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Recyclates for Sustainable Food Contact Method Development for the Validation of Migration Barriers

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Recyclates for Sustainable Food Contact Method Development for the Validation of Migration Barriers

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Abstract: Ideological changes in industrial approaches require greater ecological thinking. Regarding plastics, the integration of plastic waste into the circular economy arises from the urgent need to design and develop sustainable alternatives. The primary objective of a recycling process is to ensure that the quality of recycled plastics consistently matches that of the original product. Regional authorities and regulations require the assessment and prevention of the potential safety hazards of possible contaminants in recycling streams, recycling processes, and recycling technologies. The specific limits on migrating substances are difficult to achieve through recycling, especially in food packaging. Since food packaging accounts for the largest global share of plastic use, alternative approaches for assessing the value of recyclates as food contact materials need to be considered. One possible way to achieve this goal is barrier development via plasma-enhanced chemical vapor deposition (PECVD) to potentially prevent migration of contamination and barrier function as food contact materials. To efficiently evaluate migrations and barrier efficiencies, a novel contamination approach for virgin materials is introduced to simulate model recyclates. Achieving higher concentrations inside a virgin polypropylene matrix simplifies the analytical approaches. Further, an analysis chain regarding migration evaluation via gas chromatography coupled mass spectrometry and barrier developments are shown.

Keywords: Model Contaminants, Migration, Contaminant Characterization, Migration Barrier

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Introduction

Accounting for the largest global plastic production, packaging plastic leads to the rapid accumulation of plastic waste and significant environmental harm due to inadequate waste management. Consequently, recycling of post-consumer packaging plastics and circularity in this sector are indispensable to promote sustainability. In general, the post-consumer lifecycle and material stream of plastics determine their recycling through energy recovery and chemical or mechanical recycling processes. From an ecological and energetic perspective, mechanical recycling is advantageous, particularly when dealing with pure material streams. The primary focus of mechanical recycling is to substitute virgin materials with recyclates of consistent quality, hence the challenge of dealing with extensive sorting, materials charges, and purification efforts [1-3] Taking post-consumer recyclates into account, the resulting unknown history of the materials life cycle and origins limit their applications, as unknown impurities and miscibility's of different polymers affect the resulting quality of the recyclates. In this context, contaminants arise from various sources, including substances that form during the recycling processes, degradation of plastic composition, intentionally added substances like additives, polymeric impurities, chemical substances from both intended and unintended use [2-4]. The regulatory bodies divide contaminants into intentionally and unintentionally added substances and classify them according to their chemical nature. At the same time, regulatory bodies like the European Food and Safety Authority (EFSA) or the U. S. Food and Drug Administration (FDA) limit the quantity and quality of contaminants within the recyclate matrices respective to the application region and according to the application scenario to prevent human harm [5-7]. Therefore, to ensure suitability, an assessment of any technology application related to recyclates should be conducted before implementing these material streams in their respective fields (see Figure 1).

Figure 1. Analytical assessment to determine recyclate suitability.

Before applying technologies such as decontamination plants, it is crucial to quantitatively and qualitatively assess the contaminations present in the input stream. This assessment allows for determination of the efficiency of the decontamination technology through a subsequent re-evaluation of residual or migrating contaminants. In particular, food contact materials require high demands to meet the threshold of toxicological concerns and safety assessment limits [3]. Despite advancements in recycling pathways in recent years, mechanically recycled post-consumer polypropylene materials still fail to meet the quality threshold imposed by regulatory authorizations for the food contact material stream, which constitutes the largest share of global plastic usage. Intensive research is conducted to analyze, identify, and reduce contaminants in recycled plastics to optimize their life cycles [2,3]. A viable approach to enable the use of post-consumer recycled polypropylene in the food contact material sector is to inhibit or mitigate impurity migration by barrier applications. Therefore, a complete test path, including analyzes prior to barrier migration testing, is the key factor in efficient barrier development to meet specific application legislation thresholds.

Plasma-Based Migration Barriers

Surface coatings have been a promising approach as physical and chemical material property enhancers to suit certain applications, especially in the food contact materials sector [8]. Since avoiding degradation and migration processes are the highest disciplines for food contact materials, one possible pathway to evade these limitations is the use of surface coatings based on plasma-induced barriers [9,10]. Plasma-based barriers have a high potential to overcome gas permeation and migrations of inorganic and organic substances in packaging materials [11]. In particular, barriers by plasma-enhanced chemical vapor deposition (PECVD) inherit uniform surface properties while maintaining low operation and materials costs [10]. The PECVD represents a platform for fast coating depositions on low temperature substrates, yielding nanoscale functional coatings with outstanding chemical and physical properties. In industrial approaches, silicon-based coatings are highly valued in the application fields due to their excellent properties and efficient processabilities [10,11]. As a result, silicon oxide (SiO_x) barrier coatings became highly relevant in the packaging industry due to their excellent gas barrier properties and quick, non-destructive, and environmentally friendly deposition possibilities. By transferring the SiO_x barrier methodology of plasma-based coatings by PECVD to containers made of post-consumer recyclates, a promising pathway to preventing migration of contaminants in addition to the good gas barrier properties can be pursued (see Figure 2).

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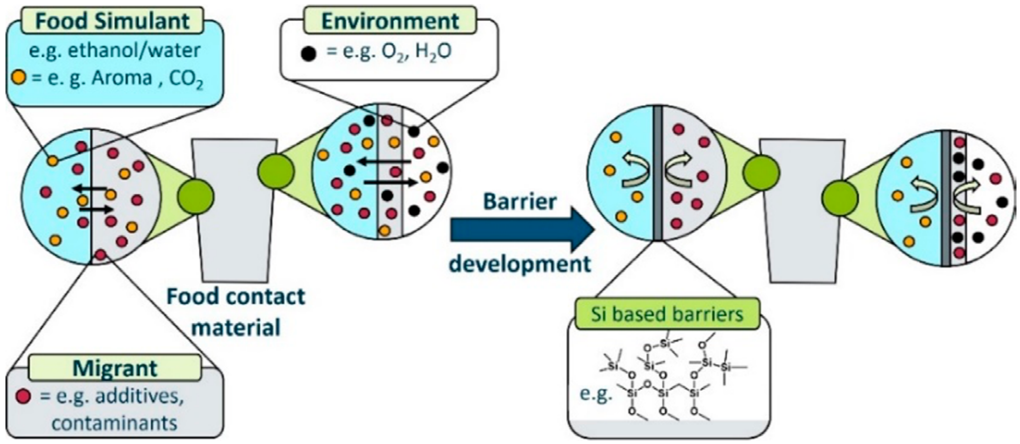

Figure 2. Concept of plasma-based barriers for migration inhibition.

According to regulatory authorizations by EFSA and FDA, the use of SiO_x coatings in food contact materials is permissible. Furthermore, the integration of nanoscale PECVD coatings into existing plastic recycling processes has been confirmed to have no adverse effects, enhancing the overall sustainability of packaging solutions [5-7]. The methodology and challenges of PECVD related to barrier deposition of Si-based barriers on recyclates can be read elsewhere [10,11].

Method Development for the Validation of Plasma-Induced Barriers

Since regulatory authorizations guide approval processes of any kind of technologies related to recyclates, barrier applications also need to meet certain thresholds of migration inhibition after testing under defined conditions [6,7]. But before taking on any approval processes on real recyclate products, the key is to understand the migration processes of chemical substances of all kinds and design barriers to prevent migration weaknesses [9,10]. To reduce the complexity of contamination matrices in real recyclates, model recyclates consisting of virgin materials contaminated with defined chemicals can be used for an efficient barrier development and barrier evaluation (see Figure 3).

Through the selection of specific chemicals, migration mechanisms and the effects of contaminants of a similar chemical nature related to the barriers and the plastic itself can be concluded. Taking the barrier evaluation into account, it is necessary to conduct an analysis chain prior to the introduced model contaminants in a designed sample, in addition to barrier development to approve barrier efficiencies. The evaluation consists of migration testing and analysis regarding the quantification and qualification of the migration of contaminants by gas chromatography coupled mass spectrometry (GC/MS) after barrier deposition. The testing procedures and analysis depend on the application fields and region and are set by official authorizations [3,5,6]. Regarding the contamination procedure, particularly for the recycling decontamination evaluation, the guidelines

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recommend introducing model contaminants known as challenge test chemicals through surrogation. This involves a specific protocol where pristine plastics are stored under defined conditions with the addition of model contaminants, followed by purification [5,6]. The resulting contaminant concentrations in the virgin plastic matrices are mostly insufficient, introducing a certain complexity for the subsequent barrier evaluation. Alongside the resulting insufficient concentration of the contaminations, only one recycling cycle is considered, neglecting further possible accumulation of contaminations by several circular recycling cycles, which are not governed by these challenge tests. To address these points, a novel contamination approach for polypropylene PP [Moplen HP640J] is conducted at the IKV along with the barrier development and analysis chain improvement strategies, hereby introducing certain chemical contaminants via compounding. By implementing effective migration barriers, the aim is to overcome contamination challenges and facilitate the reintegration of post-consumer polypropylene into the circular economy.

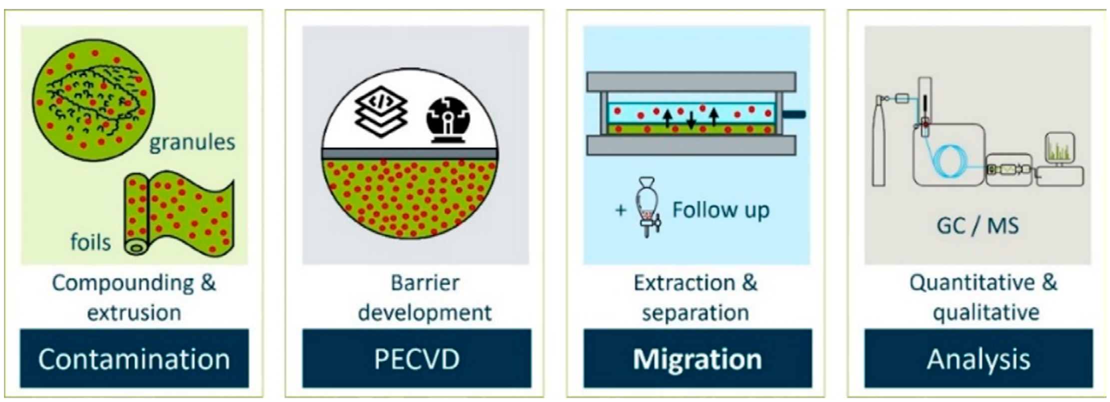

Figure 3. Method development for efficient analysis.

Novel Contamination Method

Since the novel contamination method aims to directly introduce high amounts of contaminants into the virgin PP matrix, the right choice of contaminants is crucial. Through intensive research, the contaminants were chosen respective to their volatilities and polarities in accordance with the regulatory authorities FDA and EFSA representing a broad spectrum of contaminants [5,6], while enabling rapid compounding in the PP samples under certain aspects like their solubilities or application in plastics, e.g. plasticizers. Since the accumulation of contaminants in recycled plastics can be assumed for chemicals with higher boiling points and molecular weights due to their slow evaporation and diffusion out of plastics in decontamination plants, in general contaminants with high boiling points were taken into account for this compounding approach. The volatile contaminants were selected based on their boiling points, positioned near the upper threshold of their definitional range, to ensure a significant retention within the polypropylene (PP) matrix during compounding at an elevated temperature of 180°C. Furthermore, by utilizing this strategy the

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contaminants will be more quickly introduced into the plastic matrix leading to a more efficient and flexible migration evaluation and barrier development. Through infrared spectroscopy and thermogravimetric analysis, the quantitative and qualitative characterization of the contaminants inside the PP samples are accessible (see Figure 4) [12].

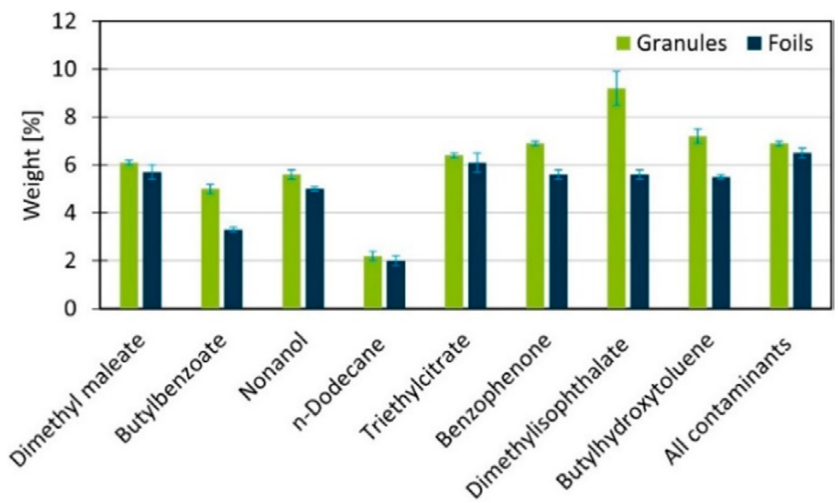

Figure 4. Content of model contaminants in the compounded and extruded PP matrices.

Regarding the differentiation of contaminants based on their polarity and volatility, specifically polar and volatile (dimethyl maleate, butyl benzoate), non-polar and volatile (nonanol, n-dodecane), polar and non-volatile (triethyl citrate, benzophenone), and non-polar and non-volatile (dimethyl isophthalate, butylhydroxytoluene), no clear trends can be observed in their incorporation into the polypropylene matrices during the compounding to granules. The variations in the resulting weight percentages can be attributed to the differing solubilities and boiling points of the contaminants introduced. Originally, a target compounding of 10 weight percent was desired. However, this was not achieved due to evaporation during the contamination procedure, uneven distribution of model substrates within the granules, and loss of contaminants in the water bath during compounding. Furthermore, the weight losses observed in contaminations during subsequent foil extrusion processes can be attributed to the volatilization occurring during thermal processing.

Migration Analysis

With respect to the barrier migration evaluation, it is imperative to conduct migration analysis in accordance with the specific food contact material testing protocols relevant to different application regions. Considering the varying application fields, testing under defined regulatory contact conditions with various food simulants is necessary to quantitatively and qualitatively evaluate the migrating substances, determining their suitability in accordance with the regulatory authorities

[3,5,6,9]. To ensure the migration testing of the novel contamination method the contaminants are characterized by GC/MS (see Figure 5).

All contaminants and the internal standard in a dichloromethane solution of 10 ng/μL are identified by their resulting mass spectra and assigned to the peaks in the resulting clean chromatogram. This demonstrates the suitability of GC/MS in the method development chain for quantifying and qualifying the migrating substances. The next steps involve performing quantifications to meet regulatory detection thresholds and validating the extractability of contaminants in food simulant matrices with dichloromethane, ensuring the analysis through GC/MS and following the suggested path to initiate barrier development.

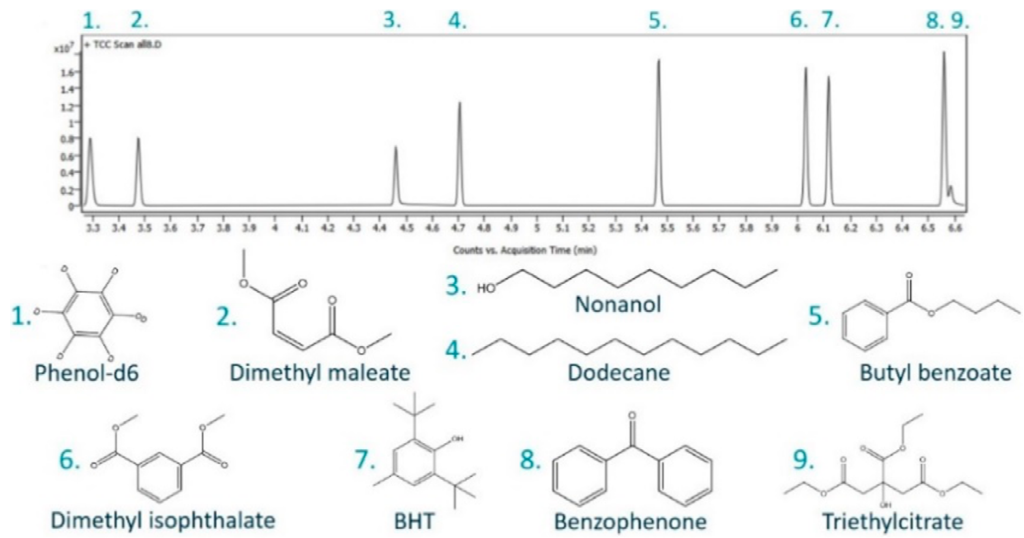

Figure 5. Gas chromatography spectrum of all contaminants and internal standard Phendol-d6.

Conclusion and Outlook

In accordance with regulations from Europe and the United States, a novel contamination method was integrated into a migration evaluation chain for the efficient development of barriers or any recycling technology. By direct compounding specific contaminants in virgin, high concentrations of PP were obtained. Further, the basis for the GC/MS analysis of the contaminants post migration were validated. Building on these fundaments, the next step involves ensuring qualitative and quantitative migration evaluation via GC/MS to facilitate efficient barrier development. The final step entails transferring the methodology to recyclates, following successful migration studies with model substrates. This will pave the way for developing barriers in recyclates for food contact materials, to achieve specific migration limits.

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