Investigations on the influence of multiple extrusion on the degradation of polyolefins

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A B S T R A C T
The importance of mechanical recycling of polymers has increased within the last decades, especially due to numerous regulations of governments all over the world. Hereby recycling quotas are enforced to pave the way towards a closed loop recycling. During its lifetime, polymers are exposed to multiple environmental factors, which can already induce degradation. However, a major factor that needs to be taken into account is the increased thermo-mechanical stress during the recycling process, which may have significant impact on the quality of recyclates as well. In the present work, polyolefins (high-density polyethylene and polypropylene) were artificially exposed to stress by continuous extrusion at varying speeds and absence or presence of stabilizers to analyze the extent to which the recycling contributes to degradation processes. These samples were analyzed for low-molecular-weight stress markers by thermodesorption gas chromatography and by high-performance liquid chromatography (both coupled to mass spectrometric detection). Depending on the extent of stress, the occurrence of odd-numbered linear alkane chains was revealed in polyethylene samples, and of oxidized branched alkanes in polypropylene samples. Correlations with molecular weight (determined by high temperature gel permeation chromatography) and with decreasing concentrations of stabilizers could be demonstrated.

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1. Introduction

Worldwide more than 400 million tons of plastic are produced every year with a rising trend. This accumulated to an amount of over 9.2 billion tons manufactured over the past 60 years [1,2]. Approximately 40% of these polymers have a life cycle of less than a month, leading to vast quantities of waste. Yet only 10% or 600 Mt of this plastic waste was recycled since the 1950s [1,3]. In the European Union (EU) 33 kg of plastic packaging waste was generated per inhabitant in 2018, leading to a total amount of 17.8 Mt of plastic post-consumer packaging waste [4,5]. Lately, the EU legislated the Directive (EU) 2018/852 to enforce higher recycling rates for materials found in packaging waste. The targets for the recycling rate of plastic waste are 50% by 2025 and 55% by 2030 [6]. To achieve these goals considerable efforts need to be set by the EU member states. In 2018, 32.5% of the total plastic post-consumer waste was recycled, in difference to this, the share for the plastic post-consumer packaging waste was significantly higher by reaching already 42%. This plastic waste mainly consisted of the polyolefins polypropylene (PP) and high- and low-density polyethylene (HDPE, LDPE) [5].

The main recycling technique is mechanical recycling including the steps sorting, washing, grinding and extrusion. All these steps can have a significant impact on the quality of the recyclates. By thorough separation of the waste, pure waste streams can be achieved, being a first step towards a recycle of good quality. A washing step is introduced to reduce non-polymer contaminations of the future recycle. After grinding, the waste flakes are compounded to obtain a homogeneous end-product in order to guarantee a uniform quality of the recycle [7,8].

The quality is the most critical criterion for polyolefin recyclates as well as a major cost driver. Today, still a low demand for polyolefin recyclates exists, mainly because of the manufacturers’ fear of inconsistent quality and unreliable product properties [9]. The quality of recyclates is not only defined by the presence or absence of polymeric or non-polymeric contaminations but also by the specific polymer properties [10–12]. These mechanical and molecular properties are affected by the exposure to thermal and mechan-
ical stress during the life-time of the polymer and by the recycling process itself [13]. By incentives of governments towards a closed loop recycling, polyolefins need to withstand the recycling not only once but many times without a significant loss of quality [14]. Therefore, it is important to investigate the impact of multiple extrusion processes on the degradation of polyolefins and how preventive measures like the addition of stabilizers can be influential for the quality of recycled materials. Recent studies on extrusion of polymers mainly focused on changes of the mechanical properties, yet in order to fully understand the polyolefin degradation chemical parameters need to be investigated as well.

Testing techniques for recyclates include mechanical testing of the tensile and tear strength, modulus, and strain at break, or differential scanning calorimetry (DSC) for the determination of polymer crystallinity and measurements of the melt-flow index (MFI). During several recycling cycles, the mechanical properties deteriorate as a consequence of the degradation of the polymer molecules, whereby the main degradation pathways are oxidation and chain scissions [15–22]. These can also be monitored by the carbonyl signal in the infrared (IR) spectra and measurements of the molecular-weight distribution by gel permeation chromatography (GPC) [23–26]. However, it still seems worth the efforts to look for alternative chemical methods to obtain additional information on the degradation behaviour in the recycling process and consequently about the quality of the material.

In this study, polyolefin materials were artificially exposed to thermo-mechanical stress by a continuous extrusion experiment performed within a time frame of 20 to 120 minutes. The resulting samples acting as surrogates for recyclates were characterized by means of high-temperature gel permeation chromatography with IR-detection (HT-GPC-IR). Subsequently, analyses by thermodesorption-gas chromatography coupled to a single quadrupole mass spectrometer (TD-GC-MS) and by high-performance liquid chromatography coupled to a quadrupole time-of-flight mass spectrometer (HPLC-QTOF-MS) were performed in order to characterise possible low-molecular-weight markers for the polymer degradation induced by the extrusion, which then were compared with real polyolefin recyclates for validating the significance. In addition, the impact of stabilizers on the quality after exposure to stress was investigated by using typical concentrations of the most abundant applied stabilizers Irgafos 168 and Irganox 1010. Finally, possible correlations of the different investigated parameters were studied to get the whole picture of the polyolefin degradation.

2. Materials and methods

2.1. Chemicals

Toluene, n-heptane and acetonitrile (ACN), all of analytical reagent grade, and formic acid (> 99%) were purchased from VWR International GmbH (Darmstadt, Germany). Tributylphosphate (97%) and ammonium formate (97%) were purchased from Sigma-Aldrich Handels GmbH (Viena, Austria). High-purity water (18 MΩ cm) was generated by a Millipore purification system (Molsheim, France). 1,2,4-trichlorobenzene (TCB) was obtained from Acros (99%, Schwerte, Germany) and was stabilized with 0.4 g L−1 butylated hydroxytoluene (>99%, Sigma-Aldrich Handels GmbH, Vienna, Austria). The polymer stabilizers (technical grade) Irganox 1010, Irgafos 168 and Cyanox 1790 were purchased from various commercial sources. Unstabilized HDPE and PP powders as well as various real polyolefin recyclates were commercially available from local manufacturers.

2.2. Instrumentation

Molecular-weight distribution was determined by a Polymer Char high-temperature gel permeation chromatograph equipped with an IFR detector (Polymer Char, Valencia, Spain). Three serially connected PIgel Oxelis columns (300 × 7.5 mm, 13 μm, Agilent Technologies, Santa Clara, California) combined with a PIgel Oxelis guard column (50 × 7.5 mm, 13 μm) were maintained at 160°C. TCB, stabilized with butylated hydroxytoluene, was used as mobile phase at a flow of 1 mL min−1. The injection volume was set to 200 μL. Total time of analysis was 40 minutes.

The analyses of the stabilizers and oxidized branched alkane species were performed on an Agilent 1260 HPLC coupled to an Agilent model 6510 quadrupole time-of-flight MS (QTOF-MS) equipped with an electrospray ionization source (Agilent Technologies, Santa Clara, California). The drying gas temperature was set to 325°C at a flow rate of 10.5 L min−1, the nebulizer to 50 psi and the capillary voltage to 3500 V. Samples were analysed in the positive mode. A Kinetex C18 column was used (50 × 3 mm, 2.6 μm, Phenomenex, Aschaffenburg, Germany), equipped with a C18 guard column (4 × 2 mm, Phenomenex, Aschaffenburg, Germany).

The following gradient elution was used for the stabilizer analysis employing 10 mM ammonium formate in H2O containing 0.1% formic acid (A) and acetonitrile with 0.1% formic acid (B): 60% B from 0 to 4 min, linear increase to 75% B between 4 and 7 min, linear increase to 87% B between 7 and 10 min, linear increase to 92% B between 10 and 14 min, hold at 92% B for 3 min, linear increase to 100% B between 17 and 20 min, hold for 2 min. The column was re-equilibrated for 2 minutes to starting conditions. Column temperature was set to 37.5°C and the flow rate to 1.2 mL min−1 using a split of 1:3 before the mass spectrometer. The injection volume was 20 μL.

The analysis of the oxidized branched alkane species was performed with a gradient elution using 10 mM ammonium formate in H2O containing 0.1% formic acid (A) and acetonitrile with 0.1% formic acid (B). Starting conditions were set to 50% A, 50% B, held constant for 2 min, followed by a linear increase to 100% B from 2 to 10 min, which was kept for 11 min. The column was re-equilibrated for 2 minutes to starting conditions. Column temperature was set to 30°C and the flow rate to 1 mL min−1 using a split of 1:3 before the mass spectrometer. The injection volume was 20 μL.

The TD-GC-MS measurements were performed with an Agilent 6890N gas chromatograph coupled to a single quadrupole 5975C XL MSD mass spectrometer (Agilent Technologies, Santa Clara, California) and a Gerstel desorption unit consisting of a TD52A autosampler, a TDS3 and a cool injection system CIS (Gerstel, Mülheim an der Ruhr, Germany). The thermodesorption was performed using a linear temperature gradient starting at 40°C to a final temperature of 280°C (held for 5 min) with a rate of 7°C min−1. The transfer line was heated to 300°C. The desorption mode applied was split (20:1). The CIS was pre-cooled to −25°C using liquid nitrogen and the temperature was linearly increased to 300°C with a rate of 12°C min−1. The GC was equipped with an Optima 5 MS column (30 m x 0.25 mm, 0.25 μm, Macherey-Nagel, Düren, Germany). Helium 5.0 was used as mobile phase with a flow rate of 1.5 mL min−1. The following temperature program of the GC oven was used: the initial temperature of 60°C was held for 1 min, followed by a linear increase of 7°C min−1 up to a temperature of 310°C, held for 5 min.

2.3. Sample preparation

4 g of polymer powder without or with 0.15 wt% Irgafos 1010, 0.15 wt% Irgafos 168 or a mixture of 0.15 wt% Irgafos 1010 and 0.15 wt% Irgafos 168 was extruded using a twin-screw com-
pounder (Haake Rheomix CTW5 Minilab II, Thermo Fisher Scientific, Waltham, USA) equipped with twin-screws (5/14 mm conical outer diameter, 109.5 mm length). The temperature was maintained at 220°C and the rotation speed was either 50 or 100 rpm to compare the influence of mechanical stress. The instrument was run in circulation mode. By using the bypass valve, samples were taken after 20, 40, 60, 80, 100 and 120 minutes. Each experiment was conducted in triplicates.

For the HT-GPC-IR analysis, about 4 mg of each sample was weighed in and 20 μL of n-heptane (diluted 1:10 with TCB) was added. Dependent on the polymer type the samples were dissolved automatically in the autosampler with 8 mL of TCB either for 120 min (HDPE) or for 180 min (PP) at a shaking speed of 3.

The analysis of stabilizers and the oxidized species of polypropylene by HPLC-QTOF-MS were performed by using 20 mg of sample, adding 440 μL toluene, 10 μL tributylphosphite (diluted 1:100 with toluene) and 50 μL internal standard (Cyanox 1790, 150 mg L⁻¹ in toluene). After an oven extraction (130°C, 60 min) the polymer was precipitated using 800 μL of ACN, followed by centrifugation. 400 μL of the clear solution was evaporated to dryness via a nitrogen stream, and subsequently reconstituted with 400 μL ACN. Samples were stored at -80°C until the analysis with HPLC to prevent shifts in concentrations by possible evaporation of solvent.

For the TD-GC-MS analysis, 20 mg sample were weighed in aluminum pans (12 × 4 × 2.7 mm, VWR International GmbH, Darmstadt, Germany) and positioned in the thermodesorption tubes, which had been conditioned by an Gerstel tubes concentrator TC 2 (Gerstel, Mülheim an der Ruhr, Germany) at 350°C for 1h.

2.4. Data evaluation

HT-GPC-IR measurements were performed using the Instrument Control software for data acquisition and GPC One for the further processing of the data. Data acquisition of the HPLC-QTOF-MS was done using Agilent MassHunter LCMS Acquisition software 10.0. The software Agilent MassHunter Qualitative Analysis B.07.00 was employed for data evaluation. MSD Chemstation was used for the data acquisition of the TD-GC-MS, and MS Chemstation Data Analysis for the evaluation of the results.

3. Results and discussion

To investigate the effects of thermal and mechanical stress on the properties of polyolefins and the occurrence of possible degradation markers induced by multiple extrusion, virgin HDPE and PP powders were extruded using a twin-screw compounder. The processing temperature was held constant at 220°C and to further study the influence of the screw speed the experiment was performed using either 50 rpm or 100 rpm. Moreover, the most common stabilizers Irganox 1010 (IX 1010) and Irgafos 168 (IF 168) were added either solely with 0.15 wt% or using a combination of both, each with 0.15 wt%, in order to identify the proposed beneficial impact of stabilization. The chemical structures of these stabilizers are shown in Fig. S1 of the electronic supplementary material (ESM). Especially IF 168 is used as processing stabilizer to prevent oxidation of the polyolefin by the decomposition of peroxides [27]. To analyze the course of degradation, samples were taken during the extrusion process after 20, 40, 60, 80, 100 and 120 minutes. For comparison of the results of these artificially stressed samples, commercially available HDPE and PP recyclates were analyzed.
3.1. Results of HT-GPC-IR

To see the changes on the macromolecular level, HT-GPC-IR analyses were performed. As expected, the degradation of polypropylene is faster than of HDPE due to the lower thermal stability. Therefore, it can be assumed that more chain scissions occur in PP than in HDPE. Interestingly, the stabilizer IF 168 showed no beneficial influence on PP as can be seen in Fig. 1. This may be due to the fact that the stabilizer is already degraded within the first 20 minutes. A synergistic effect can be observed by the mixture of both stabilizers. An influence of the extrusion speed can be seen after 20 minutes, yet this trend decreased with increasing extrusion time. After an extrusion time of 120 min, very similar results are obtained for each polypropylene sample independent of the presence of stabilizers. The GPC curves exemplarily shown for the unstabilized polypropylene extruded at a speed of 100 rpm are given in the Supplementary Material (Fig. S3). It can be seen that the time-dependent decrease of molecular weight correlates with narrower curves, resulting in a lower polydispersity index (PDI). One can conclude that especially high molecular-weight chains are prone to chain scissions. The PDI decreases faster at higher extrusion speeds.

On the contrary, the influence of stabilizers can be clearly seen for the polyethylene samples extruded with a speed of 50 rpm (see Fig. 2 in the ESM). The best results were obtained with IF 168, closely followed by IX 1010. The results of the mixture of both stabilizers showed a larger decrease of molecular weight within the first 20 minutes. Differently to 50 rpm, the results for 100 rpm are comparable for all stabilizers, yet still better than without stabilizer. Overall, a higher degree of degradation can be observed with the higher speed, but differences between the different stabilization systems are not as high as in case of polypropylene. The same is true when comparing the obtained PDIs. The curves are narrower if the speed is higher, yet there are no significant differences comparing the different stabilizers. This leads to the conclusion that the degradation of HDPE cannot be observed on the macromolecular level in detail.

3.2. Results of TD-GC-MS for HDPE samples

The polyethylene samples were further analyzed by TD-GC-MS to investigate changes at the low-molecular weight level. Using a temperature of 280°C for thermodesorption, the chromatograms of virgin HDPE materials mainly show even-numbered alkane species with chain length between C_{10}H_{22} and C_{30}H_{62}. Contrary to that, additional odd-numbered chains can be found in HDPE recyclates. The presence of species with chain lengths larger than C_{30}H_{62} can be expected, but was not investigated because their increasing boiling points make them less suited for GC analysis. A comparison of the chromatograms of virgin and recycled HDPE is displayed in Fig. 2. Two probable ways of degradation resulting in the formation of these molecules are either the cleavage of a CH_{3}-end group or the cleavage within a larger chain.

The extrusion experiments showed that with increasing extrusion time the peak areas of these odd-numbered chains obtained by integrating the corresponding peaks in the TD-GC-MS chromatograms increased. This increase was both speed- and stabilizer-dependent. A higher increase was observed at an extrusion speed of 100 rpm, and these differences between different extrusion speeds were more pronounced than expected from the HT-GPC-IR results given in part 3.1. Interestingly, with an extrusion time of 20 mins or longer, IF 168 was not capable of preventing cleavages, whereas IX 1010 or the combination of both significantly reduced the degradation as can be seen in Fig. 3.

In addition, two commercially available HDPE recyclates were analyzed for odd-numbered alkane species and compared with the artificially stressed samples. As can be seen in Fig. 4, lower amounts of odd-numbered chains could be found in recylcate 1 than in recylcate 2, but both are within the region of the artificially stressed samples. It can be concluded that these found markers might be mainly formed during the extrusion process and their amount is significantly influenced by the presence of specific stabilizers. These species can be used as parameter for the degradation of HDPE during the extrusion.

3.3. Results of HPLC-QTOF-MS for PP samples

Contrary to HDPE, TD-GC-MS is not suitable for the PP samples due to many partly overlapping peaks in the chromatogram, which could not be assigned to specific compounds. Therefore, polypropylene samples were further analyzed using HPLC coupled to a QTOF-MS. Hereby, oxidized species of low-molecular weight molecules related to polypropylene were observed only in the extruded samples but not in the virgin material. Therefore, this oxidation occurred during the extrusion process. The proposed structures for these oxidized branched alkane species are given in Fig. 5.

All identified compounds were verified by MS/MS, as example a MS/MS spectrum of the oxidized branched alkane species PP ox 5 (3,5,7,9,11,13,15,17-Octamethyloctadecane-2,4-dione) can be found in the ESM (Fig. S4). A complete separation of all peaks could be
Fig. 3. Comparison of the integrated peak areas of the odd-numbered alkane species ($C_{11}H_{24}$ to $C_{27}H_{56}$) of the extruded HDPE samples over the extrusion time in dependence of extrusion speed (top four graphs representing 50rpm and the bottom four 100 rpm) and stabilizers obtained by TD-GC-MS. All odd-numbered chains related to HDPE increased over time, yet in clear dependency of extrusion speed and stabilizer content.
achieved by a gradient elution, a chromatogram is displayed in Fig. 6.

All oxidized species of PP showed the same trend with rising peak areas over the extrusion time, exemplarily shown for the PP ox 5 in Fig. 7. Interestingly, a significantly higher degree of oxidation can be found in the samples extruded with a speed of 100 rpm although the decrease in molecular weight is faster at the lower speed of 50 rpm. It can be assumed that the degradation mechanism is dependent on the screw speed, lower speeds lead to chain scission, higher speeds to oxidation processes. At 100 rpm, an influence of the stabilizers can be observed, whereby the mixture of both stabilizers shows the best results followed by IX 1010. As already seen in the GPC data, IF 168 does not show a real benefit if compared to the data of the unstabilized PP samples. For comparison reasons, commercially available PP recyclates were analyzed to see if these oxidized species can be detected. In three different PP recyclates oxidized species could be found yet signal intensities were low, indicating that these oxidation processes were not the primary degradation pathway during the real recycling process or more recyling cycles are necessary for the formation of these species.

3.4. Results of HPLC-QTOF-MS for quantitation of stabilizers

To understand why the stabilizers differ significantly concerning their influence on the degradation of the polymers, a quantitation was performed using HPLC-QTOF-MS. A table with the resulting concentrations of the stabilizers is given in the ESM Table S1. These analyses have shown that IF 168, if present solely, was degraded within the first 20 minutes in the case of polypropylene at both extrusion speeds and in the case of polyethylene at 100 rpm. Low concentrations could be detected for HDPE at 50 rpm. High signals corresponding to the oxidized species of IF 168 indicated a fast consumption of the stabilizer during the extrusion process. The results indicate that either the stabilizer is not stable at the given temperature during the long extrusion time or significant amounts of hydperoxides and related radicals are present within the first 20 minutes leading to this fast consumption. Interestingly, if the stabilizer was present together with IX 1010, the concentration was low but detectable mostly until minute 60. This can be an explanation why no differences in the results could be seen between the unstabilized samples and the ones with IF 168 added. On the other hand, IX 1010 could be quantified in each sample, higher concentration were found if IF 168 was added as well. Different recyclates (HDPE and PP) were analyzed as well. Mainly IX 1010 and IF 168 were identified in rather low levels. This indicates that a restabilization of the polymers had not occurred during the recycling process but might be performed only later during the next processing steps.

3.5. Correlation of results

To compare the results of the different analysis methods, heat maps for each polymer (Fig. 8 for HDPE, Fig. 9 for PP) were generated. The data have been standardized by the z score.

Different correlations can be seen in the heat map, regarding the different extrusion speeds as well as the different stabilizers. The degradation of polyethylene is higher at a speed of 100 rpm, hereby the concentrations of stabilizers is lower compared to the results of 50 rpm. Therefore, it can be concluded that higher extrusion speeds favor degradation, leading to stabilizers being consumed faster. A beneficial influence can be seen for IX 1010 preventing the degradation of HDPE. Yet a combination with IF 168 did not show a synergic effect. IF 168 itself degraded mostly within the first 20 min of extrusion and could not decrease the degradation speed of the polymer. Overall, it can be seen that the decrease of molecular weight corresponds well with the increase of molecules with odd-numbered chains and decrease of the concentrations of the stabilizers. Longer extrusion times increase the degradation of the polymer, therefore more stabilizer is consumed and due to chain scissions degradation products of the polymer are formed.

Degradation pathways of polypropylene seem to be dependent on the extrusion speeds. The oxidation process of polypropylene is higher at 100 rpm although the degradation is lower, indicating that the increase of mechanical stress favors oxidation over chain scission. Hereby a beneficial influence of stabilizers towards less oxidation could be observed. Although IF 168 is used as process stabilizer against oxidation, IX 1010 showed better results. In the literature, no explanation for the different stabilizer behaviours could be found. Regarding the concentrations of the stabilizers, the behavior is similar to the polyethylene samples, higher speeds lead to greater degradation. Nevertheless, more intact stabilizers could be found throughout all PP samples compared to HDPE. Overall, it can be seen that the concentration of stabilizers correlate with the molecular weight and to the formation of oxidized branched alkane species. Yet the influence of the extrusion speed is significantly higher for the oxidation processes of polypropylene than for the chain scissions.

4. Conclusion

In this study, the degradation behaviour of the polyolefins HDPE and PP specific for the extrusion process was investigated by analysis of the formation of different chemical species after thermomechanical stress through continuous extrusion at a speed of ei-
ther 50 rpm or 100 rpm. The results of different analysis methods using HT-GPC-IR, TD-GC-MS and HPLC-QTOF-MS were compared. For polyethylene, the decrease in molecular weight could be correlated with the increase of molecules with odd-numbered chains in dependence of stabilizer concentrations. For polypropylene, two different degradation paths could be identified at different speeds. At lower speed chain scissions occurred, whereas at higher speed more oxidation processes could be observed. In order to see if these processes also occurred during mechanical recycling, commercially available HDPE and PP recyclates were analyzed. HDPE recyclates showed high amounts of molecules with odd-numbered chains, whereas in the PP recyclates oxidized species could be detected. During the lifetime of polymers, different degradations can occur dependant on various factors. Yet due to the increasing importance of repeated recycling processes, it is important to analyze degradation behaviours during the extrusion process. This study has shown that stabilization of the polymers significantly lowers the loss of recyclate quality, but clearly in dependence of the used stabilizer systems. Irgafos 168 used alone is neither in HDPE nor in PP capable of preventing degradation sufficiently due to the high speed of consumption. Sufficient stabilization during the recycling process is of major importance to reduce the detoriation of the polymer properties.
5. Declarations

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6. Author statement

Schweighuber Andrea: Conceptualization; Methodology; Validation; Writing - original draft; Visualization
Felgel-Fahrholz Alexander: Investigation
Bögl Thomas: Visualization
Fischer Jörg: Funding acquisition; Resources; Project administration
Buchberger Wolfgang: Supervision; Writing - review & editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 9. Heat maps for the results of PP, the top for 50 rpm and the bottom for 100 rpm. Red indicate the highest results, whereas blue corresponds to the lower resulting numbers. For both extrusion speeds, a decrease of molecular weight as well as of stabilizer concentration (if present) can be seen. Depending on the extrusion speed, the formation of oxidized branched alkane species can be observed.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2021.109689.

References

[1] Plastic atlas 2019: Facts and figures about the world of synthetic polymers, Heinrich Böll foundation, Berlin (2019) https://www.boell.de/sites/default/files/2019-11/Plastic%20Atlas%202019.pdf, retrieved on May 19, 2021.

[2] Morten W. Ryberg, Alexis Laurent, Michael Hauschild, Mapping of global plastics value chain and plastics losses to the environment (with a particular focus on marine environment), UN Environ. Prog. (2018) 1–99 https://wedocs.unep.org/handle/20.500.11822/2674, retrieved on May 19, 2021.

[3] Roland Geyer, Jenna R. Jambeck, Kara Lavender Law, Production, use, and fate of all plastics ever made, Sci. Adv. 3 (2017) 1–5.

[4] Eurostat, Packaging waste statistics, 2020 https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Packaging_waste_statistics#Waste_generation_by_packaging_material (accessed 30 March 2021).

[5] PlasticsEurope, Plastics - the Facts 2020, 2020. https://www.plasticsEurope.org/en/resources/publications/4312-plastics-facts-2020 (accessed 25 March 2021).

[6] European Parliament and of the Council, Directive (EU) 2018/852 of the European Parliament and of the Council of 30 May 2018 amending Directive 94/62/EC on packaging and packaging waste, 2018.

[7] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review, Waste Manag 29 (2009) 2625–2643, doi:10.1016/j.wasman.2009.06.004.

[8] K. Ragaert, L. Delva, K. van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Manag 69 (2017) 24–58, doi:10.1016/j.wasman.2017.07.044.

[9] European Commission, Communication from the Commission to the European parliament, the Council, the European economic and social committee and the committee of the regions: A European Strategy for Plastics in a, Circul. Econ. (2018).

[10] M.K. Eriksen, K. Pivnenko, M.E. Olsson, T.F. Astrup, Contamination in plastic re-
cycling: Influence of metals on the quality of reprocessed plastic, Waste Manag Res 35 (2017) 141–146, doi:10.1080/074242X16669998.

12. B. Hu, S. Serranti, N. Fraunholz, F. Di Maio, G. Bonifazi, Recycling-oriented characterization of polyolefin packaging waste, Waste Manag 33 (2013) 574–584, doi:10.1016/j.wasman.2012.11.018.

13. D. Jubiniæville, E. Esmiazadeh, S. Saikrishnan, C. Tzoganakis, T. Mekonnen, A comprehensive review of global production and recycling methods of polyolefin (PO) based products and their post-recycling applications, Sustain. Mater. Techn. 25 (2020) e00188, doi:10.1002/sust.2020.e00188.

14. M.K. Eriksen, A. Damgaard, A. Boldrin, T.F. Astrup, Quality assessment and circularity potential of recovery systems for household plastic waste, J. Indust. Ecol. 23 (2019) 156–168, doi:10.1111/jiec.12822.

15. P. Obłak, J. González-Gutierrez, B. Zupančič, A. Aulova, I. Emri, Processability and mechanical properties of extensively recycled high density polyethylene, Polym. Degrad. Stabil. 114 (2015) 133–145, doi:10.1016/j.polymdegradstab.2015.01.012.

16. L. Baltes, L. Costiuc, S. Patachia, M. Tierean, Differential scanning calorimetry—a powerful tool for the determination of morphological features of the recycled polypropylene, J. Therm. Anal. Calorim. 138 (2019) 2399–2408, doi:10.1007/s10973-019-0679-7.

17. S. Yin, R. Tuladhar, F. Shi, R.A. Shanks, M. Combe, T. Collister, Mechanical reprocessing of polyolefin waste: A review, Polym. Eng. Sci 55 (2015) 2899–2909, doi:10.1002/pen.23482.

18. N. Vidakis, M. Petousis, A. Maniadi, Sustainable additive manufacturing: mechanical response of high-density polyethylene over multiple recycling processes, Recycl 8 (2021) 4, doi:10.3390/recycling8010004.

19. L. Sun, X.Y. Zhao, Z.Y. Sun, Study on the properties of multi-extruded recycled PE and PP, Adv. Mat. Res. 1003 (2014) 96–99, doi:10.4028/www.scientific.net/AMR.1003.96.

20. R. Scaffaro, F.P. La Mantia, L. Botta, M. Morreale, N. Tz. Dintcheva, P. Mariani, Competition between chain scission and branching formation in the processing of high-density polyethylene: Effect of processing parameters and of stabilizers, Polym. Eng. Sci. 49 (2009) 1316–1325, doi:10.1002/pen.21337.

21. A.A. Mendes, A.M. Cunha, C.A. Bernardo, Study of the degradation mechanisms of polyethylene during reprocessing, Polym. Degrad. Stabil. 96 (2011) 1125–1133, doi:10.1016/j.polymdegradstab.2011.02.015.

22. L. Coulter, H.G.M. Orbon, R. Rijk, Analytical protocol to study the food safety of (multiple-)recycled high-density polyethylene (HDPE) and polypropylene (PP) crates: Influence of recycling on the migration and formation of degradation products, Polym. Degrad. Stabil. 92 (2007) 2016–2025, doi:10.1016/j.polymdegradstab.2007.07.022.

23. A.K. Dordinejad, F. Sharif, M. Ebrahimii, R. Rashedi, Rheological and thermomechanical assessment of polyethylene in multiple extrusion process, Thermochim. Acta 668 (2018) 19–27, doi:10.1016/j.tca.2018.08.010.

24. L.A. Pinheiro, M.A. Chineletto, S.V. Canevarolo, The role of chain scission and chain branching in high density polyethylene during thermomechanical degradation, Polym. Degrad. Stabil. 86 (2004) 445–453, doi:10.1016/j.polymdegradstab.2004.05.016.

25. O. Dikonomidou, M.I. Triantou, P.A. Tarantili, C. Anatolaki, N. Karonos, The effect of extrusion reprocessing on structure and properties of isotactic poly(propylene), Macromol. Symp. 321-322 (2012) 216–220, doi:10.1002/masy.201251139.

26. M.J. Abad, A. Ares, L. Barral, J. Cano, F.J. Diez, S. Garcia-Garabal, J. Lopez, C. Ramirez, Effects of a mixture of stabilizers on the structure and mechanical properties of polyethylene during reprocessing, J. Appl. Polym. Sci. 92 (2004) 3910–3916.

27. H. Zweifel, R.-D. Maier, M. Schiller (Eds.), Plastics additives handbook, Hanser, München, 2009.