

Effect of mechanical recycling on molecular structure and rheological properties of blends of Phillips and Ziegler-Natta catalyst high density polyethylene (HDPE)

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ABSTRACT

High-density polyethylene (HDPE) represents a major fraction of global plastic production and waste. Industrially, HDPE is mainly produced using Ziegler-Natta (ZN) and Phillips (P) catalysts, which yield distinctly different molecular features such as terminal vinyl groups in P-HDPE. As shown recently by our group for two blow moulding grade ZN- and P-HDPE, ZN- and P-HDPE have complementary degradation pathways during mechanical recycling. ZN-HDPE mainly undergoes chain scission, whereas P-HDPE tends to form star-like branched to crosslinked structures due to the terminal vinyl groups. This results in completely different processing properties, i.e., the complex viscosity at low frequencies increases for P-HDPE but decreases for ZN-HDPE. In realistic post-consumer waste streams, HDPE mixtures derived from both catalyst systems are inevitably, underlining the need to understand the degradation pathways of their blends. We investigate the molecular and rheological evolution of blends of ZN-HDPE and P-HDPE with varying compositions during simulated mechanical recycling in a twin-screw extruder at 210 °C and 180 rpm for 10, 20 and 30 min. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), cross-fractionation chromatography (CFC), melt flow index (MFI), small amplitude oscillatory shear (SAOS), extensional rheology as well as mechanical solid-state properties were used to analyse the recycled materials. The analysis reveals that increasing the P-HDPE to ZN-HDPE ratio leads during mechanical recycling to an increased content of star-like branched/crosslinked chains. This is quantified by a decreasing degree of crystallinity and weight average molecular weight, whereas viscosity at low frequencies drastically increased. For instance, the low-frequency viscosity of rZN-HDPE after 10 min increased by 30 % compared to vZN-HDPE, but the addition of 10 or 30 wt% of P-HDPE resulted in a viscosity increase of about 300 % and 600 %, respectively. The here presented findings provide mechanistic insight into degradation pathways in mixed-catalyst HDPE post-consumer waste streams and offer guidance for improving recycling and upcycling strategies for more realistic polyolefin waste stream mixtures.

1. Introduction

Plastic materials have become indispensable in modern society due to their versatility, durability, and low production cost. Global annual plastic production has recently exceeded ~418 million tons, with polyolefins accounting for more than half of the total demand [1]. Among polymer applications, packaging represents the largest sector, consuming approximately 35-40 % of all plastics produced worldwide. Other major applications include building and construction (~16 %),

automotive (~8-10 %), electrical and electronics (~6 %), and consumer products (~10 - 12 %) [2-4]. Packaging materials are predominantly composed of polyolefins and polyesters, including different types of polyethylene (PE), isotactic polypropylene (iPP), polyethylene terephthalate (PET), and polystyrene (PS) [5-7]. Within the polyethylene family, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) are widely used in rigid and flexible packaging due to their favourable mechanical performance, chemical resistance, and processability [8]. Despite their

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advantages, packaging plastics present significant environmental challenges due to its short service lifetimes and are often discarded after a single use [1]. Mechanical recycling is currently the most widely implemented method for recovering polyolefin waste due to its relatively low cost and energy demand compared with chemical recycling processes. However, recycling of packaging materials is complicated by e.g. contaminations, additives, and the mixing of different polymer grades [9,10]. Repeated thermal and mechanical processing can induce chemical and physical degradation, resulting in changes in molecular weight, branching structure, crystallinity, and thus rheological properties [11–15]. These structural modifications often lead to deterioration in processability and mechanical performance of recycled plastics [15–20]. Understanding degradation mechanisms is essential because they determine how polymer structure evolves during processing, use, and recycling, and thus directly control properties such as mechanical strength, toughness, and processability. When it is clear whether a polymer mainly undergoes chain scission, crosslinking, oxidation, or hydrolysis, it becomes possible to predict changes in molecular weight, viscosity and crystallinity over multiple recycling cycles [14,21–28].

High-density polyethylene (HDPE) is one of the most important polyolefins used in packaging applications such as bottles, containers, caps, and household goods [29]. It has a highly linear molecular structure with minimal short-chain branching, enabling efficient chain packing, resulting in high crystallinity, stiffness, and chemical resistance. Industrial HDPE is mainly produced via coordination polymerization of ethylene using heterogeneous Ziegler-Natta (ZN) [30,31] and Phillips (P) [32–34] catalysts, which generate polymers with different molecular weight distributions and terminal vinyl contents. These

architectural differences have a direct impact on thermo-oxidative degradation during melt processing and recycling [35]. For ZN-HDPE, degradation is typically dominated by chain scission, causing molecular weight reduction and increased melt flow. In contrast, P-HDPE, with its higher vinyl end-group content, more readily undergoes branching reactions during reprocessing, often leading to an increase in molecular weight and decreased melt flowability, as shown schematically in Fig. 1. This degradation behaviour is reported in our previous work [36] and the virgin and recycled ZN-HDPE and P-HDPE molecular changes parameter such as complex viscosity ($|\eta^*|$), molecular weight (M_w), MFI and vinyl index are given in Table 1.

In realistic post-consumer streams of PE, contaminations are considered to be other polymers as e.g., iPP, which is despite its chemical similarity not miscible. However, even for conventionally considered uncontaminated HDPE PCW, HDPE grades produced with different catalyst systems enter the same stream and cannot be practically separated by catalyst origin. As a result, mechanically recycled HDPE in the PCW stream will most of the time consist of blends of ZN-HDPE and P-HDPE, in which competing chain scission and branching reactions occur simultaneously during reprocessing. This complex interplay can significantly alter molecular weight distribution, branching topology, crystallinity, and rheological behaviour, as shown in Fig. 1. Yet the degradation mechanisms and structure-property evolution of mixed-catalyst HDPE streams has not been investigated in detail. In particular, there is a lack of systematic studies that couple detailed molecular characterization with rheology analysis under conditions representative of industrial mechanical recycling.

Rheology is a strong characterization method for the analysis of melt

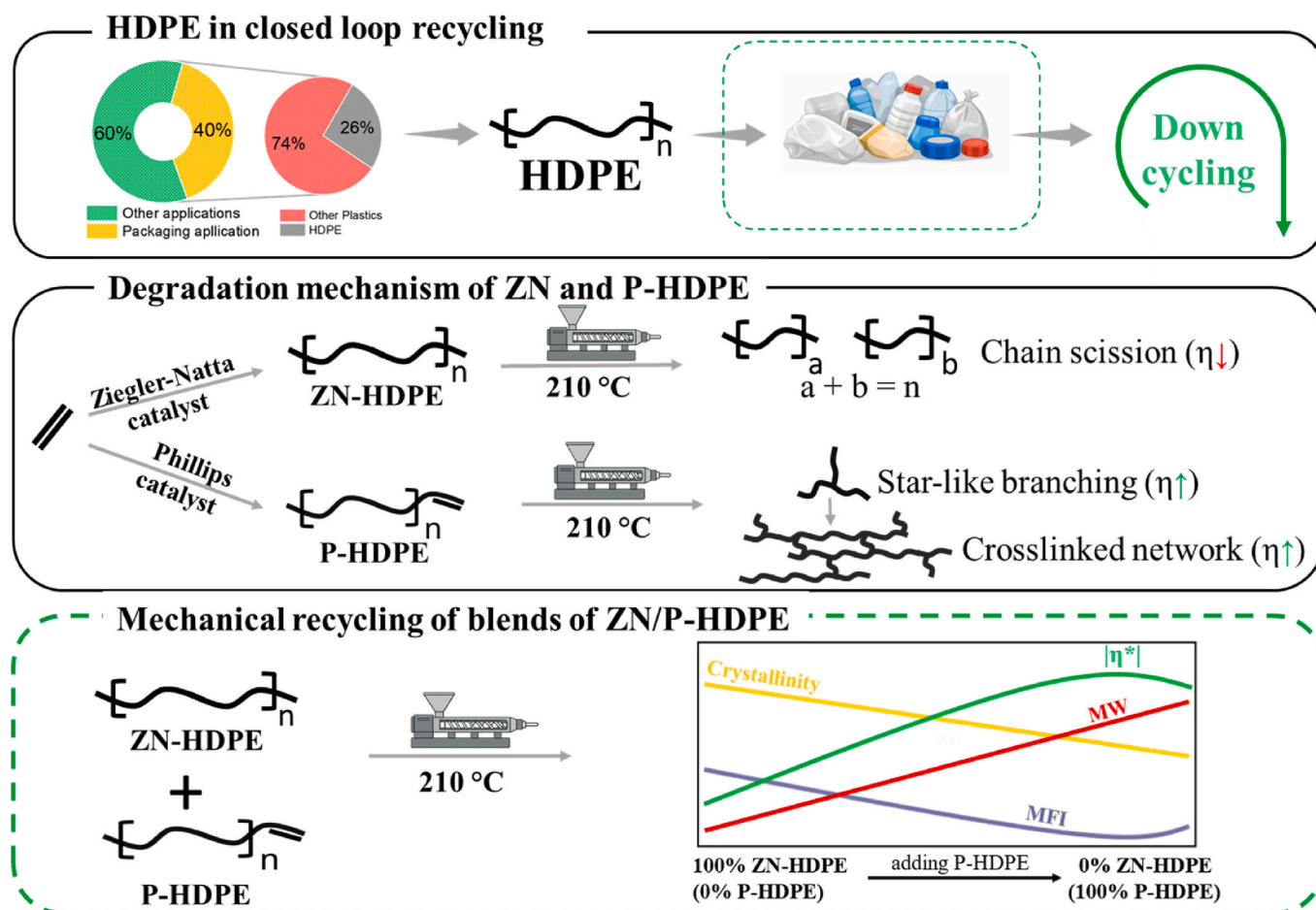


Fig. 1. Shows closed loop recycling of HDPE in packaging application, HDPE degradation mechanism and this work, the recycling outcome of mixed catalyst HDPEs (image of packaging products generated by using chatgpt).

Table 1Molecular parameters and changes quantified by MFI, FTIR, CFC, DSC and SAOS of neat virgin and recycled ZN-HDPE and P-HDPE at $t_r = 30$ min.

Material name	Grade name	MFI [g/10min]	Vinyl index	X_c [%]	T_m [°C]	M_w [kg/mol]	D	T_p [°C]	ω_{co} [rad/s]	$ \eta^* _{@0.01 \text{ rad/s}}$ [kPa s]
vP-HDPE	Lupolen 5012DX, Lyondell Basell	0.25	0.036	67	133	232	20	95.6	3.4	90.8
vZN-HDPE	Borstar BB2588, Borealis	0.25	-	72	133	273	42	94.5	7.4	95.7
100 % rZN-HDPE	-	2.15	-	71	135	94.5	9	95.2	8.3	53.4
$t_r = 30$ min										
100 % rP-HDPE	-	0.018	0.025	63.3	133.5	146	14	92.7	Branching/ crosslinking	928.2
$t_r = 30$ min										

viscosity, relaxation time spectrum and elasticity which is sensitive to molecular weight distribution and type of topologies such as linear chain, star-like branching, long chain branching and crosslinked network. According to reptation theory, M_w of a linear polymer chain depends on the crossover frequency, ω_{co} , from the rubber to the terminal regime, representing the longest relaxation time, following equation (1).

$$\frac{1}{\omega_{co}} \propto (M_w)^{3.4} \quad (1)$$

In the case of star-like branching, M_w does not follow equation (1) but M_w changes according to the molecular weight of the arms, $M_{w,a}$ as:

$$\frac{1}{\omega_{co}} \propto e^{M_{w,a}} \quad (2)$$

In this work, we examine the molecular and rheological evolution of blends of ZN-HDPE and P-HDPE under well-defined mechanical recycling conditions. Blends with different vZN- to vP-HDPE compositions are reprocessed in a twin-screw extruder at 210 °C and 180 rpm for controlled recycling times to rival industrial processing. The reprocessed materials are characterized by Fourier transform infrared spectroscopy (FTIR) to follow vinyl index, differential scanning calorimetry (DSC) to determine crystallinity and thermal transitions, and cross-fractionation chromatography (CFC) to understand changes in the molecular weight distributions. In addition, melt flow index (MFI) measurements, small-amplitude oscillatory shear (SAOS), and extensional rheology are used to probe topological changes and melt strength and to relate molecular level changes to processing relevant rheological behaviour. Elucidating the degradation behaviour of ZN-HDPE and P-HDPE blends enable the development of targeted strategies for processing mixed-catalyst HDPE waste streams. Such mechanistic understanding facilitates the rational design of more robust recycling and upcycling routes, thereby supporting the implementation of a circular economy of plastics.

2. Material and methods

2.1. Raw materials

Two blow-moulding grade virgin HDPE resins were employed in this study: vZN-HDPE (Borstar BB4588, Borealis) and vP-HDPE (Lupolen 5012DX, LyondellBasell). Both materials exhibited comparable melt flow index (MFI) of 0.23 g/10 min (vZN-HDPE) and 0.25 g/10 min (vP-HDPE), measured at 190 °C according to ASTM D1238. Both HDPE resins exhibited comparable weight-average molecular weights (M_w) although substantially different dispersity indices. They displayed quasi-identical melting temperatures ($T_m = 133$ °C) yet distinctly different degrees of crystallinity, as shown Table 1. While both materials exhibited broadly similar chemical compositions, FTIR spectra revealed a subtle but distinct absorption band at 908 cm^{-1} exclusively in the vP-HDPE, characteristic of terminal vinyl unsaturation ($-\text{CHCH}_2$).

2.2. Recycling method

Mechanical recycling was simulated using a Haake Minilab II co-

rotating twin screw extruder in the circulation mode, enabling continuous material flow within the barrel. The blends composition of 100, 95, 90, 70, 50, 30, 10, and 0 wt% vZN-HDPE with vP-HDPE were processed at 210 °C and 180 rpm for $t_r = 10, 20$, and 30 min to assess the effects of reprocessing on thermal and rheological properties. After the extrusion, recycled blends were chemically characterized by FTIR, DSC, and CFC, alongside rheological evaluation via SAOS and extensional rheology. Rheological specimens were prepared by compression moulding under vacuum at 180 °C and dimensions of 25 mm diameter and 1 mm thick disks for SAOS and rectangular films (15 × 5 × 0.5 mm) for extensional rheology analysis.

2.3. DSC

DSC analysis was conducted using a Mettler Toledo DSC1 from −80 °C to 180 °C at heating and cooling rates of 10 K/min. Melting temperature (T_m) and crystallinity (X_c) were determined from the second heating and cooling cycles, respectively. Crystallinity was calculated according to Equation (3), using $\Delta H_{m100} = 293$ J/g for 100 % crystalline HDPE [37].

$$X_c = \frac{\Delta H_m}{\Delta H_{m100}} \cdot 100 \% \quad (3)$$

2.4. FTIR

FTIR spectra were acquired using a Bruker Alpha-T spectrometer over 3600 – 600 cm^{-1} at room temperature, with 4 cm^{-1} resolution and 256 scans averaged per sample. The vinyl index (VI) was calculated according to Equation (3) [32].

$$\text{Vinyl Index} = \frac{A_{908\text{cm}^{-1}}}{A_{1465\text{cm}^{-1}}} \quad (4)$$

2.5. CFC

CFC analysis was performed using a Polymer Char system combining temperature rising elution fractionation (TREF) and high-temperature size exclusion chromatography (SEC). Samples (~8 mg) were dissolved in 1,2,4-trichlorobenzene at 150 °C for 60 min, injected into a TREF column (ceramic microbeads, void volume 2000 – 2600 μL), followed by a PLgel Olexis SEC column (7.5 × 300 mm, 13 μm). TREF crystallization proceeded from 125 °C to 35 °C at 0.5 °C/min to ensure near-equilibrium fractionation and minimize co-crystallization, with stepwise SEC analysis of eluates for molecular weight distribution determination.

2.6. MFI

The melt flow index (MFI) was measured using a device from Custom Scientific Instruments (CSI) in accordance with ASTM D1238, at a temperature of 190 °C under a load of 2.16 kg. The MFI values were determined as the mass (g) of extrudate collected over a 10 min interval.

2.7. Shear and extensional rheology

SAOS measurements were conducted using an Anton Paar MCR 702e Space Dualdrive rheometer (Austria) with 25 mm parallel-plate geometry (1 mm gap) under nitrogen atmosphere (N_2 5.0, 99.999 % purity). Strain sweep tests at 160 °C and strain amplitudes of 1–100 % were used to identify the linear viscoelastic regime, followed by frequency sweeps from 150 to 0.01 rad/s at constant strain amplitudes within the linear regime. Uniaxial extensional measurements were performed at 160 °C using the Anton Paar Universal Extensional Fixture (UXF) in the multi-drive mode at Hencky strain rates of 0.1 and 0.3 s^{-1} . Transient extensional viscosity to the linear Doi-Edwards model prediction was calculated using the IRIS software [38–41].

2.8. Tensile testing

Tensile tests were performed using a Zwick universal testing machine equipped with a 2.5 kN load cell. Dumbbell-shaped specimens with a 10 mm gauge length were tested at room temperature using a crosshead speed of 20 mm/min. For each material and processing condition, three specimens were tested, and the tensile properties were determined from the recorded stress-strain curves. The elongation at break is an engineering strain. The reported values represent the average of the three measurements.

3. Result and discussion

3.1. DSC

Thermal characterization of the recycled blends was performed using DSC to evaluate changes in crystallinity and melting behaviours. Recycling induces chain irregularities due to thermo-mechanical degradation, which leads to a reduction in crystallinity and, to a lesser extent, melting temperature. The virgin ZN-HDPE exhibits a higher crystallinity, X_c , (72 %) compared to virgin P-HDPE (67 %), indicating a more regular chain structure and efficient chain packing. Upon recycling, both materials show a decrease in crystallinity and the values are given in Fig. 2 (A) and Table S 1, 2 & 4, with reductions of approximately 7 % for rZN-HDPE and 9 % for rP-HDPE after $t_r = 30$ min, reflecting structural degradation and the formation of chain defects. The recycled blends display intermediate crystallinity values, lying between those of neat rZN-HDPE and 100 % rP-HDPE. This behaviour suggests that P-HDPE is more susceptible to structural degradation, thereby reducing the overall crystallinity of the blends. Consequently, increasing the P-HDPE content results in a progressive decline in crystallinity. For instance, incorporation of 90 % P-HDPE leads to a reduction of X_c of approximately 10 %. Relative to rZN-HDPE. In contrast, the addition of small amounts of P-HDPE (≤ 10 wt%) only slightly enhances crystallinity (by ~ 2 –4 %) compared to 100 % rZN-HDPE. This increase may be attributed to improved chain mobility or nucleation effects, which facilitate more efficient crystallization at low P-HDPE concentrations. Furthermore, increasing the recycling time ($t_r = 10$ –30 min) results in a systematic decrease in crystallinity (~ 3 –6 % at $t_r = 30$ min), consistent with progressive chain irregularities and defect formation under prolonged

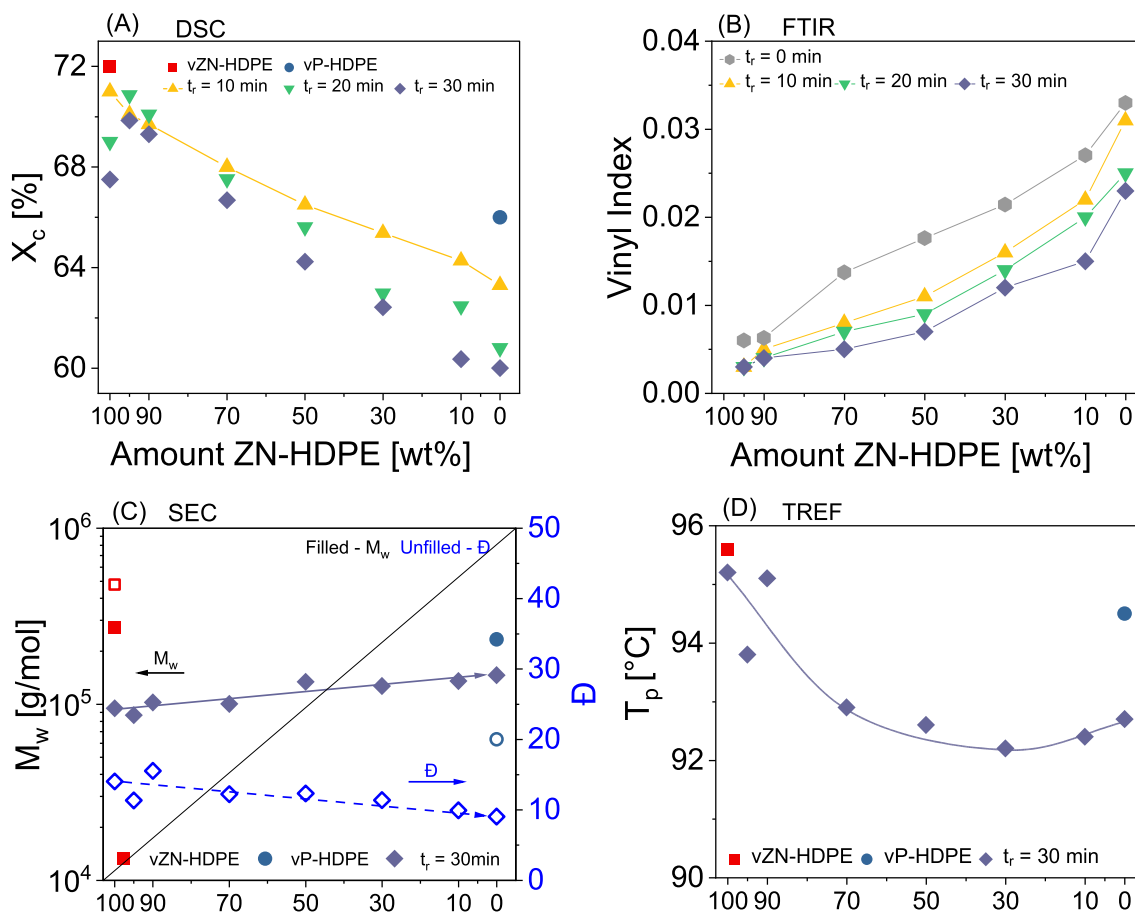


Fig. 2. Molecular characterization of recycled blends at different t_r . (A) shows crystallinity from the DSC analysis, (B) shows vinyl index from the FTIR analysis, (C) and (D) show molecular weight and peak temperature respectively from the CFC analysis.

thermo-mechanical exposure.

The melting temperatures (T_m) of vP-HDPE and vZN-HDPE were around 133 °C. After recycling, T_m gradually dropped by 3 °C as the amount of P-HDPE added to the blend increased to 70 wt%. This is primarily due to branches formed during thermal-mechanical deterioration.

3.2. FTIR

FTIR analysis was carried out to investigate the evolution of terminal vinyl unsaturation in the blends before and after recycling, as shown in Fig. 2(B) and Table S 2. The characteristic absorption band at 908 cm^{-1} , attributed to terminal vinyl unsaturation, is only present in P-HDPE, but not (significantly) in the ZN-HDPE [32,42]. Accordingly, 100 % P-HDPE exhibits a vinyl index of 0.036, indicating a significant presence of terminal unsaturation. Upon recycling at 210 °C, the vinyl index of neat P-HDPE decreases by up to 36 %, suggesting that these vinyl groups are progressively consumed through branching reactions during thermo-mechanical processing. Increasing the P-HDPE content in the blends results in a progressive increase in vinyl index, reaching up to 42 % relative to the reference. This trend indicates, that the incorporation of P-HDPE introduces additional vinyl unsaturation, which can serve as reactive sites for branching and play a critical role in governing the extent of branching reactions in the blends. Furthermore, increasing t_r leads to a systematic reduction in vinyl index across all blend compositions, indicating that prolonged thermal and mechanical exposure accelerates the reaction of terminal vinyl groups. Taken together, the results demonstrate that the addition of P-HDPE increases the availability of reactive terminal vinyl groups, while extended recycling time allows their conversion into branched structures.

3.3. CFC

Cross-fractionation chromatography (CFC), combining size exclusion chromatography (SEC) and temperature rising elution fractionation (TREF), was employed to elucidate the molecular and structural evolution of the blends after 30 min of recycling. SEC provides information on molecular weight and molecular weight distribution, whereas TREF enables assessment of branching through the peak elution temperature (T_p) [43–48]. The weight average molecular weight, M_w , and the peak temperature from TREF are shown in Fig. 2(C and D) and Table S 4. The virgin ZN-HDPE exhibits a broader molecular weight distribution ($\text{Đ} = 42$) and higher T_p compared to P-HDPE, indicating a more linear chain architecture and higher crystallinity. This observation is consistent with the DSC results, confirming the more ordered structure of ZN-HDPE.

Upon recycling, both rZN-HDPE and rP-HDPE exhibit significant reductions in T_p and M_w . The reduction in T_p (from 95.6 to 94.7 °C for rZN-HDPE and from 94.5 to 92.7 °C for rP-HDPE) further suggests increased irregularities, like branching, within the polymer chain. Extensive chain scission is indicated by the decrease in M_w of approximately 66 % and 43 % for 100 % rZN-HDPE and 100 % rP-HDPE after $t_r = 30$ min, respectively, and results in a significantly higher M_w for rP-HDPE than rZN-HDPE after $t_r = 30$ min. This can be attributed to the presence of terminal vinyl unsaturation in P-HDPE, which promotes branching reactions during recycling. For instance, blends containing 10 wt% P-HDPE exhibit an increase in M_w of approximately 8 %, compared to 100 % rZN-HDPE, which rises to ~45 % at higher P-HDPE content (90 wt%). For the recycled blends of P-HDPE and ZN-HDPE, M_w follows a semi-logarithmic relationship with the P-HDPE to ZN-HDPE ratio.

These results indicate, that while chain scission dominates in 100 % rZN-HDPE, the presence of P-HDPE introduces competing branching/chain extension reactions that increase molecular weight but reduce crystallinity. This demonstrates that the addition of P-HDPE shifts the degradation mechanism from predominantly chain scission towards a

balance between chain scission and branching, resulting in increased molecular weight and decreased T_p in the recycled blends.

3.4. MFI

The melt flow index (MFI) of the recycled blends was used to assess changes in the flow behaviour. An increase in MFI reflects enhanced flowability associated with reduced viscosity and molecular weight, whereas a decrease in MFI indicates increased viscosity, typically due to branching or crosslinking and the values are shown in Fig. 3 and Table S 1, 3 & 4. Upon recycling, 100 % rZN-HDPE shows at $t_r = 30$ min a significant increase in MFI by approximately a factor of 10, indicating dominant chain scission. In contrast, 100 % rP-HDPE exhibits a substantial decrease in MFI by a factor of ~14, suggesting the formation of star-like branched to crosslinked structures. The MFI of the recycled blends is strongly governed by composition. Incorporation of P-HDPE into ZN-HDPE leads to a progressive decrease in MFI, with values decreasing from 2.15 g/10 min for 100 % rZN-HDPE to 0.014 g/10 min for blends containing 10 wt% ZN-HDPE. Conversely, blends with low ZN-HDPE content (10 wt%) exhibit a reduction in MFI relative to 100 % rP-HDPE. The influence of t_r (10 to 30 min) further highlights the competition between chain scission and star-like branching/crosslinking. Blends containing ≥ 70 % ZN-HDPE exhibit higher MFI at longer t_r , indicating increased chain scission under prolonged thermo-mechanical exposure. In contrast, blends with lower ZN-HDPE content (< 70 %) show a decrease in MFI with increasing recycling time, suggesting continuous branching reactions in P-HDPE dominated blends.

Overall, the MFI results demonstrate that the balance between chain scission and branching is governed by both blend composition and recycling time. The addition of small amounts of P-HDPE to ZN-HDPE compensates chain scission, whereas the incorporation of P-HDPE into blends with ZN-HDPE as majority component promotes branching, thereby significantly influencing the flow behaviour and molecular structure of the recycled materials.

3.5. Shear rheology

The rheological behaviours of virgin, neat recycled, and mixed-catalyst HDPE blends was investigated using small-amplitude oscillatory shear (SAOS) frequency tests, with particular emphasis on G' and G'' as a function of angular frequency (ω), as well as complex viscosity $|\eta^*|$, as shown in Fig. 4, Figure S 1 and Figure S 2. Molecular changes were quantified using the crossover frequency (ω_{co}), defined as the frequency at which G' equals G'' , and the complex viscosity at a low frequency of $\omega = 0.01$ rad/s ($|\eta^*|_{@0.01 \text{ rad/s}}$). These parameters are highly sensitive to molecular weight and chain dynamics, thus allowing detailed assessment of the degradation mechanisms. As illustrated in Fig. 4(D), the $|\eta^*|_{@0.01 \text{ rad/s}}$ for the un-recycled blends ($t_r = 0$ min) remains relatively

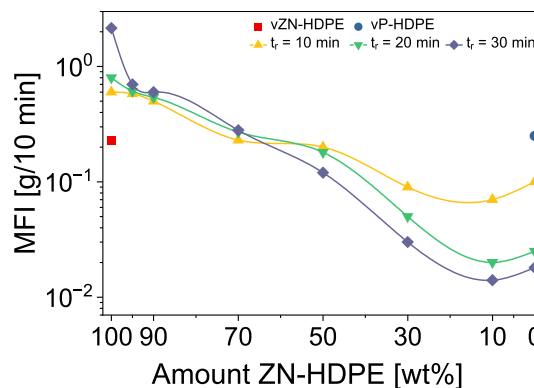


Fig. 3. MFI values for virgin HDPEs and recycled blends at different t_r of 10, 20 and 30 min.

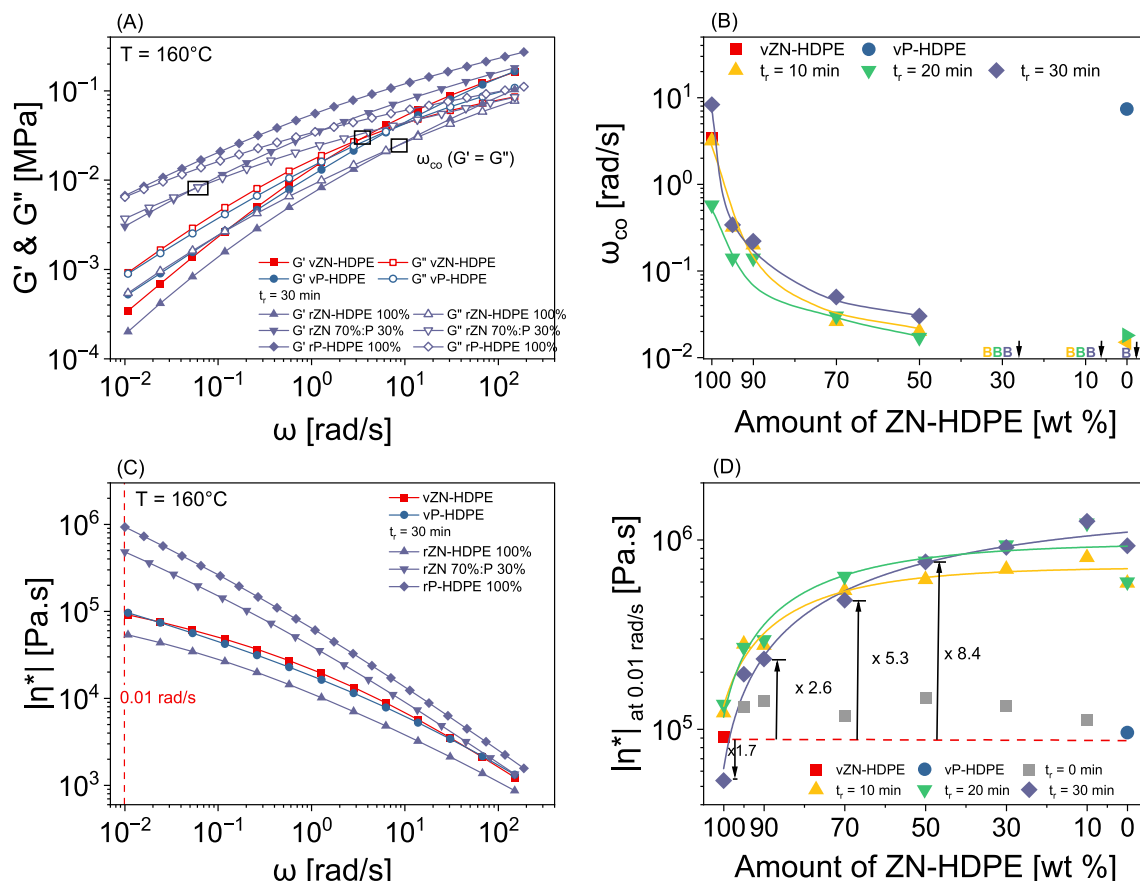


Fig. 4. SAOS frequency dependent analysis of virgin P- and ZN-HDPE and recycled HDPE blends, (A) shows G' and G'' vs ω for the virgin and recycled neat HDPEs as well as a blend containing 30 % of P-HDPE in 70 % ZN-HDPE, (B) shows ω_{co} as function of ZN-HDPE amount in the blends, (C) shows $|\eta^*|$ vs ω for the polymers from (A) and (D) shows $|\eta^*|_{@0.01 \text{ rad/s}}$ as a function of ZN-HDPE amount in the blends. Especially (B) and (D) clearly show the remarkable impact of the addition of even small amounts of P-HDPE in ZN-HDPE.

stable across all composition ratios. These values lie marginally above those of the virgin HDPE components but significantly below the corresponding reprocessed formulations. This changes indicate that the active terminal vinyl groups native to P-HDPE do not undergo significant chemical reactions in fast mixing at low screw speeds.

For 100 % rZN-HDPE, ω_{co} exhibits an initial decrease at shorter t_r (10 & 20 min), followed by an increase by a factor of 2.4 at $t_r = 30$ min, indicating dominant chain scission. In contrast, 100 % rP-HDPE shows a substantial decrease in ω_{co} by a factor of about 500 at $t_r = 10$ min, which further shifts toward lower frequencies with increasing recycling time, indicating extensive molecular weight increase or star-like branching, see equation (2). Correspondingly, $|\eta^*|_{@0.01 \text{ rad/s}}$ decreases by 41 % for 100 % rZN-HDPE and increases by a factor of ~ 10 for 100 % rP-HDPE at $t_r = 30$ min. The shift of ω_{co} towards lower frequencies reflects increased molecular weight, while a shift towards higher frequencies indicates chain scission [49–53], which is only for the ZN-HDPE consistent with the SEC analysis, and can for P-HDPE only explained by star-like branching to a low degree in crosslinked network. For the blends, the incorporation of P-HDPE results in a significant reduction in ω_{co} and a corresponding increase in $|\eta^*|_{@0.01 \text{ rad/s}}$, indicating the formation of star-like branched molecular architectures. For example, blends containing 5 wt% P-HDPE exhibit a decrease in ω_{co} by a factor of about 25 and an increase in $|\eta^*|_{@0.01 \text{ rad/s}}$ by a factor of 2 at $t_r = 30$ min compared to vZN-HDPE. This behaviour suggests that the presence of P-HDPE compensates chain scission and promotes branching, as shown schematically in Fig. 7. FTIR analysis confirms that increasing P-HDPE content leads to a higher vinyl index, thereby promoting crosslinking of the terminal double bonds to star-like branching, which is reflected in

the reduction of crossover frequency and the increase in $|\eta^*|$. At higher P-HDPE contents (≥ 70 %), ω_{co} shifts beyond the measurable range (< 0.01 rad/s), indicating extensive star-like branching to crosslinking. This is further supported by the substantial increase in $|\eta^*|$ up to a factor of 24 for blends containing 90 wt% P-HDPE, which is even higher than 100 % rP-HDPE at $t_r = 30$ min. The effect of recycling time further highlights the competition between chain scission and star-like branching/crosslinking. Blends containing ≥ 70 % ZN-HDPE exhibit higher ω_{co} and lower $|\eta^*|$ at longer recycling times, indicating increased chain scission. Conversely, P-HDPE-rich blends show increased $|\eta^*|$ with longer recycling time, indicating continuous star-like branching to crosslinking. This trend is consistent with the MFI analysis (see Fig. 7).

Overall, the results demonstrate that the addition of even small amounts of P-HDPE to ZN-HDPE compensates in their rheological behaviour chain scission by star-like branching/crosslinking of the P-HDPE chains, as reflected in decreased crossover frequency and increased complex viscosity.

This finding is of particular interest for the recycling of real HDPE PCW streams, where P-HDPE and ZN-HDPE cannot be separated, but even the addition of small amounts of P-HDPE fully dominates the reprocessability of recycled HDPE. The drastic increase in viscosity with even 5 to 10 wt% of P-HDPE to ZN-HDPE will make the reprocessability of PCW HDPE very difficult and a given extruder would need to be run much below the maximum torque to handle those changes in viscosity and to avoid screw blockage or instabilities.

3.6. Extensional rheology

While DSC, TREF, and, to some extent, SAOS rheology provide insights into chain irregularities such as short-chain branching (SCB), crystallinity and general molecular degradation, extensional rheology allows to distinguish comb like long-chain branching (LCB) like in LDPE from other branching architectures, especially star-like structures. Notably, only LCB leads to strain hardening behaviour [54–60], making extensional measurements particularly sensitive to comb-like LCB molecular architectures. As expected for linear polyethylene, both virgin P-HDPE and ZN-HDPE exhibit negligible strain hardening. This behaviour is characteristic for predominantly linear, entangled polymer chains without/with minimal LCB. For recycled 100 % rZN-HDPE and 100 % rP-HDPE after $t_r = 30$ min at 210°C , the elongational behaviour remains essentially unchanged compared to the corresponding virgin materials, indicating that recycling under those conditions does not induce significant long-chain branching. Similarly, the recycled blends exhibit negligible strain hardening across all strain rates, or for the 50:50 blend even strain softening occurs, as shown in Fig. 5. These results indicate the absence of long-chain branching in both neat and blended recycled systems. Instead, the molecular architecture is likely dominated by short-chain or star-like branching, which does not cause strain hardening. This interpretation from extensional rheology is consistent with the SAOS results, which suggest increased star-like branching without the formation of LCB, required for strain hardening.

3.7. Tensile test

Tensile tests were performed with the virgin HDPEs as well as the with blend recycled for 30 min. A summary of the tensile parameters, including ultimate tensile strength (UTS), Young's modulus (E-modulus), and elongation at break (engineering strain) for the virgin and recycled HDPE blends after $t_r = 30$ min is presented in Fig. 6, Figure S 3 and Table S 5. Comparable mechanical behaviour was observed between the two virgin grades, where vZN-HDPE and vP-HDPE exhibited ultimate tensile strengths of 29.3 ± 1.2 and 28.4 ± 1.9 MPa, and E-modulus of 446 ± 3 and 444 ± 15 MPa, respectively and elongation at break values exceeding 1000 %, indicating the high ductility characteristic of high molecular weight HDPE.

Following thermo-mechanical recycling, the two polymers exhibited markedly different mechanical responses. The rZN-HDPE 100 % showed an increase in UTS to 30.8 ± 0.5 MPa and an increase in E-modulus to 486 ± 19 MPa relative to the virgin material. The simultaneous increase in strength and stiffness suggests that recycling promoted molecular rearrangement, where shorter polymer chains packed tightly and increase the effective crystalline fraction. Nevertheless, the elongation at break decreased dramatically from 1050 % to 534 %, indicating a

substantial loss of ductility. This reduction is attributed to chain scission during recycling, which lowers the molecular weight. In contrast, rP-HDPE 100 % exhibited a clear deterioration in all tensile properties. The ultimate tensile strength decreased to 26 ± 1.2 MPa, while the E-modulus declined to 382 ± 3 MPa. Although the elongation at break (617 ± 70 %) remained higher than that of rZN-HDPE 100 %, it was still considerably lower than that of the virgin materials.

The addition of a small amount of P-HDPE (5–10 wt%) significantly influenced the tensile performance of recycled blends. Compared with rZN-HDPE 100 %, the blend containing 5 wt% of P-HDPE exhibited the highest UTS (31.7 ± 2.1 MPa) and E-modulus (517 ± 41 MPa), corresponding to increases of approximately 3 % and 6.5 %, respectively. Similarly, the blend containing 10 wt% of P-HDPE maintained a slightly higher ultimate tensile strength (31.3 ± 1.0 MPa) than rZN-HDPE 100 %, while its E-modulus (483 ± 23 MPa) remained comparable. These improvements are consistent with the higher crystallinity observed for both blend compositions compared with rZN-HDPE 100 %. The engineering strain at break increased markedly from 534 % for rZN-HDPE 100 % to 722 % and 850 % for the blends with 5 and 10 wt% of P-HDPE, respectively, indicating a substantial recovery in ductility. Further increasing the recycled P-HDPE content to 30–90 wt% progressively deteriorated the tensile performance of the blends. The blend contains 30 % of P-HDPE, UTS is decreased by approximately 4 % and it is decreased up to 12 % by addition of P-HDPE 90 % to the blend. The E-modulus and elongation of break were approximately constant for the blend contain 30 % of P-HDPE compared to rZN-HDPE 100 %. However, UTS and E-modulus subsequently decreased by 6–10 % and 7–20 % with further increases with P-HDPE content of 50–90 %. Although the engineering strain at break remained 12–26 % higher than that of rZN-HDPE 100 %, it progressively declined with increasing P-HDPE content to the blend compared with the 10 wt% of P-HDPE in the blend, indicating a gradual loss of ductility at higher blend ratios.

Overall, the tensile properties demonstrate that blend composition plays a critical role in balancing stiffness, strength, and ductility after thermo-mechanical recycling. Incorporating a small amount of recycled P-HDPE (5–10 wt%) into the blend produced the optimum mechanical performance by simultaneously enhancing the UTS, E-modulus, and engineering strain at break, which is consistent with the increased crystallinity observed for these blend compositions compared to rZN-HDPE. In contrast, further increasing the P-HDPE content to the blends progressively reduced the tensile strength and E-modulus.

4. Conclusion

High-density polyethylene (HDPE) is primarily synthesized industrially via Ziegler-Natta (ZN) and Phillips (P) catalysts, which impart distinct molecular features despite their chemical similarity, but are typically mixed in post-consumer waste streams of HDPE. In particular, P-HDPE contains a higher concentration of terminal vinyl groups, which strongly influence its degradation behaviour during mechanical recycling and promotes branching/crosslinking due to the presence of reactive terminal vinyl groups. In contrast, ZN-HDPE predominantly undergoes chain scission, resulting in reduced molecular weight and viscosity. This study demonstrates for blends of P-/ZN-HDPE with the same melt flow index for the virgin grades, that thermo-mechanical degradation is governed by the blend composition derived from different catalyst systems. Increasing the fraction of P-HDPE enhances the contribution of terminal vinyl groups and promotes star-like branching/crosslinking. This is evidenced by an increase in molecular weight, a corresponding drastic decrease in crossover frequency and a drastic increase in viscosity at low shear rates, as determined by CFC and SAOS analyses. For example, the low-frequency viscosity of rZN-HDPE after 10 min increased by 30 % compared to vZN-HDPE, but the addition of 10 or 30 wt% of P-HDPE resulted in a viscosity increase of about 300 % and 600 %, respectively. Those drastic increase in viscosity will make the reprocessability of PCW HDPE very difficult and much care

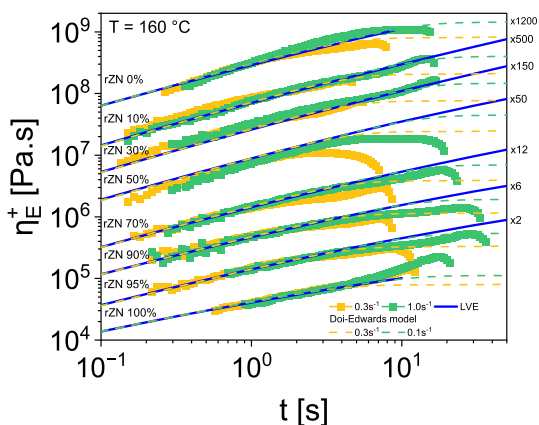


Fig. 5. Extensional viscosity of the recycled blends in the different composition of ZN-HDPE at two different strain rates of 0.1 s^{-1} and 0.3 s^{-1} .

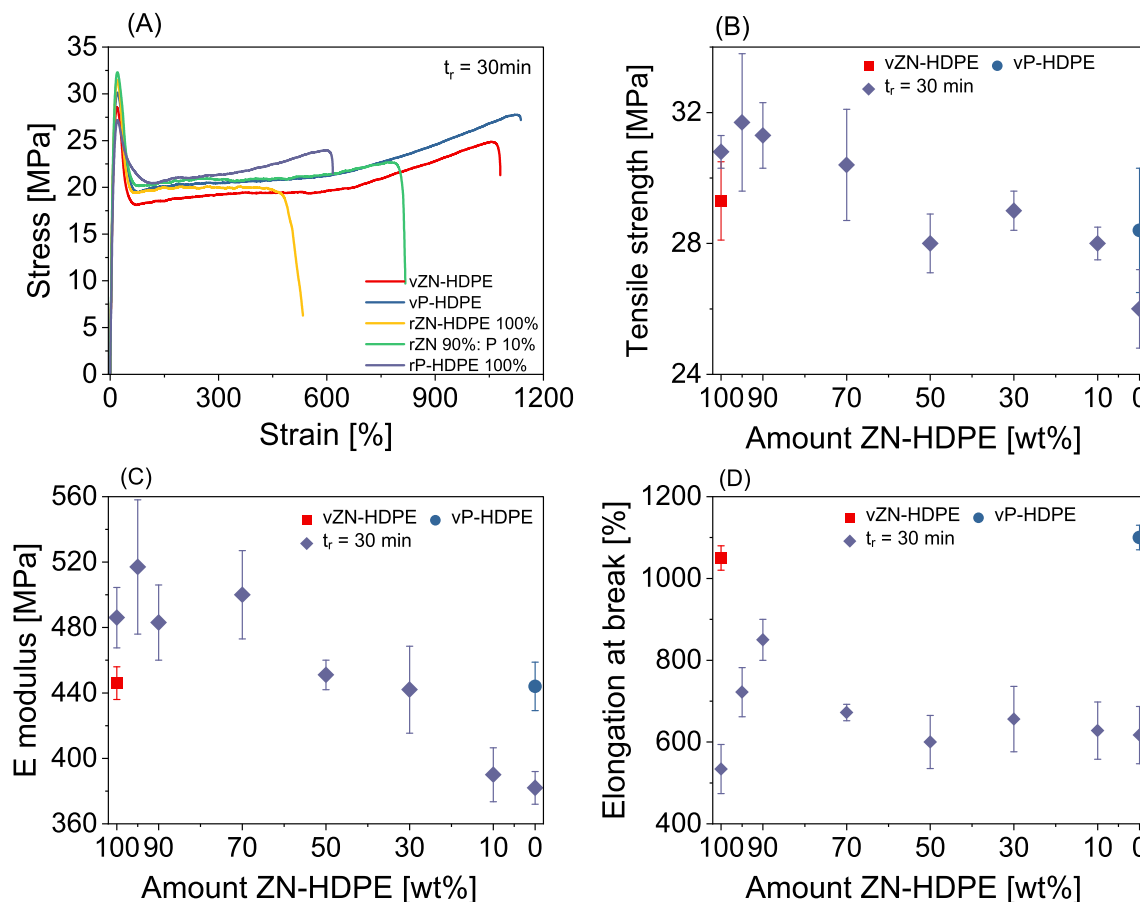


Fig. 6. Tensile properties of virgin and recycled HDPE blends reprocessed at $t_r = 30$ min: (A) representative engineering stress-strain curves, (B) ultimate tensile strength (UTS), (C) Young's modulus (E-modulus), and (D) elongation at break as a function of amount of ZN-HDPE in wt %.

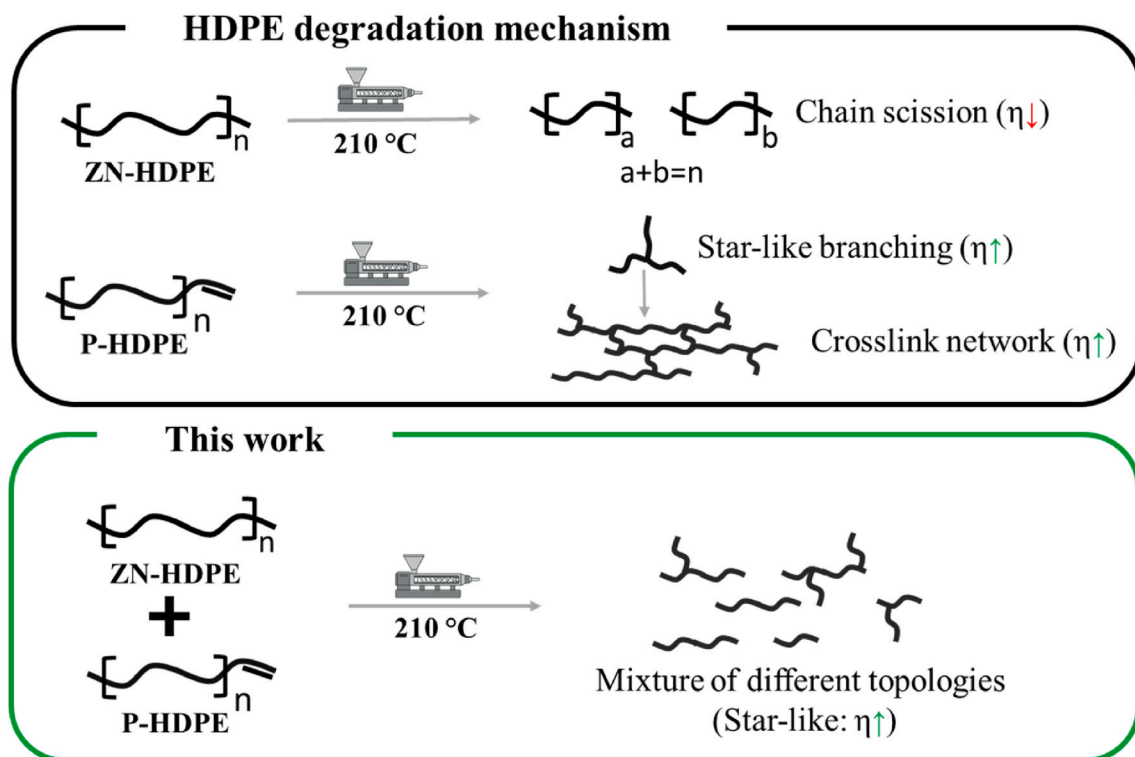


Fig. 7. The different proposed topologies after the reprocessing at 210°C for ZN-HDPE, P-HDPE and the blends of ZN-HDPE and P-HDPE.

needs to be taken to avoid screw blockage or instabilities. The results highlight that blend composition governs the balance between chain scission and star-like branching/crosslinking, see Fig. 6, which in return determines the rheological and processing behaviour of recycled HDPE. The tensile properties further demonstrated that blend composition strongly governs the mechanical performance of recycled HDPE. Incorporating a small amount of P-HDPE (5–10 wt%) into the blend provided the higher UTS, E-modulus, and engineering strain at break, which is consistent with the increased crystallinity compared to rZN-HDPE 100 %. In contrast, higher P-HDPE contents progressively reduced the UTS and stiffness. Importantly, since it is industrially impractical to separate HDPE based on polymerization catalyst type, this study mimics realistic post-industrial and post-consumer waste streams by investigating mixed HDPE systems. These insights provide a scientific basis for understanding and predicting the recycling behaviour of mixed HDPE waste, supporting the development of improved processing strategies and enabling higher-value reuse of polyethylene materials.

CRedit authorship contribution statement

Alexsandar Arumugam: Formal analysis, Investigation, Writing – original draft. **Akshai Thomas:** Formal analysis, Investigation. **Jeanine Flore Kameni Nakmanou:** Formal analysis, Investigation. **William Felipe Chaverra Ordóñez:** Data curation, Investigation. **Michael Fischlschweiger:** Funding acquisition, Methodology, Resources, Writing – review & editing. **Valerian Hirschberg:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2026.130520>.

Data availability

Data will be made available on request.

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