



Article Plastic Bottle Cap Recycling—Characterization of Recyclate Composition and Opportunities for Design for Circularity

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Received: 17 November 2020; Accepted: 10 December 2020; Published: 11 December 2020



Abstract: In line with efforts to create a circular economy of plastics, recent EU legislation is strengthening plastic bottle recycling by ambitious separate collection targets and mandatory recycled content obligations. Furthermore, explicit design requirements on the caps of bottles and composite beverage packaging have been introduced. These caps are typically made of polyethylene or polypropylene and often contain additives such as slip agents and anti-statics. Commercially available bottle cap recyclates (BCRs) as well as specifically formulated model compounds were analyzed in terms of composition by means of infrared spectroscopy, differential scanning calorimetry, and high-performance liquid chromatography. Their composition was found to be heterogeneous due to polyolefin cross-contamination, directly reflecting the diversity of cap materials present in the market. Slip agent legacy additives originating from the initial use phase were found and quantified in both commercial and model cap recyclates. This highlights the opportunity for redesigning plastic bottle caps not only in response to regulatory requirements, but to pursue a more comprehensive strategy of product design for circularity. By including considerations of polymer resin and additive choice in cap manufacturing, more homogeneous waste streams could be derived from plastic bottle cap recycling, enabling recycling into more demanding and valuable applications.

Keywords: circular economy; design for circularity; EU policy; legacy additives; mechanical recycling; plastic bottle cap; polyethylene; polypropylene; single-use plastics directive; slip agent

1. Introduction

1.1. Changing Policies and Regulatory Requirements Affecting Plastic Bottles and Their Caps

The concept of a circular economy of plastics is quickly gathering momentum [1–4] as our understanding of national [5,6], regional [7], and global [8,9] plastics flows and stocks, as well as the associated environmental burdens [10,11], is evolving. Plastic packaging in particular [3,5] is in the focus when it comes to addressing the transition from linearity to circularity. Packaging is both the main application field for single-use plastics [12] and the biggest group among different post-consumer plastic waste fractions [5,13].

Plastic bottles made of polyethylene terephthalate (PET) are a good example of well-defined post-consumer plastic waste streams that are suitable for high-quality mechanical recycling [14]. The recycling schemes and processes for PET bottles have evolved to very high standards that allow for post-consumer recyclates to be reintroduced into new food contact applications [15]. Year by year, humans produce several hundred billion plastic bottles [16]. As long as appropriate collection

schemes are in place, these bottles can be closed-loop recycled into new bottles (bottle-to-bottle) [15]. Besides that, bottles may be open-loop recycled into the textile industry (bottle-to-fiber) [17] or into thermoforming sheet products (bottle-to-sheet) [18]. Therefore, while a number of recycling paths exist for PET bottles, there seems to be no high-value reutilization path for the bottle caps, which are separated from the PET during recycling (see Figure 1).



Figure 1. The plastic bottle, its characteristics with relevance to recycling, and potential recycling paths (own illustration).

The caps, however, represent a growing waste stream and too often they find their way into the environment [19]. Growth forecasts for major packed beverage sectors such as bottled water [19] and specifically for plastic bottle caps [20,21] have been vital in pre-COVID-19 times and it seems reasonable to assume that the material volumes are set to further increase [22,23].

Most recent EU legislation on single-use plastics laid down in Directive (EU) 2019/904 [24] is going to target this segment by demanding that caps and lids of both beverage bottles and composite beverage packaging will be subject to product requirements (Article 6), extended producer responsibility (Article 8 paragraph 2), and awareness raising measures (Article 10) in future. Additionally, there will be a requirement for separate collection for recycling (Article 9) of plastic beverage bottles including their caps and lids. The separate collection target for beverage bottles is 77% by 2025 and 90% by 2029 [24]. The foreseen product requirements demand that caps and lids remain attached to the container during usage in order to avoid littering. All bottle cap manufacturers are hence confronted with the need to redesign their caps, if they are to be marketed in the EU. In view of the juxtaposition of more stringent requirements on material circularity on the one hand and quite impactful product design requirements for caps on the other hand, attention needs to be devoted to understanding the current system. Ideally, harvesting the potential benefits of increased bottle cap recycling will become a reality in the near future by making clever adjustments that combine legislatively required changes with a viewpoint of design for circularity.

The literature provides a number of examples of reuse and repurposing approaches for plastic bottles and their components. Bottles with their caps on have been investigated for their suitability as alternative building materials in the construction sector [25–27]. Post-consumer plastic bottle caps have been suggested to function as core elements in aluminum-plastics composite sandwich structures [28]. Other small- and large-scale repurposing strategies included the handcrafting of molecular models for chemistry teaching purposes out of used caps [29,30] and the utilization of caps as an alternative combustion fuel to low-quality lignite [31], respectively.

While downcycling, cascaded use, and repurposing can definitely have their justification, especially when regionally specific circumstances have to be considered, a generally more sustainable way to circulate end-of-life bottle caps is likely found in conventional mechanical recycling.

1.2. Characteristics of Plastic Bottle Cap Materials

Polymer resins specifically intended for beverage bottle caps and closures can be found in the product portfolios of most polyolefin producers. As an incomplete yet illustrative example, a survey of the relevant marketing documents and resin selection guides available from the websites of Borealis, Braskem, Dow, INEOS, LyondellBasell, SABIC, and TOTAL was used to create the overview depicted in the upper part of Figure 2. The material diversity in the caps and closure universe is huge, even if only caps for beverage containers are considered and closures for chemicals and detergent bottles or personal care products are excluded. Both high-density polyethylene (PE-HD) and different types of polypropylene (PP) homo- and copolymers are used to make screw caps for beverage containers. A tendency towards PE-HD as the material of choice for caps of pressurized beverages such as sparkling mineral water and carbonated soft drinks (CSD) can be observed [32,33]. However, the spectrum of melt flow rate (MFR) values—a very common measure to characterize thermoplastic polymers such as PE and PP—covers more than two orders of magnitude. MFR values may range from as low as 0.3 g/10 min for high-molecular weight PE-HD grades designed for lightweight caps withstanding the highest pressure levels up to about 30 g/10 min for caps of dairy products or general purpose PE-HD caps. For PP caps, the range extends to well above 50 g/10 min for highly rigid caps that are suitable for high-speed injection molding and fast cycle production.



Figure 2. Typical range of melt flow rate (MFR) values for PE-HD and PP resins for different plastic bottle cap applications and illustration of chemical structures of common slip agent additives (own illustration).

Depending on the targeted application, a number of additives are commonly employed to tailor the properties of polyolefin cap resins. These additives include processing and thermal stabilizers such as phosphites. Antioxidants such as sterically hindered phenolic compounds provide for stabilization during service life. Typically, blends of both processing and service life stabilizers are used. Occasionally, UV light stabilizers might be incorporated too. These protect the polymer itself as well as light-sensitive additives from degradation through sunlight. This can be necessary when caps are intended for outdoor applications (e.g., sports beverages) or when the regional climate demands it. All of these stabilizing additives are intrinsic components of the neat resin and they are usually not specifically mentioned in data sheets. In addition to basic stabilizer formulations, other functional additives may be used to further adjust the cap properties. In the case of PP caps, typical functional additives include nucleating agents. These are substances that promote the formation of nuclei from which faster, more uniform, and more complete crystallization of the polymer can take place [34,35]. Macroscopically, this results in faster production cycles and improved mechanical performance of PP. Anti-statics are another commonly incorporated functional additive in PP cap resins. These are substances that act on the surface of molded parts where they optimize demolding behavior and enhance storage and handling properties due to reduced electrostatic loading and dust attraction [34,35].

Finally, slip agents are very common additives in both PP and PE cap resins. In the case of PE caps, slip agents are actually the prime functional additive to be used beyond the obligatory stabilizers. On the level of additive composition, slip agents are a common feature of many bottle caps, regardless of their base polymer being PE or PP. For this reason, the fate of slip agents is of particular relevance to plastic bottle cap recycling.

Slip agents are slip-promoting additives that are incorporated to tailor service-related properties of the caps such as the opening torque which plays an important role not only for consumer comfort but also for the sealing performance [35-37]. Very common slip agents for polyolefins are behenamide (docosanamide, C₂₂H₄₅NO), erucamide (cis-13-docosenamide, C₂₂H₄₃NO), and oleamide (cis-9-octadecenamide, C₁₈H₃₅NO) as well as stearamide (octadecanamide, C₁₈H₃₇NO). These compounds belong to the group of primary fatty acid amides that are characterized by a hydrocarbon tail linked to an amide group forming the hydrophilic head of the molecule (see Figure 2). While behenamide and stearamide comprise a fully saturated hydrocarbon tail, erucamide and oleamide both contain a carbon–carbon double in *cis*-configuration. They are hence mono-unsaturated molecules.

Behenamide, erucamide, oleamide, and stearamide are all part of the Union list of authorized plastics additives and none of these compounds are subject to specific migration limits according to EU regulation No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food [38]. Among these four compounds, erucamide is the most commonly used slip-promoting additive used for plastic bottle caps [37]. However, due to its double bond, erucamide is more susceptible to oxidation and chemical degradation upon exposure to climate-related stresses such as elevated temperature and UV light or contact with ozone which is used for drinking water sterilization in some parts of the world [39,40]. The degradation products of erucamide as well as those of contaminants potentially present in commercial standard-quality erucamide have been associated with off-odor and off-taste issues in bottled water [39,41]. For this reason, other slip-promoting additives with a saturated chemical structure, e.g., behenamide, are being used besides erucamide [42]. Typical slip agent concentrations in PE-HD bottle caps have been reported at 2000 ppm [36].

Obviously, colorants and pigments are another important group of additives in plastic bottle caps, as in most other plastic products. However, coloration is a separate processing step that is typically not performed by the resin manufacturer. Color master batches are added to the polymer resins by other members of the bottle cap value chain such as a plastics converter or the brand owner.

In short, contrary to the situation of the PET bottle body, it can be argued that there seems to be a material complexity issue [43] with the caps of these bottles. Besides the difference in waste stream magnitude (a typical screw cap of a PET bottle may have a mass of 2 to 3 g, very roughly about a tenth of the respective bottle body), this material's complexity is an additional obstacle hindering effective high-quality recycling of screw caps.

It remains in doubt which applications could best be targeted by bottle cap recyclates (BCRs) to fully exploit their theoretical performance profile. Further, it is not clear what the fate of additives such as slip agents that are typically used in bottle caps might be. Are they going to end up in new products like extruded profiles, non-pressure pipes, or even bottle caps with recycled content (see Figure 1)?

Studies of the fate of additives during recycling and the potential impacts of so-called legacy additives in products with recycled content are mostly focused on chemical compounds that pose a certain level of risk to human and/or environmental health. The compounds are either subject

to specific regulations and restrictions (RoHS, REACH, food-contact approval, etc.) or they can be classified as substances of concern (SOC), substances of high concern (SHC), or substances of very high concern (SVHC). For an effective circular economy of plastics that produces and circulates high-quality plastic products with recycled content, however, it will be necessary to consider not only the fate of potentially harmful substances. Understanding the fate of typical functional additives that are used to tailor and tune properties such as in the case of slip agents in plastic bottle caps is of equal importance from a polymer engineering point of view. If functional additives are effectively transferred into the consecutive product life cycle by recycling, their presence should be made use of to contribute to product performance and to create value.

1.3. Goal and Scope

It is therefore the aim of this work to systematically investigate a number of different bottle cap recyclate formulations, both from commercial sources and from a controlled lab environment. The questions addressed herein concern the impact that changing waste stream characteristics have on the composition of bottle cap recyclates and the fate of slip agent additives found in bottle caps. Slip agents are specifically addressed as these are a common feature of many plastic bottle caps, either PE-HD or PP caps. Furthermore, they are the prime functional additive in PE-HD caps (apart from obligatory stabilizers) that form the major fraction of caps in PET beverage bottles in many countries.

2. Materials and Methods

2.1. Materials

Three distinct groups of BCRs were studied in this work in order to investigate the influence of variations in waste stream composition. The BCRs were grouped into commercial recyclates (CRs), waste model recyclates (WMRs), and virgin model blends (VMB). A description of the BCR formulations is given in Table 1.

Sample Acronym	Sample Type	Origin	Composition	Remarks
CR-1	commercial recyclate	post-consumer PET bottles	mainly post-consumer polyolefin screw caps	example of a commercially available regranulate
CR-2	commercial regrind	post-consumer PET bottles	post-consumer polyolefin screw caps	example of commercially available regrind
WMR-1	waste model recyclate	post-consumer PET bottles	mix of shredded screw caps and bottle labels	illustrates the impact of labels of PET bottles on recyclate characteristics
WMR-2	waste model recyclate	PET bottles, PE-HD bottles, composite beverage packaging	self-collected caps of used PET bottles, PE-HD bottles, and composite beverage packaging	illustrates the impact of caps of diverse packaging articles on recyclate characteristics
VMB-1	virgin model blend	virgin polymer resin from	50% PE-HD1 45% PE-HD2 2.5% PP1 2.5% PP2	simulates a recyclate with slip agent and low-level PP contamination
VMB-2	virgin model blend	virgin polymer resin from	25% PE-HD1 25% PE-HD2 25% PP1 25% PP2	simulates a recyclate with slip agent, anti-statics, and high PP fraction

Table 1.	Overview	of bottle ca	ap recyclate	(BCR)	formulations	used in	this work
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Commercial recyclates (CR) were obtained from recycling companies in Austria and Germany. The CR grades served as examples of BCRs already present in the market at the time of conducting this study. The short sign CR-1 was used for the grade Krutene-HD multicolored compound MFR 2.1–3.0 from Kruschitz GmbH (Völkermarkt, Austria), which was available in the form of granules.

It was claimed to consist mainly, but not exclusively, of post-consumer plastic bottle caps. The melt flow rate (MFR) was reported to be 2.5 g/10 min (190 °C, 2.16 kg). The short sign CR-2 was used for the regrind grade multiprop 3230 from Multiport GmbH (Bernburg, Germany), which consisted of sorted, washed, and shredded bottle caps. This regrind material has a melt flow rate between 3 and 20 g/10 min (190 °C, 5 kg) depending on the batch.

Waste model recyclates (WMRs) were defined such to highlight the impact of different waste stream compositions. The grade WMR-1 consisted of both caps and labels of post-consumer plastic beverage bottles, i.e., all non-PET plastic components of a typical PET beverage bottle. This is not a commercial product but was kindly supplied by Kruschitz GmbH (Völkermarkt, Austria). The grade WMR-2 was composed of screw caps originating from a diverse range of beverage and dairy packaging items. Specifically, the caps for WMR-2 originated from 58% PET bottles, 35% composite beverage packaging, and 7% PE-HD bottles. These caps were self-collected during the course of several months in a number of Austrian households.

Virgin model blends (VMBs) were formulated by melt blending four different commercially available virgin polyolefin resins, designated as PE-HD1, PE-HD2, PP1, and PP2. All of these are typically used for different caps and closure applications and are food contact-approved. The VMB materials served as control samples in terms of composition and presence of typical additives, specifically slip agents. VMB-1 was designed to simulate a bottle cap recyclate with low-level PP contamination of 5% by mass, whereas VMB-2 represents a heterogeneous cap recyclate with equal amounts of PE-HD and PP by mass.

PE-HD1 was a multimodal PE-HD with a density of 0.956 g/cm³ and a melt flow rate of 0.8 g/10 min (190 °C, 2.16 kg). It contains a slip agent and is specifically designed for caps and caps of carbonated soft drink bottles. PE-HD2 was a bimodal PE-HD with a density of 0.954 g/cm³ and a melt flow rate of 4 g/10 min (190 °C, 2.16 kg). It contains no slip agents and is intended for caps and closures of flat water, tea, and juices. PP1 was a PP homopolymer with a density of 0.905 g/cm³ and a melt flow rate of 25 g/10 min (230 °C, 2.16 kg). It is used to make various caps and closures and it contains both anti-static and slip additives. PP2 was a commercial PP random copolymer grade with a density of 0.905 g/cm³ and a melt flow rate of 13 g/10 min (230 °C, 2.16 kg). It contains anti-static additives and it is used for making items such as closures, lids, bottles, and containers.

2.2. Sample Preparation

The commercial recyclate CR-1 was received in sufficient amount to allow for production of an injection molded multipurpose specimen according to ISO 3167. The molding was carried out using a Victory 60 (Engel Austria GmbH, Schwertberg, Austria) injection molding machine. The processing parameters included a barrel temperature profile of 145 °C at the rear end up to 225 °C at the nozzle and a mold temperature of 30 °C. An initial injection rate of 19 cm³/s resulting in a fill time of ca. 2.7 s was chosen and a holding pressure of 700 bar and a holding time of 14 s were used.

All other recyclate formulations were processed in smaller batch sizes using lab-scale techniques due to limited material availability. The self-collected caps from beverage bottles and composite beverage packaging were rinsed with tap water to remove packaging content residues. They were then dried in air and shredded into flakes using a Pulverisette 25 cutting mill (Fritsch GmbH, Idar-Oberstein, Germany) equipped with a 4 mm sieve cassette.

The recyclate formulations CR-2, WMR-1, WMR-2, VMB-1, and VMB-2 were compounded using a Plasti-Corder Lab-Station (Brabender GmbH & Co. KG, Duisburg, Germany) equipped with a twin-screw measuring kneader 350. For each of these five formulations, approximately 200 g of flakes or granules was kneaded at 60 rpm and a temperature of 170 to 180 °C for 5 min. The resulting homogenized melt was put between two layers of aluminum foil and transferred into a hydraulic press pre-heated to 180 °C to make 1.5 mm-thick plates. The plates were cooled down to 100 °C under pressure and then cooled down to room temperature in ambient air. The kneading chamber and kneading elements were thoroughly cleaned and aluminum foils were disposed of after processing each individual material formulation to avoid cross-contamination.

Upon melt processing, the slip agent molecules are more or less evenly distributed throughout the volume of the fabricated samples. Diffusion of the slip agent molecules from the volume to the surface and subsequent formation of mono-, double-, and multi-layers represent a time- and temperature-dependent process [36,37]. Within certain limits, higher storage temperature should result in faster diffusion to the surface [44]. Hence, hot-pressed samples of all recyclate formulations except CR-1 were stored at 23, 50, and 65 °C for up to 256 h in order to facilitate slip agent diffusion.

2.3. Methods

The presence of surface-bound legacy additives in different BCR formulations was investigated by Fourier-transform infrared spectroscopy in the attenuated total reflection mode (ATR-FTIR). High-performance liquid chromatography with ultraviolet light detection (HPLC-UV) was used as a complementary method for refining the qualitative information gained from ATR-FTIR and additionally allowing for quantification of legacy additives. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were employed to supplement the compositional analysis.

2.3.1. Infrared Spectroscopy (ATR-FTIR)

The ATR-FTIR spectra were acquired within a wavenumber range from 4000 to 650 cm⁻¹, using a resolution of 4 cm⁻¹ (equivalent to a data point interval of 1 cm⁻¹), and a contact force of approximately 100 N. A total of 16 spectra were acquired and averaged for each sample and at least five samples (i.e., individual injection molded specimens, individual pieces of hot-pressed plates, or distinct locations on caps) were tested for each material. The ATR crystal was regularly cleaned with isopropanol and a new background calibration was performed. The measurements were carried out using a Spectrum 100 (PerkinElmer, Waltham, MA, USA) equipped with a UATR module.

2.3.2. High-Performance Liquid Chromatography (HPLC-UV)

High-performance liquid chromatography was used to quantify the concentrations of three typical slip agent compounds that were assumed to be present in the recyclate formulations as they are common slip-promoting additives for polyolefins in general and specifically for plastic bottle caps [35,36]. Behenamide (docosanamide, $C_{22}H_{45}NO$, CAS registry No. 3061-75-4), erucamide (cis-13-docosenamide, $C_{22}H_{43}NO$, CAS registry No. 112-84-5), and oleamide (cis-9-octadecenamide, $C_{18}H_{35}NO$, CAS registry No. 301-02-0) were chosen for analysis in this work.

The chemicals used for the HPLC-UV method included acetonitrile (VWR chemicals, >99%), water (18 M Ω , Merck Millipore Milli-Q water purification system), Cyanox 1790 (Cytec Industries) as an internal standard, behenamide (ABCR, 75%), crodamide SR/OR (Crode Chemicals), oleamide (Sigma-Aldrich, St. Louis, MO, USA, ≥99%), and toluene (VWR chemicals, 100%).

For each of the six recyclate formulations, 20 mg of polymer sample was dissolved with 450 μ L toluene and 50 μ L of internal standard (Cyanox 1790) was added. The vials were kept in the oven at 130 °C for 1 h. For the precipitation of the polymer, 800 μ L acetonitrile was added and after centrifugation, 300 μ L of supernatant was brought to dryness via a nitrogen stream and re-dissolved in 300 μ L acetonitrile. The samples were prepared in triplicates, then analyzed by HPLC-UV.

The measurements were performed on an Agilent Series 1260 Infinity HPLC system, equipped with a diode array detector (Agilent Technologies, Waldbronn, Germany). The column for separation was a Kinetex C18 column ($50 \times 3 \text{ mm}$, 2.6 µm particle size) from Phenomenex (Aschaffenburg, Germany). A binary gradient was used with acetonitrile and 18 M Ω water with a flow rate of 1.2 mL/min. The following linear gradient of acetonitrile/water was operated for elution: 60/40 from 0 to 4 min, 75/25 from 4 to 7 min, 87/13 from 7 to 10 min, 92/8 from 10 to 14 min, 92/8 from 14 to 17 min, and 100/0 from 17 to 23 min. The injection volume was 15 µL and the column temperature was maintained at 38 °C. The detection wavelength was set to 200 nm.

The determination of melting and crystallization peak temperatures via DSC was used as a method for compositional analysis complementary to ATR-FTIR. Samples with a mass of 6 to 8 mg were cut from injection molded specimens (CR-1) or hot-pressed flat plates (all other BCRs) and placed in aluminum pans with lids. A minimum of two samples were tested for each material. The temperature program included an initial isothermal of 5 min at 20 °C, followed by a first heating scan from 20 to 220 °C to erase the thermal history, a cooling scan from 220 down to 20 °C to reveal crystallization peak temperatures, and a subsequent second heating scan from 20 up to 280 °C to obtain melting peak temperatures. The heating and cooling rates were set to +10 K/min and -10 K/min, respectively. Nitrogen was used as a purge gas at a flow rate of 20 mL/min. The measurements were performed on a DSC 8500 (PerkinElmer, Waltham, MA, USA) and an empty pan was used as a baseline correction reference.

3. Results

3.1. Spectroscopic Surface Characteristics of Selected Commercial Resins and Caps

Both anti-static and slip additives are supposed to be active at the plastic surface in order to fulfill their functions. ATR-FTIR spectra collected from surface locations of granules of virgin polymer resins for cap production are depicted in Figure 3a. Except for PE-HD2, which is free of anti-static and slip additives according to its datasheet and which gives a pure PE spectrum [45], all other cap resins have absorption bands located in the spectral regions between 3400 and 3000 cm⁻¹ and from 1750 to 1600 cm⁻¹ which are highlighted by red boxes in Figure 3. These additional bands cannot be attributed either to PE or PP [45] and must hence originate from other compounds. Moreover, the respective bands were absent in all virgin resins when spectra were recorded from the bulk via measuring the cross-section instead of the surface locations of plastic granules.



Wavenumber [cm⁻¹]

Figure 3. ATR-FTIR spectra obtained from surface of virgin bottle cap resins (**a**) and from surfaces of screw caps taken from different beverage packaging items (**b**). Spectra are shown in absorbance. Baselines have been shifted arbitrarily along the vertical axis to improve visibility. Red boxes indicate absorption bands that are indicative of surface-bound additives.

The virgin PP resins PP1 and PP2 showed rather weak absorption bands due to additives. Nevertheless, a broad and flat peak between 3350 and 3180 cm⁻¹ was found for PP2 together with a sharp duplet peak at 1740 and 1730 cm⁻¹. A precise assignment was not possible in this case. For PP1, weak bands were detected at 3392, 3296, 3199, 1740, 1730, and 1646 cm⁻¹. Again, a definite assignment was not possible. According to the manufacturer, this PP homopolymer is equipped with anti-static and slip additives and the bands detected would fit to a mixture of fatty acid amides (including stearamide) and hydroxylated fatty acids [47].

bottle caps containing erucamide [36,37], and PP cast films with erucamide slip agent [48].

In Figure 3b, the spectra obtained from individual screw caps taken from the raw material supply for the WMR-2 formulation show ATR-FTIR characteristics similar to those of the virgin cap resins above. The red boxes in Figure 3 extend over both image parts (a) and (b) in order to facilitate comparison. Bands correlating with the NH₂ and C=O groups of fatty acid amides were detected in varying intensities on the cap of a sparkling water PET bottle, the cap of a carbonated soft drink (CSD) in a PET bottle, and the PE-HD cap of a composite beverage packaging for apple juice.

Notable exceptions were found in the spectrum of the sparkling mineral water bottle cap that exhibits an additional carbonyl duplet band with peaks at 1740 and 1730 cm⁻¹, corresponding to ester and aldehyde functionalities, respectively [46]. Moreover, the upper spectrum in Figure 3b representing the PP cap of carrot juice in a composite packaging contains a broad band between 3400 and 3100 cm⁻¹ with peak absorption at 3307 and 3243 cm⁻¹ instead of the two distinct NH₂ bands at 3395 and 3185 cm⁻¹ mentioned above. Together with the intensive carbonyl bands at 1739 and 1731 cm⁻¹, this points to the presence of glycerol monostearate (C₂₁H₄₂O₄, CAS registry No. 123-94-4) [47], a common mold release and anti-static agent in polyolefins [35].

In short, the presence of surface-bound additives in both selected commercial polymer resins intended for caps and closure applications and caps obtained from used beverage plastic bottles and composite beverage packaging was confirmed by ATR-FTIR.

3.2. Bottle Cap Recyclates (BCRs)

3.2.1. Polymeric Constituents of Bottle Cap Recyclates (BCRs)

Despite the fact that ATR-FTIR is a facile, fast, and potent method for polymer identification, its penetration depth is in the sub- and lower micrometer range, depending on the wavelength and angle of the incident light and the refractive indices of the used ATR crystal and the investigated material [37,45]. ATR-FTIR is hence well suited for surface and near-surface characterization, however, for the purpose of compositional analysis, it was supplemented by DSC in this work. The resulting thermograms for all recyclate formulations are plotted in Figure 4. They illustrate the heat flow between the sample and the surrounding environment as a function of temperature. Endothermal flows are positive and directed downwards; exothermal flows are negative and directed upwards. The left column in Figure 4 shows the cooling curves (a, c, e) recorded after completion of the first heating scan, whereas the right column depicts curves obtained from the second heating scan (b, d, f). Temperatures higher than 180 °C are not shown because no endo- or exothermal events were detected above this value.



Figure 4. DSC thermograms resulting from cooling and second heating scans of commercial recyclates (**a**,**b**), waste model recyclates (**c**,**d**), and virgin model recyclates (**e**,**f**). Exothermal direction is up; endothermal direction is down.

The crystallization (T_C) and melting peak temperatures (T_M) are summarized in Table 2 together with the respective values for enthalpy of crystallization (ΔH_C) and enthalpy of melting (ΔH_M). The absence of further endothermal or exothermal events at higher temperatures suggests that polyolefins form the main constituents of all recyclate formulations. Nevertheless, the presence of small amounts of other polymeric contaminants cannot be completely excluded based on these findings. Contaminations with foreign polymers that are in the lower percent range or even below 1 percent by mass are not readily detectable by means of DSC. Complimentary and more sensitive analytical methods may be employed in this case. Liquid chromatography, for instance, was shown to be a promising method for the detection of low-level contamination with polyamide 6 in polyolefin recyclates [49].

Table 2. Crystallization and melting peak temperatures and respective enthalpy values of all BCRs obtained from DSC measurements.

Sample	$T_{C} [^{\circ}C]^{1}$	$\Delta H_C [J/g]^2$	T _M [°C] ³	ΔH_{M} [J/g] ⁴
CR-1	117.2, 125.2	72.4, 25.0	131.4, 162.8	92.7, 25.8
CR-2	116.3	175.4, 0	131.4, 159.1	196.7, 1.9
WMR-1	116.5, 123.8	118.6, 7.6	131.6, 161.3	153.1, 12.7
WMR-2	116.3, 125.5	176.4, 1.1	131.3, 162.1	186.4, 2.6
VMB-1	115.6, 121.4	170.5, 0.7	130.7, 157.0	192.1, 2.5
VMB-2	115.9, 122.7	77.0, 31.2	131.0, 158.1	95.2, 25.9

¹ Crystallization peak temperature, ² crystallization enthalpy, ³ melting peak temperature, ⁴ melting enthalpy.

Based on the same consideration of lacking sensitivity for components with very low concentrations, no interference of DSC measurements with the presence of slip agents is expected. The typical

concentrations of these compounds are in the range of several hundred up to a few thousand ppm, which is still way below 1 percent by mass. Even if slip agent melting were to be observed, the melting peaks would be located at temperatures significantly below the PE-HD peaks. Erucamide and oleamide melt between 75 and 80 °C [50,51], while stearamide and behenamide have melting points slightly below and slightly above 110 °C [52,53], respectively.

The commercial recyclate CR-1 is essentially a blend of PE-HD and PP, owing to clear signals for both polymers with melting peak temperatures of 131 and 163 °C, respectively [54]. In contrast to that, the CR-2 material seems to be almost free from cross-contamination with PP. It is essentially a PE-HD material. Very flat melting peaks can be observed in the heating curves of CR-2 only upon strong magnification. The associated melting peak temperature is 159 °C.

The waste model recyclates provide a similar impression (see Figure 4c,d). The major component of both WMR-1 and WMR-2 is PE-HD. WMR-1 shows a moderate melting peak at around 161 °C and a distinct crystallization peak at 124 °C, indicating the presence of PP [54]. This is likely due to significant amounts of bottle labels as WMR-1 is made from all PET bottle parts that are separated from the actual PET bottle body by float–sink separation during reprocessing. WMR-2, which is composed of self-collected caps and, instead of labels, contains a few mass percent of caps from composite beverage packaging for juices and milk, shows weak signs of PP too. The peak temperatures are 126 °C for crystallization and 162 °C for melting and these can only be observed upon high magnification as in the case of CR-2.

The DSC curves of the virgin model recyclates are depicted in Figure 4e,f. The case of VMB-2 illustrates that even a PP content of 50 percent by mass causes only a moderate PP melting peak. This is due to both the lower average degree of crystallinity of typical PP grades compared to typical PE-HD grades and the generally lower melting enthalpy of crystalline PP domains compared to PE-HD crystallites [54]. While a value of 291 J/g is reported for theoretically perfectly crystalline PE, the corresponding value for PP is just 209 J/g [54]. Accordingly, the DSC curves of VMB-1, that contains only 5% PP, show just faint signs of PP crystallization and melting visible upon greater magnification. This is a good piece of evidence for the difficulty of adequately detecting low-level polyolefin cross-contamination by thermo-analytical methods, especially with PP being the minor component.

Enthalpy values for crystallization and melting may be used to calculate degrees of crystallinity of PE-HD and PP [54]. Furthermore, they may also be used for estimating the relative content of each of the two components [55]. The latter is of particular interest with regard to compositional analysis. The compositions of VMB-1 and VMB-2 are known (see Table 1). Their respective enthalpy values can hence be used for rough estimations based on linear regression. The regression is in this case based on two points only, which is a relevant limitation from a precision point of view. Nevertheless, comparing the ΔH_{M} values of CR-1, CR-2, WMR-1, and WMR-2 with those of the VMBs provides interesting estimates. Based on this approach, CR-2 and WMR-2 seem to have a PE-HD content of significantly above 90%. The formulation WMR-1 can be called PE-dominated due to an estimated PE-HD content of 70 to 80%, while CR-1 seems to contain only about 50% of PE-HD by mass. The commercial bottle cap regrind material (CR-2) and self-collected caps (WMR-2) are hence the least affected by polyolefin cross-contamination. In both cases, the care taken to keep bottle caps separate from other wastes either by industrial means (CR-2) or by manual action (WMR-2) likely leads to this outcome. The case of WMR-1 is an indicator that separation of bottle labels from the shredded caps is essential to keep PE-HD purity high. The commercial regranulate CR-1 demonstrates that mixing post-consumer bottle caps with other waste streams during reprocessing can have a severe impact specifically on polyolefin cross-contamination.

Another interesting observation concerns the high similarity of PE-HD crystallization and melting peak temperatures that show a maximum spread of 1.6 and 0.9 °C, respectively, for the various formulations. For the PP crystallization and melting peak temperatures, the maximum spread is 4.1 and 5.8 °C, respectively. This points to rather similar PE-HD resins in all recyclate formulations on the one hand and rather dissimilar PP resins in the various formulations on the other hand. It seems likely

that PP grades used to make bottle labels (in WMR-1) are rather different from typical PP cap resins which are present in VMB-1, VMB-2, and probably CR-1.

3.2.2. Evidence for Legacy Additives in Plastic Bottle Cap Recyclates

Whether typical plastic bottle cap additives such as anti-statics and slip agents survive the processes involved in mechanical recycling and whether they can hence be inherited by the resulting recyclates as legacy additives was investigated by ATR-FTIR analysis. The ATR-FTIR spectra of all bottle cap recyclate formulations are depicted in Figure 5. Based on the findings discussed in Section 3.1, the left column shows the spectral range from 3500 to 3050 cm⁻¹ where bands related to hydroxyl groups (e.g., glycerol monostearate) or bands related to NH₂ groups (e.g., fatty acid amides) are expected. Complementary to that, the right column shows the region from 1900 to 1450 cm⁻¹ where bands associated with the carbonyl functionalities are expected.



Figure 5. ATR-FTIR absorbance spectra of commercial recyclates CR-1 and CR-2 (**a**,**b**), waste model recyclates WMR-1 and WMR-2 (**c**,**d**), and virgin model blends VMB-1 and VMB-2 (**e**,**f**).

All curves plotted in Figure 5 show at least a certain degree of infrared absorption at 3395, 3188, 1646, and 1630 cm⁻¹. This provides a strong piece of evidence for the presence of fatty acid amide compounds in these commercial and model recyclates. It is also in good agreement with an earlier work reporting the detection of surface-bound fatty acid amide molecules in polyolefin recyclates containing post-consumer bottle caps [56].

The commercial recyclate CR-1 generated the strongest ATR-FTIR signals related to erucamide-like slip agents (including an extra band at 3312 cm⁻¹ that is not visible at other samples and that also belongs to erucamide [47]). In addition, compounds containing ester and aldehyde functionalities with peaks at 1740 and 1730 cm⁻¹ [46] were recorded. The latter could indicate the presence of anti-static additives. However, infrared activity in the carbonyl region between 1700 and 1780 cm⁻¹ could also originate from other compounds or simply from thermo-oxidative polymer degradation [57–61].

The spectra of the waste model recyclates in Figure 5c,d and those of the virgin model recyclates in Figure 5e,f show the same characteristics in both wavelength regions of interest with regard to fatty acid amide signatures. In addition to amide-related bands, WMR-1 comprises absorption in the carbonyl region at around 1715 cm⁻¹. The intensities of all these bands, however, are rather low. Interestingly, the situation did not change significantly when it was tried to support slip agent molecule migration to the surface by incubating samples at temperatures of 50 and 65 °C for 256 h. Only VMB-1, the virgin model recyclate containing 50% PE-HD with a slip agent, developed a pronounced increase in band intensities upon incubation at 50 °C (data not shown here). This was not observed at 65 °C.

Summing that up, surface-bound additives were clearly detected in one commercial bottle cap recyclate, whereas the other formulations did show only traces of additives in their ATR-FTIR spectra. However, those weak signals could be effectively reproduced. Additive accumulation at the surface is very dependent on the storage conditions [36] and future work should perhaps utilize other settings than those employed here.

3.2.3. Identification and Quantification of Selected Slip Agents as Examples of Product-Specific Legacy Additives

The average concentrations of behenamide, erucamide, and oleamide as obtained from triplicate quantification via HPLC-UV including the respective standard deviation values are depicted as a bar chart in Figure 6. It is worth mentioning, that despite the difficulties in obtaining intense and clear signals of slip agent molecules on the surfaces of CR-2, WMR-1, WMR-2, and VMB-2 by means of ATR-FTIR spectroscopy, all investigated formulations were shown to contain substantial amounts of slip additives by HPLC-UV.



Figure 6. Concentrations of slip agent legacy additives behenamide, erucamide, and oleamide in all investigated recyclate formulations determined by HPLC-UV.

Erucamide was the most abundant legacy slip agent in this study. It was the only analyzed compound being found in all tested recyclate formulations. The measured concentrations ranged from 1592 \pm 212 ppm in CR-1, the commercial bottle cap recyclate available as granules, down to 475 \pm 19 ppm in WMR-2, the blend of self-collected caps from used PET bottles and composite beverage packaging. These values are in the typical range of additive loading when using slip agents [35,37,48,62]. Specifically, erucamide and behenamide concentrations of 2000 ppm have been reported for PE-HD bottle caps for carbonated soft drinks [36].

Behenamide was detected in four out of six samples, namely in CR-1, CR-2, WMR-1, and WMR-2. While the measured concentrations in CR-2, WMR-1, and WMR-2 were rather similar with 586 ± 84 , 629 ± 42 , and 512 ± 23 ppm, respectively, the sample CR-1 contained only 64 ± 29 ppm of behenamide.

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Behenamide was not detected in the virgin model recyclates VMB-1 and VMB-2, however, its presence in all commercial and waste model recyclates indicates widespread application in plastic bottle caps or waste fractions that are intentionally or accidentally treated together with these. Nevertheless, not all caps contain slip agents. This is not only supported by the availability of bottle cap resins without any slip additive from several virgin polymer suppliers. In fact, both erucamide and behenamide were found by HPLC-UV in only one out of three sample flakes taken from the batch of shredded post-consumer bottle caps prior to melt processing them into the CR-2 recyclate formulation.

Oleamide was found exclusively in CR-1. Here, the derived concentration was 56 ± 11 ppm and was hence on the same (low) order of magnitude as the behenamide concentration in this recyclate formulation. It seems that this compound is not as widely used in bottle caps, as this is the case for erucamide and behenamide (acknowledging the fact that bottle cap composition and resulting waste fractions may be subject to both regional and seasonal variations).

4. Discussion

The compositional analysis of bottle cap recyclates revealed two main aspects. First, polyolefin cross-contamination, i.e., traces of PP in PE materials, is a fact. Second, slip agent molecules are present as legacy additives in amounts that can in some cases be comparable to typical additive loadings of virgin polymer resins and products. In both cases, feedstock composition plays a crucial role.

Polyolefin cross-contamination is a common phenomenon in post-consumer plastics recycling, which is by now well documented through analytical work on both waste fractions [1,63,64] and actual recyclates [55,56,65–67]. Despite their apparent chemical similarity, PE and PP are immiscible polymers [68,69]. When mixed together, they develop a heterogeneous morphology characterized by phase separation. The minor component forms the discontinuous phase being dispersed in the major component which forms the continuous phase. Co-continuous phases may be built up under suitable conditions of the mixing ratio (e.g., 50:50) and similar viscosities [68,69]. As long as the contaminating minor component is present at a relatively low concentration, the effects on thermal behavior (such as crystallization) and simple mechanical properties such as stiffness (E-modulus) are moderate or even negligible [55,69,70]. However, the presence of PP in PE-HD was found to influence the deformation behavior and to promote brittle failure [70]. At higher amounts of cross-contamination, a negative deviation from additive property changes was observed [69]. This means that the blend of PE-HD and PP performs worse than expected from simply adding up the properties of both components multiplied with their respective mass fractions (simple additivity). This could be a major obstacle to utilization in caps and closure applications where toughness is often required. Furthermore, a negative impact on deformation behavior might lead to significantly reduced performance in more complex and especially long-term mechanical loading cases [71] such as environmental stress crack resistance (ESCR) testing, which is of high relevance for carbonated beverage caps. The presence of polyolefin cross-contamination can hence be regarded as a severe challenge in the pursuit of high-quality and high-value recycling paths for plastic bottle cap materials. Nevertheless, results presented herein indicate that some bottle cap waste fractions such as the commercial regrind CR-2 are quite pure in terms of polyolefin cross-contamination already. With some adjustments in sorting and/or in resin choice and product design, a high-purity PE-HD waste stream could be obtained from post-consumer bottle caps in future.

The presence of various levels of slip agents in the investigated recyclates sheds light on another aspect of the quality discussion in post-consumer plastics recycling. In stark contrast to the amount of academic interest regarding the fate of substances of concern in a circular plastics economy [72], the fate of functional additives that are not necessarily harmful has not yet received significant attention in scholarly work. However, it is of very high relevance for the functioning of an economy, especially a circular one that strives to increase the amount of plastic products with ever more recycled content, to have sufficient knowledge about the factors influencing the quality and performance of these

products. Functional additives play a key role here and slip agents in recyclates derived from caps may serve as an educative example that might be extended to other groups of plastic products.

While some functional additives like slip agents are not particularly harmful, they might still give rise to rather subtle concerns, including concerns related to processing ability and product performance. For example, erucamide has been associated with the occurrence of a kind of new clothes-like odor and off-taste in bottled water [41], indicating potential issues with consumer experience. Migration of erucamide and related compounds from plastic packaging into food simulants has been documented in the literature [73,74]. This per se is no concern from a regulatory point of view as long as the so-called overall migration limit is not surpassed because behenamide, erucamide, and oleamide (as well as stearamide) are all members of the Union list of authorized additives for food contact and no specific migration limits apply [38]. Nevertheless, attention has been drawn to the fact that oleamide, for instance, is a bioactive compound that seems to affect diverse physiological processes including certain cell signaling pathways [75]. Moreover, a recent study has emphasized the risk of experimental interference and potential misinterpretation of data from bioassays and other (bio)analytical methods due to the presence of oleamide and other leachables from plastic lab ware [76]. On the other hand, erucamide and oleamide were reported to possess anti-fouling properties against marine organisms including diatoms, biofilms, and abalones, whereas oleamide seemed to be significantly more effective [77].

With a view on more technical aspects of the presence of (legacy) additives, erucamide [78], as well as combinations of behenamide and erucamide [79], was shown to interfere with the surface modification of plastics by means of corona treatment. Such treatments are used to clean and activate plastic surfaces to improve consecutive bonding, coating, or lamination processes. An atmospheric plasma, also called corona discharge, is generated by an electric field of high voltage and frequency. This corona discharge reacts with the plastic surface, thereby increasing the surface energy [80]. For PE films containing 1000 ppm of erucamide, a more intensive corona treatment in terms of higher voltage and higher number of passes was required to achieve the same surface energy as compared to a neat PE film without a slip agent. Furthermore, the presence of erucamide and/or behenamide reduced the long-term stability and promoted faster decline in the surface energy of PE films after corona treatment [79].

Another aspect to take into consideration is the interaction of different legacy additives with each other on the one hand and the interaction between legacy additives and intentionally added additives on the other hand. Detrimental interaction between erucamide and certain silica-based anti-block agents has been reported [81]. Pronounced formation of colored degradation products of erucamide was attributed to the presence of transition metal oxides and alkaline earth metal oxides which are impurities in silica minerals, and silanol groups on the surface of silica anti-block agents [81].

None of these observations might be an obstacle to recycling in general. However, they might interfere with intentions of high-quality recycling into applications where adherence to clearly defined specifications and well-defined, tailored property profiles is a must. Juan and co-workers [82] recently demonstrated very clearly that the origin and the precise type of recycled resin matter a lot for fulfilling demanding performance requirements. They analyzed blends of pressure pipe grade PE-HD with several different types of recycled PE-HD from diverse waste streams such as crates, industrial containers, and automotive fuel tanks. They found that despite similar MFR values and performance of the respective blends in short-term properties such as yield strength and flexural modulus, a pronounced difference in impact and long-term properties (that are highly relevant for pressure pipe applications) originated from contamination issues and molecular differences such as the degree of short-chain branching of the HDPEs in the used waste streams [82]. Building on observations such as this, the presence, leakage, and behavior of legacy additives such as slip agents, whether of (health) concern or not, should be considered and potentially even exploited when high-quality recycling loops are to be pursued.

Regarding the case of bottle cap recyclates, it seems very worthwhile to elucidate whether the legacy slip agents inherited to form the first product life cycle actually keep their functionality. This seems plausible insofar, as the determined concentrations of a few hundred up to about 1600 ppm are within the range of typical applications. Furthermore, the spectroscopic investigation indicates that migration to the surface takes place. What is more to that, no evidence of severe chemical degradation of the slip agent molecules was found in the spectra. To elucidate whether the typical plate-like surface layer morphology of slip agents is developed would require a more in-depth analysis, e.g., by means of atomic force microscopy [37,48]. Further, whether all this results in the desired low coefficient of friction and adequate opening torque performance of caps as expected from slip agent activity is a question that should be addressed in future research.

The aspects addressed above highlight some issues which may require further consideration and more profound analysis prior to using them as a solid argument to demand for industry action or even novel regulatory acts. They are rather meant to provide additional input for discussion and a new perspective on the role of legacy substances that are of no particular (health) concern but give rise to a number of other consequences for processing and product performance.

5. Conclusions

In the current quest for higher recycling rates of plastics, it seems crucial to adopt a comprehensive approach on material composition and quality. Aiming for sustainable material cycles that create benefits and value beyond recycling for the sole sake of recycling should be the common goal of regulatory, corporate, and engineering efforts in this context. Besides continued research into advanced sorting and processing technologies, and conventional concepts of design-for-recycling that are used in product design, another potentially more rewarding strategy might be the dedicated compositional design of well-defined and easy-to-recycle waste streams for product categories where this seems to makes sense. Products that are subject to far-reaching regulatory action (such as plastic bottles and their caps in the EU) could be a logic first choice here. The case of bottle caps and the recyclates derived thereof demonstrates that a presumably simple application, such as making closures for beverage containers, in reality gives rise to an entire family of very diverse polyethylene and polypropylene grades, which eventually result in cross-contaminated polyolefin blends when subjected to recycling. This is even more so, when not only PET bottle caps are considered alone but when caps from other beverage packaging items such as composite packaging or PE-HD bottles are taken into account too.

On the other hand, it is common practice to incorporate functional additives into virgin plastic formulations in order to tailor precisely the material characteristics and hence the final product properties for specific applications. This is one of the success factors of polymeric materials. These intentionally added substances, which provide for adequate functionality during the "first life" of a given plastic grade—such as slip agents do in certain bottle cap materials—are readily transferred into consecutive use phases by means of mechanical recycling. Evidence presented herein shows that neither washing nor melt processing are effective in removing slip agent molecules from post-consumer bottle cap materials. While methods to detect and quantify legacy additives are available, it is a case-specific question whether the presence of these substances is irrelevant and negligible, a substantial source of concern, or perhaps even an opportunity. A sufficiently high loading with slip agents inherited from the previous use phase might reduce or even eliminate the need for re-additivation after recycling.

We argue that establishing sustainable material cascades and cycles for plastics not only requires reliable knowledge of where materials destined for recycling are coming from and what else apart from their main constituents they might contain. It also requires a thorough consideration of what they could best be utilized for in a consecutive use scenario taking fully into consideration their composition, intrinsic properties, and legacy additive content. This comprehensive approach on recyclate quality anticipates multiple, potentially dissimilar cascades and life cycles and covers both the actual polymer itself and the associated additives that must not be neglected [43,72,83]. It might therefore be worthwhile to pursue an approach of rationalizing and harmonizing polymer and

additive formulations while still allowing for continuous (and maybe even concerted) innovation. Definitely, this is an approach for selected applications only, perhaps with plastic bottle caps serving as an indicative and educative example based on the current regulatory pressure (or let us call it a window of opportunity for circularity-aware redesign). In combination with optimizing the respective collection schemes and reprocessing infrastructure, this might even open a door for much needed food contact-approved polyolefin recyclates that are currently still lacking in stark contrast to PET recyclates. Additionally, this will perhaps allow the plastics recycling sector to live up to the success rationale that has been working for virgin polymers for decades: to precisely tailor materials for specific use cases. In the early 21st century, which is a crucial time for both plastics and sustainable development [84–88], this could eventually be extended to a paradigm of *tailor-making materials for specific use and reuse cases*.

Author Contributions: Conceptualization, M.G. and R.W.L.; methodology, M.G., A.S., and W.B.; investigation, M.G. and A.S.; resources, M.G.; writing—original draft preparation, M.G. and A.S.; writing—review and editing, M.G., W.B., and R.W.L.; visualization, M.G.; supervision, R.W.L.; project administration, M.G. All authors have read and agreed to the published version of the manuscript.

Funding: Open Access Funding by the University of Linz. Other than that, this research received no external funding.

Acknowledgments: The authors express their gratitude for receiving sample materials used for experiments as donations in kind from Kruschitz GmbH (Völkermarkt, Austria) and mp-bbg Multiport GmbH (Bernburg, Germany). The support by Günter Jachs (Johannes Kepler University Linz, Institute of Polymeric Materials and Testing, Austria) and Martin Reif (Kompetenzzentrum Holz GmbH, Linz, Austria) in sample preparation is highly acknowledged. Furthermore, the authors wish to thank Robert Pugstaller, Roswitha Pleiner, Christian Pleiner, Viktoria Gall, and Alexander Lovas for helping collect used plastic bottle caps.

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

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