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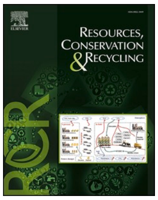

Effect of mechanical recycling on the rheological and mechanical properties of bio-based and bio-degradable polybutylene succinate

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ABSTRACT

In this study, the effect of mechanical recycling on the molecular, rheological and mechanical properties of poly (butylene succinate) (PBS) was thoroughly investigated via closed loop extrusion. Molecular characterization techniques, such as size exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR), as well as oscillatory shear rheology were used to monitor the changes associated with reprocessing. Tensile tests were also performed to quantify the evolution of mechanical properties, such as Young's modulus (E), ultimate tensile strength (σ_{ult}) and elongation at break (ε_b). The FTIR results showed significant changes of the hydroxyl groups in recycled PBS (rPBS). SEC confirmed a sudden molecular weight (M_w) drop by about 67 % and increased polydispersity with number of recycling loops (total extrusion time). On the other hand, the rheological properties, such as zero-shear viscosity (η_0), storage moduli (G'), loss moduli (G'') and longest relaxation time (τ), were significantly changed with increasing screw rotating speed (shear stresses) and extrusion (residence) time. These results highlight the importance of controlling the mechanical recycling conditions for rPBS to ensure suitable rheological and mechanical properties after mechanical recycling, as well as the need of chain extender to preserve material properties and resources.

1. Introduction

Poly(butylene succinate) (PBS) is a biodegradable, aliphatic polyester used in various applications including packaging, agriculture and biomedical fields (Huang et al., 2018; Zhang et al., 2022a). PBS is regarded as a potential replacement for polypropylene (PP) which is about 16 % of the global plastic market (Alsabri et al., 2022). This represents a huge market for PBS in the near future. Furthermore, PBS is a sustainable, bio-based and biodegradable plastic alternative, which can be produced by renewable resources, such as sugarcane, cassava and corn (Aliotta et al., 2022). Although PBS can be naturally decomposed by bacteria and fungi, the degradation rates under standard environmental conditions is around 3–8 % weight loss for PBS being exposed to environmental degradation after 120 days, leading to the production of CO_2 and water (Huang et al., 2018; Kim et al., 2005; Liu et al., 2008; Su et al., 2019). This slow degradation rate still results in the accumulation of plastic wastes. Consequently, PBS recycling become increasingly important as a means of reducing waste and conserving natural resources.

Mechanical and chemical recycling are two main approaches for plastic end-of-life management (Zhang et al., 2022b, 2022c). Mechanical recycling is based on the reprocessing (grinding and extrusion) of the material after its end of life. The processes are usually cheaper, energetically and ecologically more favorable than chemical recycling (depolymerization/purification), which also requires polymerization before being reused. For relatively uncontaminated materials, mechanical recycling is a straightforward process easy to perform which does not require complex equipment. A study from the European Chemical Industry Council (CEFIC) reported that the mechanical recycling of polymer wastes, such as polyethylene terephthalate (PET) and polyethylene (PE), can save up to 60 % of the energy required for chemical recycling (CEFIC, 2020). Mechanical recycling generates significantly

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lower emissions than chemical recycling via depolymerization when all the impacts are considered, including CO_2 release, acidification, eutrophication, photochemicals formation, etc. (Maga et al., 2019; Jeswani et al., 2021). As suggested by CEFIC, chemical recycling will complement mechanical recycling under current ecological, technological and economical consideration, especially when high purity (low contamination) application is required, such as the biomedical, pharmaceutical and food industries (CEFIC, 2020).

However, mechanical recycling can have a significant effect on the molecular properties of the material, leading to substantial difference in terms of physical, rheological and mechanical properties (tensile, fatigue, creep, etc.) (Dedieu et al., 2022; Muthuraj et al., 2014; Zhang et al., 2024). It was found that PBS, when processed above 190 °C, underwent branching/recombination degradation reactions, resulting in extrudates with higher solution viscosity and bimodal molar mass distribution (Georgousopoulou et al., 2016). However, some research reported different rheological and molecular properties of PBS after mechanical recycling. For example, the melt flow index (MFI) of recycled PBS (rPBS) was found to increase by 80 % after only 5 cycles of grinding and compression molding at 140 °C for 10 min with a pressure of 6.9 MPa (Prasoetsopha et al., 2018). This aligned with the observation reporting that the MFI increased from 3 g/10 min to 17 g/10 min with 7 repeated mechanical extrusion at a temperature range between 120–180 °C (Nomadolo et al., 2024). Besides, the molecular weight of PBS exhibited no significant change even after multiple reprocessing cycles at a temperature of 140 °C (Kanemura et al., 2012). These changes finally affected the mechanical performance of rPBS such as impact strength (Nomadolo et al., 2024) and bending strength (Kanemura et al., 2012).

The discrepancies observed are likely attributed to the variations in reprocessing conditions employed across different studies. Drawing a definitive conclusion regarding the underlying reason remains challenging due to the limited information on rPBS available in the literature. However, several researchers have thoroughly studied the degradation mechanism of polyesters during mechanical recycling, especially polyethylene terephthalate (PET) (Benvenuta Tapia et al., 2018; Cavalcanti et al., 2007; Nait-Ali et al., 2011) and polylactic acid (PLA) (Beltrán et al., 2018, 2016). These findings can be relevant to PBS as well. For example, increasing the extrusion temperature from 265 °C to 280 °C at a screw speed of 100 rpm resulted in a 10 % decrease of PET intrinsic viscosity after the same extrusion time, while the effect of screw rotation speed was less important (Asensio et al., 2020). This indicates that rPET thermal degradation is more dominant than mechanical degradation due to shearing during extrusion. Therefore, long-term exposure to high temperature plays a significant role on the rheological behavior of these recycled polymers. Furthermore, in the presence of water, hydrolytic degradation of the ester group during PET mechanical recycling is responsible for molecular weight decrease (Karayannidis and Psalida, 2000; Nait-Ali et al., 2011; Phua et al., 2011) and lower polydispersity (Phua et al., 2011), resulting in the formation of shorter chains with carboxyl and hydroxyl end groups (Awaja et al., 2004; Fashandi et al., 2008; Fechine et al., 2004). However, hydrolytically degraded polymers can be regenerated by reversible reaction, such as polycondensation and release of water (Assadi et al., 2004). Transesterification is another undesirable phenomenon leading to increased polydispersity (Lipik et al., 2010). The thermal cleavage of the ester bond in PET during extrusion also generates shorter chains with carboxyl and vinylic end groups (Masmoudi et al., 2018; Nait-Ali et al., 2011). Several works also reported that PET chain scission can be associated with mechanical stress leading to lower molecular weight (Makkam and Harnnarongchai, 2014; Phua et al., 2011; Pinheiro et al., 2017). In contrast to polyesters, studies on low density polyethylene (LDPE) showed that after 100 extrusion cycles, the MFI of LDPE decreased by a factor of 100 (Jin et al., 2012), indicating that repeated mechanical shearing and long-term exposure to high temperature led to increased molecular weight due to recombination and chain branching.

The mechanical properties of rPBS, such as tensile strength, Young's modulus and elongation at break, are also influenced by the recycling conditions. One study reported a significant drop in elongation at break drop (84 %) after a single recycling loop at 140 °C and extrusion stress 6.9 MPa for 10 min (Prasoetsopha et al., 2018). Therefore, it is mandatory not only to consider the number of reprocessing loops, but also residence time distribution related to the extruder screw speed, as well as the temperature when optimizing recycling processes for each polymer. This is important as polymer degradation (mechanisms, rates, etc.) is influenced by their chemical structure, as well as their intrinsic stability (depending on the presence of additives and contamination) towards heat, mechanical stress, oxidation, UV radiation, etc. (Jin et al., 2012; Zhao et al., 2022). Any modification on the chemical structure during recycling will generate changes in their processing and final properties.

Currently, studies on the effect of mechanical recycling conditions, such as extrusion temperature, shear rate and processing time, on rheological and mechanical properties of rPBS are limited. Furthermore, detailed information about molecular structure change during mechanical recycling is missing for rPBS. Such information is essential to understand and predict the macroscopic behavior of the recycled materials since both rheological and mechanical properties are highly dependent on molecular topology (Chimeni et al., 2018; Hirschberg et al., 2020, 2018). Consequently, the main objective of this study is to establish correlations between the evolution of PBS molecular structure during mechanical recycling under different conditions and rheological behaviours, polymer structural characteristics, and mechanical performances. In particular, rheology is the main focus as being a very sensitive tool to quantify changes in molecular weight, topology and morphology. For example, the molecular architecture of long-chain-branched PBS are well related to their rheological behavior such as strain-hardening effects (Bourg et al., 2021). Using rheological measurements, molecular changes in LDPE, such as chain scission and crosslinking during mechanical recycling, were identified which were in agreement with size exclusion chromatography (SEC) measurements (Jin et al., 2012). In addition, van Gurp-Palmen plot (vGP-plot), which is a plot of the phase angle as a function of the absolute value of the complex shear modulus, is a valuable tool to detect changes in molecular weight, polydispersity and long-chain branching (Hirschberg et al., 2023; Stefan Trinkle et al., 2002; Stefan Trinkle and Christian Friedrich, 2001). Finally, SEC and FTIR can provide direct information regarding molecular changes to confirm rheological observations (Assadi et al., 2004; Lipik et al., 2010; Makkam and Harnnarongchai, 2014; Masmoudi et al., 2018; Phua et al., 2011).

From a practical perspective, by simulating the recycling process through controlled processing conditions, the degradation process that occur during actual recycling processes can be effectively mimic. The systematic evaluation of rheological characteristics, such as viscoelastic behaviours, coupled with molecular analysis and mechanical testing, will provide valuable insights into the material's behaviors under repeated recycling conditions.

This comprehensive understanding is crucial to asses the viability of PBS as a sustainable and recyclable material, enabling us to establish guidelines for its efficient and effective reuse. By identifying the critical point where the material's properties deteriorate beyond acceptable limits, the recycling process can be optimized to maximize resource utilization and contribute to the development of a more circular and environmentally friendly economy.

2. Materials and methods

2.1. Materials and mechanical recycling

Virgin PBS (BioPBS, FD92, M_w: 149 kg/mol, PDI: 7.86) with a melting temperature $T_m = 84$ °C and a density of 1.24 g/cm^3 was obtained from Mitsubishi Chemical Corporation (Tokyo, Japan). The melt flow rate (MFR, 190 °C, 2.16 kg) is 4 g/10 min (ISO 1133). A lab-size twin-screw counter-rotating extruder (HAAKE MiniLab II, Thermo Scientific, Karlsruhe, Germany) was used for simulating PBS mechanical recycling (reprocessing).

Before closed-loop recycling, virgin PBS pellets with an ellipsoidal shape (SSA ≈ 3/mm) were dried at 80 °C for at least 12 h in an oven. For each batch, a total of 5 g was fed in the extruder which was run under different conditions of temperature (120 °C and 140 °C) and screw rotating speed (30 rpm and 100 rpm). These conditions can be commonly found for the mechanical mixing of PBS composite/blends (Bourg et al., 2021; Lule et al., 2020; Muthuraj et al., 2014). The extrusion time was also controlled by internally recirculating the material inside the extruder between 3 and 24 h to mimic different recycling generations (number of closed-loops).

Finally, the rPBS was compression molded at 120 °C for 10 min under vacuum with a 25 mm diameter disk mold for small amplitude oscillatory shear rheology. For tensile tests, a HAAKE MiniJet Pro-Piston Injection Molding System (Thermo Scientific, Karlsruhe, Germany) was used to prepare dog-bone samples (ISO 527-2-1ba). The molten rPBS was injected at 150 °C and 35 MPa with a mold at 30 °C.

2.2. Characterization

Differential scanning calorimetry (DSC) analysis was performed in a TA Q-200 (TA instrument, USA) under a nitrogen atmosphere. Samples around 5–15 mg were placed in aluminum pans and scanned using the following steps: from 20 °C to 160 °C at a heating rate of 10 K/min and subsequently cooled down from 160 °C to 20 °C at a cooling rate of 10 °C/min (2 °C/min was also used for virgin PBS to compare). The first heating cycle was used to remove the thermal history and adsorbed water. The second heating cycle was reported as the results. The data were analyzed via the TA Instrument Universal Analysis software. The crystallinity (χ) was calculated as:

$$\chi = \frac{\Delta H_m}{\Delta H_{m0}} (100) \tag{1}$$

where ΔH_m is the enthalpy of melting of the specimen and ΔH_{m0} is the melting enthalpy of 100 % crystalline PBS taken as 110.3 J/g (Chang et al., 2022).

Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo Scientific Nicolet iS50 ATR-FTIR to identify changes in the physical and chemical interactions during recycling. 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.

The molecular weight distribution of both virgin and recycled PBS was determined using size exclusion chromatography (SEC). An Agilent 1200 series was used with a four-detector configuration including UV detector, followed by multiangle laser-light scattering (MALLS) detection; the eluent passes through a differential refractive index (DRI) detector provided by Polymer Standard Service (PSS, Germany). The columns (SDV-Lux 5 μm (guard column), SDV-Lux-1000 Å, SDV-Lux 100000 Å, PSS) used in the analysis were calibrated using monodisperse liner polystyrene (PS) standards with average molecular weights ranging from 476 to 2.5 × 10^6 g/mol. The eluent was chloroform ($CHCl_3$) with a flow rate of 1 mL/min at 23 °C. Each sample was in solution with a concentration of 1 mg/mL and injected into the columns using an autosampler with 100 μL being used for each measurement.

The small amplitude oscillatory shear (SAOS) rheological properties were investigated using a strain-controlled ARES-G2 rheometer (TA Instruments, USA) in a nitrogen atmosphere ($N_2 > 99.9$ vol% with a N_2 purifier) to prevent polymer degradation at high temperatures. The experiments were conducted using a parallel plates geometry (25 mm diameter). To determine the linear viscoelastic regime, oscillatory strain sweep tests were firstly 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 90 and 180 °C. The master curves were constructed by shifting the storage modulus (G') and loss modulus (G'') to a reference temperature ($T_{ref} = 160$ °C) using the time-temperature superposition (TTS) principle in the rheometer software Trios from TA instruments.

Tensile testing was performed using a universal tensile testing machine (Hegewald & Peschke, Nossen, Germany) at room temperature. The specimens were subjected to deformation at a constant crosshead speed of 50 mm/min using a 10 kN load cell. The tests were conducted until specimen failure and the resulting stress-strain curves were used to determine the Young's modulus (E), ultimate tensile strength (σ_{ult}) and elongation at break (ε_b).

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

Fig. 1(a, b) compares the DSC thermograms of rPBS extruded under different conditions. It was observed that the materials have a similar melting temperature around 84 °C even after multiple recycling cycles. Multiple peaks can be identified for some rPBS probably due to different sizes of the crystalline structure or multiple unit cells, which needs to be investigated in the future. Although differences in the melting peak widths can be observed indicating varying molecular weight distribution (MWD), no general trend can be identified. On the other hand, Fig. 1c shows a 4 % increase of crystallinity between the virgin PBS and the one extruded for 24 h at 120 °C and 100 rpm. This slight increase could be ascribed to higher mobility of shorter polymer chains during crystallization, consequently higher crystallization rates. Polymers exposed to shear stress and high temperature are susceptible to chain scission leading to shorter polymer chains. This argument is also supported by Fig. S1a showing the effect of cooling rate on crystallization. The crystallization peak of virgin PBS can be captured at a slow cooling rate (2 °C/min), but not at a higher rate (10 °C/min). However, these peaks can be easily observed at 10 °C/min for all rPBS as shown in Fig. S1b. Longer polymer chains for virgin PBS have less mobility and consequently a lower rate to form a crystalline structure for the conditions investigated. This information indicates that the polymer chains of rPBS have higher local mobility than virgin PBS.

3.2. Rheology

Small amplitude oscillatory shear rheology combined with the time-temperature-superposition (TTS) is an effective approach to establish molecular structure-macroscopic property relationships. Therefore, Fig. 2 compares the frequency dependent master curves of the virgin and recycled PBS under different extrusion conditions to determine the effect of extrusion screw speed and temperature. All the investigated materials reach their zero-shear-viscosity (η_0) plateau within the experimental window. Fig. 2a shows that the η_0 of PBS extruded at 120 °C and 30 rpm for 6 h ($\eta_0 = 677$ Pa·s) decreased by 33 % compared to the virgin material ($\eta_0 = 1003$ Pa·s). Assuming a cubic dependence of the viscosity on the weight averaged molecular weight (M_w) for a linear polymer, this would be related to a decrease in M_w by about 10 %. Further extrusion, up to a total of 12 h, only decreased η_0 by another 9 % (η_0: from 677 to 613 Pa·s). To show maximum rheological differences between virgin and recycled PBS, an extrusion time of 12 h was selected to investigate how the screw rotating speed affects the rheological behaviors of rPBS. Fig. 2b compares the virgin material with the rPBS extruded at 30 rpm and 100 rpm with a temperature 120 °C for 12 h, respectively. It can be seen that η_0 of rPBS processed at 120 °C and 30 rpm ($\eta_0 = 613$ Pa·s) is reduced after 12 h by 38 % in comparison to virgin PBS ($\eta_0 = 1003$ Pa·s), while the reduction increases to 98 % for rPBS extruded at 120 °C and 100 rpm for 12 h ($\eta_0 = 19$ Pa·s). The effect of extrusion temperature on

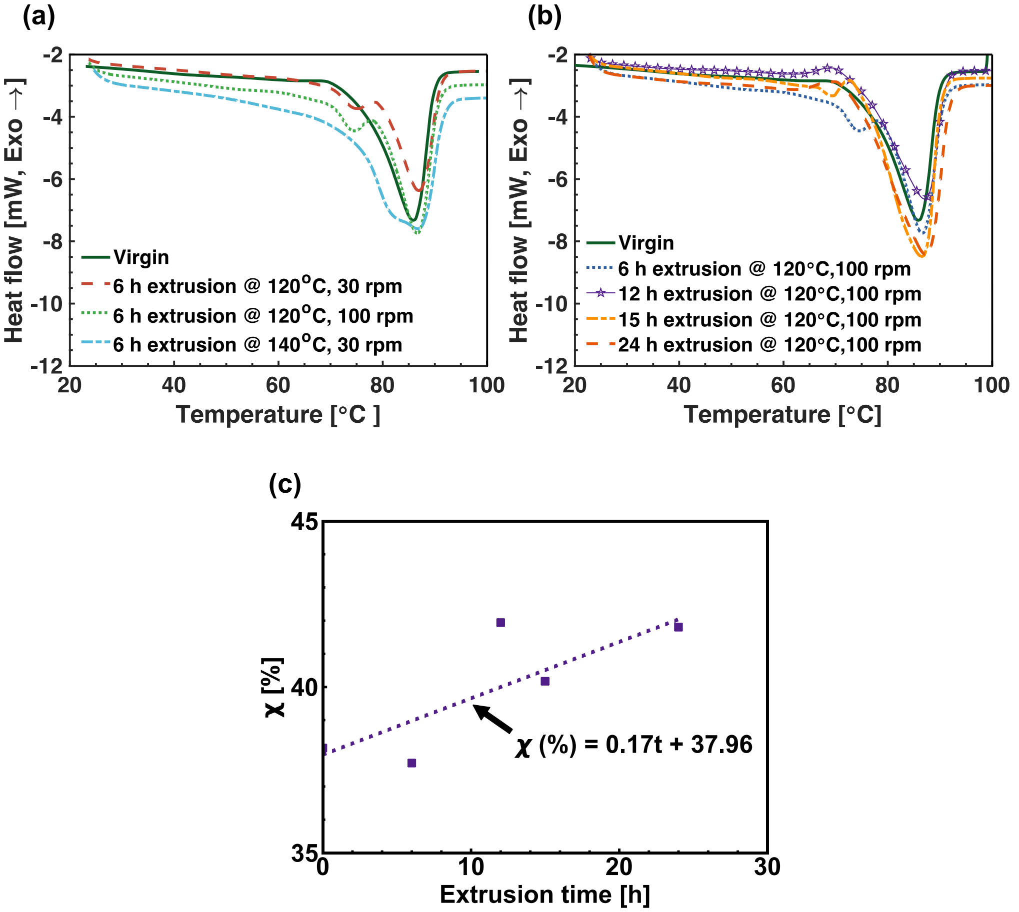

Fig. 1. (a, b) DSC thermograms of rPBS under different mechanical recycling conditions, both virgin and recycled PBS show similar melting temperature around 84 °C; (c) crystallinity as a function of extrusion time for rPBS processed at 120 °C and 100 rpm. The dash line represents a linear regression for comparison. The crystallinity of rPBS increases with the extrusion time and the rPBS extruded at 120 °C and 100 rpm for 24 h has 4 % high crystallinity compared to virgin PBS.

the rheological properties is also compared in Fig. 2c. After extrusion at 30 rpm for 6 h, the rheological behavior of rPBS between 120 °C and 140 °C shows negligible difference. It should be noted in Fig. 2b that data for rPBS at very low angular frequency is experimentally not available due to low shear stresses (sensitivity limit for current geometry: 25 mm parallel plates). To cover a similar angular frequency spectrum as for the virgin material, the experimental data were extrapolated via the Carreau-Yasuda model as shown by the dash lines. Figure S2 shows that this approach is reasonable for these materials and conditions.

From the rheological properties of rPBS under different processing parameters, the screw rotating speed seems to be the most critical processing parameter. However, limited effect of extrusion temperature is observed for the range investigated (120–140 °C). This extrusion temperature seems to be close to practical values as one must be above T_m (84 °C), but as low as possible. Nevertheless, for the conditions selected, a critical extrusion time seems to exist to initiate a substantial change in η_0. For more analysis and interpretation of the molecular mechanisms behind these observations, a focus is made on a specific set of extrusion condition as a function of extrusion time: 120 °C and 100 rpm.

Fig. 3 presents the rheological information of rPBS processed at 120 °C and 100 rpm for up to 24 h. Fig. 3a clearly shows that η_0 drops by 98 % (from 1003 to 19 Pa·s) after 12 h of extrusion compared to virgin PBS. However, the variation of η_0 after 3 h (η_0= 943 Pa·s) is negligible and a limited reduction (29 %) is observed up to 11 h (η_0= 711 Pa·s) of extrusion compared to virgin PBS (η_0= 1003 Pa·s). This indicates that the material can be recycled for some time without significant rheological changes.

More analysis can be done by using the storage (G') and loss (G'') moduli as shown in Fig. 3b. In all cases, the loss moduli dominate over the storage moduli at low frequency, as the terminal relaxation regime is reached. In the terminal regime, all the rPBS show the expected scaling behavior following a Maxwell model: G' ∝ ω^2 and G'' ∝ ω. The experimental crossover points for rPBS extruded for less than 11 h could be reached at high angular frequencies (10^3–10^4 rad/s). In contrast, G' and G" are much lower for rPBS extruder more than 11 h over the whole angular frequency range. In these cases, the G'/G'' crossover points cannot be measured and are obviously shifted towards higher angular frequencies, indicating lower M_w. These crossover frequencies are out of the experimental range due to the onset of crystallization at lower temperatures. Lower relaxation times indicate shorter polymer chains, hence severe degradation of rPBS due to thermal cleavage or shear scission.

To quantitatively determine changes in the molecular structure, the experimental data as shown in Fig. 2 were fitted to the Carreau-Yasuda model as described in the Supplementary Information to extract the parameters as reported in Table 1. It can be seen that all the rPBS have lower η_0 than the virgin one. Moreover, the substantial η_0 drops of about 98 % compared to virgin PBS (η_0= 1003 Pa·s) above 12 h of extrusion time (η_0= 19 Pa·s) is quite noticeable. It is also interesting to note that the characteristic time (τ) for the Carreau–Yasuda model for rPBS extruded above 12 h at 120 °C and 100 rpm (τ= 0.009 s) is one order of magnitude lower than for virgin PBS (τ= 0.146 s). Both information (η_0 and τ) strongly suggests a substantial decrease in molecular weight. The parameter α characterizes the width of the transition from the Newtonian plateau (low shear rate) to the shear-thinning (high shear rate) region. Table 1 reports a significant increase of α for rPBS processed

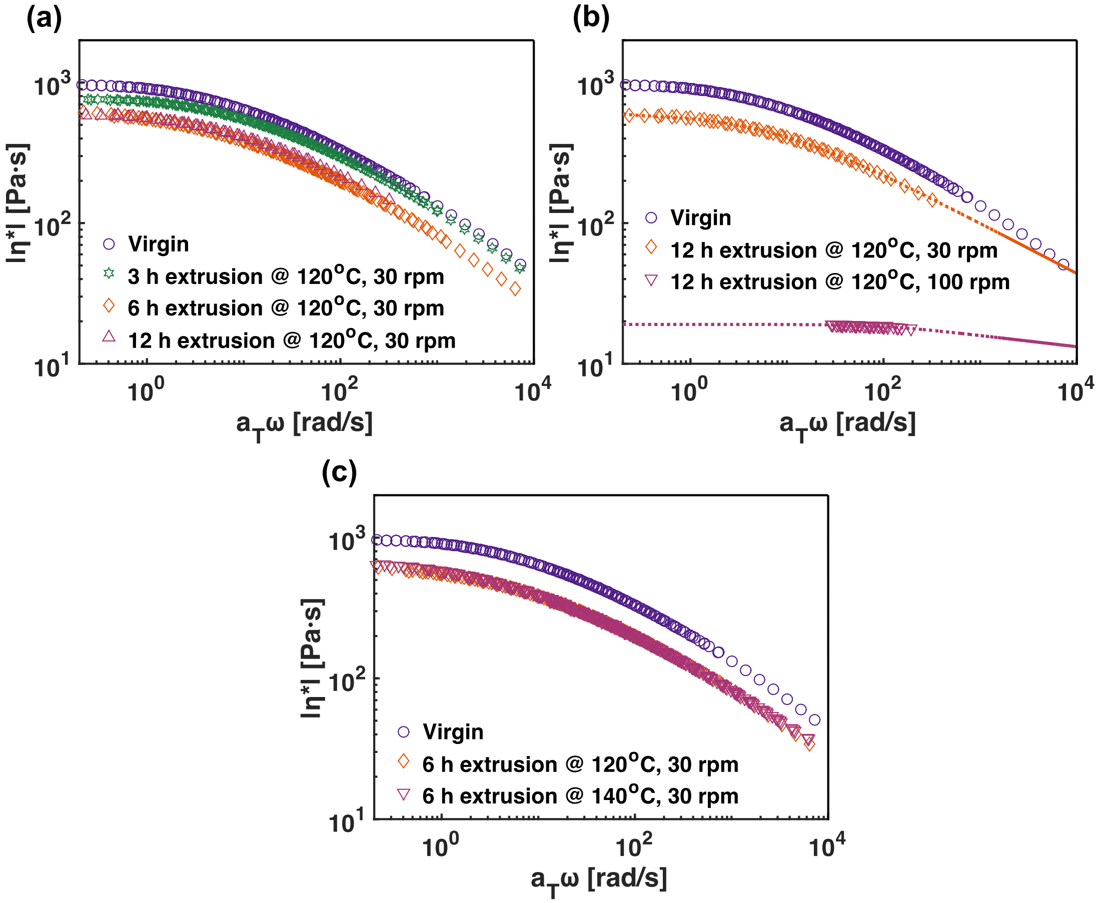

Fig. 2. Complex viscosity as a function of angular frequency for rPBS under different mechanical recycling conditions. The reference temperature for TTS is set as T_{ref} = 160 °C. The comparison indicates that both extrusion time and screw rotating speed have a more significant effect on the rheological property of rPBS than temperature in the ranges investigated.

above 11 h at 120 °C and 100 rpm. For example, a substantial increase (59 %) for α is noticed after 15 h of extrusion ($\alpha = 1.19$) compared to virgin PBS ($\alpha = 0.75$). As the parameter α can be linked to the molecular weight distribution (MWD) in general, an increasing trend indicates a MWD broadening (Mahmood et al., 2020). Finally, the power law-index (n) for rPBS extruded above 12 h ($n = 0.92$) is 51 % higher compared to the virgin PBS ($n = 0.61$), which indicates a less shear-thinning behavior for rPBS. In conclusion, all the information extracted for the viscosity curves indicates that the rPBS is less viscous and more Newtonian (less viscoelastic).

To reduce the effect of the molecular weight dependence, the van Gurp-Palmen (vGP) analysis is performed and the results are presented in Fig. S3. These data show that only the left side of the minimum can be monitored by melt rheology. Semi-crystalline PBS would require crystallization at temperatures around 40 °C (Fig. S1) to acquire data for high modulus within the vGP-plot. However, this creates a conflict with the melting temperature of 84 °C, which poses a challenge in obtaining the full vGP-plot using melt rheology.

Within experimental uncertainty, all the investigated PBS samples with the same polydispersity should superimpose regardless of their chemical nature (Stefan Trinkle and Christian Friedrich, 2001). The vertical position of the minimum in phase angle (δ) correlates with the molecular weight of polymers. Higher molecular weight correlates quantitatively with lower phase angle δ at the minimum of the rubbery plateau. Although the minimum is not observed in Fig. S3, the difference before reaching the plateau can still hold important information regarding the molecular weight change during multiple recycling processes. The rPBS samples with an extrusion time above 12 h have higher phase angles (δ) than virgin PBS and rPBS with extrusion time below 12 h for the same $|G^*|$, suggesting lower molecular weight (M_w).

For linear low-disperse polymers, η_0 is proportional to $M_w^{3.4}$ when the $M_w > M_c$ (PBS: M_c= 16 kg/mol PS equivalent) (Garin et al., 2014). So changes in M_w relative to the virgin PBS can be calculated. Fig. 4a plots these relative changes (η_0 and M_w) as a function of the extrusion time compared to the virgin PBS values (η_0^0 and M_w^0). It is observed that both relative parameters significantly start to decrease around 11 h of extrusion at 120 °C and 100 rpm leading to a sudden decrease of M_w/M_w^0 by a factor of 3 (cross symbols) compared to the virgin PBS. Increasing the screw rotating speed from 30 rpm to 100 rpm (Fig. 4b) also causes the relative zero-shear viscosity (η_0/η_0^0) and molecular weight (M_w/M_w^0) to decrease by 97 % and 64 % respectively, when the temperature and extrusion time were the same (120 °C and 12 h). This information indicates that higher shear rates and long residence times in the extruder substantially decrease the molecular weight of rPBS, and thus the rheological properties.

To further validate the conclusion from rheological observations, SEC characterization was performed. Fig. 5 presents the results for the normalized DRI response as a function of the elution volume V_e. The distribution curves of virgin PBS and rPBS processed for less than 12 h show similar peak values at $V_e \approx 40$ mL and full width at half maximum (FWHM) of ~7 mL. This suggests limited differences in their molecular weight distribution. However, V_e shifts to values between 42 - 44 mL at peak DRI response for rPBS processed above 12 h. This indicates a reduction in rPBS molecular weight (Fig. 4, black triangle) due to chain cleavage. Furthermore, the FWHM of rPBS extruded for more than 12 h increases to about 9 mL showing an increase in polydispersity. This information confirms that long exposure to both high temperature and

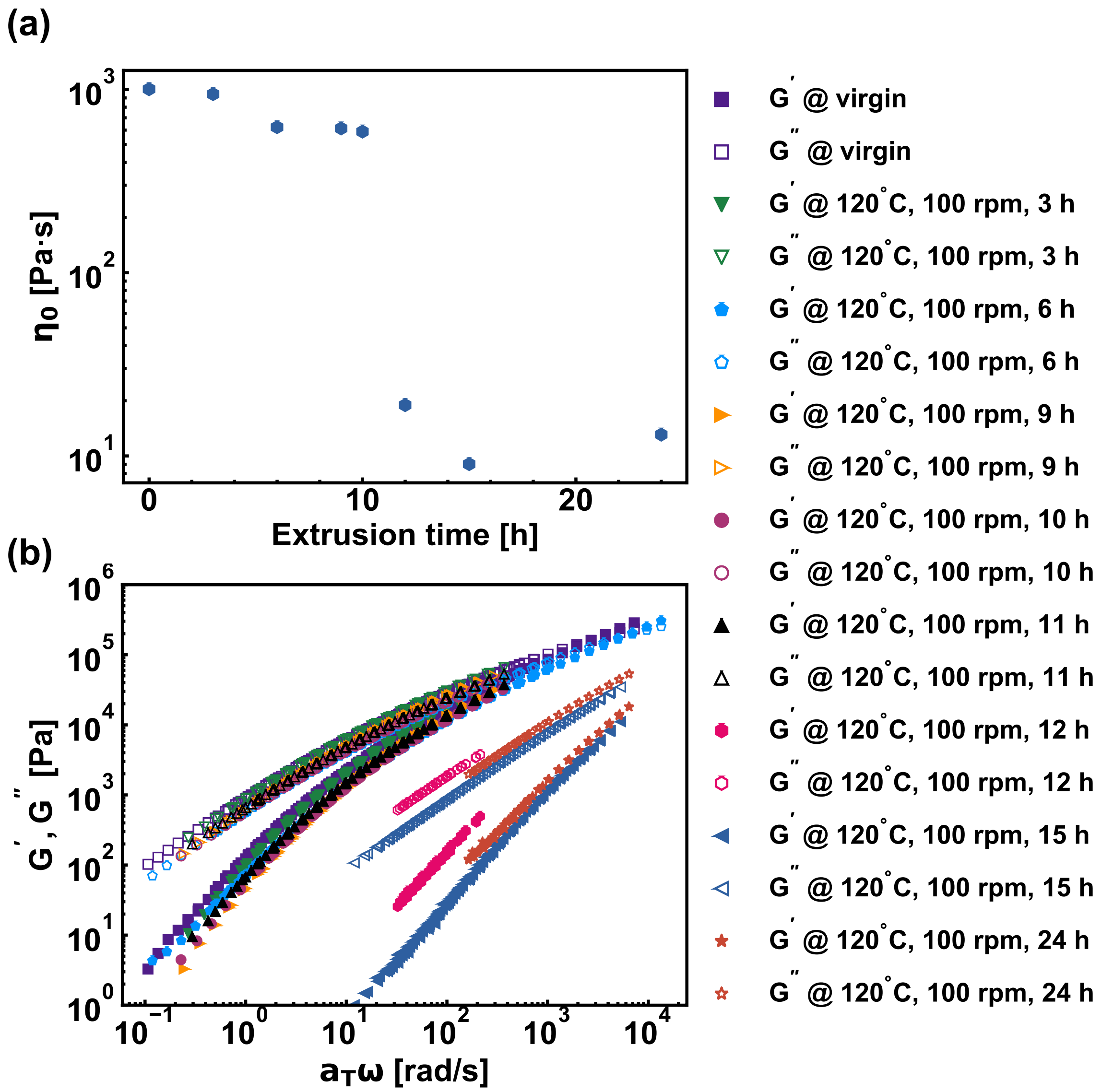

Fig. 3. (a) Zero-shear viscosity (η_0) as a function of extrusion time and (b) storage moduli G' and loss moduli G'' as a function of angular frequency. The zero-shear viscosity (η_0) of rPBS decreases by two-fold compared to virgin PBS when the extrusion time is above 12 h. The moduli also have lower values for extrusion time longer than 12 h compared to virgin PBS.

Table 1
Carreau–Yasuda parameters for PBS under different extrusion conditions.

Conditions	Extrusion time [h]	η_0 [Pa · s]	τ [s]	$\alpha(-)$	n (-)
Virgin	0	1003	0.146	0.75	0.61
120 C 30 rpm	3	799	0.098	0.73	0.60
	6	677	0.101	0.55	0.56
	12	613	0.155	0.77	0.64
120 C 100 rpm	3	943	0.131	0.81	0.64
	6	623	0.096	0.72	0.61
	9	613	0.111	1.02	0.69
	10	613	0.113	0.83	0.64
	11	711	0.112	0.80	0.64
	12	19	0.009	1.48	0.92
	15	9	0.001	1.19	0.86
	24	12	0.001	1.16	0.81
140 C 30 rpm	6	672	0.21	0.71	0.62

shear stress lead to polymer chains scission, but a small variation in polydispersity (molecular weight distribution). These results further underline the importance of careful selection of processing conditions to maintain the molecular structure of rPBS during mechanical recycling.

The activation energy of polymer melts is the minimum energy required for the chain segment to overcome the viscous resistance and start flowing. Its value also quantifies the sensitivity of rheological properties to temperature. The activation energy of viscous flow can be calculated by an Arrhenius empirical equation as (Lou et al., 2019):

$$|\eta^*| = Ae^{\frac{E_a}{RT}} \tag{2}$$

where $|\eta^*|$ is the absolute value of complex viscosity, A is the viscosity at infinitely high temperature ($|\eta^*_{infi}|$), E_a is the Arrhenius activation energy, R is the gas constant (8.314 J/mol·K) and T is the absolute temperature. By taking the natural logarithm on both side of Eq. (2), one can extract the value of E_a from the slope of ln($|\eta^*|$) - 1/T plot. The complex viscosity at constant shear frequency for a minimum of 3 temperatures can be used and the results are presented in Fig. S4. It can be seen that the activation energy changes with respect to shear frequency. Generally, E_a decreases with increasing shear rate for the virgin PBS and most of rPBS except for rPBS extruded at 120 °C and 100 rpm above 12 h. To further investigate this phenomenon, the average E_a of rPBS extruded at 120 °C

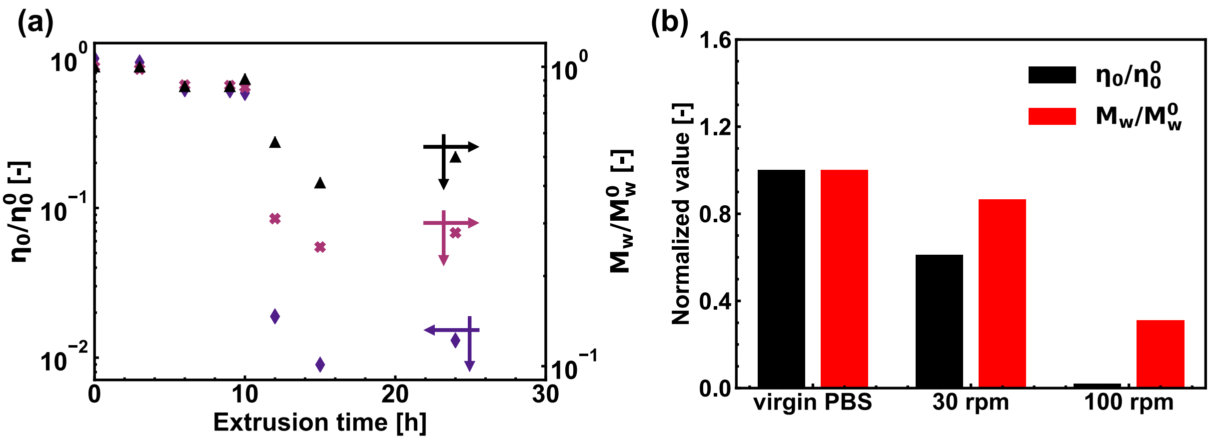

Fig. 4. (a) Zero shear viscosity (⧫: η_0) and molecular weight (Ó: M_w) values relative to the virgin PBS properties (η_0^0 and M_w^0) as a function of extrusion time for rPBS extruded at 120 °C and 100 rpm. p is SEC calibration with polystyrene (PS) standard (PS equivalent). (b) the influence of screw rotating speed on the zero-shear viscosity (η_0) and molecular weight (M_w) of PBS extruded at 120 °C and 12 h. Longer extrusion time (above 12 h) generates lower molecular weight (M_w) by a factor of ~10 and thus the zero-shear viscosity (η_0) of PBS by a factor of ~100. Increasing the screw rotating speed from 30 rpm to 100 rm decreases η_0 by 97 % and M_w by 64 % when the temperature and extrusion time are the same.

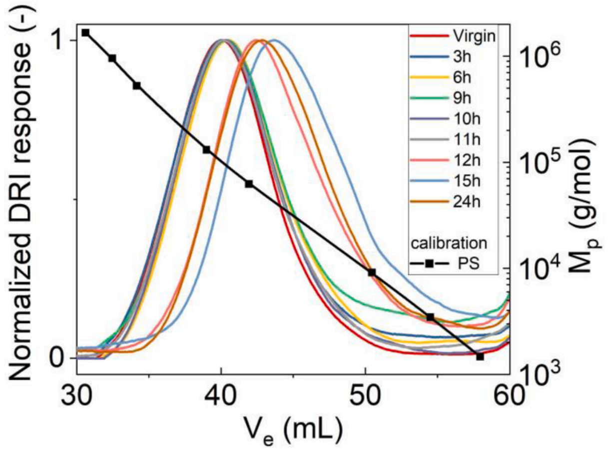

Fig. 5. Elution chromatograms of the virgin and recycled PBS detected by GPC-DRI. All the rPBS were processed at 120 °C and 100 rpm for a period between 3 and 24 h. The elution volume of rPBS with extrusion time longer than 12 h shifts from 40 mL to 42 – 44 mL indicating reduced molecular weight. The broadness of V_e distribution implies increased polydispersity of rPBS extruded more than 12 h.

and 100 rpm are summarized in Table 2 where significant increases are observed above 12 h as the viscosity becomes less sensitive to temperature change. This is probably due to the high mobility of shorter chains becoming less temperature dependent.

3.3. *Fourier-transform infrared spectroscopy (FTIR)*

The observation from both SAOS rheology and SEC confirmed that chain scission occurred during mechanical recycling of PBS. This leads to the ask about their origin with respect to chemical changes during mechanical recycling. Fourier-transform infrared spectroscopy (FTIR) spectroscopy is a powerful analytical tool to determine changes in the functional groups of PBS during mechanical recycling. However, the quantification of spectral information can be challenging due to varying background and noise. To overcome this issue, the baseline can be corrected by asymmetrical least squares smoothing methods.

Table 2
Activation energy of rPBS processed at 120 C and 100 rpm between 3 and 12 h.

Condition	Extrusion time [h]	Activation energy [kJ/mol]
120 C, 100 rpm	0	14.6
	3	15.6
	6	20.2
	9	10.7
	12	33.2
	15	32.9
	24	26.0

Fig. 6 presents the baseline-corrected ATR-FTIR spectrum of PBS after normalizing to their maximum peaks, respectively. The peak at 956 cm^{-1} corresponds to the bending of the –CO—OH of the terminal acid group. The absorption band around 1044 cm^{-1} is attributed to the -O-C—C- stretching vibration, while the peaks around 1160 cm^{-1} and 1210 cm^{-1} arise from the -C-O—C- stretching of the ester bonds. The sharper and more intense band around 1711 cm^{-1} is due to the carbonyl group -C = O which arise from the stretching of both the amorphous and crystalline domains of ester carbonyl groups as observed by de Matos Costa et al., 2020 and Mallardo et al., 2016. In the region between 2800 cm^{-1} and 3000 cm^{-1}, the asymmetric stretching of the -CH- groups is identified. A very week absorption band between 3500 cm^{-1} and 3600 cm^{-1} is assigned to the hydroxyl groups (-O-H). Although the intensity of peaks below 3500 cm^{-1} varies between virgin PBS and rPBS, no general trend was observed. However, the intensity of hydroxyl groups in rPBS extruded for more than 6 h is generally stronger than for virgin PBS as shown in Fig. 7.

This increase of hydroxyl groups could be associated to possible hydrolysis with remaining traces of water (Lee et al., 2008). More likely, the thermal degradation causes a random scission of the in-chain ester links resulting in the formation of vinyl ester and carboxyl end groups (Venkatachalam et al., 2012). During the mechanical recycling process, PBS is subjected to elevated temperature, pressure, mechanical stresses (shear and elongation), and potential exposure to water (air humidity) during the cleaning process. Water can facilitate the cleavage of ester bonds during extrusion. This correlation between the changes in the hydroxyl and carbonyl bands observed in the FTIR spectra provides strong evidence for the occurrence of ester bond rupture, hydration, or chemically more precise "saponification" as a PBS degradation mechanism during mechanical recycling. Likewise, this can explain the decrease of molecular weight of highly recycled PBS as observed via SEC. However, this hypothesis will be further investigated in future studies by using more chemical analysis, such as nuclear magnetic resonance spectroscopy (NMR), to unveil more details on the degradation mechanisms during mechanical recycling of PBS, with a focus on

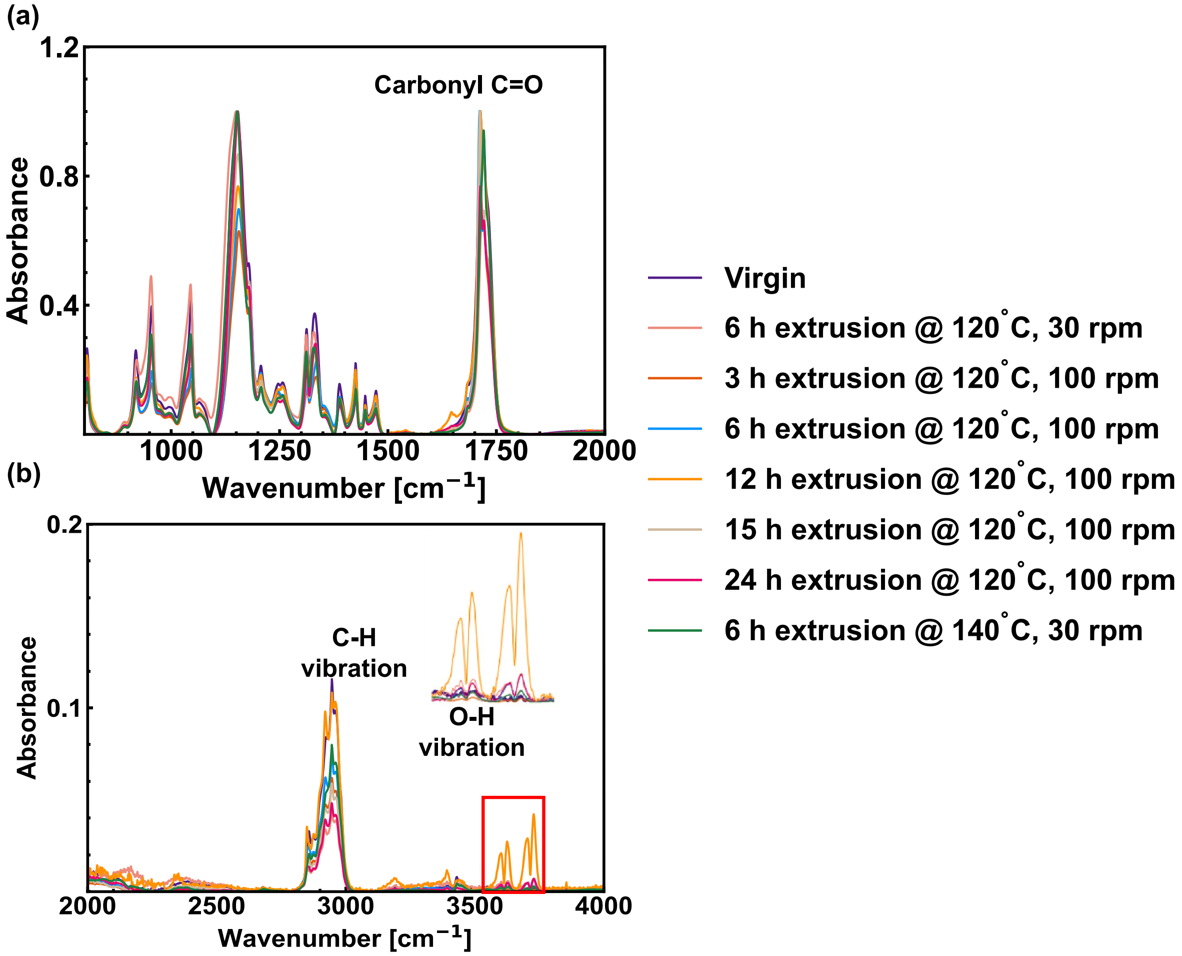

Fig. 6. ATR-FTIR spectra of virgin and rPBS processed under different conditions (120 °C and 140 °C; 30 and 100 rpm) for a period between 3 h and 24 h: (a) 800–2000 cm^{-1} and (b) 2000–4000 cm^{-1}.

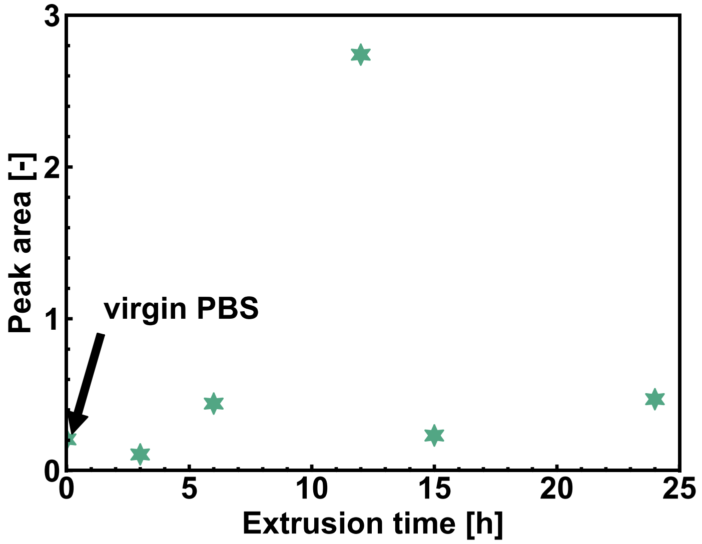

Fig. 7. Change of -O-H groups resonance relative peak area of PBS as a function of extrusion time at 120 °C and 100 rpm. The peak area is calculated by integrating the absorbance signal of -O-H groups between the wavenumber of 3570 cm^{-1} and 3750 cm^{-1} in ATR-FTIR spectra. In general, the -O-H of rPBS has stronger signal than virgin PBS which can be associated with hydrolysis due to remaining traces of water in PBS or more likely the scission (saponification) of ester links.

molecular changes after 11 h of extrusion time.

3.4. Tensile properties

The mechanical properties in the solid state (below T_m) highly depend on the molecular structure, as well as the morphology and size of the crystalline structure. Tensile tests were performed at 50 mm/min and room temperature. Fluctuations are found in the stress-strain curves in Fig. 8 due to necking and plastic deformation or defects (Kuang et al., 2022). It is interesting to see in Fig. 8a that the elongation at break is significantly decreased for rPBS that was extruded above 12 h at 120 °C and 100 rpm. However, no clear trend can be concluded for other

Table 3
Tensile properties of virgin and mechanically recycled PBS.

Conditions	Extrusion time [h]	E [MPa]	σ_{ult} [MPa]	Elongation at break [%]
Virgin	0	271.3	16.9	220.7
120 C, 100 rpm	6	283.8	18.0	265.9
	12	311.8	13.6	5.8
	15	298.6	5.4	2.0
	24	249.3	9.9	4.8
120 C, 30 rpm	6	222.9	21.9	328.6
140 C, 30 rpm	6	262.7	21.8	204.1

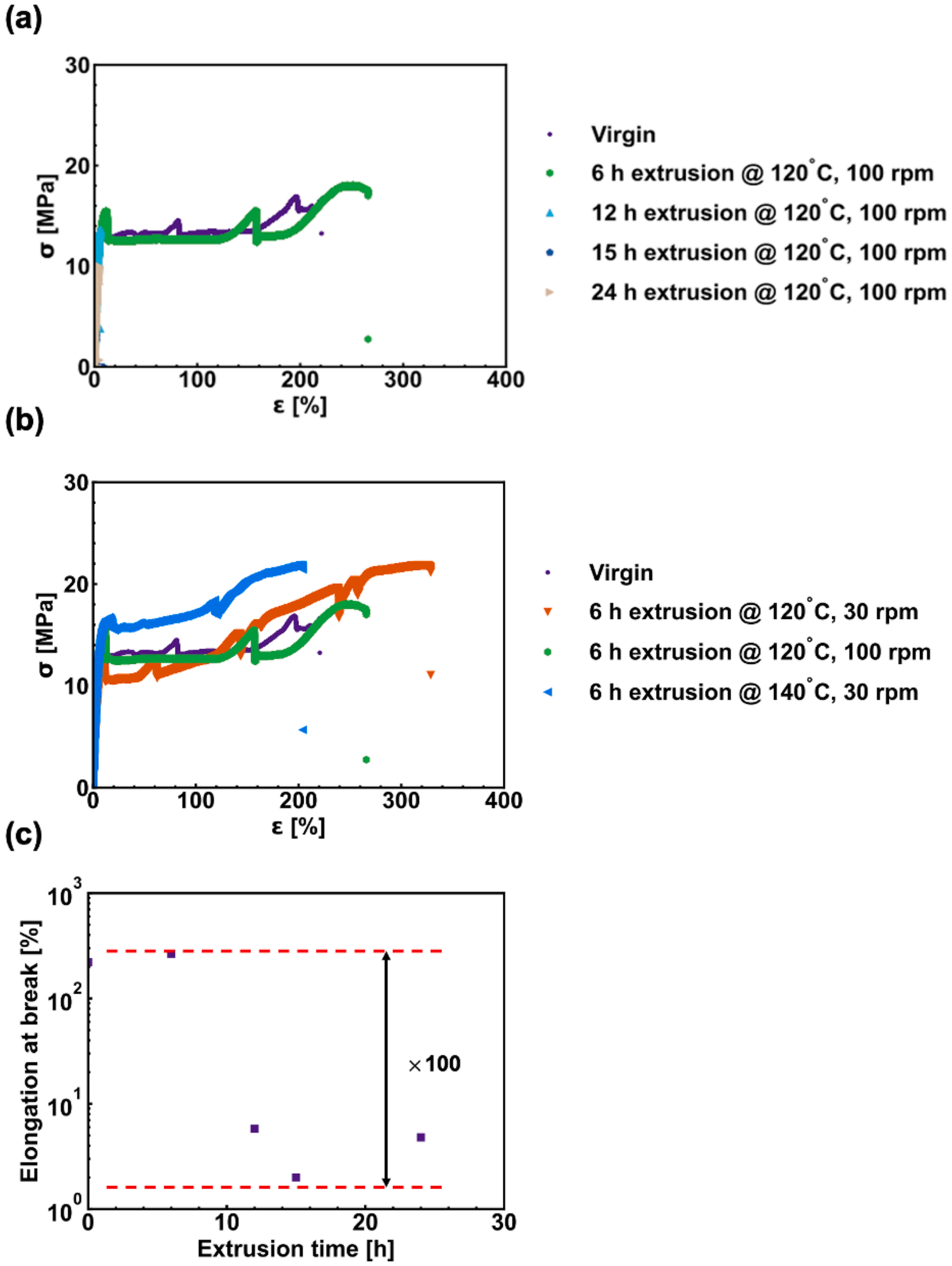

Fig. 8. Stress-strain curves of rPBS processed at: (a) 120 °C and 100 rpm for different time; (b) different temperatures (120 °C, 140 °C) and screw rotating speed (30 rpm, 100 rpm) for 6 h; (c) elongation at break as a function of extrusion time for rPBS extruded at 120 °C and 100 rpm. Mechanical extrusion has a significant effect on the elongation at break of rPBS. The largest difference between virgin PBS and rPBS (extrusion time > 15 h) can reach 100 times.

conditions including different temperature or screw rotating speed in Fig. 8b. To be quantitative, the key tensile properties are summarized in Table 3 where negligible effect of the extrusion time or condition on the Young's modulus *E* is observed. But significant reduction (more than 40 %) is observed for the ultimate tensile strength of rPBS processed at 120 °C and 100 rpm above 15 h compared to the virgin PBS. Moreover, the elongation at break of rPBS extruded at 120 ℃ and 100 rpm above 15 h decreased by a factor of 100 when compared to the virgin PBS as more clearly seen in Fig. 8c. Lower elongation at break is mainly due to chain scission as confirmed via rheological measurement and SEC, resulting in a very brittle material. In conclusion, the tensile properties significantly dropped above a critical recycling time (around 12 h) depending on the conditions used (temperature and screw speed).

4. Conclusion

This work investigated the effect of different mechanical recycling conditions on the molecular, rheological and mechanical properties of recycled poly(butylene succinate) (rPBS). The experiments were conducted using a lab-scale twin-screw extruder using different temperatures (120 °C and 140 °C), screw rotating speed (30 rpm and 100 rpm) and time (3 h to 24 h) to simulate different mechanical recycling generations.

The thermal properties of the material were analyzed using differential scanning calorimetry (DSC), while changes in the molecular structure and processing properties were studied using small amplitude oscillatory shear rheology (SAOS) tests. The results were used to understand the evolution of the molecular structure with processing and the molecular structure of the material was characterized using size exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR) to monitor chemical changes. Finally, mechanical tensile tests were performed at room temperature to determine the effect of mechanical recycling on the properties of rPBS.

The results suggested that high screw rotating speed (100 rpm) and long extrusion time (above 12 h) significantly decreased the viscosity of regenerated PBS (rPBS). The zero-shear viscosity (η_0) decreased by 98 % for rPBS processed at 120 °C and 100 rpm for 12 h compared to virgin PBS, which indicates a reduction in molecular weight of about 70 %. The characteristic time (τ) extracted from the Carreau-Yasuda shear viscosity model also decreased by a factor of 100. Such changes can be attributed to substantial polymer chains scission during mechanical extrusion, which was confirmed by increased crystallinity observed via DSC. SEC results also showed a reduction in molecular weight with increased polydispersity for rPBS processed at high temperature, high shear rate and for long time. Finally, FTIR analyses showed significant changes in hydroxyl groups indicating chain scission from ester bonds resulting from shear stress or thermal cleavage.

In terms of mechanical properties, the Young's modulus (E) remained mostly unchanged, but the tensile strength (σ_{ult}) for rPBS processed at 120 °C and 100 rpm above 15 h was reduced by more than 40 % compared to virgin PBS. But the elongation at break of rPBS was found to be more affected with decreases by a factor of up to 100 compared with virgin PBS.

So the main conclusion is that mechanical recycling via melt extrusion of rPBS resulted in chain scission which significantly modified the rheological and mechanical properties of the polymer. However, this phenomenon mainly occurred for long extrusion time (more than 12 h) and high screw speed (100 rpm) for the conditions investigated. These results indicate that PBS can be recycled several times without significant changes in its processing and overall properties, which makes it interesting to recycle.

These findings can be related to real-case scenarios by considering the actual recycling conditions used in industrial settings or recycling facilities. These conditions can be mapped to the simulated processing time, temperature, and screw speed (rpm) in this study. By establishing such correlation, it is possible to estimate a practical maximum number of recycling generations that can be performed under these specific conditions while maintaining the desired material properties.

Furthermore, these findings can shed light on potential strategies to mitigate the loss of molecular weight and mechanical performance during recycling. For instance, if specific processing conditions and additives are found to be more effective in preserving the polymer's molecular structure and properties, these insights can guide the optimization of recycling processes and development of more sustainable recycling practice and circular economy.

However, these preliminary results did not answer all the questions and future studies should focus more on the degradation mechanisms during PBS mechanical recycling (extrusion), as well as to study other processing methods (injection molding, thermoforming, calendering, etc.). A careful analysis of the functional groups should also be performed to follow other properties such as permeability, color, fatigue, creep, etc. This would make it possible to determine specific functional groups changes as fingerprints of degradation. Finally, a complete understanding of the degradation mechanisms would help to design suitable additives to preserve the properties and applications of recycled PBS, as well as other polymers in general.

CRediT authorship contribution statement

Jian Zhang: Formal analysis, Investigation, Writing – original draft. **Valerian Hirschberg:** Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Michael Pollard:** Formal analysis, Investigation, Methodology, Writing – review & editing. **Manfred Wilhelm:** Resources, Supervision, Validation, Writing – review & editing. **Denis Rodrigue:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, 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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2024.107741.

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