



Effect of mechanical recycling on molecular structure and rheological properties of high-density polyethylene (HDPE)

Jian Zhang^{a,b,d}, Valerian Hirschberg^{b,c,**}, Anika Goecke^b, Manfred Wilhelm^b, Wei Yu^d, Michael Orfgen^e, Denis Rodrigue^{a,*}

^a Department of Chemical Engineering and CERMA, Université Laval, 1065 Avenue de La Médecine, Quebec, G1V 0A6, Canada

^b Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, Karlsruhe, 76131, Germany

^c Institute for Technical Chemistry, Technical University Clausthal, Arnold-Sommerfeld-Str., 438678, Clausthal-Zellerfeld, Germany

^d Advanced Rheology Institute, Department of Polymer Science and Engineering, State Key Laboratory for Metal Matrix Composite Materials, Shanghai Jiao Tong University, Shanghai, 200240, PR China

^e Ernst-Berl-Institut für Technische und Makromolekulare Chemie, TU Darmstadt, Peter-Grünberg-Str. 8, 64287, Darmstadt, Germany

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ABSTRACT

This study investigates the degradation of high-density polyethylene (HDPE) during successive closed-loop mechanical recycling via multiple extrusion. The main objective is to perform a comprehensive analysis of the rheological property changes associated with molecular characteristics. High temperature size exclusion chromatography (SEC) was performed first showing that more than 95% mass recovery was obtained after every mechanical recycling generation, thus excluding the possibility of extensive crosslinking in the rHDPE investigated. Then, small amplitude oscillatory shear (SAOS) measurements revealed significant increases of the zero-shear viscosity (η_0) by up to six-times, especially at a later stage between the 4th and 8th recycling cycles. Additionally, the van Gurp-Palmen (v-GP) plots suggest long chain branching due to the generation of free radicals during mechanical recycling, as radicals are created by chain scission. Extensional rheological measurements showed no detectable strain hardening effect, which is in contradiction with the hypothesis of an ill-defined long chain branched structure. This assumption is further corroborated through nuclear magnetic resonance (NMR) analyses, which detect branching sites in both ^{13}C and ^1H spectra. Moreover, the 'branch-on-branch' (BoB) constitutive model yields insights into the molecular topologies present within the recyclates, including different structures such as star-shaped and comb-type configuration. Overall, this study provides in-depth insights into topological changes during the mechanical recycling of HDPE, most likely from linear to a randomly branched, star-like structure, which is of fundamental interest for polyolefin polymer reprocessing; i.e. HDPE recycling.

1. Introduction

The global plastic waste crisis has brought attention to the urgent need for a transition from a linear plastics economy to a circular one [1, 2]. This shift aims at maximizing the value and lifespan of plastics while minimizing their environmental footprint via several innovations including the use of biobased/biodegradable materials and the 3R concept: reduction, reuse, and recycle [3]. A switch towards bioplastics as a viable alternative to petroleum-based plastics is still currently facing undeniable challenges. These challenges are at different levels including

cost, processability, availability, potential competition with food stock and required performances/properties [4–8]. Among the various recycling approaches, mechanical recycling plays a crucial role in achieving an environmentally and economically sustainable plastic economy [9–12]. In general, a remolding step (e.g. extrusion) is possible for linear and branched materials, but not for crosslinked polymer materials.

High density polyethylene (HDPE) is widely used in various applications due to its advantageous properties including high strength, chemical resistance, versatility, availability, and low cost [13]. The annual global production of HDPE was around 67 million tons in 2022,

* Corresponding author.

** Corresponding author. Department of Chemical Engineering and CERMA, Université Laval, 1065 Avenue de La Médecine, Quebec, G1V 0A6, Canada.

E-mail addresses: valerian.hirschberg@kit.edu (V. Hirschberg), Denis.Rodrigue@gch.ulaval.ca (D. Rodrigue).

and a 10% global increase is expected in 2023 [14]. However, the increasing accumulation of HDPE waste poses significant environmental challenges. Mechanical recycling offers a promising solution by transforming HDPE waste directly into valuable secondary raw materials [1]. Nevertheless, it is essential to determine the quality and performance of recycled HDPE (rHDPE) as mechanical recycling can generate some degradation associated with the reprocessing conditions. Furthermore, mechanical recycling has some limitations, such as contamination, variations in molecular weight and chain structure; i.e. polymer topology [11,12,15,16]. This is why a complete understanding and optimization of the processing equipment and conditions are of the utmost importance to ensure consistent quality and performance of rHDPE products.

Extensive research has been conducted to investigate the degradation of different grades of HDPE during mechanical recycling [17–21]. During the recycling process the material is exposed to thermo-mechanical and thermo-oxidative conditions, leading to various reactions such as chain scission, branching, and finally crosslinking [9]. In general, chain scission is the dominant phenomenon regardless of the extrusion temperature [18], but in a thermo-oxidative atmosphere, a competition between chain scission, branching and crosslinking reactions occurs for HDPE [17]. Chain branching can occur during mechanical recycling, but at a lower level compared to chain scission [18, 19]. However, these findings are highly dependent on the polymer grade and extrusion conditions such as temperature, shear rates and duration. Other studies reported that thermo-mechanical degradation at higher temperatures tends to initiate chain scission of longer chains due to their higher entanglement density and consequently a larger force along the chain. As a result, macroradicals are formed and subsequently react with the vinyl terminal unsaturation of other chains, leading to the formation of branched molecules [20–22]. This phenomenon seems to be grade dependent, as Philips type HDPE exhibits a higher level of branched chains compared to the Ziegler-Natta type [22].

The extent of polymer degradation related to recycling is influenced by several factors such as extrusion velocity, time, temperature, and oxygen content. Increasing their level can promote the formation of low molecular weight-chains (or polymers), long chain branching, volatile products, formation of carbonyl-, ether- and olefinic groups, as well as insoluble material due to crosslinking. It is important to note that molecular weight increases and decreases can occur simultaneously as competitive phenomena [23].

The degradation process of HDPE begins with chain scission induced by shear/thermal treatment, forming macroradicals; e.g. of C–C bonds for terminal C-radicals, C–H bonds for in-chain radicals, etc. Subsequently, these radicals undergo disproportionation and/or recombination reactions, resulting in branched and/or crosslinked structures [24, 25]. Such degradation can be macroscopically assessed and quantified by mechanical and rheological properties which are functions of molecular characteristics; e.g. molecular weight and molecular topology. These molecular parameters can be determined via multiple methods, but the most prominent methods are size exclusion chromatography (SEC), Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy, rheology etc. For instance, chain cleavage is known to increase the melt flow index (MFI) [17,19,26], and a reduction of the zero-shear viscosity [18], both parameters associated with lower weight-average molecular weight (M_w) [9,18,23]. On the other hand, chain branching and crosslinking lead to lower MFI [24], and higher shear/extensional viscosity [9,17,20], related to higher M_w [18,22,23]. Extrusion over a long duration, at high temperature and at high shear rates in mechanical recycling results in a higher carbonyl concentration originating from aldehydes, ketones and carboxylic acids, as well as lower vinyl concentration as determined via FTIR. This finding is attributed to polymer chains oxidation and the recombination of polymer chains/macroradicals, respectively [22].

In summary, the degradation of HDPE during mechanical recycling involves a complex balance between chain scission and branching. One

way to determine these changes is via relationships between the rheological and molecular properties during mechanical recycling [27,28].

Previous studies provided valuable insights into the degradation of HDPE properties during mechanical recycling, including rheological and mechanical properties [18,23,24,29–31]. However, there is a lack of research investigating the degradation occurring after successive mechanical recycling, which more accurately mimics the expected recycling scenario in the near future. However, solely relying on SAOS rheology and SEC measurements using only simple SEC detectors (e.g. DRI or viscosity detector) may not be sufficient to determine whether branching occurs during reprocessing. Furthermore, the information obtained regarding the branching structure, such as comb or star topologies during mechanical recycling, is limited.

To address these gaps in the literature, the present study investigates the topological changes associated with the mechanical recycling of HDPE. This is done through a comprehensive analysis combining rheology, SEC, FTIR and nuclear magnetic resonance (NMR) ^1H and ^{13}C measurements. By simultaneously following the rheological properties and molecular characteristics of the material during closed-loop mechanical recycling in a small lab extruder, a more comprehensive understanding of the degradation mechanisms is obtained to identify the specific topological changes. The information obtained provides highly valuable insights into the evolution of HDPE's topological structure and contributes to a deeper understanding of the degradation processes involved in mechanical recycling.

2. Materials and methods

2.1. Materials and mechanical recycling

High density polyethylene (HDPE) (M_w : 94.5 kg/mol, \bar{D} :5.1) with a melting temperature $T_m = 132$ °C was obtained from Service Conseil Sinclair (Canada). The original material was provided as flakes made from post-consumer origin and composed of ground rigid bottles (mixed colors). The melt flow rate (MFR, 190 °C, 2.16 kg) is 6.7 g/10 min (ASTM D1238) and the density 0.96 g/cm³ at 20 °C. The mechanical recycling was performed on a Leistritz ZSE-27 (40 L/D) co-rotating twin-screw extruder with a flat temperature profile (170 °C) with a screw (27 mm diameter) rotating speed of 60 rpm leading to an average residence time of 90 s [2]. The recycled HDPE (rHDPE) was cooled down in a water bath (to room temperature) before being pelletized. The samples were produced via compression molding (Carver automatic press) at 140 °C for 10 min under vacuum with a 13 mm diameter and 1 mm thickness disk mold for small amplitude oscillatory shear (SAOS) rheology and with a rectangular shape (length: 20 mm, width: 10 mm, thickness: 0.5 mm) for uniaxial extensional viscosity measurement.

2.2. Characterization

Small amplitude oscillatory shear (SAOS) rheological properties were investigated using a strain-controlled ARES-G2 rheometer (TA Instruments, USA) in a nitrogen atmosphere ($\text{N}_2 > 99.9$ vol% with a N_2 purifier) to prevent polymer degradation at high temperatures. The experiments were conducted using a parallel plates geometry (13 mm diameter and 1 mm gap). To determine the linear viscoelastic regime, oscillatory strain sweep tests were first performed at a constant angular frequency ($\omega = 100$ rad/s) for a strain range of $\gamma_0 = 0.1$ –100%. Then, oscillatory shear frequency sweeps in the linear regime were conducted at temperatures between 140 and 180 °C. The master curves were constructed by shifting the storage modulus (G') and loss modulus (G'') to a reference temperature ($T_{\text{ref}} = 180$ °C) using the time-temperature superposition (TTS) principle and the rheometer software (Trios, TA instruments, USA). The extensional rheology measurement was performed with the extensional viscosity fixture (EVF) at $T = 140$ °C at a Hencky strain rate of $\dot{\epsilon} = 10$ s⁻¹.

The molecular weight distribution of HDPE was determined using

high temperature size exclusion chromatography (HT-SEC). A PolymerChar system was used with a four-detector configuration including two IR detectors, followed by multiangle laser-light scattering (MALS) detection and a four-capillary bridge viscometer. The 3 mixed bed columns (Tosoh TSKgel HT2, 30 μm , 7.8 \times 300 mm) protected by a guard column (Tosoh, 30 μm , 7.5 \times 75 mm) were calibrated using low dispersity polystyrene (PS) standards with peak molecular weights (Mp) ranging from 890 g/mol to 1 \times 10⁷ g/mol. The eluent was 1,2,4-trichlorobenzene (TCB) with a flow rate of 1 mL/min at 150 $^{\circ}\text{C}$ (stabilized with butylated hydroxytoluene, BHT). Each sample was dissolved in solution at a concentration of about 1 mg/mL and injected (injection volume of 200 μL) into the columns using an autosampler. The solution was not filtered before injection. Signals from all detectors were processed by GPCOne, an integrated software package from PolymerChar.

To identify possible branching and oxidation products in rHDPE, Fourier transform infrared spectroscopy (FTIR) with DTGS detector was done on a Thermo Scientific Nicolet iS50 ATR. The analysis was performed at room temperature with a scanning range from 800 to 4000 cm^{-1} and a spectral resolution of 4 cm^{-1} . For each spectrum, 64 scans were accumulated and the absorbance was recorded as a function of the wavenumber. Additionally, the HDPE samples (ca. 10 mg) were dissolved in 1 mL of 1,1,2,2-TCE- d_2 at high temperature (373 K [32]) for ^1H and ^{13}C nuclear magnetic resonance (NMR) characterization. The prepared solutions were analyzed by a Bruker AVANCE III HD 700 MHz NMR spectrometer. Mnova v14.3 (Mestrelab Research) was used for data processing.

3. Results and discussion

3.1. Rheological properties

The combination of small amplitude oscillatory shear (SAOS) rheology and time-temperature-superposition (TTS) provides an effective method to establish relationships between molecular structures and macroscopic properties. Fig. 1(a) compares the frequency dependent absolute value of the complex viscosity of recycled HDPE from different generations under identical extrusion conditions to determine the effect of extrusion cycles. At high angular frequencies, the complex viscosity shows limited difference among the different extrusion generations. Such differences increase with decreasing angular frequency. This means that the mechanical recycling of HDPE causes negligible change in the shear viscosity for the selected processing shear rate (e.g. typical industrial processing condition are around shear rates of 100–1000 s^{-1}) and temperature (170 $^{\circ}\text{C}$), which is in agreement with the literature [9]. To compare the zero-shear viscosity (η_0) of HDPE from different extrusion generations, the experimental data were fitted to the Carreau-Yasuda model (Fig. A1) and the zero-shear viscosity (η_0) is plotted in Fig. 1(b). Limited changes (below 20%) in η_0 are observed from the 1st to 4th generation of rHDPE. However, a 6-fold increase of η_0 is observed between the 4th (3580 Pa s) and 8th (23,120 Pa s) generation. Assuming linear chains and a cubic dependence of η_0 on the weight average molecular weight (M_w), this would correspond to an increase in M_w by about 82% towards the 8th generation. Similarly, after 8 to 16 cycles of mechanical extrusion, η_0 reaches a plateau. Please note that 10 cycles would be equivalent to 900 s residence time in the extruder at 170 $^{\circ}\text{C}$. Such rheological changes must be linked to variations in the molecular structure during mechanical extrusion. Consequently, unless chain extension occurs and the M_w increases, higher

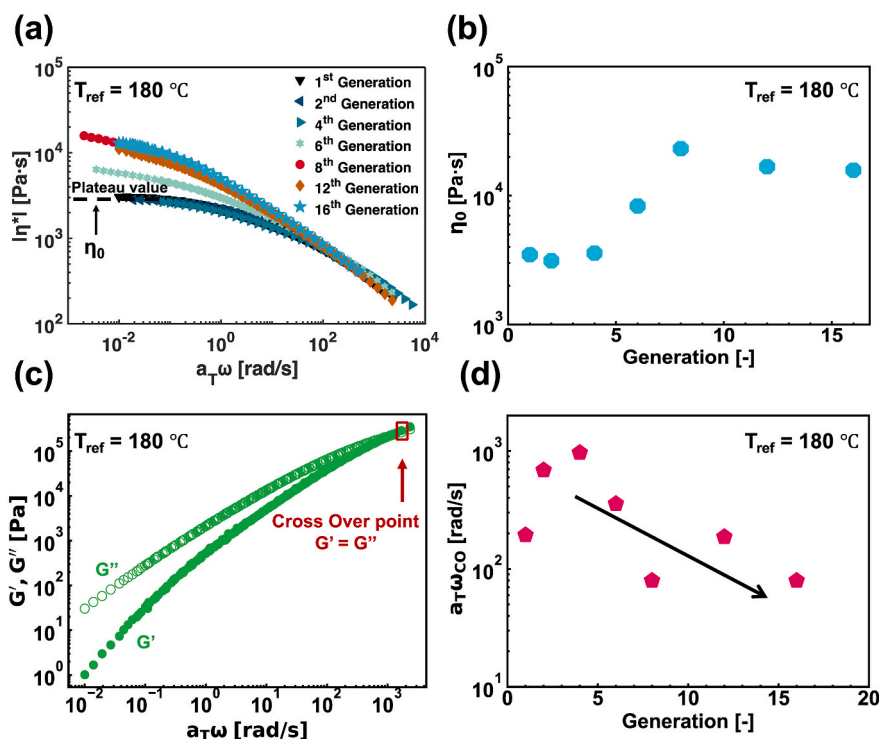


Fig. 1. (a) Absolute value of the complex viscosity as a function of shifted angular frequency for rHDPE under identical mechanical recycling conditions. The reference temperature for TTS is set as $T_{\text{ref}} = 180$ $^{\circ}\text{C}$. (b) Zero-shear viscosity (η_0) as a function of the extrusion generations. The results show a 6-fold increase of η_0 only between the 4th and 8th generation out of a total of 16 generations. (c) Graphical definition of the cross-over point ($G' = G''$) in a master curve of the virgin HDPE. (d) Cross-over frequency ($a_T\omega_{\text{CO}}$) as a function of the generation number. The arrow is only for visual guidance. The complete raw data for G' and G'' as a function of angular frequency is shown in Fig. A2. In general, the cross-over frequency decreases with recycling generation indicating an increase of the relaxation time (τ) of polymer chains. This behavior can be associated with longer chain or branched chain structures and is consistent with the zero-shear viscosity increase. The black line with the arrow is only for visual guidance.

η_0 associated with mechanical recycling must be related to branching or crosslinking.

The variation in the cross-over frequency across different recycling generations shows an inverse correlation as observed in Fig. 1(c and d). This correlation implies that rHDPE with a higher number of extrusion generations exhibits a longer chain relaxation time (τ). This longer relaxation time can be attributed to increased constraints on the polymer chains mobility, potentially arising from increases in the molecular weight of linear chains, as well as branched or crosslinked structures. However, an increase in molecular weight of about 80% for linear chains is not likely and not confirmed by SEC indicating marginal change in M_w , as the uncertainty associated with SEC is around 10%. Consequently, the observed increase in viscosity and lower cross-over frequency can be attributed to a long-chain branched topology. It is known, that for stars or combs, the relaxation time increases exponentially with increasing arm length [33,34]. Thus, a decrease in the cross-over frequency is indicative of branching. In addition, the slope of G' in Fig. A2 decreases by 14% and 20% for the 6th and 16th recycling generations respectively, compared to the first generation. This observation supports the presence of branched structures, leading to a wider distribution of relaxation time. This wider distribution contributes to a more gradual transition from an elastic to a viscous behavior.

The evidence presented indicates a dominant branching process during mechanical extrusion. However, the decrease trend in the zero-shear viscosity (Fig. 1(b)) and the increasing crossover frequency (Fig. 1(d)) observed up to the 4th recycling generation suggest a competition between chain scission and branching [35].

To further reveal the topological structure changes of rHDPE with the number of extrusion generations, the van Gurp-Palmen (v-GP) plots are shown in Fig. 2. The v-GP plot enables to investigate the frequency dependent viscoelastic properties, independent of their molecular weight at first approximation [36]. The presence of a second minimum or a shoulder at low $|G^*|$ values can be caused by either branching or a bimodal chain distribution for linear polymers [37,38]. The high and low $|G^*|$ minimum correspond, in a branched topology, to the relaxation of the arm and backbone, respectively. The curves change from a concave shape (1st, 4th and 6th generation) to convex (12th and 16th generation) with shoulders. Compared to the v-GP plot of branched model systems, similarities between the rHDPE from the 12th and 16th generations and data reported in the literature for branched systems, such as combs or asymmetric stars, is striking [38,39].

In Fig. 2(b), $|G^*|$ at a phase angle of 60° ($|G^*|_{\delta=60^\circ}$), which is a parameter often used in industry to quantify branching, is plotted as a function of extrusion generations. The absolute value $|G^*|_{\delta=60^\circ}$ shows marginal changes up to the 4th generation due a competition (equilibrium) between chain scissor and branching. However, the decreasing trend with further extrusion generations can be related to an increase in

either arms' length or a higher number of arms as observed in previous studies [38,39]. Therefore, the assumption that chain branching occurred during the mechanical recycling of HDPE seems reasonable.

To investigate the elongation viscosity, melt strength was also quantified in addition to SAOS. The melt strength refers to the ability of a material to resist deformation under extensional flow, indicating the resistance of its molecular chains to flow and stretching. Strain hardening, a characteristic increase of the stress to elongational deformation, occurs for PE only when a polymer chain is stretched between at least two branching points. It can thus be used to determine the presence of long-chain branching [40–43]. Consequently, this fingerprint is used to identify different topological structures in rHDPE. The time-dependent tensile stress growth coefficient for extrusion generation 1, 6, 8 and 16 are shown in Fig. 3. At a Hencky strain rate $\dot{\epsilon} = 10 \text{ s}^{-1}$, no significant strain hardening is observed in all the rHDPE. This is at first surprising since branching in the rHDPE is expected to cause strain hardening. Possible explanation for this result is the degree of branching in the rHDPE being similar or lower than the original (linear) matrix or the generation of (a-)symmetric star-like structures.

3.2. Molecular characterization by size exclusion chromatography (SEC)

Although rheological measurements offer valuable insights into the

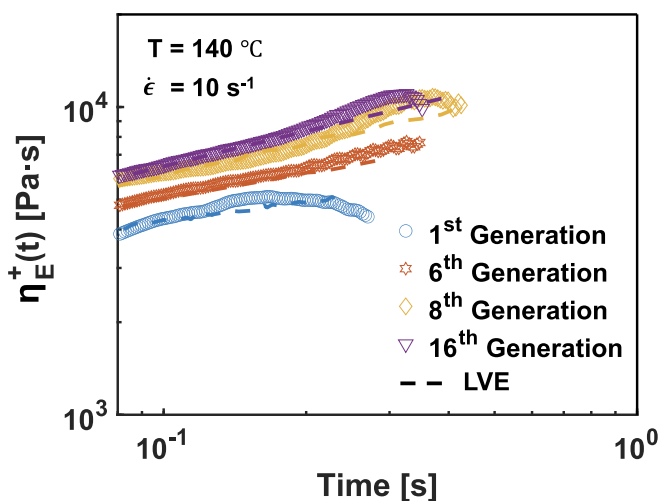


Fig. 3. Time-dependent tensile stress growth coefficient $\eta_E^+(t)$ for recycled HDPE from different extrusion generations measured at 140°C and $\dot{\epsilon} = 10 \text{ s}^{-1}$. No strain-hardening effect is observed for these rHDPE for the temperatures and strain rates applied.

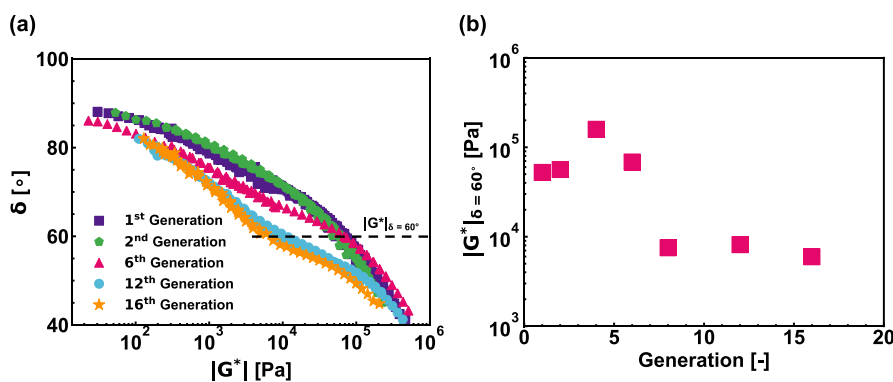


Fig. 2. (a) van Gurp-Palmen (v-GP) plot (phase angle δ as a function of the absolute complex modulus $|G^*|$). With increasing number of extrusion generations, the shape of the v-GP-plots changes from concave to convex and gradually reveals a shoulder (12th and 16th generation) indicating chain branching. (b) $|G^*|_{\delta=60^\circ}$ as a function extrusion generation indicating higher molecular weight of side arms by either increasing arm length and/or number of arms in a branched system.

topological structure of rHDPE, ambiguities remain regarding the exact changes in the molecular mass distribution and branching. To reach a more specific conclusion, an additional molecular characterization is needed. First, Fig. 4(a) presents the mass recovery observed during SEC measurement to investigate crosslinking. In particular, a significant proportion (>95%) of the dissolved HDPE in TCB is recovered from the column. This clearly shows that no extensive crosslinking occurs in the samples even after 16 extrusion cycles, as highly crosslinked polymers are unable to dissolve in the solvent and be recovered after the size exclusion chromatography. This strongly suggests that chain branching dominantly occurs during the mechanical recycling for the conditions used. Several other parameters, such as changes in the rheological properties and the absence of gelation, support the presence of chain branching in the recycled HDPE. These findings provide evidence of structure modifications in the form of chain branching during rHDPE reprocessing.

Understanding the development of chain branching during mechanical extrusion is of high importance as it offers valuable guidance for future kinetic studies. Investigating the mechanisms and dynamics of chain branching in this context can provide insights into the processes and help to optimize the extrusion conditions for specific recycle properties. The molecular weight distributions (MWD) presented in Fig. 4(b) show minimal variation between the different generations.

Quantitative analysis of the molecular information, including M_w and \mathcal{D} , is shown in Fig. 4(c). The data reveal that M_w decreases by 11% from the 1st generation ($M_w = 95$ kg/mol) to the 16th generation ($M_w = 85$ kg/mol). However, the dispersity remains relatively constant from generation to generation ($\mathcal{D} = 4.5$ –5). This suggests that mechanical recycling decreases the weight average molecular weight (M_w), but maintains a relatively consistent dispersity across the different generations under the applied conditions.

3.3. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR)

To assess the chemical changes in rHDPE, Fig. 5 presents the FTIR spectra which can detect chain degradation. Characteristic peaks appear at 2850 cm^{-1} and 2912 cm^{-1} corresponding to the CH stretching in $-\text{CH}_2-$ groups. Another notable peak at 1470 cm^{-1} represents the CH bending band of CH_2 groups, while the peaks at 722 cm^{-1} indicates the CH_2 rocking mode within the CH_2 groups forming the backbone structure. However, no peaks around 1720 cm^{-1} (indicative of carbonyl groups formed due to thermo-oxidation) are present in the rHDPE

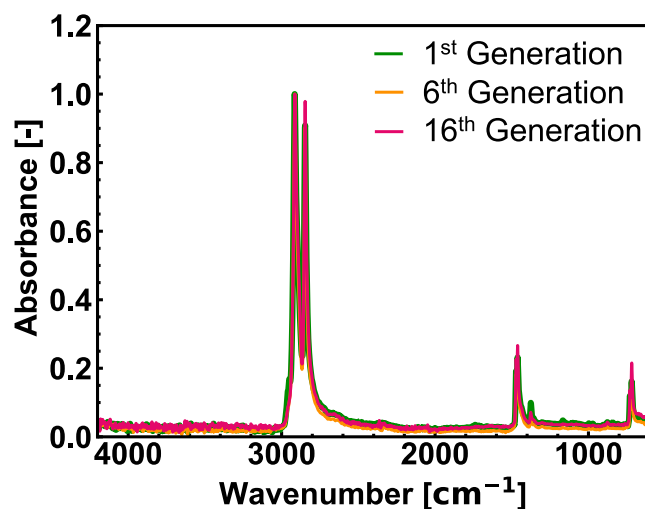


Fig. 5. ATR-FTIR spectra of reprocessed HDPE. There is no obvious effect of oxidation identified in the spectra of the recyclates.

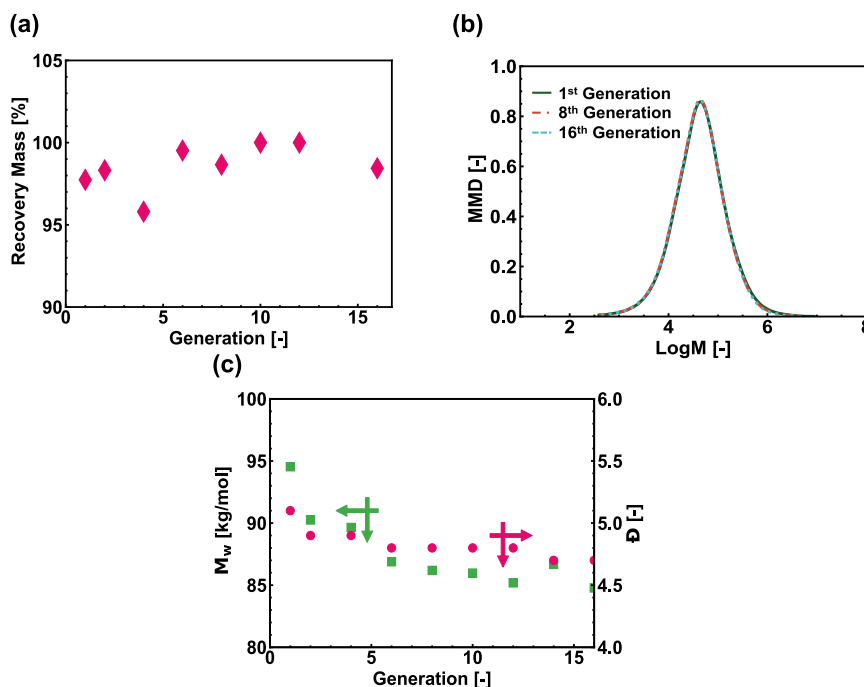


Fig. 4. (a) Mass recovery from high temperature SEC measurements as a function of the recycling generation. A significant amount (>95%) of mass is recovered during SEC measurement after 4 extrusion generations indicating that negligible crosslinking occurred in the samples. (b) Molar mass distribution (MMD) of rHDPE from different generations, M in g/mol. (c) Weight averaged molecular weight (M_w) and polydispersity index (\mathcal{D}) as a function of extrusion generations. The apparent M_w decreases by 11% from the 1st generation ($M_w = 95$ kg/mol) to the 16th generation ($M_w = 85$ kg/mol). However, the dispersity was almost constant (less than 5% variation) between the generations.

(see Fig. A3). This suggests that no oxidative degradation occurred during mechanical recycling under the conditions used in this study.

Fig. 6 displays the ^1H and ^{13}C NMR spectra of both virgin and recycled HDPE, which have undergone multiple cycles (6th and 16th) of mechanical extrusion. The most prominent resonance peaks are observed at 1.4 ppm in ^1H NMR (Fig. 6(a)) and 30 ppm in ^{13}C NMR (Fig. 6(b)). These peaks correspond to the methylene (CH_2 -) groups found in the backbone or branched chains of HDPE. But additional peaks around 46 ppm are observed in the ^{13}C spectra of the recyclates, which are absent in the original HDPE spectrum. These peaks could originate from either a CH_2 -group (typically seen in the range of 15–55 ppm) or a CH - group (typically observed in the range of 20–60 ppm) [44]. This suggests an increased presence of branching for the recycled HDPE compared to the original material. This increase in branching leads to an increase in CH_3 - end groups and is further supported by the appearance of more intense peaks in ^1H spectra between 0.7 and 1.3 ppm in the recycled samples compared to the original HDPE. Furthermore, the number of end-groups containing CH_3 - increases as the branched content increases as evidenced by the peak at 1.3 ppm in Fig. 6(a). This peak

most likely corresponds to the CH_2 - group (typically found in the range of 1.2–1.4 ppm) and overlaps with a potential peak originating from CH_3 . Another piece of evidence for increased branching is the emergence of a peak associated with a CH - group (branching point), typically seen at 1.4–1.7 ppm, which is visible in the recyclates but not in the original HDPE (Fig. 6(a)).

On the other hand, the ^1H spectra of the recycled samples indicate the presence of oxidation products. The minor peaks observed in the range of 2.0–2.5 ppm can be attributed to protons adjacent to carbonyl groups. Additionally, the peaks between 3.7 ppm and 4.3 ppm are indicative of protons adjacent to the oxygen in carbonyl-groups, including ether (R-O-CH , 3.2–3.8 ppm) and ester (R-(CO)-OCH , 3.5–4.8 ppm) [45,46]. The semi-quantitative comparison of chemical groups in ^1H spectra can be found in Table 1. This information is corroborated by the ^{13}C spectra, which exhibit peaks around 35–65 ppm and even higher chemical shift (120–140 ppm in Fig. 6(b)) corresponding to vinyl or aromatic groups or any carbon atom adjacent to oxygen in a carbonyl group [45,46]. This information is not available from FTIR spectra (Fig. 5), due to the limited selectivity of IR

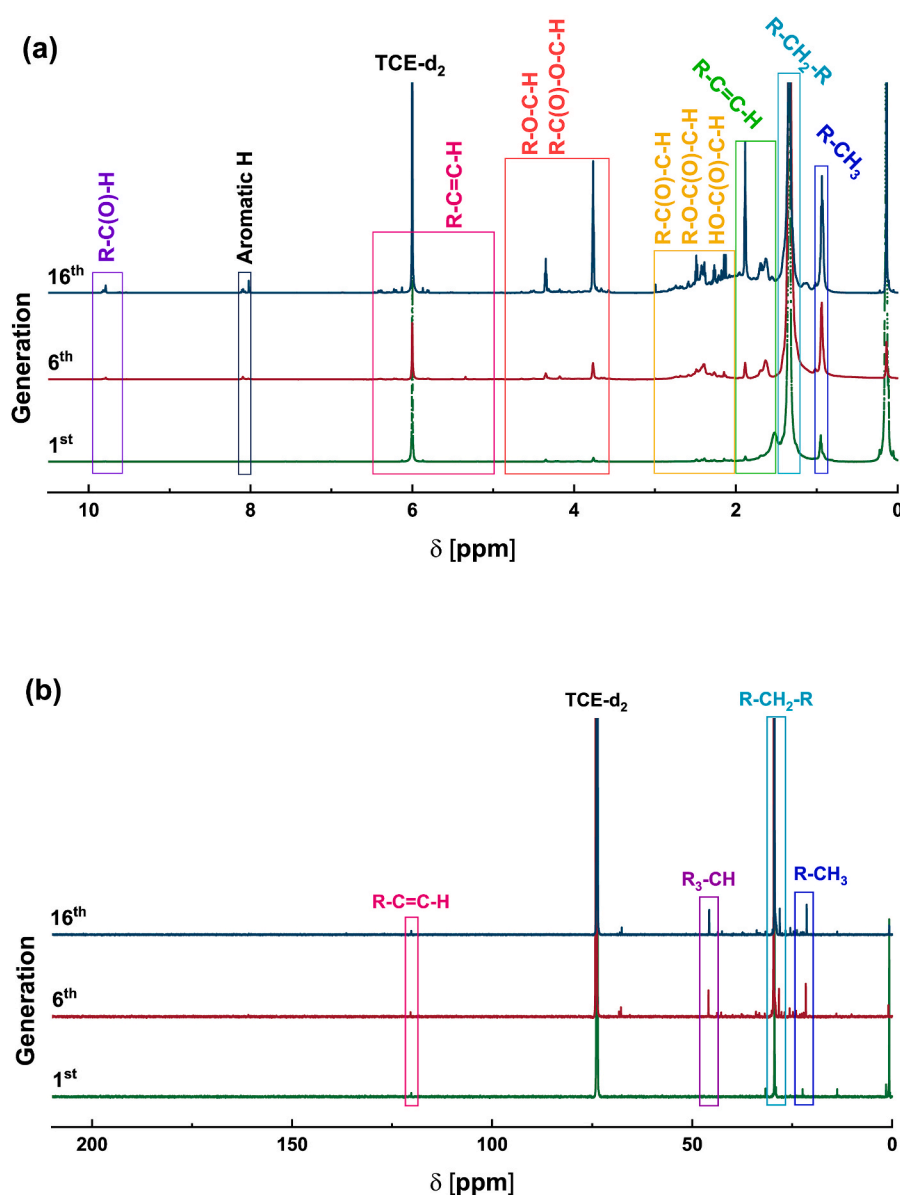


Fig. 6. NMR spectra of the original, 6th and 16th generation of rHDPE: (a) ^1H and (b) ^{13}C . Possible branching points are found from CH_2 - and CH_3 - groups in the recyclates due to the appearance of a peak around 46 ppm. The NMR spectra also identify possible oxidation during mechanical recycling.

Table 1

Integration range and normalized integrals for the different chemical groups identified in the ^1H NMR spectra. The respective spectra are shown in Fig. 6.

ppm-range	Protons	Integral		
		1st Generation	6th Generation	16th Generation
0.50–10.5	Total	100	100	100
0.85–1.00	R-CH ₃	2.56	4.68	6.72
1.20–1.50	R-CH ₂ -R	84.94	77.29	45.72
1.50–2.00	R-C=C-H	7.64	5.80	14.37
2.00–3.00	R-C(O)-C-H	1.38	6.87	14.51
3.50–4.85	R-O-C(O)-C-H	0.47	1.84	5.58
	R-O-C-H			
	R-C(O)-O-C-H			
5.00–6.50	R-C=C-H	5.19	1.59	8.20
8.00–8.15	Aromatic H	0.01	0.12	0.28
9.70–9.85	R-C(O)-H	0.01	0.07	0.21

spectroscopy. Furthermore, IR spectroscopy is not quantitative and needs calibration, as the intensity (integral) of a peak also depends on the electrical dipole moment of the investigated structure.

Based on the information obtained via rheological and molecular characterizations, there is strong indication that branching occurs during the mechanical recycling of HDPE under the experimental conditions studied. However, the topological structure of these branched chains remains elusive and challenging to elucidate via experimental techniques alone. To shed more light on this ambiguity, the branch-on-branch (BoB) model based on molecular dynamics will be used. This model aims to characterize the linear viscoelastic behaviour of rHDPE and offers a means to explore the topological structure changes within the material.

3.4. Proposed chain topology

Despite the rheological measurements in shear and elongation, as well as molecular characterization via SEC, FTIR and NMR suggesting possible chain branching during mechanical recycling, the exact composition and chain topology remain unclear due to the statistical nature of this problem. The recyclates are most likely composed of thousands of different polymer molecules, each having different chain structures. Conventional methods, such as SEC, FTIR and NMR, struggle to provide detailed topological information. However, rheological analyses, especially linear viscoelasticity coupled with constitutive modelling [34,42,47–50], can provide valuable insight into different topological features. This is because rheology amplifies subtle differences in molecular structure in a non-linear way, while spectroscopy often responds linearly to molecular changes. Constitutive models based on molecular dynamics, such as the “branch-on-branch” (BoB) model [51–57], are able to provide accurate descriptions of the linear viscoelastic behavior of polymers with varying chain topologies using a suitable set of model parameters; e.g. branching kinetics, activation energies, etc. [58]. The fundamental concept behind the BoB constitutive model is the hierarchical relaxation of branched structures [59]. This model can generate relaxation spectra by calculating the stress relaxation modulus, considering the effects of different relaxation pathways along the branched molecule occurring at various time scales during the relaxation process [51]. The relaxation pathways include processes such as relaxation occurring more rapidly than the entanglement time, arm-retraction, side arm motion, retraction of compound arm, reptation and constraint-release Rouse motion. Using this comprehensive BoB model, it becomes possible to predict the linear viscoelastic behaviour of branched polymers with diverse topological structures. These structures may include symmetric-star, asymmetric-star, H-type, comb, Cayley tree-like chains, etc. Numerous studies

showed that the BoB model provides accurate predictions of the linear viscoelastic behavior of branched chains when compared to the experimental results of model branched polymers over several decades of dynamic range [51,58,60]. A deviation below 7% between experimental results and model predictions of moduli is evident for the BoB model, but this may vary for the lower end of the frequency region. For a more detailed understanding of the model and algorithm, please refer to the original publication [51].

To differentiate the composition and chain structure within the recyclates, the BoB model was used to fit the oscillatory shear rheological data, including the dynamic modulus, phase angle and complex viscosity. The key challenge lies in determining the appropriate molecular structure for various compositions. Based on the experimental findings, it appears that the current recyclates do not exhibit long chain branching structures, offering valuable guidance in selecting potential molecular topologies. Therefore, the recyclates may consist of linear, star-shaped and comb-like molecules. The modelling results of linear viscoelasticity of the linear (original) and branched (recycled) HDPE are presented in Fig. 7(a and b). The predicted lines provide an excellent description of the experimental data and suggest that the investigated recyclates contain both linear and branched structures, such as star-shaped and comb-like (Table 2). However, the linear viscoelastic behavior of branched polymers cannot be well described by linear topology alone as shown in Fig. 7(b). This confirms the presence of branched structures in the recyclates. Based on the v-GP plots comparing the experimental results with BoB-B model prediction as shown in Fig. 7(c), this confirms the model’s suitability in capturing the random (short) chain branching topology evident in rheological characterizations. This analysis represents a promising direction for further investigations into the degradation/branching kinetics of (mechanical) recycling processes in terms of determination and quantification.

From all the information obtained, a conclusive picture of the topological evolution of HDPE with increasing mechanical recycling is possible. Thermo-mechanical degradation plays a crucial role in the mechanical recycling of HDPE, leading on the one hand to chain scission and a subsequent slight decrease in molecular weight as observed via SEC characterization. On the other hand, as the material goes through more mechanical extrusion cycles, random branching develops resulting in higher viscosity.

A comparison of the v-GP plots of rHDPE with a branched-structure model system shows some similarities and a random-branched mechanism can be used to explain the phenomena occurring during the mechanical recycling of HDPE. Investigations by SEC and NMR also support this hypothesis. From the rheological BoB constitutive model, it is possible to predict compositions and molecular topologies, such as star/comb-shaped or randomly branched structures, within the recyclates. Consequently, a mechanism involving the formation of random branches, especially short chain branching, within the polymer chains, similar to a star/randomly branched structures, rather than a long chain branched structure due to the absence of strain hardening in elongational flow is possible. Based on these conclusions, typical structures are proposed in Fig. 8.

These findings provide valuable insights into the complex processes occurring during the mechanical recycling of HDPE. The results of thermo-mechanical degradation are chain scission and random branching having also an effect on the molecular weight distribution. The rheological behavior and molecular spectroscopy also help to unravel the underlying mechanisms to understand, detect and even quantify the properties changes during mechanical recycling.

4. Conclusion

Mechanical recycling of high-density polyethylene (HDPE) through successive extrusion cycles gradually modifies its topological structure. This study investigated in details the mechanisms involved by following changes in the molecular structure and rheological behavior using small

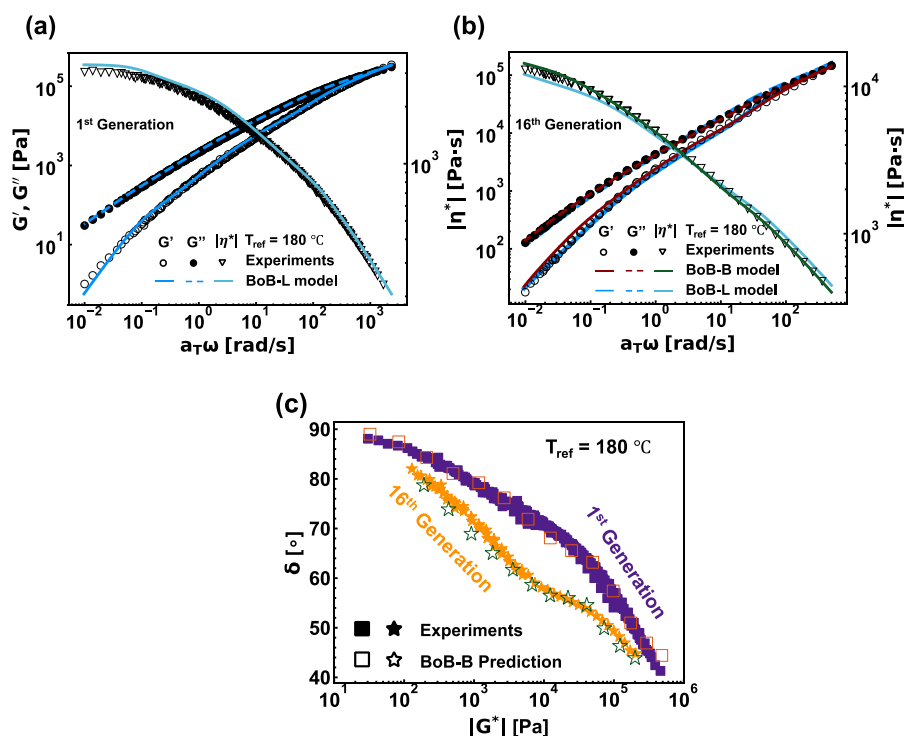


Fig. 7. Linear viscoelastic G' , G'' and $|\eta^*|$ master curves at $T = 180\text{ }^\circ\text{C}$ for the original and 16th generation recycled HDPE. (a) The BoB model can fit the first-generation HDPE assuming only a linear topology (BoB-L). (b) For the 16th generation, additional branched components, such as asymmetric star and comb-like molecules, each about 10% vol., are needed in the model (BoB-B) to better predict the experimental data. (c) Examination of the v-GP plot, comparing experimental findings with predictions from the BoB-B model, reinforces the model's suitability in accurately capturing the random (short) chain branching topology as observed via rheological characterizations.

Table 2

Parameters used to fit the linear viscoelastic curves for the original and the 16th recycled HDPE samples.

HDPE	Linear chain		Star-like topology		q^c	Comb-like topology			
	φ^a	M_w/\bar{D}	φ	M_a/\bar{D}^b		φ	M_a/\bar{D}	M_b/\bar{D}^b	q
Original	1	94.5/5.1	–	–	–	–	–	–	
Recycled	0.8	85/5.1	0.1	L:85 S:42.5/5.1 ^d	3	0.1	42.5/5.1	85/5.1	6

^a φ stands for the volume fraction of each component.

^b M_a and M_b are the molecular weight of the side arm and backbone, respectively. The units for all molecular weights are $\text{kg}\cdot\text{mol}^{-1}$. \bar{D} is the polydispersity (PDI).

^c q is the arm number.

^d L and S are abbreviations for long chain and short chain, respectively. Here, the short chain is defined as half M_w of the long chain.

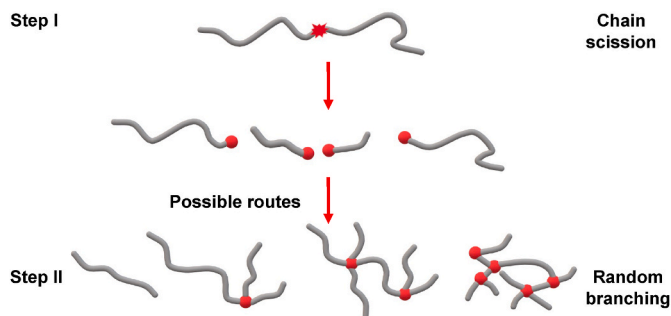


Fig. 8. Proposed chain dynamics of HDPE during mechanical recycling. Fragments formed during mechanical extrusion develop randomly branched structures, such as star-like and comb-shaped chains, according to the information obtained from analytical characterizations and the BoB modeling.

amplitude oscillatory shear (SAOS) and elongation rheology tests. In addition, high temperature size exclusion chromatography (HT-SEC), Fourier transform infrared (FTIR) spectroscopy and one dimensional ^1H , ^{13}C nuclear magnetic resonance (NMR) provided information on the molecular characteristics. The combined results enabled the analysis of topological and chemical structure changes of recycled HDPE.

The results revealed that for the first 4 recycling cycles in the extruder at $170\text{ }^\circ\text{C}$ and a typical residence time of 90 s, no significant change in the rheological properties occurred, but an increase of the zero-shear viscosity (η_0) by a factor of 6 occurred between cycles 4 and 8. However, SEC measurements indicated a 11% decrease in the weight average molecular weight M_w between the 1st and 16th generation. A thorough analysis of the rheological behaviors was performed via v-GP plots where possible chain branching in the rHDPE material was detected. Since no strain-hardening effect was observed under uniaxial extension, dominant long-chain branching can be ruled out, but rather short chain branching could take place. Furthermore, extensive cross-linking (gelation) can also be eliminated since more than 95% mass recovery from SEC characterization was obtained for all the recyclates. Instead, the presence of randomly branched structures is most likely to

occur, as confirmed via ^1H and ^{13}C NMR spectra. Furthermore, a rheological model (branch-on-branch, BoB) was used to determine the possible branching topologies (star-shaped and other randomly branched structures and compositions) in the recyclates.

Thermo-mechanical degradation results in the formation of a random-branching structure, including short chain branching contributing to the increased viscosity observed. However, a more comprehensive kinetic study of the degradation mechanism during mechanical recycling (extrusion) is still lacking. Furthermore, linking molecular evolution during mechanical recycling with mechanical properties is of importance for future studies. Thus, a complete understanding of the degradation mechanism would enable the design of suitable additives to preserve the properties and applications of recycled HDPE, as well as other polymers in general. These additives might include radical scavengers or other polymer additives to control the mechanical properties in both the melt and solid state.

CRediT authorship contribution statement

Jian Zhang: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Valerian Hirschberg:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis, Conceptualization. **Anika Goecke:** Writing – original draft, Formal analysis. **Manfred Wilhelm:** Writing – review & editing, Supervision, Resources. **Wei Yu:** Writing – review & editing, Software, Methodology. **Michael Orfgen:** Writing –

original draft, Formal analysis. **Denis Rodrigue:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendices.

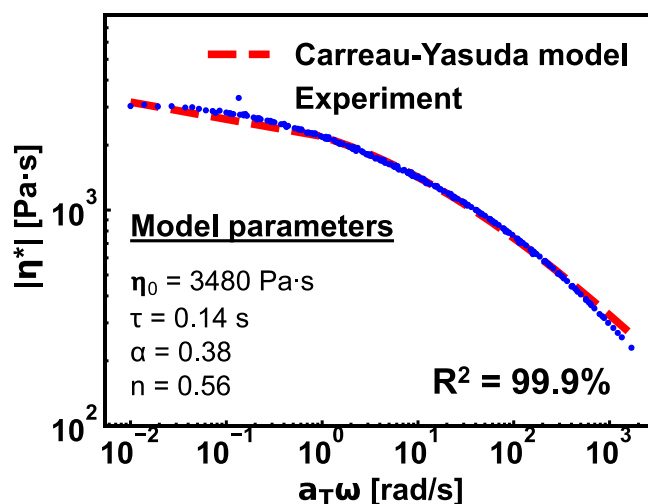


Fig. A1. Comparison between the experimental data and prediction from the Carreau-Yasuda model (Eq. (A1)). The experimental data are obtained from the SAOS rheological measurements of the 2nd rHDPE extruded at 170 °C and 60 rpm for 90 s. The fitting parameters are $\eta_0 = 3480$ Pa s, $\tau = 0.14$ s, $n = 0.56$ and $\alpha = 0.38$.

The value of the complex viscosity ($|\eta^*|$) as a function of angular frequency (ω) can be approximated by the Carreau-Yasuda model which can capture the features of experimental results as:

$$|\eta^*(\omega)| = \eta_0 [1 + (\tau\omega)^\alpha]^{\frac{n-1}{\alpha}} \quad (\text{A1})$$

where,

η_0 is the zero-shear viscosity,

τ is a characteristic time,

n is the power-law index in the shear-thinning region,

α is a parameter related to the width of the transition between the zero- and shear-thinning regions.

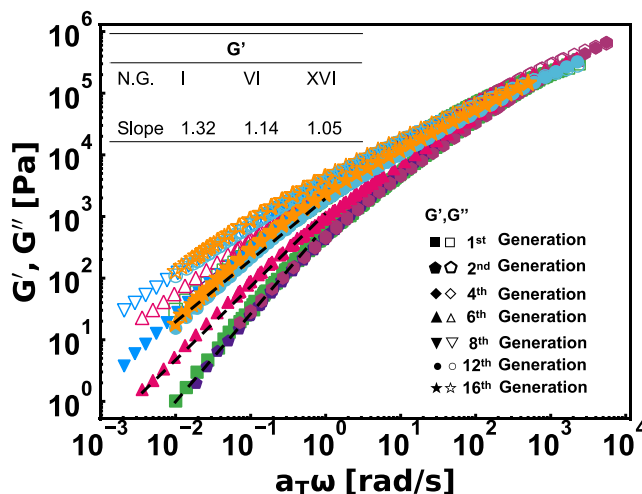


Fig. A2. Storage modulus (G') and loss modulus (G'') of rHDPE from different recycling generations. The reference temperature for TTS is set as $T_{ref} = 180$ °C.

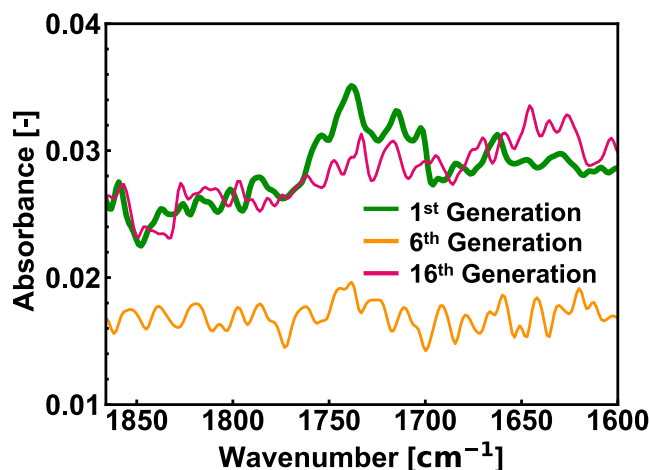


Fig. A3. ATR-FTIR spectra of reprocessed HDPE. There is no obvious effect of oxidation identified in the spectra of the recyclates. The spectra region between 1600 and 1850 cm^{-1} has been magnified to enhance spectral resolution and sensitivity. There are no discernible peaks around 1720 cm^{-1} indicative of carbonyl groups formed due to thermo-oxidation present in all the rHDPE samples.

Branch-on-Branch modeling

The Branch-on-Branch (BoB) simulation was conducted with the RepTate ToolKit. The configuration file describing the composition and molecular morphology can be accessed through Mendeley Data, Zhang, Jian (2023), “PolyConfig”, Mendeley Data, V2, <https://doi.org/10.17632/5xz2n6cmsh.2>.

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