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Exploration de la recyclabilité mécanique en boucle fermée, d'un polymère biodégradable pour des applications d'emballage alimentaire

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UNIVERSITÉ DE MONTPELLIER

La vie c’est comme une bicyclette,

il faut avancer pour ne pas perdre

l’équilibre.

Albert Einstein

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Valorisation des travaux de recherche

Published articles.

I. Dedieu, S. Peyron, N. Gontard, C. Aouf (2022). *The thermo-mechanical recyclability potential of biodegradable biopolyesters: Perspectives and limits for food packaging application*. Polymer testing 111, 107620. DOI 10.1016/j.polymertesting.2022.107620

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron (2022). *Recycled poly(hydroxybutyrate-co-valerate) as food packaging: effect of multiple melt processing on packaging performance and food contact suitability*. Journal of Polymers and the Environment.

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron (2022). *Mechanical recyclability of biodegradable polymers used for food packaging: case study of PHBV*. Food Additives and Contaminants: Parts A. DOI 10.1080/19440049.2022.2122589

Articles waiting for submission.

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron. *Investigation of sorption mechanisms of chemical contaminants in PHBV-based food packaging materials: impact on closed-loop recycling opportunities*. En préparation pour soumission dans Food packaging and shelf life.

Articles in progress.

I. Dedieu, C. Bonnenfant, S. Peyron, N. Gontard, C. Aouf. *Decontamination of PHBV-based materials: investigation of an adapted contaminant panel in recycling assessment and impact of quercetin as additive*.

Posters in international congress.

I. Dedieu, S. Peyron, C. Aouf. *Mechanical recyclability of polyhydroxyalkanoates (PHAs) for food packaging application*. VII international seminar Biopolymers and Sustainable Composites, Valencia (Spain) March 4-5, 2020.

Oral presentation in national congresses.

I. Dedieu, S. Peyron, C. Aouf. *Mechanical recycling: determination of process conditions and limitations for food packaging applications*. 48èmes Journées d'études des polymers, Porquerolles (France), October 3-8 2021.

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron. *Prospects and challenges of the mechanical recycling of Polyhydroxybutyrate-co-valerate for food packaging applications*. 17èmes journées scientifiques et industrielles du Goupe Français des Polymères, Marseille (France), April 7-8 2022.

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron. *Evaluation of the closed-loop mechanical recycling of Polyhydroxybutyrate-co-valerate for food packaging applications*. Journées de Printemps du GDR Durabilité des Matériaux Biosourcés, Grenoble (France), May 11-13 2022.

Oral presentation in international congresses.

I. Dedieu, C. Aouf, S. Gaucel, S. Peyron. *Mechanical recycling of polyhydroxyalkanoates for food contact applications*. European Polymer Congress, Prague (Czech Republic), June 26 – July 1 2022.

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Abbreviations

PHBV: poly(hydroxybutyrate-co-hydroxyvalerate)

PET: polyethylene terephthalate

PP: polypropylene

HDPE: high density polyethylene

PLA: poly(lactic acid)

EFSA: european food safety authority

FCM: food contact material

FDA: food and drug administration

SEC: size exclusion chromatography

DEHA: N, N-diéthyl hydroxylamine

DSC: differential scanning calorimetry

TGA: thermogravimetric analysis

PO2: oxygen permeability

WVP: water vapor permeability

SML: specific migration limit

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Depuis la seconde moitié du XXème siècle, le plastique a infiltré la plupart des domaines de notre vie, se rendant indispensable dans le quotidien de tous les foyers, et ce, indépendamment de la condition sociale. En effet, cette famille de matériaux synthétiques aux nombreux avantages (peu cher, léger, résistant et polyvalent), a peu à peu remplacé tous les matériaux traditionnels et/ou naturels, facilitant la vie du consommateur au quotidien, et lui permettant de se moderniser plus et plus vite. Depuis les années 1950, environ 8,3 milliards de tonnes de plastiques ont été produits, dont 56 % depuis les années 2000 avec une demande et une consommation qui ne cessent de croître d'année en année [1]. Cependant, à l'aube du XXIème siècle, parallèlement à cette croissance exponentielle, de nombreuses inquiétudes vis-à-vis de l'utilisation massive de ces plastiques commencent à émerger. Ces inquiétudes portent tout d'abord sur l'origine pétro-sourcée de ces matériaux, dont la ressource fossile se raréfie et dont l'extraction pollue notre environnement. La seconde inquiétude est liée à leur devenir après utilisation, ou ce qui est appelé communément leur fin de vie. En effet, ces matériaux sont trop faiblement recyclés (avec seulement 35 % des plastiques recyclés en Europe en 2020) [2] alors qu'une grande partie s'accumule dans l'environnement, où ils vont subsister durant des temps très longs. La longévité des plastiques dans l'environnement est si importante qu'ils sont utilisés comme indicateur de notre ère géologique [3]. Ces plastiques se fragmentent ensuite jusqu'à l'échelle de micro et nano particules difficiles à extraire et vont se retrouver dans nos écosystèmes et dans toutes les échelles trophiques. Ces particules sont susceptibles d'engendrer de nombreux effets délétères sur l'environnement et sur la santé des organismes vivants bien que ces effets soient encore peu connus [4]. Si aucune initiative n'est prise et si rien ne change, il est attendu qu'en 2050 il y ait plus de plastique dans les océans que de poissons… [5, 6]

Afin de faire face à ces problématiques, de nombreux collectifs et organismes publiques tentent de réduire cette consommation massive des matériaux plastiques dits « conventionnels » pétrosourcés, via différentes règlementations des usages, mais aussi en orientant l'innovation vers des alternatives plus durables. Ainsi, de nombreuses initiatives sont engagées vers le développement de matériaux plastiques moins impactants, tels que les bioplastiques. Ces bioplastiques sont des polymères issus de ressources

naturelles et renouvelables et/ou sont des polymères biodégradables/compostables en milieu naturel. Actuellement, ces bioplastiques représentent 1 % du marché mondial du plastique et 2 % du marché européen, mais cette part devrait fortement augmenter [7]. Une augmentation des bioplastiques bio-sourcés analogues aux polymères conventionnels (drop-in) tels que le bio-PET ou les bio-PE est attendue dans les prochaines années, puisque ces bioplastiques sont susceptibles de suivre les mêmes filières (procédés de production, usage, recyclage etc) que leurs homologues conventionnels. Cependant, ces bioplastiques ne sont pas biodégradables et auront, par conséquent, le même impact en termes de pollution à long terme. Des efforts doivent donc être faits pour développer des bioplastiques bio-sourcés et biodégradables (qui sont à ce jour moins bien maîtrisés), afin de minimiser l'impact de la production et de la fin de vie des plastiques. Dans cette optique, les poly(hydroxyalkanoates) (PHAs) sont une famille de biopolyesters bio-sourcés et biodégradables considérés comme prometteurs. Les projets GLOPACK, ResUrbis et USABLE sont des exemples de projets européens H2020, ayant pour objectif d'évaluer les potentialités d'usage des PHAs, y compris dans le domaine de l'emballage alimentaire, en amont de leur implémentation sur le marché. Le projet USABLE, dans lequel se place ce travail, est un projet qui rassemble 25 partenaires européens (dont 15 industriels). Il a pour objectif de développer des emballages en plastiques bio-sourcés et biodégradables, obtenus à partir de résidus secondaires de l'industrie agro-alimentaire et d'un procédé à faible empreinte environnementale, et présentant un cycle de vie durable et entièrement circulaire. En effet, les emballages représentent environ 40 % de la demande en plastique, et sont souvent à usage unique et à durée de vie courte, ce qui entraîne une augmentation rapide des déchets de ce secteur [1]. Prenant en compte les contraintes des différentes voies d'usage, le projet vise à développer 8 prototypes d'emballage présentant les propriétés pertinentes et adaptées à chaque application des secteurs ciblés allant de l'alimentaire au pharmaceutique. L'appréhension du cycle de vie de ces produits, de la production des matériaux à leur fin de vie est présentée figure 1. Par une approche d'ingénierie inverse, les PHAs produits à partir des résidus de l'industrie agro-alimentaire seront fonctionnalisés, formulés (ajout de charges ou d'additifs) et manufacturés pour répondre aux besoins des utilisateurs finaux de l'emballage.

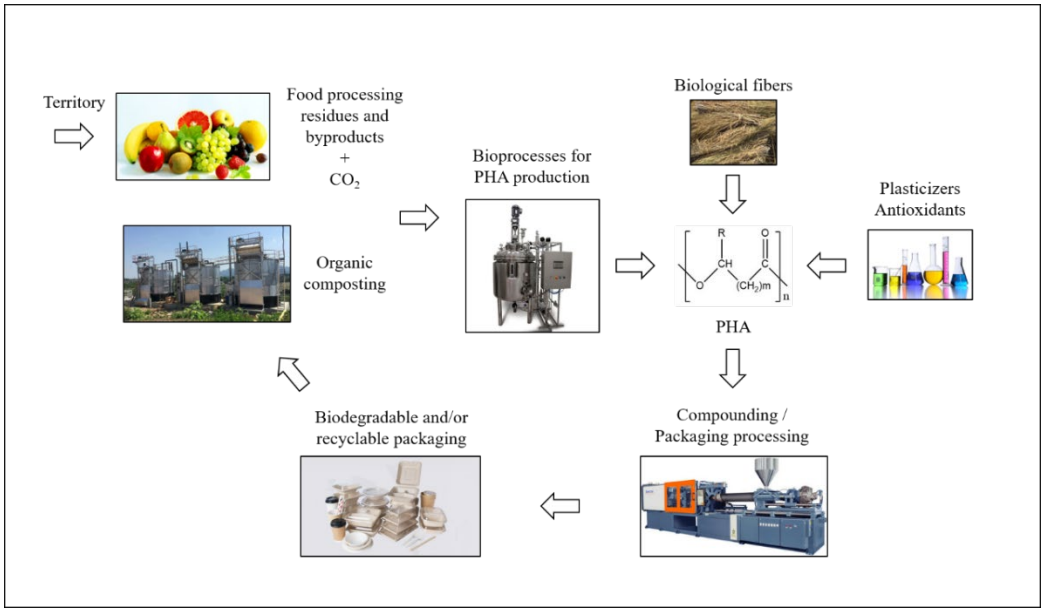


Figure 1. Concept visuel du projet.

Pour atteindre ces objectifs, le projet USABLE se décline en sept « Work Packages » (WPs), dont deux, distinctement dédiés à la coordination et à la diffusion et communication. Les cinq autres représentent le cœur scientifique et technique du projet, comme présenté figure 2.

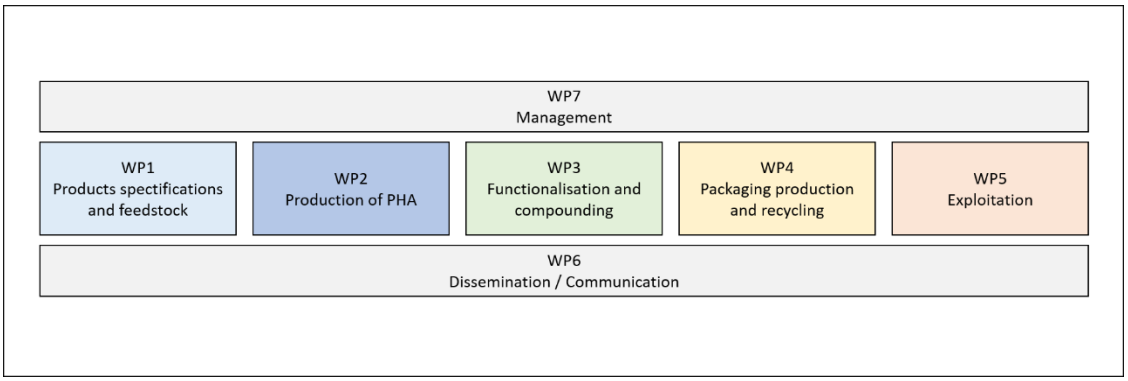


Figure 2. Distribution des « Work Packages » du projet USABLE.

L'interconnexion des différents Wps s'illustre assez bien. Ainsi, le WP1 a pour objectif de collecter les données et informations nécessaires aux autres WPs, comme les spécifications utiles pour les applications finales telles que le design, la fin de vie etc. Le WP2 est axé sur la production par voie microbienne des PHAs afin d'en optimiser les procédés de synthèse et d'extraction. Obtenus par fermentation bactérienne, les polymères résultants ont des caractéristiques directement liées à l'origine et la composition des cultures et des matières premières employées. De plus, l'impact des différents flux

(eau/matière/énergie) et des méthodes d'extraction/purification sur l'environnement et sur le prix des futurs matériaux est évalué. Dans le WP3, les PHAs sont fonctionnalisés pour répondre aux cahiers des charges des emballages finaux. Afin de modifier leurs propriétés physico-chimiques, différentes méthodes sont mises en œuvre, telles que l'ajout d'additifs (plastifiants biodégradables, antioxydants), l'addition de charges ou le mélange avec d'autres polymères (autres PHAs, PLA). Les formulations les plus performantes et pertinentes, en termes de faisabilité technique sont ensuite optimisées et mises à disposition pour le WP4. Dans ce WP, des articles d'emballage cibles sont produits et caractérisés pour leur recyclabilité et leur biodégradabilité, ce qui permet de déterminer leur devenir et l'impact environnemental de leur cycle de vie. Le WP5 est consacré à l'analyse des risques environnementaux, économiques et sanitaires via les résultats collectés dans les WPs techniques.

Cette thèse s'inscrit dans le WP4 du projet et s'intéresse à l'étude de la fin de vie d'un polymère de la famille des PHAs : le Poly(hydroxy-butyrate-co-valerate) (PHBV). Elle a pour objectif d'étudier la recyclabilité mécanique du PHBV, en boucle fermée, pour des applications d'emballage alimentaire. Le recyclage mécanique consiste à remettre en forme le matériau via un passage à l'état fondu, et un recyclage en boucle fermée signifie que le matériau recyclé sera utilisé pour les même applications que le polymère vierge à condition que sa qualité et ses propriétés d'usage soient préservées. Parmi les différentes voies de fin de vie possible pour un plastique, il a été démontré que le recyclage mécanique représente l'option la plus respectueuse de l'environnement et la plus rentable économiquement [8, 9]. Cette option permet à la fois de réduire le recours à la matière première vierge, et de diminuer la quantité de déchets rejetée dans l'environnement. Dans le cas du PHBV, où l'étape de production reste encore assez coûteuse, cette option conduirait également à une diminution du prix du matériau, le rendant plus compétitif sur le marché.

Cependant, le recyclage mécanique d'un polymère bio-sourcé et biodégradable, en boucle fermée et pour des applications d'emballage alimentaire soulève de nombreux verrous. Tout d'abord et indépendamment des questions scientifiques, le déploiement à grande échelle d'un procédé de recyclage repose sur l'existence d'un flux important de matière et donc un volume élevé de déchets d'emballages à traiter, et la mise en place de filières de tri. Cette question relève des organismes et collectivités locales

et territoriales et ne sera pas traitée dans cette thèse. D'un point de vue scientifique, deux verrous majeurs sont à lever. Tout d'abord, la plupart des polymères bio-sourcés et biodégradables et notamment le PHBV, sont thermiquement sensibles à la température [10]. L'application d'un procédé de recyclage mécanique nécessitant des températures élevées, risque de dégrader le polymère et ainsi altérer ses propriétés, limitant l'utilisation du recyclat pour les mêmes applications. D'autre part, le contact alimentaire impose de nombreuses contraintes règlementaires notamment en Europe, afin de garantir la sécurité du consommateur [11, 12]. Ainsi, un matériau recyclé ne pourra emballer un nouvel aliment, que s'il ne présente aucune contamination résiduelle susceptible d'engendrer un risque pour la santé du consommateur. Ces contraintes et règlementations sont déjà en vigueur dans le cas du recyclage mécanique des emballages alimentaires conventionnels et notamment les bouteilles en PET [13]. Les procédés de recyclage existant présentent une étape de décontamination spécifique aux applications alimentaires, afin de garantir l'élimination des contaminants chimiques et biologiques susceptibles de se trouver dans les emballages usagés. En tenant compte de tous ces aspects, le recyclage mécanique du PHBV a été abordé, dans cette thèse, en découplant les deux étapes majeures des procédés de recyclage classique existants : l'étape de remise en forme du matériau à l'état fondu (étape d'extrusion) et l'étape de décontamination du matériau à l'état solide. Le découplage de ces deux étapes permettant de mieux comprendre les mécanismes afin de mieux répondre aux questions scientifiques, et d'appréhender les actions à mettre en œuvre.

L'objectif de cette thèse est donc de comprendre et de décrire le comportement du PHBV au cours de l'opération de recyclage mécanique, en intégrant les critères essentiels dans l'évaluation des performances d'un emballage alimentaire. L'approche repose sur la mise en évidence des relations entre les modifications de structure du polymère (longueur de chaînes, niveau d'interaction et d'organisation du réseau) induites lors du traitement thermo-mécanique et les propriétés d'usage du matériau issu de ce traitement (propriétés mécaniques, propriétés de transport et d'inertie). Cet objectif se décline ainsi en deux questions scientifiques majeures :

(i) l'impact de la remise en œuvre (à l'état fondu) du PHBV sur ses propriétés structurales et fonctionnelles

(ii) l'aptitude au contact alimentaire du PHBV à l'issue des traitements de contamination/décontamination. Pour répondre à cette deuxième question, nous avons opté pour l'étude et la compréhension des mécanismes de transfert opérant lors des différentes étapes d'un procédé de recyclage en boucle fermée (figure 3). Ainsi, la contamination potentielle du PHBV a été décrite par un mécanisme de sorption des molécules chimiques, tandis que la décontamination de ces mêmes molécules lors du recyclage a été simplifiée par un mécanisme de désorption. Enfin, la migration de ces molécules dans l'aliment a été abordée afin d'étudier l'aptitude au contact alimentaire du polymère recyclé.

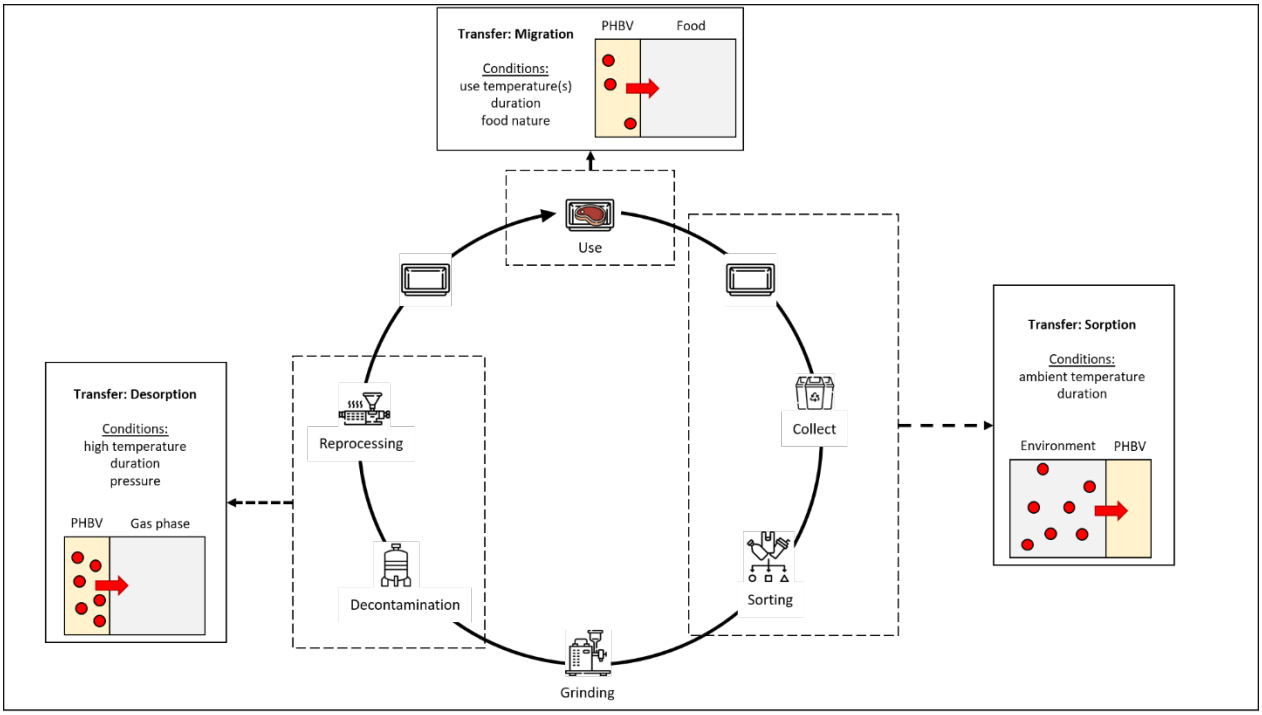


Figure 3. Rôle des mécanismes de transfert dans l'étude d'un cycle de recyclage mécanique en boucle fermée du PHBV.

L'approche stratégique suivie lors de cette thèse se reflète dans l'agencement des différents chapitres du manuscrit et est schématisée figure 4.

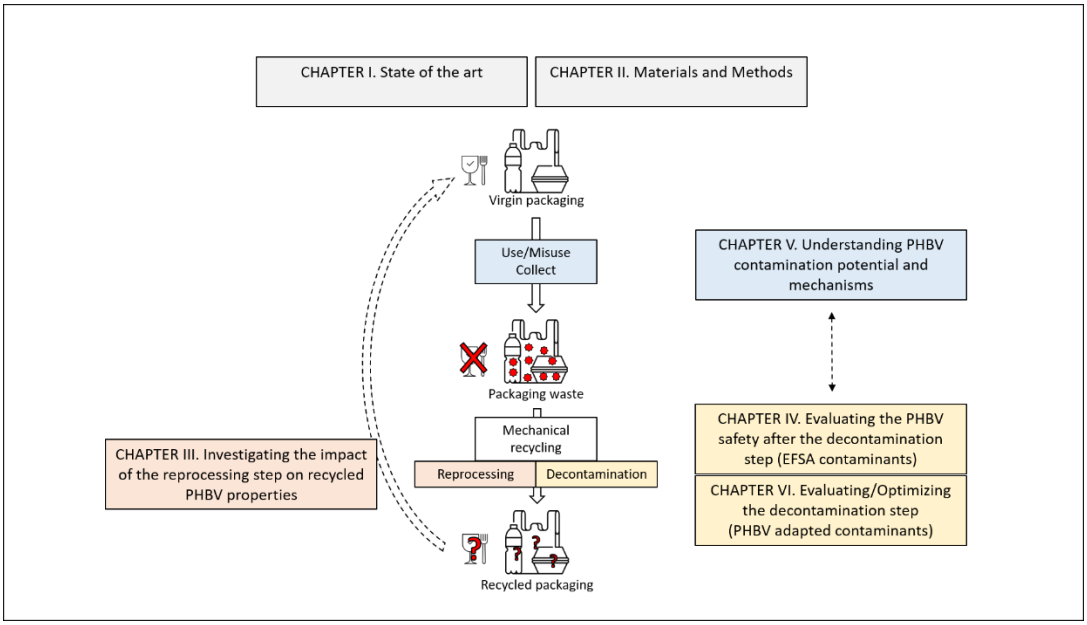


Figure 4. Objectifs scientifiques et découpage du manuscrit de thèse

Le **chapitre I**, aura pour objectif de définir les différentes notions abordées dans cette thèse (emballages alimentaires, bioplastiques, recyclage mécanique…), et à positionner ces travaux dans le cadre des travaux antérieurs réalisés dans le même contexte. Le **chapitre II** regroupera l'ensemble des matériels et méthodes utilisés lors des études développées dans les 4 chapitres suivants. Le **chapitre III** a pour objectif de répondre à la première question scientifique : l'impact de l'étape de remise en œuvre du PHBV sur ses propriétés. Il s'agit d'évaluer la dégradation thermique du matériau lors du procédé d'extrusion successif, et de mesurer son impact sur les propriétés structurales et d'usage, ainsi que, sur l'aptitude au contact du PHBV.

Les chapitres IV, V et **VI** tendent à répondre à la deuxième question scientifique relative à la contamination/décontamination du matériau pour l'application d'emballage alimentaire.

Dans un premier temps, le **chapitre IV** présentera une évaluation de l'aptitude au contact du PHBV après décontamination, en se basant sur la règlementation européenne existante pour le recyclage en boucle fermées des bouteilles de PET. Dans cette règlementation, l'évaluation du matériau se fait via un « challenge test » où le polymère artificiellement contaminé par un panel de contaminants modèles, est soumis à un traitement thermique censé éliminer ces contaminants. La contamination résiduelle

déterminée est ensuite comparée à une concentration maximale tolérée dans un emballage (cette concentration est modélisée en fonction du polymère et de l'application visée).

Dans un second temps, la contamination potentielle réelle du PHBV sera évaluée dans le **chapitre V**. En effet, au regard de ses caractéristiques intrinsèques, le PHBV présente une capacité de contamination différente de celle du PET, remettant en cause l'utilisation du panel de contaminant modèles déterminé par la règlementation européenne. Différents tests de sorption de nouveaux contaminants sur le PHBV seront effectués afin de comprendre et d'évaluer les mécanismes de sorption relatifs à ce polymère spécifiquement.

Enfin, dans le **chapitre VI**, le PHBV sera soumis à un panel de contaminants plus large, répondant à ses spécificités. L'efficacité de la décontamination de ces nouveaux contaminants sera évaluée et comparée aux résultats obtenus dans le chapitre IV. En parallèle une tentative d'optimisation de la décontamination sera réalisée, via l'ajout d'un additif/ stabilisant naturel dans le polymère.

Dans cette thèse, de manière générale, les phénomènes opérants dans les différents procédés et étapes du cycle de recyclage mécanique d'un emballage alimentaire, ont été simplifiés par les principaux mécanismes de transfert décrits dans la figure 3. Ces transferts sont déterminants dans la compréhension de la recyclabilité du polymère, avec un impact important de la nature des différents constituants (compartiments d'échange, contaminants chimiques) et des conditions opératoires.

CHAPTER I. STATE OF THE ART

CHAPTER I. STATE OF THE ART (Review)

A major part of this chapter was the subject of a review intituled “The thermo-mechanical recyclability potential of biodegradable biopolyesters: Perspectives and limits for food packaging application”, published in Polymer Testing journal (DOI 10.1016/j.polymertesting.2022.107620). To complete the chapter, additional paragraphs have been added concerning the definition of food packaging and its regulation.

1. Plastic food packaging

1.1. Definition and generalities

Since the early 1900’s, the discovery of fossil-based polymers, especially thermoplastics has been the main driver behind the development of plastic industry. Strong, inexpensive, lightweight and versatile, plastics are used in thousands of products that add comfort, convenience and safety to our everyday lives. The current world production of plastic is about 370 million tons[14, 15], with an annual growth in consumption of about 5 %[16]. European plastics production accounts for 16 % of the global market, with approximately 57.9 million tons in 2019[14, 15]. Packaging is the largest end-use market segment, accounting for just over 40 % of total plastic usage. Polyolefins such as low and high density polyethylene (LDPE and HDPE) and polypropylene (PP), along with polyesters like polyethylene terephthalate (PET) are the most used thermoplastics in packaging sector[17, 18]. These fossil-based materials are in ever-increasing demand because of their desirable thermal stability, mechanical properties and their good barrier properties to carbon dioxide and oxygen.

Indeed, a material intended for food packaging applications must have certain properties regarding the performance and food safety of the final product. First of all, the polymer must have a certain capacity to be shaped into packaging, and be capable of providing mechanical protection for the packaged food conservation and transportation. The material must also have certain transfer properties, i.e. a capacity to allow/slow down the transfer of gas and/or water vapour molecules through the packaging in order to limit the degradation of the food, and to preserve its nutritional, sanitary and organoleptic properties. Finally, the most important polymer constraint is the regulatory health aspect.

This safety aspect imposes to the material a certain inertia towards the food in order to guarantee the safety of the consumer as explained below. All these requirements will strongly depend on the specificities of the packaged food. Indeed, a packaging for strawberries will not have the same constraints and requirements as a packaging for cookies.

1.2. Regulation framework

Plastic materials and articles intended to come into contact with food are subject to specific regulations. First of all, all Food Contact Materials (FCMs) must be manufactured following the Regulation (EC) 2023/2006 (about the good manufacturing practices), which requires the establishment of a quality assurance system for the manufacture, processing and distribution of materials and articles intended to be in contact with food [19]. In addition, Europe has a harmonized legal framework for the safety of FCMs with the Regulation (EC) 1935/2004 whose main purpose is to define the principle of inertness required for all materials intended for use in contact with food [20]. The Article 3 of this regulation states that these FCMs cannot release constituents into food at levels which may endanger human health or involve changes in the composition, smell or taste of the food. These constituents involve any substance of the packaging such as polymer constituents, additives, fillers or neo-formed compounds. Regulation (EU) 10/2011 translates the requirements of Regulation 1935/2004 to plastics, by setting out the specific conditions for compliance testing and the maximum permitted migration limits [12]. Article 5 of this regulation states that only substances included in the Union list for authorized substances may be intentionally used in plastic materials intended to be in contact with food. These substances are submitted to an overall migration limit stated in Article 12 and to a specific migration limit stated in Article 11, with restrictions and specifications in the Annex 1 of the regulation. For additional precisions, this regulation extended FCM to the following categories: (I) (part of) materials exclusively from plastics, (II) plastic multi-layer materials held together, (III) materials that can be printed and/or covered by a plastic coating, (IV) plastic coatings or layers, forming gaskets in caps and closures and (V) plastic layers in multi-material of multi-layer materials. At present, bioplastics (both biobased and biodegradable) are considered to be the same as petroleum-based synthetic plastics and are not subject to any specific guidelines or recommendations. Therefore, like all

other plastic materials intended to be in contact with food and entering the European market, they must comply with the requirements of these three regulations.

1.3. Single use plastic pollution and official initiatives

Rapidly increasing production of single-use plastic products overwhelms the world's ability to deal with them, with the emergence of severe environmental consequences. In 2019, 17.8 MT of food and drink packaging were collected in Europe, with 18.5 % landfilled, 39.5 % incinerated and 42 % down-cycled, while the non-collected waste is still accumulated in the environment [14]. Plastic incineration generates toxic emissions, carbon dioxide and methane, which contribute to worldwide climate change [21] and air pollution. But the crucial consequence of linear plastic waste management is the persistent and invasive particles pollution interfering with our ecosystem and entering in food-feed chains. Plastics that are not incinerated are doomed to persist for centuries, slowly fragmenting into micro and nano-particles. These particles are able to absorb and transport ubiquitous organic pollutants and to diffuse in all environmental compartments including air, water, and living being's organs (by translocation) [22, 23]. Then numerous public and private initiatives are implemented to develop a plastic circular economy.

Over the past decade, more and more EU initiatives and regulatory measures to reduce the environmental impact of single-use plastics have been put in place. Indeed, because of the problems related to their accumulation, Directive (EU) 2019/904 prohibits the marketing of plastic straws, plates and cutlery for single use in the EU, since July 2021 [24]. Products made from oxo-degradable plastic are also concerned. Also, this directive set out forecasts for better recycling of bottles with the objective of a selective sorting of 77% of plastic bottles in 2025 and up to 90% in 2030. By the same deadline, bottles will have to be made from at least 30% recycled plastics. In addition, EU has claimed that an important target is to reuse or recycle all plastic packaging entering the European market by 2030 [25]. Last April, the French government published the 3Rs strategy (Reduce, Reuse, Recycle), which calls for the extension of reuse and recycling to all types of single-use plastics, with a priority on food packaging aiming for even more ambitious targets than those set in Europe [26].

All of the above safety requirements are applicable to recycled plastics intended to come into contact with food. Thus, closed-loop mechanical recycling for food packaging applications is regulated by the Regulation (EU) 282/2008 [11]. Excluded from this regulation are materials recycled from plastic products not used on the manufacturing site, or recycled materials intended to be used behind a plastic functional barrier (in compliance with Directive 2002/72/EC now repealed by the regulation 10/2011/EC). Recycled plastic materials can only be on the EU market if they contain recycled plastic obtained from a recycling process which has already been authorized according to Regulation (EU) 282/2008 (Article 3). This authorization requires that (1) the raw material meets the requirements of the plastic FCMs and that (2) these raw materials come from a closed circuit free of contamination or that it is demonstrated that the process is capable of reducing such contamination to a level that does not pose a risk to human health. To meet these requirements, the European Food Safety Authority (EFSA) has published guidance on the submission of a dossier for the safety assessment of a recycling processes [13]. To date, only PET-based materials have been the subject of a scientific opinion on the criteria to be used for safety evaluation of a mechanical recycling process for manufacture of materials in contact with food [27]. This safety evaluation is investigated by conducting “challenge tests”, whose principle is detailed in the last part of this chapter.

1.4. Bioplastics as alternatives

As mentioned earlier, at present, almost all national and European initiatives to combat plastic pollution are focused on recycling. Nevertheless, it should be noted that the term “recycling” is most often improperly used for plastic as large-scale recycling such as mechanical recycling, is not applicable an unlimited number of time. The quality of the recycled plastic decreases after the first treatment cycle and the best recyclable plastic such as PET is doomed to end quickly as a persistent waste[28, 29]. Processes called “recycling” are most often “down-cycling” or “re-using loops” since the process is not part of a closed loop of upgrading. The development of biodegradable plastics to substitute persistent conventional petrochemical plastics gives hope that such environmental and health problems might be solved or at least reduced. Biodegradation ensures that the waste is fully converted in a reasonable time into harmless molecules such as carbon dioxide and water, being able to reintegrate the carbon cycle

via the photosynthesis[30]. Biodegradation means that no persistent particles of plastic waste will jeopardize our eco-systems and health in the future in many possible ways including their uptake, accumulation in organs or pollutant transport. However, up to now, biodegradable plastics are contrasted with recycled plastic. Recycling and biodegradation are considered as two separate and not compatible end of life options, which is not clearly supported by any scientific data. It is time to move beyond these bias and to consider that the recycling of biodegradable polymers could advantageously upgrade their biodegradation in a complementary way. On this basis, the waste hierarchy applied to the specific case of biodegradable packaging materials can be considered according to the prioritization model presented in Figure 5. Beyond the question of carbon savings, each pathway is associated with a time scale for which thermo-mechanical recycling technologies appears most valuable because of their convenience compared to the more expensive and time-consuming chemical recycling technologies[31].

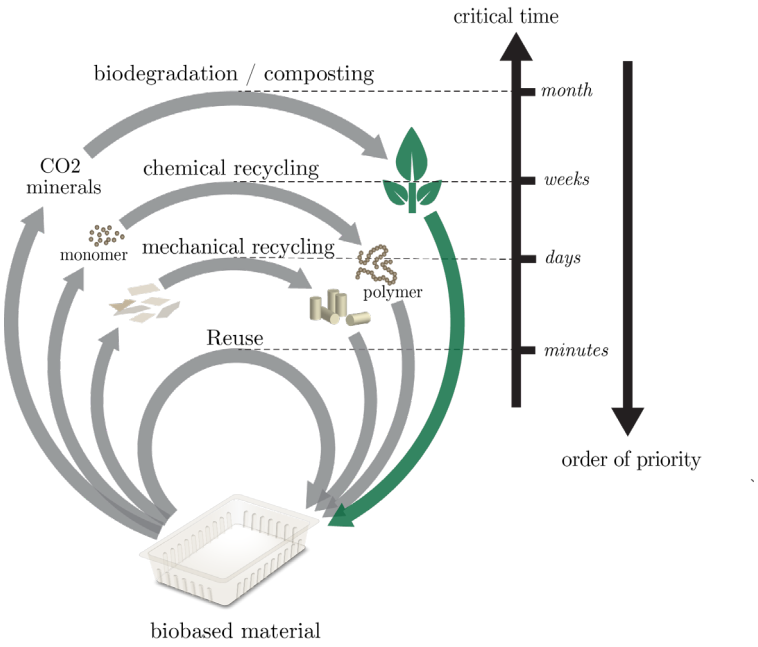


Figure 5. Waste hierarchy approach applied to biodegradable packaging materials

In order to clarify the recycling ability of existing biodegradable plastic, the current review was undertaken. Our long-term vision is to contribute to resources saving while avoiding the production of persistent plastic waste, by promoting re-using loops of biodegradable plastic before biodegradation.

Biodegradable and compostable polymers were classified into four categories[32] (I) naturally occurring polymers such as starch, cellulose, proteins… ; (II) biopolymers produced directly by natural or genetically modified organisms, such as microbial polyesters ; (III) polymers obtained from the conventional/chemical transformation of bio-based monomers, such as PLA ; (IV) polymers chemically synthesized from fossil-based monomers. A large number of biodegradable and compostable polymers have been produced recently and many of them are promising candidates to replace fossil-fuel-derived plastics in different applications. Among them, polyesters such as polylactide acid (PLA), polyhydroxyalkanoates (PHAs), bio-polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) are undergoing a dynamic development[33, 34] (figure 6).

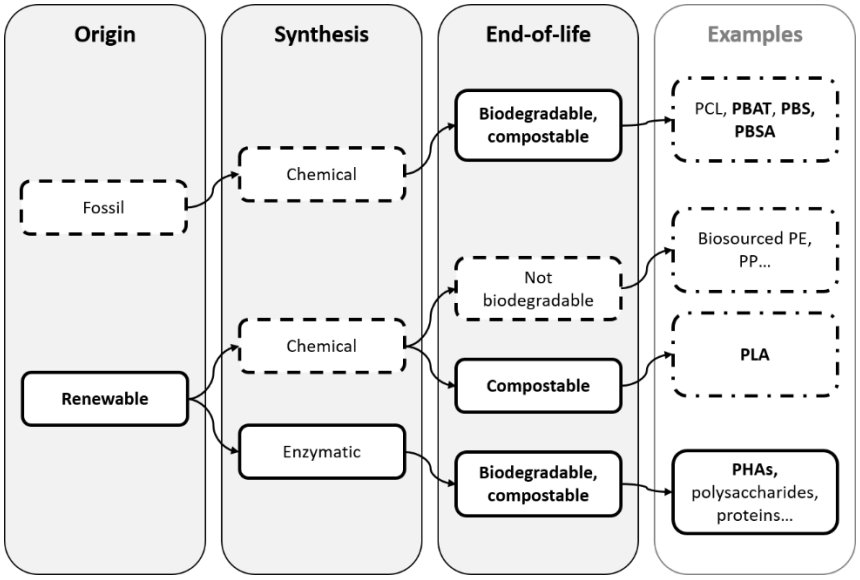


Figure 6. Main groups of bioplastics according to Berthet[34].

According to European Plastics, the global capacity of bioplastic production was 2.11 million tons in 2019 (accounting for about 1 % of plastics produced) and is forecasted to reach 2.44 million tons in 2024[15]. The global PLA market was estimated to 300 Kt in 2019, and is expected to reach 330 Kt by 2024 [35]. Current global production of PHAs is about 25 320 tons which account for 1.2 % total bioplastics compared to 13.4 % for PBAT and 4.3 % for PBS. However, due to its significant growth, it is expected to reach 6.6 % of total bioplastic production in 2024[36, 37]. Thanks to technological advances in the productivity and functionality of PLA, several large companies such as McDonald's®, Bayer, DuPont, Nike, Danone... have already started to integrate its containers and packaging into their

products[38, 39]. For instance, Danone® is changing their yogurt cup from conventional PP to PLA, improving their packaging carbon footprint by 25 % and DuPont® PLA materials are used in the production of cups, trays and films. This, together with the growing consumer demand for biodegradable plastics[40] is causing the production of these polymers to take off and probably exceed estimates.

As a consequence, biodegradable/compostable polymers will be increasingly used for common application like bottles, trays, packaging, etc. Hence, they would likely end up in waste streams and composting facilities which could not assimilate increasing flows of these polymers. Furthermore, Gioia et al. reported that biodegradation and composting of biodegradable plastics should be restricted to specific applications[41]. For example, biodegradation of agricultural mulch film where material fragmentation leads to soil contamination, or composting of food waste collection bags where separation between organic matters and plastics is not possible. For all these reasons, it would be advisable to promote solutions offering the possibility to extend the service lives of these materials, or to obtain added value before finally discarded them into biodegradable products facilities.

Previews reviews have focused on mechanical and chemical recycling of PLA and PLA derivatives[42-45]. This review covers the studies dealing with the mechanical recyclability of the main promising biodegradable polyesters PLA, PHAs, PBAT and PBS within the last ten years. A deep focus is given to relationship between chemical structure and polymer macroscopic properties during reprocessing steps. With a view to the potential use of these biodegradable polyesters as food packaging, their decontamination ability will be discussed. The limitations likely to be encountered by the bioplastics recycling sector, and some challenges to be faced in the future will be presented.

2. End-of-life and life cycle assessment (LCA)

Different end of life (EOL) channels for plastic waste are now in place. (I) Landfilling is one of the oldest waste treatments based on the burial of post-used plastic.[46]. (II) Incineration. The aim of this technology is to produce energy from plastic waste, since the calorific value of plastics such as polyolefins or polyvinyl is similar to that of fuel or oil used for its production[47, 48]. (III) Mechanical recycling includes waste sorting, size reduction, cleaning (or decontamination) and polymer

remodeling[49]. This process is called primary recycling or closed-loop recycling and implies that performances and functionality of recycled materials are equivalent to the original virgin plastic (With a regular supply, only the recycling of PET and HDPE bottles is economically viable today[50]). The technology that currently prevails is secondary recycling (down cycling) which leads to a product with lesser value than to original plastic[51]. (IV) Chemical recycling, or tertiary recycling, involves the degradation of the polymer chain into monomer units (depolymerization) or randomly ruptured fragments (oligomers). The chain rupture is carried out either by solvolysis or thermodegradation (pyrolysis)[52, 53].

Several studied have examined the environmental burden of the existing waste management options for both biodegradable and non-biodegradable plastics, based on the assessment of carbon footprint and the use of nonrenewable energy. For all plastics, mechanical recycling seems to be the favorable option, especially when it produces virgin-quality recyclates [9, 54-58].

K. Changwichan et al.[8] have implemented eco-efficiency (E/E) indicator to compare landfilling, composting, mechanical recycling and incineration of takeaway food boxes made from PLA, PHA or PBS. E/E indicator is recognized as a single indicator which includes both economic and environmental aspects, with a view to increasing economic benefit while reducing environmental impact. Out of the four end-of life (EOL) options, 100 % mechanical recycling showed the highest E/E values for all the bioplastic boxes. This high E/E value is mainly due to the avoidance of bioplastic production step which is responsible for negative environmental impacts (eutrophication, acidification, land use…) and high costs. For the three polyesters tested, recycled PLA showed the highest E/E followed by PBS and PHA. In other words, the mechanical recycling of these polyesters and particularly PLA has shown a lower environmental impact and a higher economic benefit compared to the other EOL scenarios.

LCA analyses also support this outcome particularly because of the carbon savings that such a process can provide. Rossi et al.[59] concluded that landfill and industrial composting of PLA result in the worst environmental impact compared to mechanical recycling. This can be explained by the fact that recycling technology allows the polymer to be regenerated and reused, while composting leads to its replacement which is associated to the impact of the whole production process again (figure 7) [9].

Even within recycling processes, chemical recycling has shown higher impacts due to the environmental burden associated with the re-polymerization step[60]. As an example, mechanical recycling spends 1.60 MJ of fossil energy to produce 0.96 Kg of PLA, which is 4 times lower than energy used for recycling the same amount of PLA through chemical process[9].

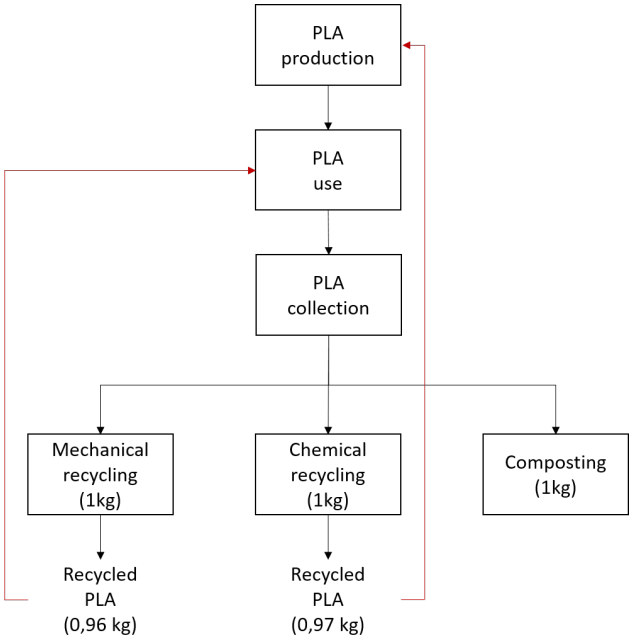


Figure 7. PLA conversion yield through different end-of-life options according to Cosate de Andrade et al.[9].

It is important to note that none of LCA studies has considered the deterioration of material properties within the mechanical processing and no standard test methods for the evaluation of the quality of the resulting recyclates have been developed. Thus, LCA identifies mechanical recycling as the preferred option in the short term over other waste management techniques, but the possibility of recycling the polymer by chemical or organic processes (AD, composting) could be useful in the long term (after several cycles of mechanical treatment). Today, LCA analyses do not provide a clear answer as to the combination of different end-of-life scenarios to reduce the environmental impact of biodegradable materials[61].

The study of degradation mechanisms during mechanical reprocessing and potential unlocking of these issues are the topic of the next part.

3. Mechanical recycling: reprocessing ability of biodegradable polymers

From a technical point of view, mechanical recycling which requires low investment, is an eco-friendly technology and is relatively simple to set up and applied. However, it often results in products whose properties are much poorer than those of the starting material. The degree of deterioration of the polymer properties as a function of the reprocessing cycles is an important techno-economic criterion which defines the recirculation potential of the material through mechanical recycling[31]. This section will first shed light on the impact of mechanical recycling on the structure and properties of PLA, PHA, PBS and PBAT, with a focus on degradation mechanisms of these polyesters (Niaounakis et al. reported the patents related to the mechanical recycling of aliphatic polyesters, but these patents only focus of the mechanical recycling of PLA[62]) . Then, the different methods that have been attempted to improve the properties of recyclates will be examined. It should be noted that no industrial recycling process has been implemented yet for this type of plastic. Hence, in all the studies presented herein, the term "recycling" refers to the material reprocessing, by means of extrusion or compounding, at lab scale.

3.1. Impact of the mechanical recycling on structure-properties of biodegradable polyesters

It has been noted that the majority of articles devoted to the mechanical recyclability of these "biodegradable" polyesters focus on PLA, probably due to the relative maturity of its production technology and its better establishment in the plastics market, compared to other biodegradable plastics. Although we reported, in an almost exhaustive way, all the articles published, in this field, on the four mentioned polyesters, we worked exclusively during this thesis on the recyclability of PHAs, and more particularly of PHBV. There were two main reasons for this choice. First, PHAs are biobased polymers, produced in nature by bacterial fermentation. They are biocompatible and with good barrier properties, making them good candidates to replace conventional plastics in food packaging applications. Second, PHAs are fully biodegradable in natural environments. Unlike PLA and PBS, they are completely mineralized in soil within a short time, and are the only polymers that have shown degradation in marine environments [63]. Even after cycles of reuse and recycling (which should be investigated), their ultimate end-of-life option is to return carbon to the soil or the environment, without any hazardous

consequences. Although the diffusion of PHAs is currently limited by their high cost, several initiatives are being taken to overcome this problem, such as the use of agricultural residues as raw material, or the optimization of extraction and purification processes [64]. Today, the Chinese producer Tianan® produces good quality PHB and PHBV for researchers.

3.1.1. Mechanical recyclability and degradation mechanisms of PLA

PLA is a biopolymer obtained from the polycondensation of lactic acid or from the ring-opening polymerization of lactide (a cyclic dimer of lactic acid). PLA monomer derives from the fermentation of sugar feedstock, corn, etc, with a predominance of L-isomer in nature. Commercial PLA with high crystallinity is generally based on a 100 % L-lactide isomers. The co-polymer with a few proportion of the D-lactide isomer is rather amorphous[18, 65]. The two largest producers of PLA are NatureWorks and Mitsui Chemical, although some others companies produce smaller outputs. PLA presents optical and mechanical properties generally considered as similar to those of PS and PET and is approved by FDA for food-contact application [66]. PLA is widely described as a biodegradable plastic. However, this polymer is less susceptible to environmental degradation than other aliphatic polyesters. It was evidenced that its degradation is mainly due to abiotic hydrolysis rather than to microbial attack[67]. For this reason, PLA can only degrade under industrial composting conditions, including anaerobic conditions and elevated temperatures[68, 69].

The mechanical recycling of PLA has been investigated at lab-scale by means of injection[44, 70, 71] and extrusion[72-74] , during one[75], three[73], five[76], and ten[74] processing cycles. All studies showed a gradual decrease in M_w, which enhanced the mobility of the polymer chains and increased crystallization during cooling[76]. The cold-crystallization (T_{cc}) can be decreased down to 10 °C from the initial values, due to the liability of recyclates to nucleate crystalline domains, at lower temperatures, as a consequence of the presence of shorter chains generated by the degradation[42]. However, the influence of successive reprocessing cycles on glass transition temperature (T_g) and melting point (T_m) of PLA remained very limited.

With regard to changes in mechanical properties during reprocessing, various results have been reported. After seven injection cycles, Pillin et al.[71]observed that neither material strength in elastic

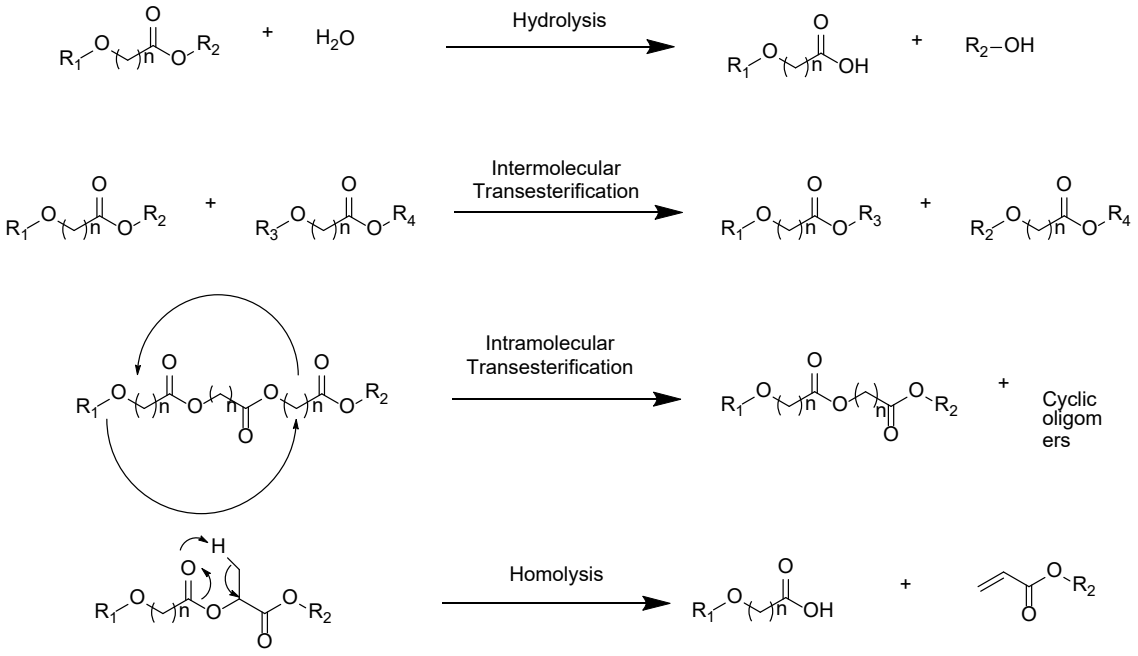
domain, nor tensile modulus were affected by the thermomechanical treatment. Tensile modulus value remained constant as the potential decrease in M_w was probably balanced by the increase in crystallinity. However, stress and strain at break decreased from 66 MPa to 25 MPa, and from 6 % to 0.8 %, respectively. In contrast, Zenkiewicz et al.[74] showed a slight decrease of 8.3 % for stress at break and an unchanged strain at break after ten extrusion cycles. This was confirmed by Badia et al[70]. and Lopez et al. [44] studies which reported that no significant modifications occurred in stress-strain at break of PLA over five reprocessing cycles. These variations between studies could be attributed to the variation in the ratio of D/L lactide isomers in PLA. In general, PLA reprocessing affected the macroscopic mechanical properties, resulting on materials with increased brittleness and stiffness[70, 71, 74].

By investigating water vapor and oxygen transmission rates versus extrusion number, it has been observed that permeability through PLA films significantly rise with the extrusion number. After ten extrusion cycles, the relative increase of transmission rates of water vapor and oxygen were 39 % and 18 %, respectively[74].

The influence of the washing step on properties of PLA recyclates was pointed out by Beltràn and coworkers[77]. In order to approach the real conditions of mechanical recycling, virgin PLA samples were first subjected to an accelerated aging process including photochemical and thermal degradations. Then, a portion of these samples was washed with a sodium hydroxide aqueous solution. Finally, all the samples were reprocessed by extrusion and compression molding. After one cycle, the recycled PLA, without washing step presented a small decrease in the intrinsic viscosity in comparison with the virgin polymer (around 5 %). However, the intrinsic viscosity of the washed PLA was 20 % lower than that of virgin PLA and 16 % lower than that of recycled PLA without washing. This suggests that different factors contribute to the structural degradation of recyclates, including ageing, chemical washing and thermomechanical treatment.

Other studies questioned the influence of thermomechanical multi-processing on microbial degradation of PLA and it was found out that PLA recyclates are still industrially compostable after several cycles[73].

During thermal processing, PLA polymer is mainly subjected to chain scission reactions leading to a decrease in molecular weight and an increase in cold crystallization. Generally, the thermal degradation of PLA follows the postulated mechanistic routes of polyesters which are: (I) hydrolysis; in the presence of water; the cleavage of the ester linkages giving rise to carboxylic acid and hydroxyl linear oligomers. (II) intramolecular transesterification leading to the formation of cyclic or linear oligomers. (III) intermolecular transesterification which interchange ester units between different chains causing a variation in M_w distribution. (IV) homolytic chain scission at temperatures above melting[78] . The analysis of PLA recyclates by MALDI-TOF-MS revealed that the repeated thermomechanical treatments resulted on hydrolytic and homolytic chain rupture along with intermolecular transesterification mechanisms[78] . Mechanical forces taking place during the reprocessing (e.g. shear and elongation deformation during extrusion cycles) are converted in additional heat input, enhancing thermal degradation[78, 79] (Figure 8). In the presence of oxygen, the thermo-oxidative degradation is governed by intramolecular transesterification in first stage and radical degradation in the second stage initiated by the lowest dissociation energy of tertiary CH bond[80].



The most reported degradation products for PLA, PHA, PBS and PBAT

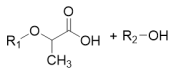
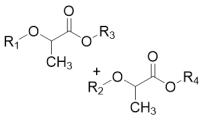
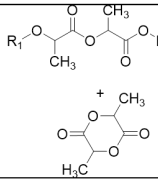
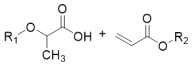
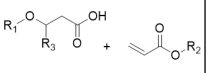
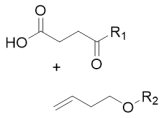
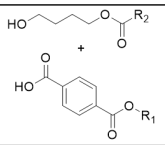
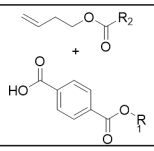
Mechanism / Polymer	Hydrolysis	Intermolecular transesterification	Intramolecular transesterification	Homolysis	Reference
PLA					46, 47
PHA PHB: $R_3 = CH_3$ PHBV: $R_3 = CH_2\text{-}CH_3$	——	——	——		58, 60, 65
PBS	——	——	——		77
PBAT		——	——		81

Figure 8. Thermal degradation mechanisms of aliphatic polyesters.

3.1.2. Mechanical recyclability and degradation mechanisms of PHAs

PHAs are a family of biopolyesters, produced by bacterial fermentation of sugars and lipids. This class of polymer includes a variety of molecular structure depending on the type of bacteria, the monomer used as substrate and the process parameters. The most widespread PHAs are the homopolymer polyhydroxybutyrate (PHB) and the copolyester polyhydroxybutyrate-co-hydroxyvalerate (PHBV)[81] (table 1). Some companies such as Tianan (China), Kaneka (Japan), Telles (USA) and Cheil Jidang (South Korea) produce PHAs at industrial scale, from 2,000 to 50,000 tons/year[82]. For the time being, PHAs represent a low volume of the biopolymer market but they are attracting commercial interest[83], as they exhibit thermomechanical properties close to those of polypropylene. PHAs present good barrier properties against oxygen and water vapour (table 2), compliance with food contact material regulations and biocompatibility, making them suitable for food packaging applications[18, 82]. In natural environment such as soil, lake water and marine water, PHAs

degrade in 5-6 weeks into water, carbon dioxide and biomass[16, 84]. However, global use and industrialization of PHAs are still limited due to the high production costs, inducing high price.

Table 1. Mechanical properties of PHAs depending of HV content. [85-87]

	Mechanical properties		
	Tensile strength (MPa)	Elongation at break (%)	Young Modulus (GPa)
PHB	40	6	1.7 – 3.5
PHBV 3%	39	6.2	1.2
PHBV 10 %	25	20	1.2
PHBV 20%	20	50	0.8

Table 2. Water vapour and oxygen permeability of some plastics used in packaging. [86, 88]

	PWV x 10^{14} ($g.m.m^{-2}.s^{-1}.Pa^{-1}$)	PO2 x 10^{17} ($mol.m.m^{-2}.s^{-1}.Pa^{-1}$)
PHB	11.4 – 57.1	0.95 – 4.75
PHBV	11.4 – 34.3	2.38 – 6.65
PLA	57.1 – 80.0	7.13 – 11.9
LDPE	6.7 – 8.7	23.8 – 95.1
HDPE	1.7 – 3.5	12.5 – 46.8
PET	5.8 – 22.9	0.48 – 2.38
PP	2.3 – 4.6	23.8 – 47.6
PS	11.3 – 45.6	47.6 – 71.3

Unlike PLA, only few studies have been carried out on the mechanical recyclability of PHAs probably due to their good biodegradability and their still limited market share. PHAs are known to be very sensitive to thermal degradation during melt processing due to the narrow temperature window between melting and degradation temperatures. PHB decomposes easily near its melting point[89]. After several grinding or extrusion cycles, there is a rapid decrease in molecular weight associated with a dramatic drop in viscosity at temperatures just above its melting point[90-92]. As consequence, significant change in mechanical properties was observed. After the third cycle, tensile strength decreased above 50 % and elongation at break has declined so much that it impeded further extrusion[91]·[93]. However, neither Young's modulus, nor melting and glass transition temperatures were affected by heat treatments.

The random β-elimination scission has been widely regarded as the main degradation mechanism of PHB, based on a typical structures of degradation products, namely crotonic acid and oligomers with crotanate end-groups (Figure 4)[94]. Later on, an E1cB (**E**limination **U**nimolecular **c**onjugate **B**ase) elimination mechanism proceeding via α-deprotonation by a carboxylate anion to

produce the same products was proposed[95]. β-elimination scission and/or E1cB elimination produce a large number of carboxylic compounds which would auto-catalyze the random degradation. These carboxylic compounds randomly attack ester groups on polymer chains to induce transesterification reactions, resulting on the reproduction of carboxyl groups associated with a remarkable decrease in molecular weight[10].

The auto-acceleration of the random degradation is dependent on carboxylic groups self-proliferation in bulk. The unzipping reaction occurring at the end of molecules is a 0^{th}-order reaction, just kinetically favored scission of polymer chains that repeatedly generate a large number of crotonic acids. This is an ideal self-proliferation reaction of carboxyl compounds and is the key factor in the auto-accelerated random degradation[96, 97] .

The mechanical recyclability of PHBV with different % valerate was tested at laboratory scale in two studies. Zembouai et al.[98] monitored the behavior of PHBV with 3 % HV content, during 6 extrusion cycles at 180 °C. Zaverl and coworkers[99] investigated the effect of 5 extrusion cycles, at 170 °C, on properties of PHBV with 14 % HV content. They both reported a decrease in M_w (22,9 % for PHBV-3 %, after 6 cycles and 16,6 % for PHBV-14 %, after 5 cycles). It was observed that the mechanical properties (tensile strength, elongation at break and toughness) slightly decreased in the case of PHBV-3 %, making it a little more brittle after multiple processing cycles, while PHBV-14 % maintained its mechanical properties up to the fourth cycle. Thermal properties did not change during reprocessing, except for melting enthalpy of PHBV-3 %, which increased by 9 %. This is due to the decrease in M_w which enhances the polymer chains mobility and induces higher crystallization. The increase of the amount of valerate (up to about 10 %) leads to a decrease of copolymer melting point (172 °C for PHBV-3 % against 156 °C for PHBV-14 %), which results in improvement in ductibility and flexibility and enhancement of its workability and thermal stability.

As for PHB, the degradation mechanism of PHBV is dominated by a random β-elimination reaction involving a six-membered ring transition state[10, 100]. For both PHB and PHBV, the presence of oxygen did not induce or accelerate the degradation reactions at melting temperature[101].

3.1.3. Mechanical recyclability and degradation mechanisms of PBS

PBS is a biopolymer produced from the condensation of succinic acid and 1,4-butadediol. In the past, PBS was exclusively obtained from fossil raw materials, but can be now entirely biobased thanks to the production of its monomers by bacterial fermentation, succinic acid and 1,4-butanediol resulting respectively from the fermentation of sugars like glucose and dextrose[102, 103]. Companies producing PBS in commercial scale of 20,000 tons/year are Mitsubishi Chemicals, Hexing Chemical and Xinfu Pharmaceutical[89]. PBS mechanical properties present similarities with those of PP and PE, with a melting point exceeding 100 °C which proved to be suitable for applications requiring high temperatures. Its copolymers PBSA and PBST show higher flexibility, making them potential candidates for a wide panel of food packaging applications[89]. According to the European standard DIN EN 13432, PBS is biodegradable and compostable[104, 105]

The mechanical recycling of polybutylene succinate (PBS) was simulated by repeated polymer extrusion for up to seven times, followed by granulation[106]. In such conditions, the Melt Flow Rate (MFR) of PBS doubled already after one reprocessing cycle. This correlated with GPC analysis results, which showed a significant decrease in M_n (virgin 78832, after 7 cycles 57866) and M_w (virgin 156157, after 7 cycles 119796). PBS structural degradation resulted on decrease in tensile strength and strain at break by up to 24 % and 32 % respectively. At ambient temperature, Young's modulus showed a marginal increase with the increasing number of reprocessing cycles (increase by maximally 7 % of the initial value) and no impact was observed on storage modulus. These results may be related to general soft and flexible material features in this temperature range. Thermal parameters such as glass transition and melting temperatures were not altered by repeated treatments. However, a change in the shape of the melting peak has been noticed. A distinct double peak was observable for virgin PBS, which is most probably caused by polymorphism and may also involve a melt-crystallization. In comparison, the reprocessing yielded a single melting peak with a preceding exothermal effect. Others studies report the same changes of melting peak with decreasing of PBS molecular weight[107].

In other studies dealing with PBS reprocessing by means of 3 cycles of compression[108] and 5 cycles of extrusion[109], viscosity and M_w of polymer were found to decrease after the first extrusion run. However, they strongly increased thereafter[108]. Also, a decrease in crystallinity was

observed[109]. This was attributed to the occurrence of branching/recombining reactions that increased the viscosity and disrupted the regularity of polymer chains.

Degradation mechanism of PBS within multiple processing cycles was not investigated. Only few studies have examined the mechanism of PBS thermal degradation in absence and presence of oxygen[110, 111]. Without oxygen influence, The thermal degradation of PBS is mainly governed by β-elimination mechanism[112]. Rizzareli and co-workers[111] investigated the thermo-oxidative degradation of PBS under atmospheric air at 170 °C for up to 6h. The structure modification and oligomer end-groups produced during polymer degradation were identified using MALDI-TOF-MS analysis. It contributed to establish the global degradation mechanism, described in figure 9. The initial step consists of a hydrogen abstraction from the methylene group adjacent to the ester linkage, leading to the formation of an hydroperoxide intermediate. Unstable hydroperoxide derivative undergo elimination of hydroxyl radical to produce oxy radical which can decompose into oligomers with different end-groups through different routes. A comparison with PBS behavior under nitrogen confirmed that oxygen is a key parameter in the degradation process.

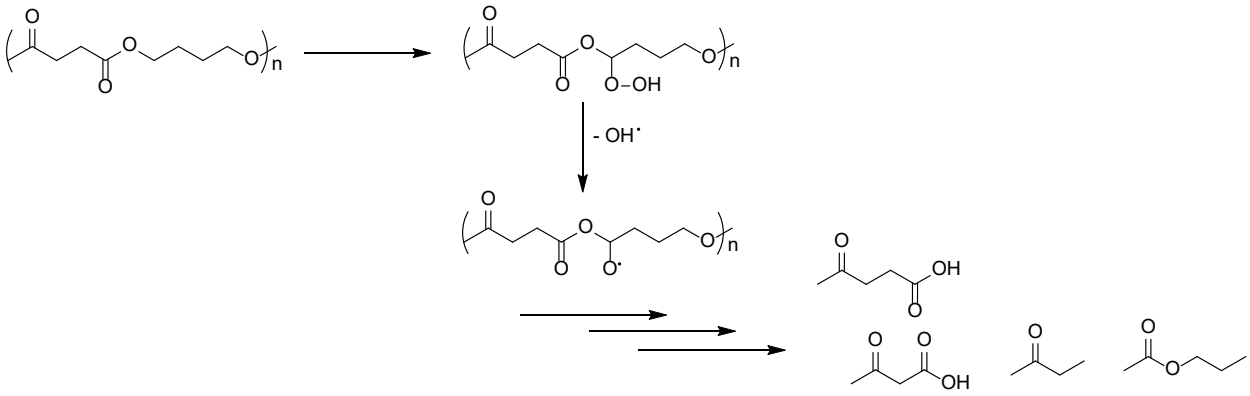


Figure 9. Overall thermal-oxidation processes in PBS according to Rizzarelli et al.[111].

3.1.4. Mechanical recyclability and degradation mechanisms of PBAT

PBAT (poly(butylene-adipate-co-terephtalate)) is an aliphatic-aromatic co-polyester, synthetized by polycondensation of 1,4-butanediol (BDO) with both adipic and terephthalic acids (AA and PTA). It is mainly produced by BASF (Germany), KINGFA (China) and Novamont (Italy) at a rate of less than 60,000 tons/year[113]. Although PBAT is synthesized from fossil-based derivatives, it can

cover a wide range of packaging applications as it exhibits properties similar to those of low density polyethylene thanks to the aromatic unit in the molecule chain[114], and it completely biodegrades in soil[115]. Despite this, expending PBAT producing is still hampered by its high production cost (between PLA and PHAs) and low thermomechanical resistance. One of the strategies to improve the mechanical properties of PBAT is the increasing of the terephthalate content. However, a specific ratio between terephthalate and aliphatic components (30-50mol% of terephthalate units) should be respected in order to maintain the biodegradability of the polymer [41, 114]. Because of its relatively poor performance, very few studies have been conducted on the PBAT recycling. Scaffaro et al. found that the addition of organoclays to PBAT polymer under UV irradiations enhances the polymer crosslinking, leading to the formation of porous structure, which can be further used for the production of high-value Materials. In this case, also, the biodegradability of the material is affected[116]. The thermal degradation of PBAT is mainly governed by an oxidative chain scission as discussed in several studies. Thus, after extrusion at 180, 190 and 200 °C[117] or after processing on a torque rheometer at 180 °C and 200 °C for 10 min[118], a decrease in molecular weight and viscosity was observed, indicating the thermodegradation of PBAT governed by scission chain reactions probably competed with cross-linking reactions (figure 4). Chaves and Fechine[118] reported an increase of absorbance at 400 nm of PBAT solution after processing at 180 or 200 °C, which may be due to an increase of chromophore groups or cross-linking in polymer. The same processing under nitrogen flow[117, 119] and/or with the use of antioxidants additives[118] showed a lower reduction in molecular weight and viscosity, which confirms the influence of oxygen in the degradation process. Chain scission mechanisms of PBAT were proposed by Al-Itry and coworkers[117] as depicted in figure 4.

On the other hand, a study reported by Signori and Bronco[119] revealed that processing PBAT in a mixer at temperature range of 150 °C - 200 °C during 10 min did not affect the molecular weight and thermal properties of the polymer. This may be attributed to the relatively mild processing conditions compared to the other studies.

3.2. Tentative to upgrade polyesters properties during mechanical recycling

Although the treatments described above do not simulate realistic conditions of the mechanical recycling process, the various studies highlighted the structural degradation of PLA, PHA, PBS and PBAT under the influence of thermal, thermomechanical and thermo-oxidative treatments.

In order to prevent or minimize degradation during these "recycling" processes, different strategies have been considered including thermal and chemical treatments, or the production of blends, bio-composites or nanocomposites based on bio-polyesters.

3.3. Thermal and chemical treatments

Several studies have examined the potential effect of some thermal and chemical treatments on the improvement of PLA properties after reprocessing. By choosing appropriate temperatures between 75 °C and 135 °C range, it is possible to modify the amorphous-to-crystalline ratio of PLA during processing. Thus, Carrasco et al.[75] and Nascimento et al.[120] subjected PLA samples, previously extruded and injected during one cycle, to thermal annealing at 120 °C during 6h. The resulting increase of crystallinity induced an increase of Young modulus and yielded strength, while a decrease of elongation at break was observed. The use of additives is a common strategy to improve the material processability. Since the thermal degradation mechanisms of biopolyesters are often enhanced by the presence of oxygen, many studies investigated the addition of antioxidants to stabilize them during recycling. These antioxidants may have the capacity to trap free radicals, limiting oxidative phenomenon and maintaining thereby polymer chain length. For instance, the addition of quinones or tropolone to PLA at 200 °C, under air, led to the effective stabilization of thermal and mechanical properties[71, 121]. Typical antioxidant stabilizers (Irganox® and Irgafos®) were also added to PBS[109] and PBAT[118]. The thermo-mechanical degradation was suppressed for PBS and strongly reduced for PBAT. Properties of recycled PLA was significantly improved by the use of phosphites [122, 123]. The use of chain extenders and branching agents by reactive extrusion has also proven its efficiency. The addition of multifunctional epoxides to PLA[117, 124, 125] or PBAT[117] contributed to the stabilization of molecular weight of these polyesters, improving thereby their mechanical, thermal and rheological properties.

3.4. Polymer blends

Since this review is specifically dedicated to biodegradable polyesters, blends made by adding non-biodegradable polymers are not discussed here and the focus is on the interest of blends combining virgin and recycled polymers sources.

The properties of blends made up of cleaned post-consumer PLLA bottle flakes and virgin PLLA resin were assessed[126]. After cleaning, blends were extruded and thermoformed into trays, to be then characterized. Up to 40 % PLLA recycled content, no significant difference was observed in M_w, thermal and mechanical properties of blends with just slight difference in sheets color.

La Mantia et al. [127] investigated the effect of five extrusion cycles on the thermal, rheological and mecanical properties of PLA/PBAT blend (45:55 wt%). Througout the processing cycles, an increase in the visosity was observed and correlated with the presence of branched macromolecules in PBAT. Regarding the mecanical properties, the elastic modulus increased while the elongation at break decreased with the number of extrusions, due to the decrease in molecular weight and the increase in crystallinity mainly in the PBAT phase. However, the five extrusion cycles did not significantly affect the thermomechanical properties of the blend, indicating that it can withstand more reprocessing cycles.. The addition of PBS to PLA to improve its thoughness and crystallization has been widely studied. These blends offer specific material properties. However, their favored biphasic composition, mainly leads to a restriction of their applications [128]. Thus, in PLLA/PBS blend (50:50wt%), PBS nodules were included in PLLA matrix, acting as crystallization nuclei agents. After seven injection cycles of the blend, an increase of the crystallinity and a drop of the elongation at break were observed, and correlated with PLLA degradation. On the other hand, Young's modulus and the tensile strength remained relatively stable [129].

The melt molding recycling of PLA/PHBV (50:50 wt%) blend was studied by Zembouai et al.[98] up to six repeated processing cycles. Mn value of the blend was only reduced by 4.8 % after six reprocessing cycles and the stability was relatively improved compared to the neat PHBV. Mechanical properties were maintained after processing cycles as tensile modulus and strain at break did not significantly change. However, the crystallization enthalpy of the blend increased from 32.9 J g-1 in the first cycle to 46.5 J g-1 after the sixth one, reveling a decrease in the molecular weight of PHBV

which enhanced the polymer chain mobility and the crystallization kinetic. The addition of PLA may be a promising route to the thermomechanical stabilization of PHBV. In the same vein of PHBV stabilization, a blend of PHBV/PBS (50:50 wt%) was produced and processed six times by extrusion[130]. Blend viscosity was higher than that of neat polymers and crystallinity and mechanical properties were kept constant during recycling. This may be ascribed to chemical interactions between PHBV and PBS chains which delayed the PHBV degradation. However, seven cycles extrusion of PHBV/ PBAT blend (35:65 wt%) resulted in a considerable increase in MFR after only three processing cycles. This was associated to a growing band intensities in the wavenumber range between 3200 and 3600 cm-1 in FT-IR fingerprint, indicating the formation of carboxylic groups. This exceptional strong rise in flowability was not reflected in the results of GPC which revealed a rather moderate decrease in Mn and slight increase in Mw. Due to moderate processing temperatures (between 135 °C and 150 °C), degradation is not likely for PHBV but repeated processing provoked hydrolytic degradation of PBAT leading to a dramatically decrease in viscosity[106].

Table 3. Review of the impact of multiple reprocessing, on biodegradable biopolyesters and their blends

Polymer Group /blend	Polymer material	Reprocessing conditions	Thermomechanical properties	Ref
PLA	PLLA [Biomer]	Injection-molding at 175-195°C	After 5 cycles, tensile strength from 64.1 to 58.7 MPa, Young's modulus stables at 2.6 GPA, elongation at break, from 3.4 to 3.0%. From the 6th cycle, sharp decrease in tensile strength and elongation at break.	[44]
	PLA (4.2% D-lactide content) [Natureworks]	Injection-molding at 160-190°C	After 2 cycles, viscous molar mass is maintained, and it showed 50% decrease at the 5th cycle. After 5 cycles: decrease in the Young's modulus of 28%, overall increasing fashion of strain at break (10%), the impact resistance decreased by 10% after the first cycle, remaining unchanged after. Decrease of the cold crystallization temperature from the second cycle (drop of 6°C). Loss of PLA performance after the second cycle.	[70]
	PLLA [Biomer]	Injection-molding at 175-190°C	After 5 cycles, decrease of T_g from 66 to 56°C, appearance of crystallization during cooling after 2 cycles, decrease of M_w by 50% after 3 cycles. Therefore, a rapid decrease of PLA performances was observed.	[71]
	PLA [Natureworks]	Extrusion (temperature not mentioned)	Mechanical properties decreased with extrusion numbers: after 10 cycles, impact strength decreased by 20%, and tensile test at break by 8%. MFR of the sample extruded 10 times was threefold higher than that of neat PLA. T_g was not affected. Cold crystallization temperature decreased from 125 to 115°C. Tonset after one extrusion was 339°C, and after 10 extrusions, it reached 332°C. This recycled PLA is suitable to be used as additive to the neat PLA.	[74]
	PLA [Natureworks]	Extrusion (145-190°C) + Injection (180-210°C)	Extrusion + injection of neat PLA caused: increase in MFI from 7 to 10.7 g/10min, yellowish color, decrease in M_w from 212 to 162 KDa, degradation temperature was slightly lower for processed	[75]

			material 325°C (compared to 331°C for virgin PLA), significant increase in elongation at break (32-35%).	
	PLA (4.2% D-lactide) [Natureworks]	Extrusion + compression molding at 180°C	After 5 cycles: decrease in M_w from 289 to 154 KDa, very slight increase in T_g, strong decrease in tensile modulus and ultimate stress at both 20°C and 50°C. No additional chemical functions (end groups) appearance.	[76]
	PHB [BIOCYCLE]	Extrusion + compression molding at 170°C	After 3 cycles: decrease in tensile strength at break above 50%, increase in crystallinity after the first cycle (even more after the 2nd and 3rd cycles), Tmax corresponding to degradation temperature was maintained at 297°C, no modification in the chemical structure of the polymer.	[91]
	PHBV (3% HV) [Tianan]	Extrusion (single screw) at 175-180°C	After 3 cycles: decrease in M_n from 299 to 260 KDa, complex viscosity drastically reduced, slight decrease in tensile modulus from 4.3 to 3.8 GPa due to the enhancement in crystallinity, decrease in strain at break with more brittle material. Degradation from the 3rd cycle.	[98]
	PHBV (14% HV) [Zeneca Bioproducts]	Extrusion (twin screw) at 170°C	Properties maintained up to the 4th cycle. After 4 cycles: decrease in M_w from 337 to 281 KDa, no modification in tensile strength, crystallinity rate was reduced from 54% to 42%, slight modification in Tonset.	[99]
PBS	PBS [Bionolle]	Extrusion (twin screw) at 160-210°C	MFR reduplicate after 1 cycle. After 7 cycles, decrease in M_w from 156 to 119 KDa, T_g and melting temperatures not altered by reprocessing, modification in the shape of melting peak due to molecular degradation, at room temperature no significant change in storage modulus neither in Young's modulus, decrease in tensile strength and strain at break by 24 and 32% respectively. Loss of material properties throughout recycling.	[106]
	PBS [Natureplast]	Extrusion at 190-210°C	After the 3rd cycle: viscosity increased by up to 31% indicating the occurrence of branching/recombination without crosslinking, decrease in M_w by about 20%, significant increase in the crystallization temperature up to 16°C.	[109]

Blend	PLA/PBS (50:50wt%)	injection molding at 190°C	After 7 cycles: a drop in the viscosity by -65%, decrease in PLA M_W, PBS accelerate the cold crystallization of PLA from cycle 4, stability of mechanical properties especially for stiffness and tensile strength. PBS is less degraded than PLA.	[129]
	PLA/PHBV (50:50wt%)	Extrusion at 175-180°C	After 6 cycles: M_n is reduced by 4.8% due to stabilization effect of PLA, increase in crystallization enthalpy from 33 to 46 J g^{-1} due to the crystallization of PHBV, decrease in storage modulus by 9%, biphasic morphology of the blend, which does not affect its mechanical properties. Incorporation of PLA improved PHBV properties.	[98]
	PHBV/PBAT (35:65wt%)	Extrusion at 140°C	After only 3 cycles: MFR increased by 328%, shift of melting value to higher temperatures, increase in crystals size. Degradation mainly occurred in PBAT, with a phase separation in the blend.	[106]

3.4.1. Biocomposites and nanocomposites

The use of fibers and particles to reinforce biodegradable polyesters is a common strategy to improve the performance, the water sensitivity and the sustainability of these polymers while reducing the often high production costs. The production of reinforced PLA has been widely reported, while the recyclability of such materials is still under investigation.

The mechanical recycling of PLA compounded with 30 wt% of wood fibers was simulated through repeated extrusion and injection moulding[131]. Compared to neat PLA, the bio-composite was able to sustain five cycles of reprocessing without a significant drop in its mechanical properties, except for elongation at break. Its degradation occurred after the sixth or seventh cycle. However, the ageing of the bio-composite through immersion in water at 50 °C, clearly affected the morphology of the bio-composite, accelerating its degradation under reprocessing conditions. The reinforcement effect of natural fibers was highlighted in other studies. Composites consisting of 30 % (v/v) PLA and 70 % (v/v) cellulose fibers were prepared by compression moulding and ground to be used as fillers for virgin PLA[132]. The reprocessing of these materials by repeated cycles of injection moulding showed that the composite material with 20 wt% filler could be processed six time, with an acceptable reduction in mechanical properties while the composite with 50 wt% filler suffered a significant degradation already after one cycle of injection moulding. Bio-composites based on PLLA and flax fibers, with fiber content of 20 and 30 wt%, have shown mechanical properties close to those of glass fiber/PP composite and superior to hemp/PP and sisal/PP materials[133]. After several injection cycles of PLLA/flax fiber composites, the mechanical properties were conserved until the third injection, even if polymer M_w and fiber length were slightly reduced. Bourmaud et al.[129] studied the recycling ability of a 50:50 wt% blend of PLLA-PBS, containing 30 wt% of flax fiber, through seven successive injection cycles. As expected, the introduction of flax fibers induced a strong increase of composite viscosity due to the fiber-polymer and fiber-fiber interactions restricting chain mobility. The mechanical properties during the first three injection cycles were maintained enough to consider recycling as an end-of-life option for these composites. On the other hand, Lopez and co-workers[44] reported that PLLA reinforced with 30 wt% cellulosic fibers obtained from a softwood chemithermo-mechanical pulp (CTMP) is an un-

recyclable material since the mechanical properties of the composite strongly decreased after just one processing cycle, made it too brittle to be reprocessed. The large water affinity of CTMP fibers might cause an increase in the water content and then a faster hydrolytic degradation of the matrices.

Concerning nanocomposites, some studies investigated the main effects of reprocessing PLA with nanoparticles such as cellulose nanocrystals (CNCs)[134] and nanofibers (CNF)[135], non-organic nanoparticles such as clay[136] or chalk[137], or carbon nano-sources like Graphene nano-patelets (GnP)[138].

Cellulose nanocrystals are widely used for the reinforcement of PLA matrix[134]. However due to their hydrophilic nature, they often agglomerate and initiate degradation of the PLA backbone. To improve the dispersion of the CNCs, Dhar and co-workers[134] employed radical initiator dicumyl peroxide (DCP) to covalently crosslink PLA and CNCs. The resulting nanocomposite was processed by extrusion three times. NMR and FTIR structural analysis revealed the formation of C-C covalent linkages between PLA and CNCs during reactive extrusion. This led to improved processability, and higher melt and thermal stabilities of PLA-CNC nanocomposites. The maximum degradation temperature increased by ~7-12 °C, and viscosity and storage modulus were improved by ~10 and ~50 times, respectively.

In the study conducted by Heidarian and co-workers, recycled PLA was reinforced by bagasse CNFs with a diameter of 35 nm[135]. Nanocomposites containing 1 and 3 wt% CNF have shown a good dispersion of nanofibers in the matrix and a drastic improvement in recycled PLA mechanical properties, especially for Young's modulus and strength at break. Nevertheless, recycled PLA with 3 % CNF showed a slower biodegradability, compared to the neat polymer. This was attributed to the more diffusion resistance ability of compounds due to the presence of nanocellulose in the polymer amorphous domain.

The influence of thermomechanical treatments on PLA/mineral nanocomposites was studied through repeated extrusion cycles. Composites of PLA with nanoclay were reported to have better thermal stability and improved barrier properties compared to neat PLA[136]. Nanocomposites based on PLA and chalk ($Ca\ CO_3$) 30 wt% were found to be mechanically reprocessable up to six times without suffering significant change in mechanical and thermal properties[137]. PLA reinforced with GnP was

submitted to five extrusion cycles[138] and the presence of GnP reduced the degradation rate of nanocomposite throughout the recycling processes.

The presence of nanoparticles provides better PLA stability during thermomechanical treatments. However, the biodegradability of the resulting nanocomposites must be questioned in view of the possible impact of non-biodegradable nanomaterials on the action of the microorganisms involved.

3.5. Conclusions about mechanical "recycling" of biopolyesters

To date, all the studies on the mechanical recycling of biodegradable bioplastic are based on thermomechanical reprocessing, and are still performed at laboratory scale, since no industrial facility is yet available. The post-consumer recycling of bioplastics materials may be implemented, as soon as the commercial volumes and sales increase sufficiently to cover the investments required to install separate recycling streams. However, their thermal and thermos-oxidative instability is an obstacle to their mechanical recycling, condemning them to be down-cycled (despite certain efforts to stabilize them). Key innovation is to design closed-loop recycling strategies able to preserve the quality of recyclates and to promote their utilization in food and beverage packaging sector.

Next section will discuss the challenge and limitations related to the closed-loop recycling of biodegradable polyesters in food packaging applications.

4. Mechanical recycling: decontamination of biodegradable polymers

Recycled plastic intended to food contact requires special attentions and is subject to specific regulation by the European Commission as stated above (Section 1.3). The issue of consumer safety is at the heart of the regulatory framework which must ensure the harmlessness of recycled materials. Post-consumer plastic may contain undesirable contaminants due to previous packaging use and/or domestic misuse, to contaminations during waste disposal (cross-contaminations, presence of non-food grade polymers), and also to the presence of additives and polymer degradation products. The persistence of these contaminants in the recycled packaging may pose a risk to human health by migrating into food.

Therefore, mechanical recycling processes for food contact applications are subject to regulations and must meet specific requirements to ensure the safety of recycled packaging.

4.1. Safety of recycling processes for food contact plastic packaging

As mentioned above (Section 1.2), according to article 3 of the framework regulation (EC) No 1935/2004, any food contact material should not transfer constituents to food in quantities which could endanger human health, change the composition of the food or deteriorate its organoleptic characteristics. In the absence of specific directives or regulations, the application of this inertia principle for biodegradable materials is covered by regulation (EC) N°10/2011[12], which sets out the procedures for checking the compliance of plastic materials. For all materials produced from a recycling process, the main concern about their suitability for food contact is their possible post-usage contamination. Post-consumer plastic packaging may contain a range of substances that can accumulate throughout the packaging life, from production (additives), use/misuse, and recycling (degradation products) [139, 140].

Considering that the contaminants are very diverse and that it is not possible to test every packaging, the safety of the final product is ensured by controlling the quality of the raw material and the efficiency of recycling process to remove contaminants [141]. Thus, in Europe, each recycling process must be evaluated by EFSA (European Food Safety Authority), in order to obtain an authorization for the production of food-contact recycled plastic by submitting an evaluation following specific guidelines [13].

The decontamination efficiency of the recycling process is evaluated by specific challenge tests. These tests are implemented according to a worst-case scenario simulating high levels of contamination in plastic waste [142]. Most technologies, designed for bottle-to-bottle recycling of PET, rely on cleaning steps to reduce contaminant levels mainly by a thermal treatment under vacuum or inert gas to promote contaminant desorption. This thermal treatment usually occurs in the solid state (flakes or pellets incubated in a reactor) and sometimes in the melt phase (in the extruder)[140]. Surface treatment with non-hazardous chemicals are also found in some recycling processes. At process output, concentrations of residual surrogates (C_{res}) are analyzed to assess the cleaning efficiency, and compared

to a modelled surrogate concentration (C_{mod}) which represent the maximum surrogate concentration in plastic that corresponds to an acceptable upper limit of dietary exposure whose threshold is set to avoid any toxicological effect. C_{mod} is calculated by generally recognized diffusion models overestimating the real migration of contaminant into food. To satisfy the evaluation criterion, the recycling process has to demonstrate its ability to decontaminate the contaminated plastic up to a residual concentration (C_{res}) not higher than the modelled concentration (C_{mod}) [143]. Surrogates are organic compounds (also known as "model contaminants") with different molecular weights, volatilities and polarities, with a variety of functional groups, representative of possible chemical classes of contaminants concern. Several studies have been carried out to identify and quantify the potential contamination of collected plastics. PET is the most frequently studied material. In Europe, the EU project FAIR-CT98-4318, provided a set of PET surrogates such as Toluene, Chlorobenzene or Phenyl cyclohexane, as a result from extensive experimental and analytical experiments [144]. A review of the literature data can also be found in a report from Franz et al. [145].

From 2010 to 2018, EFSA evaluated more than 130 processes for food-contact recycled plastics In most cases, the evaluated processes concern PET recycling, since it presents a relatively high inertness and resistance to higher temperature than other polymers, it does not need much additives like antioxidants and plasticizers, and all PET raw materials are food grade [146]. The other recycling processes mainly refer to polyolefins (PP and/or HDPE) which require further cleaning because of their higher permeability to contaminants, and a higher migration rate (into food) compared to PET. In addition, polyolefins are much less temperature resistant, making more challenging their effective decontamination. However, it is not relevant to use the same surrogate panel as PET for the polyolefins challenge tests, since the barrier properties are strongly different [139]. To date, EFSA has not received applications for any others types of plastic. From 1990 to 2018, the US FDA has given 206 favorable opinions with 153, 22, and 21 submissions referred to PET, PS, and polyolefins food contact recycling processes respectively.

4.2. Food safety of recycled biodegradable biopolymers

As the market of biodegradable biopolymers is still very emerging, their mechanical recycling has not been addressed yet, and even less for food applications. Indeed, mechanical recycling of biodegradable plastics is a controversial issue. The supporters of this type of recycling claim that commercial biodegradable biopolymers such as PLA degrade slowly under ordinary conditions, even in the presence of microorganisms, with the risk to contribute to plastic soup in the future. Biodegradable plastics disposed in landfills may lead to methane and CO_2 emissions, with a negative climate impact. Further, the recycling of biopolymers is crucial in reducing the consumption of renewable resources needed for the synthesis of the corresponding monomers. At the opposite, the mechanical recycling opponents point out two main limitations which might curb the implementation of such process. First, bioplastics represent today less than 1 % of the total amount of plastics, and it is not realistic to develop separate recycling streams for them to date. So, when they end up in mixed fraction (with other plastics) or in residue during sorting, they are not currently isolated and are eventually incinerated[147]. Indeed, to preserve the quality of recycled PET, the PLA contamination should be maintained below 0.1%[148]. In the case of PP, the amount of PLA or PHB should not exceed 5% [149]. Moreover, they argue that the recyclates resulting from such materials show lower mechanical and thermal properties compared to original plastics and do not produce secondary material of high quality. The arguments of the detractors of the mechanical recycling of biodegradable plastics can be now considered as unfounded. The increase in PLA and PBS production will lead to the new separate recycling stream that should be implemented in the short to medium term (it is estimated that one type of bioplastic should reach 5-10% volume within plastic recycling system[150]). In addition, in the case of mixed plastic waste streams, biobased and biodegradable polymers can be sorted out by employing NIR (Near Infra-Red) technology. For example, at a commercial scale, PLA has been sorted by means of NIR , with a minimum sorting efficiency of 97,5 % [151]. On the other hand, the polymer degradation during the recycling process is not something peculiar to bioplastics. Even conventional plastics are prone to degrade under recycling conditions. If feeding with virgin plastic was the solution adopted to improve the quality of recycled oil-based plastics, it is imperative not to be restricted to this idea, and to exploit the wide field of opportunities that bioplastics recycling still offers. For instance, it would be interesting to strengthen

studies in additives and stabilizers, especially natural molecules and macromolecules. These latter are not harmful for environment and human health and can play an important role in improving bioplastics for durable uses by providing cost reduction, reinforcement, increasing thermal resistance and crystallization rate, inhibiting oxidation… Another option is to invest on the implementation of combined valorization techniques. For example, favoring chemical and biological recycling, after several cycles of mechanical recycling.

Even more, many challenges remain to achieve mechanical closed-loop recycling of biodegradable plastics. With regards to their particular transfer properties and their ability to absorb different substances , the well-known approaches used for PET seems not be adequate to ensure the safety to of biodegradable biopolymers[140]. There is a need of further studies dealing with the possible contaminants specific to these polymers and to implement specific challenge tests with an adequate representative panel of surrogates with different polarities and molecular weight. The decontamination of higher molecular weight contaminant should be carefully assessed since the desorption efficiency decreases with an increasing in contaminants molecular weight.

5. Conclusion

Although gathered under a common generic denomination, bio-plastics and biodegradable plastics integrate a great variety of polymers. Their different structures provide a reactivity and differentiated properties which defines the opportunities and options for their end-of-life treatments. This review covers the studies dealing with the mechanical recyclability of the main promising biodegradable biopolyesters, PLA, PHAs, PBAT and PBS within the last ten years. The study of degradation mechanisms during reprocessing steps highlighted the structural degradation of all studied polymers under the influence of thermal, thermomechanical and thermos-oxidative treatments. It is assumed that the quality grade of the output raw material from the recycling process determines its range of use for food and non-food applications. If different methods have been attempted to improve the properties of recycled polymers including thermal and chemical treatments, production of blends, bio-composites or nano-composites, all these strategies raise new concern about their impact on the

recycling process and on the suitability for food contact of the packaging derived from the secondary material

Despite the promising preliminary results on the mechanical reprocessing of biodegradable biopolymers, the closed-loop recycling for food applications is still not studied. It seems certain that the approach currently used for assessing the safety of PET recycling technologies cannot be extrapolated to the biopolyesters. In addition to the economic and logistical considerations specific to each territory, the emergence of a recycling system for biopolyester-based materials requires indispensable technological progress, such as (I) the improvement of the performance of the processes which should as far as possible avoid/limit the degradation of more sensitive bio-polyesters than PET and (II) the provision of guidelines describing how to evaluate these processes, particularly in terms of decontamination efficiency. In this way, the safety assessment of the mechanical recycling process should be deeper investigated, taking into account the polymer specificities (transport and barrier properties) in order to implement an adequate challenge test.

CHAPTER II. MATERIALS AND METHODS

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1. Materials

1.1. *Polymeric matrix*

The polymer used was poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) powder with 3 mol% of 3-hydroxyvalerate (HV) (Figure 10). It was purchased from Nature plast (France) under the PHI003 commercial grade, a pure uncompounded powder produced from pure culture. The same batch EDW 2300 was used for all materials studied in this thesis. Main properties of PHBV are reported in Table 4, according to the supplier. Molecular weight of PHBV powder was measured and Mw > 1100000 g/mol. The polymer powder was stored away from any source of air, moisture, light and heat to prevent any moisture intake.

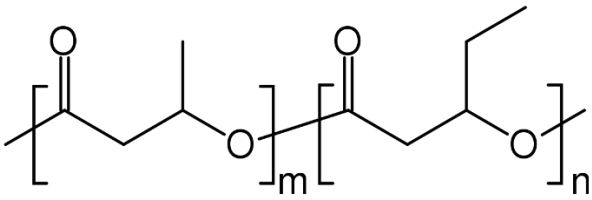


Figure 10. Formula of PHBV.

Table 4. Main characteristics of PHBV

	Method	Unit	Value
General properties			
Density	ISO 1183		1.25
MFI (190 °C ; 2.16 kg)	ISO 1133	g/10min	5-15
Optical properties			Opaque
Thermal properties			
Melting temperature	DSC	°C	170-176
Mechanical properties			
Stress at elastic limit	ISO 527	MPa	31
Stress at break	ISO 527	MPa	39
Strain at break	ISO 527	%	2
Young's modulus	ISO 527	MPa	2800-3500
Flexural modulus	ISO 178	MPa	3520-4170

1.2. *Contaminants, calibration standards and additives.*

Nucleating agent (98 % boron nitride), solvents (methanol, 95 % ethanol), contaminants (listed below), internal measurement standards (listed below) and polyphenolic additive (95 % quercetin) were purchased from Sigma-Aldrich.

The named "EFSA panel of contaminants" was set according to the FDA and EFSA guidelines for PET recycling with the following list of surrogates: toluene, chlorobenzene, methyl salicylate, phenylcyclohexane, benzophenone, methyl stearate and DEHA. This panel aim to have a range of molecular weight and polarity representative of potential PET contaminants of concern, their diffusion and sorption behavior [27, 152]. Others contaminants were also used in order to present a higher polarity or molecular weight than those of FDA and EFSA guidelines. The list of surrogates is: gallic acid,

catechin, ferulic acid, polyethylene glycol 200 (PEG 200) and Irganox 1076. Surrogates parameters are reported in Table 5.

Table 5. Surrogates contaminants parameters.

	Surrogate contaminants	CAS number	Molecular weight (Mw in g/mol-1)	Polarity (Log Kaw)
EFSA panel	Toluene	108-88-3	92	2.7
	Chlorobenzene	108-90-7	113	2.8
	Methyl salicylate	119-36-8	152	2.6
	Phenylcyclohexane	827-52-1	160	4.8
	Benzophenone	119-61-8	182	3.2
	Methylstearate	112-61-8	298	8.4
	DEHA	103-23-1	371	8.1
Higher polarity	Gallic acid	149-91-7	170	0.7
	Catechin	154-23-4	290	1.5
	Ferulic acid	537-98-4	194	1.5
	PEG 200	107-21-1	190-210	1.1
Higher molecular weight	Irganox 1076	2082-79-3	531	13.4

3,5-Di-tert-4-butylhydroxytoluene (BHT) was used as internal measurement standard for GC analysis of EFSA contaminants panel. Vanillic acid and PEG 550 were used as internal measurement standard for HPLC analysis of phenolic compounds and PEG 200 respectively. Uvitex OB was used as internal measurement standard for HPLC analysis of Irganox 1076.

1.3. *Food simulants*

Three different food simulants were chosen for specific migration tests according to the Regulation (EU) 10/2011 [12] in order to evaluate the food safety of the reprocessed PHBV. These three

simulants were chosen according to the characteristics of the PHBV, the namely, 96% Ethanol to simulate fatty food, 3% acetic acid to simulate acidic food and Tenax (60/80 mesh) as solid dry food simulant, all supplied from Sigma-Aldrich.

2. Production of polymeric materials

PHBV, boron nitride and quercetin additive were dried at 60 °C during 24h before any thermal processing in order to remove potential water content.

Neat PHBV was produced from the extrusion of a mixture of PHBV powder with 0.5wt% of boron nitride. To produce PHBV-Q material, a mixture of PHBV powder with 0.5wt% of boron nitride and 1wt% of quercetin was extruded. Extrusion was carried out in a lab scale Thermo scientific Process 11 parallel twin-screw micro-compounder (Thermoscientific, Karlsruhe, Germany), equipped with a L/D ratio of 40, a screw diameter of 11mm, and a 3 mm rod die. The temperature profile set at 180°C was uniform from the feeding to the die, and the screw profile is described in Figure 11 according to Vandi et al. [153]. The screw speed was set at 150 rpm, with a residence time of approximately 2 min. After granulation, the pellets were dried at 60 °C for 24h, then neat PHBV and 12x12 cm PHBV-Q films with an average thickness of 300 µm were produced by thermo-compression using heated hydraulic press (20T, Pinette Emidecau Industries). The temperature was 180 °C and the pressure was first set at 5 bars for 1 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30 s. Produced films were then cooled down at ambient temperature.

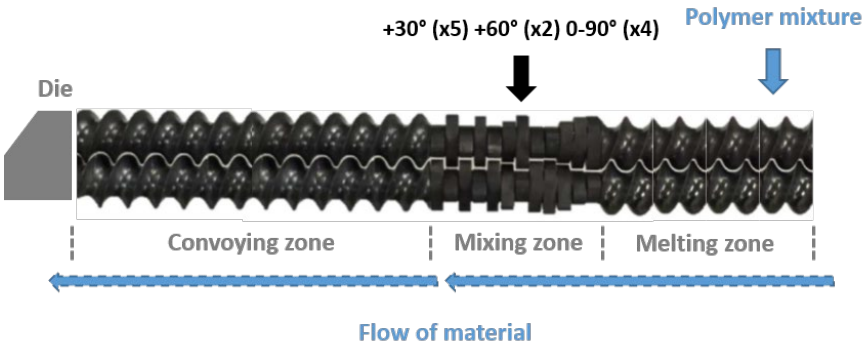


Figure 11. Twin-screw profile according to Vandi et al. [153].

3. Mechanical recyclability: reprocessing cycles of PHBV films

Mechanical recycling was simulated by reprocessing the material following the extrusion procedure as described above. Four processing cycles were performed in order to simulate four successive mechanical recycling processes as shown in Figure 12. After each cycle, the granulating process was carried out at room temperature and the granulated product was dried at 60 °C for 24h. Pellets were thermoformed in PHBV films following the thermo-compression process previously described, before being characterized.

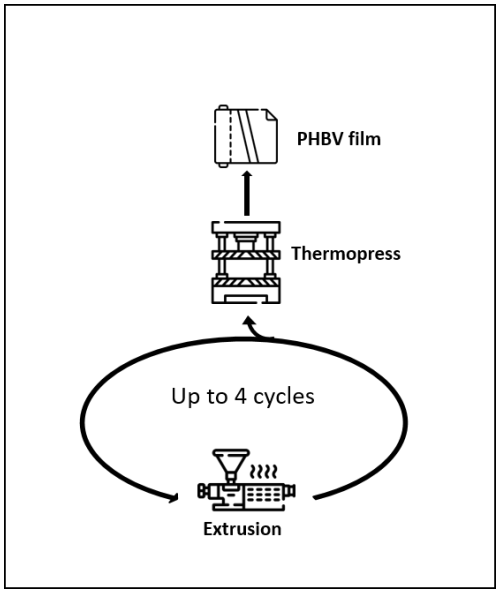


Figure 12. Schematic description of reprocessing model method.

4. Mechanical recyclability: PHBV films decontamination

4.1. *Contamination procedure*

According to the contamination protocols for challenge tests, polymer flakes should be soaked in a surrogates solution until a sorption equilibrium is reached [154]. For polymer contamination with EFSA contaminant panel, solid contaminants (benzophenone and methylstearate) were dissolved in the liquid contaminants (toluene, chlorobenzene, methylsalicylate, phenylcyclohexane, DEHA) without the use of additional solvent, and stirred until a homogeneous solution was obtained. For higher polarity contaminants, Surrogates contaminants were dissolved in methanol, at a concentration of 9 $mg.mL^{-1}$ and 23 $mg.mL^{-1}$ for phenolic compounds (catechin, gallic acid, ferulic acid) and PEG200 respectively, and

stirred until a homogeneous solution was obtained. In a sealed container, this surrogate's mixture was dropped on polymer flakes (1.5 cm squares) at a concentration of 500 mg of surrogates per kg of flakes. Containers were stored for 10 days at 40 °C with continuous rotatory agitation until a sorption equilibrium is reached. After 10 days, the contamination level was evaluated by measuring the surrogate concentration in the flakes.

4.2. *Decontamination process*

Decontamination of the contaminated flakes was performed in a glass oven (Buchi, B-585) at elevated temperature and under vacuum (< 20 mbar). The experimental process is schematized in Figure 13. As a function of the contaminants group (EFSA panel, High polarity molecules), different time/temperature combinations were tested. Temperatures ranged from 100°C to 160°C, and the processes lasted from 3 to 72h (specific conditions are described in the respective chapters).

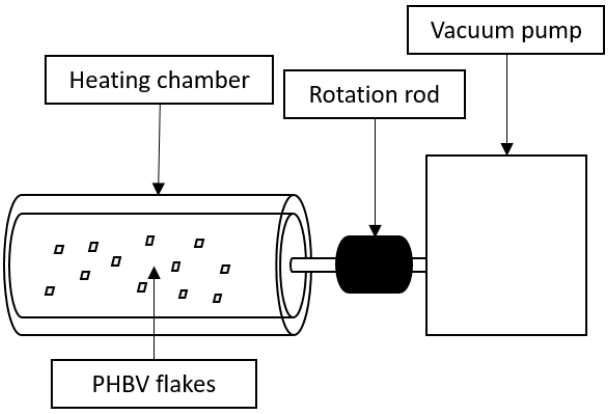


Figure 13. Scheme of the PHBV flakes decontamination process.

4.3. *Extraction method*

The surrogate concentrations in the polymer flakes after contamination and decontamination were determined using the following extraction method: PHBV flakes (0.3 g) were placed in a glass vial and 5 ml of methanol were added. Samples were then stored for 1 day at 40 °C under magnetic agitation to extract the surrogates from the polymer matrix. All the extracts were obtained in triplicate. For EFSA contaminants panel, extracts were analyzed using an Agilent 7890A GC equipped with a 7693A Automatic Sampler and a flame ionization detector (FID). A total of 1 µL of the extract was injected into the GC equipped with a HP-5 (5%-phenyl)methylpolysiloxane capillary column of 32 mm ID and

30 m length. Carrier gas was nitrogen (8.11 mL.min^{-1}) and the chromatographic conditions were as follows: initial oven temperature was maintained at 40 °C for 5 min, and subsequently heated from 40°C to 270°C at a rate of 6 °C.min^{-1} to 270 °C, where it was held for 15 min. The injector temperature was 250 °C. The peaks identification and product quantification were based on the use of the different surrogates as external standards (calibration curves with concentration range of 10 – 45 mg.L^{-1}), as well as the use of BHT at 30 mg.L^{-1} as an internal standard. For higher polarity contaminants (phenolic compounds and PEG200) extracts were analyzed using an Acquity UPLC (Waters, Milford, MA) liquid chromatography system, equipped with a photodiode array detector (DAD) and a mass spectrometer. The Waters column was 100 mm x 2.1 mm, HSS T3, particles size was 1.8 µm. The solvent used were A (99.9 % H_2O and 0.1% HCOOH v/v) and B (80 % CH_3CN; 19 % H_2O; 1% HCOOH) with a flow rate of 0.55 mL.min^{-1}. The injection volume was 2 µl and DAD was set at 280 nm in order to detect gallic acid, catechin and ferulic acid. The Acquity UPLC system was coupled online with a Bruker amazon X electrospray ionization (ESI) ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany). The nebulizer pressure was 3.03 bar; the temperature of the drying gas was set at 200 °C with a 12 L.min^{-1} flow; and the capillary voltage was set at −5.5 kV. The mass spectra were acquired over a mass range of 50− 2000 Th in the positive ion mode. The mass spectrum acquisition speed was set at m/z 8100 s^{-1}. The target mass was tailored to each reaction between m/z 100 and 900. PEG 200 was detected and quantified by integrating the mass spectrometry peak at 300 m/z. The peaks identification and quantification were based on the use of the different surrogates and quercetin as external standards (calibration curves with concentration range of 10 - 45 mg. L^{-1}), as well as the use of vanillic acid and PEG 550 at 30 mg.L^{-1} as an internal standard.

4.4. *Decontamination measurements*

The decontamination efficiencies were determined for each surrogate by comparing the surrogate concentration in the flakes after decontamination with the initial concentration before heat treatment (see equation 1).

$$Decontamination\ efficiency\ = (1 - \frac{sample\ concentration}{initial\ concentration}) \times 100 \qquad (1)$$

4.5. *Safety assessment*

For EFSA contaminant panel, residual concentration of contaminant, C_{res}, is then calculated by applying the decontamination efficiency percentage to a reference contamination level. Reference contamination level in the PET feedstock set in the literature at 3 mg.kg^{-1} and was used here [27].

4.5.1. Estimation of diffusion coefficients

Diffusion coefficients of each surrogate were estimated, from experimental desorption kinetic curves at each decontamination temperature, using Fick's second law. Diffusion is assumed to be isotropic and flakes are considered as infinite plane sheets, leading to a mono-directional diffusion equation. Surrogates' desorption takes place in a constantly renewed medium (vacuum) then null boundary condition is used. Initial surrogate concentrations are supposed to be uniform in the films. Surrogate desorption is described by the analytical solution of the diffusion equation, given by Crank [155]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\} (2)$$

where M_t and M_∞ (mg) are the mass of the diffusing molecule which desorb from the polymer at time t and at infinite time, respectively, D is the diffusion coefficient of the diffusing molecule in the polymer (m^2.s^{-1}), t is the time of the desorption (s), L is the thickness of the film (m).

The numerical simulations were carried out using the Matlab software and the lsqnonlin function, to estimate the diffusion coefficient.

4.5.2. Determination of experimental partition coefficient

PHBV flakes were contaminated following the contamination procedure (section 4.1). After a quick ethanol rinsing to eliminate surface contamination, material samples (145 ± 20 µm) were immersed in 100 mL of ethanol 95 % as food simulant, in a surface/volume ratio of 6 dm^2.L^{-1}, at 40 °C for 10 days under magnetic agitation. Then, an aliquot of food simulant was collected and analyzed in GC following the same procedure described in the previous section (4.3). Experimental partition

coefficient ($K_{P/F}$) of the contaminants between the polymer matrix and the food simulant, were calculated from equation (3)

$$K_{P/F} = \frac{C_{P,\infty}}{C_{F,\infty}} \frac{\rho_P}{\rho_F} \quad (3)$$

where $C_{P,\infty}$ and $C_{F,\infty}$ (mg.kg^{-1}), are the equilibrium concentrations of contaminant in the polymer and in the food simulant, respectively, ρ_P and ρ_F (kg.m^{-3}) are the density of polymer and food simulant, respectively.

4.5.3. Estimation of acceptable residual concentration of contaminant

For each surrogate, C_{mod} represents the residual concentration in the recycled PHBV resulting in a migration that does not exceed the dietary exposure threshold defined as 0.0025 µg/kg bw/day [156]. Thus, C_{mod} represents the maximal surrogate content in recycled PHBV which ensure the food safety and is calculated by modelling using the following migration model from the JRC publication [157] in equation (4):

$$C_{mod} = SML * \frac{V_F \rho_F}{A} \left\{ \rho_P d_p \left(\frac{\alpha}{1+\alpha} \right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-D_P t \frac{q_n^2}{d_p^2} \right) \right] \right\}^{-1} \quad (4)$$

where SML is the Specific Migration Limit (mg.kg^{-1}), $C_{mod}$is the maximum initial concentration in the polymer (mg.kg^{-1}) , V_F is the volume of food (m^3), D_P is the diffusion coefficient of migration in the polymer (m^2.s^{-1}), d_p is the thickness of the polymer (m), A is the area of polymer in contact with food (m^2), q_n are the non-zero, positive roots of equation (5)

$$\tan q_n = -\alpha \, q_n \quad (5)$$

and α is calculated from equation (6)

$$\alpha = \frac{1}{K_{P/F}} \frac{V_F}{V_P} \quad (6)$$

where V_P is the volume of the polymer (m^3).

Standard test conditions were used for contact with food simulant and parameters used were taken from the EFSA regulation on PET migration modelling [27]. The food contact material was considered as a 100 % recycled polymer of 300 µm thickness. Food contact ability was assessed after

10 days at 40 °C in a food simulant (density of 1000 kg.m^{-3}), with a surface area to volume ratio of 6 dm^2 (0.06 m²) polymer to 1 kg food simulant.

5. Mechanical recyclability: evaluation of the contaminants affinity with PHBV polymer

5.1. *Sorption isotherms*

Sorption isotherm experiments were performed with different contaminants concentration gradients, at 20°C. Specifically, 0.3 g of PHBV flakes (1.5×1.5 cm) were placed in glass vials and 5 mL of contaminant solutions were added under magnetic stirring. Benzophenone, ferulic acid and Irganox 1076 were added in concentration ranges of 1-125 g.L^{-1} ,1-50 g.L^{-1} and 2-6 g.L^{-1} respectively. 95% ethanol was used as solubilizing medium of the contaminants, and is also considered as food simulants, mainly used to replace vegetable oil. After reaching the sorption equilibrium, PHBV flakes were immersed in 5 mL of methanol in order to extract the contaminants sorbed in the polymer matrix. Extraction was conducted for 24 h at 40 °C, under magnetic agitation (300 rpm). The supernatant solutions were filtered and placed in 1.5 mL glass vials and the equilibrium concentrations of the three contaminants were determined. All experiments were performed in triplicate.

Benzophenone and ferulic acid quantification was performed by injecting the solutions in Ultimate 3000 UHPLC (Thermofisher) liquid chromatography system, equipped with a photodiode array detector (DAD), set at 280 nm. The Waters column was 100 mm × 2.1 mm, HSS T3, with particles size of 1.8 µm. The solvents used were A (99.9 % H2O and 0.1% HCOOH v/v) and B (80 % CH3CN; 19 % H2O; 0.1% HCOOH) with a flow rate of 0.55 mL/min; and the injection volume was 2 µL. The peaks identification and product quantification were based on the use of the different contaminants as external standards (calibration curves with concentration range of 10 – 45 mg.L^{-1}). Vanillic acid was used at 30 mg.L^{-1} as internal standard.

Irganox 1076 concentration was determined by recording the absorbance of the samples at 230 nm, after injection in Alliance HPLC system (Waters) equipped with an Alltima C18 column (250 m ×

2.1 mm, 5 µm) protected with a Alltima C18 (7.5 mm × 2.1 mm, 5 µm) column guard. The solvent used was 55 % (v/v) aqueous acetonitrile at a flow rate of 0.3 mL.min^{-1} at 50 °C, and the injection volume was 2 µL. Product quantification was based on the use of Irganox 1076 as external standards (calibration curves with concentration range of 10 – 45 mg.L^{-1}). Uvitex OB was used at 30 mg.L^{-1} as internal standard.

Linear regression has been drawn for each contaminant isotherm, and experimental partition coefficients ($K_{P/L}$) of the contaminants between the liquid food simulant and the polymer were determined as the slope of the regression curves, using the Origin software.

5.2. *Sorption kinetics and estimation of Diffusion coefficients*

Sorption kinetics experiments were conducted in order to determine the diffusion coefficient of contaminants. In 30 mL glass vials, PHBV flakes (1.5 cm squares, 0.3 g) were immersed in a 95% ethanol solution, saturated with each contaminant. The saturated stock solutions had a concentration of 133 g.L^{-1} for Benzophenone, 50 g.L^{-1} for ferulic acid and 6 g.L^{-1} for Irganox 1076. Vials were hermetically sealed and submitted to magnetic agitation (300 rpm) at room temperature (20 °C). PHBV samples were, then, collected at specified time intervals, rinsed with 95 % ethanol and dried with absorbent paper. Then, PHBV flakes were immersed in 5 mL of methanol in order to extract the contaminants sorbed in the polymer matrix. Extraction was conducted for 24 h at 40 °C, under magnetic agitation (300 rpm). After filtration, the supernatant solutions were placed in 1.5 mL glass vials and quantification was carried out in the same way described previously for sorption isotherms. All experiments were performed in duplicate.

Diffusion coefficients of each diffusing surrogate were estimated, by fitting experimental sorption kinetic curves with mathematical model from Fick's second law. The samples were considered as one-dimensional infinite plane sheets with a negligible diffusion from the borders of the flakes. Sorption took place in a saturated solution of surrogate, then constant boundary conditions may be assumed. Initial surrogate concentrations were supposed to be uniform in the solution and null in the film. Surrogate sorption may be described by the equation (2) (section 4.5.1), where M_t and M_∞ are the

masses (mg) of the diffusing molecule in the polymer at time t and at the equilibrium state, respectively, D is the diffusion coefficient of the diffusing molecule in the polymer ($m^2.s^{-1}$), t is the time of the sorption (s) and l is the half thickness of the film (m).–In order to calculate the apparent Diffusion coefficient D, the asymptotical mass uptake M_∞ at equilibrium was calculated from the known initial concentration in the solution and the partition coefficient (determined above). In order to take into account the heterogeneity of experimental standard deviations along the kinetic, a weighted root mean squared error was used for estimation of D. Weights were set as the inverse of experimental variance.

The numerical simulations were carried out using the Matlab software and the lsqnonlin function, to estimate the diffusion coefficient.

5.3. *Sorption profiles*

5.3.1. Sorption simulation

Concentration profiles of each contaminant through the polymer thickness were modelled for different time in PHBV and in PET, in order to compare the sorption behaviour of these two different polymers. As for sorption kinetics experiments, the simulation involved 1.5×1.5 cm films immersed in contaminants saturated ethanolic solutions. The initial concentrations were 133 $g.L^{-1}$ for Benzophenone, 50 $g.L^{-1}$ for ferulic acid and 6 $g.L^{-1}$ for Irganox 1076. Contaminant concentration in initial solutions being very high, it was considered that the conditions at the borders remained constant. Thus, the contaminant sorption at time t (s), and position x (m) into the film described by $x \in [-l, l]$, with l the half thickness of the film (m), is given by the following equation, provided by Crank [155]:

$$\frac{C_{x,t} - C_0}{C_\infty - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right\} \cos\frac{(2n+1)\pi x}{2l} \quad (7)$$

where $C_{x,t}$ is the concentration in diffusing substance in the polymer ($mg.cm^{-3}$) at time t and depth x, C_∞ is the concentration in diffusing substance in the polymer at the equilibrium state ($mg.cm^{-3}$), C_0 is the initial concentration in diffusing substance in the polymer, here considered to be null, D is the diffusion coefficient of the diffusing molecule in the polymer ($m^2.s^{-}1$). They were obtained from sorption kinetic experiments for PHBV and from the literature for PET. As there is initially no

contaminant in the polymer, the equilibrium concentration C_∞ in the polymer can be calculated from the known initial concentration in the solution and the partition coefficient assuming no loss due to transfer to the headspace or leaks. The numerical simulations were carried out using the Matlab software.

5.3.2. Sorption measurements by Raman spectroscopy

In addition to modelling, the sorption profile of benzophenone in PHBV was determined experimentally by sorption kinetics followed by the evaluation of its concentration in the polymer thickness using Raman spectroscopy.

Sorption was carried out by immersing 1.5×1.5 cm films in 5 mL of saturated ethanolic solution of benzophenone (133 $g.L^{-1}$). Vials were sealed and submitted to a continuous magnetic agitation at 20 °C. Polymer flakes were, then, collected at 0.5 h and 1.5 h in order to obtain concentration profiles at non-equilibrium state. They were rinsed with 95 % ethanol and dried with absorbent paper. Then, small polymer lamellae were cut through the thickness of the flakes and placed on a microscope slide before being characterized by Raman spectroscopy (figure 14).

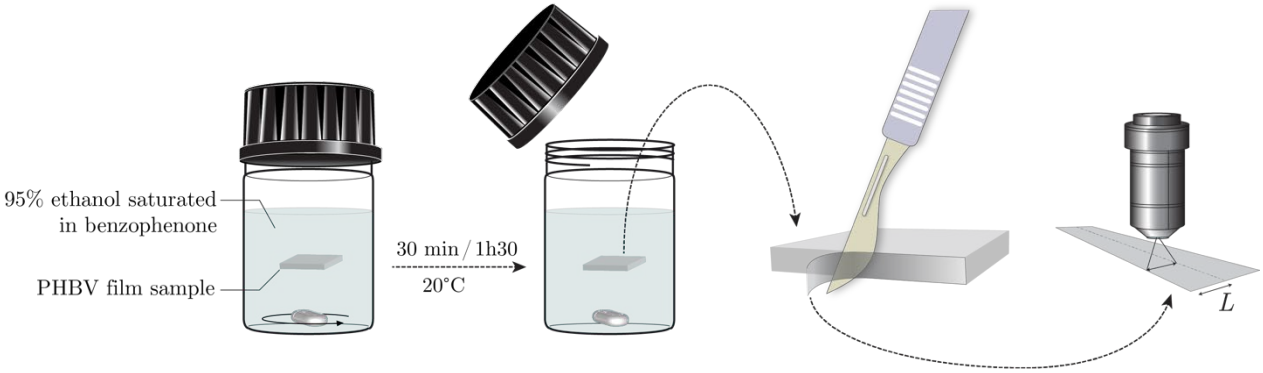


Figure 14. Experimental method for the evaluation of the concentration profile of benzophenone in the thickness of PHBV by Raman spectroscopy.

Raman spectra were recorded between 95 and 3500 cm^{-1} Raman shift, using a confocal Raman micro spectrometer Almega (ThermoElectron). The configuration was: excitation laser He-Ne with λ_0 = 633 nm, grating 500 grooves/mm, pinhole 25 µm, objective 50×, numerical aperture (NA) 0.8 and focal distance (f) 380 µm. A total of 9 spectra were realized in the half thickness of the samples with a

step of 17 µm. The collection time was 10 s and each spectra was replicated 4 times. All spectra were pre-treated with Omnic v7.1 (ThermoElectron) and the processing included a multipoint linear baseline correction. The relative content of Benzophenone was evaluated using the height of the Benzophenone specific peak (1695 cm^{-1}) assigned to the C=O group, normalized by the height of the PHBV specific peak (1761 cm^{-1}) related to the C=O group of the ester function.

As in the previous section, samples were considered as infinite films with uniform initial contaminant concentration in the solution and zero initial concentration in the sample. Assuming in addition that concentration can be obtained from intensities through a linear relationship, equation 7 can be used to estimate the Diffusion coefficient of Benzophenone from experimental normalized intensity profiles instead of concentration profiles. The normalized intensity at equilibrium I_∞ was taken from experimental value at the boundary of the sample.

The numerical simulations were carried out using the Matlab software and the lsqnonlin function, to estimate the diffusion coefficient.

6. Characterization methods

6.1. *Size Exclusion Chromatography (SEC)*

PHBV average molecular weight (Mw) and number-average molecular weight (Mn) were determined by SEC performed in the University of Bologna (Italy). Samples were placed in sealed tubes and dissolved in Hexafluoro-2-propanol/Chloroform mixture (95:5) at a concentration of 1 $mg.mL^{-1}$. SEC analyses were carried out in a HP 1100 Series equipped with a PL gel 5 µm Minimixed-C column. Injection volume was 20 µL and chloroform flow rate was 0.3 $mL.min^{-1}$. Detection was performed by means of refractive index and UV detectors. The calibration of the instrument was done with polystyrene standards, and all the sample analyses were performed in triplicates.

6.2. *Differential Scanning Calorimetry (DSC)*

DSC analyses were carried out using a TA Instruments (Q200 modulated DSC, TA Instruments) calorimeter under a nitrogen atmosphere with a flow rate of 50 $mL.min^{-1}$ and a heating rate of 10 °C.min-

[1]. Around 8 mg of sample was used for each analysis and all experiments were done in duplicate. The samples were subjected to the following thermal schedule. First heating from -30 to 200 °C, with stabilization for 3 min; then cooling down up to -30 °C with again a stabilization for 3 min; followed by a second heating scan up to 200 °C. The melt crystallization temperature (*Tc*) was determined from the cooling scan whereas the melting temperature (*Tm*) and the melting enthalpy (*ΔHm*) were obtained from the second heating scan after erasing the thermal history. Overall theoretical degree of crystallinity (*Xc*) was calculated from the melting enthalpy according to the following equation:

$$Xc\ (\%) = \frac{\Delta Hm}{\Delta H°(PHBV)} \quad (8)$$

where ΔH0 is the melting enthalpy of 100% crystalline PHBV, i.e. 109 J/g [158].

6.3. *Thermal Gravimetric Analysis (TGA)*

TGA was carried out using a Mettler apparatus (TGA2) equipped with a XP5U balance (precision of 0.0001 mg). Around 8 mg of sample were heated at 10 °C.min^{-1} from 25 °C to 800 °C under nitrogen flow of 50 mL.min^{-1}. Three replicates were scanned for each sample. Mass loss and first derivative of mass loss were recorded as a function of temperature, and the maximum degradation temperature (*Tdeg*), corresponding to the temperature at which the degradation rate was maximum was measured.

6.4. *Mechanical properties*

ISO½ samples were cut from the films obtained by thermocompression. Tensile properties of samples were measured using a tensile tester (Zwick BZ2.5/TN1S) with a cross-head speed of 1 mm.min^{-1}. Young's modulus, elongation at break as well as tensile strength were calculated from strain-stress curves with the Matlab program, taking account an effective cross section of 22 mm. Ten replicates were scanned for each reprocessing cycle.

6.5. *Transfer properties*

The Oxygen permeability (PO_2) of the reprocessed films was determined in triplicate at 23 °C and 50% relative humidity, using an O_2 permeation chamber equipped with an integrated PSt6-type

sensor (PreSens Precision Sensing GmbH). Figure 15 describes this system consisting of two chambers separated by a grid where the film is placed with an open testing area of $1{,}26.10^{-3}$ m^2. After applying nitrogen flesh on both sides of the film to remove the surrounding oxygen, the lower chamber was exposed to an oxygen flow of 50 $mL.min^{-1}$, while the upper chamber was hermetically closed. By permeation, the O_2 molecules could pass through the film where the sensor stood, the system measured oxygen ingress in % for five days. PO_2 ($mol.m/m^2.s.Pa$) was calculated according to the following equation :

$$PO_2 = \frac{J\ x\ e}{A\ x\ \Delta P} \quad (9)$$

where J ($mol.s^{-1}$) is the flux of gas passing through the film, e is the film thickness (m), A, the permeation area (m^2) and ΔP, the differential partial pressure of the permeant gas across the film (Pa).

The water vapor permeability (Pwv) of films was determined according to a modified ASTM procedure (ASTM E96 – Standard test methods for water vapor transmission of materials). Analyses were conducted at 23 °C and a relative humidity gradient of 0 to 100% with five replicates per sample. Film samples, with 9,08 cm^2 area were hermetically sealed in 50 mL glass permeation cells containing 40 mL of distilled water, and were placed in a desiccator containing silica gel, for 10 days as shown in Figure 15. Pwv ($mol.m/m^2.s.Pa$) was calculated according to the following equation:

$$P_{wv} = \frac{J\ x\ e}{A\ x\ \Delta P} \quad (10)$$

where J ($mol.s^{-1}$) is the flux of water vapor passing through the film, e is the film thickness (m), A, the permeation area (m^2) and ΔP, the differential water vapor pressure between the cell and the dessicator (Pa).

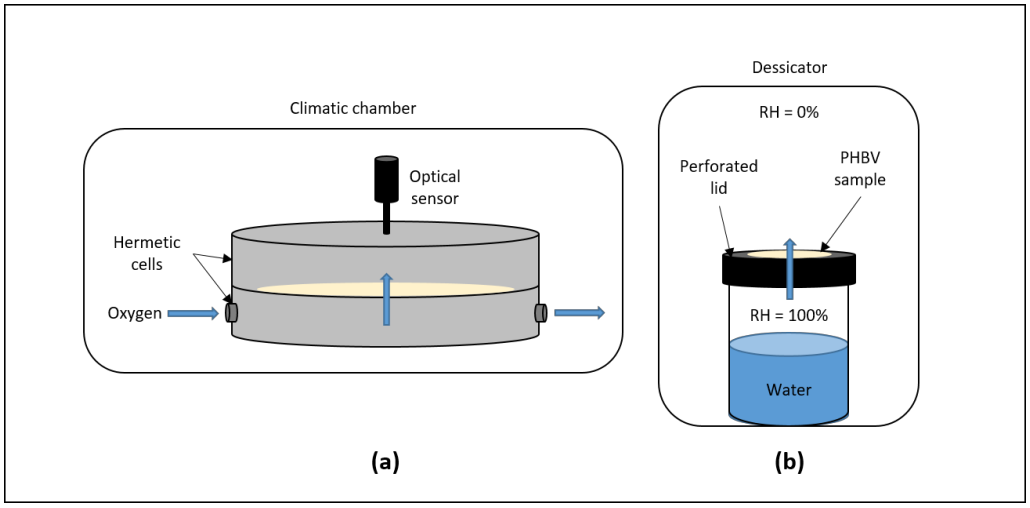


Figure 15. Schematic description of the permeation test method for (a) oxygen transfer and (b) water vapor transfer.

6.6. *Specific migration*

In order to evaluate the suitability for food contact of reprocessed PHBV, crotonic acid migration was assessed in three different food simulants following the recommendation of European regulation EU 10/2011 on plastic materials and articles intended to come into contact with food [12]. The Namely, 95% Ethanol to simulate fatty food, 3% acetic acid to simulate acidic food and Tenax as solid dry food simulant. The migration level of crotonic acid was mesasured by desorption tests as shown in Figure 16. According to European standard EN 10/2011, films disks of 2.8 cm diameter were immersed in 95% ethanol or 3% acetic acid, with a surface/volume ratio of 6 $dm^2.L^{-1}$. In the case of Tenax, a film of 3x2 cm was placed into Petri dish and completely covered by the simulant (0.24 g corresponding to 4 $g.dm^{-1}$). All samples were stored at 40 °C for 10 days under magnetic stirring for liquid simulants.

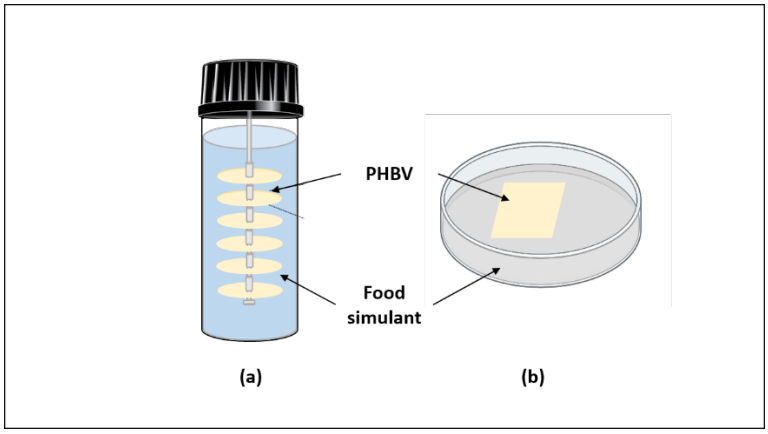


Figure 16. Specific migration test in (a) liquid food simulant and (b) solid food simulant.

Crotonic acid was quantified in each food simulant after 10 days of contact by means of UPLC-DAD analysis. For detection purposes, Ethanol 95% samples were concentrated 67 times. A standard addition procedure was applied to acetic acid 3% samples, since it cannot be easily evaporated. Tenax samples were submitted to an extraction with 5 ml methanol, during 4 days at 40 °C and under magnetic stirring. The extracts were subsequently concentrated 5 times. All the samples were then, injected in Acquity UPLC (Waters, Milford, MA) liquid chromatography system, equipped with a photodiode array detector (DAD). The Waters column was 100 mm x 2.1 mm, HSS T3, particles size was 1.8 µm. The solvent used were A (99. % H_2O and 0.1% HCOOH v/v) and B (80% CH_3CN ; 19 % H2O ; 0.1% HCOOH) with a flow rate of 0.55 ml/min. The injection volume was 2 µl and DAD was set at 210 nm in order to detect the concentration of crotonic acid which was used as external standard.

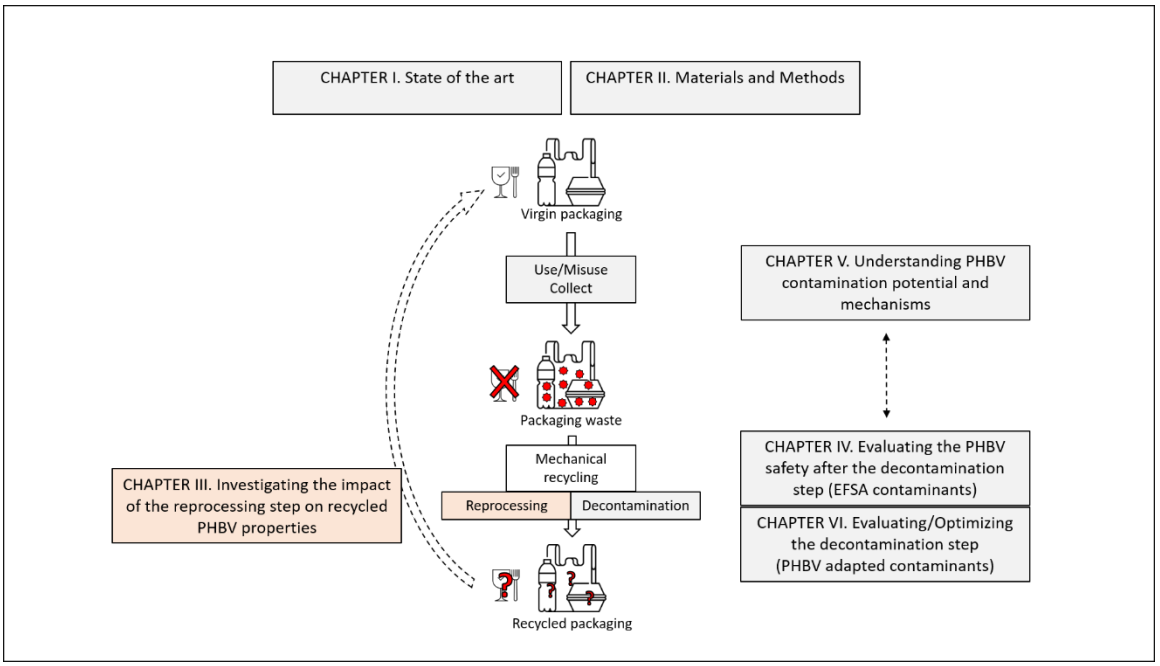
7. Statistical analysis

All the statistical analyses and data visualization were performed in R (RStudio, 2021). The variables were checked for normality (Shapiro-Wilk test). The significance of results was examined by one-way analysis of variance (ANOVA) followed by a Tukey test with a confidence interval of 95%. Then, the significant differences between the data were defined.

CHAPTER III. INVESTIGATING THE IMPACT OF THE REPROCESSING STEP ON RECYCLED PHBV PROPERTIES

CHAPTER III. INVESTIGATING THE IMPACT OF THE REPROCESSING STEP ON RECYCLED PHBV PROPERTIES (Article 1)

Ce chapitre a pour objectif d'étudier l'impact de la remise en œuvre sur les propriétés du PHBV, aussi bien en terme de performance que de sécurité alimentaire. Cette remise en œuvre, qui s'opère à l'état fondu, consiste généralement en un procédé d'extrusion du matériau afin de le remettre en forme. Les températures et contraintes de cisaillement élevées opérant lors du procédé étant susceptibles de dégrader le polymère, celui-ci peut présenter en sortie des propriétés amoindries par rapport au polymère vierge. Ceci aurait pour conséquence de compromettre la réutilisation du polymère recyclé en boucle fermée (recyclage « bottle to bottle »). De plus, dans le cadre d'application d'emballage alimentaire, les molécules néoformées (issues de la dégradation du matériau), si elles sont présentes, devront respecter les propriétés d'inertie vis-à-vis de l'aliment, édictées par la règlementation européenne 10/2011. Afin d'évaluer l'aptitude du PHBV à être remis en œuvre plusieurs fois, le polymère a été soumis à 4 cycles d'extrusion successifs, à l'issu desquels il a été caractérisé. Cette caractérisation a porté sur les propriétés structurales, d'usage (capacités mécaniques et barrières) et d'inertie, permettant de statuer sur l'aptitude du PHBV à être réutilisé pour des applications similaires.



Recycled poly(hydroxybutyrate-co-valerate) as food packaging: effect of multiple melt processing on packaging performance and food contact suitability

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Abstract

This study examines the opportunity of using recycled poly(hydroxybutyrate-co-valerate) (PHBV) as food packaging. The recyclability was evaluated by assessing the effect of repeated polymer processing (up to four extrusion cycles) on the structural and barrier properties of the material, as well as its ability to produce neo-formed chemicals susceptible to migrate into food. It was shown that increasing the number of processing cycles results in a decrease of the polymer molecular weight, leading to a decrease of mechanical properties, balanced by a maintenance of the crystalline structure and of the thermal stability. The oxygen and water vapour transfer properties were also maintained after four cycles suggesting that r-PHBV-based packaging can retain its property and use panel. The specific migration of crotonic acid, one of the main products of the thermomechanical degradation of the PHBV was measured in three different food simulants. In all cases, it did not exceed the specific migration limit (SML) set at 0.05 mg/Kg food, revealing the food contact suitability of non-contaminated recycled PHBV under test conditions.

Keywords: bioplastics; polyhydroxybutyrate-co-valerate; mechanical recycling; food packaging; suitability

1. Introduction

Plastic, with its unique set of properties (versatile, flexible, strong, cheap…) has become one of the most popular material since the second half of the 20th century. At the same time, this success is turning into an environmental and health disaster due to the plastic waste accumulation and the

widespread diffusion of persistent plastic fine particles, even in living organisms [159]. Packaging is the largest end-use market segment, accounting for over 40% of total plastic usage [160]. These fossil-based materials are in ever-increasing demand due to their desirable thermomechanical and barrier properties, yet they are beyond the world's capacity to handle. In 2019, 17.8 Mt of food and drink packaging were collected in Europe, with 18.5% landfilled, 39.5% incinerated and 42% down-cycled [161]. Landfill and incineration are still mainly used despite the Circular Economy Package adopted in 2017 by the European commission, which promotes a circular economy for plastics. In the frame of waste hierarchy, prevention should be considered as first priority, followed by preparing for re-use, materials recovery (mechanical and chemical recycling) and organic recycling. Energy recovery and disposal should be the last options envisaged [4]. Therefore, there is a gap between the current plastic waste management and the circular economy principles. This gap is even greater for alternative plastics, namely biobased and biodegradable plastics. These emerging plastics such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and polybutylene succinate (PBS) are increasingly entering the food packaging market thanks, in particular, to their deployment by major agri-business groups through a wide range of applications [162]. However, post-consumer biodegradable packaging are mainly directed towards the energy recovery lines (i.e. incineration) and are not recovered in an industrial composting facilities, as they cannot be assimilated to biowaste of natural origin according to many national standards. Yet, biobased and biodegradable plastics are likely to follow the different end-of-life options and should be incorporated in a hierarchal end-of-life system that prioritizes material recycling, leading to a recovery of economic value. LCA studies and TESA (Techno-Economic Sustainability Analysis) which are based on the assessment of mechanical recyclability, economic viability, common environmental/technico-economic sustainability criteria, confirm that the organic recycling of biodegradable and bio-based plastics should be only considered when mechanical and chemical recycling are not possible [8, 9, 31, 54, 163]. The mechanical recycling process consists in reprocessing the polymer waste, *via* a step of reshaping in the molten state, most often by extrusion. In the case of materials intended to food contact applications, specific requirements should be respected in order to ensure the safety of the recycled material. In EU, EFSA published in 2011, the criteria to be used to ensure the safety of food contact recycled PET, involving an additional decontamination step consisting in cleaning and heat treatment.

This decontamination step should be extrapolated to all other recycled plastics intended for food contact applications [27].

From a technical point of view, several investigations have addressed the mechanical recyclability of some biobased and/or biodegradable plastics. These studies, mainly focused on thermomechanical reprocessing of PLA, concluded that the thermal and mechanical properties are altered beyond a certain number of cycles [42, 44]. Only Briassoulis et al. have employed Techno-economic sustainability analyses (TESA) to address the feasibility of recycling food packaging biomaterials in a closed-loop system [31]. Among the promising biopolymers, polyhydroxyalkanoates (PHAs) have received particular attention thanks to their biocompatibility and biodegradability under natural conditions [16, 18]. Recent studies (from 2010 to 2020) on the biodegradation of PHAs in soil and marine environments were compiled in the review by Meereboer et al. The authors showed that depending on the nature of the soil and the temperature and moisture conditions, PHAs can reach up to 80% degradation in 80 to 100 days [63]. This family of bio-polyesters of microbial origin contains several homo- and copolymers with varying thermal and mechanical characteristics. Polyhydroxybutyrate-co-valerate (PHBV) is one of these copolymers, which has a great potential. During the biotechnological production, feeding and nutrient ratios may impact the valerate content which can vary from 0 to 24% inducing a modulation of the mechanical properties and flexibility of the copolymer [164]. Overall, PHBV has mechanical properties close to polypropylene and polystyrene (in terms of strength and elasticity but not flexibility), barrier properties close to those of PET, and its compliance with food contact material regulations, make it a good candidate to replace conventional plastics in the rigid food packaging category [18, 82, 165].

Although PHBV is biodegradable, this end-of-life option does not necessarily have to be favoured and can fully co-exist with possible material recycling which allows a reduction of production costs and saving raw materials and carbon.

When considering the closed-loop mechanical recycling of PHBV for food contact applications. Two questions arise (1) how many processing cycles can PHBV withstand without losing its mechanical and barrier properties, and without producing any neo-formed chemicals (NIAS) that could migrate into food, inducing toxicity to the consumer. (2) is the mechanical recycling process capable of removing

post-consumer contaminants due to previous packaging use or misuse, to comply with recycled packaging safety regulation. The second question involving the assessment of the decontamination efficiency through a challenge test will be the subject of a future work.

This study will focus on the effect of the multiple processing cycles on the evolution of the PHBV functional properties, as well as the formation of neo-formed chemicals.

Only very few studies investigated the modification of PHBV properties after reprocessing. Indeed, five cycles of extrusion followed by injection moulding at 170 °C [99] resulted in the maintenance of PHBV properties, except for a slight decrease in the fifth cycle. However, six cycles of extrusion at 180 °C led to thermal degradation of the polymer, reflected in a decrease in the molecular weight of PHBV and an increase in its crystallinity rate [98]. In the absence of a specific recommendation, PHBV-based materials are approved for food contact provided that the level of migration of crotonic acid, the main thermal degradation product of PHBV, does not exceed the permitted limit of 0.05 mg/kg food (CE/10/2011) [12].

The purpose of the present work is to investigate the functional properties of PHBV after several recycling loops, as well as the potential occurrence of crotonic acid at concentrations that may exceeds the recommended threshold. The integrated approach implemented in this study consists of monitoring the evolution of the structural characteristics of PHBV-based material (crystallinity rate and molecular weight of the polymer chains) in relation to the functional properties of the packaging (barrier and mechanical properties) throughout the reprocessing cycles and establishing an initial opinion on the opportunity of applying mechanical recycling in compliance with safety recommendations.

2. Experimental

2.1. Materials

PHBV with 3 mol% of 3-hydroxyvalerate (HV) was purchased from Nature plast (France). It corresponds to the PHI003 commercial grade, a pure uncompounded powder produced from pure culture. According to the manufacturer, PHBV has the following properties: density = 1,25 g.cm^{-3}, Tm = 170-176 °C. Molecular weight of PHBV powder was measured and Mw > 1100000 g/mol. Boron

nitride 98 % was purchased from Merck. Crotonic acid (98 %), ethanol (96 %), acetic acid (>99 %) and poly(2,6-diphenyl-p-phenylene oxide) under the trade name of Tenax (60/80 mesh) were supplied from Sigma-Aldrich.

2.2. Reprocessing cycles

PHBV powder was mixed with 0.5 wt% of Boron Nitride as a nucleating agent. To improve the mechanical properties of polymers, nucleating agents are often used, such as Hyperform HPN-20E used for HDPE, to reduce cycle time and improve blow moulding performance [166]. Then, the mixture was dried at 60 °C for 24h prior to extrusion. Extrusion was carried out in a parallel twin screw microcompounder Process 11 (Thermoscientific), at 150 rpm with a uniform processing temperature of 180 °C from the feeding to the die. The residence time of PHBV in the extruder did not exceed 3 min. Four processing cycles were performed in order to simulate the mechanical recycling. After each cycle, the granulating process was carried out at room temperature and the granulated product was dried at 60 °C for 24h. PHBV films with an average thickness of 300 µm were produced by thermocompression using a heated hydraulic press (20T, Pinette Emidecau Industries). About 6 g of pellets from each processing cycle were placed in a mould between two Teflon sheets and pressed with heating plates stabilized at 180 °C. The temperature was 180 °C and the pressure was first set at 5 bars for 1 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30. The resulting films were finally air cooled at room temperature.

After thermocompression of the PHBV films and before any characterization of the material, all samples were conditioned at a temperature of 25 °C and under an atmosphere with a relative humidity of 50% during 2 weeks in order to allow the secondary crystallization of PHBV [167].

2.3. Characterization methods

2.3.1. Size Extrusion Chromatography (SEC)

SEC was used to determine the evolution of PHBV molecular weight throughout the reprocessing cycles. Samples were placed in sealed tubes and dissolved in a 95/5 Hexafluoro-2-propanol/Chloroform

mixture at a concentration of 1mg/mL. Gel permeation chromatography (GPC) measurements were performed by a HP 1100 Series equipped with a PL gel 5 µm Minimixed-C column. The instrument, provided with a refractive index and UV detectors, worked using chloroform as eluent. The calibration of the instrument was constructed with polystyrene standards. The sample analyses were performed in triplicates. The weight-average molecular weight (*Mw*) and number-average molecular weight (*Mn*) were obtained from the SEC analysis and the polydispersity index (*PDI*) was calculated as Mw/Mn, using the software Excel 2016.

2.3.2. Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a TA Instruments (Q200 modulated DSC, TA Instruments) calorimeter under a nitrogen atmosphere with a flow rate of 50 mL.min^{-1} and a heating rate of 10 °C.min^{-1}. Around 8 mg of sample was used for each analysis and all experiments were done in duplicate. The samples were subjected to the following thermal schedule. First heating from -30 to 200 °C, with stabilization for 3 min; then cooling down up to -30 °C with again a stabilization for 3 min; followed by a second heating scan up to 200 °C.

The melt crystallization temperature (*Tc*) was determined from the cooling scan whereas the melting temperature (*Tm*) and the melting enthalpy (*ΔHm*) were obtained from the second heating scan after erasing the thermal history. Overall theoretical degree of crystallinity (*Xc*) was calculated from the melting enthalpy according to the following equation:

$$Xc\ (\%) = \frac{\Delta Hm}{\Delta H°(PHBV)} \quad (8)$$

where *ΔH0* is the melting enthalpy of 100% crystalline PHBV, i.e. 109 J/g [158].

2.3.3. Thermal gravimetric analysis (TGA)

TGA was carried out using a Mettler apparatus (TGA2) equipped with a XP5U balance (precision of 0.0001 mg). Around 8 mg of sample were heated at 10 °C.min^{-1} from 25 °C to 800 °C under nitrogen flow of 50 mL.min^{-1}. Three replicates were scanned for each sample. Mass loss and first derivative of

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ISO½ samples were cut from the films obtained by thermocompression. Tensile properties of samples were measured using a tensile tester (Zwick BZ2.5/TN1S) with a cross-head speed of 1 $mm.min^{-1}$. Young's modulus, elongation at break as well as tensile strength were calculated from strain-stress curves with the Matlab program, taking into account an effective cross section of 22 mm. Ten replicates were scanned for each reprocessing cycle.

2.3.5. Transfer properties

The Oxygen permeability (PO_2) of the reprocessed films was determined in triplicate at 23 °C and 50% relative humidity, using an O_2 permeation chamber equipped with an integrated PSt6-type sensor (PreSens Precision Sensing GmbH). This system consists of two chambers separated by a grid where the film is placed with an open testing area of $1{,}26.10^{-3}$ m^2. After applying nitrogen flesh on both sides of the film to remove the surrounding oxygen, the lower chamber was exposed to an oxygen flow of 50 $mL.min^{-1}$, while the upper chamber was hermetically closed. By permeation, the O_2 molecules could pass through the film where the sensor stood. The system measured oxygen ingress in % for five days. PO_2 ($mol.m/m^2.s.Pa$) was calculated according to the following equation :

$$PO_2 = \frac{J \, x \, e}{A \, x \, \Delta P} \quad (9)$$

where J ($mol.s^{-1}$) is the flux of gas passing through the film, e is the film thickness (m), A, the permeation area (m^2) and ΔP, the differential partial pressure of the permeant gas across the film (Pa).

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40 mL of distilled water, and were placed in a desiccator containing silica gel, for 10 days. Pwv (mol.m/m^2.s.Pa) was calculated according to the following equation :

$$P_{wv} = \frac{J\ x\ e}{A\ x\ \Delta P} \quad (10)$$

where J (mol.s^{-1}) is the flux of water vapour passing through the film, e is the film thickness (m), A, the permeation area (m^2) and ΔP, the differential water vapour pressure between the cell and the desiccator (Pa).

2.3.6. Migration tests

In order to evaluate the suitability for food contact of reprocessed PHBV, crotonic acid migration was assessed in three different food simulants following the recommendation of European regulation EU 10/2011 on plastic materials and articles intended to come into contact with food [12]. These are, 95% Ethanol to simulate fatty food, 3% acetic acid to simulate acidic food and Tenax as solid dry food simulant. The migration level of crotonic acid was measured by desorption tests. According to European standard EN 10/2011, films disks of 2.8 cm diameter were immersed in 95% ethanol or 3% acetic acid, with a surface/volume ratio of 6 dm^2.L^{-1}. In the case of Tenax, a film of 3x2 cm was placed into Petri dish and completely covered by the simulant (0.24 g corresponding to 4 g.dm^{-1}). All samples were stored at 40 °C for 10 days under magnetic stirring for liquid simulants.

Crotonic acid was quantified in each food simulant after 10 days of contact by means of UPLC-DAD analysis. For detection purposes, Ethanol 95% samples were concentrated 67 times. A standard addition procedure was applied to acetic acid 3% samples, since it cannot be easily evaporated. Tenax samples were submitted to an extraction with 5 ml methanol, during 4 days at 40 °C and under magnetic stirring. The extracts were subsequently concentrated 5 times. All the samples were then, injected in Acquity UPLC (Waters, Milford, MA) liquid chromatography system, equipped with a photodiode array detector (DAD). The Waters column was 100 mm x 2.1 mm, HSS T3, particles size was 1.8 µm. The solvent used were A (99. % H_2O and 0.1% HCOOH v/v) and B (80 % CH_3CN; 19 % H2O; 0.1%

HCOOH) with a flow rate of 0.55 mL/min. The injection volume was 2 µL and DAD was set at 210 nm in order to detect and quantify crotonic acid which was used as external standard.

2.4. Statistical analysis

Statistical analyses and data visualization were performed in XLSTAT (Addinsoft, 2019). The variables were checked for normality (Shapiro-Wilk test). The significance of results was examined by one-way analysis of variance (ANOVA) followed by a Tukey test with a confidence interval of 95 %. Then, the significant difference between the data had been defined.

3. Results and Discussion

3.1. Structural properties

The evolution of the molecular weight (Mw), polydispersity and crystallinity parameters of PHBV during the processing cycles is shown in table 6. Cycle 0 corresponds to the first extrusion cycle transforming PHBV powder into pellets.

Table 6. Molecular weight and crystallinity parameters of PHBV films after the reprocessing cycles. Values represented are mean ± standard deviation.

PHBV	Mw (g/mol)	PDI	Tc (°C)	Tm (°C)	Xc (%)	Tdeg (°C)
Cycle 0	$827206^{a} \pm 21831$	$3.8^{a} \pm 0.4$	$125.3^{a} \pm 0.2$	$177.6^{a} \pm 0.4$	$87.7^{a} \pm 0.7$	$300.2^{a} \pm 0.9$
Cycle 1	$815486^{a} \pm 29939$	$3.7^{a} \pm 0.1$	$126.1^{ab} \pm 0.1$	$177.7^{a} \pm 1.0$	$88.1^{a} \pm 0.6$	$299.4^{a} \pm 2.4$
Cycle 2	$683572^{b} \pm 20411$	$3.6^{a} \pm 0.3$	$126.3^{ab} \pm 0.5$	$177.7^{a} \pm 1.0$	$88.0^{a} \pm 0.4$	$300.8^{a} \pm 0.6$
Cycle 3	$662609^{b} \pm 36669$	$3.4^{a} \pm 0.4$	$126.6^{b} \pm 0.4$	$177.8^{a} \pm 0.9$	$89.2^{a} \pm 0.6$	$302.0^{a} \pm 1.2$
Cycle 4	$627822^{b} \pm 15349$	$3.3^{a} \pm 0.4$	$127.1^{b} \pm 0.1$	$177.3^{a} \pm 0.8$	$89.4^{a} \pm 0.4$	$299.3^{a} \pm 0.1$

As *Mw* of PHBV commercial powder is > 1100000 g/mol, it is worth to note that the first extrusion cycle (corresponding to cycle 0) induced the most dramatic degradation of the polymer, decreasing its molecular weight by almost 25 %. Subsequently, PHBV *Mw* decreased with the number of processing cycles. At the end of the fourth cycle, PHBV polymer lost ~25 % of its *Mw*. As previously described, the high temperatures and the shear stress that polymer undergone during the reprocessing result in a progressive chain scission , mainly attributed to the beta-elimination mechanism [10, 100]. The constant value of the polydispersity index (PDI) of the polymer observed over the five extrusion cycles supports the hypothesis of the random nature of the chain scission reactions in the polymer. The crystallinity parameters *i.e* crystallization temperature (*Tc*), melting temperature (*Tm*) and crystallization rate (*Xc*) were respectively determined from cooling and second heating scans of PHBV films visible in figure 17. The crystallization rate of the polymer did not significantly evolve throughout the processing cycles. However, a slight increase in the crystallization temperature *Tc* was observed from the third cycle, indicating that the crystallization is occurring more easily when the number of cycles increases. An easier crystallization process is likely due to the reorientation of the polymer fragments after the chains scission[70, 168]. On the other hand, the crystallization rate as well as the melting temperature remained constant over the five processing cycles. Zembouai et al. [98] have observed an increase in crystallinity rate after processing PHBV with 3 wt% valerate content over six cycles of extrusion, while Zaverl et al. [99] described an opposite behaviour in the case of the copolymer exhibiting a valerate percentage of 14 %, under similar processing conditions. Since these two studies also simulated the PHBV reprocessing via a polymer extrusion process, the crystallinity evolution is

then likely due to the valerate content, in the absence of any nucleating agent. In our case, the use of boron nitride seems to govern the nucleation process, causing slight evolution in crystallization rate, *Tm* and *Tc*, despite the significant degradation of polymer chains. The melting temperature (*Tm*) remained almost constant, meaning that the fusion of crystalline fraction takes place in the same way over the reprocessing cycles. Polymer degradation should decrease the spherulites size, but the nucleation seems to be not affected by the polymer degradation in the presence of the nucleating agent [169]. This was confirmed by the constant shape of the unimodal melting peak indicating a relative stability of the distribution of the crystallite sizes [169]. The constant melting temperature at around 177 °C implies that the process temperature scale can be kept the same at 180 °C during the five cycles. Since the polymer degradation might be enhanced when its processing occurs higher from its melting temperature, the previously observed differences in polymer degradation cannot therefore be explained by differences in the melting temperature during the process [169].

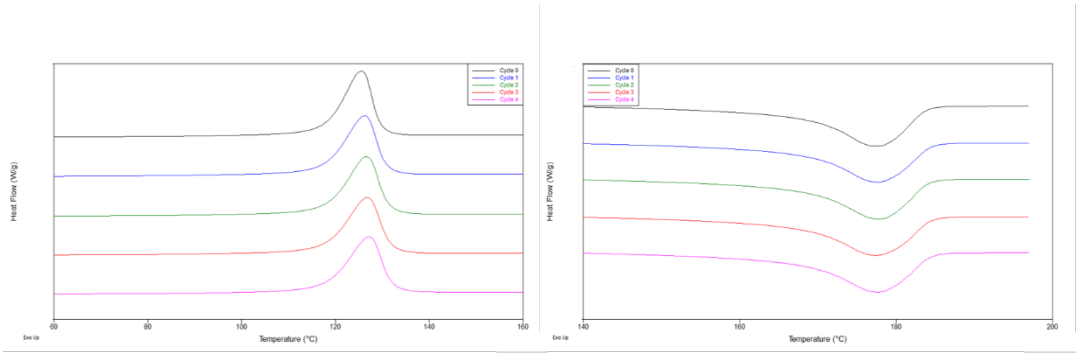


Figure 17. PHBV DSC curves over four extrusion-compression cycles (a) cooling scan and (b) second heating scan.

The thermal gravimetric analysis (TGA) showed almost the same degradation maximum temperatures for samples of different reprocessing cycles with no significant change has been detected over the reprocessing cycles as shown in figure 18. Previous studies reported the same trend in PHA or PLA reprocessing [74, 99]. This may be explained by the relative stability of the crystallinity degree [170].

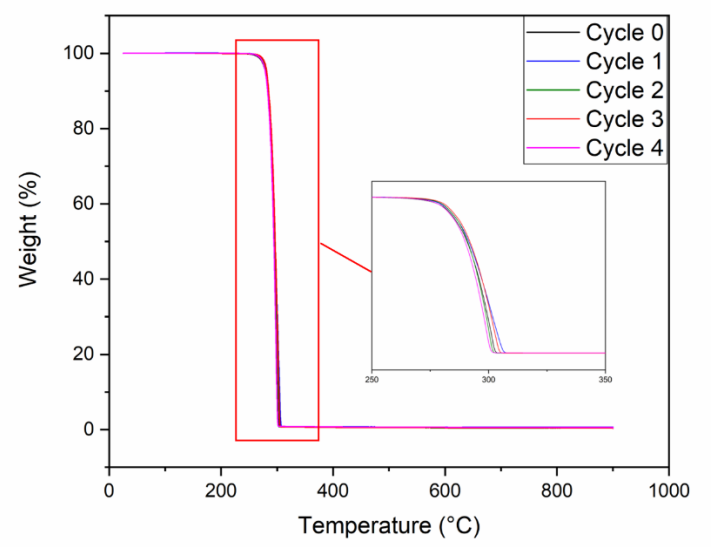


Figure 18. PHBV ATG curves over four extrusion-compression cycles.

These results showed that despite a significant decrease in the polymer molecular weight, the crystalline behaviour and the thermal stability have evolved very slightly over the processing cycle. This observation is consistent with studies focusing on the impact of reprocessing on the thermal behaviour of PHA [98, 99]. However, in the context of food packaging applications, functional properties (mechanical and barrier) as well as the safety of the reprocessed materials should be taken into account in order to ensure compliance with quality requirements and regulation.

3.2. Mechanical properties

Figure 19 shows pictures of the film samples obtained over successive cycles and reveals that the reprocessed materials do not present any obvious visual changes. The macroscopic optical properties such as colour, opacity and smooth texture do not appear to be altered by the reprocessing.

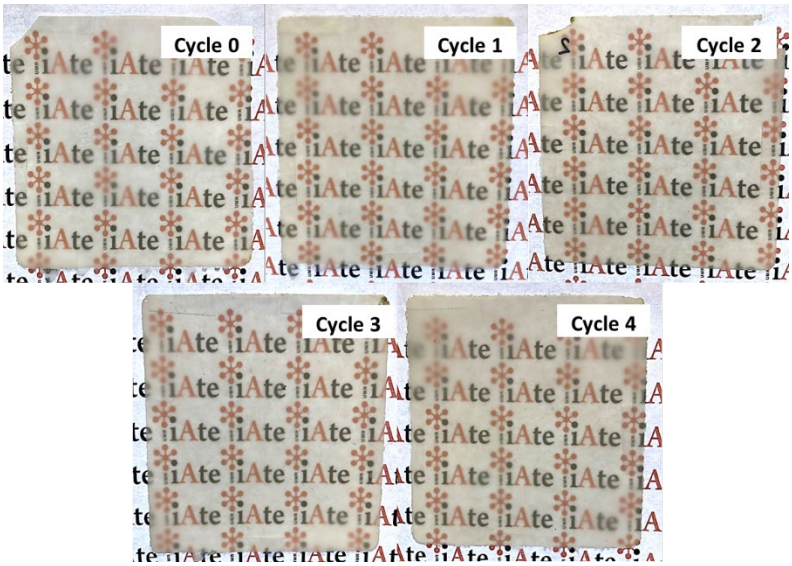


Figure 19. PHBV films over four extrusion-compression cycles.

The mechanical properties of the material reflect its ability to provide a high-performance packaging for food and define which types of packaging (bottles, trays, flexible bags, etc.) can be produced. Based on these tensile tests, the evolution of the mechanical properties of the materials over the processing cycles are summarized in table 7, and the tensile stress vs. strain curves are shown in figure 20.

Table 7. Evolution of the mechanical properties after reprocessing cycles. Values represented are mean ± standard deviation.

Sample	Young modulus (MPa)	Tensile strength (Mpa)	Strain at break (%)
Cycle 0	$1148^{ab} \pm 38$	$39.9^{a} \pm 1.5$	$6.2^{a} \pm 0.3$
Cycle 1	$1068^{a} \pm 59$	$40.0^{a} \pm 0.7$	$6.8^{a} \pm 0.2$
Cycle 2	$1143^{ab} \pm 57$	$38.4^{ab} \pm 1.8$	$6.4^{a} \pm 0.7$
Cycle 3	$1199^{b} \pm 61$	$36.0^{b} \pm 3.4$	$4.1^{b} \pm 0.5$
Cycle 4	$1197^{b} \pm 121$	$36.5^{b} \pm 2.5$	$4.7^{b} \pm 1.4$

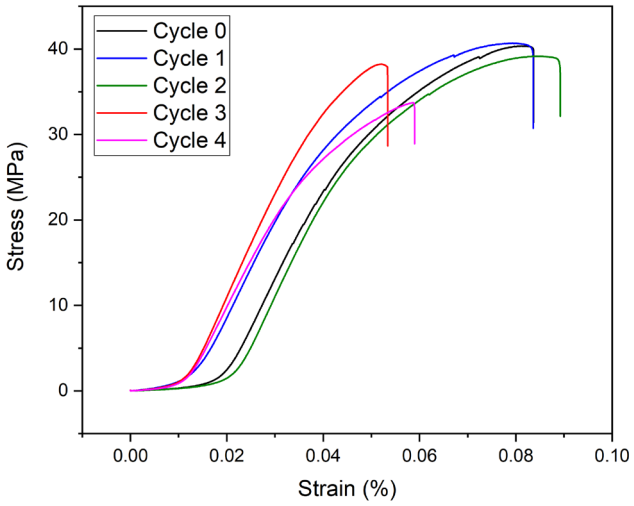


Figure 20. Stress vs strain curves of PHBV depending on the number of reprocessing cycles.

These values confirm that PHBV can be considered as a brittle and stiff material, which exhibits low ductility due to its high crystallinity. Compared to other semi-crystalline polymers, mechanical properties of PHBV reflect a rigid and fragile behaviour from the first cycle. Over the processing cycles and especially after the third one, a slight increase in young's modulus (~ 4.8 %) and a decrease in both tensile strength (~ 8 %) and strain at break (~ 25.2 %) were observed. These variations indicate a reprocessing-induced embrittlement of PHBV. Most studies about reprocessing of biopolymers such as PLA, PBS or PHB reported that thermal reprocessing results in no or low influence on Young's modulus, supposing that the value remains stable since the decrease of molecular weight is balanced by an increase of crystallinity [106, 170]. However, a gradual drop in the tensile strength and strain at break values are observed. In our case, the increase of crystallinity is less pronounced than the decrease of molecular weight, which may explain the slight variation of the Young's modulus, but the decrease in tensile strength and strain at break revealed a decrease of mechanical properties, due to the polymer chain scission.

Yet, these modifications being limited, the reprocessed materials present sufficiently preserved performances for the targeted applications. In reality, the stiffness of PHBV limits its applications to the packaging of solid food, as trays or jars.

3.3. Transfer properties

Oxygen and vapour permeability measurements are considered as indicator of barrier properties that reflect the effectiveness of the packaging in extending the shelf life of the packaged product. Figure 21 shows the evolution of the oxygen and water vapour permeability of PHBV films over the processing cycles, and demonstrates the lack of detrimental effect of the four successive reprocessing steps.

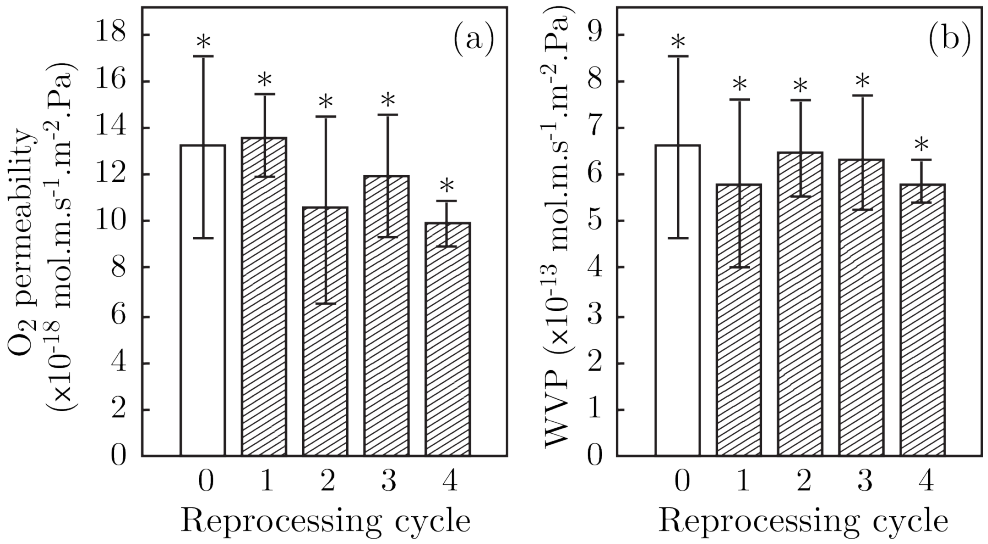


Figure 21. Oxygen (a) and water vapour (b) permeabilities of PHBV films depending of the number of reprocessing cycles.

Oxygen permeability showed a slight downward trend although these variations are not significant. This is consistent with the slight increase of crystallinity (Table 6) as the permeation of molecules takes place in the amorphous phase. These values appear to be in agreement with previous measures reported on similar materials [171-173] and are characteristic of a good barrier material against gas and water vapour transfer, with low permeabilities (close to those of PET materials) [165]. A high variability of permeability measurements was observed which can be partially explained by the heterogeneity of the materials, induced during their thermoforming. It is worth noting that the small variation in material permeability (well below a factor of ten) does not impact the shelf life of the packaged food regardless of the system considered. Therefore, the reprocessing of PHBV did not have an influence on the performance of the packaging in terms of barrier properties.

3.4. Food contact suitability: occurrence of neo-formed chemicals

As any material intended to come into contact with food, PHBV-based packaging must meet the inertness criteria defined in the European framework regulation (UE/1935/2004) and consequently must not transfer any substance that may present a danger for human health [12]. The issue of the suitability for food contact of a biosourced and biodegradable material such as PHBV cannot be raised on the same basis as a conventional plastic material since it is, in principle, free of additives. Therefore, compliance should be assessed on the unique basis of measuring the migration of non-intentionally added substances (NIAS). In the case of a compound present in the positive list of authorized substances (EU/10/2011), the migration of this substance must not exceed the specified specific migration limit that was set on the basis of toxicological data.

It is well-known that the thermomechanical degradation of PHVB obeys to random chain scission mechanism with crotonic acid (but-2-enoic acid) as one of the major low molecular weight degradation products[10, 100]. Crotonic acid is referenced in the positive list of authorized substances with a specific migration limit (SML) of 0.05 mg/kg food (CE/10/2011) [12]. As consequence and although food-grade PHBV contains in principle a concentration of crotonic acid below the permitted threshold [174], the production and release of crotonic acid in food over reprocessing cycles must be considered as a critical point of safety concern. All the more so as oligomers may migrate and be hydrolysed (*in vivo* or *ex vivo*) then further exposure could occur. As PHBV is a rigid and stiff material, its application is a priori limited to rigid packaging such as trays and jars, mainly dedicated to solid foodstuff (e.g. meat, cheese, yogurts or dry food). To simulate the foodstuff that could be packed in PHBV, three food simulants have been selected, namely, ethanol 95 % for fatty food, acetic acid 3 % for acid food and Tenax for dry food [12]. Table 8 summarizes the specific migration of crotonic acid in the different food simulants as function of processing cycle number.

Table 8. Specific migration of crotonic acid from processed PHBV into food simulants*

Processed PHBV	Crotonic acid specific migration (mg/kg 95% ethanol)	Crotonic acid specific migration (mg/kg 3% acetic acid)	Crotonic acid specific migration (mg/kg tenax)
Cycle 0	0.015 ± 0.001	< 0.01	< 0.001
Cycle 2	0.018 ± 0.001	< 0.01	< 0.001
Cycle 4	0.042 ± 0.002	< 0.01	< 0.001

*For 3 % acetic acid and tenax measurement, the migration of crotonic acid was not detectable. Values are given as being below the detection limit of the method

Migration of crotonic acid in 95 % ethanol, increased with the number of processing cycles, reaching 0.042 mg/Kg after the fourth cycle. However, in both 3 % acetic acid and Tenax, the amount of crotonic acid was barely detectable by the methods used with values below of 0.01 mg/Kg in acetic acid 3 % and less than 0.001 mg/Kg in tenax. These results indicate that crotonic acid resulting from the thermomechanical degradation of re-processed PHBV (see table 6 for chain scission) is readily released in 95 % ethanol, whereas it does not migrate into aqueous acetic acid and even less into solid food simulant. This is consistent with previous safety assessment of poly(hydroxybutyrate-co-hexanoate) (PHBH) from EFSA, where the overall migration and the specific migration of crotonic acid were evaluated in various food simulant [175, 176]. Overall migration was found to be higher in 95 % ethanol while it was lower in 3 % acetic acid and not detectable in tenax. These results confirm the conclusion of Angelier *et al.* (2020) [177] that, based on global migration measurements, contact with ethanol 95 % constitutes the worst conditions of use for PHBV-based materials. In addition, EFSA has issued an opinion stating that EtOH 95% is not a suitable food simulant for such polar polymers and that migration into it should not be considered since it essentially gives total extraction [175].

From a regulatory stand-point, the specific migration of crotonic acid proves not exceed the specific migration limit of 0.05 mg/Kg in the three food simulants used in this study suggesting that, after 4 processing cycles, virgin PHBV (without additives) could be considered to have no health concerns. However, it is important to keep in mind that reprocessing of PHBV was conducted at laboratory small-scale and do not accurately reflect the industrial process conditions including, in particular, a potentially much longer residence time of the polymer in the extrusion chamber. As

consequence, the values measured in food simulants must be regarded with care and attention as they could come alarmingly close to the SML after four processing cycles.

The assessment of the food contact suitability of PHA-based recycled materials is not currently covered by any EU directive or guidance from the European health authorities. For this reason, we need to be vigilant in assessing the risk associated with recycled PHBV materials by integrating the evaluation of neo-formed compounds and the evolution of inertness properties that evolve with the structural modifications generated by the thermal treatment cycles. We should not only apply the challenge test approach inspired by PET bottle-to-bottle recycling.

4. Conclusion

The prospect of recycling PHBV-based food packaging is an issue that requires the consideration of many criteria. The approach applied in this investigation is based on a comprehensive assessment of the impact of repeated extrusion-compression cycles (up to four cycles) on the functional properties and the safety (through the assessment of neo-formed products) of the resulting packaging. Gas and mass transfer properties are at the heart of these issues as they determine the barrier performance and the food contact suitability of recycled materials. Thermo-mechanical treatments applied to the material induce multiple structural modifications at the molecular level such as random chain scission and probable depolymerisation which need to be considered with respect to their effects on these transfer properties. While these macromolecular breakdowns induce a mechanical embrittlement of the material, they do not induce any significant variation of the water vapour and oxygen permeability values, which leads to the conclusion that multiple recycling does not dramatically change the usability of PHBV materials as food packaging for solid foodstuff (as trays and jars). Apart from market and infrastructure considerations, the main technological barrier to the deployment of mechanical recycling technology applied to PHBV-based food packaging is probably related to the release of the crotonic acid produced by the chain depolymerization and subject to a low migration limit. This point of concern is all the more important at a time when the European Commission is opening a consultation on a draft amendment to the evaluation provisions for recycled plastic. The aim of this initiative is to extend the recycling of plastics intended to come into contact with food, currently restricted to PET, to other resins and thus to

extend it to other packaging waste. The first draft submitted for public consultation proposes an evolution of provisions for the appropriate evaluation of non-PET materials including increased vigilance on residual incidental contamination. Unlike the challenge test procedure used for PET, which does not take into account the presence of neo-formed contaminants during the process, the future alternative approach is based on designed sampling strategy to obtain the best possible estimate of the average contaminant level in a batch of rec. The specific migration values of crotonic acid are highly dependent on the type of food and storage conditions. However, the thermal treatment applied to post-consumer PHBV packaging will have to be finely optimized in order to avoid any excessive production of crotonic acid within a concentration limit in the sample batch which is not defined at present.

Statements & Declarations

Funding

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Competing Interest

The authors declare that they have no competing financial interest of personal relationship that could influence the work reported in this paper.

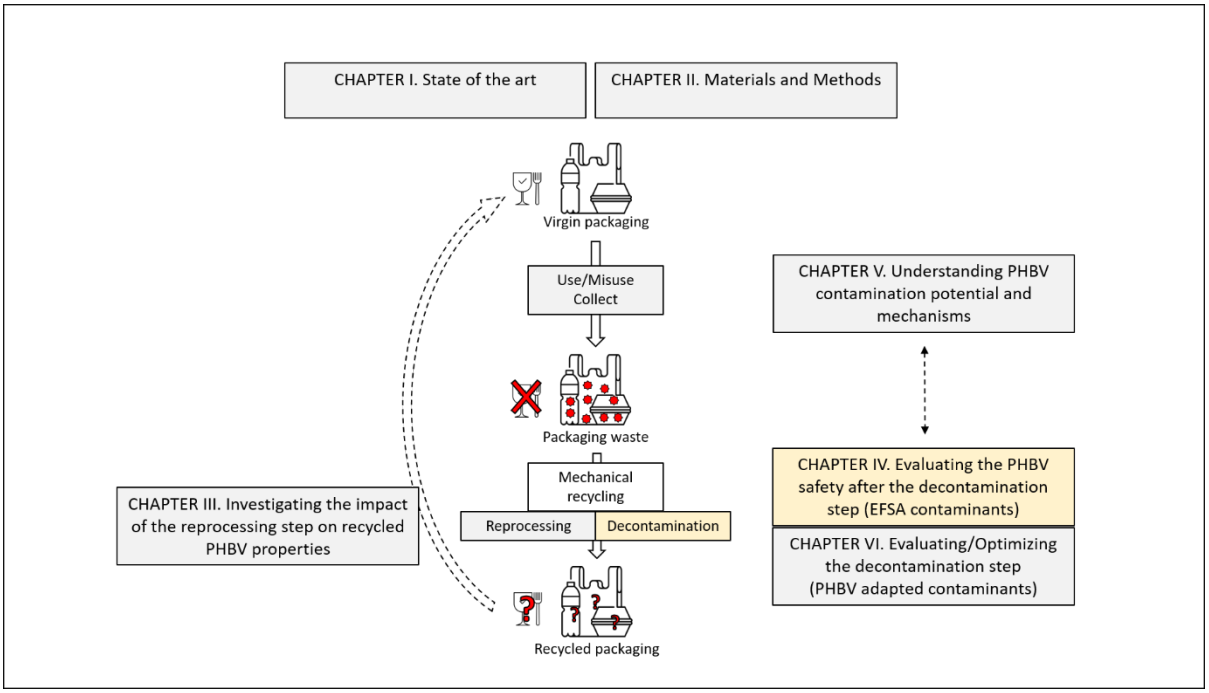
Conclusion

La recyclabilité mécanique du PHBV a été évaluée en mesurant l'impact de la remise en œuvre répétée du polymère, sur ses différentes propriétés. Comme attendu, le polymère a subi une dégradation progressive au cours des 4 cycles successifs d'extrusion. Cependant, l'impact sur ses propriétés d'usage (propriétés mécaniques et de transfert) s'est révélé plutôt modéré. L'inertie du polymère, a été mesurée via l'évaluation de la migration spécifique de l'acide crotonique, produit néoformé issu de la dégradation du PHBV. Au contact d'aliments acides ou solides, cette inertie n'est pas impactée. Cependant, en présence du simulant alimentaire, l'éthanol 95 %, la migration de l'acide crotonique a augmenté avec le nombre de cycles d'extrusion, compromettant, potentiellement, le ré-usage du matériau après 4 cycles. L'éthanol 95%, souvent utilisé pour substituer les huiles végétales, provoque un gonflement du polymère, induisant, ainsi, une migration plus importante de l'acide crotonique. Au-delà de ce fait, il est nécessaire d'accroitre la vigilance quant à l'inertie du PHBV après remise en œuvre. De plus, dans le cadre du recyclage mécanique des emballages à usage alimentaire, une vigilance particulière doit être portée sur la contamination accidentelle, ou provoquée par les résidus alimentaires, tel que décrit dans le chapitre IV.

CHAPTER IV. EVALUATING THE PHBV SAFETY AFTER THE DECONTAMINATION STEP (EFSA CONTAMINANTS)

CHAPTER IV. EVALUATING THE PHBV SAFETY AFTER THE DECONTAMINATION STEP (EFSA CONTAMINANTS) (Article 2)

Ce chapitre a pour objectif d'évaluer l'aptitude au contact alimentaire du PHBV après un procédé de décontamination. Afin de réaliser cette évaluation, nous nous sommes basés sur la règlementation européenne existante, élaborée pour le recyclage en boucle fermée des bouteilles en PET. Dans cette réglementation, il est établi que tout matériau recyclé en vue d'une utilisation en contact avec les aliments, devra provenir d'un procédé de recyclage évalué et autorisé par l'EFSA. Dans ce chapitre, la même procédure sera appliquée au PHBV. Ainsi, le matériau sera contaminé, avec le même panel de contaminants représentatifs identifiés pour le PET, avant d'être soumis à un procédé de décontamination thermique, sous vide. A l'issu de ce procédé, l'aptitude au contact alimentaire du matériau, pour des applications d'emballages ciblées, sera évaluée. Afin de valider le procédé de décontamination, le PET sera utilisé comme contrôle.



Mechanical recyclability of biodegradable polymers used for food packaging: case study of PHBV

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Abstract

For the purpose of mechanical recycling for food contact applications, decontamination of PHBV polymer was performed under different temperatures and time conditions. As expected, increasing the decontamination temperature and duration increased the decontamination efficiency, but also the degradation of the polymer. Thus, the combination 160°C/6h was selected as the optimal conditions that maximize contaminants removal while minimizing polymer degradation. Then, the safety of the recycled PHBV under these conditions was assessed, in accordance with EFSA regulation based on bottle-to-bottle PET recycling. Decontamination of low molecular weight molecules such as toluene, chlorobenzene, and methylsalicylate was nearly complete with residual concentrations below the modelled concentrations allowed in the polymer when the adult scenario was considered. However, the higher molecular weight and lower volatility molecules exhibited acceptable decontamination efficiencies, but their residual concentrations in the polymer exceeded the maximum concentrations of no concern. The presence of these molecules allows the use of nearly 21% recycled PHBV in the new materials to meet safety criteria. It is important to keep in mind that this work, never done before, is a preliminary work on mechanical recycling of PHBV, mainly based on extrapolation of PET conditions and regulations. Much more research needs to be done to improve the decontamination process, the barrier properties of PHBV or to think about a short recycling line for PHBV.

Keywords: bioplastics; polyhydroxybutyrate-co-valerate; mechanical recycling; food packaging;

suitability

1. Introduction

In 2020, the plastic demand in Europe was estimated at 49 Mt with almost 40% attributed to packaging [2]. For several years, packaging has accounted for the largest share of 60% of plastic waste generation [178], with serious impacts on the environment, ecosystems and human health . One key goal of the circular Economy Action Plan (CEAP) adopted by the European commission in 2015 and revised in 2020, was “tackling packaging and packaging waste”. This general principle applies in particular to the European packaging and packaging waste directive (PPWD) 94/62/EC (1994, reinforced in 2018) which sets that by December 2025 at least 65wt% of all packaging waste must be recycled, with a target of 5% increase of recycling by 2030 [179]. Currently, the dominant technology for plastic recycling is mechanical recycling, which is considered as the most environmentally friendly and economical end-of-life scenario, according to LCA studies [9, 54]. However, the concept of recycling, i.e. closed loop recycling, is often confused with down-cycling, where the product obtained after processing is of lesser quality. According to Ellen MacArthur Foundation, only 2% of plastic packaging is being kept within the closed loop [180], mainly limited to bottle-to-bottle applications of polyethylene terephthalate (PET) and some HDPE (high density polyethylene) bottles, with a maximum of two recycling cycles.

For closed-loop mechanical recycling of food contact materials (FCM), the issue of food safety must be addressed and the ability of the recycling process to remove post-consumer contaminants must be studied in order to satisfy the compliance requirements defined in Commission Regulation EU 10/2011 [12] and in Commission Regulation EC 282/2008 [11]. Contaminants can be divided into polymer residues, such as additives and polymer degradation products, contaminants from food, and post-consumer contaminants related to the misuse of the packaging. For example, during use, substances from food components may migrate into packaging, while misuse occurs when packaging is reused to store non-food or toxic substances. Contamination can also occur during the waste collect and sorting steps. As mentioned above, due to the maturity of the closed-loop PET recycling market and technologies, the European Food Safety Authority (EFSA) has exclusively published opinions on the safety assessment of the mechanically recycled PET bottles for direct food contact [156, 181-183] and

several studies (based on surveys) have been conducted to establish the main sources of contaminations as well as the chemical structures of the contaminants [184]. As a result, model substances were selected to represent the real-case contaminants by covering a wide variety of functional chemical groups. These contaminants are listed in EFSA and FDA (US Food and Drug Administration) regulations [152].

The evaluation of PET recycling processes is based on the measurement of decontamination efficiency resulting from the comparison between the residual concentration of contaminants measured in the recycled polymer (C_{res}) and a modelled concentration in this polymer (C_{mod}) set on the basis of a toxicological threshold [156]. The evaluation is part of "challenge tests" approach which consist in subjecting artificially contaminated plastic samples to the recycling process before analyzing the residual concentration of these contaminants. The model contaminant concentrations are established by means of migration models and correspond to the substance concentrations, in the packaging, able to contaminate the food at the set toxicity threshold. It results from a tolerable intake of 0.0025 µg/kg bw/day which is considered as the threshold of toxicological concern for genotoxic compounds proposed by EFSA [185]. When C_{res} is lower than C_{mod}, the recycled PET is not considered of safety concern, and the recycling process is evaluated as safe under the specified conditions of use [27]. Considering that the dietary exposure of consumers to the chemical substances should not exceed reference values, there is a question of whether the contaminants panel identified for PET can be extrapolated to other polymers which exhibit different transport properties. The few studies conducted on HDPE contamination concluded that due the structural difference between PET and HDPE, other substances with higher Mw may be of concern in the case of HDPE and that the challenge test with the PET contaminants panel is not appropriate for all polymers [140].

While the lack of knowledge on the safety assessment of recycled regular plastics such as PE and PP is notable, the gap is even deeper for alternative plastics, namely biobased and biodegradable plastics. Today, there are no regulations regarding the safety assessment of recycled biodegradable plastics in contact with food. Yet, there is a great interest and growing demand for these plastics, which will soon lead to an accumulation of their waste. In addition, it is important to note that biodegradation and mechanical recycling are not incompatible end of life options, but complementary ways to save resources, reduce production costs while avoiding the generation of persistent plastic wastes. In addition,

the EU mentioned that an important goal is to either reuse or recycle all plastics packaging entering the EU market by 2030 [25]. This means that, at the end, all food packaging materials (plastics and bioplastics) must be recycled in a closed-loop. Among emerging biodegradable plastics, polyhydroxyalkanoates (PHA) is one of the most attracting polymer families for food packaging applications, involving several homo- and copolymers with varied properties. Polyhydroxybutyrate-co-valerate (PHBV) is one such copolymers, which has attracted a lot of interest due to its polypropylene-like mechanical and barrier properties [186]. Mechanical recycling of PHBV for food contact applications has never been investigated before and only few studies have addressed the effect of multiple processing cycles on thermomechanical properties of the polymer, showing the decrease in molecular weight and embrittlement of the polymer after a number of cycles [98, 99]. These investigations also shown that the generation of crotonic acid, one of the major thermal degradation products of PHA, increased with the number of processing cycles. Due to its toxicity concern, crotonic acid is subject to migration limit and must be considered in the safety assessment of recycled PHBV.

This study will provide new insights into the feasibility of using recycled PHBV as food contact material. A super-cleaning recycling process will be undertaken for PHBV-based material and its decontamination efficiency will be evaluated. In the absence of specific recommendation for biodegradable polymers, the decontamination efficiency of PHBV will be evaluated according to PET-based regulation, using the approach and contaminants panel applied for PET, the reevaluation of the PHBV contaminants panel being the subject of a future work. Before evaluating the safety of the polymer, different decontamination conditions were tested (different temperature/time combinations). The degradation of the polymer during the decontamination process was studied by monitoring the thermomechanical properties of the polymer. The optimal decontamination conditions resulted from a compromise between the highest contaminants removal and the lowest polymer degradation.

2. Materials and Methods

2.1. Materials

PHBV powder with 3 mol% of 3-hydroxyvalerate (HV) was purchased from Nature plast (France). It corresponds to the PHI003 commercial grade, a pure uncompounded powder produced from pure culture. According to the manufacturer, PHBV has the following properties: density = 1250 kg.m^{-3}, Tm = 170-176 °C.

Nucleating agent (boron nitride), contaminants (listed below), solvents (methanol, ethanol), and 3,5-Di-tert-4-butylhydroxytoluene (BHT) as internal measurement standard for GC analysis were purchased from Sigma Aldrich France.

In order to follow the FDA and EFSA guidelines, PHBV flakes were spiked with a set of surrogate contaminants, which should have a range of molecular weight and polarity representative of potential contaminants of concern, their diffusion and sorption behavior [27, 152]. Today, EFSA publications refer mainly to PET recycling, with the following list of surrogates: toluene (92 g.mol^{-1}), chlorobenzene (113 g.mol^{-1}), methyl salicylate (152 g.mol^{-1}), phenylcyclohexane (160 g.mol^{-1}), benzophenone (182 g.mol^{-1}), methyl stearate (298 g.mol^{-1}) and DEHA (371 g.mol^{-1}).

2.2. Production of PHBV films

PHBV powder was mixed with 0.5 wt% of Boron Nitride as a nucleating agent and the mixture was dried at 60 °C for 24h prior to extrusion. Extrusion was carried out in a parallel twin screw microcompounder Process 11 (Thermoscientific), at 150 rpm with a uniform processing temperature of 180 °C from the feeding to the die. Granulation was carried out at room temperature. The granulated product was dried at 60 °C for 24h, then PHBV films with an average thickness of 300 µm were produced by thermocompression using a heated hydraulic press (20T, Pinette Emidecau Industries). The temperature was 180 °C and the pressure was first set at 5 bars for 1 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30. Flakes were then produced by cutting the films into 1.5×1.5 cm squares.

2.3. Contamination procedure of PHBV flakes

According to the contamination protocols for challenge tests, polymer flakes should be soaked in a surrogates solution until a sorption equilibrium is reached [154]. For PHBV flakes contamination, solid contaminants (benzophenone and methylstearate) were dissolved in the liquid contaminants (toluene, chlorobenzene, methylsalicylate, phenylcyclohexane, DEHA) without the use of additional solvent, and stirred until a homogeneous solution was obtained. In a sealed container, this surrogate's mixture was dropped on PHBV flakes (1.5 cm squares) at a concentration of 500 mg of surrogates per kg of flakes. Then, the container was stored for 10 days at 40 °C with continuous rotatory agitation. After 10 days, the contamination level is evaluated by measuring the surrogate concentration in the flakes as described in section 2.4.2.

2.4. Decontamination of PHBV flakes

2.4.1. Decontamination process

Decontamination of the contaminated flakes was performed in a glass oven (Buchi, B-585) at elevated temperature and under vacuum (< 20 mbar). The experimental process is schematized in figure 13. In order to optimize the process, different temperature/time combinations were tested. thus, PHBV flakes were introduced in the heating chamber and rotated, under vacuum, at 100 °C, 130 °C, 145 °C and 160 °C (temperatures lower than the PHBV melting temperature) during 3, 6, 20, 48 and 72 hours.

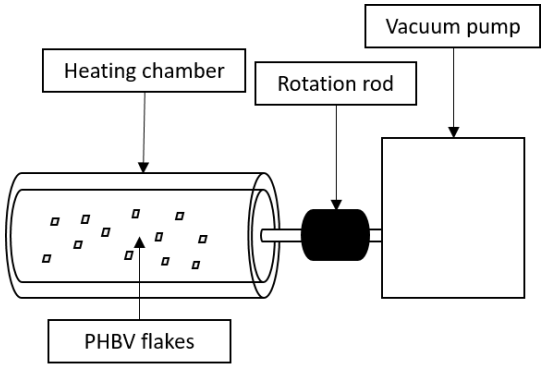


Figure 13. Scheme of the PHBV flakes decontamination process.

2.4.2. Extraction method

The surrogate concentrations in the polymer flakes after contamination and decontamination were determined using the following extraction method: PHBV flakes (0.3 g) were placed in a glass vial and 5 ml of methanol were added. Samples were then stored for 1 day at 40 °C under magnetic agitation to extract the surrogates from the polymer matrix. The extracts, obtained in triplicate were analyzed using an Agilent 7890A GC equipped with a 7693A Automatic Sampler and a flame ionization detector (FID). A total of 1 µL of the extract was injected into the GC equipped with a HP-5 (5%-phenyl)methylpolysiloxane capillary column of 32 mm ID and 30 m length. Carrier gas was nitrogen (8.11 mL.min-1) and the chromatographic conditions were as follows: initial oven temperature was maintained at 40 °C for 5 min, and subsequently heated from 40°C to 270°C at a rate of 6 °C.min-1 to 270 °C, where it was held for 15 min. The injector temperature was 250 °C. The peaks identification and product quantification were based on the use of the different surrogates as external standards (calibration curves with concentration range of 10 – 45 $mg.L^{-1}$), as well as the use of BHT at 30 mg.L-1 as an internal standard.

2.4.3. Decontamination efficiencies of PHBV flakes

The decontamination efficiencies were determined for each surrogate by comparing the surrogate concentration in the flakes after decontamination with the initial concentration before heat treatment (see equation 1).

$$Decontamination\ efficiency\ = (1 - \frac{sample\ concentration}{initial\ concentration}) \times 100 \qquad (1)$$

Residual concentration of contaminant, C_{res}, is then calculated by applying the decontamination efficiency percentage to a reference contamination level. Reference contamination level in the PET feedstock set in the literature at 3 $mg.kg^{-1}$ and was used here [27].

2.4.4. Estimation of diffusion coefficients

Diffusion coefficients of each surrogate were estimated, from experimental desorption kinetic curves at each decontamination temperature, using Fick's second law. Diffusion is assumed to be isotropic and flakes are considered as infinite plane sheets, leading to a mono-directional diffusion

equation. Surrogates' desorption takes place in a constantly renewed medium (vacuum) then null boundary condition is used. Initial surrogate concentrations are supposed to be uniform in the films. Surrogate desorption is described by the analytical solution of the diffusion equation, given by Crank [155]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\} (2)$$

where M_t and M_∞ (mg) are the mass of the diffusing molecule which desorb from the polymer at time t and at infinite time, respectively, D is the diffusion coefficient of the diffusing molecule in the polymer ($m^2.s^{-1}$), t is the time of the desorption (s), L is the thickness of the film (m).

Estimation of the diffusion coefficients was performed by minimizing the root mean square error (RMSE) between experimental and simulated desorbed mass. It is worth noting that, for each contaminant, it was assumed that full desorption occurs at least asymptotically. Consequently, the asymptotic desorbed mass, M_∞ , was taken constant and equal to the initial mass of contaminant in the film, so that the diffusion coefficient was the only unknown parameter. The numerical simulations were carried out using the Matlab software and the lsqnonlin function, to estimate the diffusion coefficient.

2.5. Determination of experimental partition coefficient

PHBV flakes were contaminated following the contamination procedure (section 2.3). After a quick ethanol rinsing to eliminate surface contamination, material samples (300 ± 20 µm) were immersed in 100 mL of ethanol 95 % as food simulant, in a surface/volume ratio of 6 $dm^2.L^{-1}$, at 40 °C for 10 days under magnetic agitation. Ethanol 95% was selected as one of the representative food simulants, which often replaces vegetable oil. It represents the worst case scenario for PHBV applications [187]. Then, an aliquot of food simulant was collected and analyzed in GC following the same procedure described in the previous section (2.4). Experimental partition coefficient ($K_{P/F}$) of the contaminants between the polymer matrix and the food simulant, were calculated from equation (3)

$$K_{P/F} = \frac{C_{P,\infty}}{C_{F,\infty}} \frac{\rho_P}{\rho_F} (3)$$

where $C_{P,\infty}$ and $C_{F,\infty}$ (mg.kg-1), are the equilibrium concentrations of contaminant in the polymer and in the food simulant, respectively, ρ_P and ρ_F (kg.m-3) are the density of polymer and food simulant, respectively.

2.6. Migration predictive modelling: determination of C_{mod}

For each surrogate, C_{mod} represents the residual concentration in the recycled PHBV resulting in a migration that does not exceed the dietary exposure threshold defined as 0.0025 µg/kg bw/day [156]. Thus, C_{mod} represents the maximal surrogate content in recycled PHBV which ensure the food safety and is calculated by modelling using the following migration model from the JRC publication [157] in equation (4):

$$C_{mod} = SML * \frac{V_F \rho_F}{A} \left\{ \rho_P d_p \left(\frac{\alpha}{1+\alpha} \right) \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-D_P t \frac{q_n^2}{d_p^2} \right) \right] \right\}^{-1} (4)$$

where SML is the Specific Migration Limit (mg.kg^{-1}), $C_{mod}$is the maximum initial concentration in the polymer (mg.kg^{-1}) , V_F is the volume of food (m^3), D_P is the diffusion coefficient of migration in the polymer (m².s^{-1}), d_p is the thickness of the polymer (m), A is the area of polymer in contact with food (m²), q_n are the non-zero, positive roots of equation (5)

$$\tan q_n = -\alpha\, q_n \ (5)$$

and α is calculated from equation (6)

$$\alpha = \frac{1}{K_{P/F}} \frac{V_F}{V_P} \ (6)$$

where V_P is the volume of the polymer (m^3).

Standard test conditions were used for contact with food simulant and parameters used were taken from the EFSA regulation on PET migration modelling [27]. The food contact material was considered as a 100 % recycled polymer of 300 µm thickness. Food contact ability was assessed after 10 days at 40 °C in a food simulant (density of 1000 kg.m^{-3}), with a surface area to volume ratio of 6 dm^2 (0.06 m²) polymer to 1 kg food simulant.

2.7. Characterization of the thermomechanical properties of PHBV flakes after decontamination process

2.7.1. Size exclusion chromatography (SEC)

After decontamination, the average molecular weight (Mw) and number-average molecular weight (Mn) were determined by SEC performed in the University of Bologna (Italy). Samples were placed in sealed tubes and dissolved in Hexafluoro-2-propanol/Chloroform mixture (95:5) at a concentration of 1 $mg.mL^{-1}$. SEC analyses were carried out in a HP 1100 Series equipped with a PL gel 5 µm Minimixed-C column. Injection volume was 20 µL and chloroform flow rate was 0.3 $mL.min^{-1}$. Detection was performed by means of refractive index and UV detectors. The calibration of the instrument was done with polystyrene standards, and all the sample analyses were performed in triplicates.

2.7.2. Mechanical testing

The tensile strength, Young's modulus and elongation at break were measured according to DIN EN ISO 527-1 using INSTRON 68 SC-5 device with a load cell of 2kN. Measurements were performed on dog bone shaped film specimens (width of 4 mm and gauge length of 22 mm) which were inserted with an effective length of 40 mm between the clamps at the beginning of the tests. The samples were tested under a monoaxial tension with a cross head speed of 10 $mm.min^{-1}$. Ten replicates were realized for each measurement.

2.8. Statistical analysis

Statistical analyses and data visualization were performed in R (RStudio, 2021). The variables were checked for normality (Shapiro-Wilk test). The significance of results was examined by one-way analysis of variance (ANOVA) followed by a Tukey test with a confidence interval of 95%. Then, the significant difference between the data was defined.

3. Results and discussion

3.1. Determination of the decontamination efficiencies

In order to determine the optimal temperature/duration combination for the PHBV flakes decontamination, materials were submitted to thermal treatment under vacuum at different temperatures (100, 130, 145, and 160°C) for 3, 6, 20, 48 and 72h. The EFSA surrogate panel was used and the decontamination efficiency of each compound under the different conditions is represented in figure 22. Note that the surrogates are ranked from the lowest to the highest molecular weight, from toluene to DEHA, and the results at 48 and 72 h are not shown because no evolution in the decontamination efficiencies was noted after 20h (visible in supporting data table S1).

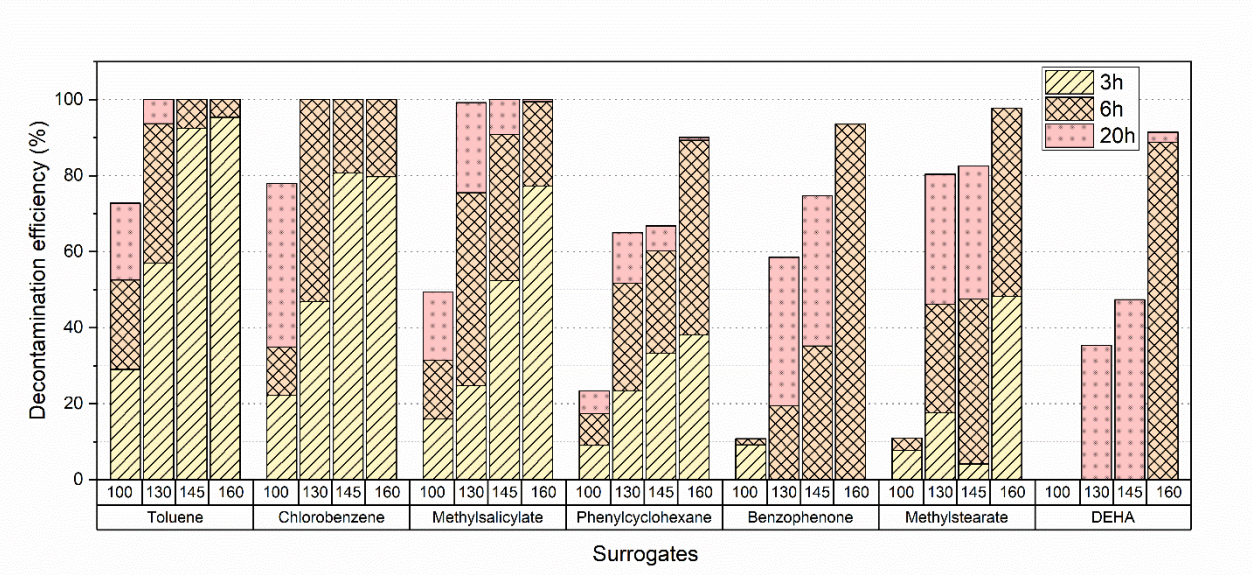


Figure 22. Evolution of decontamination efficiencies as a function of decontamination temperature and duration (additional raw data with standard deviation in supporting data, table S1)

First, it is observed that higher temperatures and longer residence time led to better decontaminations, regardless the surrogate used. It is assumed that the decontamination of contaminants results from their diffusion within the materials followed by their desorption and volatilization at the surface. Increase of the decontamination is related to the increase of the diffusion coefficient of the surrogate in the polymer for increasing temperature [188]. The effect of temperature on the surrogate's diffusivities during decontamination is detailed in the Arrhenius plot Figure 23, with activation energies

ranging from 50 to 81 kJ.mol^{-1} (diffusion coefficient and activation energy values are shown in supporting data, table S2). Generally, a 2- to 4-fold increase of diffusivity was observed between 130°C and 160°C. However, the increase in decontamination efficiency is not strictly correlated to this increase of diffusivity. For compound with high volatility (i.e. toluene and Chlorobenzene), the diffusion should be the limitant mechanism. So, the decontamination is diffusion-driven and D is the main determining factor. Conversely, for the other high molecular weight molecules with vaporisation temperatures higher than the treatment temperature, it can be assumed that decontamination is only slightly dependent on diffusivity. Thus, depending on molecules properties (size, volatility etc), the effect of diffusivity increasing with temperature will not have the same impact on their decontamination efficiency.

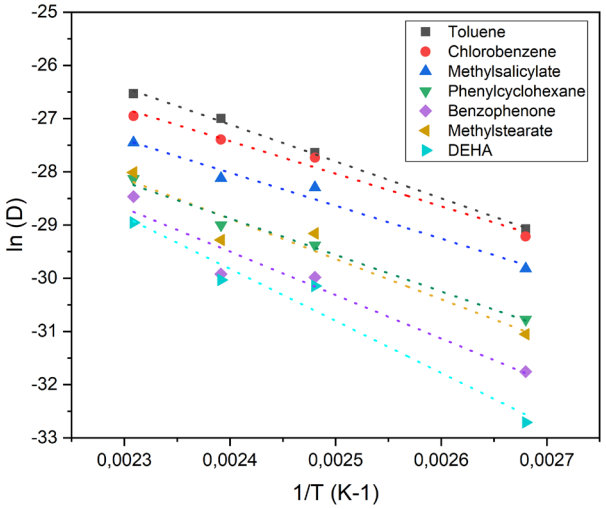


Figure 23. Estimated diffusivities of surrogates in PHBV during decontamination. Arrhenius plot of estimated diffusivities against decontamination temperature.

Secondly, higher is the molecular weight (Mw) of the surrogate, lower is its decontamination efficiency. Toluene, chlorobenzene and methylsalicylate, with the lowest M_ws (from 92 to 152 g.mol^{-1}) were completely removed at all temperatures tested, except at 100 °C. However, only the treatment at 160 °C allowed an efficient decontamination (more than 80 %) of the other surrogates. Indeed, the increase of the molecular weight of a compound decreases on one hand its diffusion coefficient (see supporting data Table S2), limiting its diffusion in the polymer matrix, and on the other hand its volatility, reducing its desorption under vacuum which is the limiting step in decontamination process.

At 160°C, a minimum duration of 6h is necessary to obtain the highest decontamination of the four heaviest molecules of the panel (phenylcyclohexane, benzophenone, methyl stearate and DEHA). However, this decontamination level does not evolve even for durations reaching 72h. This could be attributed to the modification of the polymer structure during the decontamination process. Indeed, the thermal instability of PHBV polymer at temperatures close to its melting point is well known [189]. Thus, the thermal degradation translated by molecular chains scission and an increase in the crystallinity could have an impact on the diffusion of the molecules in the polymer matrix, hindering their desorption [100].

Regarding the decontamination, the best efficiency is obtained at 160°C for a duration in the range [6h, 20h], providing a possible strategy for PHBV recycling. On the other hand, a limited alteration of the thermomechanical properties of the recycled material will guarantee its performance during future usage. The evolution of the properties of decontaminated PHBV will therefore be discussed in the next section.

For the decontamination process of 6 h at 160 °C, the decontamination efficiencies of each contaminant are ranging from 89.29 % to 100 %. Under similar decontamination conditions, i.e temperature close to the melting point and residence time of few hours, PET decontamination was found to be much higher than for PHBV [181-183]. This may be explained in part by the decontamination temperatures which lead to increase the chain mobility and also the diffusion of the contaminants in the polymer matrix, and are highly dependent on the melting temperature of the polymer [146]. Then for PET which have a melting temperature near to 250 °C, decontamination may be performed at higher temperature, leading to an increase of the contaminants desorption and a better decontamination. The higher decontamination of PET may also be ascribed to the difference between PET and PHBV namely their nature (PET is in a glassy state while PHBV is in a rubbery state at ambient temperature) which lead to higher barrier properties for PET than for PHBV. Therefore, PET will potentially sorb less strongly the contaminants, and thus its decontamination will be faster and more efficient. In the opposite case, HDPE which is also in a rubbery state at ambient temperature but melts at temperature of about 130 °C, presents much lower decontamination efficiencies than our results on PHBV, for the less volatile molecules [190].

3.2. Evolution of the thermomechanical properties of PHBV under decontamination conditions

The evolution of the PHBV Mw and tensile properties were monitored at decontamination temperatures of 130, 145 and 160 °C, for different durations (since decontaminations efficiencies at 100 °C were very low).

Figure 24 shows the evolution of the normalized PHBV molecular weight samples after decontamination tests.

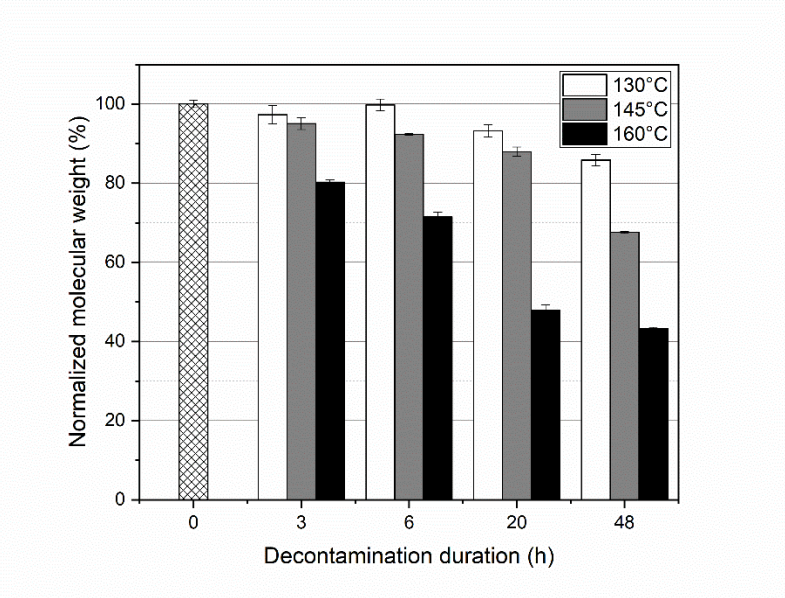


Figure 24. Evolution of normalized PHBV molecular weight after decontamination at 130, 145 and 160°C for 3, 6, 20 and 48 h.

A decrease in the PHBV molecular weight is observed with increasing temperature and decontamination time. At 130 °C, the polymer Mw decreased slightly from 0 to 48h. However, a more pronounced decrease was noticed for higher temperature, with a mass loss of 12% after 20h at 145 °C and of 28.5%, after 6h at 160 °C. As previously mentioned, high temperatures are responsible of PHBV thermal degradation reflected by polymer random chains scission, mainly attributed to a beta-elimination mechanism[10, 100].

One of the major products of the random chain scission of PHBV is crotonic acid (but-2-enoic acid) [10, 100]. It is considered as a neoformed chemical (NIAS) and is submitted to migration

regulation into food as it is referenced in the positive list of authorized substances [12]. Figure 25 shows the normalized concentration of crotonic acid in the polymer, depending on decontamination temperature and duration.

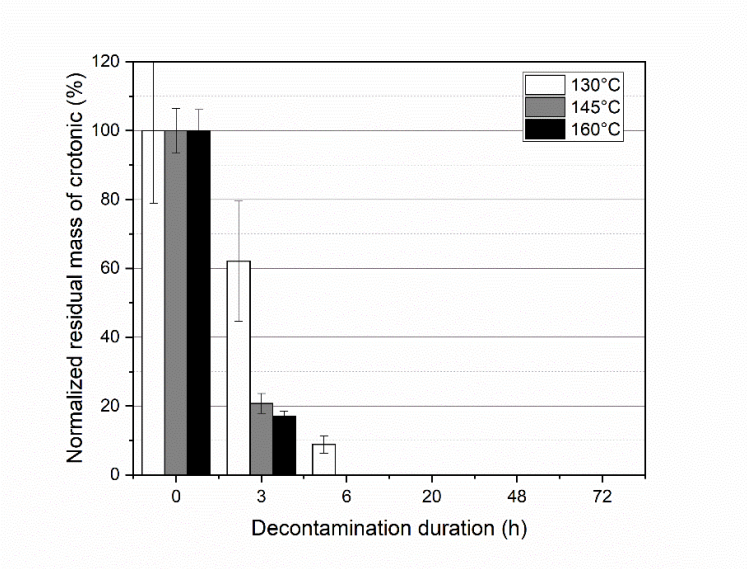


Figure 25. Evolution of crotonic acid concentration in PHBV, as a function of decontamination temperature and duration

Surprisingly, increasing the decontamination temperature and duration did not lead to the presence of more crotonic acid in the recycled material despite of greater structural degradation. No crotonic acid has been detected from 6h at 145 °C and 160 °C and from 20h at 130 °C. Crotonic acid generation is likely more pronounced at higher temperatures. However, its low molecular weight, even lower than that of toluene (M_w = 86 g/mol) facilitates its desorption from the polymer matrix during the decontamination process, especially at higher temperatures. Then, the level of exposure of this neoformed chemical appears negligible and precludes any consumer safety concerns.

The impact of the Mw decrease on the tensile properties of PHBV was investigated and results are shown in figure 26. As Young's modulus remained stable under the different decontamination conditions tested, only the evolution of the elongation at break (a) and the tensile strength (b) is depicted. It is important to note that tensile test measurements could not be performed after 48h at 160 °C because of the very high brittleness of the samples.

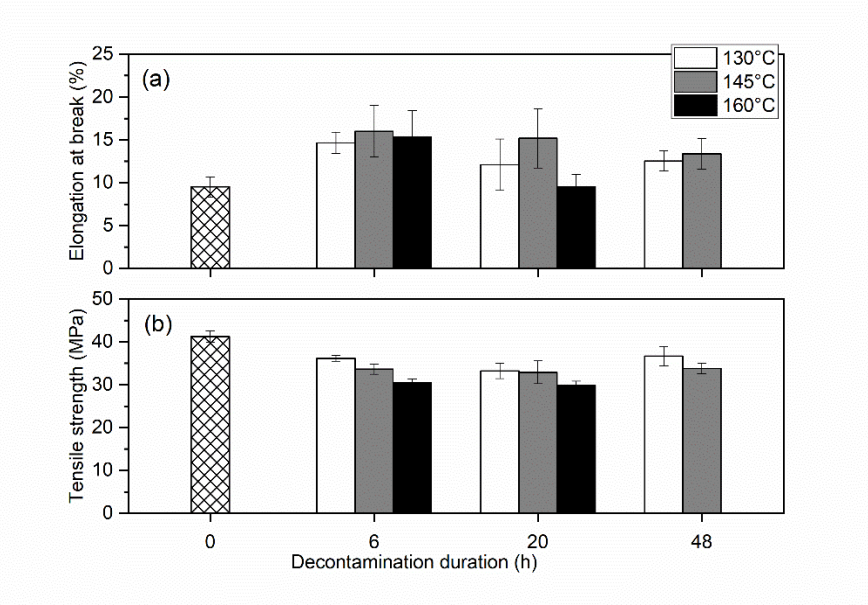


Figure 26. Evolution of PHBV mechanical properties (a) the elongation at break and (b) the tensile strength depending on decontamination temperature and duration

The stability of the Young's modulus under the different decontamination conditions attests that the decrease in polymer Mw did not significantly impact its elasticity (shown in supporting data Figure S1).

An increase in elongation at break is observed at the different temperatures/residence times tested. This mechanical behaviour is probably due to the plasticization effect by the PHBV oligomers resulting from the polymer chain scission as previously seen in polymer plasticization with oligomeric polyesters [191]. On the contrary, a significant decrease in tensile strength with increasing decontamination temperature and time is related to material embrittlement, mainly caused by a decrease in chain length and a possible increase in crystallinity.

Decontamination processes of PET at temperatures close to its melting point were also responsible of decrease of molecular weight and increase of crystallinity [192]. However, the chain scission also observed during the thermal decontamination treatment applied to PET can be compensated by their reconstruction/elongation according to the reversible reaction of esterification. This so-called solid-state polycondensation processes is nearly always in the PET recycling processes, in order to give to recycled PET, the same material properties as virgin ones [193]. Moreover, the decontamination

processes of PET flakes usually take less time than for PHBV, e.g. between 1 and 2 hours, leading to lower degradation of the polymer.

Considering the decontamination efficiencies and the structural evolution of the polymer under the applied decontamination conditions, the combination 160°C/6h seems to be the optimal couple guaranteeing an efficient decontamination without causing significant damage to the polymer structure. On this basis, the decontamination efficiencies should be expressed through residual concentrations (C_{res}) and compared to the authorized concentration limits (C_{mod}) in order to assess the polymer safety.

3.3. Safety assessment of recycled PHBV-based material for food contact application

The EFSA safety assessment of recycled plastics is mainly based on three elements. (i) input concentration of surrogates in collected plastic (ii) the cleaning efficiency of the recycling process and (iii) the level of exposure of the consumer towards potentially residual surrogates [193].

First, the presence and concentration of any substances, including also additives and neo-formed products, from the material use/misuse/collect, is considered. In the case bottle-to-bottle recycling approach, EFSA assumed that the maximum input concentration of surrogates is 3 mg/Kg (derived from the European project recyclability [184]). In the absence of any supply chain, surveys and studies for the biodegradable polymers and considering that the paths of treatment of the biodegradable materials is at present common to that of the synthetic plastic materials, this value of reference can be by default taken in consideration in the case of PHBV. The issue of exposure to neoformed compounds produced during the recycling process is excluded from consideration in the case of the current reference recommendation, presumably because of the thermal stability of PET.

Secondly, the evaluation of the decontamination efficiencies is performed by the means of challenge test, consisting in intentional contamination and decontamination of the considered plastic by the recommended panel of contaminant surrogates. Then as a sort of normalizing measure, the decontamination efficiency is calculated on the basis of the residual concentration (C_{res}) of each contaminant quantified in the recycled polymer in comparison with the input concentration of 3 mg/Kg.

Finally, the exposure to the residual substances for the relevant consumer is considered according the maximum dietary exposure level of 0.0025 µg/Kg body weight/day, threshold for DNA-reactive mutagens and/or carcinogens. From this level, a maximum allowable migration value can be deducted for each scenario (infant, toddler and adult) from migration modelling into a corresponding concentration of contaminant in the plastic (Cmod). Due to the brittle nature of PHBV, trays and jars applications appear to be the only possible containers for food applications which rather corresponds to packaging of products consumed by toddlers and adult's classes. Two scenarios were considered, toddlers and adults, with SML of 0.15 $\mu g.kg^{-1}$ food and 0.75 $\mu g.kg^{-1}$ food respectively [27, 156], with 95 % ethanol as food simulant. Within these scenarios, simulations were conducted distinctly (1) with a high solubility theoretical value of the contaminants in the Food according a worst-case scenario ($K_{P/F}$ = 1) [157] and (2) according a most realistic approach based on experimentally determined $K_{P/F}$. To calculate C_{mod}, due to absence of Piringer parameters for PHAs food contact materials, the actual diffusion coefficients (D_P) in PHBV at 40 °C in 95 % ethanol were extracted from literature [194]. The use of actual diffusion coefficients prevents the overestimation of the C_{mod} value, generally used in such approaches.

On these basis, calculation of recycling suitability of PHBV based material considering both toddlers and adult's scenarios are gathered in table 9.

Table 9. Decontamination efficiencies, from the challenge test, residual concentrations of the surrogates in the recycled PHBV (C_{res}) and modelled concentrations of the surrogates in PHBV (C_{mod}) corresponding to a modelled migration of 0.15 µg/kg food (toddler's scenario) and 0.75 µg/kg food (adult's scenario) after 10 days at 40°C, with a good solubility of the migrant in food simulant ($K_{P/F}$ =1).

Surrogates	Decontamination efficiency (%)	C_{res} for 100% rPHBV (mg/kg PHBV)	C_{mod} (mg/kg PHBV) for toddlers scenario	Maximum % of rPHBV to fulfil the criteria	C_{mod} (mg/kg PHBV) for adults scenario	Maximum % of rPHBV to fulfil the criteria
Toluene	100.00	0	0.007	100.0	0.034	100.0
Chlorobenzene	100.00	0	0.007	100.0	0.034	100.0
Methylsalicylate	99.44	0.017	0.007	41.8	0.034	100.0
Phenylcyclohexane	89.29	0.321	0.007	2.2	0.034	10.6
Benzophenone	93.52	0.194	0.007	3.6	0.034	17.4
Methylstearate	97.76	0.067	0.007	10.4	0.034	50.5
DEHA	88.89	0.333	0.007	2.1	0.034	10.2

As discussed previously, the desorption of the lower molecular weight contaminants from PHBV was very efficient, due to their volatility, with complete decontamination of toluene and chlorobenzene. Thus, their residual concentrations (C_{res}) after recycling were lower than the corresponding modelled concentration in PHBV (C_{mod}) for both toddlers and adult's scenario. Due to their lower vapour pressure, the decontamination was less effective for higher molecular weight contaminants, leading to higher residual concentrations after decontamination (C_{res}) than the corresponding modelled concentrations (C_{mod}), especially for phenylcyclohexane and DHEA. Therefore, despite the acceptable thermomechanical properties of the material, the use of 100% recycled PHBV raises safety concerns. For the toddler's scenario (corresponding to a maximum 0.15 µg contaminant/kg

food), the condition to do not exceed to maximum tolerable amount of DEHA is to include only 2.1% of recycled PHBV in the new material. In the case of the adult's scenario, C_{mod} in the polymer is higher than in the toddler's scenario due to the higher Tolerable Daily Intake (TDI) defined for this population category but only allows the introduction of 10.2% of recycled PHBV in the final packaging to fulfill the suitability for food contact application.

From the phenomenological point of view, the decontamination process can be described as the result of the diffusion of contaminants within the material and their subsequent desorption/volatilization on the surface. On this basis, it is clear that the transfer properties of the polymers largely determine the degree of decontamination of the material and clearly explain the differences in behaviour observed between PHBV and PET. Two remarks must be pointed out regarding C_{mod} values of the contaminants in recycled PHBV material *i.e.* (1) the modelled concentrations C_{mod} are very low compared to those in PET (from 0.13 to 0.47 mg/kg PET for toddlers scenario after 1 year at 25 °C) [182, 183] what is likely due to the lower barrier properties of PHBV, as the diffusion coefficient of contaminants in PHBV ($D_{app} \sim 1.10^{-14}$ $m^2.s^{-1}$) is 10^4 higher than that in PET ($D_{app} \sim 1.10^{-18}$ $m^2.s^{-1}$), which may accelerate their migration in food [194, 195]. (2) C_{mod} in PHBV have the same value regardless of the contaminant and its molecular weight what can be explained by this rapid diffusion of contaminants in PHBV matrix where they fast reach an equilibrium. As consequence, the C_{mod} value was proportional to partition coefficient of the substances between the polymer and the food ($K_{P/F}$) and is not impacted by their diffusivity in the material.

In order to discriminate the behavior of each contaminant and to estimate as accurately as possible the content of recycled PHBV allowed to be used in the composition of a packaging, alternative C_{mod} values in PHBV were calculated on the basis experimentally determined coefficient partitions. Table 10 shows the experimental values of the partition coefficients of the contaminants between the polymer and the food simulant (ethanol 95%). As the decontamination of Toluene and Chlorobenzene is complete, these substances are no longer of concern and are not represented in the following results.

On the basis of the experimental values of $K_p/_F$ (Table 10), C_{mod} were re-calculated for both toddlers and adult's scenarios, and the results are reported in Table 11.

Table 10. Experimental partition coefficient of contaminants between the polymer and the food simulant (95% ethanol)

Contaminant	Partition coefficient $K_{P/F}$
Methylsalicylate	39.0 ± 5.0
Phenylcyclohexane	72.2 ± 8.0
Benzophenone	18.1 ± 6.8
Methylstearate	64.6 ± 12.5
DEHA	62.9 ± 19.3

Table 11. Decontamination efficiencies, from the challenge test, residual concentrations of the surrogates in the recycled PHBV (C_{res}) and modelled concentrations of the surrogates in PHBV (C_{mod}) corresponding to a modelled migration of 0.15 µg/kg food (toddler's scenario) and 0.75 µg/kg food (adult's scenario) after 10 days at 40°C, with an experimental solubility of the migrant in food simulant ($K_{P/F}$) according to table 10.

Surrogates	Solubility of the migrant in food simulant	Decontamination efficiency (%)	C_{res} for 100% rPHBV (mg/kg PHBV)	C_{mod} (mg/kg PHBV) for toddlers scenario	Maximum % of rPHBV to fulfil the criteria	C_{mod} (mg/kg PHBV) for adults scenario	Maximum % of rPHBV to fulfil the criteria
Methylsalicylate	39.0	99.44	0.017	0.011	65.8	0.057	100.0
Phenylcyclohexane	72.2	89.29	0.321	0.015	4.7	0.077	23.8
Benzophenone	18.1	93.52	0.194	0.009	4.6	0.044	22.7
Methylstearate	64.6	97.76	0.067	0.014	20.9	0.072	100.0
DEHA	62.9	88.89	0.333	0.014	4.2	0.071	21.3

As expected, the integration of experimental values of partition coefficients into the migration model led to an increase in the C_{mod} values and thus an increase in the allowable residual contamination levels. As reported in previous calculations, the use of 100 % recycled PHBV for adults is allowed if

the post-consumer polymer is contaminated with the substances represented by toluene, chlorobenzene and methylsalicylate molecules. The other four model contaminants with higher molecular weights (i.e. Phenylcyclohexane, Benzophenone, Methylstearate, DEHA) produce higher levels of residual contamination associated with a level of exposure that may be considered of concern in the event of 100% recycled PHBV-based packaging. In accordance with the recommendations for PET, it appeared therefore only possible to include 21% recycled material in the composition of packaging for an adult population.

At first glance, the lack of safety of mechanically recycled PHBV could discourage efforts and investment in the setting up of closed-loop recycling lines for PHBV intended for food contact. However, we should keep in mind that the entire approach used in this work, including the contaminants selection, the cleaning treatments and the modelling calculations was inspired by the bottle-to-bottle mechanical recycling of PET. This default approach was guided by the lack of specific recommendation for biodegradable polymers and leads to conclusions close to previous investigations on synthetic polymers with low barrier properties towards low molecular weight organic pollutants. The 3 $mg.Kg^{-1}$ standard contamination level used for PET, which has been established through random sampling of packaging waste (REF), is may be not representative of the contamination extent of PHA packaging waste. The different inertness properties of PHA compared to PET can lead to contamination by other substances in other concentrations. Lower and higher contamination levels will have obviously a significant impact on the residual contamination (Cres) and consequently on the final percentage of recycled PHBV incorporated in a new packaging which is directly proportional to the level of contamination of incoming stream.

In a study conducted by Palkopoulou et al. (2016), it was indicated that PET approach cannot be extrapolated to others polymers such as polyolefins with respect to different properties towards contaminants sorption and desorption behavior [140]. The results presented in this study support this observation and lay the foundations for a revision of the approach applied to PET to biodegradable polyester-based materials. It is clear that the effectiveness of the decontamination technologies developed for PET is based on (1) the inertness properties of the polymer, which provides a high diffusive barrier to high molecular weight pollutants, and (2) the thermal properties, which require the

PET to be melted at high temperatures to promote the vaporization of any contaminants. The transposition of this approach based on decontamination encounters this double constraint. The low barrier properties of this type of material result in easier sorption and diffusion of a wide range of pollutants, and the lower melting temperature prevents their removal by volatilization. While it is well established that the diffusion coefficient is related to the molecular weight of the diffusing substances, the identification of a molecular structural parameter to describe/predict the volatilization of molecules on the surface seems more difficult to elucidate under the heat treatment conditions applied in the mechanical recycled process. The analysis of PHBV behaviour towards a broad range of contaminants with different Mw and polarities is must necessarily be the subject of further in-depth research. Improving the quality grade of the secondary material therefore requires the development of new advanced technologies better adapted to the characteristic transport properties of PHBV. In this respect, facilitated material transfers should be considered as an asset that should be exploited.

4. Conclusion

The mechanical recycling of polymers used in food packaging is a necessary challenge, particularly in the context of roadmaps and regulations currently being implemented in Europe. While closed-loop recycling of food packaging including biodegradable materials should undoubtedly be favoured, it implies reprocessing technologies and procedures for assessing the quality grade of the secondary raw material specific to each type of material. This work explores the opportunities for decontamination of recycled PHBV material following a strategy inspired by the one implemented in the PET bottle-to-bottle mature technology. The probability of misuse of PHBV-based post-consumer packaging and the fact that collection routes are common to all plastic packaging justifies the use of the same model pollutant panel used in the PET decontamination assessment procedure.

This work shows that the implementation of a decontamination technology requires a compromise based on the implementation of a thermal treatment whose severity prevents any significant degradation of the polymer while allowing the removal of pollutants susceptible to be absorbed by the material during its life cycle. The limits of the development of such technology are thus set by both the thermal stability of the polymer and the sorption/desorption properties of the material. In the specific

case of PHBV, which is subject to degradation reactions even at low processing temperatures, the incorporation rates of recycled secondary material cannot exceed 21% under food contact conditions according to the most realistic use patterns.

The expected benefits appear too limited to consider the development of a specific PHA upgrade pathway. Improving the quality grade of the secondary material therefore requires the development of new advanced technologies better adapted to the low inertness properties of PHBV. In this respect, facilitated material transfer should be considered as an asset to be exploited in a future strategy to optimize desorption based on alternative methods using solvent, CO2, or supercritical fluid extractions; or performing the decontamination during a melt-state step after an additional washing step [196, 197]. Investigations on a Solid State Polycondensation (SPP) may also be relevant to increase the quality of recycled PHBV, as done in PET recycling. The ester bonds may potentially be reformed by reversible esterification, which will depend on the reactivity and mobility of the polymer chains end as seen in poly-lactic acid PLA studies [198].

Finally, it could be relevant to create a controlled, short and closed chain for the recycling of PHBV, in order to control and reduce the input contaminants. Mechanical recycling would therefore not require a decontamination step, as seen in the short chain recycling of high-density polyethylene and polypropylene [199].

Statements & Declarations

Funding

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Competing Interest

The authors declare that they have no competing financial interest of personal relationship that could influence the work reported in this paper.

Supporting data

Table S1. Decontamination efficiencies (mean and standard deviation) depending on decontamination temperature and duration

		100 °C	130 °C	145 °C	160 °C
Toluene	3h	29.1 ± 9.3	57.0 ± 11.9	92.5 ± 2.2	95.4 ± 4.9
	6h	52.6 ± 11.4	93.7 ± 0.3	100.0 ± 0.0	100.0 ± 0.0
	20h	78.8 ± 2.6	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	48	95.4 ± 0.5	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	72	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
Chlorobenzene	3h	22.2 ± 16.9	46.9 ± 13.6	80.7 ± 4.4	79.7 ± 6.5
	6h	34.9 ± 23.1	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	20h	78.0 ± 2.3	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	48	95.8 ± 0.4	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	72	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
Methylsalicylate	3h	15.9 ± 10.7	24.8 ± 11.0	52.4 ± 6.2	77.3 ± 3.5
	6h	31.4 ± 7.9	75.5 ± 3.1	90.9 ± 0.5	99.5 ± 0.0
	20h	49.4 ± 4.2	99.2 ± 0.4	100.0 ± 0.0	100.0 ± 0.0
	48	88.2 ± 0.4	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
	72	94.5 ± 1.9	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0
Phenylcyclohexane	3h	9.1 ± 8.7	23.5 ± 11.0	33.3 ± 2.7	38.1 ± 10.7
	6h	17.4 ± 4.6	51.8 ± 3.8	60.2 ± 3.1	89.3 ± 0.3
	20h	23.4 ± 2.5	65.0 ± 5.1	66.8 ± 6.8	90.1 ± 2.5
	48	51.6 ± 1.4	81.6 ± 2.0	88.6 ± 1.6	92.3 ± 3.7
	72	63.8 ± 4.1	92.1 ± 1.1	98.1 ± 1.0	95.8 ± 0.9

Benzophenone	3h	9.2 ± 9.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	6h	10.8 ± 3.4	19.4 ± 5.7	35.2 ± 2.3	93.6 ± 0.2
	20h	3.0 ± 2.9	58.5 ± 12.1	74.7 ± 4.3	91.4 ± 1.3
	48	48.6 ± 3.7	84.4 ± 2.2	76.2 ± 0.8	93.5 ± 1.7
	72	34.0 ± 8.7	85.7 ± 2.6	86.7 ± 6.2	98.9 ± 0.2
Methylstearate	3h	7.8 ± 7.8	17.7 ± 8.3	4.2 ± 5.5	48.2 ± 9.9
	6h	11.0 ± 6.1	46.2 ± 3.8	47.5 ± 1.9	97.8 ± 0.1
	20h	10.8 ± 8.6	80.4 ± 7.3	82.6 ± 3.7	96.2 ± 0.8
	48	42.7 ± 2.1	91.8 ± 0.6	93.3 ± 0.5	97.8 ± 1.0
	72	55.7 ± 4.0	93.1 ± 1.3	97.0 ± 1.9	99.2 ± 0.2
DEHA	3h	0.0 ± 0.0	0.5 ± 6.2	0.0 ± 0.0	0.0 ± 0.0
	6h	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	88.9 ± 0.4
	20h	0.0 ± 0.0	35.3 ± 10.8	47.4 ± 9.5	91.4 ± 1.8
	48	11.0 ± 0.7	81.5 ± 1.9	88.6 ± 1.1	93.8 ± 2.5
	72	19.4 ± 5.1	90.8 ± 1.2	96.0 ± 2.1	96.3 ± 1.0

Table S2. Surrogates diffusion coefficients depending on temperature, and resulting activation energy

	Diffusion coefficient ($m^2.s^{-1}$)				Activation energy ($kJ.mol^{-1}$)
	100°C	130°C	145°C	160°C	
Toluene	2.4E-13	9.9E-13	1.9E-12	3.0E-12	57.6
Chlorobenzene	2.1E-13	9.0E-13	1.3E-12	2.0E-12	50.8
Methylsalicylate	1.1E-13	5.2E-13	6.1E-13	1.2E-12	51.5
Phenylcyclohexane	4.3E-14	1.7E-13	2.5E-13	6.1E-13	57.0
Benzophenone	1.6E-14	9.5E-14	1.0E-13	4.3E-13	67.9
Methylstearate	3.3E-14	2.2E-13	1.9E-13	6.8E-13	62.9
DEHA	6.2E-15	8.1E-14	9.1E-14	2.7E-13	81.3

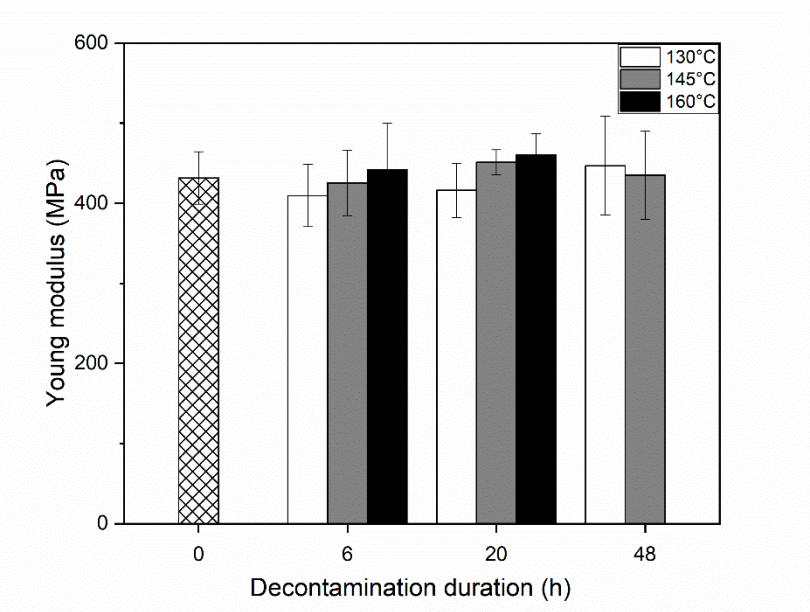


Figure S1. Evolution of PHBV young modulus depending on decontamination temperature and duration

Complementary results (not cited in the article)

The decontamination process was applied to PET samples, as well. The aim was to validate this process by comparing its decontamination efficiency to the results found in the literature.

PET pellets were purchased from TK Chemicals (Korea) with the following properties: density = 1390 $kg.m^{-3}$ and Tm = 244-248 °C. In order to remove water and avoid hydrolysis, they were dried at 60 °C during 24h before thermoprocessing,. Then, PET films with an average thickness of 300 µm were produced, at temperature of 255°C, following the procedure described for PHBV film production (section 2.2). After, PET flakes were produced by cutting the films into 1.5x1.5 cm squares. PET flakes were contaminated following the contamination procedure stated in section 2.3, before undergoing the decontamination process. The decontamination was performed in the same equipment showed in figure 13, under vacuum, at 220 °C and samples were collected at 1.5, 3, 6 and 20 hours. The surrogate concentrations in the polymer flakes after contamination and decontamination were determined using the following extraction/analysis method: PET flakes (0.3 g) were placed in a glass vial and 5 ml of a solution of methanol/dichloromethane 50:50 (v/v) were added. Samples were then stored 24 h at 40 °C under magnetic agitation to extract the surrogates from the polymer matrix. Solvents mixture was then evaporated in a rotary evaporator IKA RV 3 (Germany) at 30 °C, and extracts were solubilised again, in 5 ml of methanol, before analysis in an Agilent 7890A GC, under the same conditions described in section 2.4.2. Residual concentrations of surrogates, obtained in triplicate are represented in figure 27, after normalisation.

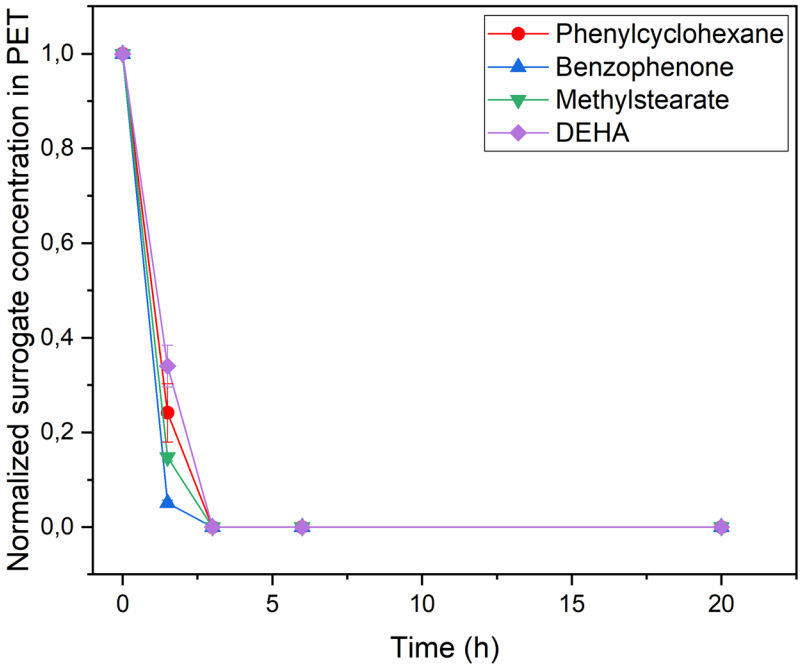


Figure 27. Evolution of residual surrogates concentration in PET, as a function on decontamination duration.

First, it is noted that toluene, chlorobenzene and methylsalicylate molecules, with the lowest molecular weight were not detected after 1.5 h of decontamination. As seen previously for PHBV, these molecules, due to their high volatility, are rapidly desorbed from the polymer and their complete decontamination is quickly achieved. The other surrogates took a little longer to be desorbed from the material, but after 3 hours of decontamination, no residue remained. These results demonstrated the good performance of the decontamination process used, as similar results have been reported in the literature [146, 200, 201]. Thanks to PET structure, the contaminants are generally sorbed near to the surface, reducing the time required for their desorption [146]. Being consistent with what has been reported in the literature, these results validate the performance of the PHBV decontamination process.

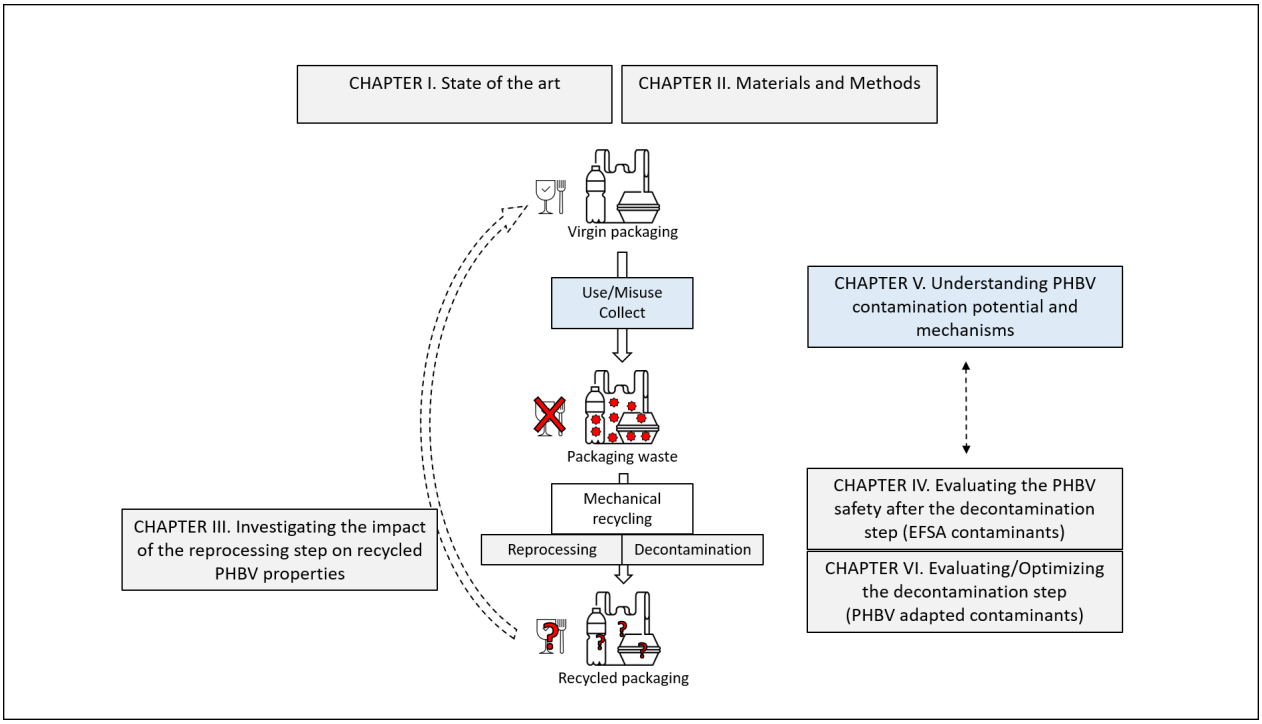
Conclusion

Dans ce chapitre, le potentiel du PHBV à être recyclé en boucle fermée pour des applications d'emballage alimentaire a été évalué. Pour cela, la stratégie établie par l'EFSA pour le recyclage du PET « bottle-to-bottle » a été utilisée et adaptée au PHBV. Ainsi, le PHBV a été volontairement contaminé par le panel de contaminants modèles identifié pour le PET, puis décontaminé selon un procédé inspiré des procédés existants pour le PET. Les résultats ont montré qu'un compromis devait être trouvé entre efficacité de décontamination et le maintien des propriétés d'usage du polymère. En effet, une décontamination efficace requière des températures et des temps de résidence élevés, ce qui altère significativement la structure du polymère. Ainsi, malgré la performance du procédé (qui a donné des résultats similaires à la littérature pour le PET), les concentrations résiduelles de certains contaminants dans le PHBV ont excédés les valeurs limites établies par la règlementation. Par conséquent, les taux d'incorporation de PHBV recyclé ne peuvent pas dépasser 21 % pour les conditions les plus favorables testés dans cette étude. Il est donc nécessaire, à l'avenir, de développer des conditions d'usage, de collecte et de décontamination, adaptés aux contraintes de ce matériau.

CHAPTER V. UNDERSTANDING PHBV CONTAMINATION POTENTIAL AND MECHANISMS

CHAPTER V. UNDERSTANDING PHBV CONTAMINATION POTENTIAL AND MECHANISMS (Article 3)

Ce chapitre a pour objectif d'évaluer la contamination propre au PHBV. En effet, au regard de sa structure et de ses caractéristiques spécifiques, le PHBV devrait présenter une capacité de contamination différente de celle du PET, ce qui remettrait en cause le choix du panel EFSA pour le challenge test. Afin d'évaluer cette différence, trois contaminants de référence seront choisis dans ce chapitre, l'un représentant le panel de l'EFSA, ainsi que deux autres avec des polarités et des masses moléculaires plus élevées. Différents tests de sorption de ces contaminants dans le PHBV seront menés et les propriétés de transfert du matériau seront caractérisées. Enfin, ces propriétés seront utilisées pour simuler une contamination réelle qui sera comparée à celle du PET, mettant ainsi en évidence les différences de comportement de ces deux matériaux. Dès lors, la pertinence de l'application de l'approche du PET aux autres polymères et particulièrement les polymères biodégradables sera discutée notamment vis-à-vis de l'utilisation du panel de contaminant modèles déterminé par la règlementation européenne, mais aussi vis-à-vis de l'application des mêmes procédés de décontamination.



Investigation of sorption mechanisms of chemical contaminants in PHBV-based food packaging material: impact on closed-loop mechanical recycling opportunities

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Abstract

In the case of closed-loop mechanical recycling of food packaging, the identification of chemical and biological substances that contaminate post-consumer materials is crucial in order to develop/adapt decontamination technology. So far, almost all contamination studies have been conducted on collected PET bottles, and the results have been extrapolated to other polymers.

In this work, the sorption mechanisms of contaminants on the biodegradable polymer PHBV were studied. Three contaminants (benzophenons, ferulic acid and Irganox 1076), with molecular weights ranging from 182 to 530 g/mol and polarity (K_{ow}) from 1.5 to 23.0 were selected. Experimental measurements of their respective partition ($K_{P/L}$) and diffusion (D) coefficients, under realistic conditions of use (contact with food simulants), allowed the modelling of their concentration profile in the thickness of the material. It was shown that the sorption in the core of PHBV of these three molecules is reached after a few hours/days. On the contrary, the same model applied to PET revealed a very slow sorption (several years), and only at the surface of the material. This was attributed to the structural differences of the two polymers in terms of chain mobility, polarity, ... This study highlights the fact that the behaviour of each polymer towards contaminants is directly related to its structure under given conditions of use, and it is a mistake to continue to address the decontamination processes of all polymers, based on the nature and level of contamination of PET.

Keywords: food packaging; contamination; transfer mechanisms; bioplastics; polyhydroxybutyrate-co-

valerate

1. Introduction

For several years, the European union has been trying to deal with the environmental disaster caused by the accumulation of plastic waste, by enacting laws and decrees that essentially aim to encourage reuse and recycling [179]. Plastic packaging, which accounts for nearly 40% of plastic production, and which has a very short lifetime, is particularly concerned by these new laws. Today, the most mature and promising recycling technology, is mechanical recycling, which appears to be the most economically viable and least environmentally impactful option according to LCA studies [9, 57, 58]. However, to date, only 2% of plastic packaging is mechanically recycled in a closed-loop system, and almost all of this is bottle-to-bottle PET recycling [202].

Closed-loop mechanical recycling implies that the recycled polymer will be used for similar food packaging applications. Therefore, it must comply with the requirements for general safety aspects of food packaging materials, as defined in Commission Regulation EU 10/2011 [12]. In other words, it must not contain contaminants in a concentration that could harm human health, or alter the organoleptic characteristics of food. There are multiple routes of contamination of food packaging, as it can be contaminated with chemicals when in contact with food, through misuse by consumers with non-food substances, or through cross-contamination with other containers during waste collect and sorting. To date, all contaminants identification work has been done for PET through surveys [184], and a panel of model contaminants has been grouped into European Food Safety Authority (EFSA) and US Food and Drug Administration (FDA) regulations to represent the different contaminant structures detected in PET waste. Therefore, any recycling process, including a decontamination step, capable of reducing the concentration of these contaminants to a level below the toxicity threshold, is allowed by EFSA and FDA [193].

Due to the lack of data on plastic contamination, this evaluation system, which is very effective for PET bottles, is often applied to other materials, such as HDPE milk bottles, with a simple adaptation of the reference contamination level [193]. However, some studies on the contamination of post-

consumer polyolefins have reported the presence of contaminants with molecular weights up to 300, 421 and 663 $g.mol^{-1}$ which is higher than the PET EFSA panel, which includes substances with a molecular weight not exceeding 230 $g.mol^{-1}$ [140]. The contamination of a polymer matrix depends primarily on, (1) the affinity of the contaminant for the polymer, reflected by its partition coefficient between the polymer P and the external medium L ($K_{P/L}$) and (2) the diffusion of the contaminant in the polymer core, highlighted by its diffusion coefficient (D). Since polyolefins and PET are in a rubbery and glassy state, respectively, under usage conditions (depending on Tg values), the mobility of the polymer chains, which plays a role on the diffusion of molecules, is different. As a result, compared to PET, polyolefins have poor barrier properties, and are susceptible to be contaminated with a wider range of molecules, including higher molecular weights substances [203]. On this basis, the decontamination process, directly related to the safety assessment, and exclusively based on PET bottle studies, is not appropriate for other polymers with different structures and transport properties [140].

Biosourced and biodegradable plastics are gradually investing the plastics market. Their biodegradability, which makes them an ideal solution against the accumulation of plastic, should not prevent their involvement in the circular economy system of plastics. Indeed, their recycling would save resources and reduce production costs. Within this category of plastics, polyhydroxyalkanoates (PHAs) are an emerging class of bioplastics, which have the main advantage of being fully biodegradable in natural environments [186]. Poly(hydroxybutyrate-co-valerate) (PHBV), a copolymer belonging to the PHA family, has mechanical and barrier properties, allowing it to replace some conventional plastics such as PP or LDPE, in food packaging applications [204]. However, closed-loop recycling of PHBV, including a safety assessment, has never been studied before. Before studying decontamination and safety assessment, it is crucial to reveal the behavior of PHBV towards contaminants, not limited to the EFSA PET panel. Indeed, PHBV has a much lower Tg than PET, so it has weaker barrier properties towards high molecular weight substances. In addition, it has a higher polarity than PET due to its few polar functions [13, 14], as shown by the water contact angle measurements of 60° and 79° for PHBV and PET, respectively [15] [16]. Therefore, PHBV can potentially be contaminated with polar substances that are also not considered by the EFSA panel.

The objective of this work is to investigate the affinity of PHBV to chemical substances with different molecular weights and polarity. Thus, it was contaminated with three distinct substances: (1) benzophenone, a contaminant of the EFSA panel for PET, (2) ferulic acid with a higher polarity and (3) Irganox 1076, a contaminant of higher molecular weight. In order to understand the contamination mechanisms, the sorption and diffusion coefficients of the selected contaminants were determined from isotherms and sorption kinetics, performed under contact conditions with ethanol, used as a food simulant. These coefficients were then integrated into diffusion models to establish the concentration profiles of the contaminants in the thickness of the material in order to evaluate their penetration depth. Finally, these theoretical results were confronted with experimental measurements of concentration profiles, using a Raman micro-spectrometer.

2. Materials and methods

2.1. Materials

PHBV with 3 mol% of 3-hydroxyvalerate (HV) was purchased from Natureplast (France) under the commercial grade of PHI003. According to manufacturer, PHBV has a density of 1.25 $g.cm^{-3}$ and a melting temperature of 170-176 °C.

Boron nitride, as PHBV nucleating agent and solvents (95% Ethanol, Methanol) were purchased from sigma Aldrich.

The selected model contaminants are benzophenone, ferulic acid and Irganox 1076. Their parameters such as molecular size (M_w) and polarity (expressed as Log K_{ow}) are reported in Table 12. 95 % ethanol was used as solvent for contaminant dissolution (it is also considered as food simulant in European regulation). Vanillic acid and Uvitex OB were used as internal measurement standards for liquid chromatography analyses. All these chemicals were purchased from Sigma Aldrich.

Table 12. Contaminants parameters

Contaminant	Mw (g.mol-1)	Log Kow
Benzophenone	182.0	3.2
Ferulic acid	194.2	1.5
Irganox 1076	530.9	23.0

2.2. Preparation of PHBV films

PHBV powder was mixed with 0.5 wt% of Boron Nitride and the mixture was pre-dried during 24 h at 60 °C in order to remove the potential water content. The extrusion was carried out in a parallel twin screw microcompounder Process 11 (Thermoscientific), at 150 rpm with a constant temperature of 180 °C from the feeding to the die. Then, granulation was performed at room temperature and pellets underwent another drying step at 60 °C for 24 h. PHBV films with an average thickness of 350 ± 20 µm were produced by thermo-compression at 180 °C using a heated hydraulic press (20T, Pinette Emidecau Industries). The pressure was first set at 5 bars for 5 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30 s. PHBV films were stored 2 weeks at room temperature and under a controlled relative humidity of 50 % in order to complete the crystallization of the film structure.

2.3. Sorption isotherms

Sorption isotherm experiments were performed with different contaminants concentration gradients, at 20°C. Specifically, 0.3 g of PHBV flakes (1.5×1.5 cm) were placed in glass vials and 5 mL of contaminant solutions were added under magnetic stirring. Benzophenone, ferulic acid and Irganox 1076 were added in concentration ranges of 1-125 $g.L^{-1}$,1-50 $g.L^{-1}$ and 2-6 $g.L^{-1}$ respectively. 95% ethanol was used as solubilizing medium of the contaminants, and is also considered as food simulants, mainly used to replace vegetable oil. After reaching the sorption equilibrium, PHBV flakes were immersed in 5 mL of methanol in order to extract the contaminants sorbed in the polymer matrix.

Extraction was conducted for 24 h at 40 °C, under magnetic agitation (300 rpm). The supernatant solutions were filtered and placed in 1.5 mL glass vials and the equilibrium concentrations of the three contaminants were determined. All experiments were performed in triplicate.

Benzophenone and ferulic acid quantification was performed by injecting the solutions in Ultimate 3000 UHPLC (Thermofisher) liquid chromatography system, equipped with a photodiode array detector (DAD), set at 280 nm. The Waters column was 100 mm × 2.1 mm, HSS T3, with particles size of 1.8 µm. The solvents used were A (99.9 % H2O and 0.1% HCOOH v/v) and B (80 % CH3CN; 19 % H2O; 0.1% HCOOH) with a flow rate of 0.55 mL/min; and the injection volume was 2 µL. The peaks identification and product quantification were based on the use of the different contaminants as external standards (calibration curves with concentration range of 10 – 45 $mg.L^{-1}$). Vanillic acid was used at 30 $mg.L^{-1}$ as internal standard.

Irganox 1076 concentration was determined by recording the absorbance of the samples at 230 nm, after injection in Alliance HPLC system (Waters) equipped with an Alltima C18 column (250 m × 2.1 mm, 5 µm) protected with a Alltima C18 (7.5 mm × 2.1 mm, 5 µm) column guard. The solvent used was 55 % (v/v) aqueous acetonitrile at a flow rate of 0.3 $mL.min^{-1}$ at 50 °C, and the injection volume was 2 µL. Product quantification was based on the use of Irganox 1076 as external standards (calibration curves with concentration range of 10 – 45 $mg.L^{-1}$). Uvitex OB was used at 30 $mg.L^{-1}$ as internal standard.

Linear regression has been drawn for each contaminant isotherm, and experimental partition coefficients ($K_{P/L}$) of the contaminants between the liquid food simulant and the polymer were determined as the slope of the regression curves, using the Origin software.

2.4. Sorption kinetics and estimation of Diffusion coefficients

Sorption kinetics experiments were conducted in order to determine the diffusion coefficient of contaminants. In 30 mL glass vials, PHBV flakes (1.5 cm squares, 0.3 g) were immersed in a 95% ethanol solution, saturated with each contaminant. The saturated stock solutions had a concentration of

133 g.L^{-1} for Benzophenone, 50 g.L^{-1} for ferulic acid and 6 g.L^{-1} for Irganox 1076. Vials were hermetically sealed and submitted to magnetic agitation (300 rpm) at room temperature (20 °C). PHBV samples were, then, collected at specified time intervals, rinsed with 95 % ethanol and dried with absorbent paper. Then, PHBV flakes were immersed in 5 mL of methanol in order to extract the contaminants sorbed in the polymer matrix. Extraction was conducted for 24 h at 40 °C, under magnetic agitation (300 rpm). After filtration, the supernatant solutions were placed in 1.5 mL glass vials and quantification was carried out in the same way described previously for sorption isotherms. All experiments were performed in duplicate.

Experimental sorption kinetics were used to estimate the diffusion coefficients of each contaminant, based on fitting experimental data with a suitable analytical solution of Fick's second law. The samples were considered as one-dimensional infinite plane sheets with a negligible diffusion from the borders of the flakes. Sorption took place in a saturated solution of contaminant, then constant boundary conditions were assumed. Initial contaminant concentrations were assumed to be uniform in the solution and null in the film. Contaminant sorption can be described by the following equation (2), provided by Crank [155]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right\} (2)$$

Where M_t and M_∞ are the masses (mg) of the diffusing molecule in the polymer at time t and at the equilibrium state, respectively, D is the diffusion coefficient of the diffusing molecule in the polymer (m^2.s^{-1}), t is the time of the sorption (s) and l is the half thickness of the film (m).

In order to calculate the apparent Diffusion coefficient D, the asymptotical mass uptake M_∞ at equilibrium was calculated from the known initial concentration in the solution and the partition coefficient (determined above). In order to take into account the heterogeneity of experimental standard deviations along the kinetic, a weighted root mean squared error was used for estimation of D. Weights were set as the inverse of experimental variance.

The numerical simulations were carried out using the Matlab software and the lsqnonlin

function, to estimate the diffusion coefficient.

2.5. Sorption profile

2.5.1. Sorption simulation

Concentration profiles of each contaminant through the polymer thickness were modeled for different time in PHBV and in PET, in order to compare the sorption behavior of these two different polymers. As for sorption kinetics experiments, the simulation involved 1.5×1.5 cm films immersed in contaminants saturated ethanolic solutions. The initial concentrations were 133 $g.L^{-1}$ for Benzophenone, 50 $g.L^{-1}$ for ferulic acid and 6 $g.L^{-1}$ for Irganox 1076. Contaminant concentration in initial solutions being very high, it was considered that the conditions at the borders remained constant. Thus, the contaminant sorption at time t (s), and position x (m) into the film described by $x \in [-l, l]$, with l the half thickness of the film (m), is given by the following equation, provided by Crank [155]:

$$\frac{C_{x,t} - C_0}{C_\infty - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right\} \cos\frac{(2n+1)\pi x}{2l} \quad (7)$$

where $C_{x,t}$ is the concentration in diffusing substance in the polymer ($mg.cm^{-3}$) at time t and depth x, C_∞ is the concentration in diffusing substance in the polymer at the equilibrium state ($mg.cm^{-3}$), C_0 is the initial concentration in diffusing substance in the polymer, here considered to be null, D is the diffusion coefficient of the diffusing molecule in the polymer ($m^2.s^-1$). They were obtained from sorption kinetic experiments for PHBV and from the literature for PET. As there is initially no contaminant in the polymer, the equilibrium concentration C_∞ in the polymer can be calculated from the known initial concentration in the solution and the partition coefficient assuming no loss due to transfer to the headspace or leaks. The numerical simulations were carried out using the Matlab software.

2.5.2. Sorption measurements by Raman spectroscopy

In addition to modelling, the sorption profile of benzophenone in PHBV was determined experimentally by sorption kinetics followed by the evaluation of its concentration in the polymer thickness using Raman spectroscopy.

Sorption was carried out by immersing 1.5×1.5 cm films in 5 mL of saturated ethanolic solution of benzophenone (133 $g.L^{-1}$). Vials were sealed and submitted to a continuous magnetic agitation at 20 °C. Polymer flakes were, then, collected at 0.5 h and 1.5 h in order to obtain concentration profiles at non-equilibrium state. They were rinsed with 95 % ethanol and dried with absorbent paper. Then, small polymer lamellae were cut through the thickness of the flakes and placed on a microscope slide before being characterized by Raman spectroscopy (figure 14).

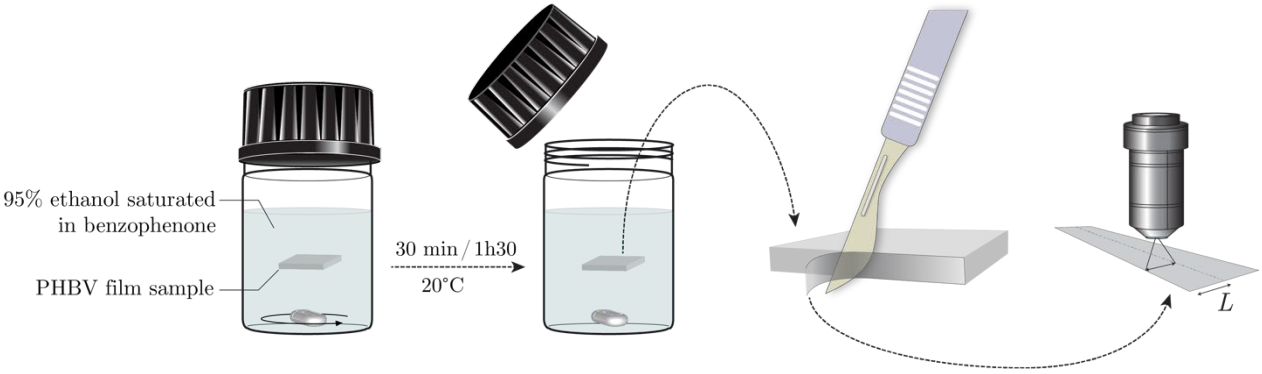


Figure 14. Experimental method for the evaluation of the concentration profile of benzophenone in the thickness of PHBV by Raman spectroscopy.

Raman spectra were recorded between 95 and 3500 cm^{-1} Raman shift, using a confocal Raman micro spectrometer Almega (ThermoElectron). The configuration was: excitation laser He-Ne with λ_0 = 633 nm, grating 500 grooves/mm, pinhole 25 µm, objective 50×, numerical aperture (NA) 0.8 and focal distance (f) 380 µm. A total of 9 spectra were realized in the half thickness of the samples with a step of 17 µm. The collection time was 10 s and each spectra was replicated 4 times. All spectra were pre-treated with Omnic v7.1 (ThermoElectron) and the processing included a multipoint linear baseline correction. The relative content of Benzophenone was evaluated using the height of the Benzophenone specific peak (1695 cm^{-1}) assigned to the C=O group, normalized by the height of the PHBV specific peak (1761 cm^{-1}) related to the C=O group of the ester function.

As in the previous section, samples were considered as infinite films with uniform initial contaminant concentration in the solution and zero initial concentration in the sample. Assuming in addition that concentration can be obtained from intensities through a linear relationship, equation 7 can

be used to estimate the Diffusion coefficient of Benzophenone from experimental normalized intensity profiles instead of concentration profiles. The normalized intensity at equilibrium I_∞ was taken from experimental value at the boundary of the sample.

The numerical simulations were carried out using the Matlab software and the lsqnonlin function, to estimate the diffusion coefficient.

3. Results and Discussion

3.1. Partition coefficients of contaminants in PHBV

Sorption isotherms of the contaminants in PHBV were conducted during 4 days for Benzophenone and 7 days for Ferulic acid and Irganox 1076, and the results are reported in Figure 28. These contact times were set on the basis of preliminary experiments aimed at characterizing the minimum times required to reach the equilibrium state of the system for each contaminant. Sorption isotherms presented an overall linear trend without reaching any steady state, suggesting that saturation limit of contaminants in PHBV was never reached in our experimental conditions. Linear regression models were employed to fit the sorption isotherms and showed a good fit (dashed lines), with R^2 ranged from 0.987 to 0.998. This isotherm model is the simplest equation describing sorption from a liquid onto a homogeneous solid phase dominated by a partition process, then the good fit indicated that partition in the case of PHBV did not depend on solution concentration in these conditions [205].

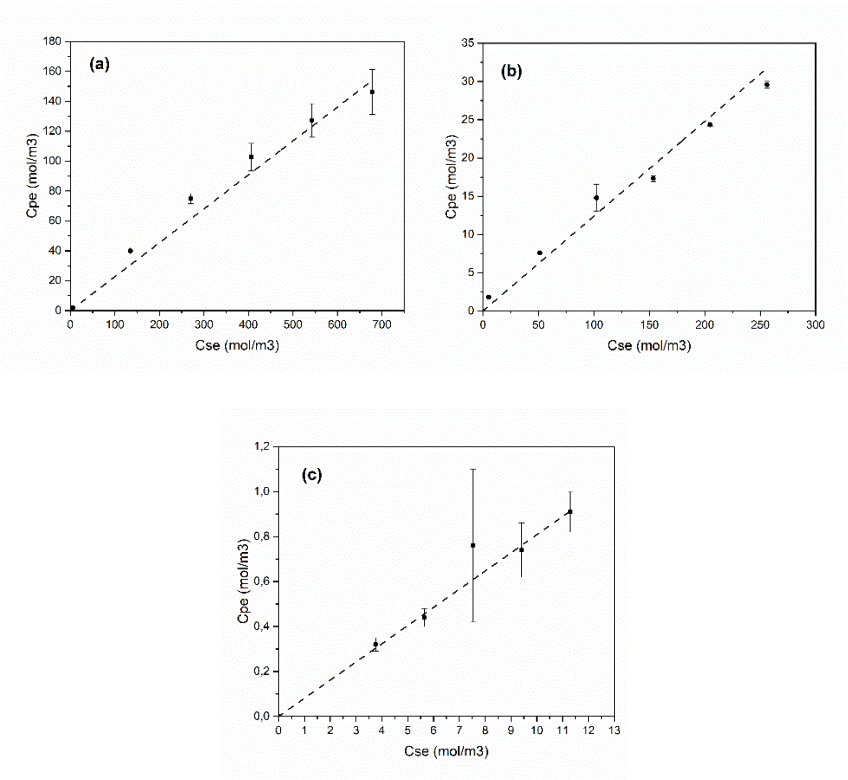


Figure 28. Sorption isotherms of Benzophenone (a) Ferulic acid (b) and Irganox 1076 (c) in PHBV at 20°C. Cpe and Cse representing the contaminant equilibrium concentration in the polymer and the solution respectively.

In order to describe the sorption capacity of PHBV, partition coefficients $K_{P/L}$ were calculated from the linear regression model, and are reported in Table 13. The affinity of PHBV for contaminants followed the order Benzophenone > Ferulic acid > Irganox 1076. The partition phenomenon of a molecule in a polymer depends more specifically on the interactions between the contaminant and the polymer matrix. This interaction, which reflects the concept of affinity between the two compounds, is particularly influenced by the hydrophilic/lipophilic balance of the contaminant and the polarity of the matrix. The high affinity of the different contaminants for the packaging material could be attributed to specific interactions between chemicals and polymers substituents, such as hydrogen bonding, hydrophobic of π-π interactions [206, 207]… Regarding the molecular weight of the three contaminants, PHBV seems to present a higher affinity for chemicals with molecular weight not exceeding 200 g/mol. Irganox with, Mw = 530 g/mol was less adsorbed/sorbed in the polymer. For contaminants of close molecular weight, namely benzophenone and ferulic acid, it appears that PHBV has a higher affinity for

benzophenone, which presents a moderate polarity (K_{ow} = 3.2, compared to ferulic acid K_{ow} = 1.5). This is confirmed by the Hansen coefficients values, where the polar component of PHBV (8.8 $MPa^{½}$)[208] is similar to that of benzophenone (8.6 $MPa^{½}$)[209], and significantly different from that of ferulic acid (5.7 $MPa^{½}$)[210], suggesting a lower overall compatibility.

Table 13. Partition coefficients of contaminants in PHVB in ethanol at 20°C

Contaminant	Partition coefficient (KP/L)
Benzophenone	0.227
Ferulic acid	0.124
Irganox 1076	0.081

3.2. Diffusivity of contaminants in PHBV

Further experiments and simulations have been conducted for sorption in solutions of ethanol saturated in contaminants. Therefore, due to the relative poor sorption of PHBV regarding solution concentration, the concentration conditions in the border of the samples will supposed to be constant.

Sorption kinetics of the contaminants in the PHBV matrix were performed for 7 days for Benzophenone and 9 days for ferulic acid an Irganox 1076. Experimental data were fitted with the sorption kinetic model (Equation 2) to determine the apparent diffusion coefficient of each contaminant. The equilibrium concentrations of the contaminants in the polymer have been deducted from the initial concentration in the solution and the partition coefficient determined in the previous section. Experimental and simulated curves are shown in Figure 29.

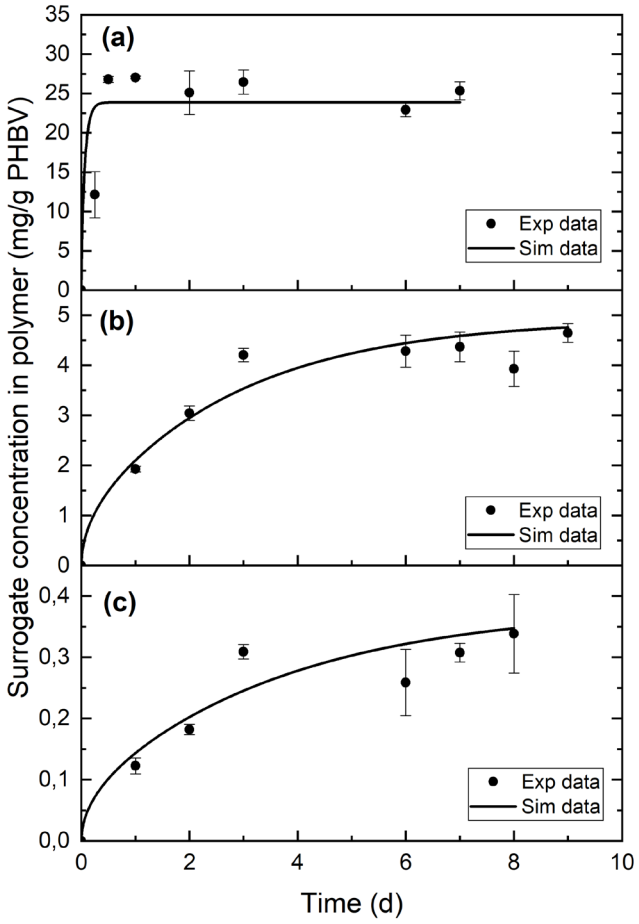


Figure 29. Experimental (points) and simulated (plain lines) sorption kinetic curves of Benzophenone (a), Ferulic acid (b) and Irganox 1076 (c) in PHBV at 20°C.

Under the investigated conditions, the sorption of any contaminants in PHBV flakes was fast with an equilibrium state reached between few hours and 6 days (figure 29). It is worth noting that the experimental sorption kinetics presented heterogeneous standard deviation, which justified the use of weighted root mean squared error (w-RMSE), instead of the classical unweighted root mean squared error (RMSE), for estimation of diffusivities. The apparent diffusion coefficients for Ferulic acid and Irganox 1076 were independent on the use of w-RMSE or RMSE. Due to the faster sorption and higher experimental uncertainty obtained for Benzophenone, w-RMSE led to significantly higher diffusivity. On this basis, the estimation of the apparent diffusion coefficient (D_{app}) of each contaminant in PHBV is reported in Table 14.

Table 14. Apparent Diffusion coefficients of contaminants in PHVB at 20°C.

Contaminant	Apparent diffusion coefficient (m2.s-1)	Root mean squared error
Benzophenone	$2.25e^{-12}$	$1.7e^{-1}$
Ferulic acid	$5.92e^{-14}$	$1.5e^{-2}$
Irganox 1076	$4.48e^{-14}$	$2.0e^{-3}$

The sorption kinetic of a chemical from a liquid to a solid phase, generally, occurs in the following way: (1) diffusion and convection of the molecule in the liquid solution, (2) reversible or irreversible adsorption on the solid surface and (3) diffusion into the solid matrix. In the case of the sorption in a condensed solid phase such as a PHBV film, the diffusion of the substance into the polymer is generally considered as the rate-limiting step since the diffusion in the liquid phase and its adsorption on the polymer surface are fast, even more in a turbulent environment where the transfer resistance at the interface can be considered negligible [211]. Therefore, the apparent diffusivity of a chemical through the entire sorption process is mainly governed by the diffusion in the polymer phase.

Several factors are known to control diffusion of chemical in polymeric matrices among which the most impactful are : (1) The chemical structure of the diffusing substance, in terms of molecular weight, molar volume, functional groups and their repeating pattern, (2) the polymer mobility that is affected by the molecular weight, degree of crystallinity, degree of cross-linking, extent of unsaturation and glass transition temperature and (3) the temperature [211]. Based on the simple fact that the driving force responsible for the mobility of a diffusing substance is compensated by the frictional force of a viscous medium, the relationship of proportionality between the diffusion coefficient and the molecular weight of the compound is commonly accepted [212, 213].

In the investigated case, it is observed that Irganox 1076 with the higher molecular weight showed the lowest diffusivity in PHBV matrix. However, it is important to note that the apparent diffusion coefficient of benzophenone and ferulic acid are different by a factor of almost 40 even though these two compounds have almost identical molecular weights. This suggests that the additional

influence of the polarity of the molecules or a plasticization of the material by the diffusing substance, at high concentration, results in a modification of its transfer properties. In addition, the diffusivity coefficients values in PHBV are much higher than those reported on PET for molecules of similar molecular weight [195], and the high transfer rates that occur in the PHBV imply that there is contamination in the core of the material. The diffusion of molecules, with different polarities, into the depth of the polymer matrix is related to the hydrophilic nature and low barrier properties of PHBV polymer[193]. This fact which is completely excluded from any consideration in the challenge test approach applied to PET recycling, must be taken into consideration in the development of an accurate cleaning technology applied to direct PHBV food contact recycled material.

3.3. Modelling the concentration profile in the thickness of materials integrating experimental values of D and $K_{P/L}$

In order to assess the depth of contaminants penetration through the materials thickness, the concentration profiles were simulated based on the diffusion models described in the equation (7), at different times of contact for PHBV and PET, and are shown in Figure 30. The profiles in PHBV were simulated using the experimental values of the diffusion and partition coefficients of the contaminants. Sorption profiles in the PET were simulated using contaminants' diffusion from the Piringer equation and a partition coefficient of 1 (*i.e* equal solubility between the polymer and the solvent), assuming a very low influence of $K_{P/L}$ due to the low diffusivity of the contaminants in the material [214]. Concentration profiles though the flakes thickness were modelled in PHBV in the range of 1-6 hours for Benzophenone and in the range of 1-6 days for ferulic acid and Irganox 1076. In PET, it was at 1 and 1.10^3 days for Benzophenone and ferulic acid and at 1 and 1.10^4 days for Irganox 1076.

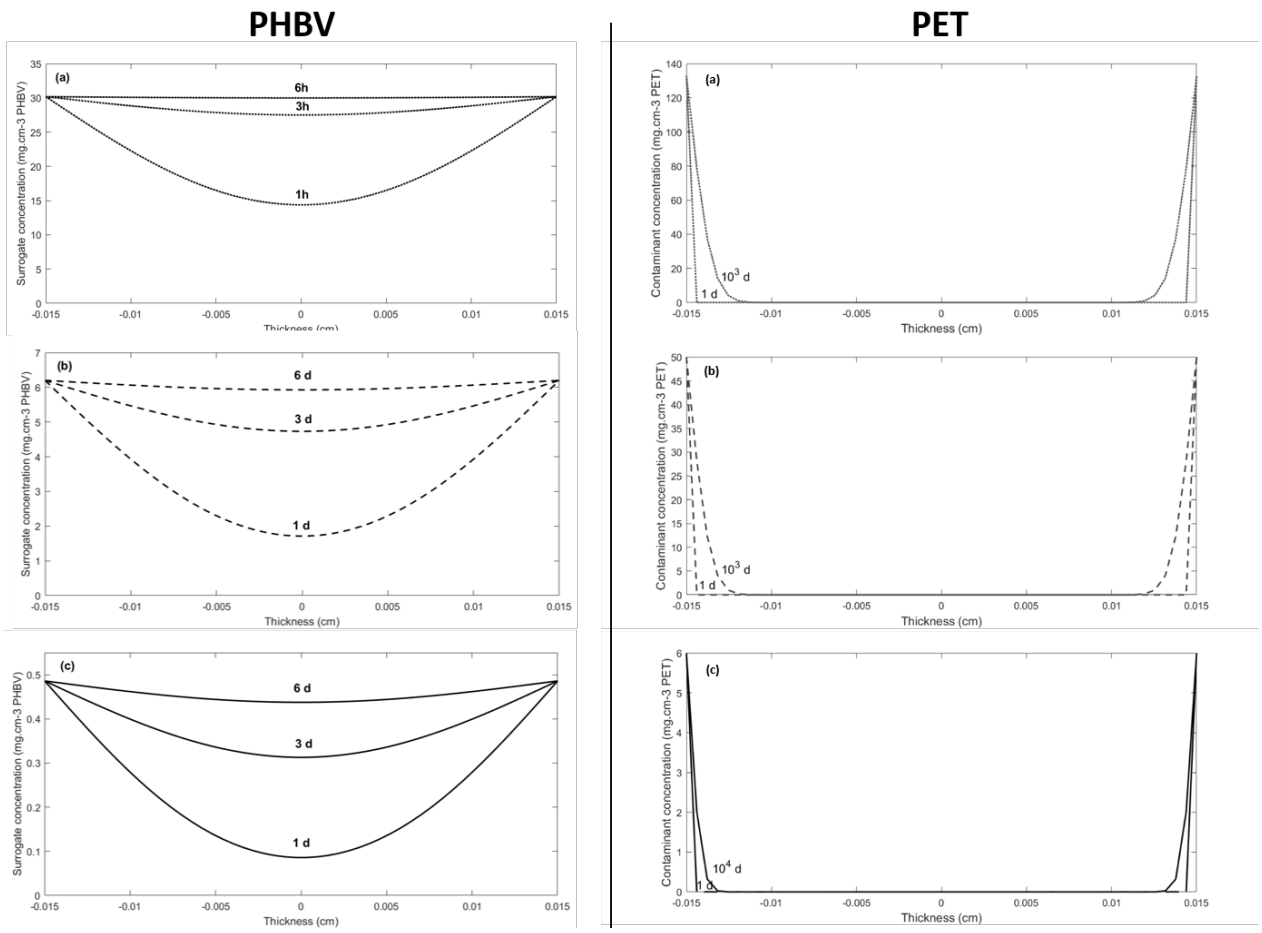


Figure 30. Modelled curves of contaminant sorption in polymer as a function of time and polymer thickness. Sorption of Benzophenone (a), Ferulic acid (b) and Irganox 1076 (c) in PHBV and PET for the left and right columns respectively.

Concentration profiles in PHBV at room temperature showed that all three contaminants were completely sorbed into the core of the material in a relatively short time. Benzophenone sorption reached equilibrium in less than one day. The sorption of ferulic acid and Irganox 1076 reached equilibrium in six days, due to their lower diffusivity in the polymer. In PET, in the other hand, the sorption of all contaminants is very long process. After 1000 days of contact at room temperature, the contaminants are still concentrated on the surface and are far from reaching the core of the polymer. The dynamic properties of the material and the mobility of the polymer chains proved to be very determining and can explain the differences in behaviour observed between the two types of polymers. In the case of semi-crystalline polymers, it is well established that the movement of low molecular weight molecules takes place in the amorphous parts of the material and, according to the widely accepted theory of free

volumes, the degree of crystallinity is considered to be a determining parameter. Since the amorphous free-volume of glassy polymers is dense and well organized, the lack of mobility of the glassy polymer chains such as PET prevents the diffusion of compounds [193]. The concentration profiles obtained for the two types of polymers clearly show the predominant influence of diffusion coefficient of the contaminants on their distribution in the thickness of the packaging material. The very low diffusivity values described for PET, ranging 1.10^{-18} to 1.10^{-22} m^2/s [195], thus, result in a very low depth of contaminants penetration. Considering that potential contaminations are likely to occur during contact use or during post-consumer sorting and reprocessing, the strategy used during the recycling operation is therefore very favourable to the decontamination process since PET exhibits a glassy structure at room temperature (*i.e.* during the contamination stages) and a rubbery state during the decontamination process.

In contrast, rubbery polymers present amorphous free-volume fractions with a greater freedom of movement of the polymer chains, where chemical are expected to diffuse easily, due to the flexible structure [140, 203]. Thus, although PHBV has a very high degree of crystallinity (Xc ~ 80 %), the facilitated diffusion in its amorphous parts induces contamination of the core material. It is important to note that PHBV, unlike PET, has a low glass transition temperature and therefore remains in a rubbery state throughout its life cycle (contamination/decontamination). This must be taken into account when defining the rates applied during the decontamination step, which may require a longer residence time in the vacuum reactor or extrusion chamber.

In order to validate the principle that diffusion and partition coefficient values extracted from sorption isotherms can be used to simulate/predict the contamination of materials after food contact, experimental profiles of benzophenone concentration in PHBV were established using a Raman micro-spectrometer. The comparison was made after 0.5 and 1.5 hours of contact (Figure 31). These low times were chosen in order not to reach the sorption equilibrium of Benzophenone in the polymer and to be able to accurately determine the diffusion coefficients.

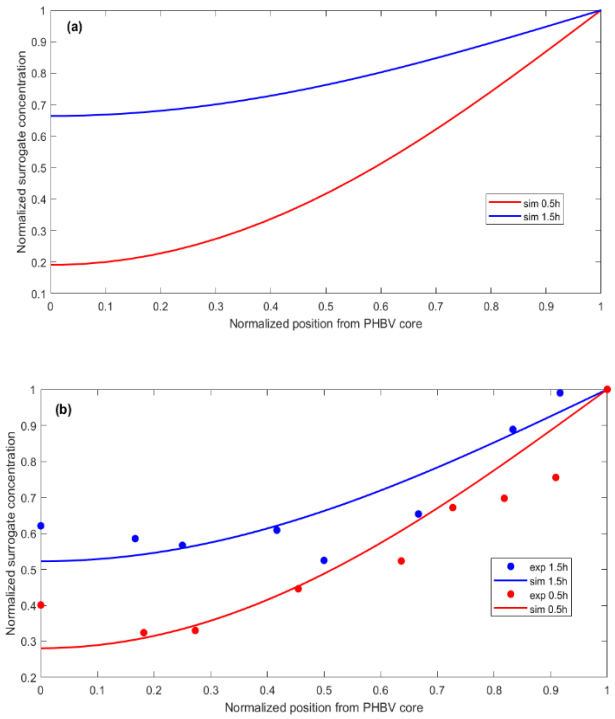


Figure 31: Benzophenone concentration profile in PHBV (a) simulated profile from kinetics/isotherms of Raman analysis data (b) experimental and simulated profile from sorption test.

The fitting curves of experimental spatial distribution data estimated a Benzophenone diffusion coefficient of $2.52e^{-12} \pm 1.46e^{-12}$ which is very close to the diffusion coefficient obtained from sorption kinetics ($D= 2.25e^{-12}$). Thus, the results presented in figure 31 clearly demonstrate that the actual level of contamination measured by the experimental route is similar to the level predicted on the basis of parameters previously extracted from the sorption isotherm.

Therefore, this preliminary study suggests that the approach of using transfer parameters extracted from sorption isotherms and kinetics can be considered as an alternative pathway to establish a contamination profile in a polymer, in a worst-case scenario. This finding may support the strategy generally employed for consumer health protection purposes of using overestimated diffusivity values in models, such as that proposed by Piringer. However, while this approach has proven to be effective in assessing/overestimating material transfer involving synthetic polymers such as PET, it may be of limited application in the particular case of PHBV. The results of this study show that PHBV is capable of absorbing polar compounds that are usually excluded from synthetic polymeric materials, and have a

behaviour that cannot be easily anticipated based on their molecular weight alone. This first investigation on PHBV sorption behaviour revealed a high potential for contamination by various substances due to its properties. Thus, the contamination potential has to be determinate based on the structure of the polymer, as in the case of glassy polymers such as PET which will only be contaminated in the surface, with low molecular weight and apolar substances, and rubbery polymers which can be fully contaminated with a wider range of substances. Polymers polarity must also be taken into account, with the possibility of potential sorption of additional polar substances. Therefore, the challenge test approach currently implemented for the recycling of food contact PET cannot be extrapolated to all others polymers, and decontamination protocols must be adapted to the particular behaviour of the PHBV. While the decontamination of glassy polymers has proven to be very effective with a simple thermal process or by removing the contaminated surface layer, the decontamination of rubbery polymers is much more difficult, due to the high contamination down to the polymer core.

4. Conclusions

The development of closed-loop recycling of biodegradable food packaging materials, such as PHBV, depends on ensuring consumer safety and therefore on controlling the level of exposure to contaminants that may be incorporated into the material at different stages of its life cycle. This control must be exercised over both (i) the nature and concentrations of potential contaminants in post-consumer materials and (ii) the cleaning efficiency of the recycling technology. This work provides preliminary insights into the first critical issue by exploring the risks of contamination of PHBV during their contact with food, in relation with their structure and transport properties. The high capacity of PHBV to be contaminated by a wide range of organic compounds, including high molecular weight molecules (>300 Da) and polar substances demonstrates the limitations of the transposition of the challenge test developed for bottle-to-bottle PET recycling, and raises the question of a wider and more representative panel of contaminants. Studies on PHBV contamination from future collect/sorting chains should be conducted when PHBV would be present on the market and should allow for a better assessment of PHBV-specific contamination risks.

This work also lays the foundation for the development of technologies suitable for the decontamination of PHBV materials during their recycling. The sorption and diffusion of polar and high molecular weight non-volatile compounds in the core of the films requires the development of alternative cleaning technologies to the volatilization processes. Decontamination technologies should be optimized as a function of the contamination behaviour of the polymer, as the polymer properties may also impact the desorption behaviour. Further careful scientific studies, with a wider contaminants panel are needed to conclude on the safety of a mechanical process, depending on polymer nature and properties.

Statements & Declarations

Funding

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Declaration of interest statement

The authors declare that they have no competing financial interest of personal relationship that could influence the work reported in this paper.

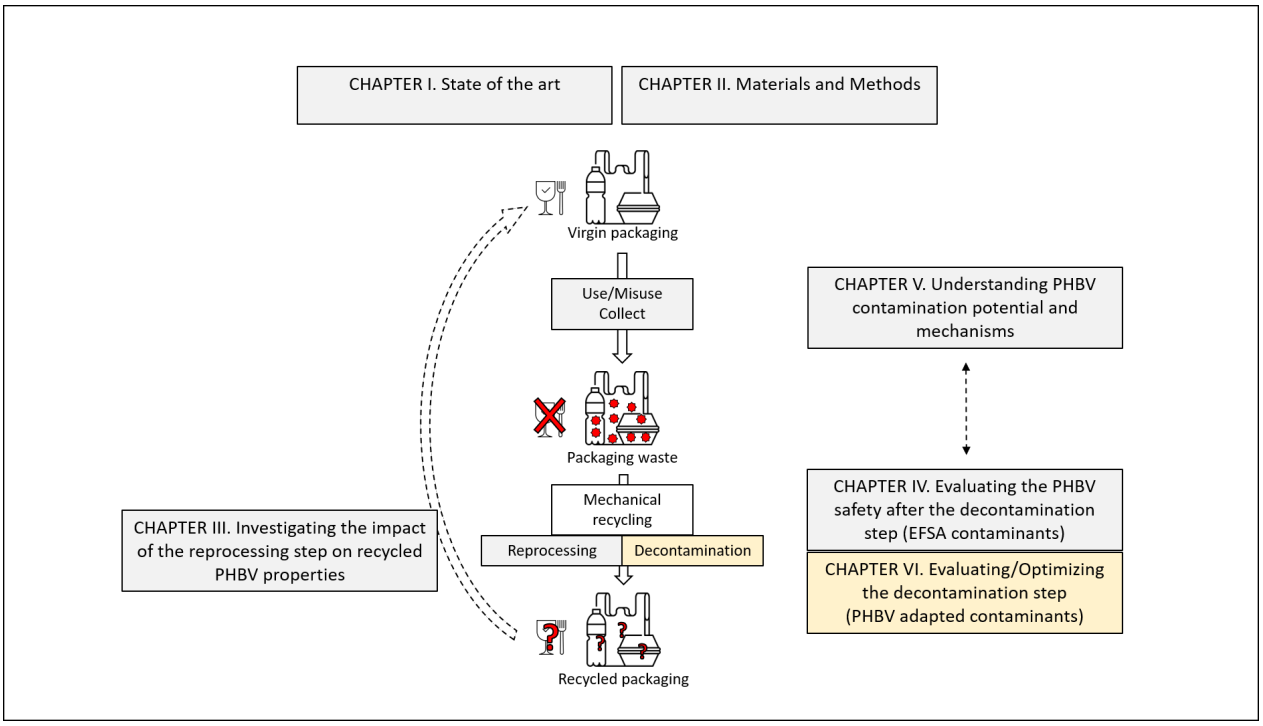
Conclusion

Dans ce chapitre, le développement du recyclage mécanique en boucle fermée de matériaux d'emballage alimentaire biodégradables a été abordé sous l'angle de leur exposition aux contaminants au cours de leur cycle de vie. Ce travail a permis d'explorer les risques de contamination du PHBV en fonction de sa structure et de ses propriétés de transport. La forte capacité du PHBV à être contaminé par une large gamme de composés organiques, y compris des molécules de haut poids moléculaire (>300 Da) et des substances polaires, démontre les limites de la transposition des « challenges tests » développés pour le recyclage des bouteilles en PET, et pose la question d'un panel de contaminants plus large et plus représentatif. Cette différence de comportement entre polymère, peut être attribuée à la différence de nature/structure des matériaux, et doit inciter à porter l'attention sur la mise en place d'approches spécifiques. Des études sur la contamination du PHBV dans les futures chaînes de collecte/tri devraient être menées lorsque le PHBV sera présent sur le marché et devraient permettre une meilleure évaluation des risques de contamination spécifiques au PHBV. Les techniques de décontamination elles, doivent être optimisées en fonction de cette spécificité de comportement des matériaux.

CHAPTER VI. EVALUATING/OPTIMIZING THE DECONTAMINATION STEP (PHBV ADAPTED CONTAMINANTS)

CHAPTER VI. EVALUATING/OPTIMIZING THE DECONTAMINATION STEP (PHBV ADAPTED CONTAMINANTS) (Article 4)

Pour faire suite aux chapitres précédents, qui ont démontré que le panel de contaminants modèles appliqués au PET n'était pas adapté au PHBV, ce chapitre a pour objectif d'évaluer l'aptitude au contact du PHBV dans des conditions « plus proches de la réalité ». Ainsi, le polymère sera soumis à un panel de contaminants plus élargi et plus adapté à ses capacités de sorption. Des contaminants avec des poids moléculaires et des polarités plus élevés que les contaminants établis par l'EFSA, seront testés et l'efficacité de décontamination sous différentes températures sera évaluée. En parallèle la protection du polymère de la dégradation engendrée par le traitement thermique sera tentée via l'addition du stabilisant naturel, la quercétine. L'impact de la présence de cet additif sur l'efficacité de décontamination, ainsi que sur l'intégrité structurelle du polymère sera étudié.



Decontamination of PHBV material intended for food contact applications: relevance of the contaminants panel and the role of quercetin as additive

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Abstract

The closed-loop recyclability of PHBV materials for food contact applications was investigated. Going beyond the EFSA contaminant panel (established for bottle-to-bottle PET recycling), PHBV was contaminated with polar contaminants, namely gallic acid, catechin, ferulic acid and PEG 200. Due to the low volatility of these molecules and hydrogen bonding interactions with the polymer, their decontamination efficiencies were well below safety limits. After 48h at 160°C, a decontamination of 25.9 % for gallic acid, 68.5 % for catechin, 67 % for ferulic acid and 86.8 % for PEG 200 was reached. To increase the temperature/decontamination time combination, quercetin was used as a thermal stabilizer. The presence of quercetin decreased contaminant removal (-8.5 % for gallic acid, -57.4 % for catechin, -18.7 % for ferulic acid, and -31.9 % for PEG200), for shorter decontamination times, by generating hydrogen bonds and π-stacking interactions with the contaminants. With longer decontamination times, a great degradation of the polymer occurred (-83 % Mw and -45 % Xc), accelerated by the presence of quercetin.

Keywords: mechanical recycling; polyhydroxybutyrate-co-valerate; decontamination; food packaging; quercetin.

1. Introduction

The recycling of food packaging plastics, considered single-use plastics, is at the heart of the European and French strategies to reduce plastic waste for the period 2025-2040 [25, 215]. Last April, the French government published the 3Rs strategy (Reduce, Reuse, Recycle), which calls for the

extension of recycling to all types of single-use plastics, with a priority on food packaging [26]. In terms of recycling, mechanical recycling is mainly targeted as it is the most implemented and mature technology, with important economic and environmental benefits [216].

However, mechanical recycling is often confused with down-cycling, where the recycled materials are of lower quality and cannot withstand the endless recycling loops, ending up in landfills or incineration facilities. Indeed, only 2% of plastic packaging is been kept within a closed-loop system [202]. One of the solutions to reduce the pressure on raw materials and prevent the accumulation of plastic waste is to consider closed-loop recycling of plastics that, at the end of their life cycle, do not present any danger to human health or the environment. The recycling of biodegradable plastics should therefore be studied. Indeed, recycling is often opposed to biodegradability, although these two end-of-life options are complementary. Combined in an integrated system, recycling creates an after-use economy, while biodegradability eradicates definitively the issues of the environmental spreading of the persistent plastic waste.

To date, almost all closed-loop mechanical recycling technologies have been developed for polyethylene terephthalate (PET) bottle-to-bottle applications [193]. To ensure safety, the European Food Safety Authority (EFSA) evaluates and issues an opinion on any recycling process which aims at decontaminating post-consumer PET during the recycling process. Until 2021, approximately 180 EFSA opinions have been published [193]. The evaluation is part of a "challenge test" approach which consists in doping the plastic with known contaminants, and analysing their elimination through the recycling process, mainly based on a thermal treatment under vacuum or gas flow [146]. The recycled plastic is considered safe if the residual concentration of contaminants does not exceed the limits corresponding to the toxicity thresholds [27]. For PET, model substances with different chemical structures (such as toluene, chlorobenzene, methyl salicylate, methyl stearate… etc.) have been selected to simulate the real-case contaminants mainly identified in post-consumer food packaging. These substances are listed in EFSA and FDA (US Food and Drug Administration) regulations [152].

While closed-loop recycling of other plastics such as PE and PP is still challenging [140], no work has been done on biodegradable plastics, and in particular on one of the promising biosourced, biocompatible and biodegradable plastics, poly(hydroxybutyrate-co-valerate). PHBV is a co-polyester

produced by microorganisms, with interesting mechanical and barrier properties that make it a good substitute for conventional polypropylene in rigid packaging. In recent decades, it has gained significant attention and its production is constantly increasing [165].

To initiate a study on the closed-loop recyclability of PHBV, two points need to be raised: (i) the compatibility of the EFSA contaminant panel (established for PET) with PHBV, with the possibility of extrapolating the results obtained for PET. (ii) the quality of the recycled PHBV after the decontamination process.

First, the contamination is highly dependent on the polymer intrinsic properties. Unlike PET, polyolefin are rubbery at room temperature, with much lower barrier properties. This results in greater diffusion of contaminants into their matrix and the possibility of contamination by higher molecular weight substances, as established by Palkopoulou et al. [140]. Rubbery PHBV, which is more polar than PET and PE, could be contaminated not only by higher molecular weight substances, but also by more polar molecules. Therefore, the EFSA panel of contaminants should be extended in the case of PHBV.

Second, PHBV is known to be a thermal sensitive polymer which undergoes random chain scissions close to its melting temperature [10, 100]. Therefore, the decontamination process should be tailored to maximize contaminant removal, while minimizing degradation of the polymer structure. One option to improve the stability of the polymer is the addition of a thermal stabilizer.

This work will therefore have two objectives. The first will be dedicated to the evaluation of the efficiency of our thermal treatment process on the removal of a larger panel of contaminants, containing molecules of higher polarity and lower volatility (in comparison to those of EFSA panel). The selected molecules are gallic acid, catechin, ferulic acid and PEG 200. This follows a previous study on the decontamination efficiency of the EFSA substances panel [87]. In parallel, the impact of decontamination conditions on the structural evolution of the polymer will be evaluated. Depending on the structural behaviour of the polymer, the use of quercetin as a natural thermal stabilizer will be studied. Quercetin is a natural and non-toxic polyphenolic compound that has already proven its effectiveness as a thermal stabilizer in the manufacture of PHBV [217] and other polymers [218], preventing chain scission caused by heat and oxidation. To link the two parts, the role of quercetin on

the affinity of polymers for contaminants as well as on the efficiency of decontamination will also be studied.

2. Materials and methods

2.1. Materials

PHBV with 3 mol % of 3-hydroxyvalerate units (HV) in the form of pure uncompounded powder was obtained from Nature plast (France) under the commercial name of PHI003. According to the manufacturer, it has a true density of 1.25 $g.cm^{-3}$ and a melting temperature of 170-176 °C.

Nucleating agent (boron nitride, 98 %), polyphenolic additive (quercetin, 95 %), chemical contaminants (listed below), solvents (methanol, 99.8 % and ethanol, 99.8 %), vanillic acid 97 % and PEG 550 (as internal measurement standards for HPLC, and mass spectrometry analyses for phenolic contaminants and PEG 200 respectively), were purchased from Sigma Aldrich France. PHBV flakes were spiked with a set of surrogate contaminants, which aim to present a higher polarity than those of FDA and EFSA guidelines. The list of surrogates is: gallic acid, catechin, ferulic acid and polyethylene glycol 200 (PEG 200). Their physical-chemical properties, and those of quercetin additive are reported in Table 15.

Table 15. Contaminants and quercetin (additive) physical-chemical properties.

Substance	M_w (g.mol^{-1})	Log K_{aw}	Vapor pressure (mmHg)	δd [MPa$^{1/2}$]	δp [MPa$^{1/2}$]	δh [MPa$^{1/2}$]	Ref.
Quercetin	302	1.5	2.8 10-14	23.0	15.8	25.0	[219, 220]
Gallic acid	170	0.7	1.3 10-7	22.2	8.9	23.5	[219, 221]
Catechin	290	1.5	0.3 10-5	13.3	4.5	19.7	[219, 220]
Ferulic acid	194	1.5	2.7 10-6	22.7	5.7	15.6	[210, 219]
PEG 200	190-210	1.1	0.09	16.6	5.7	16.8	[219, 222]

The compatibility of the contaminants with quercetin, based on Hansen parameters, was determined from equation 11 [223]:

$$\Delta\bar{\delta} = \sqrt{(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \qquad (11)$$

With δ_d the dispersive energy component, δ_p the polar energy component and δ_h the hydrogen bonding energy component.

2.2. Production of neat-PHBV and PHBV-quercetin (PHBV-Q) films

Before thermal processing, PHBV, quercetin and Boron nitride powders were dried at 60 °C during 24h in order to remove potential water content. Neat PHBV was produced from the extrusion of a mixture of PHBV powder with 0.5wt % of boron nitride. To produce PHBV-Q material, a mixture of PHBV powder with 0.5wt % of boron nitride and 0.3wt % of quercetin was extruded. Extrusion was carried out in a lab scale Thermo scientific Process 11 parallel twin-screw micro-compounder

(Thermoscientific, Karlsruhe, Germany), equipped with a L/D ratio of 40, a screw diameter of 11mm, and a 3 mm rod die. The temperature profile set at 180°C was uniform from the feeding to the die, and the screw profile was the one described in [153]. The screw speed was set at 150 rpm, with a residence time of approximately 2 min. After granulation, the pellets were dried at 60 °C for 24h, then neat PHBV and 12x12 cm PHBV-Q films with an average thickness of 300 µm were produced by thermos-compression using heated hydraulic press (20T, Pinette Emidecau Industries). The pressure was first set at 5 bars for 1 min, for melting the pellets, then progressively increased from 5 to 150 bars in 30 s before stabilization at 150 bars during 30 s. Flakes from PHBV and PHBV-Q films were produced by cutting the films into squares of 1.5X1.5.

2.3. Contamination procedure of PHBV and PHBV-Q flakes

Surrogates contaminants were dissolved in methanol, at a concentration of 9 mg. mL^{-1} and 23 $mg.mL^{-1}$ for phenolic compounds and PEG200 respectively, and stirred until a homogeneous solution was obtained. In sealed containers, this surrogate's mixture was dropped on PHBV and PHBV-Q flakes at a concentration of 500 mg of surrogates per kg of flakes. Containers were stored for 10 days at 40 °C with continuous rotatory agitation until a sorption equilibrium was reached. After 10 days, the contamination level was evaluated by measuring the surrogate concentration in the flakes.

2.4. Decontamination procedure of PHBV and PHBV-Q flakes

2.4.1. Decontamination process

Decontamination of the contaminated flakes was performed at elevated temperature and under vacuum (< 20 mbar) in a glass oven (Buchi, B-585). The experimental process, already described in a previous study [87] is schematized in Figure 13. Polymer flakes were introduced in the heating chamber, under vacuum and rotation, at 130 °C, 145 °C and 160 °C, during 6, 20 and 48 hours for neat PHBV and at 160°C, for 6 and 48 hours for PHBV-Q.

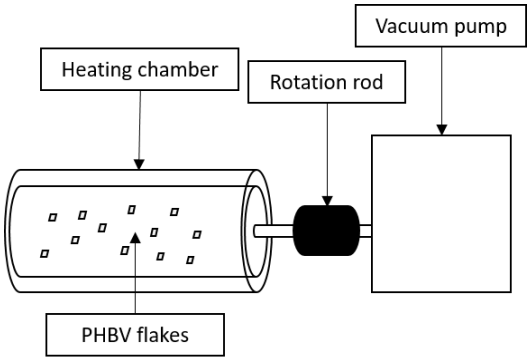


Figure 13. Scheme of the PHBV and PHBV-Q flakes decontamination process according to Dedieu et al. [87]

The surrogate and quercetin (the additive) concentrations in the polymer flakes after contamination and decontamination were determined using the following extraction method: 5 mL of methanol were added to 0.3 g of both PHBV material flakes in a glass vial, and samples were stored at 40 °C for 24 hours under magnetic agitation. All the extracts, obtained in triplicate, were analysed using an Acquity UPLC (Waters, Milford, MA) liquid chromatography system, equipped with a photodiode array detector (DAD) and a mass spectrometer. The Waters column was 100 mm x 2.1 mm, HSS T3, particles size was 1.8 µm. The solvent used were A (99.9 % H_2O and 0.1% HCOOH v/v) and B (80 % CH_3CN; 19 % H_2O; 1% HCOOH) with a flow rate of 0.55 $mL.min^{-1}$. The injection volume was 2 µl and DAD was set at 280 nm in order to detect gallic acid, catechin and ferulic acid. The Acquity UPLC system was coupled online with a Bruker amazon X electrospray ionization (ESI) ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany). The nebulizer pressure was 3.03 bar; the temperature of the drying gas was set at 200 °C with a 12 $L.min^{-1}$ flow; and the capillary voltage was set at −5.5 kV. The mass spectra were acquired over a mass range of 50− 2000 Th in the positive ion mode. The mass spectrum acquisition speed was set at m/z 8100 s^{-1}. The target mass was tailored to each reaction between m/z 100 and 900. PEG 200 was detected and quantified by integrating the mass spectrometry peak at 300 m/z. The peaks identification and quantification were based on the use of the different surrogates and quercetin as external standards (calibration curves with concentration range of 10 - 45 mg. L^{-1}), as well as the use of vanillic acid and PEG 550 at 30 $mg.L^{-1}$ as an internal standard.

2.4.2. Decontamination efficiencies

The decontamination efficiencies were determined for each surrogate by comparing the surrogate concentration in the flakes after decontamination with the initial concentration before heat treatment (equation 1).

$$Decontamination\ efficiency\ = (1 - \frac{sample\ concentration}{initial\ concentration}) \times 100 \qquad (1)$$

2.5. Characterization of the physical-chemical properties of PHBV and PHBV-Q flakes after decontamination process

2.5.1. Size exclusion chromatography (SEC)

After decontamination, the average molecular weight (*Mw*) and the number-average molecular weight (*Mn*) were determined by SEC performed in the University of Bologna (Italy). 5mg of each sample were placed in sealed tubes with 2 mL of Chloroform ($CHCL_3$) for 24 hours. Then, 10 drops of hexafluoroisopropanol (HFIP) were added in order to achieve a solvent ratio of 95:5 (v/v), and the mixture was stirred for 2 hours before to be filtered over 45µm nylon filter. SEC analyses were carried out in a UHPLC HP 1100 Series with a PL gel 5 µm Minimixed-C column. Injection volume was 20 µL and chloroform flow rate was 0.3 $mL.min^{-1}$. Detection was performed by means of refractive index and UV detectors. Instrument calibration was done with polystyrene standards, and all the sample analyses were performed in triplicates.

2.5.2. Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a calorimeter DSC series Q200, TA Instruments, under a nitrogen atmosphere (50 $mL.min^{-1}$) with a heating rate of $10°C.min^{-1}$.

Around 8 mg of sample was used for each analysis and all experiments were done in triplicate. to determine the crystallization rate and the thermal properties, the following heating/cooling protocol was used: first heating from -30 to 200 °C, with stabilization for 3 min; then cooling down up to -30 °C with again a stabilization for 3 min; followed by a second heating scan up to 200 °C.

The melting temperature (*Tm*), the crystallisation temperature (*Tc*) and the apparent melting enthalpy (*ΔHm*) were determined from the DSC curves from the second cool-heat cycle, using the Universal Analysis 2000 Software by TA Instruments.

The crystallinity rate (Xc) was calculated from the melting enthalpy according to equation 8.

$$Xc(\%) = \frac{\Delta Hm}{\Delta H_m^\circ} \times \frac{100}{w} \qquad (8)$$

Where : *ΔHm* is the melting enthalpy of the polymer matrix, w is the polymer weight fraction in the sample and ΔH_m° is the theorical melting enthalpy of the polymer assumed to be 100% crystalline, ΔH_m°= 109 J.g^{-1} for PHBV [158].

2.6. Statistical analysis

Statistical analyses and data visualization were performed in R (RStudio, 2021). The variables were checked for normality (Shapiro-Wilk test). The significance of results was examined by one-way analysis of variance (ANOVA) followed by a Tukey test with a confidence interval of 95 %. Then, the significant difference between the data was defined.

3. Results and discussion

3.1. Decontamination of neat PHBV film

Decontamination of PHBV from gallic acid, catechin, ferulic acid and PEG 200 was conducted at different temperature/time combination, in order to determine the optimal decontamination conditions. PHBV flakes were submitted to thermal treatment, under vacuum, at different temperature (100, 130, 145, 160 °C) for 6, 20 and 48h. Decontamination efficiency of each contaminant, under the different conditions is represented in Figure 32.

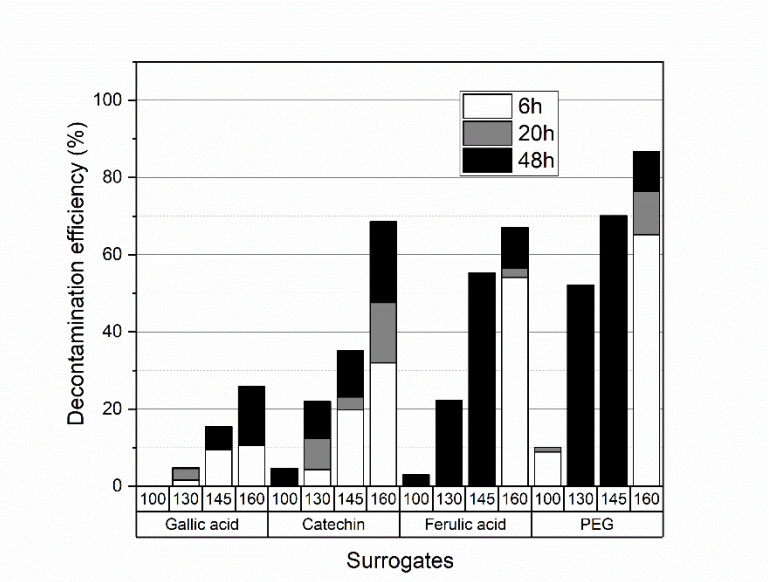


Figure 32. Decontamination efficiency of gallic acid, catechin, ferulic acid and PEG 200 as a function of decontamination temperature and duration.

First, it was observed that the decontamination efficiency increased with the treatment time and temperature for each contaminant. This has already been reported in a previous work when the decontamination of PHBV from the EFSA panel (the model surrogates used for the PET challenge test) was studied [87]. It has been shown that increasing temperature leads to an increase in contaminant diffusion and volatility, which are well known to respectively influence the diffusion and desorption of a chemical from a polymer matrix. The most efficient decontaminations were obtained for the highest temperature and duration, with 25.9% decontamination for gallic acid, 68.5% for catechin, 67% for ferulic acid, and 86.8% for PEG 200 after 48h, at 160°C. Under these conditions, the decontamination of chemical substances from the polymer occurs via two successive steps: (1) the diffusion of the contaminant within the material and (2) their subsequent desorption and volatilization from the surface. The nature of the polymer, such as polarity, free volume and chain mobility, as well as that of the molecule, such as molecular weight, polarity and shape, play a major role in the diffusion process. The volatility of the molecule is also responsible of its desorption from the polymer surface.

From the decontamination kinetics (data not shown), it is clear that the decontamination of these molecules does not follow a Fickian diffusion behaviour. Thus, this process is not only a combination of diffusion/volatilization phenomena, but seems to be governed by the physical-chemical parameters

of the contaminants and their interactions with the polymer. The molecular weight of each contaminant as well as its polarity (expressed as Log K_{aw}) and vapour pressure are shown in Table 15.

In terms of contaminant properties, molecular weight (M_w) does not appear to govern the decontamination of molecules, since gallic acid with the lowest M_w is less decontaminated than catechin with the highest M_w. Thus, other physicochemical parameters can affect the molecule/polymer affinity, and consequently the decontamination efficiency. Gallic acid is the contaminant with the highest polarity (showing a better affinity for the polar PHBV) and the lowest vapour pressure, which may limit its diffusion and its volatilization respectively, explaining its lowest decontamination compared to the other substances. PEG 200, whose polarity is close to that of catechin and ferulic acid, is by far the most volatile compound in the panel, which showed the most effective decontamination.

In addition to the individual characteristics of the polymer and the contaminants, the chemical interactions between the two can play a crucial role in the decontamination process. Apart from PEG 200, the other contaminants (gallic acid, catechin and ferulic acid) belong to the polyphenols family. These compounds are prone to form intermolecular hydrogen bonds due to their phenolic hydroxyls which are good hydrogen donors. In the presence of hydrogen acceptors like PHBV (with its carbonyl groups), they can form hydrogen bonds [224] with an energy of 6-30 KJ/mol [225]. Moreover, it has been shown that polyphenols with gallate moieties (which is the case of gallic acid) form 40 % more hydrogen bonds than those without (catechin and ferulic acid) [226]. This is another argument explaining the lower decontamination of these compounds and especially gallic acid. On the other hand, phenolic intermolecular hydrogen bonds could also be formed, since polyphenols can be both hydrogen donors and acceptors [227]. These complex interactions inevitably act as a brake on polymer decontamination.

As a result, the efficiency of PHBV decontamination with these polar molecules, under these conditions is far from satisfactory and the recycled materials pose safety concerns [87]. However, the use of polar aprotic (non-hydrogen donor) molecules should be considered to complete this study.

As a solution, it can be argued that higher temperature and/or decontamination time can increase the diffusion of molecules within the polymer matrix and help break the hydrogen bonds formed, thereby improving decontamination. However, extending the decontamination time to temperatures at or above

160°C will inevitably result in significant polymer degradation. Indeed, in the previous work dealing with the PHBV decontamination from EFSA molecules panel, it has been shown that exposing the polymer to 160°C during 48h resulted in decrease in M_w by 57 %, and decrease in Tensile strength and Elongation at break by 100 %, making the material too brittle [87].

Therefore, the condition to move to more drastic decontamination conditions is to stabilize the polymer to prevent or reduce its thermal degradation. One of the methods used is the addition of thermal stabilizers. Quercetin as an additive, was chosen for two reasons. It is a natural biocompatible polyphenol that does not interfere with the biodegradability of PHBV, and it has already proven to be an effective thermal stabilizer in the production of PHBV films [228]. Due to the hydrogen bonds formed with the polymer, the formation of the six-membered ring, a precursor of the thermal degradation mechanism, was prevented [217].

In the next section, the decontamination efficiency as well as the structural evolution of PHBV will be studied, in the presence of quercetin as an additive at 0.3 wt %.

3.2. Impact of quercetin on the decontamination efficiency and thermal properties of PHBV film

Before evaluating the effect of quercetin on the thermal stabilization of the PHBV film during the decontamination process, its role on the decontamination efficiency was first studied. Thus, the decontamination of PHBV-Q film from the same surrogates was performed at 160°C (the highest temperature) for 6 and 48h. The decontamination efficiency results are shown in Figure 33.

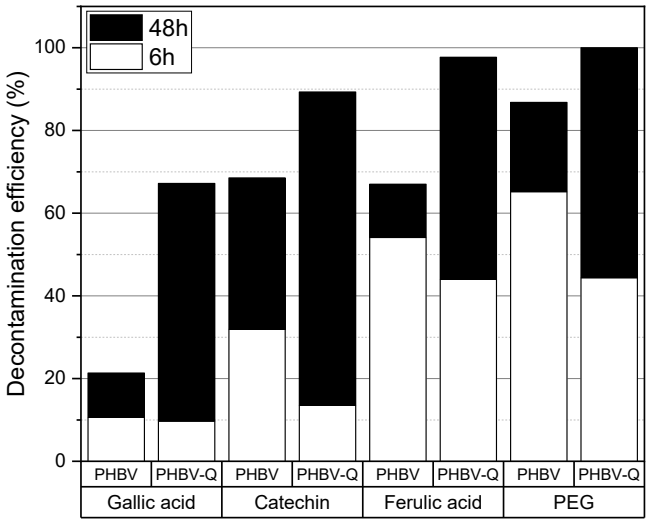


Figure 33. Decontamination efficiency of gallic acid, catechin, ferulic acid and PEG 200 of PHBV and PHBV-Q after 6 and 48h at 160°C.

First, it is important to remind that quercetin was incorporated into the material during the production process of the film (by extrusion). Thus, the polyphenol crystals were homogenously distributed in the polymer matrix with strong hydrogen bonds between the two [217]. During all the decontamination process, the amount of quercetin initially loaded in the film remained unchanged (Quercetin concentration: 3.23 ± 0.08 mg. g^{-1} at 0h, 3.32 ± 0.31 mg.g^{-1} at 6h and 3.29 ± 0.07 mg.g^{-1} at 48h). This means that the interactions between quercetin and PHBV were strong enough to remain stable during heat treatment.

Regarding the decontamination efficiency, it was found that the presence of quercetin delayed the removal of contaminants after 6h at 160 °C, compared to neat PHBV. Indeed, the decontamination percentage decreased by about 8.5%, for gallic acid, 57.4 % for catechin, 18.7 % for ferulic acid and 31.9 % for PEG200. Since quercetin is a polyphenolic compound homogeneously distributed in the polymer matrix, it is easy to consider that besides the interactions that could occur between the contaminants and the polymer (discussed above), the phenolic contaminants could also interact with quercetin via hydrogen bonds and π-stacking interactions. These complex interactions require more energy to break down [229], that 160 °C for 6h would allow.

To confirm this assumption, the affinity of the different contaminants with PHBV and PHBV-Q films was compared. For this, the percentage of sorption of the contaminants on the two films was calculated and the results were summarized in Table 16.

Table 16. Evolution of sorption percentage of contaminants on PHBV and PHBV-Q films

	Pourcentage of sorption			
Contaminants	Gallic acid	Catechin	Ferulic acid	PEG 200
PHBV	77.3 ± 2.4	67.4 ± 1.5	84.6 ± 4.5	81.2 ± 0.6
PHBV-Q	96.1 ± 3.8	82.6 ± 2.4	100.0 ± 4.9	80.6 ± 5.2
Evolution	+ 18.8 %	+15.2 %	+15.4 %	-0.6 %

As can be seen, the presence of quercetin resulted in approximately 15-18% higher sorption of phenolic contaminants due to the interactions discussed above. In addition, it has been shown in a previous work that the addition of quercetin at 0.5wt% decreased the crystallinity rate from 82% to 79% [217], which creates more amorphous phase, capable of being contaminated.

The affinity of quercetin and phenolic contaminants was also expressed by Hansen solubility parameters which are used to estimate the type of interactive forces responsible for the compatibility between substances. These physical-chemical parameters are composed of three parts: dispersive energy component (δd), polar energy component (δp) and hydrogen bonding energy component (δh) [209]. The higher the deviation of the Hansen parameters of two substances, the lower their compatibility. This deviation may be reflected by the $\Delta\bar{\delta}$ factor, whose low value indicates good compatibility between the two substances. Using this factor, the compatibility of quercetin with each contaminant was determined (Table 17).

Table 17. Factor compatibility of the contaminants with Quercetin.

	$\Delta\bar{\delta}$
Gallic acid	7.1
Catechin	15.8
Ferulic acid	13.8
PEG 200	14.5

Due to the close Hansen parameters between quercetin and gallic acid (especially dispersive and hydrogen components), the latter was most impacted by the presence of the additive. Ferulic acid and catechin contamination of the polymer was also increased by the addition of quercetin, with almost similar compatibility with the additive. PEG 200 decontamination decreased by 32 %, despite low compatibility with quercetin (Tables 16 and 17). As PEGs have a well-known plasticizing effect on polymers [230, 231], it can be considered that the plasticizing effect of PEG 200 was higher in the presence of quercetin.

Surprisingly, the trend was reversed when the decontamination time was extended to 48h; In this case, the decontamination efficiencies were higher in the presence of quercetin. The higher release of contaminants from PHBV-Q film after 48h could be related to the structural evolution of the polymer. Table 18 shows the change in molecular weight and polymer crystallinity caused by the heat treatment.

Table 18. Molecular weight and crystallinity changes of PHBV and PHBV-Q depending on decontamination duration at 160 °C.

	Molecular weight change (%)		Crystallinity change (%)	
Time (h)	PHBV	PHBV-Q	PHBV	PHBV-Q
6	-28.50 ± 1.13	-35.14 ± 1.67	+ 22.82 ± 1.95	+23.01 ± 0.91
48	-56.73 ± 0.33	-83.82 ± 0.12	+ 36.58 ± 1.38	+45.48 ± 3.62

After 48h of decontamination PHBV-Q have lost 83 % of its molecular weight against 53 % for PHBV. Moreover, the crystallinity rate increased by 45 % for PHBV-Q, compared to 36% for PHBV. The decrease in molecular weight accompanied by an increase in crystallinity reveals the degradation of the polymer via a random chain scission mechanism [101]. Thus, it appears that contrary to expectations, quercetin accelerated the thermal degradation of PHBV. Hence, the polymer chain scission increased the mobility of the chain, allowing easier release of contaminants. However, the acceleration of polymer degradation by quercetin is not fully understood and requires further investigation.

In summary, this preliminary study reveals that the use of quercetin had an impact on decontamination efficiency and polymer stability, but not in the desired manner. However, considering that quercetin was bound to contaminants by hydrogen bonds, it was shown that a heat treatment at 160 °C for 6h was not able to break these bonds. On the other hand, the suitability of a material for a food contact application depends on its ability to release contaminants into food. Therefore, we can ask whether binding with quercetin would not slow down the migration of contaminants into food. Future studies on the contact of these recycled materials with food simulants should be conducted to answer this question.

4. Conclusion

Evaluation of the decontamination of the PHBV material with an extended panel of contaminants was studied in this article. Polar protic contaminants showed high affinity to the polymer through hydrogen bonding interactions, resulting in a low level of decontamination.

The use of quercetin as a thermal stabilizer increased the affinity of the contaminants to the polymer and decreased the decontamination efficiency after 6h of thermal treatment. Extending the decontamination time to 48h led to extensive degradation of the polymer making it impossible to reuse.

Further research should be conducted on polar aprotic contaminants and the role of quercetin in slowing the migration of contaminants into foods.

Complementary results

Decontamination process of neat PHBV was also investigated with surrogates owing higher molecular weight than those of EFSA panel. Irganox 1076 (M_w = 530 g.mol^{-1} and K_{aw} = 0.9) and Irganox 1010 (M_w = 1178 g.mol^{-1} and K_{aw} = 1.2) were purchased from Sigma Aldrich (France) and were dissolved in methanol, at a concentration of 8 mg.mL^{-1}. PHBV flakes were then contaminated with this solution, following the protocol described in section 2.3. Decontamination of the contaminated flakes was performed by means of the experimental process shown in section 2.4, under the same conditions of temperature and duration. The surrogates' concentrations in the polymer flakes after contamination and decontamination, were detrmined after extraction, as previously described: 5 mL of methanol were added to 0.3 g of PHBV material flakes in a glass vial, and samples were stored at 40 °C for 24 hours under magnetic agitation. All the extracts, obtained in triplicate, were analysed using an Alliance HPLC system (Waters) equipped with an Altima C18 column (250 mm x 2.1 mm, 5-µm) column guard. Compounds were separated with 55 % aqueous acetonitrile at a flow rate of 0.3 mL.min^{-1} at 50 °C. Absorbance was recorded at 230 nm to quantify the surrogates' concentration. The peaks identification and quantification were based on the use of the two Irganox as external standards (calibration curves with concentration range of 10 - 45 mg.L^{-1}), as well as the use of BHT at 30 mg.L^{-1} as an internal standard. Decontamination efficiencies were determined for each surrogate by comparing the initial concentration in PHBV flakes with the residual concentration after decontamination (equation 1 in section 2.4), and results are shown in figure 34.

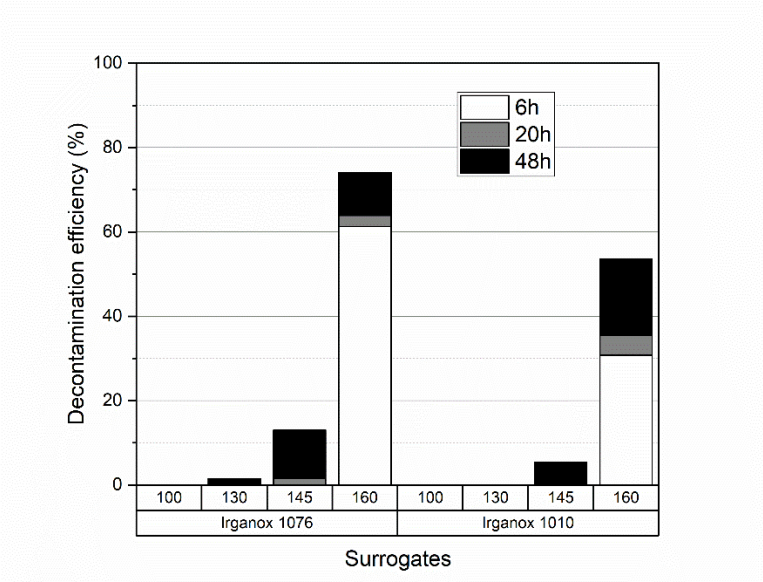


Figure 34. Decontamination efficiency of Irganox 1076 and Irganox 1010 as a function of decontamination temperature and duration

As seen previously for phenolic compounds, the decontamination efficiency of the process increased with the treatment time and temperature, due to the potential impact on surrogate diffusion and volatility. This is not the case for Irganox surrogates, with very little or no decontamination for temperatures below 160°C. This is because the processing temperature must be high enough to counteract the high molecular weight and low volatility of these contaminants. The highest decontamination efficiencies were found for the harshest process conditions (48 hours of heat treatment at 160 °C), with 72.5 % for Irganox 1076 and 50.8 % for Irganox 1010. These values, as well as the desorption kinetics (not shown) are similar to those found in the decontamination of phenolic substitutes, highlighting a non-fickian decontamination behaviour.

In terms of contaminant properties, molecular weight (M_w) seems to govern the decontamination of theses contaminants, which otherwise present similar polarity. Irganox 1010 which has higher molecular weight than Irganox 1076, shows a lower decontamination, probably due to the negative impact of the molecular weight on compounds diffusion and volatility. Finally, these decontamination values still appear very low compared to the values found in the EFSA panel study.

Conclusion

Dans ce chapitre, le potentiel du PHBV à être recyclé en boucle fermée pour des applications alimentaires a été réévalué, en complément des travaux réalisés dans le chapitre IV. Cette nouvelle approche a consisté à prendre en compte un panel de contaminants plus large en terme de polarité et de masse moléculaire. En effet, ces contaminants, non pris en compte dans le cadre du PET de par son caractère apolaire et son inertie, sont toutefois susceptibles d'être sorbés par le PHBV comme développé dans le chapitre précédent. Lors de leur décontamination, ces contaminants ont montré un comportement différent de celui du panel de l'EFSA, avec une désorption qui ne suit plus un comportement fickien, et une décontamination bien moins importante. Ces différences peuvent être attribuées aux différentes caractéristiques des contaminants (masse moléculaire, polarité, volatilité…) lesquelles sont susceptibles d'impacter notamment leur liaison avec la matrice polymère, leur diffusion et leur volatilisation. Afin d'améliorer cette décontamination, l'application de conditions plus sévères pourrait être envisagée mais la dégradation du PHBV aux températures élevées restreint l'augmentation de ce barème temps/température. Ainsi, l'ajout d'un additif naturel a été testé afin de protéger le polymère de la dégradation lors de ce procédé. Les résultats de cette étude ont montré que l'ajout de quercétine a conduit à lier plus fortement les contaminants dans le matériau, conduisant dans un premier temps à une décontamination moins efficace. En augmentant la durée du traitement thermique en présence de quercétine, la décontamination a été plus importante, mais la dégradation du polymère également, le rendant difficilement exploitable.

GENERAL DISCUSSION, CONCLUSIONS AND PROSPECTIVE

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1. Rappel des objectifs

La production de matériaux plastiques ne cesse de croître d'année en année, engendrant une diminution des ressources et une accumulation des déchets non biodégradables dans l'environnement. Le domaine de l'emballage alimentaire est plus que concerné par ces problématiques, puisqu'il représente environ 40 % de la demande et que la plupart des articles en plastiques ont une durée de vie courte engendrant une production rapide des déchets. Ainsi, la mise en place d'alternatives plus respectueuses de l'environnement dans ce domaine devient une nécessité afin de remplacer les plastiques persistants, prédominant actuellement sur le marché.

Les plastiques biosourcés et biodégradables pourraient à priori permettre de limiter les dégâts engendrés par la production et la fin de vie des plastiques conventionnels. Leur développement et leur mise sur le marché est donc l'une des alternatives durables envisagées par les politiques actuelles. C'est dans cet objectif que le projet USABLE, financé par l'Union Européenne, vise à étudier le potentiel d'une famille de biopolyesters biodégradables les poly(hydroxyalkanoates) (PHAs) à substituer les polymères conventionnels pour des applications d'emballage alimentaire. Dans une approche d'économie circulaire, les différents volets du cycle de vie du polymère sont explorés, au regard des contraintes technico-économiques existantes. La fin de vie des matériaux élaborés est un point crucial de cette approche en terme d'impact environnemental et économique. Parmi les différentes voies pouvant être empruntées par les déchets d'emballage, le recyclage mécanique semble être l'option la plus favorable environnementalement et économiquement parlant, et ce malgré le caractère biodégradable de ces polymères.

L'objectif de cette thèse était de comprendre et décrire le comportement du PHBV au cours de l'opération de recyclage en intégrant tous les critères considérés dans l'évaluation des performances d'un emballage alimentaire. L'approche repose sur la mise en évidence des relations entre les modifications de structure du polymère (longueur de chaînes, niveau d'interaction et d'organisation du

réseau) induites lors du traitement thermomécanique et les propriétés d'usage du matériau issus de la matière secondaire (propriétés mécaniques, propriétés de transport et d'inertie).

Cette thèse s'est ainsi focalisée sur deux questions scientifiques majeures :

- L'étude de l'impact de la remise en œuvre (à l'était fondu) du PHBV sur ses propriétés structurales et fonctionnelles
- L'étude de la contamination/décontamination du PHBV, et son aptitude au contact alimentaire à l'issu du son traitement. Cette deuxième question se déclinant en plusieurs questions sous-jacentes.

Dans le cadre de cette étude, le recyclage a été abordé en découplant les deux étapes majeures des procédés de recyclage classique existants : l'étape de remise en forme du matériau à l'état fondu (étape d'extrusion) et l'étape de décontamination du matériau à l'état solide. Le découplage de ces deux étapes permet de mieux comprendre les mécanismes afin de mieux répondre aux questions scientifiques.

2. Principaux résultats

Les premiers travaux (Chapitre III) ont consisté à explorer l'étape de remise en forme du matériau, en évaluant l'impact de celui-ci sur les propriétés structurales et sur les propriétés d'usage du PHBV. De par sa nature (polyester biodégradable), le PHBV est sensible aux températures élevées, il est donc important de mesurer sa dégradation lors de l'application de cette étape du procédé, qui porte le polymère à sa température de fusion tout en lui appliquant des contraintes mécaniques. Afin de simuler l'effet de plusieurs cycles de remise en œuvre (i.e. plusieurs cycles de recyclage mécanique), le polymère a été soumis à 4 cycles d'extrusion successifs et ses différentes propriétés ont été mesurées à travers les cycles.

Les résultats ont montré une dégradation de la structure du matériau au fur et à mesure des cycles de remise en œuvre, avec une diminution significative de la masse moléculaire du polymère dû à un mécanisme de rupture de chaîne bien décrit dans la littérature. Malgré que ces ruptures macromoléculaires aient induit une fragilisation du matériau, elles n'ont cependant pas entraîné de variation significative des valeurs de perméabilité à la vapeur d'eau et à l'oxygène, ce qui a permis de

conclure que de multiples remises en œuvre n'ont pas modifié radicalement l'utilisation des matériaux PHBV comme emballage alimentaire pour les denrées solides (comme les barquettes et les pots) comme présenté dans le tableau 19.

Tableau 19. Effet de la remise en œuvre sur les propriétés structurales et fonctionnelles du PHBV.

	Masse moléculaire	Contrainte à la rupture	Déformation
Cycle 2	- 17.4 %	- 3.8 %	+ 3.2 %
Cycle 4	- 24.1 %	- 8.5 %	- 24.2 %

En ce qui concerne l'aptitude au contact du polymère remis en œuvre, la migration de l'acide crotonique, monomère produit lors de la dégradation du PHBV et soumis à une limite de migration spécifique, a été mesurée dans différents simulants alimentaires. Ces valeurs de migration, présentées dans le tableau 20, ont montré une forte dépendance au type d'aliment, avec une migration dans les aliments gras qui tend significativement à augmenter tandis qu'elle ne fut pas détectée dans les autres simulants.

Tableau 20. Effet de la remise en œuvre sur la migration de l'acide crotonique dans différents simulants alimentaires.

	Simulant d'aliment gras	Simulant d'aliment acide	Simulant d'aliment solide
Cycle 2	+ 0.2 %	+ 0.0 %	+ 0.0 %
Cycle 4	+ 1.8 %	+ 0.0 %	+ 0.0 %

Cependant, ce résultat doit être vérifié puisque l'impact de l'utilisation d'un simulant gonflant le polymère peut être discuté. L'impact du changement d'échelle du procédé, et des autres étapes du recyclage mécanique sur la dégradation pouvant induire une dégradation supplémentaire du polymère, il serait important d'optimiser les traitements thermiques appliqués aux emballages en PHBV après

usage, afin d'éviter toute production excessive d'acide crotonique pouvant entraîner une migration supérieure à la limite garantissant la sécurité du consommateur.

L'utilisation d'un matériau en polymère recyclé pour des applications d'emballage alimentaire ne nécessite pas seulement que ce polymère présente des propriétés d'usage suffisamment maintenues pour permettre la performance de l'emballage (conservation et protection de l'aliment), mais aussi que ce polymère soit apte au contact alimentaire. Cette aptitude au contact alimentaire sous-entend que le matériau ne soit pas susceptible de présenter un danger pour la santé humaine, ou d'entraîner une modification inacceptable des propriétés des denrées emballées. Dans le cadre du recyclage mécanique, afin de satisfaire le critère d'inertie du matériau, celui-ci doit être suffisamment décontaminé au vu des molécules chimiques qu'il est susceptible de sorber lors de sa précédente utilisation.

Ainsi, dans un premier temps, des travaux du Chapitre IV ont consisté à évaluer la décontamination du PHBV et son aptitude au contact, en suivant les lignes directrices de la règlementation européenne mise en place pour le PET. Le PHBV a été soumis à un procédé de décontamination inspiré des procédés existants pour les polymères conventionnels, après contamination par un panel de contaminants modèles, où différentes conditions de durée et de température ont été testées. Les résultats ont montré qu'une température suffisamment élevée (160 °C) et une durée suffisamment longue (6h) étaient nécessaires pour obtenir une décontamination élevée. Cependant, l'application d'une telle température durant plus de 6h a engendré une dégradation significative de la structure moléculaire du polymère et de ses propriétés mécaniques comme présenté dans le tableau 21. Cependant, contrairement à ce qui pouvait être attendu, l'augmentation des température et durée de décontamination n'a pas conduit à une augmentation de la quantité d'acide crotonique mesurée, et ce malgré l'augmentation de la dégradation. Ceci, peut-être expliqué par le fait que la faible masse moléculaire de l'acide crotonique ait favorisé sa désorption. Ainsi, l'augmentation de la production de ce monomère néoformé ne semble pas, dans ce procédé, engendrer de problème de sécurité alimentaire.

Tableau 21. Evolution des propriétés structurales et mécaniques du PHBV en fonction de la durée de décontamination à 160 °C

Durée de décontamination à 160 °C	Masse moléculaire	Contrainte à la rupture
6h	- 28.5 %	- 26.2 %
20h	- 52.1 %	- 27.8 %
48h	- 56.7 %	n.a

L'aptitude au contact du PHBV soumis à une décontamination de 6h à 160 °C a donc été évaluée. Les contaminants présentant les plus faibles poids moléculaires ont été presque ou totalement décontaminés, avec des concentrations résiduelles autorisées lorsque le scénario adulte est considéré. La décontamination des contaminants de poids moléculaire plus élevé et de volatilité plus faible s'est révélée plutôt efficace, mais les concentrations résiduelles dans le polymère se sont avérées supérieures aux concentrations maximales autorisées pour l'utilisation de 100% du polymère recyclé dans un nouveau produit. Le tableau 22, présente les différents pourcentages de PHBV recyclé autorisés après décontamination dans les conditions appliquées, et selon le scénario envisagé. En effet, la concentration maximale en contaminant autorisée dans le polymère va dépendre de nombreux paramètres comme (a) la migration de ce dernier depuis le polymère dans l'aliment, et (b) l'exposition du consommateur à ces contaminants, engendrée par son alimentation. Dans le cadre du PET, la migration du contaminant dans l'aliment dépend fortement de sa diffusion dans celui-ci dans les conditions testées. Cependant dans le cas du PHBV, la diffusivité des contaminants étant beaucoup plus élevée, l'équilibre/partition entre le polymère et l'aliment est rapidement atteint dans ces conditions. Ainsi, le coefficient de partition devenant le facteur prédominant au détriment de la diffusivité des contaminants, des coefficients de partitions expérimentaux ont été appliqués au lieu du coefficient standard utilisé dans le cadre du PET, dans l'objectif de simuler un scénario plus réel.

Tableau 22. Comparaison du pourcentage de PHBV recyclé autorisé dans un nouvel emballage, selon le scénario envisagé.

	Scénario le plus défavorable		Scénario plus réel	
Type d'application	Enfants	Adultes	Enfants	Adultes
Pourcentage maximal de PHBV recyclé autorisé dans un nouveau matériau	2.1 %	10.2 %	4.2 %	21.3 %

Dans le scénario le plus favorable, les résultats ont montré que seulement 21 % du PHBV recyclé pourrait être utilisé dans les nouveaux matériaux afin de respecter les critères de sécurité alimentaire. Ces faibles résultats sont majoritairement dus à la diffusion rapide des contaminants dans l'aliment, ce qui engendre des valeurs de concentrations maximales autorisées plus faibles que celles mesurées pour le PET. Ces résultats pourraient à première vue, décourager les efforts portant sur le recyclage du PHBV. Cependant, ces premières recherches soulèvent de nombreux points de vigilance à ne pas oublier. Premièrement, dû à l'absences de cadre dédié aux polymères biodégradables, l'approche utilisée dans cette étude a été inspirée du recyclage des bouteilles en PET, dont les propriétés présentent de nombreuses différences avec celles du PHBV. Le PET, polymère vitreux à température ambiante, va présenter une inertie bien plus élevée que le PHBV qui lui est caoutchoutique et donc présente une certaine mobilité de chaîne facilitant la diffusion des contaminants. Ainsi, la contamination potentielle du PHBV pourrait bien être différente de celle du PET, en terme quantitatif (niveau de contamination) et en terme qualitatif (nature des contaminants). Une contamination plus faible ou plus élevée en quantité, aura un impact significatif sur la quantité résiduelle après décontamination, ce qui impactera de même la quantité maximale de polymère recyclé autorisée. La question d'un panel de contaminants plus adapté au PHBV sera quant à elle développée dans le chapitre suivant. Il convient également de noter que les propriétés thermiques du PHBV (température de fusion) contraignent la décontamination à opérer à des températures bien inférieures à celles du PET, ce qui a un impact non négligeable sur la diffusion, la volatilisation et donc la décontamination des contaminants. Ainsi, le développement de

nouvelles technologies alternatives destinées à faciliter les transferts dans le matériau (extractions, lavage etc) pourrait être une stratégie pour optimiser la désorption. Mener des recherches sur la polycondensation à l'état solide pourraient également être utile pour améliorer la qualité du PHBV recyclé, comme c'est le cas pour le recyclage du PET.

Dans un second temps, le chapitre V a porté sur l'étude de la contamination réelle du PHBV en caractérisant la sorption de trois contaminants : un contaminant représentatif du panel de l'EFSA et deux contaminants présentant respectivement une polarité et une masse moléculaire plus élevées que celles du panel. Dans un premier temps, la caractérisation des paramètres influençant la sorption des contaminants dans le PHBV, présentés dans le tableau 23, a permis de mettre en évidence une affinité du polymère avec les contaminants, qui semble dépendre des caractéristiques de ces derniers. De plus, la diffusivité des contaminants semble être le facteur prédominant dans la vitesse d'atteinte de l'équilibre de sorption puisque la diffusion est bien connue comme le phénomène limitant dans les processus de sorption.

Table 23. Paramètres des contaminants et caractérisations de leurs propriétés de transfert dans le PHBV à température ambiante.

Contaminant	Masse moléculaire (M_w en g/mol)	Polarité ($\log K_{aw}$)	Coefficient de partition ($K_{P/L}$)	Coefficient de diffusion (D en m^2/s)	Temps d'atteint de l'équilibre de sorption (en jours)
Benzophénone	182.0	3.2	0.227	$2.25.10^{-12}$	<1
Acide férulique	194.2	1.5	0.124	$5.92.10^{-14}$	6
Irganox 1076	530.9	23.0	0.081	$4.48.10^{-14}$	6-7

Dans un second temps, à l'aide des paramètres mesurés, les profils de sorption des contaminants dans le PHBV ont été simulés en fonction de la durée de sorption et de l'épaisseur du matériau, et comparés avec ceux du PET. Ces résultats visibles figure 30, ont démontré que les trois contaminants sont sorbés au cœur du PHBV, atteignant l'équilibre en des temps relativement courts, tandis que dans le PET, la sorption s'opère seulement en surface, sur des temps très longs. Ces résultats peuvent être

attribués à la différence de nature des matériaux, puisque le PHBV, polymère caoutchoutique à température ambiante, présente une mobilité de chaîne plus élevée que celle de la matrice du PET qui lui est vitreux et présente des chaînes plus rigides. Cette mobilité de chaîne permet notamment une diffusion et donc une contamination plus rapide des molécules.

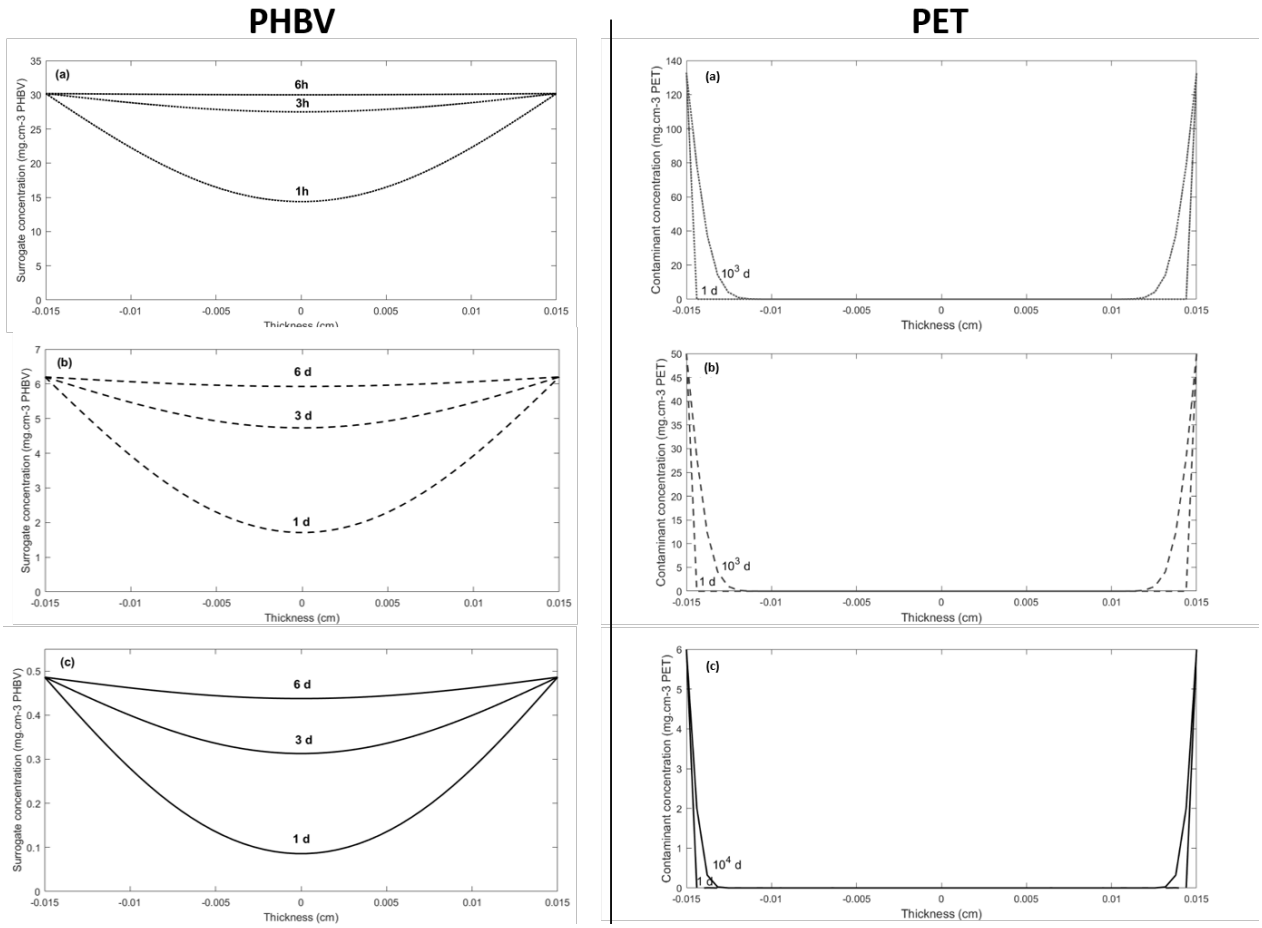


Figure 30. Profils de sorption simulés en fonction de la durée de sorption et de l'épaisseur du matériau. Sorption de Benzophénone (a), Acide férulique (b) et Irganox 1076 (c) dans le PHBV colonne de gauche et dans le PET colonne de droite.

Dans un dernier temps, ce même profil de sorption a été réalisé expérimentalement sur la sorption de la Benzophénone dans le PHBV. La bonne corrélation des résultats expérimentaux et des résultats simulés permet non seulement de valider ces résultats, mais aussi de poser les bases stables d'une approche rapide permettant de caractériser l'aptitude à la contamination d'un matériau donné.

Enfin, au vu des résultats précédents, une première investigation de la décontamination du PHBV portant sur un panel de contaminants plus large que celui étudié dans le chapitre IV, a été conduite dans le chapitre VI. Allant au-delà du panel de contaminants de l'EFSA, ces contaminants, non pris en compte dans le cadre du PET de par son caractère apolaire et son inertie, sont toutefois susceptibles d'être sorbés par le PHBV comme développé dans le chapitre précédent. Dans un premier temps, le PHBV a été contaminé avec des contaminants modèle d'une classe de molécules protiques de polarité plus élevée. En raison de leur faible volatilité et de leur capacité à interagir avec le polymère via des liaisons hydrogènes, les efficacités de décontamination mesurées furent bien inférieures à celles du panel de l'EFSA, avec des efficacités allant de 25.9 à 86.8 % après 48 h de décontamination à 160 °C. Si l'on se réfère à l'approche utilisée actuellement pour l'accréditation des procédés, ces faibles pourcentages entraîneraient une contamination résiduelle élevée, induisant une potentielle impossibilité du polymère recyclé à être utilisé comme emballage alimentaire. Afin d'améliorer cette décontamination, l'ajout d'un additif naturel, la quercétine a été testée en tant que stabilisateur thermique de la matrice polymère, afin de limiter la dégradation de celui-ci et ainsi permettre l'utilisation de conditions de décontamination plus sévères. Les résultats, tableau 24, montrent que contre tout attente, l'utilisation de la quercétine comme additif a augmenté l'affinité des contaminants avec le polymère et a diminué l'efficacité de la décontamination après 6h de traitement thermique. L'augmentation de la durée de traitement jusqu'à 48h, a conduit à une dégradation importante du polymère rendant sa réutilisation impossible. Dans le cadre de la sécurité alimentaire des matériaux recyclé, il serait donc intéressant après 6h de décontamination à 160 °C, d'étudier l'impact de la liaison de la quercétine au contaminants sur la migration de ces derniers dans l'aliment, puisqu'un ralentissement de cette migration pourrait permettre des concentrations résiduelles plus élevées.

Tableau 24. Impact de l'utilisation de quercétine comme additif, sur l'efficacité de décontamination et la dégradation du PHBV. AG : Acide gallique ; CAT : Catéchine ; AF : Acide férulique ; PEG : PEG 200.

Durée de décontamination	Evolution de la décontamination (%)								Evolution de la masse moléculaire (%)	
	PHBV				PHBV + quercétine				PHBV	PHBV + quercétine
	AG	CAT	AF	PEG	AG	CAT	AF	PEG		
6h	+10.6	+32.0	+54.1	+65.2	+9.7	+13.6	+44.0	+44.4	- 28.5 %	- 35.1 %
48h	+25.9	+68.5	+67.0	+86.8	+67.2	+89.3	+97.7	+100	- 56.7 %	- 83.8 %

La décontamination de contaminants représentatifs de classes de molécules de masse moléculaire plus élevée que le panel de l'EFSA a également été étudiée. De la même manière que pour les contaminants polaires, les efficacités de décontamination mesurées furent inférieures à celles du panel de l'EFSA, avec des efficacités entre 50.8 et 72.5 % après 48h à 160 °C. Il est intéressant de noter que dans ce cas, pour les décontaminations effectuées à des températures inférieures à 160 °C, les efficacités furent quasi nulles ou très faibles, ceci pouvant s'expliquer par le fait que la température de traitement doive être suffisamment élevée pour contrecarrer le poids moléculaire élevé et la faible volatilité de ces contaminants, qui limitent fortement leur désorption.

Ainsi, lors de leur décontamination, ces contaminants ont montré un comportement différent de celui du panel de l'EFSA, avec une désorption qui ne suit plus un comportement fickien, et une efficacité de décontamination bien moins importante. Ces différences peuvent être attribuées aux différentes caractéristiques des contaminants (masse moléculaire, polarité, volatilité…) lesquelles sont susceptibles d'impacter notamment leur liaison avec la matrice polymère, leur diffusion et leur volatilisation.

Ainsi, cette thèse a permis d'apporter de nombreuses réponses vis-à-vis des futurs challenges liés au recyclage des polymères biodégradables, afin de faire face aux enjeux environnementaux et sanitaires.

3. Perspectives

L'approche utilisée en première partie de cette thèse, a permis de monter que l'application de cycles répétés de remise en œuvre à l'état fondu n'impacte pas radicalement l'utilisation des matériaux en PHBV comme emballage alimentaire d'aliments solides. Cependant, les conditions des procédés utilisés à l'échelle laboratoire n'engendrent pas les mêmes contraintes thermomécaniques que les celles des procédés industriels. Ainsi, la dégradation du matériau pourrait être plus importante et devra être mesurée. La migration de l'acide crotonique, produit néoformé par cette dégradation pourrait aussi augmenter, selon le type d'aliment emballé et les conditions de stockage, pouvant limiter l'aptitude au contact du PHBV recyclé à des applications spécifiques. Le traitement thermique appliqué aux emballages en PHBV post-consommation devra être finement optimisé afin d'éviter toute production excessive d'acide crotonique dans une limite de concentration non définie à ce jour.

Il convient de rapporter cependant, que dans un second temps, l'étape de décontamination a montré que ce même acide crotonique était désorbé du matériau. Il serait donc important de quantifier la quantité d'acide crotonique présent dans le matériau final, afin d'évaluer l'aptitude au contact réelle de l'emballage après un cycle de recyclage complet. Cette aptitude au contact étant aussi régie par la décontamination du matériau, qui n'a conduit dans cette étude qu'à de faibles pourcentages de PHBV recyclé autorisés dans de nouveaux emballages, il serait intéressant d'évaluer la décontamination finale du matériau en fin du procédé de recyclage complet. En effet, l'étape de remise en œuvre, qui porte le matériau à des température plus élevées que le procédé de décontamination, pourrait augmenter la décontamination finale du matériau et ainsi améliorer sa réincorporation dans de nouveaux produits. Dans un même temps, l'application successive de ces deux étapes est aussi susceptible d'aggraver la dégradation du matériau, contraignant sa réutilisation, ce qui devra donc également être évalué. Afin d'améliorer la qualité finale du PHBV recyclé, l'utilisation d'une étape de polycondensation à l'état solide (SPP) pourrait être étudiée comme c'est le cas dans le recyclage du PET, puisque les liaisons esters peuvent potentiellement être reformées par estérification réversible, ceci dépendant de la réactivité et de la mobilité des chaînes polymères, comme cela a été observé dans les études sur l'acide poly-lactique (PLA).

En ce qui concerne l'évaluation de la sécurité du PHBV recyclé, le risque de contamination du PHBV par des molécules non représentées dans le panel de l'EFSA ayant été démontré, il s'avère nécessaire de déterminer des règles d'évaluation spécifiques dédiées à chaque polymère. En effet, les caractéristiques d'un polymère le rendent plus ou moins susceptible de sorber diverses molécules et l'évaluation de cette contamination potentielle pourrait à priori se faire au moyen de techniques de caractérisation rapides (cinétiques et isothermes de sorption). En regard de la contamination du matériau (rapide/lente, en profondeur/en surface, contaminants volatiles/non volatiles), l'adaptation du procédé de décontamination pourrait permettre d'améliorer le potentiel d'un matériau à être recyclé. Dans le cas du PHBV qui est contaminé à cœur, rapidement, par des molécules de taille et de polarité diverses, les techniques de désorption des contaminants devraient se baser sur des méthodes alternatives facilitant le transfert des molécules telles que des extractions par solvant, CO2 ou fluide supercritique. L'étude d'une étape de décontamination à l'état fondu, ou de l'addition d'une étape de lavage pourrait également être envisagées. Une autre approche pourrait être d'inclure le recyclage mécanique du polymère, pour les cas d'une utilisation en circuit court, où les conditions sont suffisamment contrôlées pour éviter toute contamination excessive du matériau (et notamment le mauvais usage par le consommateur).

La limite de cette approche utilisée pour le PHBV, est qu'à l'échelle industrielle, la mise en place d'une filière de recyclage en boucle fermée se doit d'être dédiée à l'ensemble des PHAs, famille de polymères de caractéristiques et de comportements présentant une variabilité importante. L'application de conditions standards des procédés de recyclage, nécessaire à la mise en place d'une filière unique, pourrait se voir contrainte par cette variabilité des différents polymères, qui présentent des conditions de mise en œuvre/dégradation différentes, mais aussi des propriétés de transfert différentes (de par leur cristallinité). L'application de ces conditions standard à un mélange de divers PHAs pourrait donc ainsi influencer la qualité du recyclat final. Un des prérequis du recyclage mécanique pour des applications d'emballage alimentaire étant que la matière utilisée soit apte au contact alimentaire, il reste encore à déterminer et évaluer les PHAs susceptibles d'être concernés par cette filière, puisqu'à ce jour seuls 2 PHAs (des copolymères de PHBH, numéro CAS 147398-31-0) ont reçu cette évaluation de sécurité alimentaire [175, 176].

Cette thèse apporte de manière générale, une vision de l'ensemble des verrous liés à la mise en place du recyclage mécanique d'un polymère biodégradable et le développement d'une méthodologie pouvant être appliquée en première approche. Ces verrous étant fortement dépendant de la nature et des spécificités du polymère, celui-ci devra d'abord être caractérisé. De sa nature (caoutchoutique/vitreuse, polaire/apolaire, cristalline/amorphe etc..) dépendront ses propriétés de transfert/inertie et ainsi, sa capacité à être contaminé, décontaminé mais aussi sa capacité à relarguer des substances dans l'aliment au contact. Les caractéristiques thermomécaniques du polymère, pourront elles permettre de mettre en évidence la résistance ou non de celui-ci aux conditions appliquées dans les différents procédés, et ainsi le risque de dégradation de ses propriétés. Comme cité précédemment, la mise en place de procédés adaptés aux contraintes de chaque matériau pourrait être un levier permettant le recyclage efficient et viable d'un polymère.

D'autres verrous moins scientifiques sont aussi à prendre en compte dans la mise en place d'une filière de recyclage comme l'adéquation aux règlementations politiques qui tendent plutôt à valoriser la biodégradation des plastiques biodégradables plutôt que leur recyclage. La faisabilité de la mise en place de l'ensemble de la filière (collecte, tri, puis procédés de recyclage) peut être également un frein à son développement, ainsi que l'acceptabilité des matériaux recyclés par le consommateur.

Enfin, parmi les lecteurs les plus réticents au développement du recyclage des plastiques biodégradables, certains diront à juste titre que selon la hiérarchie des déchets et le bon sens, la priorité doit être de réduire l'utilisation des plastiques dans notre quotidien. Cet objectif doit évidemment être le cœur des actions menées conjointement par les consommateurs et par les entités impliquées (entités règlementaires, de recherche, industrielles etc), en opérant un fort changement des modes de consommation (développement du vrac, des matériaux réutilisables ou de la consigne par exemple). Cependant, la lenteur et/ou la lourdeur de cette transition à certains niveaux (comme la restauration collective par exemple), nécessite la mise en place d'alternatives décarbonées tels que les PHAs, en remplacement des plastiques conventionnels. L'intérêt du recyclage de ces polymères biodégradables reste donc crucial puisqu'il représente une réelle voie d'intérêt dans leur développement et pas seulement un moyen de limiter les dégâts engendrés par notre consommation plastique. A la question aussi simple

que concrète que l'on arrive à se poser à la fin de cette thèse : « peut-on espérer recycler les PHAs à l'avenir ? » il est à l'heure actuelle encore difficile de répondre. Bien que les résultats présentés dans cette étude ne fassent pas émerger un optimisme franc à ce propos, il convient de rappeler que les PHAs sont encore au début de leur histoire, où tout reste à faire et à optimiser, à l'instar du développement des polymères conventionnels avant leur expansion mondiale. Dans ce but, la recherche scientifique se doit donc non seulement de produire des connaissances fondamentales mais aussi d'apporter des réponses pour avancer dans la meilleure direction possible pour le monde de demain.

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Exploration de la recyclabilité mécanique en boucle fermée, d'un polymère biodegradable pour des applications d'emballage alimentaire

La diminution des impacts environnementaux liés aux plastiques est un des problèmes majeurs actuels notamment dans le domaine de l'emballage alimentaire. Dans l'objectif de lier l'utilisation de matériaux moins éco-efficients tout en diminuant les impacts environnementaux, cette thèse vise à explorer la possibilité de recycler mécaniquement en boucle fermée un polymère biosourcé et biodégradable (le PHBV) pour des applications d'emballage alimentaire. L'objectif est de comprendre et décrire le comportement du PHBV au cours de l'opération de recyclage, en intégrant les critères essentiels dans l'évaluation des performances d'un emballage alimentaire. La question se focalise sur deux questions scientifiques majeures : (i) l'impact de la remise en œuvre (à l'état fondu) du PHBV sur ses propriétés structurales et fonctionnelles ; (ii) l'aptitude au contact alimentaire du PHBV à l'issue des traitements de contamination/décontamination. Suivant un découplage des deux étapes principales d'un procédé de recyclage (remise en œuvre et décontamination), la première partie de ces travaux a pour but de mesurer l'évolution des performances du matériau après plusieurs cycles de remise en œuvre. Par la suite, la décontamination du matériau a été étudiée dans un premier temps en regard de la règlementation existante pour les polymères conventionnels et les risques liés à l'exposition du consommateur ont été évalués. Dans un second temps, dans une approche plus dédiée aux caractéristiques du PHBV, la contamination potentielle réelle du matériau a été évaluée avant d'étudier une nouvelle fois la décontamination conséquente.

Mots clés : bioplastiques ; polyhydroxybutyrate-co-valerate ; recyclage mécanique ; aptitude au contact alimentaire ; propriétés de transfert

Exploring the closed-loop mechanical recyclability of a biodegradable polymer for food packaging applications

The reduction of environmental impacts related to plastics is one of the major current problems, especially in the field of food packaging. In the aim of using less eco-efficient materials while decreasing environmental impacts, this thesis aims to explore the possibility of the closed-loop mechanical recycling of a biosourced and biodegradable polymer (PHBV) for food packaging applications. The objective is to understand and describe the behavior of PHBV during the recycling operation, integrating the essential criteria in the evaluation of the performance of a food packaging. The question focuses on two major scientific issues: (i) the impact of the reprocessing (in the molten state) of the PHBV on its structural and functional properties; (ii) the suitability for food contact of the PHBV after the contamination/decontamination treatments. Following a decoupling of the two main steps of a recycling process (reprocessing and decontamination), the first part of this work aims at measuring the evolution of the material performances after several reprocessing cycles. Then, the decontamination of the material was studied in a first step with regard to the existing regulation for conventional polymers and the risks related to the exposure of the consumer were evaluated. In a second step, in an approach more dedicated to the characteristics of the PHBV, the real potential contamination of the material was evaluated before studying again the consequent decontamination.

Keywords: bioplastics; polyhydroxybutyrate-co-valerate; mechanical recycling; food contact ability; transfer properties