the adhesive formulation are listed in the appendix of the EU Regulation 10/2011. As these two chemicals are not carcinogenic, mutagenic, or toxic for reproduction, the regulation states that their use in an intermediate layer of the packaging is acceptable, provided that it can be ensured by using a functional barrier that less than 0.01 mg of the substance is released into 1 kg of the packed goods. As described in the Material and Methods section, 121 mg/kg and 36 mg/kg residual *N*-(2-hydroxyethyl)maleimide were determined in the maleimide polymer. For the furfuryl functionalized prepolymer, about 15 mg/kg residual content of furfurylamine was repeatedly determined. Since the two polymers were mixed in the form of a two-component adhesive, the concentrations of furfurylamine and *N*-(2-hydroxyethyl)maleimide were reduced. With the ratio of the two polymers used in the present case, 9 mg/kg residual content of furfurylamine and 14 mg/kg/47 mg/kg residual content of *N*-(2-hydroxyethyl)maleimide were thus present in the adhesive. The following migration predictions were carried out with these concentrations as initial concentrations in the adhesive layer.

In the case of a PET-PE laminate, which is very common on the packaging market, it can be assumed that the PE side of the laminate faces the filling material, as this is the sealable side. Therefore, the following section investigates how the migration of the residual contents of furfurylamine and *N*-(2-hydroxyethyl)maleimide of the adhesive through a PE film in a PET-PE-laminate is to be assessed. Assuming that in such a package a 45-μm thick PE film is the only barrier to the contents, the migration scenarios for furfurylamine and *N*-(2-hydroxyethyl)maleimide shown in Figure 7 could be modelled. In the case of furfurylamine, the lag time, i.e., the time after which the first molecules have migrated into the food at 23 °C, is 95 s, while in the case of *N*-(2-hydroxyethyl)maleimide, lag time is 187 s. For furfurylamine, the final concentration was set after 25 min with an amount of 0.005 mg furfurylamine per kg of foodstuff. For *N*-(2-hydroxyethyl)maleimide, the final concentration was reached after 40/50 min with 0.007 mg/kg *N*-(2 hydroxyethyl)maleimide in the best case and 0.025 mg/kg in the worst case.

Thus, the migrants penetrated the PE barrier to food almost immediately, which shows that PE does not act as a suitable barrier against the migrants. Even if the thickness of the PE was increased from 45 μm to 1000 μm, i.e., more than 22 times as thick, the lag-time is 13 h for furfurylamine and 26 h for *N*-(2-hydroxyethyl)maleimide. Thus, even such unrealistically thick PE layers do not represent a sufficient barrier for the lifetime of most packaging purposes.

The speed at which the migrant passes into the food also depends on the speed at which it migrates from the adhesive to the PE layer. This speed is influenced by the diffusion coefficient of the migrant in the adhesive. The previous simulations were carried out, as indicated under Material and Methods, under the assumption that the migrant in the adhesive has the same diffusion coefficient as in PE. With this assumption, a very high mobility of *N*-(2-hydroxyethyl)maleimide and furfurylamine is observed in the adhesive and thus a fast transition into the neighboring polymer layers is assumed. This assumption creates a worst-case scenario, but a slower transition would be realistic because it can be assumed that the free volume in the adhesive is lower than in PE because of the stronger intermolecular interactions and crosslinking and because of relatively high structural affinity of the migrants to the adhesive system [37]. To assess the effect of this worst-case estimation, the order of magnitude of the diffusion coefficient of PE was gradually adjusted to the magnitude of the diffusion coefficient in PET. Figure 8 shows the time-dependent concentration of the migrant in the food under this variation of the diffusion coefficient in the adhesive in a PET-PE laminate.

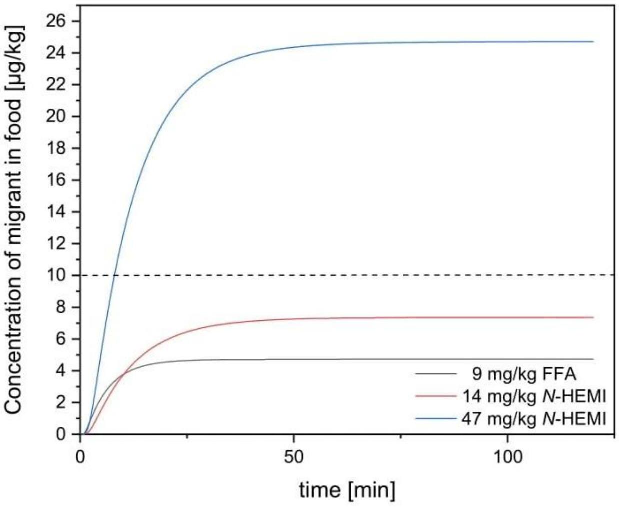


Figure 7. Visualization of the time-dependent concentration of migrants in food using a PE barrier of 45 µm at 23 °C over 120 min. The concentration curves are shown for a residual content of 9 mg/kg furfurylamine (black) and 14 mg/kg and 47 mg/kg NHEMI (red and blue) in the adhesive. The dotted line indicates the legally prescribed limit value.

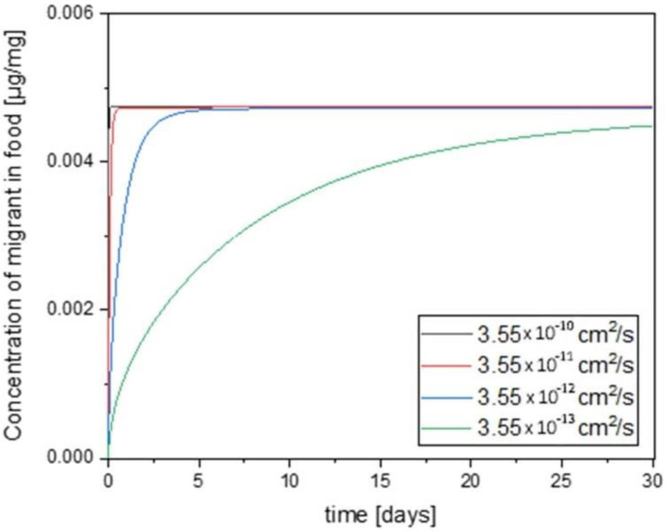


Figure 8. Time-dependent increase in concentration of furfurylamine in food in a PET-PE laminate using different diffusion coefficients of the migrant in the adhesive at 23 °C.

The lag time remains the same if the diffusion coefficient in the adhesive is varied, as this has little influence on the molecules that come directly from the boundary layer. However, the supply of migrants is slowed down, which means that the maximum concentration in the food is reached more slowly. If the diffusion coefficient in the adhesive was 3.60×10^{-12} cm^2/s, the maximum concentration would be reached after about 2 days, while diffusion coefficient of 3.60×10^{-13} cm^2/s will cause the final concentration to be reached after about 25 days.

The actual diffusion coefficient for furfurylamine should be between the assumed values 3.60×10^{-9} cm^2/s and 3.60×10^{-13} cm^2/s. The exact value would have to be determined separately, but is probably irrelevant in the present situation, as the maximum concentration is also reached within one day at 3.60×10^{-10} cm^2/s and 3.60×10^{-11} cm2/s. Should the diffusion coefficient of furfurylamine be in the order of 3.60×10^{-12} cm^2/s and 3.60×10^{-13} cm^2/s, a possibly relevant time delay could occur.

Figure 7 showed that despite the rapid lag-time at room temperature, the maximum amount of furfurylamine that can pass into the foodstuff is 0.005 mg/kg at an initial concentration of 9 mg/kg in the adhesive. In the case where a residual content of 14 mg/kg *N*-(2-hydroxyethyl)maleimide is present in the adhesive, the maximum concentration that can be transferred to the food in the current packaging layout is 0.007 mg/kg, which is also below the limit value. The situation is different with a residual content of 47 mg/kg *N*-(2-hydroxyethyl)maleimide in the adhesive. Here, the amount that can migrate into food is 0.025 mg/kg and the limit value would therefore be exceeded. For furfurylamine and *N*-(2-hydroxyethyl)maleimide it could be determined that in the present packaging design the limit value is not exceeded if the residual content of *N*-(2-hydroxyethyl)maleimide and furfurylamine in the adhesive is lower than 30 mg/kg.

Accordingly, the synthesis conditions of the adhesive and quality controls must guarantee that this threshold is not exceeded. The same also applies to the multilayer structure PET-aluminum-PE, since the adhesive directly contacts the PE layer facing the food.

Since migrants pass through PE so quickly into the food, the barrier effect of EVOH on migrants is examined below. For this purpose, it is first of all necessary to determine the diffusion coefficients of the migrants and structurally related molecules through EVOH, since the use of the diffusion coefficients determined according to Piringer would result in an overestimation of the values in this case.

3.3. *Diffusion Coefficients*

The diffusion coefficients were determined from the lag times of the applied permeants through the PE/EVOH/PE film according to Equation (1). Due to the fact that EVOH is a low diffusive polymer, temperatures of 61 °C up to 81 °C have to be applied. At lower temperatures, the diffusion through the PE/EVOH/PE film was too slow and the permeated amounts were below the analytical detection limits if any of the molecules was able to overcome the barrier. Permeation through the PE layer at such high temperatures is much faster, which means that the lag times of the PE layers are negligible under the applied temperature conditions. Therefore, the experimentally determined diffusion coefficients are related to the EVOH layer. The applied temperatures are above the T_g of EVOH. Below T_g, diffusion in glassy state is lower which means that the experimentally determined diffusion coefficients can be considered as a worst-case. The experimentally determined D_P values for the applied 38 substances are given in Tables S7–S11 and are shown in Figure 9, where it can be seen that the tested substances show correlations between their molecular volume (V) and their diffusion coefficients D_P. Similar correlation has been found in previous studies on the same method [25–27]. The applied substances followed the Arrhenius relationship (Equation 2) from which the activation energies of diffusion were derived for 15 of the 38 applied substances. The other substances follow the same relationship. However, the temperature range was too small or the amount of diffusion coefficients was less than four kinetic points, which was the minimum amount of individual diffusion coefficients for the calculation of the activation energies. These strict rules are necessary. Otherwise, the activation energies of diffusion will show too high uncertainty. The activation energies of diffusion are given in Table S12 in the Supporting Information.

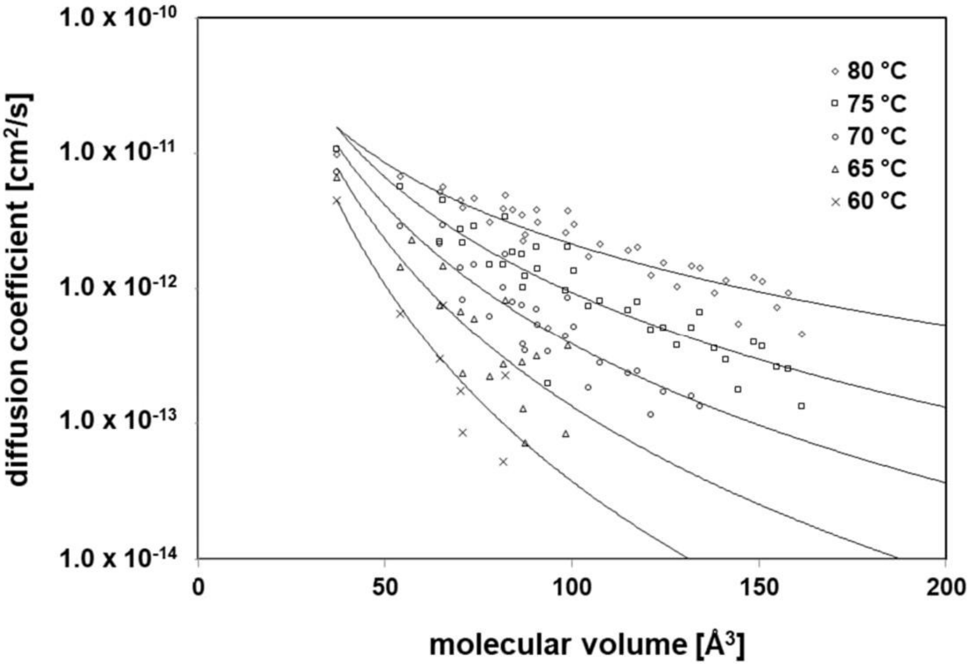


Figure 9. Correlation between the molecular volume (V) of the permeants and their diffusion coefficients (D_P) in EVOH films at various temperatures.

3.4. Activation Energies of Diffusion

E_A and the D_0 values for each permeant were calculated from the Arrhenius relationship (Equation 2). The results show good linearity for the investigated permeants, which indicates that the diffusion process follows Fick's laws of diffusion, and that the swelling of the polymer by the permeants can be excluded under the experimental conditions in this study. For E_A and D_0 the results are given in Table S13. Figures 10 and 11 show a correlation of the E_A to the V and the D_0 of the investigated permeants, respectively. From both correlations, the slope and the intercept of the correlations were derived which are the basis of the prediction of the diffusion coefficients at low temperatures, e.g., 23 °C is the temperature applied in the diffusion modelling (see below). The prediction of the diffusion coefficients is based on the method published by Welle [31] and based on Equation (3).

$$D_P = b\left(\frac{V}{c}\right)^{\frac{a-\frac{1}{T}}{d}} \tag{3}$$

where D_P is the diffusion coefficient (in cm^2/s), V is the molecular volume (in Å^3), T is the temperature (in K), and the parameters a to d the slope and the intercepts of the above correlations between V and E_A and D_0 versus E_A with a = 2.77×10^{-3} 1/K, b = 1.60×10^{-11} cm2/s, c = 38.82 Å^3), and d = 3.36×10^{-5} 1/K.

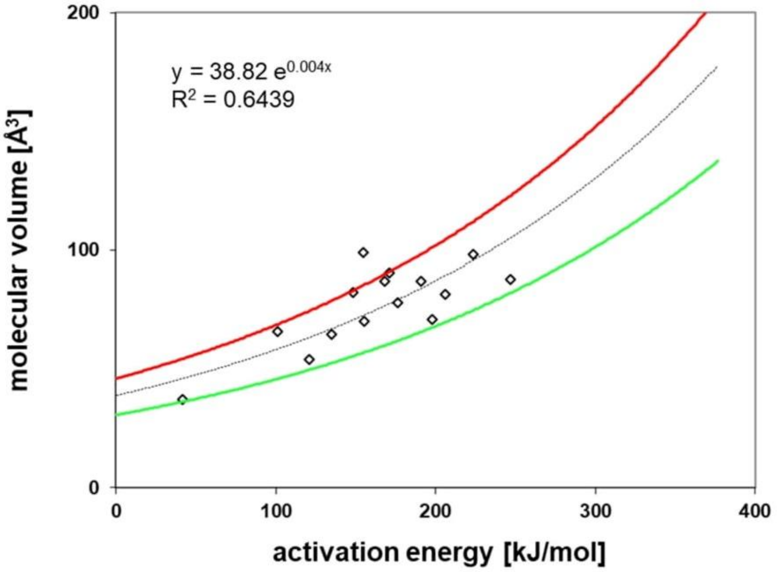


Figure 10. Correlation between the activation energy of diffusion (E_A) and the molecular volume (V) of the test permeants.

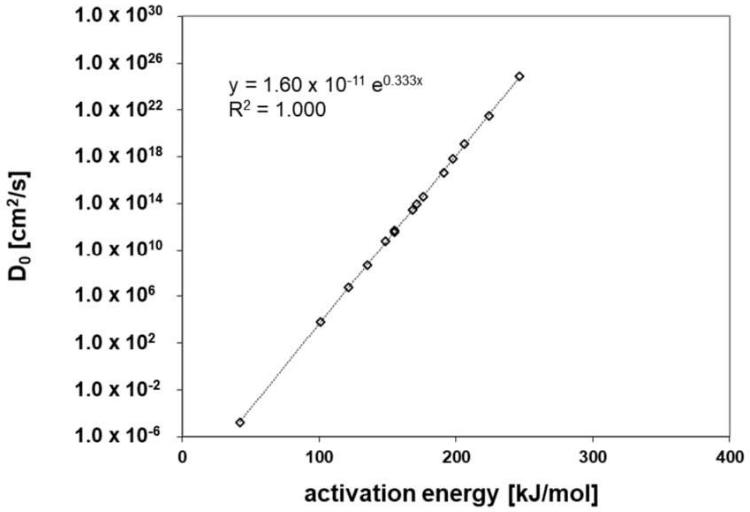
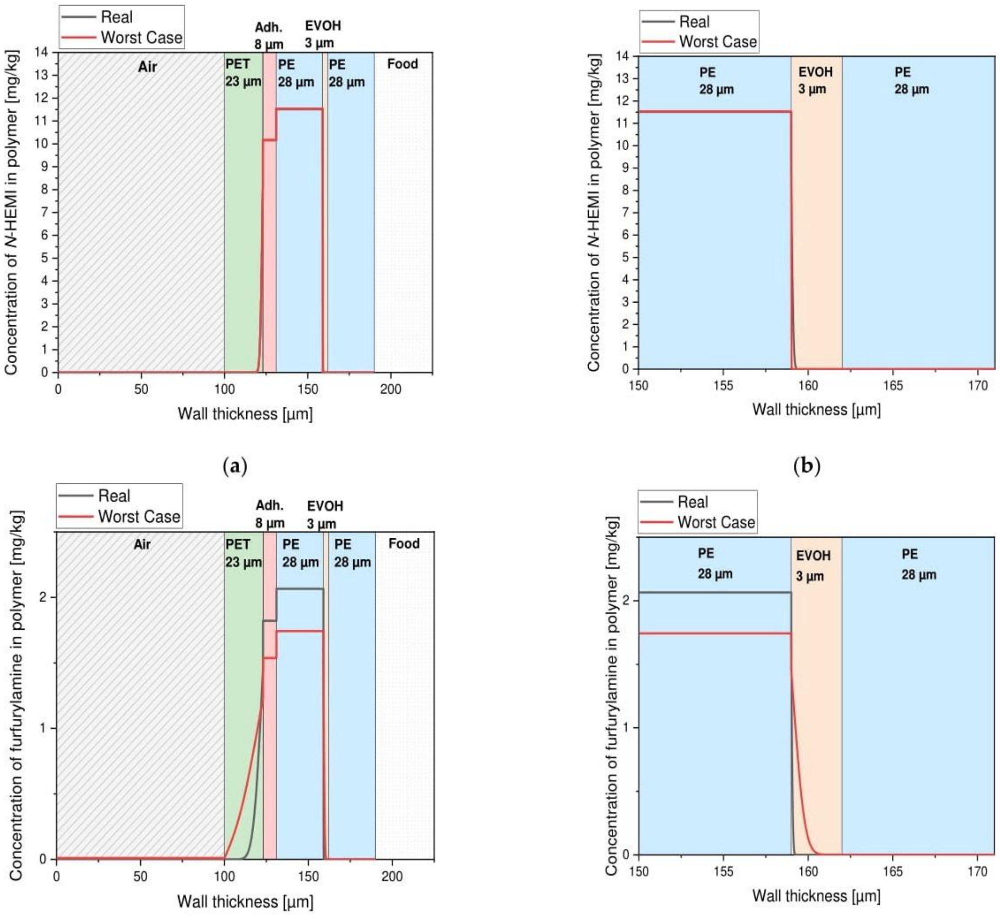


Figure 11. Correlation between the activation energy of diffusion (E_A) and the pre-exponential factor (D_0) of the test permeants.

3.5. Migration Modelling of N-(2-hydroxyethyl)maleimide and Furfurylamine through EVOH

The diffusion coefficients predicted for furfurylamine and *N*-(2-hydroxyethyl)maleimide for PET [31] and EVOH (this study, from Equation (1)) at 23 °C were used to discuss the migration through PE/EVOH/PE-barrier instead of PE, facing the packed food. We have to predict the diffusion coefficients of both molecules, because experimentally the diffusion coefficients were available only at temperatures of 60 °C and above. This is an indication, that both PET and EVOH are good barrier polymers for organic substances.

Figure 12 depicts the concentration profiles of *N*-(2-hydroxyethyl)maleimide (13 a + b) and furfurylamine (13 c + d) in a PET-PE/EVOH/PE laminate (see material and methods) after one year at 23 °C.



(**a**) (**b**)

(**c**) (**d**)

Figure 12. Concentration profile of migrants in the film structure PET-PE/EVOH/PE after one year at 23 °C. (**a**) Concentration profile for the migrant *N*-(2-hydroxyethyl)maleimide (*N*-HEMI), both in a worst-case and in a realistic scenario. For better recognition of the barrier effect of EVOH, the area of the EVOH layer is shown enlarged in (**b**). (**c**) Worst-case and realistic concentration profile for furfurylamine. An enlarged representation of the barrier effect of EVOH is shown in (**d**).

It can be seen that the concentration of migrants in the adhesive and the adjacent PE layer is high and decreases sharply from the interfaces with PET and EVOH. Since diffusion into PE is very fast, the migrants are distributed very quickly between the adhesive and the adjacent PE film. The higher concentrations in PE can be explained by the fact that the concentration is given in mg/kg and PE has a lower density than the adhesive. Since the diffusion coefficients for *N*-(2-hydroxyethyl)maleimide in PET and EVOH are so low, the *N*-(2-hydroxyethyl)maleimide migrates only 7.4 µm from the adhesive/PET interface into the PET and only 0.6 µm from the PE/EVOH interface into the EVOH within one year.

Because of the faster diffusion of furfurylamine, it penetrates further into PET and EVOH. Through the 23-µm thick PET layer, furfurylamine has a lag time of about one year according to the worst-case scenario, whereas the 3 µm EVOH barrier is not overcome after one year.

Figure 13 shows the correlation between the thickness of the EVOH barrier and the lag times of the two migrants at 23 °C, where the layer thickness has, according to Equation 1., a quadratic effect on the lag time. Even in the worst-case scenario of furfurylamine, a 1.5-µm thick layer of EVOH ensures a lag time of 3 years, a reasonable time for most packaging purposes. However, such thin EVOH layers are not common, as they would be difficult to extrude [38]. Ordinary EVOH layer thicknesses start at around 3 µm, and would thus provide a lag time of 9.13 years (realistic scenario) or 513 years (worst case scenario) for furfurylamine. In the case of *N*-(2-hydroxyethyl)maleimide the lag times are 476 years (worst-case scenario) or even around 26,500 years in the realistic scenario. Since even the lowest breakthrough time of 9.13 years determined for furfurylamine in the worst-case scenario is more than sufficient for normal packaging purposes, EVOH is a suitable barrier for the adhesive.

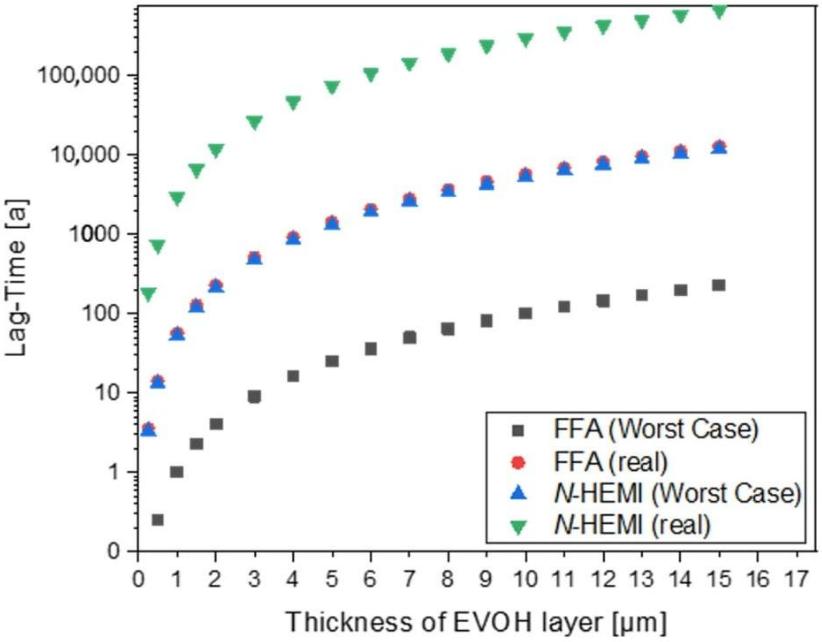


Figure 13. Dependence of the lag time of *N*-(2-hydroxyethyl)maleimide (*N*-HEMI) and furfurylamine on the layer thickness of EVOH at 23 °C.

However, in terms of recyclability, however, the use of PE/EVOH/PE compounds makes only limited sense. While low concentrations of EVOH have only a minor impact on the quality of the recycled material, PE-EVOH compounds with an EVOH content >5% are not considered recyclable [39,40]. Assuming that the thinnest possible extrudable EVOH layer is about 3 µm thick, the adjacent PE layers would have to be at least 30-µm thick each. However, in the case of a PET tray with a PE/EVOH/PE layer (e.g., used for products with antioxidant requirements) [41], where the PET could be made available for recycling by separating the PE-EVOH portion, it would also be a gain to recycle only the PET portion, as this has the decidedly higher mass portion. From this point of view, it would also be reasonable to use a PE/EVOH/PE film with an EVOH content >5%. In addition, the PE/EVOH/PE portion could be recycled by mixing it into a PE fraction to dilute the EVOH content.

4. Conclusions

Multilayer packaging fulfils an important function in the packaging market, but is under constant criticism because it usually cannot be recycled. However, they can be made recyclable by using a reversible crosslinking packaging adhesive with Diels-Alder-adducts, which would have to meet all legal requirements and must not endanger the safety of the consumer. With the formulation used in this work, for the laminates PET-PE, PE-aluminum, and PE-aluminum bond strength between 2 and 3 N/15 mm could be achieved, which is supposed to be sufficient for most packaging purposes. The separation of the material components for recycling takes place in heated solvent, in which the Diels–Alder adducts open and the components are then solvated in the solvent.

For furfurylamine and *N*-(2-hydroxyethyl)maleimide, the two chemicals that are according to the EU Constitution 10/2011, not allowed to reach a concentration of 0.01 mg per kg of food, diffusion models had been used to predict the diffusion behavior of the multilayer packaging materials. Using the diffusion coefficients according to the Piringer model it can be shown that the lag-time of furfuryl alcohol and *N*-(2-hydroxyethyl)maleimide through 45-μm thick PE at 23 °C is only a few minutes. For packaging applications, therefore, this would not be considered a functional barrier against the two migrants. However, whether the limit value of 0.01 mg/kg per kg of foodstuff specified in the EU Regulation 10/2011 is exceeded depends on the residual content of the migrants in the foodstuff. Provided that the content of both substances in the adhesive is below 30 mg/kg the limit of 0.01 mg/kg in food is not exceeded.

To investigate, how an EVOH barrier can affect the migration of the two chemicals, the diffusion coefficients of the migrants through PET and EVOH and activation energies of diffusion had to be determined. Based on these data, the prediction of the diffusion coefficients of furfurylamine and *N*-(2-hydroxyethyl)maleimide (or any other organic migrant) was possible according to the Welle prediction model. It could be shown that EVOH acts as a good functional barrier and a 3-μm thick EVOH layer provides an effective barrier against migrants for food purposes.

In summary, it can be said that the modified adhesive formulation has the necessary bond strength and the principle of recyclability by means of the solvent-based recycling process is given. The migration modelling showed that the use of the adhesive behind an EVOH barrier should be possible without restrictions under food law. In order to be able to make statements about the feasibility of the lamination and the recycling process on a larger scale, experiments have to be carried out on a small pilot scale. These and experiments on the behavior of the adhesive during packaging processing will be covered in a future publication.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4360/12/12/2988/s1. Figure S1. Chemical structure of the maleimide-prepolymer. Figure S2. Chemical Structure of the furan-prepolymer. Table S1. Adhesion strength of the 5 test specimens. F gives the average force and Fmax the maximum force of the sections selected for evaluation. Fa represents the measured initial force. Table S2. Mean values, standard deviations, and variation coefficients von F, Fmax, and Fa of the five test specimens. Table S3. Adhesion strength of the five test specimens. F gives the average force and Fmax the maximum force of the sections selected for evaluation. Fa represents the measured initial force. Table S4. Mean values, standard deviations, and variation coefficients von F, Fmax, and Fa of the five test specimens. Table S5. Adhesion strength of the five test specimens. F gives the average force and Fmax the maximum force of the sections selected for evaluation. Fa represents the measured initial force. Table S6. Mean values, standard deviations, and variation coefficients von F, Fmax, and Fa of the five test specimens. Figure S3. Spectra of the delaminated PET films and the untreated film. Figure S4. Spectra of the delaminated PE films and the untreated film. Table S7. Diffusion coefficients (DP) in EVOH for the homologous row of 1-alcohols. Table S8. Diffusion coefficients (DP) in EVOH for the homologous row of 2-ketones. Table S9. Diffusion coefficients (DP) in EVOH for oxygen-containing heterocycles. Table S10. Diffusion coefficients (DP) in EVOH for aromatic substances. Table S11. Diffusion coefficients (DP) in EVOH for the homologous row of formate esters determined from PE/EVOH/PE film. Table S12. Activation energies of diffusion EA and pre-exponential factors D_0 determined within this study. Table S13. Prediction of diffusion coefficients of furfurylamine and *N*-(2-hydroxyethyl)maleimide.

Author Contributions: K.M.A.K. planned and carried out the polymer syntheses, produced and analyzed the laminates, conducted the recycling experiments, and performed the migration modeling. She also conceived and wrote the manuscript, except for the chapters on diffusion coefficients and activation energies. F.W. determined the diffusion coefficients for PET and EVOH and the activation energies for diffusion and wrote the corresponding chapters in the manuscript. J.E. performed the lag time experiments necessary to determine the diffusion coefficients. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Special thanks goes to Morchem S.A., which provided its laboratories and isocyanate prepolymers for the production of a suitable furfurylamine functionalized prepolymers. Additional thanks go to the technical team members of the Materials Development department for corona treatment and the laboratory team of the Materials Development department for providing laboratory equipment. We also thank Anita Gruner for performing the GC-MS measurements.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wagner, J.R. (Ed.) *Multilayer Flexible Packaging*, 2nd ed.; Elsevier: Oxford, UK, 2016; ISBN 9780323371001.
2. Morris, B.A. The Science and Technology of Flexible Packaging. In *Multilayer Films from Resin and Process to End Use*; Elsevier William Andrew: Amsterdam, The Netherlands, 2017; ISBN 0323242731.
3. Nonclercq, A. *Mapping Flexible Packaging in a Circular Economy*. Final Report. 2016. Available online: https://ceflex.eu/resources/ (accessed on 12 February 2020).
4. Singh, P.; Wani, A.; Langowski, H.-C. *Food Packaging Materials*; CRC Press: Boca Raton, FL, USA, 2017; ISBN 978-1-4665-5994-3.
5. Ragaert, K.; Delva, L.; van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste Manag.* **2017**, *69*, 24–58. [CrossRef] [PubMed]
6. Kaiser, K.; Schmid, M.; Schlummer, M. Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling* **2018**, *3*, 1. [CrossRef]
7. Dixon, J. *Packaging Materials*; ILSI: Brussels, Belgium, 2011; ISBN 9789078637264.
8. *A European Strategy for Plastics in a Circular Economy*; European Commisson: Brussels, Belgium, 2018.
9. Kaiser, K.M.A. Recycling of multilayer packaging using a reversible cross—Linking adhesive. *J. Appl. Polym. Sci.* **2020**, *137*, 49230. [CrossRef]
10. Banea, M.D. Debonding on Demand of Adhesively Bonded Joints: A Critical Review. *Rev. Adhes. Adhes.* **2019**, *7*, 33–50. [CrossRef]
11. Woidasky, J.; Schmidt, J.; Auer, M.; Sander, I.; Schau, A.; Moesslein, J.; Wendler, P.; Kirchenbauer, D.; Wacker, D.; Gao, G.; et al. Photoluminescent Tracer Effects on Thermoplastic Polymer Recycling. In *Advances in Polymer Processing 2020, Proceedings of the International Symposium on Plastics Technology, Berlin, Heidelberg, 10 March 2020*; Hopmann, C., Dahlmann, R., Eds.; Springer: Berlin/Heidelberg, Germany, 2020; pp. 1–13. ISBN 978-3-662-60809-8.
12. Woidasky, J.; Moesslein, J.; Wendler, P.; Kirchenbauer, D.; Wacker, D.; Gao, G.; Lang-Koetz, C. Kunststoffidentifikation und-sortierung in der Circular Economy durch Fluoreszenzmarker. *Chemie Ingenieur Technik* **2020**, *92*, 441–451. [CrossRef]
13. Kosior, E.; Mitchell, J. Chapter 6—Current industry position on plastic production and recycling. In *Plastic Waste and Recycling: Environmental Impact, Societal Issues, Prevention, and Solutions*; Letcher, T.M., Ed.; Academic Press: Cambridge, MA, USA, 2020; pp. 133–162. ISBN 978-0-12-817880-5.
14. Brunner, S.; Fomin, P.; Kargel, C. Automated sorting of polymer flakes: Fluorescence labeling and development of a measurement system prototype. *Waste Manag.* **2015**, *38*, 49–60. [CrossRef] [PubMed]
15. Ahmad, S.R. A new technology for automatic identification and sorting of plastics for recycling. *Environ. Technol.* **2004**, *25*, 1143–1149. [CrossRef] [PubMed]
16. Pla.to GmbH. Die Pla.to GmbH und die Hochschule Zittau/Görlitz entwickeln ein innovatives Recyclingverfahren für die Trennung von Folien aus Altverpackungen. 2019. Available online: https://www.plato-technology.de/downloads/ (accessed on 12 February 2020).
17. National Center for Biotechnology Information—PubChem. Furfuryl Alcohol. Available online: https://pubchem.ncbi.nlm.nih.gov/compound/Furfuryl-alcohol (accessed on 9 November 2020).
18. The European Commission, COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *OJ* **2011**, *L12*, 1–89.
19. Stepanski, H.; Leimenstoll, M.C. *Polyurethan-Klebstoffe. Unterschiede und Gemeinsamkeiten, 1. Ed. 2016*; Springer: Berlin/Heidelberg, Germany, 2016; ISBN 9783658122706.
20. National Center for Biotechnology Information—PubChem. 1-(2-Hydroxyethyl)-1H-pyrrole-2,5-dione. Available online: https://pubchem.ncbi.nlm.nih.gov/compound/1-_2-Hydroxyethyl_-1H-pyrrole-2_5-dione (accessed on 19 November 2020).
21. Institute for Occupational Safety and Health of the German Social Accident Insurance. GESTIS Substance Database—Furfurylamine. Available online: http://gestis.itrust.de/nxt/gateway.dll/gestis_en/000000.xml?f=templates&fn=default.htm&vid=gestiseng:sdbeng (accessed on 23 October 2020).
22. Heo, Y.; Sodano, H.A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **2014**, *24*, 5261–5268. [CrossRef]

23. Duan, H.-Y.; Wang, Y.-X.; Wang, L.-J.; Min, Y.-Q.; Zhang, X.-H.; Du, B.-Y. An Investigation of the Selective Chain Scission at Centered Diels–Alder Mechanophore under Ultrasonication. *Macromolecules* **2017**, *50*, 1353–1361. [CrossRef]
24. Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Sun, P.; Joncheray, T.; Zhang, Y. Synthesis of linear polyurethane bearing pendant furan and cross-linked healable polyurethane containing Diels–Alder bonds. *New J. Chem.* **2014**, *38*, 770–776. [CrossRef]
25. Ewender, J.; Welle, F. Determination and Prediction of the Lag Times of Hydrocarbons through a Polyethylene Terephthalate Film. *Packag. Technol. Sci.* **2014**, *27*, 963–974. [CrossRef]
26. Ewender, J.; Welle, F. Functional Barrier Performance of a Polyamide-6 Membrane towards n -Alkanes and 1-Alcohols. *Packag. Technol. Sci.* **2016**, *29*, 277–287. [CrossRef]
27. Ewender, J.; Welle, F. Diffusion Coefficients of n-Alkanes and 1-Alcohols in Polyethylene Naphthalate (PEN). *Int. J. Polym. Sci.* **2019**, *2019*. [CrossRef] [PubMed]
28. Roduit, B.; Borgeat, C.H.; Cavin, S.; Fragnière, C.; Dudler, V. Application of Finite Element Analysis (FEA) for the simulation of release of additives from multilayer polymeric packaging structures. *Food Addit. Contam.* **2005**, *22*, 945–955. [CrossRef] [PubMed]
29. *Polyurethane; mit 126 Tabellen*, 3rd ed.; Oertel, G.; Becker, G.W.; Braun, D. (Eds.) Hanser: Munich, Germany, 1993; ISBN 3446162631.
30. Begley, T.; Castle, L.; Feigenbaum, A.; Franz, R.; Hinrichs, K.; Lickly, T.; Mercea, P.; Milana, M.; O'Brien, A.; Rebre, S.; et al. Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Addit. Contam.* **2005**, *22*, 73–90. [CrossRef] [PubMed]
31. Welle, F. A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2013**, *129*, 1845–1851. [CrossRef]
32. Kaushiva, B.D. *Structure-Property Relationships of Flexible Polyurethane Foams*; Virginia Tech: Blacksburg, VA, USA, 1999.
33. The Dow Chemical Company. Laminating Adhesives for Flexible Packaging. In *Science that Connects*; The Dow Chemical Company: Midland, MI, USA, 2016.
34. Da Silva, L.F.; Öchsner, A.; Adams, R.D. *Handbook of Adhesion Technology*; Springer: Berlin/Heidelberg, Germany, 2011; ISBN 9783642011689.
35. Kinloch, A.J. Adhesion and Adhesives. In *Science and Technology*; Springer: Berlin/Heidelberg, Germany, 1987; ISBN 9789048140039.
36. Dole, P.; Feigenbaum, A.E.; La Cruz, C.d.; Pastorelli, S.; Paseiro, P.; Hankemeier, T.; Voulzatis, Y.; Aucejo, S.; Saillard, P.; Papaspyrides, C. Typical diffusion behaviour in packaging polymers—Application to functional barriers. *Food Addit. Contam.* **2006**, *23*, 202–211. [CrossRef] [PubMed]
37. Rafailovich, M.H.; Sokolov, J. Networks: Diffusion. In *Encyclopedia of Materials: Science and Technology*; Buschow, K.H.J., Ed.; Elsevier: Amsterdam, The Netherlands, 2001; pp. 6111–6113. ISBN 9780080431529.
38. Dunn, T. Manufacturing Flexible Packaging. In *Materials, Machinery, and Techniques*; William Andrew: Oxford, UK; Waltham, MA, USA, 2015; ISBN 0323265057.
39. Huang, C.-H.; Wu, J.-S.; Huang, C.-C.; Lin, L.-S. Morphological, Thermal, Barrier and Mechanical Properties of LDPE/EVOH Blends in Extruded Blown Films. *J. Polym. Res.* **2004**, *11*, 75–83. [CrossRef]
40. PlastEurope. New Guidelines for Barrier Polytheylene Film/"RecyClass" Tests Show EVOH Concentrations Compatible for Recycling. Available online: https://www.plasteurope.com/news/RECYCLING_t243864/ (accessed on 3 September 2020).
41. Anukiruthika, T.; Sethupathy, P.; Wilson, A.; Kashampur, K.; Moses, J.A.; Anandharamakrishnan, C. Multilayer packaging: Advances in preparation techniques and emerging food applications. *Compr. Rev. Food Sci. Food Saf.* **2020**, *19*, 1156–1186. [CrossRef]

8. Production of a PET//PE-LD laminate using a reversibly cross-linking packaging adhesive and recycling on a small-scale technical plant

by Katharina M. A. Kaiser and Tanja Ginzinger

To take the next step to large-scale application, laminate production and recycling was scaled up to a small-scale technical plant. Therefore, firstly larger quantities of the furan and maleimide prepolymers of the formulation from Chapter 7 were synthesized in order to produce 300 linear meters of a PET//PE laminate on a pilot line for coating and laminating.

The laminate adhesion exhibited by the laminate after curing of the adhesive is strong enough to provide substrate failure of the PET in the T-peel test. Thus, the laminate adhesion obtained here is better than in the previous publication, which is mainly due to the fact that machine lamination is bubble-free, unlike manual lamination. After a short-term temperature exposure of 160 °C, as occurs during the sealing of packaging, it still exhibits high bond adhesion and shows that the processing of the packaging would not lead to disintegration of the packaging.

After delamination in the small-scale solvent recycling plant, density separation was performed, producing an PE-LD fraction and a PET fraction, but each still containing a residual content of the other polymer. In the case of the PE-LD, the residual PET can be separated by melt filtration during re-granulation to yield a PE-LD granulate from which a recycled film can be produced.

By characterizing the PE-LD film by infrared spectrometry, differential scanning calorimetry, tensile test, determination of melt index and molecular weight, the influence of the recycling process on the polymer could be determined. The recycled PE-LD exhibits crosslinking due to the repeated recycling, but the crosslinking is much lower than described for PE-LD in literature. Also the mechanical properties do not show the typical behavior of crosslinked PE, but rather the behavior of plasticized material. Sum of the analytical results indicate that the solvent attenuates the crosslinking of the PE-LD during extrusion and instead has a plasticizing effect. The PET pellets, on the other hand, exhibit about 10% molar mass degradation after re-granulation and turbidity in places, which can be justified by the PE that has not been separated. For further processing of the PET, a complete separation of the residual PE-LD or the addition of a compatibilizer would be necessary.

Recycling **2021**,*6*(3), 47, DOI: 10.3390/recycling6030047

Author Contributions: K. Kaiser planned and carried out the polymer syntheses, planned and supervised the lamination and the recycling of the laminate, conceived and wrote the manuscript. T. Ginzinger organized the drying of the delaminated films and the extrusions.

recycling MDPI

Article

Production of a PET//LDPE Laminate Using a Reversibly Crosslinking Packaging Adhesive and Recycling in a Small-Scale Technical Plant

Katharina M. A. Kaiser [1,2,*] and Tanja Ginzinger [2]

[1] TUM School of Life Sciences Weihenstephan, Technical University of Munich, Weihenstephaner Steig 22, 85354 Freising, Germany
[2] Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Strasse 35, 85354 Freising, Germany; tanja.ginzinger@ivv.fraunhofer.de
* Correspondence: katharina.kaiser.gap@googlemail.com

Abstract: Multilayer packaging is an important part of the packaging market, but it is not recyclable with conventional methods since it is made of different thermodynamically immiscible materials. In this work, it was shown that it is possible to produce a PET//LDPE laminate in a pilot plant for lamination by using an adhesive consisting of maleimide- and furan-functionalized polyurethane prepolymers that cure through the Diels–Alder reaction. The material could then be delaminated in a small-scale recycling plant using a solvent-based recycling process by partially opening the Diels–Alder adducts through the influence of temperature. The PET and LDPE could be recovered without any adhesive residues before each material was regranulated, and in the case of the PE, a film was produced via cast film extrusion. The obtained PET granulate exhibited a slight, approximately 10%, decrease in molecular weight. However, since small amounts of LDPE could not be separated, compatibilization would still be required here for further use of the material. The obtained LDPE film was characterized by means of infrared spectrometry, differential scanning calorimetry, tensile testing, determination of the melt index, and molecular weight. The film showed lower crosslinking than usual for LDPE recycling and exhibited good mechanical properties. In this work, it was thus shown that upscaling of the laminate production with the modified adhesive and also its recycling at the pilot plant scale is possible and thus could be an actual option for recycling multilayer packaging.

Keywords: multilayer packaging; recycling; reversibly crosslinking adhesive; Diels–Alder

check for updates

Citation: Kaiser, K.M.A.; Ginzinger, T. Production of a PET//LDPE Laminate Using a Reversibly Crosslinking Packaging Adhesive and Recycling in a Small-Scale Technical Plant. *Recycling* **2021**, *6*, 47. https://doi.org/10.3390/recycling6030047

Academic Editor: Francesco Paolo La Mantia

Received: 19 May 2021
Accepted: 5 July 2021
Published: 13 July 2021

1. Introduction

Our globally interconnected economic and trade system shapes today's food industry, causing long transport distances and storage times for food. A special role is played by multilayer packaging, in which different materials are combined in a layered structure, thus making it possible to create customized property profiles [1,2]. For example, defined barriers against oxygen and thus longer shelf life can be created; sealable packaging or certain optical properties can be produced, which is why multilayer packaging is an important part of the packaging market. However, since multilayer packaging is not recyclable due to its different components, new solutions are being sought [3]. Since replacement with monomaterials is often not easily possible and according to the European Plastics Strategy all packaging should be reusable or recyclable by 2030, other solutions have to be found [4].

To address this problem, there are several approaches that involve either processing the different materials together or separating them [3]. Joint processing yields blends that often have good mechanical properties only with the use of compatibilizers, and where the change in mechanical properties makes closed-loop recycling difficult to imagine [3,5–8].

In order to separate the different components for the recycling of multilayer packaging, polymers can be systematically dissolved out of mixed waste fractions by using selective solvents. This approach is suitable for a broad variety of mixed inputs, but the recovery of the polymer from the solvent can be quite energy consuming [3]. For the delamination of multilayer packaging, another approach to separate the different materials from each other, several approaches already exist, but these are often limited to certain structural designs, like packaging structures containing aluminum or the mechanism of delamination has not yet been elucidated [3,9–12]. One method for generating recyclability for a variety of multilayer packagings is to use reversibly crosslinking adhesives to produce delaminable packaging that can then be separated from each other by a solvent-based recycling process. Debondable adhesives can be based on different principles. These include adhesives filled with reactive fillers that are able to expand or heat up, causing delamination. Reversibly crosslinking adhesive systems are often based on the incorporation of Diels–Alder adducts into the network [13,14]. The Diels–Alder reaction is a [4 + 2] cycloaddition in which a diene and a dienophile react reversibly. Here, the reaction between furan and maleimide groups is the most studied system [15–17]. In this study, as in two previous ones [18,19], a polyurethane adhesive containing Diels–Alder adducts was used to produce packaging laminates. These laminates could then be delaminated using a suitable solvent treatment and thus be separated for recycling.

In the first publication on this subject, typical material combinations used in packaging (PET//PE, PET//aluminum, PE//aluminum) were bonded on a laboratory scale by a packaging adhesive containing Diels–Alder adducts and also recycled on a laboratory scale. The adhesive here consisted of polyurethane-based isocyanate prepolymers functionalized with *N*-(2-hydroxyethyl)maleimide and furfuryl alcohol. With the additional use of a crosslinker molecule with three furan groups, a crosslinked packaging adhesive could thus be prepared via the Diels–Alder reaction. The retro reaction in a heated solvent ensures that the adhesive becomes thermoplastic again and can thus be dissolved in a solvent-based recycling process. Thus, composite separation takes place with no adhesive residues remaining on the composite materials [18].

In another publication, the adhesive formulation was adapted to replace the potentially carcinogenic furfuryl alcohol and the toxicologically unevaluated crosslinker molecule. This was done by using the noncarcinogenic furfurylamine and generating crosslinking via side chains of the polymers. By means of migration modeling, it was possible to check how far compliance with food regulations can be ensured when the adhesive is used in packaging [19].

Since the previous studies were only performed on a laboratory scale, the feasibility of this principle on a small technical scale will now be demonstrated in the present work. For this purpose, laminate production was scaled up to the pilot plant for lamination in order to produce 300 linear meters of a PET//LDPE laminate. The PET//LDPE laminate was selected for upscaling because it is one of the most relevant laminate types in the packaging market, frequently used in the packaging of snacks, meat, and dairy products and nonfood products [20], and the adhesive formulation showed good bonding in the laboratory tests for this packaging structure. After curing the adhesive, the 300 linear meters of the laminate can be delaminated in a small-scale recycling plant and the individual laminate components can then be reprocessed into granules or a film. A further aim of this work is to check to what extent sealing, as a typical processing step for packaging, influences the performance of the adhesive and what effects this could have.

2. Materials and Methods

2.1. Preparation of the Adhesive

The chemicals used to prepare the adhesive were purchased from different suppliers. For the production of the maleimide-functionalized prepolymer, 4,4′-methylenediphenyl diisocyanate (MDI) (98%) was purchased from Alfa Aesar (Ward Hill, MA, USA) and used without further preparation, provided that dimer formation could be excluded. Polypropylene glycol (Mw = 1000 g/mol) from Merck (Darmstadt, Germany) was used as the diol component and dried at reduced pressure and slightly increased temperature before use. To functionalize the maleimide prepolymer, a Diels–Alder and retro-Diels–Alder reaction was used in a three-step process [21,22]. The solvent methyl ethyl ketone ($\geq$99.5%) was purchased from TH Geyer and, if necessary, dried with a molecular sieve (4 Å) to a H_2O content <50 mg/kg and stored under nitrogen ($H_2O \leq 50$ mg/kg).

2.1.1. Furan-Functionalized Prepolymer

A schematic representation of the preparation of the furan-functionalized prepolymer is given in Figure 1.

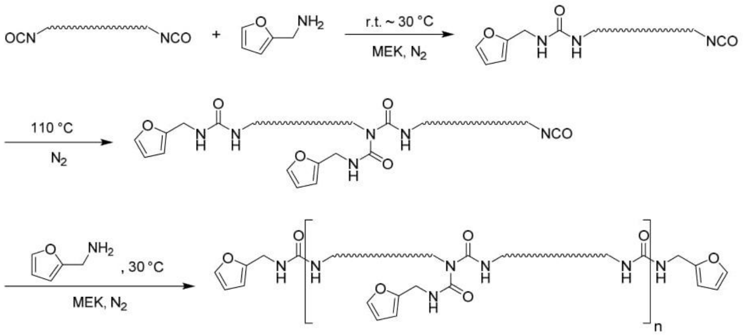


Figure 1. Reaction scheme for the preparation of the furan-functionalized prepolymer.

An amount of 575 g of isocyanate prepolymer (solids content, 401 g, 164 mmol, 3.00 NCO equiv.) was set under nitrogen in a three-necked flask equipped with a mechanical stirrer. Then, under vigorous stirring, 10.6 g (109 mmol, 10.1 mmol, 1.00 equiv.) of furfurylamine diluted in methyl ethyl ketone (MEK) was added in such a way that the temperature did not exceed 30 °C. After the reaction mixture was subsequently stirred for 30 min at room temperature, the oil bath was heated to 110 °C while evaporating the contained solvent. The mixture was kept at this temperature until the isocyanate band at 2264 cm^{-1} in the IR spectrum no longer decreased, indicating that all urea groups had reacted with isocyanate groups, while a yellow coloration of the mixture gradually appeared. By subsequently cooling the mixture to about 70 °C, 75 mL of MEK can be added, thus keeping the polymer stirrable. By adding 10.6 g (109 mmol, 10.1 mmol, 1.00 equiv.) of furfurylamine in 37.5 mL of MEK, the reaction was terminated by functionalizing the remaining NCO groups.

The fully functionalized polymer yielded the finished product obtained in the form of a clear, yellowish, viscous polymer solution with a solids content of 80%.

IR $\tilde{\nu}$ = 3315 (br), 2971 (m), 2937 (m), 2876 (m), 1713 (s), 1597 (m), 1531 (s), 1475 (w), 1460 (w), 1413 (m), 1372 (m), 1308 (m), 1219 (s), 1169 (m), 1066 (s), 1018 (m), 937 (w), 817 (w) 767 (w), 732 (w), 630 (m).

SEC	Furan-functionalized prepolymer	Mw	40,174 g/mol	PDI	2.70

This polymerization was carried out in a similar way to the method of Du et al. [23].

2.1.2. Maleimide-Functionalized Prepolymer

A schematic representation of the preparation of the maleimide-functionalized prepolymer is given in Figure 2.

To prepare the maleimide-functionalized prepolymer, 135 g of MDI (540 mmol, 3 equiv.) was first weighed in a three-necked flask flooded with N_2 and heated to 50 °C. Then, 360 g of polypropylene glycol 1000 (360 mmol, 2.00 equiv.) was added to the colorless liquid obtained, leading to an increase in the temperature of the reaction mixture due to the exothermic nature of the reaction. Once the temperature stopped increasing, the reaction mixture was heated to 80 °C until the isocyanate band in the IR spectrum stopped decreasing, indicating an end to the reaction. An amount of 50.7 g (360 mmol, 2.00 equiv.) of *N*-(2-hydroxyethyl)maleimide was then added to the mixture. The reaction was kept at 80 °C until the NCO signal disappeared. At the end, 140 mL of MEK was added for better handling.

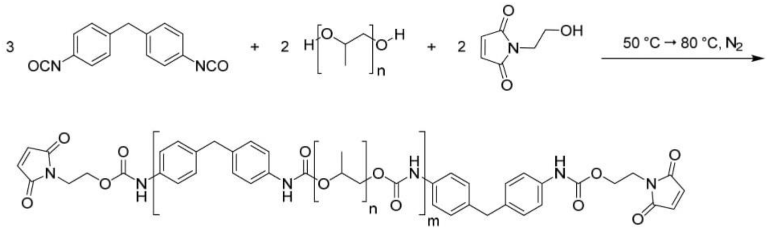


Figure 2. Reaction scheme for the preparation of the maleimide prepolymer.

The product was obtained in the form of a clear, yellow, and viscous polymer.

IR $\tilde{\nu}$ = 3301 (br), 2971 (m), 2868 (m), 1711 (s), 1598 (m), 1531 (s), 1451 (w), 1411 (m), 1373 (m), 1343 (w), 1309 (m), 1221 (s), 1076 (vs), 1017 (s), 926 (m), 821 (m), 768 (w), 696 (m).

SEC	Maleimide-functionalized prepolymer	Mw	14,488 g/mol	PDI	1.81

2.1.3. Preparation of the Adhesive Mixture

An amount of 0.57 kg (0.31 mol of maleimide groups, 1.00 equiv.) of the maleimide prepolymer, dissolved in 140 g of MEK, was weighed in a vial together with 0.73 kg (0.38 mmol of furan groups, 1.00 equiv.) of the furan polymer, dissolved in 183 g of MEK. This mixture was diluted with another 2.7 L of MEK by stirring. In this way, a low-viscous, pale-yellow solution with 30% solids content was obtained.

2.2. Production of the PET//PE Laminate

The laminates were produced in a pilot plant for the lacquering and lamination of web materials by means of a roll-to-roll process. With the exception of the convection dryer, all components of the line were supplied by Jakob Weiß & Söhne (Sinsheim, Germany). An overview of the individual elements of the system can be found in Figure 3. The facility has two corona devices for the pretreatment of the films, making in-line treatment of both LDPE and PET possible. The feed film was chosen to be the PET film (23 µm, Hostaphan® RNK), while the LDPE (45 µm, Hanita) film was chosen to be the lamination film. The strength of the corona treatment of the PET film was 300 watts/5 m/min; that of the LDPE film was 600 watts/5 m/min, which created a surface tension >40 mN/min in both cases. The drying of the solvent was achieved with a convectional dryer made by the company Drytec Co. (Hamburg-Norderstedt, Germany) with 8000 m^3/h of air circulation at 30 °C. The adhesive systems were applied with a gravure roller system, with blunt pyramids having a depth of 0.203 mm.

The layer thickness of the applied adhesive was determined by analyzing microtome cuts. For this purpose, 20 µm thick microtome cuts were made with the Jung Autocut 2055 device from Leica Microsystems GmbH (Wetzlar, Germany), which were then analyzed with an optical microscope with lenses having 40× and 200× magnification.

The adhesive was cured (Figure 4)) at 23 °C over a period of 7 days.

IR (cured adhesive) $\tilde{\nu}$ = 3299 (br), 2971 (m), 2872 (m), 1724 (s), 1702 (s), 1598 (m), 1532 (s), 1458 (w), 1413 (m), 1374 (m), 1342 (w), 1310 (m), 1222 (s), 1072 (vs), 1018 (s), 930 (m), 853 (s), 817 (m), 767 (m), 730 (m), 716 (m).

2.3. Recycling of the Laminate

The solvent formulation used was developed by CreaCycle GmbH (Grevenbroich, Germany) based on the Hansen solubility parameters and taking into account other factors, such as the commercial availability of the ingredients and the risk to users and the environment [16]. It is a polar protic solvent, but the exact chemical compositions are property of CreaCycle GmbH.

Figure 3. Schematic illustration of the used pilot plant for lacquering and lamination.

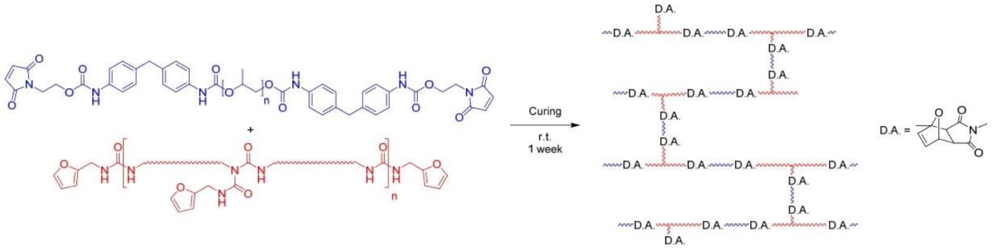


Figure 4. Crosslinking reaction of the two adhesive components during the curing process.

2.3.1. Shredding of the Film

The film was shredded using a Wanner Compact C13.20sv cutting mill from Wanner Technik GmbH. The size of the flakes was predetermined by the insertion of a perforated screen with a hole diameter of 6 mm. The flakes obtained had a size distribution of about 0.2 cm^2 to about 0.7 cm^2.

2.3.2. Delamination of the PET//PE Film

In order to open the Diels-Alder adducts in such a way that the adhesive can be removed (Figure 5), an amount of 10.3 kg of input material was treated in two batches in a dissolving kettle. For the first batch, 80 kg of solvent was first heated to 105 °C, and then 5.42 kg of the shredded material was added. The same was done for the second batch, with 70 kg of solvent and 4.88 kg of the material. The material was then stirred at this temperature for 20 min and then pumped out of the vessel. Density separation was then performed in a drum by skimming the floating fraction from the top and draining the sinking fraction from the bottom of the drum.

After pressing the materials to reduce the solvent content, the material was then prepared for further processing by predrying in the drying oven.

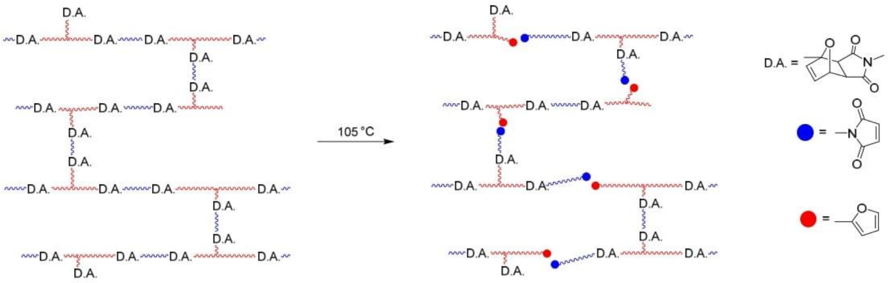


Figure 5. Partial opening of Diels–Alder adducts under the recycling conditions.

2.3.3. Degassing and Granulation

Before the material was further processed, it was predried at 105 °C and <50 mbar, which reduced the solvent content to 94% in the case of PE and 97% in the case of PET. Degassing and granulation were carried out with a corotating ZK 27 T × 24 D twin-screw extruder made by Collin Lab & Pilot Solutions GmbH (Maitenbeth, Germany) with a length-to-diameter ratio of 24:1 and a screw speed of 150 rpm. The input material was fed in the compounder with a twin-screw feeder. To decrease the amount of residual solvent, two degassing units were installed into the extruder. For the treatment of LDPE and PET, different conditions were used.

For LDPE in the degassing zones, a pressure of 22–30 mbar/4.5–6 mbar was achieved. The strand die had a diameter of 3 mm. Both a 315 µm support screen and a 50 µm screen were used for melt filtration, causing the melt pressure to increase between 76 and 180 bar. The machine data for the degassing and granulation of LDPE can be seen in Table 1.

Table 1. Machine data for LDPE degassing and granulation.

Feeding Unit	**Temperature (°C)**						
(kg/h)	**Zone 1**	**Zone 2**	**Degassing Zone 1**	**Degassing Zone 2**	**Zone 4**	**Zone 5**	**Zone 6**
0.5–0.6	100	200	200	200	200	200	205

For PET in the degassing zones, a pressure of 2.7 mbar/8.7 mbar was achieved. The strand die had a diameter of 3 mm, while the melt pressure was at around 12 mbar. The machine data for the degassing and granulation of PET can be seen in Table 2.

Table 2. Machine data for PET degassing and granulation.

Feeding Unit	**Temperature (°C)**						
(kg/h)	**Zone 1**	**Zone 2**	**Degassing Zone 1**	**Degassing Zone 2**	**Zone 4**	**Zone 5**	**Zone 6**
0.4	140	260	243	243	243	243	243

The strands were pelletized directly with a strand pelletizer from Collin Lab & Pilot Solutions GmbH (Maitenbeth, Germany).

2.3.4. Flat Film Extrusion

The recycled LDPE film was produced on a coextrusion line for flat films from Collin Lab & Pilot Solutions GmbH (Maitenbeth, Germany) using a clothes hanger distributor. The production was carried out at a constant haul-off speed of 1.8 m/min. The rotation speed of the screw was 65 rpm, and the target thickness of the film was 45 µm. The machine data for the cast film extrusion can be seen in Table 3.

Table 3. Machine data for LDPE cast film extrusion.

Feeding Unit	Temperature (°C)					
(kg/h)	**Zone 1**	**Zone 2**	**Degassing Zone 1**	**Degassing Zone 2**	**Adapter**	**Chill Roll**
1.2	30	180	220	240	240	60

2.4. Analytical Methods

2.4.1. Characterization by Infrared Spectroscopy

Infrared spectroscopic measurements were recorded using an ATR measurement unit (Golden Gate, PerkinElmer, Shelton, CT, USA) and a Fourier-transform infrared spectrometer (FTIR) from PerkinElmer (Shelton, CT, USA). Ten scans were performed for each measurement with a wavelength range of 4000 to 600 cm^{-1}. The corresponding software, Spektrum One, was used for evaluation. Since the contact pressure could not always be set quite the same when measuring the individual IR spectra, the intensities of the individual spectra differed somewhat. Therefore, the decreasing absorption bands of the maleimide group of the different spectra were not directly comparable. Quantification of the decrease in the intensity of the maleimide absorption band at 696 cm^{-1} was performed by relating it to the band of constant size at 767 cm^{-1}. To do this, the intensities of the signal at 767 cm^{-1}, setting a baseline from 791 to 743 cm^{-1}, and the signal at 696 cm^{-1}, setting a baseline from 702 to 667 cm^{-1}, were determined in the individual absorption spectra.

The ratio of the intensities (696:767 cm^{-1}) between the two bands in the uncured spectrum was determined to be 0.8861, and 0.0524 in the cured spectrum. The *Degree of curing* was therefore determined using Equation (1).

$$Degree\ of\ curing = \frac{ratio\ \left(696\ \text{cm}^{-1} : 767\ \text{cm}^{-1}\right)}{(0.8861 - 0.0524)} \quad (1)$$

2.4.2. Determination of the Molecular Weight

Size-exclusion chromatography (SEC) measurements were performed to determine the molecular weight of the adhesive polymers, PET and LDPE. In the case of the PET and the adhesive polymers, 40 µL of a solution prepared from 50 mg of sample and 10 mL of THF (in the case of adhesive polymers) or HFIP (in the case of PET) were injected using an ASI-100 Automate Sample Injector Unit from Dionex Corporation (Sunnyvale, CA, USA). To determine the molecular weight of the adhesive polymers, this procedure was modified slightly, and instead, 40 µL of the recycling solution was injected directly after delamination. Calibration was performed using a polystyrene (THF) or poly(methyl methacrylate) (HFIP) standard of narrow molecular weight distribution (PSS, Polymer Standards Service, Mainz, Germany), and the measurement was performed at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ (Bischoff HPLC Compact Pump) according to DIN 55672-1 at 40 °C. The separation column used was the GPC/SEC column SDV, linear M, 300 × 8 mm, 5 µm, 100 Å from PSS. The evaluation of the measurement results was carried out with the PL Cirrus GPC/SEC software (version 1.2). An error of ±5% was assumed as the error for the Mw determined according to this protocol [24].

High-temperature SEC measurements of LDPE were performed in 1,2,3-trichlorobenzene. The oven system used was the PL-GPC 220 with an integrated DRI detector from Polymer Laboratories (Church Stretton, UK) coupled to a Dawn Heleos II multiangle static light scattering (MALS) detector from Wyatt Technology Corporation (Santa Barbara, CA, USA). Two PLgel Olexis separation columns, 300 × 7.5 mm, from Agilent Technologies (Santa Clara, CA, USA) were used for separation. The flow rate was 1.0 mL/min, and the set measurement temperature was 150 °C. Astra 7.0 software (Wyatt Tech Corp, Santa Barbara, CA, USA) was used for the interpretation of the results.

2.4.3. Headspace Gas Chromatography

The experiments for determining the residual solvent content were performed on a Clarus 500-TRAP with a FID detector. The initial temperature was 50 °C for 4 min, and the sample was then heated to 320 °C at 20 °C/min and held for 5 min. The evaluation was carried out with Chromeleon Software.

2.4.4. T-Peel Test

T-peel tests were carried out to check the bond adhesion. These were performed on a Schenck Trebel universal testing machine type RM 50 from Bischoff Prüftechnik GmbH (Solingen, Germany). For the measurement, the laminate was cut into 15 mm wide strips perpendicular to the lamination direction. The measurement was carried out in such a way that there was an angle of 90° between the separated strips and the unseparated part of the laminate. The measuring range was 60 mm, whereby a measuring range of 5 and 60 mm was used for the evaluation of the measurement, provided that no substrate failure occurred.

The measuring speed was 50 mm/min. The evaluation was carried out with the Test&Motion program of the company Doli Elektronik GmbH (Münsingen, Germany).

2.4.5. Differential Scanning Calorimetry

Thermal analyses were performed using a “DSC 3+” instrument manufactured by Mettler Toledo (Columbus, OH, USA). For all measurements, two heating runs were performed at a N_2 purge gas rate of 20 mL/min and constant heating and cooling rates of 10 K/min. The amount of sample weighed in was about 12 mg each. Evaluation was performed with the STARe software from Mettler. The second heating run was used for evaluation in each case. The degree of crystallinity (Xcr) was estimated using Equation (2), assuming that the enthalpy of fusion of 100% crystalline PE $\Delta H_{100\%}$(PE) = 293 J/g was used and for PET $\Delta H_{100\%}$(PET) = 140 J/g [25,26].

$$X_{cr} = \frac{\Delta H_f}{\Delta H_{100\%}} \cdot 100\% \tag{2}$$

2.4.6. Determination of the Melt Flow Index (MFI)

The MFI measurements for LDPE were carried out on a MeltFlow @on unit from Karg Industrietechnik (Krailling, Germany). The parameters set were in accordance with ASTM D 1238, and the tests were carried out accordingly at 190 °C and 2.16 kg.

2.4.7. Determination of the Viscosity of the Adhesive

The viscosity of the prepared adhesive was determined in two different ways. The first method used to determine viscosity was according to ISO 2431-No4 with a VF2049-769 viscosity cup of TQC (Rotterdam, the Netherlands). With this method, the viscosity of adhesives can be determined by the time it takes for the liquid to flow out of the cup. In addition, viscosity was determined using an Anton Paar Physica MCR 301 rheometer from Anton Paar AG (Graz, Austria) with a plate–plate measuring system with a diameter of 25 mm. The selected shear rate of the measurement was 50 $1 \cdot s^{-1}$ at a temperature of 23 °C. The measuring gap was 0.25 mm, and the sample volume used was 200 µL.

This measuring system was also used to estimate the pot life based on DIN EN ISO 10364. The pot life was defined as the time in which the viscosity doubles, as this would probably no longer lead to a streak-free application. For this purpose, measurements of the sample were performed at the beginning at intervals of 2 h and then twice a day.

2.4.8. Tensile Test

The mechanical properties of the films were tested on a Z005 tensile testing machine (AllroundLine) from Zwick GmbH & Co. KG at 23 °C and 50% RH according to DIN EN

ISO 527-1. For this purpose, at least 5 strips of each film were prepared in the machine direction with a defined width of 15 mm.

2.4.9. Sealing Test

In order to check the effect of temperature on the adhesive during sealing, sealing tests were carried out with an HSG-CC heat sealer from Brugger Feinmechanik GmbH (Munich, Germany). For this purpose, 15 mm wide test strips were first cut from the laminate perpendicular to the laminate direction, as in the T-peel test, so that the tabs of the LDPE and PET could subsequently be used to perform the T-peel test. The test strips were inserted individually into the sealing device so that the sealing jaws hit the laminate in such a way that the application edge of the adhesive was affected. The parameters set in the sealing device were 160 °C, 1 s, and 80 bar.

3. Results and Discussion

3.1. Preparation of the Laminate

As in a previous publication, the formulation was chosen in such a way that no carcinogenic, mutagenic, or reprotoxic chemicals were required to functionalize the prepolymers; moreover, no crosslinking molecule was necessary [19]. This was achieved by the fact that the furan-functionalized prepolymer contains furan side chains and thus, on average, three functional groups. The maleimide prepolymer, on the other hand, is linear (see Figure 6)). When formulating the two prepolymers in MEK, care was taken to ensure that the physical properties of the adhesive were similar to the parameters of commercial adhesives in order to guarantee an unproblematic and even application of the adhesive in the laminating process. Therefore, a solids content of 30% was selected, at which, according to ISO 2432-No4, the adhesive needed 19.6 s, which was in the same order of magnitude as the times commercial solvent-based packaging adhesives needed. On the rheometer, this corresponded to a viscosity of 40 Pa·s at a shear rate of 50 $1{\cdot}s^{-1}$. The pot life of the adhesive was determined by the change in viscosity of the 30% solution over time due to the crosslinking of the adhesive to about 24 h.

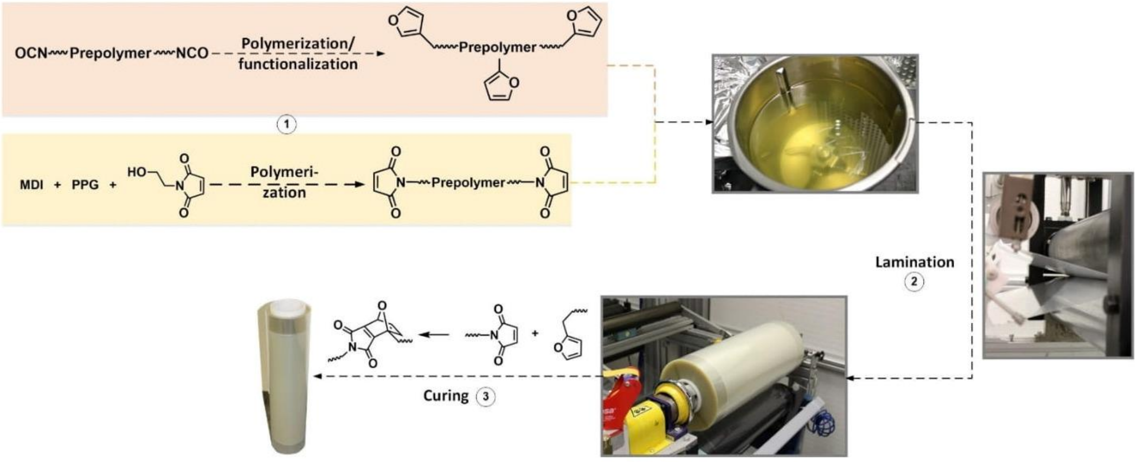


Figure 6. Overview of the individual steps in laminate production. Step 1 represents the production of the adhesive, step 2 the lamination of the PET film with the LDPE film, and step 3 the curing of the adhesive.

To ensure that the stresses that affected the laminate in the laminating machine did not lead to problems during winding, care was taken that the adhesive was sufficiently tacky. Therefore, polypropylene glycol was used as the diol component for the maleimide prepolymer, which made the prepolymer a viscous liquid that led to tackiness of the formulation.

By processing this adhesive on the laminating line described in Materials and Methods, 300 linear meters of a PET//LDPE laminate could be produced. Using microtome sectioning, the thickness of the adhesive was determined to be 6.5 µm (compare Figure 7), thus slightly exceeding the typical layer thicknesses of conventional packaging adhesives, which were around 2–5 µm [27].

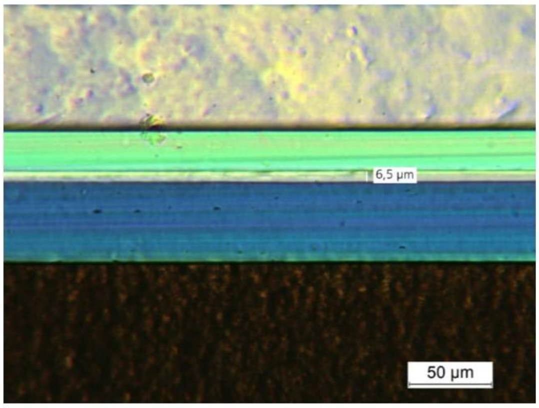


Figure 7. Microtome cut of the produced PET–PE laminate. The green material layer represents the PET film, the blue one the LDPE film.

The curing process of the adhesive, the last step of the preparation of the laminate, was followed by infrared spectroscopy. Here, the decrease. of the ring deformation mode of the maleimide group at 696 cm^{-1} could be followed [28]. It was determined that 73.8% of the isocyanate groups had already reacted after 1 day, and 88.3% after 2 days. Since the isocyanate band disappeared completely after 7 days, it was assumed that after this time had elapsed, the Diels–Alder reaction was completed (see Figure 8).

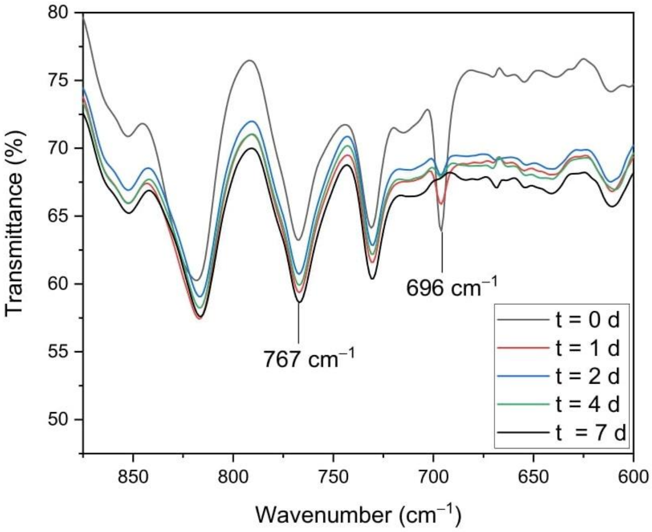


Figure 8. Decrease of the ring deformation mode of the maleimide group at 696 cm^{-1} over a time period of 7 days.

The bonding of the PET//LDPE laminate was tested using the T-peel test (see Figure 9). It was found that each of the five test strips had a substrate failure of the PET, which implies that the bond was stronger than the cohesion of the PET. This means that the bonding in this case was stronger than in the previous publication [19], although the same adhesive formulation and the same adhesive layer thickness were chosen. However, in contrast to manual lamination, machine lamination allowed an even application of the adhesive and lamination without any air bubbles. At 6.5 µm, the application of the adhesive was slightly thicker than in most commercial cases of packaging laminates, where the adhesive layer thickness is usually around 3 µm [27]. With a lower adhesive layer thickness, a decrease in bond adhesion was also to be expected. However, since in many cases an adhesive strength of 2 N/15 mm would already be sufficient, it should also be possible to use a thinner adhesive layer.

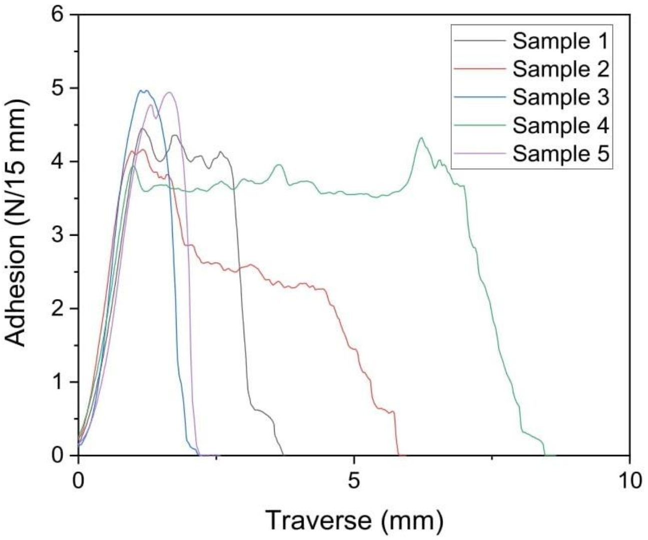


Figure 9. T-peel test results of the cured PET//LDPE laminate.

3.2. *Behavior of the Adhesive during the Sealing Process*

Since a mere laminate does not yet constitute packaging, it must be converted into a packaging in a thermomechanical processing step such as sealing to form a pouch or thermoforming to form a tray. For the adhesive, however, this means that it has to withstand thermal stress. Therefore, the influence of short-term high-temperature exposure of sealing jaws on the crosslinking of the adhesive was examined here. The conditions chosen for this were a temperature of 160 °C with a sealing time of 1 s, which can be considered typical sealing conditions for LDPE [29].

It can be seen that the ring deformation mode of the maleimide group at 696 cm^{-1} reappeared (see Figure S1). From the ratio of this absorption band, it was possible to estimate that about 62% of the Diels–Alder adducts had undergone the retro-Diels–Alder reaction. By recording another IR spectrum 10 days after the sample was sealed, it was shown that the adhesive was re-crosslinking. According to the literature, it would be expected that the re-crosslinking does not take place completely since residual amines can react with the maleimide groups at 70 °C and above in a Michael addition [30,31].

However, since the degree of crosslinking is determined via the absorption band of the maleimide group, this effect cannot be detected here. Since the residual content of furfurylamine was only about 15 ppm and the functionalization of the NCO groups was complete, it can be expected that the maleimide was not blocked in relevant amounts [19].

In order to test the influence of the partial opening of the Diels–Alder adducts by the temperature effect of the sealing test on the bond adhesion of the laminate, a T-peel test was performed directly after temperature exposure by the sealing jaws. Figure 10 shows the measurement curves of the T-peel tests.

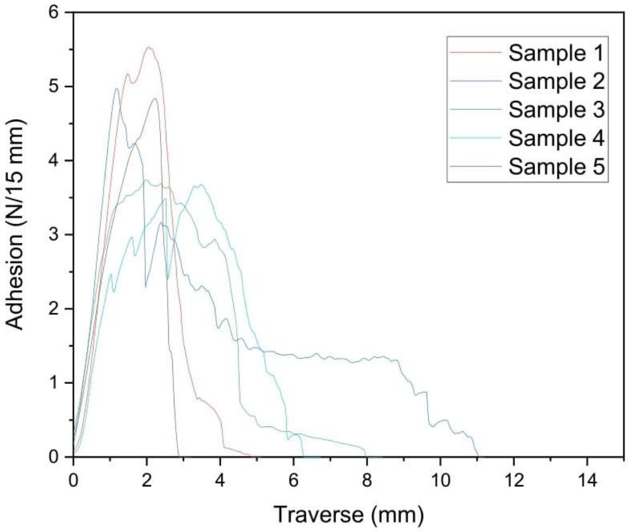


Figure 10. T-peel test results of PET//LDPE laminate after temperature exposure at 160 °C for 1 s in the sealing machine.

Here, too, as in the T-peel tests of the nonsealed samples, an immediate substrate failure of the PET film occurred. This means that even with a reduced crosslink density of the adhesive after the sealing treatment, there is still sufficient crosslink density in the adhesive to ensure cohesion in the adhesive. This shows that even directly after thermal processing of the packaging, laminate adhesion is still present, which is why there is no risk of unwanted delamination in this step.

3.3. *Recycling of the PET//LDPE Laminate in a Small-Scale Technical Plant*

The individual steps of the recycling process are shown in Figure 11 and include six steps: (1) shredding of the film, (2) solvent treatment, (3) density separation, (4) predrying of the material, (5) degassing and granulation, and (6) extrusion of the recycled film.

3.3.1. Step 1—Shredding

Shredding provided a size distribution of about 0.2 cm^2 to about 0.7 cm^2, which was a smaller size than in previous publications, in which the dimensions were 1 × 1 cm. This is because the material has to be fed into the extruder in step 5, and this is easier to carry out with smaller flake sizes. The smaller flake size also reduces the time needed for solvent treatment, as the dissolution of the adhesive proceeds via the cut edges of the flakes, and the area of the cut edges increases with decreasing flake size. However, the size distribution of the flakes influences the duration of delamination.

3.3.2. Step 2—Solvent Treatment of the Shredded Material

Step 2, the dissolving step itself was carried out for 20 min at 105 °C in a stainless steel vessel with a capacity of 100 L. The ratio between film and solvent was chosen so that the shredded films were completely covered with solvent.

In contrast to previous publications, in which laboratory-scale experiments were carried out, the solvent used in this pilot plant experiment was not dimethyl sulfoxide but an optimized proprietary CreaSolv® solvent from CreaCycle GmbH. Like DMSO, this solvent has the property of being able to dissolve the polymers of the adhesive, but it does not have the disadvantages associated with DMSO, such as the smell or the freezing point close to room temperature. Instead, it is characterized by a high flash point, which allows convenient and economical transport and storage, and a comparatively low evaporation enthalpy, which is favorable for solvent recycling.

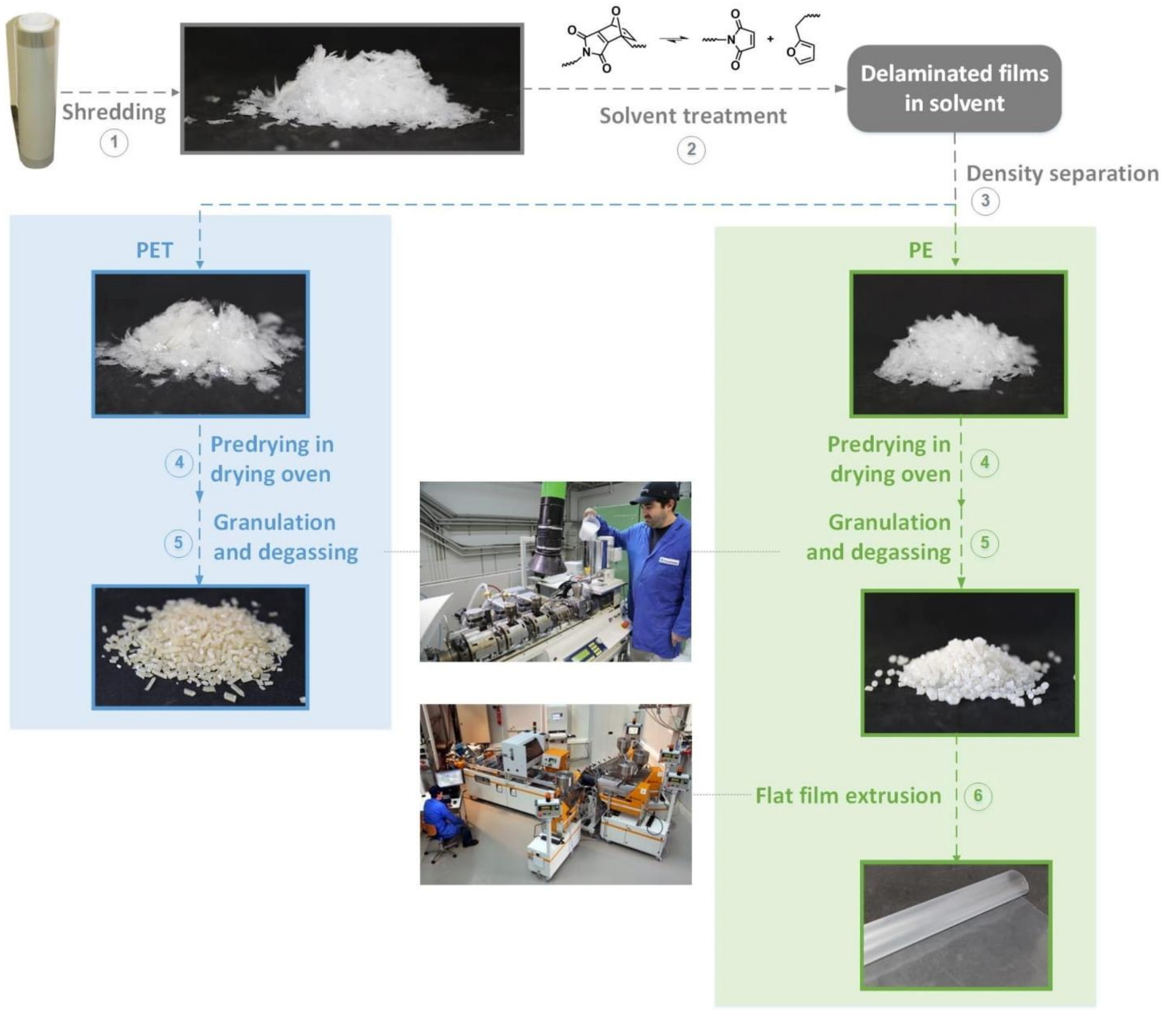


Figure 11. Overview of the individual steps of the recycling process.

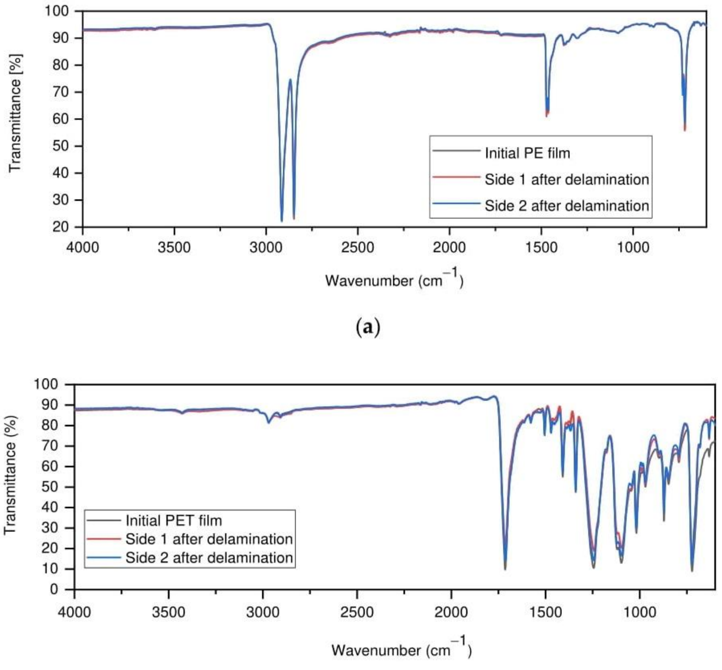
The time required for delamination in the solvent was determined in advance by laboratory-scale tests in which the time required for the delamination of particularly large flakes was determined in a dissolution test. In order to estimate the influence of a treatment time of 20 min at 105 °C, a test strip of the cured adhesive was exposed to these conditions in the drying oven, and an IR spectrum was recorded immediately afterwards. Here, too, as after treatment with the sealing device, an increase in intensity of the maleimide absorption band can be observed. From the ratio of the maleimide absorption band to the band at 767 cm^{-1} compared with the ratio of the two bands in the uncured adhesive, we found that 35% of all Diels–Alder adducts had undergone the retro reaction and were therefore present in their opened form (see Figure S2). Since the adhesive formulation was chosen in such a way that each furan-functionalized prepolymer carried on average three functional groups, the opening of 35% of the adducts should also be sufficient to cancel the crosslinking of the adhesive. In this IR experiment, however, the adhesive was heated to 105 °C in the oven, whereas in the actual recycling experiment, the temperature effect would take place in the presence of a solvent. In the solvent, once an adduct is opened, the functional groups can be surrounded by a solvate shell and thus washed away from the interlayer of the composite, becoming less likely due to dilution. It is also conceivable that the kinetics of the retro-Diels–Alder reaction could be affected since it is known that the solvent has an influence on the kinetics of the Diels–Alder reaction [17,31–35]. However, Widstrom et al. [36] performed studies on the kinetics of the retro-Diels–Alder reaction between a maleimide and furan in different solvents and could not demonstrate any influence. Therefore, it could be assumed that in the present case, there was also no influence on the kinetics of the retro-Diels–Alder reaction due to the solvent. However, it must be taken into account that the retro-Diels–Alder reaction does not necessarily take place in the solvated state, since the adhesive is crosslinked and thus initially not soluble, and is also embedded between layers of LDPE and PET. It can therefore be assumed that the retro-Diels–Alder reaction takes place to a relevant extent without interactions with the solvent or at most in a swollen state. A reliable statement on how the solvent influences the kinetics of the reaction and the mass transfer cannot be made without further investigations. The partial opening of the adducts can also be demonstrated by SEC measurements. The adhesive molecules in the recycling solvent directly after completion of the dissolution step show an elution peak in the SEC measurement, with Mw 44,470 g/mol. If the two prepolymers are freshly dissolved together and a SEC measurement is performed, an elution peak resulting from the superposition of the two prepolymers is shown, with Mw of 26,916 g/mol. This would indicate that more than one in three Diels–Alder adducts would be open. However, these two values can only be compared with a limited extent since a branched polymer is obtained due to the incomplete openings of the adducts, and branched molecules have smaller radii of gyration, and thus, smaller molar masses are determined than are actually present [37]. Therefore, estimation by IR spectroscopy seems to provide a more reliable result.

IR spectra were recorded on both sides of the dried flakes to check whether the adhesive could be completely removed. For this purpose, especially large flakes were selected from a sample of both fractions, as these have longer delamination times and should therefore be most likely to have adhesive residues on larger flakes. Figure 12a shows a spectrum of the original LDPE film and also spectra taken on both sides of a delaminated LDPE film. It can be seen that on both sides of the recovered LDPE film, there is no evidence of adhesive even where the most intense bands of adhesive at 1711, 1531, and 1072 cm^{-1} would be expected. The same can be observed with the spectra of PET (Figure 12b). Therefore, it can be assumed that there is no residue of the adhesive on the surfaces of the films.

3.3.3. Step 3—Density Separation

Step 3 of the recycling process is the density separation. Therefore, subsequent to the solvent treatment, the flakes and the solvent were pumped into a barrel where a floating layer of LDPE and a sunken fraction of PET could be identified. Before the LDPE fraction was skimmed off with a sieve, the LDPE layer was stirred several times to give PET flakes, which might have been lying on the LDPE flakes and were thus prevented from sinking, the opportunity to sink. The sink fraction was then removed via an outlet at the bottom of the barrel and separated from the solvent. Both the floating and the sinking fractions were mechanically pressed out to reduce the solvent content.

In order to evaluate the effectiveness of the composite separation, the mass fractions of the floating, sinking, and solvent fractions; their experimentally determined solvent content; and the solids content calculated from them are given in Table 4.



(**a**)

(**b**)

Figure 12. IR spectra of both sides of a delaminated film ((**a**) PE, (**b**) PET) and the respective starting film as reference.

Table 4. Overview of the quantities of the floating and sinking fractions obtained after density separation and the solvent fraction containing the adhesive.

	Quantity	Solvent Content	Solid Content	Ratio of the Solid Content	Theoretical Ratio
	kg	(%)	(kg)		
Floating fraction	6.8	32.1	4.6	5.8	5.1
Sinking fraction	3.7	17.3	3.0	3.8	3.9
Solvent fraction	146	99.4	0.8	1	1

The solids content of the solvent can be attributed to the dissolved adhesive. The theoretical ratio of the fractions to each other was calculated on the basis of the layer thicknesses of PET, LDPE, and the adhesive and their densities. Comparing the ratio of the obtained quantity fractions with the theoretically expected ratio, it was noticeable that the actually obtained quantity of LDPE exceeded the theoretically expected one, while the actually obtained quantity of PET was lower than expected. This would indicate that a relatively high proportion of PET must be contained in the floating fraction.

To validate this, the LDPE content in both the floating and sinking fractions was dissolved out with a selective solvent. It was found that the floating fraction, which consisted of PE, still contained 3% PET. However, the PET fraction still contained 15% LDPE. This contradicts the estimation based on the theoretical mass fractions. The reason for the incorrect estimation could be, for example, that it is difficult to take a representative, homogeneous sample to determine the solvent content.

The reason for the remaining PET in the LDPE floating fraction could be air bubbles adhering to the PET or PET flakes lying on LDPE flakes. The LDPE content in PET can also be partly explained by the LDPE flakes being prevented from rising by the PET flakes. The handling of the density separation may also have caused LDPE to enter the PET fraction, because when the PET fraction was drained off at the bottom of the barrel, LDPE was also carried from the floating fraction into the sinking fraction. These two problems should be reduced by cyclonic separation equipment, which is specifically designed for density separation of materials. Nevertheless, it cannot be excluded that a certain amount of LDPE was not yet delaminated from the PET, which could mean that the duration of the solvent treatment would still have to be extended.

3.3.4. Step 4, 5, and 6—Drying Granulation and Flat Film Extrusion

The two fractions obtained are predried before they are further processed in the extruders, whereby a solids content of 94% could be achieved for the PE floating fraction and 97% for the PET sinking fraction. This reduces the influence of the solvent on the extrusion and enables a low residual solvent content. During the pelletizing of the LDPE, a melt screen could be installed in the extruder to remove the remaining PET. Since the LDPE has a lower melting point than PET, it was not possible to remove the LDPE residue during PET pelletizing.

To remove the solvent from both materials, a vacuum was applied in the extruder for degassing. In this way, LDPE granulate with a residual solvent content of 219 ppm and PET granulate with a residual solvent content of 4 ppm were obtained. The LDPE granulates were extruded into a film with a target thickness of 45 µm like the initial film.

3.3.5. Recovery of the Adhesive and the Solvent

A recovery of the adhesive from the solution would be theoretically conceivable and could be performed, for example, by precipitation from solution or by distillation. In practice, however, such a procedure would not be very practical. The reason for this is that the equilibrium of the Diels–Alder reaction at room temperature would shift on the side of the adduct, and the adhesive would thus crosslink again. If the process were to be used for post-consumer packaging, the solution would contain printing ink and other impurities, such as packaging residues in addition to the adhesive. This would make recovery of the adhesive even more impractical.

The adhesive solution obtained through the recycling process is also not suitable for the direct production of a new laminate for various reasons. One obvious reason is that a solids content of 0.6% is far too low, and as in the production of the laminate, a solids content of 20%–50% would rather be necessary. However, even if this solids content could be achieved by concentrating the solution, the solution would not be suitable for lamination, as low-boiling solvents such as ethyl acetate or MEK must be used for this purpose.

Therefore, the solution is distilled to recover the solvent, but the adhesive would be discarded as a distillation residue.

For the process to be both ecologically sound and economical, it is necessary to recycle the solvent by distillation. Because the solvent has a low enthalpy of vaporization and a low vapor pressure at room temperature, recovery of the solvent is possible with relatively low energy consumption and low solvent losses.

3.3.6. Characterization of the Recovered PE

Both the LDPE regranulate and the recycled film are colorless but exhibit a slight haze.

Figure 13 shows the IR spectra of LDPE after granulation and film extrusion with the spectrum of the initial film as a reference. It can be seen that some additional absorption bands appeared due to the extrusion processes. These were more intense in the spectrum of the recycled film than in the spectrum of the granulate since one more extrusion had to be performed for the film. At 1750 cm^{-1}, a carbonyl absorption band can be observed, which indicates the presence of ketones or aldehydes and is typical for oxidative degradation processes in LDPE [38–40]. Furthermore, two additional absorption bands were found in the 1300–1000 cm^{-1} region, indicating the presence of C–O groups, which is also typical for oxidative processes [38,39].

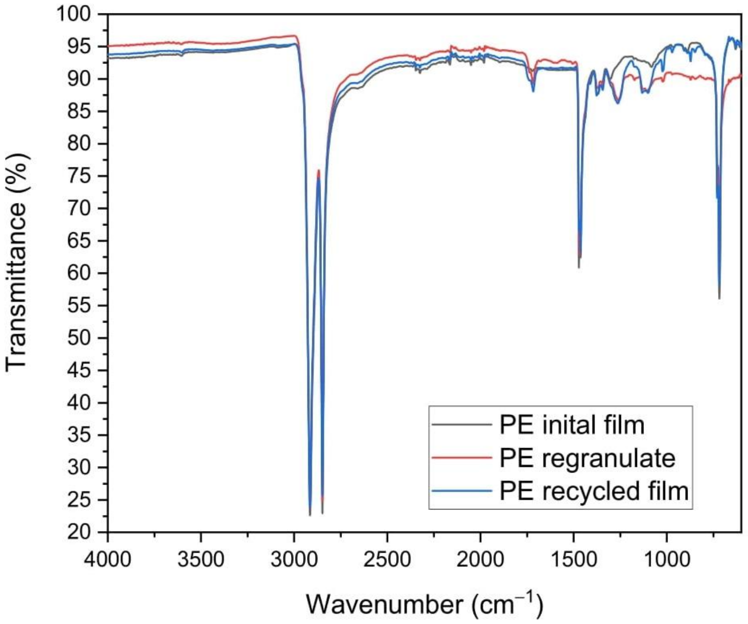


Figure 13. FTIR spectrum of the commercial LDPE film used to make the laminate, the LDPE regranulate, and the recycled film.

The thermal behavior of the virgin materialcompared with the recycled material was investigated by means of DSC measurements. The melting temperature in both cases was 109.74 °C, which shows that there was no effect on the melting temperature and the crystallization temperature also remained constant, which was 100.89 °C for the virgin material and 101.08 °C for the recycled material. This observation is consistent with the expectations, as it is described in the literature that no significant differences can be observed between the melting and crystallization temperatures of multiextruded LDPE and untreated LDPE [26]. Jin et al. also describe that the percentage of crystallinity Xcr of the multiextruded LDPE remains basically constant for up to 40 extrusion cycles and only then starts to decrease [26]. In the present case, the degree of crystallinity of the PE starting film was 38.97%, and that of the recycled film was 38.42%. There was, therefore, a decrease of 1.41% in the degree of crystallinity, which was probably due to unavoidable differences in the evaluation. The DSC measurement curves of LDPE and the data obtained from them are given in the supporting information in Figure S3 and Table S1.

Figure 14 shows the influence of degassing/granulation and flat film extrusion on MFI and molecular weight. The literature reports that both chain scission and molecular enlargement occur simultaneously during thermal degradation of LDPE, but that crosslinking predominates over degradation, which is why extrusions lead to a decrease in MFI [26,41]. This is consistent with the values shown in Figure 14, where a decrease in MFI is observed after both regranulation and extrusion of the recycled film. However, the MFI decreases reported in the literature and also the value of the reference obtained by granulating the commercial LDPE film not treated with solvent are much stronger than for the recyclate. This indicates that the residual solvent hinders the crosslinking that normally occurs during extrusion. The reason for this could be that the solvent molecules increase the distance between the molecular chains, making crosslinking more difficult. The results of the SEC measurement confirm the conclusion that extrusion in the presence of the solvent leads to a much weaker increase in molecular weight. On the other hand, with the reference where no solvent is present, the molecular weight increases strongly. This is also reflected in an increase in the polydispersity index. For the samples extruded in the presence of solvent molecules, the polydispersity index does not change significantly, from which it can be concluded that the comparatively high MFIs of the delaminated material do not result from chain degradation.

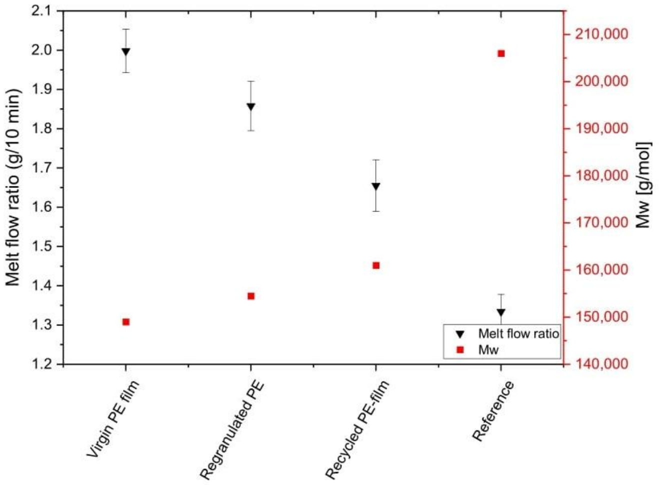


Figure 14. Change in MFI and molecular weight after regranulation/cast film extrusion of the delaminated LDPE compared with the commercial LDPE film used to produce the laminate (virgin LDPE film) and the regranulated virgin film (reference).

Table 5 shows the results of tensile testing of the recycled film and the virgin LDPE film used for lamination parallel to the extrusion direction.

Table 5. Overview of the results of the tensile test of the recycled and the initial LDPE film.

	Young Modulus Et	**Ultimate Tensile Strength σB**	**Elongation at Break ϵB**
	MPa	**MPa**	**%**
Initial LDPE	206 ± 13.6	31.3 ± 1.56	201.9 ± 38.1
Recycled film	133 ± 12.8	28.9 ± 0.74	244.1 ± 26.0

It can be seen from the literature that due to crosslinking, an increase in tensile strength and ultimate tensile strength would be expected for recycled LDPE [39,42]. However, since the LDPE in the present case, as demonstrated by SEC, was only subjected to slight crosslinking, no increase in tensile strength could be observed. Instead, the measured sample exhibited a lower tensile strength and lower Young’s modulus than the virgin film. The reason for this could be a plasticizing effect of the residual solvent. The increase in free volume between the polymer chains due to plasticizing molecule leads to deformation at lower forces, making the material less elastic and thus having a lower Young’s modulus and also a lower tensile strength [43,44]. At the same time, the elongation of plasticized materials increases because the weakening of intermolecular interactions reduces the stiffness and increases the flexibility of the film [45–47]. The typical behavior of plasticized polymers also includes an increase in elongation. This tendency can also be observed in the present case, although the high standard deviation does not allow any concrete statement on this. However, it must be taken into account here that the commercial film has a thickness of 45–47 µm, while the recycled film does not quite reach the target thickness of

45 μm and is rather between 42–43 μm thick. While this difference in thickness is taken into account in the tensile strength, this is not possible with elongation. With a film thickness of 45 μm of the recycled film, an even higher value for the elongation would therefore be expected [48,49].

The influence of the solvent on the quality of the LDPE can be reduced by reducing the solvent content prior to feeding into the extruder. This can be achieved by further optimizing the predrying or by carrying out an extraction of the solvent. The solvent content can also be further reduced by optimizing the degassing during granulation, thus further reducing its influence.

The properties of the recycled film should theoretically allow it to be used again in packaging applications. For food applications, it would first have to be checked whether the food law requirements can be met. According to EU Regulation 10/2011, this would involve guaranteeing that no more than 30 mg of solvent can pass into 1 kg of food, which is why it may only be possible to use the film behind a functional barrier [50].

3.3.7. Characterization of the Recovered PET

The PET obtained was in the form of a predominantly transparent granule, which, however, exhibited a slight yellow coloration and also a whitish turbidity in some sections. Yellowing is more frequently observed in recycled PET and can be attributed to thermo-oxidative processes [51,52]. The whitish haze is due to residual LDPE that could not be removed during density separation. Since the melting point of LDPE is below that of PET, melt filtration is not possible in this case.

The influence of the recycling process on the molecular weight of PET is shown in Table 6. Here, it can be seen that the solvent treatment and the predrying had no discernible influence on the molecular weight of the PET. During regranulation, however, a slight reduction in molecular weight took place. The determined weight-averaged molar mass of the regranulate was 36,653 g/mol and thus just below the assumed error range of 10% of the starting material, which has a Mw of 41,564 g/mol.

Table 6. Influence of the individual recycling steps on the molecular weight of PET.

Initial PET Film	Delaminated Material	Predried Material	Regranulated PET
g/mol	**g/mol**	**g/mol**	**g/mol**
40,485 ± 2025	41,564 ± 2078	40,359 ± 2018	36,653 ± 1833

It is well known that the Mw of PET often decreases during extrusion in recycling processes. In the case of pure PET, this can occur due to the presence of water in the form of hydrolytic chain scission or thermal chain scission [53]. One reason why only slight molar mass degradation occurred in the present case may be the thorough predrying of the material prior to extrusion or the maximum extrusion temperature of 260 °C, which is lower than the temperature of 280 °C usually mentioned as extrusion temperature for PET in the literature [53].

The spectrum of the regranulated PET shows some differences from the spectrum of the virgin material. For one thing, changes can be observed in the C–H region between 3000–2800 cm^{-1}. In the regranulate, two newly appeared bands at 2907 cm^{-1} and at 2853 cm^{-1} can be seen, which can be attributed to the LDPE content in the PET fraction. On the other hand, the other PE-typical bands at 1463 and 718 cm^{-1} are not found, probably because their intensity is lower and there are overlaps in the fingerprint region. The bands of PET in the C–H region shift slightly and change their intensities, which can be attributed to either chain scissions, conformational changes, or both [54,55]. The bands with wavelengths 1470, 1340, 1118, 970, and 845 cm^{-1} significantly lost intensity somewhat, while the bands at 1370, 1044, and 898 cm^{-1} significantly gained intensity. These bands are characteristic of the trans or gauche rotational conformers of the ethylene glycol moiety in

PET [55]. Since both conformers are found in the amorphous portion of the polymer, only the trans conformer is found in the crystalline phase. Since in the present case the absorption bands characteristic of the trans conformer decreased, this indicates that the regranulate has a higher amorphous fraction than the PET film used for laminate production. It is known from the literature that as a consequence of molar mass degradation during extrusion, an enrichment of trans conformers, and thus an increase in the overall degree of crystallinity, occurs [54–56]. Therefore, the increase in gauche content occurring in this case after the extrusion step must have a cause other than chain degradation. Another possible explanation could be that the crystallization of PET is disturbed by the contamination with LDPE. It has been reported in the literature that this is possible even though the two polymers are immiscible with each other [57].

However, this assumption can be ruled out on the basis of the DSC curves. The DSC measurement of the PET granulate shows that during the first heating process, a postcrystallization of the PET took place, which means that the conclusions drawn from the IR spectrum regarding the crystallinity were correct and the degree of crystallization of the regranulated PET was 13.91%.

During the second heating run, however, no postcrystallization of the PET could be detected. The degree of crystallization determined from the measurement curve of the second heating process was 34.09%, which was 2% higher compared with the degree of crystallinity of the virgin film, which was 33.21%.

This means that the LDPE content did not hinder the crystallization of the PET in general, but that the cooling process during the production of the granulate prevented the crystallization. The fact that, in addition, the melt temperatures for both virgin and recycled material were 253.73 °C and 253.81 °C, respectively, shows that molar mass degradation has no effect on the thermal properties of PET. Additionally, it is worth mentioning that the LDPE content of the granulate is not visible in the DSC curve, which means that the LDPE content cannot crystallize. The DSC curves of the PET and the measurement data determined from them can be found in the Supplementary Information in Figures S4 and S5 and Table S2.

It should be possible to reduce the proportion of LDPE in PET using cyclonic separation, but it is nevertheless unlikely that the LDPE can be completely removed. Thus, in order to still be able to achieve good mechanical properties, the addition of compatibilizers might be necessary [7,58]. Such improved treatment or compatibilization of PET could then also lead to the possibility of reusing it in packaging applications. However, the food law restrictions already described for LDPE also apply here.

4. Conclusions

As multilayer packaging has a significant presence in the packaging market due to its versatile properties and advantages, its nonrecyclability is a highly discussed problem. However, if the individual materials are bonded with a reversibly crosslinking adhesive, the packaging can be separated into its individual components, and these can then be recycled individually.

Since this concept has so far only been pursued on a laboratory scale, this work shows that upscaling of laminate production to a pilot plant for lacquering and lamination and delamination and subsequent recycling of the laminate on a small-scale technical plant are possible. The generated bond adhesion of the laminate is >4 N/15 mm and is so good that there is substrate failure of the PET film when performing the T-peel test. Delamination of the composite and subsequent further processing made it possible to produce PET and LDPE regranulate, and the LDPE regranulate was also used to produce a recycled film. The characterization of the material shows good properties of LDPE and suitability for reapplication as film. In order to ensure high-quality reuse of the PET, the residual LDPE content in this fraction would have to be achieved, for example, by means of adapted density separation (e.g., by cyclonic separation), or the addition of a compatibilizer would have to be considered. By optimizing these process steps and extending this principle to other packaging laminates, a future model for recycling multilayer packaging and thus increasing recycling rates could be developed.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/recycling6030047/s1: Figure S1: Comparison of the ring deformation band of the maleimide group at 696 cm^{-1} of the cured adhesive exposed to 160 °C for 1 s and the cured/uncured adhesive. Figure S2: Comparison of the ring deformation band of the maleimide group at 696 cm^{-1} from the cured adhesive exposed to 105 °C for 20 min and the cured/uncured adhesive. Figure S3: DSC curve of the initial PE film (green) and recycled PE film (blue). Figure S4: DSC curve of initial PET film (blue) and regranulated PET (green). Figure S5: DSC curves of the recycled PET. Shown are the first heating run in black, the cooling curve in red, and the second heating run in blue. Table S1: Data from DSC evaluation of initial PE film and recycled PE film. Table S2: Data from DSC evaluation of initial PET film and reganulated PET.

Author Contributions: K.M.A.K. planned and carried out the polymer syntheses and planned and supervised the lamination and the recycling of the laminate. She also conceived and wrote the manuscript. T.G. organized the drying of the delaminated films and the extrusion of the materials. Both authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in supplementary material.

Acknowledgments: Special thanks goes to Morchem S.A., especially to Cristina Ventayol, which provided isocyanate prepolymers for the production the furfurylamine-functionalized prepolymer. Additionally, many thanks goes to Petra Treppe and the Polymer Separation Group at the Leibniz-Institut für Polymerforschung Dresden e.V./Stellenbosch University for the HT-SEC measurements of LDPE. Thanks goes also to Norbert Rodler and the technical team members of the Materials Development for their support with the laminate production and the technical team of the Recycling Department for their support with the recycling of the laminate. We also thank David Bauer for performing GPC and HS-GC measurements and Kerstin Müller for proofreading.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wagner, J.R. (Ed.) *Multilayer Flexible Packaging*, 2nd ed.; William Andrew is an imprint of Elsevier: Oxford, UK, 2016; ISBN 9780323371001.
2. Morris, B.A. *The Science and Technology of Flexible Packaging: Multilayer Films from Resin and Process to End Use*; Elsevier Ltd: Oxford, UK, 2017; ISBN 0323243258.
3. Kaiser, K.; Schmid, M.; Schlummer, M. Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling* **2018**, *3*, 1. [CrossRef]
4. European Commisson. *A European Strategy for Plastics in a Circular Economy*; Brussels, Belgium, 2018. Available online: https://www.oneplanetnetwork.org/initiative/european-strategy-plastics-circular-economy (accessed on 12 July 2021).
5. Benhamida, A.; Kaci, M.; Cimmino, S.; Silvestre, C.; Duraccio, D. Evaluation of the Effectiveness of New Compatibilizers Based on EBAGMA-LDPE and EBAGMA-PET Masterbatches for LDPE/PET Blends. *Macromol. Mater. Eng.* **2010**, *295*, 222–232. [CrossRef]
6. Martínez, J.G.; Benavides, R.; Guerrero, C. Polyethylenes/PET blend compatibilization with maleic anhydride modified polyethylenes obtained by a UV preirradiation process. *J. Appl. Polym. Sci.* **2007**, *104*, 560–567. [CrossRef]
7. Zhang, Y.; Zhang, H.; Guo, W.; Wu, C. Effects of different types of polyethylene on the morphology and properties of recycled poly(ethylene terephthalate)/polyethylene compatibilized blends. *Polym. Adv. Technol.* **2011**, *22*, 1851–1858. [CrossRef]
8. Araujo, L.M.G.; Morales, A.R. Compatibilization of recycled polypropylene and recycled poly (ethylene terephthalate) blends with SEBS-g-MA. *Polímeros* **2018**, *28*, 84–91. [CrossRef]
9. Benzing, K.; Fleig, J.; Feiss, D.; Rott, H. Separating Aluminum-Containing Composites, Eg For Recycling Packaging Materials, Involves Treatment with Alkali Solution to Dissolve Aluminum and Precipitate Other Materials. DE10102554, 19 January 2002.
10. Chui, Y.; Lee, M.; Kim, H. A Recycling Method of Multilayer Packaging Film Waste. EP1683829A1, 26 July 2006.
11. Samorì, C.; Cespi, D.; Blair, P.; Galletti, P.; Malferrari, D.; Passarini, F.; Vassura, I.; Tagliavini, E. Application of switchable hydrophilicity solvents for recycling multilayer packaging materials. *Green Chem.* **2017**, *19*, 1714–1720. [CrossRef]
12. Cinelli, P.; Schmid, M.; Bugnicourt, E.; Coltelli, M.B.; Lazzeri, A. Recyclability of PET/WPI/PE Multilayer Films by Removal of Whey Protein Isolate-Based Coatings with Enzymatic Detergents. *Materials* **2016**, *9*, 473. [CrossRef] [PubMed]

13. Banea, M.D. Debonding on Demand of Adhesively Bonded Joints. In *Progress in Adhesion and Adhesives*; Mittal, K.L., Ed.; Scrivener: Hoboken, NJ, USA, 2020; pp. 33–50; ISBN 9781119749882.
14. Sanyal, A. Diels-Alder Cycloaddition-Cycloreversion: A Powerful Combo in Materials Design. *Macromol. Chem. Phys.* **2010**, *211*, 1417–1425. [CrossRef]
15. Gandini, A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, *38*, 1–29. [CrossRef]
16. Khan, N.I.; Halder, S.; Gunjan, S.B.; Prasad, T. A review on Diels-Alder based self-healing polymer composites. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *377*, 12007. [CrossRef]
17. Carneiro de Oliveira, J.; Laborie, M.-P.; Roucoules, V. Thermodynamic and Kinetic Study of Diels-Alder Reaction between Furfuryl Alcohol and N-Hydroxymaleimides-An Assessment for Materials Application. *Molecules* **2020**, *25*, 243. [CrossRef]
18. Kaiser, K.M.A. Recycling of multilayer packaging using a reversible cross-linking adhesive. *J. Appl. Polym. Sci.* **2020**, *137*, 49230. [CrossRef]
19. Kaiser, K.M.A.; Ewender, J.; Welle, F. Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law. *Polymers* **2020**, *12*, 2988. [CrossRef] [PubMed]
20. GVM Gesellschaft für Verpackungsmarkforschung. *Flexible Plastic Packaging Market in Germany and in Europe: Trends and Perspectives until 2021 by Product Categories*; GVM Gesellschaft für Verpackungsmarkforschung: Mainz, Germany, 2017.
21. Heo, Y.; Sodano, H.A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **2014**, *24*, 5261–5268. [CrossRef]
22. Duan, H.-Y.; Wang, Y.-X.; Wang, L.-J.; Min, Y.-Q.; Zhang, X.-H.; Du, B.-Y. An Investigation of the Selective Chain Scission at Centered Diels–Alder Mechanophore under Ultrasonication. *Macromolecules* **2017**, *50*, 1353–1361. [CrossRef]
23. Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Sun, P.; Joncheray, T.; Zhang, Y. Synthesis of linear polyurethane bearing pendant furan and cross-linked healable polyurethane containing Diels–Alder bonds. *New J. Chem.* **2014**, *38*, 770–776. [CrossRef]
24. Friedhelm Gores, P.K. Tips & Tricks: GPC/SEC: Examining accuracy and precision in GPC/SEC. *Column* **2008**, *2*, 20–23.
25. Dostál, J.; Kašpárková, V.; Zatloukal, M.; Muras, J.; Šimek, L. Influence of the repeated extrusion on the degradation of polyethylene. Structural changes in low density polyethylene. *Eur. Polym. J.* **2008**, *44*, 2652–2658. [CrossRef]
26. Jin, H.; Gonzalez-Gutierrez, J.; Oblak, P.; Zupančič, B.; Emri, I. The effect of extensive mechanical recycling on the properties of low density polyethylene. *Polym. Degrad. Stab.* **2012**, *97*, 2262–2272. [CrossRef]
27. Mieth, A.; Hoekstra, E.; Simoneau, C. *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*; Publications Office of the EU: Luxembourg, Luxembourg, 2016.
28. Turkenburg, D.H.; van Bracht, H.; Funke, B.; Schmider, M.; Janke, D.; Fischer, H.R. Polyurethane adhesives containing Diels-Alder-based thermoreversible bonds. *J. Appl. Polym. Sci.* **2017**, *134*. [CrossRef]
29. Planes, E.; Marouani, S.; Flandin, L. Optimizing the heat sealing parameters of multilayers polymeric films. *J. Mater. Sci.* **2011**, *46*, 5948–5958. [CrossRef]
30. Scutaru, A.M.; Wenzel, M.; Gust, R. Bivalent bendamustine and melphalan derivatives as anticancer agents. *Eur. J. Med. Chem.* **2011**, *46*, 1604–1615. [CrossRef]
31. Bai, N.; Saito, K.; Simon, G.P. Synthesis of a diamine cross-linker containing Diels–Alder adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer. *Polym. Chem.* **2013**, *4*, 724–730. [CrossRef]
32. Otto, S.; Blokzijl, W.; Engberts, J.B.F.N. Diels-Alder Reactions in Water. Effects of Hydrophobicity and Hydrogen Bonding. *J. Org. Chem.* **1994**, *59*, 5372–5376. [CrossRef]
33. Yadav, V.K.; Prasad, D.L.V.K.; Yadav, A.; Yadav, K. On the solvent- and temperature-driven stereoselectivity of the Diels–Alder cycloaddition reactions of furan with maleic anhydride and maleimide. *J. Phys. Org. Chem.* **2021**, *34*. [CrossRef]
34. Froidevaux, V.; Borne, M.; Laborbe, E.; Auvergne, R.; Gandini, A.; Boutevin, B. Study of the Diels–Alder and retro-Diels–Alder reaction between furan derivatives and maleimide for the creation of new materials. *RSC Adv.* **2015**, *5*, 37742–37754. [CrossRef]
35. Ruiz-Lopez, M.F.; Assfeld, X.; Garcia, J.I.; Mayoral, J.A.; Salvatella, L. Solvent effects on the mechanism and selectivities of asymmetric Diels-Alder reactions. *J. Am. Chem. Soc.* **1993**, *115*, 8780–8787. [CrossRef]
36. Widstrom, A.L.; Lear, B.J. Structural and solvent control over activation parameters for a pair of retro Diels-Alder reactions. *Sci. Rep.* **2019**, *9*, 18267. [CrossRef] [PubMed]
37. Scholte, T.G.; Meijerink, N.L.J. Gel permeation chromatography on branched polymers. *Brit. Poly. J.* **1977**, *9*, 133–139. [CrossRef]
38. Gaston, F.; Dupuy, N.; Marque, S.R.A.; Barbaroux, M.; Dorey, S. One year monitoring by FTIR of γ-irradiated multilayer film PE/EVOH/PE. *Radiat. Phys. Chem.* **2016**, *125*, 115–121. [CrossRef]
39. Czarnecka-Komorowska, D.; Wiszumirska, K.; Garbacz, T. Films ldpe/lldpe made from post—Consumer plastics: Processing, structure, mechanical properties. *Adv. Sci. Technol. Res. J.* **2018**, *12*, 134–142. [CrossRef]
40. Almond, J.; Sugumaar, P.; Wenzel, M.N.; Hill, G.; Wallis, C. Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. *Polymers* **2020**, *20*, 369–381. [CrossRef]
41. Yin, S.; Tuladhar, R.; Shi, F.; Shanks, R.A.; Combe, M.; Collister, T. Mechanical reprocessing of polyolefin waste: A review. *Polym. Eng. Sci.* **2015**, *55*, 2899–2909. [CrossRef]
42. Mendes, A.A.; Cunha, A.M.; Bernardo, C.A. Study of the degradation mechanisms of polyethylene during reprocessing. *Polym. Degrad. Stab.* **2011**, *96*, 1125–1133. [CrossRef]
43. Lim, H.; Hoag, S.W. Plasticizer effects on physical-mechanical properties of solvent cast Soluplus®films. *AAPS PharmSciTech* **2013**, *14*, 903–910. [CrossRef] [PubMed]

44. Sanyang, M.; Sapuan, S.; Jawaid, M.; Ishak, M.; Sahari, J. Effect of Plasticizer Type and Concentration on Tensile, Thermal and Barrier Properties of Biodegradable Films Based on Sugar Palm (Arenga pinnata) Starch. *Polymers* **2015**, *7*, 1106. [CrossRef]
45. Jantrawut, P.; Chaiwarit, T.; Jantanasakulwong, K.; Brachais, C.H.; Chambin, O. Effect of Plasticizer Type on Tensile Property and In Vitro Indomethacin Release of Thin Films Based on Low-Methoxyl Pectin. *Polymers* **2017**, *9*, 289. [CrossRef]
46. Fishman, M.L.; Coffin, D.R.; Konstance, R.P.; Onwulata, C.I. Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydr. Polym.* **2000**, *41*, 317–325. [CrossRef]
47. Muscat, D.; Adhikari, B.; Adhikari, R.; Chaudhary, D.S. Comparative study of film forming behaviour of low and high amylose starches using glycerol and xylitol as plasticizers. *J. Food Eng.* **2012**, *109*, 189–201. [CrossRef]
48. West, S. *The Effect of Process Parameters on the Mechanical and Optical Properties of Cast Film*; McMaster University: Hamilton ON, Canada, 2005.
49. Macauley, N.J.; Harkin-Jones, E.M.A.; Murphy, W.R. The influence of extrusion parameters on the mechanical properties of polypropylene sheet. *Polym. Eng. Sci.* **1998**, *38*, 662–673. [CrossRef]
50. The European Commission. *Commission Regulation (EU) No 10/2011: Of 14 January 2011 on Plastic Materials and Articles Intended to Come into Contact with Food*; Brussels, Belgium, 2011; Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32011R0010 (accessed on 12 July 2021).
51. Berg, D.; Schaefer, K.; Koerner, A.; Kaufmann, R.; Tillmann, W.; Moeller, M. Reasons for the Discoloration of Postconsumer Poly(ethylene terephthalate) during Reprocessing. *Macromol. Mater. Eng.* **2016**, *301*, 1454–1467. [CrossRef]
52. Ladasiu Ciolacu, C.F.; Roy Choudhury, N.; Dutta, N.K. Colour formation in poly(ethylene terephthalate) during melt processing. *Polym. Degrad. Stab.* **2006**, *91*, 875–885. [CrossRef]
53. Awaja, F.; Pavel, D. Recycling of PET. *Eur. Polym. J.* **2005**, *41*, 1453–1477. [CrossRef]
54. Sammon, C.; Yarwood, J.; Everall, N. An FT–IR study of the effect of hydrolytic degradation on the structure of thin PET films. *Polym. Degrad. Stab.* **2000**, *67*, 149–158. [CrossRef]
55. López, M.d.M.C.; Ares Pernas, A.I.; Abad López, M.J.; Latorre, A.L.; López Vilariño, J.M.; González Rodríguez, M.V. Assessing changes on poly(ethylene terephthalate) properties after recycling: Mechanical recycling in laboratory versus postconsumer recycled material. *Mater. Chem. Phys.* **2014**, *147*, 884–894. [CrossRef]
56. Donelli, I.; Taddei, P.; Smet, P.F.; Poelman, D.; Nierstrasz, V.A.; Freddi, G. Enzymatic surface modification and functionalization of PET: A water contact angle, FTIR, and fluorescence spectroscopy study. *Biotechnol. Bioeng.* **2009**, *103*, 845–856. [CrossRef] [PubMed]
57. Pracella, M. Crystallization of Polymer Blends. In *Handbook of Polymer Crystallization*; Piorkowska, E., Rutledge, G.C., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 287–326. ISBN 9781118541838.
58. Delva, L.; Deceur, C.; van Damme, N.; Ragaert, K. Compatibilization of PET-PE blends for the recycling of multilayer packaging foils. In Proceedings of the Europe/Africa Conference Dresden 2017—Polymer Processing Society PPS, Dresden, Germany, 27–29 June 2017; p. 30005.

9. Discussion

To achieve the EU's goal of making all packaging on the EU market reusable or recyclable by 2030, it is necessary to redesign non-recyclable packaging or establish new recycling technologies. Among the non-recyclable packaging, multilayer packaging is particularly relevant, as it has a high presence on the packaging market and can therefore represent a relevant adjusting screw for increasing the recycling rates.

The use of a Diels-Alder adhesive as an interlayer between different materials in multilayer packaging could be able to allow their separation and thus enable a delamination approach for a wide range of multilayer packaging.

To verify whether the recycling of multilayer packaging by delamination using Diels-Alder adhesives is indeed an option, the questions from Chapter 5 were answered in Chapters 6-0. In the following, the questions from chapter 5 are revisited and the main statements of these chapters are discussed.

1. **Is it possible to formulate Diels-Alder adhesives so that they can be used to make packaging laminates and then delaminate them with a solvent treatment? How is the behavior of the adhesive influenced by the length of the prepoylmer, the curing temperature and the substrates of the laminate?**

This question was investigated using an adhesive system consisting of linear maleimide- or furan-functionalized prepolymers of different lengths polymerized from 4,4'-MDI and a polyesterdiol. Crosslinking of the adhesive was achieved by using a molecule with three furan groups. This system was chosen for the study for different reasons: MDI was chosen as the isocyanate because its very low vapour pressure reduces its hazards during handling compared to the other major isocyanates and makes it suitable for laboratory handling. [48] There is little information in the literature about diols used in commercial packaging adhesives. After preliminary tests with various polyethers, polyesters and polyether-polyester copolymers, the caprolactone diol was selected because it gives a prepolymer that is readily soluble in methyl ethyl ketone (MEK) and ethyl acetate when polymerized with MDI, and preliminary lamination tests showed promising adhesive properties. Using these starting materials, prepolymers of different lengths were synthesized and used to produce PET//PE-LD, PET//aluminum and PE-LD//aluminum laminates by adding the crosslinker molecule.

The results of the T-peel tests (Chapter 6, Table 3) of these different laminates indicate that the increased curing temperature has a positive effect on the bond adhesion. For the aluminum laminates, a decrease in bond strength with increasing length of the adhesive molecules can be observed, while no such effect is observed for the polymer/polymer laminates.

However, since the specimens are hand-laminated, some of them have air inclusions of various dimensions, and the thickness of the adhesive cannot always be reproduced exactly, nor is the thickness within a specimen always constant. Therefore, to verify the observed trends, machine-laminated specimens that do not contain voids would have to be prepared.

Since the T-peel test is the standard method in the industry for determining the adhesion of films, this method was also used here. However, it is not really suitable for comparing adhesion between different substrates, as the different materials dissipate different amounts of energy and thus influence the measured values. [49] For example, since PE-LD is more prone to elastic and plastic deformation compared to PET or aluminum, laminates with PE-LD dissipate more energy during the T-Peel test, which is reflected in an increase in the measured adhesion value. Thus, the laminate bond strengths measured in Chapter 6, which tend to be higher for PE-LD laminates, can therefore presumably be attributed to some extend to the measurement methodology.

When observing delamination in DMSO at 105 °C (Chapter 6, Figure 6), it was noticed that the time to delamination also depends on the laminate type and the faster the solvent diffuses through the substrate, the faster the laminate delaminates. The stronger the barrier of the substrates, the stronger the influence over the cut edges during delamination. Furthermore, the length of the prepolymers and also the temperature of the curing of the laminate, and thus the different exo/endo ratios of the Diels-Alder adducts, also play a role on the duration of delamination.

2. **Is it possible to implement this principle while taking food law requirements into account?**

Since the use of CMR chemicals in packaging adhesives is only permitted in approved exceptional cases, a way was sought to avoid the use of the potentially carcinogenic furfuryl alcohol. One way to do this was seen in the use of furfurylamine which is not labeled as carcinogenic. However, replacing the furfuryl alcohol with the amine derivative is not possible without further modification of the formulation, as a drastic deterioration in the solubility of the adhesive components in ethyl acetate and MEK was observed after the formation of the urea groups, especially with the cross-linking formulations. To generate crosslinking in a different way, a reaction pathway was chosen in which the partial functionalization of a linear isocyanate prepolymer allows the formation of biuret groups and thus the formation of side chains. In this way, using a prepolymer formulation from Morchem SA, a soluble furan prepolymer with an average of three furan groups was prepared, over which crosslinking can be generated.

The bond strength achieved by this adhesive (Chapter 7, Figure 6, Table 5) for the laminates PET//PE-LD, PE-LD//aluminium and PE-LD//aluminium is between 2 and 3 N/15 mm and therefore sufficient for most packaging purposes. Delamination of the material components of the input cut to about 1 cm^2 was carried out in DMSO at 105 °C within 40 min (Chapter 7, Table 6), with partial opening of the Diels-Alder adducts and subsequent solvation of the components in the solvent.

Diffusion models had been used to predict the diffusion behavior of furfurylamine and *N*-(2-hydroxyethyl)maleimide in the multilayer packaging materials. The Piringer diffusion coefficients give a lag time of only a few minutes for furfurylamine and *N*-(2-hydroxyethyl)maleimide at 23 °C through 45 µm thick PE-LD (Chapter 7, Figure 7). The barrier effect of PE-LD is therefore not sufficient to act as a functional barrier against both of the migrants. This would not change even if unrealistically thick PE-LD layers were used or unrealistically low diffusion coefficients of the migrants in the adhesive were assumed. However, whether the limit of 0.01 mg of the migrants per kg of food specified by the EU can be exceeded depends not only on the barrier, but also on the residual content of the migrants in the adhesive. It could be determined that if the content of both substances in the adhesive is below 30 mg/kg, the limit value of 0.01 mg/kg in the food is not exceeded in a PET//PE-LD (23 µm//45 µm) laminate (Chapter 7, Figure 7). Based on the experimentally determined diffusion coefficients predicted according to the Welle prediction model, it could be shown that EVOH is a good functional barrier against the migrants and already 3 µm EVOH strongly delays the transition into the food (Chapter 7, Figure 12). Furfurylamine has higher diffusion coefficients than *N*-(2-hydroxyethyl)maleimide and therefore has a lower lag-time. However, through 3 µm of EVOH, the lag-time of furfurylamine at 23 °C is 9.1 years even in the worst-case scenario (Chapter 7, Figure 13). As this is an unrealistically long time for common packaging applications, it can be generally said that the use of the described adhesive behind a 3 µm thick EVOH layer is safe, regardless of the residual content of furfurylamine and *N*-(2-hydroxyethyl)maleimide.

The third question aims to determine whether laminate production with Diels-Alder adhesive and also recycling of the laminate can be carried out on a larger scale, as this is the next step towards commercial implementation of the process.

3. **Is it possible to transfer the principle from laboratory scale to pilot scale in such a way that the recyclates could be reused in a packaging application?**

It was shown that the formulation used can be processed in the same way on the pilot plant for lamination and lacquering as conventional solvent-based polyurethane adhesives, provided that the solids content is adjusted so that viscosities are like those of commercially available adhesives. Compared to hand lamination, better bond adhesion could be achieved via lamination on the pilot line for lacquering and lamination, since hand lamination does not allow defect-free lamination compared to machine lamination.

Processing of the film involving a short-term temperature exposure of 160 °C for 1.3 seconds does cause partial opening of the Diels-Alder adducts, but good bond adhesion is maintained, which means that the processing would not lead to failure of the packaging (Chapter 8, Figure 10). After delamination and density separation, PE-LD particles can still be found in the PET fraction and PET particles in the PE-LD fraction. While the PET fraction can be separated from the PE-LD fraction by melt filtration during granulation, the PE-LD cannot be separated from the PET fraction in this way due to its lower melting point.

Therefore, in the tests carried out in this work, a PET granulate has been obtained that contains a residual PE-LD content and would therefore not be suitable for further use in this form. For this, an optimized density separation would have to reduce the PE-LD content very considerably, or a compatibilization would be necessary. However, it was possible to re-extrude a film from the PE-LD granulate, which, however, due to interactions with the solvent, has slightly plasticized properties compared to the virgin film and a weaker increase in molecular weight than expected for recycled PE-LD (Chapter 8, Figure 14, Table 5).

9.1. Conclusion

In conclusion, it is possible to produce packaging laminates with polyurethane-based Diels-Alder adhesives and produce bond strengths that can compete with commercial ones. When exposed to temperature in a solvent, the Diels-Alder adducts can be opened in sufficient numbers to allow the adhesive to be solvated and the laminate to delaminate. For an adhesive prepared using furfurylamine and *N*-(2-hydroxyethyl)maleimide, the limit concentration in food prescribed for these two chemicals can be met (PE-LD 45 µm, 23 °C), provided the residual concentration in the adhesive is below 30 mg/kg. If this is not the case, the transition into the food can be greatly delayed by an EVOH barrier. By upscaling the PET//PE-LD laminate production, the adhesive was shown to process like conventional commercial solvent-based polyurethane packaging adhesives. By recycling on a small scale, a PET regranulate can be obtained and an PE-LD film that would be suitable again for use in packaging purposes and thus suitable to close the loop.

However, in order for the present approach to actually contribute to an increase in recycling rates, a number of open scientific questions must be clarified and some basic requirements must be met. These are outlined in Chapter 10.

10. Outlook

In order for packaging laminated with Diels-Alder adhesives to actually establish itself on the market and thus contribute to increasing recycling rates, a number of unresolved scientific, technical and commercial issues would first have to be clarified and some basic requirements met.

Some topics already mentioned in chapters 6-0 could be further deepened and optimized on a scientific level and thus contribute to an actual implementation on the market. This includes that a more detailed investigation of the influence of the solvent on the quality of the recyclates would be beneficial. This includes that the a more detailed investigation of the influence of the solvent on the quality of the recyclates would be beneficial. In the case of PE-LD, the solvent seems to interact reactively with the polymer and thus change the mechanical properties. By elucidating the mechanism, ways could be found to prevent this if necessary and improve the quality of the recycled PE-LD.

In order to optimize the delamination, an analysis of the rate-determining step of this would be useful. The rate-determining step could be the opening of the Diels-Alder adducts and the diffusion of the solvent. In the case that the opening of the adducts is decisive for the speed of the delamination, a modification of the adhesive system could cause a lowering of the temperature of the retro-Diels-Alder reaction and thus an acceleration of the opening of the adhesive network.

Another important factor that could be scientifically investigated would be the influence of impurities such as food residues and printing inks that are to be expected in post-consumer recycling. How these behave in the recycling process is difficult to assess due to their versatility and would have to be simulated in test series with different degrees of contamination and pretreatment processes.

To extend the application of the adhesive to other relevant multilayer structures, further development work for suitable adhesive formulations based on the identification of suitable diol/isocyanate components might be necessary.

One of the technical prerequisites for increasing recycling rates through the use of Diels-Alder adhesives is the sortability of delaminable packaging. For recycling, sortability is a basic requirement which includes the existence of a processing infrastructure for high-quality recycling. For this purpose, it would have to be possible to sort delaminable multilayers into a separate fraction, and the sorting system would have to be adapted accordingly: Since it can be assumed that flexible multilayer packaging will primarily be sorted into the mixed plastic soft fraction generated by wind sifting, it would be necessary to subsequently re-sort this fraction on a sensor basis. Since multilayer packaging cannot necessarily be distinguished from monomaterial polyolefin packaging by near-infrared (NIR) sorting, other sensor-based sorting technologies would be necessary. The possibility of marking packaging with detectable tags is promising. There are various ways of doing this, with chemical tracers, which have spectroscopic properties such as fluorescence under UV light [50,51] and digital watermarks being the focus of interest. [52] These can be integrated into the packaging by incorporating the chemicals into the plastic or label, or by applying the digital watermarks to the surface. [53] A sorting fraction generated in this way could subsequently be delaminated by solvent treatment.

Two scenarios are conceivable for this:

On the one hand, it could be possible to sort the individual laminate types into their own fractions. In this way, similar to the demonstration test in Chapter 8, recycling both the polyolefin fraction and the fraction of the polymer with the heavier density could be an option. However, unlike the experiment in Chapter 8, impurities would have to be expected, which means that appropriate optimization of the process would have to be carried out. The prerequisite for carrying out this scenario would be that a sufficient quantity of the respective composite is available on the packaging market to make targeted sorting or separate recycling profitable. However, in order to actually achieve a good quality of the sinking fraction, it would be important, especially for this method, to optimize the density separation, e.g. by using cyclonic separation.

Another possibility could be to delaminate different laminate types bonded with Diels-Alder adhesives in a combined solvent treatment. Here it would have to be taken into account that, as described in Chapter 6, the laminate structure also has an influence on the delamination time and that the adhesive formulation also has to be adapted for other substrate materials, which can also influence the delamination time. According to this method, the sink fraction would contain a mixture of different polymers, which makes further recycling of these difficult to imagine. In order to obtain a recyclable floating fraction, either care would have to be taken to ensure that only laminates with PE as polyolefin component end up in the fraction or, alternatively, a sorting out of PP from the floating fraction would have to be considered. The disadvantage of this method would be that the sinking fraction could not be further processed due to its heterogeneity, but on the other hand it would be more conceivable that this method would produce a sufficiently large sorting fraction to allow economically viable recycling.

In addition to the scientific and technical issues that still need to be clarified, there are also a number of points to consider with regard to the economics of the process. These include the price of the adhesive, which is strongly dependent on the proportion of maleimide and furan groups, the process energy required for the steps of the recycling process, and the infrastructure required. When optimizing the process, it must be ensured that the effort involved does not exceed the ecological and economic benefits of recycling.

11. Summary

Since it is generally not possible to recycle multilayer packaging by means of classic mechanical recycling, new approaches are being sought to recycle these. One approach is to delaminate the packaging into its individual layers, which makes it possible to recycle the different components separately. Therefore, the objective of this work was to develop a reversibly crosslinking Diels-Alder adhesive for packaging laminates and thus produce multilayer laminates that can be delaminated by means of solvent and temperature exposure in a tailor-made recycling process.

As a first step, adhesives were synthesized that consist of maleimide- and furan-functionalized prepolymers of different chain lengths and a trifunctional crosslinker molecule and cure via the Diels-Alder reaction. This adhesive was used to produce PET//PE-LD, PET//aluminum and PE-LD//aluminum laminates that subsequently were separated by treatment in heated solvent without adhesive residues on the surface of the films detectable by infrared spectroscopy.

The results of the investigations indicate that the laminate adhesion of the studied formulation depends on the type of film and on the temperature of curing. The behavior during delamination seems to be influenced by the type of bonded films, the length of the prepolymers and the curing temperature.

As a second step, the adhesive formulation was adapted in such a way that, in addition to the necessary diisocyanate- and diol-component, it is only necessary to use the two other chemicals furfurylamine and *N*-(2-hydroxyethyl)maleimide, neither of which are categorized as carcinogenic, mutagenic or toxic for reproduction. As for these two chemicals legally a limit value of 0.01 mg/kg for the migration into food is prescribed, migration modelling was used to show that PE-LD (45 µm) does represent only a poor functional barrier to the migrants. However, the limit value can still be complied with, provided that the residual concentration of migrants in the adhesive is a maximum of 30 mg/kg. At higher concentrations, an EVOH-barrier can prevent the chemicals from passing into the food, whereby the use of 3 µm EVOH can extend the lag-time of the migrants to at least 9 years (r.t.).

Upscalability was verified by producing a PET//PE-LD laminate using the adhesive on the pilot line for coating and lamination and then delaminating it on a pilot line for solvent-based recycling. Laminate production on the pilot line indicates that the processability of the adhesive is no different from commercial solvent-based polyurethane packaging adhesives, provided the solids content is selected to match the viscosity and the formulation allows sufficient tack.

Delamination also works on a larger scale, but because the input material is shredded by a machine, there is a greater distribution of the size of the film flakes, which affects the duration of delamination. Since PE-LD residuals in the PET fraction cannot be separated by melt filtration during pelletizing, in order to guarantee a good quality of the PET fraction, the density separation following delamination has to be optimized with suitable equipment. In the case of the PE-LD fraction, good recyclate quality can also be expected despite residual PET content, since separation of the PET during melt filtration is possible. However, the properties of the recycled PE-LD undergo a change when extruded in the presence of residual solvent.

In order to be able to contribute to an increase in recycling rates by implementing the process, the application of the adhesive would have to be extended to other laminate types, the process parameters of the upscaling would have to be further optimized and a new sorting path would have to be established in the sorting process of post-consumer packaging.

12. Zusammenfassung

Da es im Allgemeinen nicht möglich ist, mehrschichtige Verpackungen durch klassisches mechanisches Recycling zu verwerten, wird nach neuen Ansätzen für deren Recycling gesucht. Ein Ansatz besteht darin, die Verpackungen in ihre einzelnen Schichten zu delaminieren, was eine getrennte Verwertung der verschiedenen Komponenten ermöglicht. Ziel dieser Arbeit war es daher, einen reversibel vernetzenden Diels-Alder-Klebstoff für Verpackungslaminate zu entwickeln und damit Mehrschichtverbunde herzustellen, die in einem maßgeschneiderten Recyclingverfahren durch Lösungsmittel- und Temperatureinwirkung delaminiert werden können.

In einem ersten Schritt wurden Klebstoffe synthetisiert, die aus Maleimid- und Furan-funktionalisierten Präpolymeren unterschiedlicher Kettenlänge und einem trifunktionalen Vernetzermolekül bestehen und über die Diels-Alder-Reaktion aushärten. Mit diesem Klebstoff wurden PET//PE-LD-, PET//Aluminium- und PE-LD//Aluminium-Verbundfolien hergestellt, die sich anschließend durch Behandlung in erhitztem Lösungsmittel ohne infrarotspektroskopisch nachweisbare Klebstoffrückstände auf der Folienoberfläche trennen ließen.

Die Ergebnisse der Untersuchungen zeigen, dass die Laminathaftung der untersuchten Formulierung vom Folientyp und von der Aushärtungstemperatur abhängt. Das Verhalten bei der Delaminierung scheint von der Art der verklebten Filme, der Länge der Präpolymere und der Aushärtungstemperatur beeinflusst zu werden.

In einem zweiten Schritt wurde die Klebstoffrezeptur so angepasst, dass neben der notwendigen Diisocyanat- und Diolkomponente nur noch die beiden anderen Chemikalien Furfurylamin und *N*-(2-Hydroxyethyl)maleimid verwendet werden müssen, die beide nicht als krebserregend, erbgutverändernd oder fortpflanzungsgefährdend eingestuft sind. Da für diese beiden Chemikalien gesetzlich ein Grenzwert von 0,01 mg/kg für die Migration in Lebensmittel vorgeschrieben ist, wurde anhand von Migrationsmodellierung gezeigt, dass PE-LD (45 µm) nur eine schlechte funktionelle Barriere für die Migranten darstellt. Dennoch kann der Grenzwert eingehalten werden, sofern die Restkonzentration der Migranten im Klebstoff maximal 30 mg/kg beträgt. Bei höheren Konzentrationen kann eine EVOH-Barriere den Übergang der Chemikalien in das Lebensmittel verhindern, wobei die Verwendung von 3 µm EVOH die lag-time der Migranten auf mindestens 9 Jahre (r.t.) verlängern kann.

Die Hochskalierbarkeit wurde durch die Herstellung eines PET//PE-LD-Laminats und die anschließende Delaminierung auf einer Pilotanlage für lösungsmittelbasiertes Recycling überprüft. Die Herstellung des Laminats mit Diels-Alder-Polyurethan-Klebstoff auf einer Pilotanlage zur Beschichtung und Kaschierung zeigt, dass sich der Klebstoff in seiner Verarbeitbarkeit nicht von handelsüblichen lösungsmittelbasierten Polyurethan-Verpackungsklebstoffen unterscheidet, sofern der Feststoffgehalt entsprechend der Viskosität gewählt wird und die Formulierung eine ausreichende Klebkraft ermöglicht.

Die Delaminierung funktioniert auch im größeren Maßstab, aber da das Ausgangsmaterial maschinell zerkleinert wird, kommt es zu einer stärkeren Größenverteilung der Folienschnippsel, was die Dauer der Delaminierung beeinflusst. Da PE-LD-Reste in der PET-Fraktion nicht durch Schmelzefiltration während der Granulierung abgetrennt werden können, muss die Dichtetrennung nach der Delaminierung mit geeigneten Geräten optimiert werden, um eine gute Qualität der PET-Fraktion zu gewährleisten. Bei der PE-LD-Fraktion ist trotz Rest-PET-Gehalt eine gute Rezyklatqualität zu erwarten, da eine Abtrennung des PETs durch eine Schmelzefiltration möglich ist. Allerdings verändern sich die Eigenschaften des rezyklierten PE-LD, wenn es in Gegenwart von Restlösemittel extrudiert wird.

Um mit der Umsetzung des Verfahrens zu einer Steigerung der Recyclingquoten beitragen zu können, müsste die Anwendung des Klebstoffs auf andere Laminattypen ausgeweitet, die Prozessparameter des Upscaling weiter optimiert und ein neuer Sortierweg im Sortierprozess von Post-Consumer-Verpackungen etabliert werden.

13.References

The references of the individual publications are listed separately at the end of each publication.

1. Braun, D. *Kleine Geschichte der Kunststoffe;* Hanser: München, 2013, ISBN 9783446436862.
2. Geyer, R.; Jambeck, J.R.; Law, K.L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3*, e1700782, doi:10.1126/sciadv.1700782.
3. Statista GmbH. Annual production of plastics worldwide from 1950 to 2020: (in million metric tons). Available online: https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/ (accessed on 3 January 2022).
4. World Economic Forum, Ellen MacArthur Foundation and McKinsey & Company. *The New Plastics Economy Rethinking the Future of Plastics*: *Rethinking the Future of Plastics*, 2016.
5. PlasticsEurope Association of Plastics Manufacturers. *Plastics -the Facts 2020*: *An analysis of European plastics production, demand and waste data*, 2020.
6. Heinrich-Böll-Stiftung, Bund für Umwelt und Naturschutz BUND. *Plastikatlas 2019*: *Daten und Fakten über eine Welt voller Kunststoff*, 2020.
7. Morris, B.A. *The science and technology of flexible packaging*: *Multilayer films from resin and process to end use;* Elsevier Ltd: Oxford, United Kingdom, s.l., 2017, ISBN 0323243258.
8. *Multilayer flexible packaging;* Wagner, J.R., Ed., Second edition; William Andrew is an imprint of Elsevier: Oxford, UK, 2016, ISBN 9780323371001.
9. European Commisson. *A European Strategy for Plastics in a Circular Economy*, Brussels, 2018.
10. *Gesetz über das Inverkehrbringen, die Rücknahme und die hochwertige Verwertung von Verpackungen*: *VerpackG*, 2017.
11. Kaiser, W. *Kunststoffchemie für Ingenieure*: *Von der Synthese bis zur Anwendung*, 1. Aufl.; Carl Hanser Fachbuchverlag: s.l., 2011, ISBN 3446430474.
12. Bonten, C. *Plastics technology*: *Introduction and fundamentals;* Hanser: Munich, Cincinnati, 2019, ISBN 9781569907672.

13. Anukiruthika, T.; Sethupathy, P.; Wilson, A.; Kashampur, K.; Moses, J.A.; Anandharamakrishnan, C. Multilayer packaging: Advances in preparation techniques and emerging food applications. *Compr. Rev. Food Sci. Food Saf.* **2020**, *19*, 1156–1186, doi:10.1111/1541-4337.12556.
14. Ebnesajjad, S.; Khaladkar, P.R. *Fluoropolymer applications in chemical processing industries*: *The definitive user's guide and databook*, 2nd ed.; William Andrew Publishing: S.l., 2017, ISBN 0323447163.
15. Selke, S.E.M. Packaging: Polymers in Flexible Packaging. In *Reference Module in Materials Science and Materials Engineering*; Hashmi, S., Ed.; Elsevier: Amsterdam, 2016, ISBN 9780128035818.
16. Dixon, J. *Packaging materials;* ILSI: Brussels, 2011, ISBN 9789078637264.
17. Tukker, A. *Plastics waste*: *Feedstock recycling, chemical recycling and incineration;* Rapra Technology Ltd: Shawbury, U.K, 2002, ISBN 9781859573310.
18. Julia Vogel, Franziska Krüger, Matthias Fabian. *Background Chemical Recycling*, 2020.
19. *Fraunhofer IVV*. Available online: https://www.ivv.fraunhofer.de/en/recycling-environment/recycling-plastics.html.
20. Institute cyclos-HTP. *Verification and examination of recyclability*: *Requirements and assessment catalogue of the Institute cyclos-HTP for EU-wide certification (CHI-Standard)*, 2019. Available online: https://www.cyclos-htp.de/publikationen/a-b-katalog/.
21. Sarah Tschachtli, Thorsten Pitschke, Siegfried Kreibe, Alexander Martin. *Recyclingfähigkeit von Verpackungen*: *Konkretisierung Untersuchungsrahmen und Kriterienkatalog*, 2019.
22. *Mindeststandard für die Bemessung der Recyclingfähigkeit von systembeteiligungspflichtigen Verpackungen gemäß § 21 Abs. 3 VerpackG;* Stiftung Zentrale Stelle Verpackungsregister, Ed., 2019.
23. Kaiser, K.; Schmid, M.; Schlummer, M. Recycling of Polymer-Based Multilayer Packaging: A Review. *Recycling* **2018**, *3*, 1, doi:10.3390/recycling3010001.
24. Bayer, O. Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane). *Angew. Chem.* **1947**, *59*, 257–272, doi:10.1002/ange.19470590901.

25. Stutz, H. Kunststoff-Handbuch, Band 7: Polyurethane. Von G. Oertel . Carl Hanser Verlag, Miinchen 1993. 763 S. mit 564Abb. u. 126 Tab. geb., DM 368,-. *Chemie Ingenieur Technik* **1995**, *67*, 354, doi:10.1002/cite.330670327.
26. Meier-Westhues, U. *Polyurethanes*: *Coatings, adhesives and sealants;* Vincentz Network: Hannover, 2007, ISBN 3878703341.
27. Stepanski, H.; Leimenstoll, M.C. *Polyurethan-Klebstoffe*: *Unterschiede und Gemeinsamkeiten*, 1. Aufl. 2016; Springer Vieweg: Wiesbaden, 2016, ISBN 9783658122706.
28. Szycher, M. *Szycher's handbook of polyurethanes*, 2. ed.; CRC Press / Taylor & Francis: Boca Raton, Fla., 2013, ISBN 1439839581.
29. Dunn, T. *Manufacturing flexible packaging*: *Materials, machinery, and techniques;* William Andrew: Oxford, England, Waltham, Massachusetts, 2015, ISBN 0323265057.
30. Flexible Packaging Europe. *FPE Guideline on Use of Isocyanate-based Polyurethane Adhesives in Packaging Laminates (Issue 2.7)*, 2016.
31. The European Commission. COMMISSION REGULATION (EU) No 10/2011: of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Official Journal of the European Union*.
32. Banea, M.D. Debonding on Demand of Adhesively Bonded Joints: A Critical Review. *rev adhes adhesives* **2019**, *7*, 33–50, doi:10.7569/RAA.2019.097304.
33. Ciardiello, R.; Martorana, B.; Lambertini, V.G.; Brunella, V. Iron-based reversible adhesives: Effect of particles size on mechanical properties. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science* **2018**, *232*, 1446–1455, doi:10.1177/0954406217736552.
34. Jana Kolbe, Thomas Kowalik, Matthias Popp, Monika Sebald, Oliver Schorsch, Stefan Heberer, Markus Pridoehl, Guido Zimmermann, Andreas Hartwig, Erwin Born. Curable bonded assemblies capable of being dissociated.
35. Lebedeva, N.V.; Sanders, S.N.; Ina, M.; Zhushma, A.P.; Olson, S.D.; Rubinstein, M.; Sheiko, S.S. Multicore expandable microbubbles: Controlling density and expansion temperature. *Polymer* **2016**, *90*, 45–52, doi:10.1016/j.polymer.2016.02.050.

36. Mi Jung Rheem; Hyejun Jung; JinUk Ha; Sung-Hyeon Baeck; Sang Eun Shim. Suspension polymerization of thermally expandable microspheres using low-temperature initiators. *Colloid Polym Sci* **2017**, *295*, 171–180, doi:10.1007/s00396-016-3993-5.
37. Haydon, D. ElectRelease – electrically disbonding epoxy adhesive. *Assembly Automation* **2002**, *22*, 326–329, doi:10.1108/01445150210446175.
38. Michael D. Gilbert. Electrically disbonding materials.
39. Froidevaux, V.; Borne, M.; Laborbe, E.; Auvergne, R.; Gandini, A.; Boutevin, B. Study of the Diels–Alder and retro-Diels–Alder reaction between furan derivatives and maleimide for the creation of new materials. *RSC Adv.* **2015**, *5*, 37742–37754, doi:10.1039/C5RA01185J.
40. Clayden, J.; Greeves, N.; Warren, S.G. *Organic chemistry*, Second edition; Oxford University Press: Oxford, 2012, ISBN 0199270295.
41. Brückner, R. *Reaktionsmechanismen*: *Organische Reaktionen, Stereochemie, moderne Synthesemethoden*, 3. Auflage, Nachdruck 2015; Springer Spektrum: Berlin, Heidelberg, 2015, ISBN 3662456834.
42. Rainer Herges, T.W. Pericyclische Reaktionen: Cycloadditionen und Diels-Alder-Reaktion. Available online: http://www.chemgapedia.de/vsengine/vlu/vsc/de/ch/2/vlu/pericyclische_reaktionen/diels_alder.vlu/Page/vsc/de/ch/2/oc/reaktionen/formale_systematik/pericyclische_reaktionen/cycloadditionen/reaktivitaet.vscml.html.
43. Vollhardt, K.P.C.; Schore, N.E. *Organic chemistry*: *Structure and function*, 5. ed.; W.H. Freeman: New York, NY, 2007, ISBN 0716799499.
44. Wu, D.Y.; Meure, S.; Solomon, D. Self-healing polymeric materials: A review of recent developments. *Progress in Polymer Science* **2008**, *33*, 479–522, doi:10.1016/j.progpolymsci.2008.02.001.
45. Wang, S.; Urban, M.W. Self-healing polymers. *Nat Rev Mater* **2020**, *5*, 562–583, doi:10.1038/s41578-020-0202-4.
46. Kaiser, K.M.A. Recycling of multilayer packaging using a reversible cross-linking adhesive. *J Appl Polym Sci* **2020**, *137*, 49230, doi:10.1002/app.49230.

47. Kaiser, K.M.A.; Ewender, J.; Welle, F. Recyclable Multilayer Packaging by Means of Thermoreversibly Crosslinking Adhesive in the Context of Food Law. *Polymers (Basel)* **2020**, *12*, doi:10.3390/polym12122988.
48. Allport, D.C.; Gilbert, D.S.; Outterside, S.M. *MDI and TDI*: *A safety, health and the environment : a source book and practical guide;* J. Wiley: New York, 2010, ISBN 9780470862162.
49. Kinloch, A.J.; Lau, C.C.; Williams, J.G. The peeling of flexible laminates. *Int J Fract* **1994**, *66*, 45–70, doi:10.1007/BF00012635.
50. Woidasky, J.; Sander, I.; Schau, A.; Moesslein, J.; Wendler, P.; Wacker, D.; Gao, G.; Kirchenbauer, D.; Kumar, V.; Busko, D.; et al. Inorganic fluorescent marker materials for identification of post-consumer plastic packaging. *Resources, Conservation and Recycling* **2020**, *161*, 104976, doi:10.1016/j.resconrec.2020.104976.
51. Woidasky, J.; Auer, M.; Schmidt, J.; Kusch, A.; Gasde, J.; Lang-Koetz, C.; Wiethoff, S.; Sander, I.; Schau, A.; Richards, B.S.; et al. „Tracer-Based-Sorting“ in der Verpackungs-Abfallwirtschaft. *MÜLL und ABFALL* **2021**, doi:10.37307/j.1863-9763.2021.07.05.
52. Gian DeBelder. *HolyGrail: tagging packaging for accurate sorting and high-quality recycling*, 2019. Available online: https://www.newplasticseconomy.org/news/presenting-three-pioneer-projects-led-and-run-by-participants-of-the-new-plastics-economy.
53. Schyns, Z.O.G.; Shaver, M.P. Mechanical Recycling of Packaging Plastics: A Review. *Macromol. Rapid Commun.* **2021**, *42*, e2000415, doi:10.1002/marc.202000415.