Mechano-Optical Characterization of Extrusion Flow Instabilities in Styrene-Butadiene Rubbers: Investigating the Influence of Molecular Properties and Die Geometry

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The extrusion flow instabilities of two commercial styrene-butadiene rubbers are investigated as they vary in isomer content (1,4-cis, 1,4-trans, and 1,2 conformation) of the butadiene monomer and the molecular architecture (linear, branched). The investigated samples have similar multimodal molecular weight distribution. Two geometries of extrusion dies, slit and round capillary, are compared in terms of the type and the spatial characteristics of the flow instabilities. The latter are quantified using three methods: a highly pressure sensitive slit die, online and offline optical analysis. The highly pressure-sensitive slit die has three piezoelectric pressure transducers (Δt = 10⁻³ s and Δp = 10⁻⁵ bar) placed along the die length. The characteristic frequency (f_{Char}) of the flow instabilities follows a power law behavior as a function of shear rate to a 0.5 power for both materials, f_{Char} ≈ f_{app}^{0.5}. A qualitative model is used to predict the spatial characteristic wavelength (λ) of the flow instabilities from round capillary to slit dies and vice versa. Slip velocities (V_s) are used to quantify the slippage at slit and round capillary dies as well.

The influence of molecular properties and die geometry in capillary rheometry has challenged for the quality of a product.[1–7] As the extrusion throughput is increased, extrudate can change appearance from a smooth and transparent to matte and afterward to various kinds of surface and/or volume distortions.[5,8–10] Typical names for the flow instabilities, as the shear rate increases, are sharkskin, stick-slip, and gross melt fracture (GMF). Attempting to define these regions, Gansen et al.[11] and Naue et al.[8,9] defined the surface and volume distortions referred to slit die (rectangular cross-section area) geometry. Sharkskin is defined as high frequency (f_{Char} = 20 Hz for a specific linear low density polyethylene at 140 °C,[12] and within our study f_{Char} = 15 Hz for a specific styrene-butadiene rubber (SBR) at 120 °C) with small amplitude surface distortions. The amplitude of the distortions should be smaller than the thickness of the extrudate for the sharkskin instability. The conventional pressure transducer of a capillary rheometer is not able to capture the high frequency and low amplitude pressure fluctuations during sharkskin instability. Stick-slip instability is characterized by alternating smooth and/or sharkskin regimes as well as irregular distortions at the extrudate surface and volume. It is accompanied by slow pressure (p) fluctuations of Δp/p ≈ 25% for p = 200 bar mean pressure, measured by a conventional pressure transducer in the barrel of a capillary rheometer. GMF is characterized by distortions of the entire extrudate and therefore can be classified as a volume instability. No typical pattern in space and time has been observed for GMF.[10] Gross melt fracture is not further investigated within this presented study.

The influence of die geometry in capillary rheometry has been experimentally and numerically discussed in the literature.[13–20] Experimental studies[15,16] have shown that the onset and the type of flow instabilities are significantly affected by the die geometry even at a similar range of shear rates. For this reason, both slit (rectangular cross-section area) and round capillary (circular cross-section area) dies are used in this investigation. A power law model[13] is used to describe the shear stress dependency as a function of shear rate, followed by
implementation into the volumetric flow rate equation as suggested by Mooney.\cite{3,23} Consequently, analytical equations for the slip velocity are obtained and used to quantify the slippage at both die geometries (slit and round capillary).\cite{8,9}

In the last 15 years, an online highly pressure-sensitive in situ mechanical detection slit die has been developed to characterize the flow instabilities during extrusion.\cite{10,30,32,22–28} This system was designed for coupling to both capillary rheometers and lab size extruders.\cite{8,9} This slit die is equipped with three highly sensitive piezoelectric pressure transducers (Tr) along the die. These transducers are able to detect minor pressure fluctuations ($\Delta p \approx 10^{-5}$ bar) which appear at the onset of the flow instabilities, and they are associated with the distortions at the extrudate surface.\cite{8,9} During the onset of stick-slip instability an average stick-slip velocity $V_{\text{stick-slip}}$ needs to be defined. The development of a pressure drop along the slit die during the stick-slip is recorded by the three transducers. Palza et al.\cite{12} suggested to cross-correlate the time-dependent pressure signal of two transducers, thus the cross-correlation time $\tau_{\text{CC}}$ can be obtained. As the distance between two transducers is known $L_{\text{cc}}$, the time needed for the stick-slip instability to cross two transducers can be computed by the cross-correlation function (CCF). Hence, the average stick-slip velocity is obtained, $V_{\text{stick-slip}} = L_{\text{cc}} / \tau_{\text{CC}}$.

Several qualitative models have been used to predict the spatial characteristic wavelength of flow instabilities. Wang et al.\cite{29} Barone et al.\cite{30} and Inn et al.\cite{31} have modeled the characteristic sharkskin wavelength for capillary dies. Wang et al.\cite{29} and Barone et al.\cite{30} have studied linear low density polyethylene (LLDPE) samples which exhibit pronounced sharkskin instability. Both studies quantify the spatial characteristic wavelength $\lambda$ of flow instabilities as $\lambda = \tau^* V$, where $V$ is the average extrude velocity and $\tau^*$ is the characteristic time periodicity. A more complex analytical expression has been proposed by Inn et al.\cite{31} studying polybutadiene (PBD) samples. They used Cogswell\cite{32} approach to estimate the amount of stretching deformation on the surface of the extrudate at the die exit region. All of those qualitative models\cite{29–31} have been developed based on visual observations of extrudates immediately after the die exit.

In the present study, two commercial styrene-butadiene random copolymers with similar multimodal MWD, chemical composition but different isomer content (1,4-cis, 1,4-trans, and 1,2 conformation) of the butadiene monomer and different molecular architecture (linear, branched) are investigated. The difference in isomer content of butadiene and molecular architecture of the two samples is related to different types of flow instabilities. Additionally, size-exclusion chromatography (SEC), $^1$H-nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and a newly developed low field SEC-NMR coupling have been performed to gain insight into the molecular properties of the two SBR samples. Thereafter, the samples were extruded through the described highly pressure-sensitive slit die with length of $L = 30$ mm and a rectangular cross-section area of $0.5 \times 5$ mm$^2$ ($H \times W$), and a series of three round capillary dies with aspect ratio of $L/D = 5, 10, 15$ with diameter of $D = 2$ mm coupled to a Göttfert RG 50 capillary rheometer. The extrudate characteristics, such as the spatial wavelength and the characteristic time periodicity (or frequency), have been analyzed using the pressure fluctuations provided by the highly pressure-sensitive slit die. In addition, offline and online optical analyses for both die geometries were performed.\cite{8,9,26,28} First, the time characteristic frequency (or periodicity) was obtained by Fourier transform (FT) analysis of the in situ mechanical pressure fluctuations. Second, transmission polarization microscopy and incident light microscopy were used to quantify the spatial characteristic wavelength $\lambda$ of the instabilities on the extrudate surface and according to $\lambda = \tau^* V$, the instability characteristic time periodicity $\tau^*$ is obtained. Third, an online optical analysis method is presented based on the space-time diagrams\cite{26,31–33} capable to obtain the characteristic time periodicity without using estimated values such as the average extrude velocity. Finally, those three differently obtained periodicities are compared to each other. Additionally, this work modifies the proposed model for the spatial characteristic wavelength $\lambda$ as discussed by Wang et al.\cite{29} and Barone et al.\cite{30} and makes it capable to predict the wavelength for slit dies as well. Thus, this qualitative model allows us to predict the characteristic wavelength $\lambda$ of flow instabilities changing from capillary to slit dies and vice versa.

2. Experimental Section

Two commercial SBR, named SBR A and SBR B, were investigated in this study. The samples were characterized using SEC and high field NMR spectroscopy (400 MHz, 9.4 Tesla, $^1$H). The glass-transition temperature $T_g$ of the samples was investigated via DSC.

To determine the relative molecular weight distribution (MWD) of the SBRs, the SEC was calibrated with polystyrene standards. The elution volume multimode distributions of the two samples are presented in Figure 1. The distributions displayed that the two samples have similar elution volume distributions.

![Figure 1. Normalized differential refractive index (DRI) detector response as a function of the elution volume for both SBR samples as obtained by SEC. The inset is the molecular weight distribution (MWD) of both samples. This SEC is equipped with an analytical column with length of 300 mm and inner diameter of 8 mm.](image-url)
The heating/cooling rate was 5 K min\(^{-1}\) obtained by high field NMR and DSC, respectively. The glass-transition temperature of the two investigated SBR samples is listed in Table 1. Besides, the overall molecular weight (MW) component, presented at elution volume of 20 and 22.5 mL.

For the bimodal fraction (elution volume of 10–15 mL), the relative weight compositions of the two modes are similar as well (Table 1). The weight average molecular weights \(M_w\) of the respective components differ by a factor of 3 and almost 2.5 for SBR A and B, respectively (Table 1). However, at 145 °C the SBR A did not present stick-slip resistance.

One of the most important properties of any elastomer is its glass-transition temperature, \(T_g\). As discussed previously, \(T_g\) is controlled in SBRs by adjusting the monomer ratio of styrene to butadiene and the isomer of the butadiene units as well. DSC characterization was used to investigate the \(T_g\) of the SBR samples (Table 2). Each of the samples has only one glass transition temperature, thus phase separation is not detectable at a large length scale (i.e., \(l > 3–5\) nm) in these two systems.

The capillary extrusion temperature was chosen similar to typical industrial processing conditions for SBR polymers, that is, 120 °C for both of the samples. Owing to the appearance of different types of flow instabilities, where SBR A displays sharkskin and SBR B displays sharkskin and stick-slip, SBR A was tested at 145 °C as well. Thus, it was studied under the same temperature difference from the \(T_g\) as the SBR B. However, at 145 °C the SBR A did not present stick-slip instability in the entire range of the investigated apparent shear rates, from \(\dot{\gamma}_{app} = 10^0–10^2\) s\(^{-1}\). The temperature difference with respect to \(T_g\) at 120 °C is 156.3 °C for the SBR A and 180.7 °C for the SBR B. It is known\(^{[4]}\) that more than 100 °C above the \(T_g\), the effect of the butadiene isomer is neglectable compared to the influence of topological constraints (entanglements) and molecular architecture (i.e., branching).

### 3. Characterization Techniques

In this section, techniques which have been used and developed to characterize the flow and the process behavior of the investigated samples are presented.

#### 3.1. Oscillatory and Extensional Rheology

Rheological experiments were carried out in the linear and nonlinear regime using a TA Instruments ARES-G2.

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**Table 1.** Molecular weight characteristics of the two investigated SBR samples.

| Name    | Elution volume [mL] | Weight percent [wt%] | \(M_w\) [kg mol\(^{-1}\)] | \(M_n\) [kg mol\(^{-1}\)] | \(D\) |
|---------|---------------------|----------------------|---------------------------|---------------------------|------|
| SBR A   | 10.0–15.0           |                      | 286                       | 391                       | 1.36 |
| High MW\(^{a}\) | 10.0–12.5       | 26.6                 | 688                       | 757                       | 1.10 |
| Medium MW\(^{a}\) | 12.5–15.0     | 68.4                 | 258                       | 260                       | 1.02 |
| Low MW\(^{a}\)  | 20.0–22.5           | 5.0                  | 0.46                      | 0.65                      | 1.40 |
| SBR B   | 10.0–15.0           |                      | 287                       | 390                       | 1.35 |
| High MW\(^{a}\) | 10.0–12.5       | 26.0                 | 610                       | 650                       | 1.05 |
| Medium MW\(^{a}\) | 12.5–15.0     | 68.0                 | 252                       | 256                       | 1.01 |
| Low MW\(^{a}\)  | 20.0–22.5           | 6.0                  | 0.42                      | 0.60                       | 1.42 |

\(^{a}\)The weight percent is calculated by the DRI detector as a function of elution volume assuming that the two peaks have similar chemical composition; \(^{b}\)The weight percent is calculated from the 2D SEC-NMR data presented in Figure 6.

**Table 2.** Chemical composition in weight percentage (wt%) and the glass-transition temperature of the two investigated SBR samples obtained by high field NMR and DSC, respectively.

| Name    | Styrene [wt%] | Butadiene 1,2 [wt%] | Butadiene 1,4 (cis and trans) [wt%] | \(T_g\) [°C] |
|---------|---------------|---------------------|--------------------------------------|-------------|
| SBR A   | 23.5          | 47.3                | 29.2                                 | −36.3       |
| SBR B   | 16.3          | 25.2                | 58.5                                 | −60.7       |

\(^{a}\)The heating/cooling rate was 5 K min\(^{-1}\) with a temperature range of −90 and 160 °C. The second heating run was analyzed.
(New Castle, DE) strain-controlled rheometer. For the oscillatory frequency sweep experiments, the rheometer is equipped with a grooved plate-plate geometry, with a diameter of 8 mm to reduce slippage. The SBR samples were tested by an isothermal time sweep which has been performed at 120 °C, $\omega/2\pi = 1$ Hz and strain amplitude of $\gamma_0 = 3\%$. The storage modulus $G'$ stayed constant within 5% at 110 kPa for more than 2 h which confirms the thermal stability of the samples. Small amplitude oscillatory shear (SAOS) frequency sweep tests were performed within $\gamma_0 = 1–3\%$ strain amplitude in the linear viscoelastic (LVE) regime to obtain the magnitude of the complex viscosity, storage and loss moduli in a wide range of temperatures from −45 to +120 °C. Moreover, the nonlinear rheological behavior of the samples was investigated by uniaxial extensional rheology. The extensional viscosity fixture (EVF) was coupled to the ARES-G2 rheometer, and the transient extensional viscosity of the samples was determined at 120 °C.

### 3.2. Capillary Rheology

Capillary rheology of the samples was studied using a Göttfert RG 50 capillary rheometer (Buchen, Germany) equipped with a home-built highly pressure-sensitive slit die system, including a series of conventional round capillary dies as well. The slit die comprises a series of three highly pressure-sensitive piezoelectric (Kistler 6182CA) pressure transducers (Tr) distributed along the slit die. Each transducer is located, at (Tr1) 5 mm, (Tr2) 15 mm, and (Tr3) 25 mm from the die entrance (Figure 2). Two types of extrusion dies were compared in this study: a slit (rectangular cross-section area) die and round capillary (circular cross-section area) dies. The extrusion slit die has a rectangular cross-section of width, $W = 5$ mm and height, $H = 0.5$ mm, over a length of $L = 30$ mm. Consequently, the aspect ratios are $W/H = 10$ and $L/H = 60$. The three round capillary dies have diameter of $D = 2$ mm and aspect ratios of $L/D = 5, 10, 15$. In the highly pressure-sensitive slit die, the sensing element (piezoelectric transducers) diameter is 2.5 mm and provides the in situ detection of the mechanical pressure fluctuations. The piezoelectric transducer system provides time and pressure resolutions, of $\Delta t = 10^{-3} \text{s}$ and $\Delta p = 10^{-3} \text{bar}$ up to nominal pressure of $p = 2000 \text{ bar}$.

### 3.3. Optical Analysis of Extrudates

Figure 2. Schematic representation of the capillary rheometer and the highly pressure sensitive slit die. Marked transducers: Tr0 – conventional pressure transducer, Tr1 – Tr3 – Kistler (6182CA) highly sensitive piezoelectric pressure transducers. The ex situ online optical visualization system (camera) is placed at a distance of $\approx3.5 \text{ cm}$ below the die exit and $\approx12 \text{ cm}$ from the extrudate surface. The $x_3$ is the direction of the width ($W$), and the $x_1$ is the direction of the height ($H$).

Offline optical analysis of the collected extrudates was carried out by transmission polarized microscopy and incident light microscopy at room temperature. Transmission polarized microscopy is a contrast-enhancing technique allowing to evaluate the surface structure of the extrudate, which uses polarizing filters. The polarizing filters select a single orientation among all waves which composes of the light and drives it through the investigated sample. Incident light microscopy is the method of choice for the imaging of specimens, specifically surfaces that remain opaque even at thickness of 30 μm.

A Keyence VHX 900F (Osaka, Japan) and a Zeiss Axiophot (Oberkochen, Germany) microscopes were used in this study. The Keyence VHX 900F microscope is equipped with two zoom lenses and magnification range between 20 and 2000. The Zeiss Axiophot microscope is equipped with two objectives of 2.5 and 10, and one ocular magnification of ten times, which result in 25 and 100 times optical magnification. Cylindrical-shaped extrudates, obtained by the round capillary die, were studied via the incident light microscopy where high-resolution images are obtained. Rectangular-shaped extrudates, obtained by the slit die, were investigated using the transmission polarized microscope owing to their thin thickness of about $\approx0.5 \text{ mm}$.

Assuming a change on the extrudate surface structure after the extrusion, an online optical method is implemented to overcome this problem. The online optical setup consists of a Pentax XP (Tokyo, Japan) camera as an online extrudate optical monitoring system. The camera is positioned $\approx3.5 \text{ cm}$ below the slit die exit, perpendicular to the extrudate width (front view, $x_1-x_2$, Figure 2). The lens consists of a Sigma 105 mm DC Macro EX...
(Kawasaki, Japan), thus allowing appropriate magnification while positioned at a distance of ~12 cm from the extrudate. Full high-definition (1920 × 1080 pixels) video recordings at 60 frames per second (fps) were acquired for 5–7 min during extrusion via an online remote acquisition system. Offline and online optical imaging are used to determine the spatial and time characteristics of extrudate patterns as mentioned before.

The basic principle for constructing space–time visualization from online optical observations is presented and exemplified in Figure 3.

The video is recorded with frame dimensions $W_v \times H_v$ and a frame (acquisition) rate of $f_{va}$. A line of pixels (px) at a fixed position along $x_1$ can be extracted successively from each frame of the movie (Figure 3a) and added to a newly created image (Figure 3b). Hence, one axis corresponds to the width of the video frame $W_v$ and the other to the experimental time $t$, with the distance between each line of pixels determined by $1/f_{va}$. An example is shown in Figure 3c for the SBR A sample at 120 °C and $\dot{\gamma}_{app} = 7$ s$^{-1}$. The space–time diagram allows an easier extraction of grayscale intensity variations for long data sets and better identification of the characteristic time periodicity $\tau_s$ of the flow instability, as it does not use estimated values like the extrudate velocity, explained next.

In Figure 4, an example of a stick-slip instability is presented. Figure 4a represents the extrudate obtained by the slit die ($H = 0.5$ mm, $W = 5$ mm, and $L = 30$ mm), which results from one pressure oscillation during stick-slip instability of SBR B at $\dot{\gamma}_{app} = 100$ s$^{-1}$ and 120 °C. The first part of the extrudate is sharkskin instability and represents the stick part, that is, the pressure increases for about $\sim 30$ s from $p = 200$ to 250 bar (Figure 4b). The second part has volume and surface distortions not accounted through commonly used nomenclature and represents the slip part, that is, the rapidly decreased pressure for about $\sim 10$ s from 250 to 200 bar (Figure 4b). The slip part presents regular distortions on the side of the extrudate as well, these distortions are characterized by this study as side slide instabilities (Figure 4a). The time duration of the stick-slip instability depends on the shear rate. Typically, as the shear rate is increased, the stick-slip instability happens faster. In Figure 4b, the mechanical pressure fluctuations during stick-slip instability are observed under the same conditions, the shaded area with the four pressure oscillations has been video recorded. The space–time diagram constructed by the recorded video is shown in Figure 4c, where the four stick-slip events are presented. The stick and slip parts are indicated in the space–time diagram as well.

4. Modeling

In this section, the fitting of the steady-state viscosity as a function of wall shear rate, the modeling of the slip velocity, and the characteristics (in time and space) of the flow instabilities are presented. The steady-state viscosity obtained by the capillary rheometer is fitted by the Carreau model [38] (Equation (1)) to quantify the difference between the two samples. Moreover, the shear-thinning regime of the investigated samples obtained by the oscillatory frequency sweeps is fitted by a power law model (Equation (2)). Then, this power law function is included [3] to the volumetric flow rate equation suggested by Mooney [21] (Equation (3)) to obtain analytical equations and predict the slip velocity for both dies geometries (Equations (4) and (5)). Finally, a modified version (Equation (13)) of the model proposed by Wang et al. [29] and Barone et al. [30] is presented for the spatial characteristic wavelength of extrudates obtained by round capillary die, to predict the spatial characteristic wavelength for extrudates obtained by slit die as well.

4.1. Viscosity Models

Using the Cox-Merz rule (explained below) where $\eta(\dot{\gamma}) = \eta(\dot{\omega})$, with the numerical values of $\dot{\gamma} = \dot{\omega}$ (Figure 8), [30] a Carreau model [38] Equation (1), is used to fit the steady-state viscosity data from capillary rheometry for each material. In
addition, a power law model, Equation (2), fits the shear rate dependent (shear-thinning) magnitude of the complex viscosity data from the rotational rheometer. Thus, $K$ and $n$ are material-dependent parameters and are used for the computation of the slip velocity. The fitting values of the models are listed in Table 3.

$$\eta(\gamma) = \frac{\eta_0}{\left[1 + (\tau\gamma)^{\frac{1-m}{2}}\right]^m}$$

(1)

$$[\eta'(\omega)] = K\gamma^{n-1}$$

(2)

where $\eta_0$ is the zero shear viscosity, and $\tau$ is the longest characteristic relaxation time of the material.

Table 3. Carreau (Equation (1)) and power law (Equation (2)) fitting parameters obtained at 120 °C.

| Name   | $m$ | $\tau$ [s] | $\eta_0$ [kPa s] | $n$ | $K$ [kPa] |
|--------|-----|-------------|-------------------|-----|-----------|
| SBR A  | 0.13| 0.35        | 55                | 0.17| 180       |
| SBR B  | 0.17| 0.90        | 140               | 0.19| 210       |

4.2. Slip velocity

Mooney[21] derived the following general formula (Equation (3)) for the volumetric flow rate $Q$ of a round capillary die of radius $R$ and length $L$. Assuming[21] steady-state conditions, well-developed velocity profile, and an incompressible non-Newtonian flow in the presence of wall slip which is assumed to be solely a function of the wall shear stress[3]

$$Q = \pi R^2 V_s + \frac{\pi R^4}{\sigma_w} \int_0^t \dot{\gamma} \sigma_{yw} d\sigma_{yw}$$

(3)

In Equation (3), $\sigma_y$ is the shear stress and $\sigma_w$ is the wall shear stress (at radius $r = R$). The first term describes the volumetric flow rate of slippage, and the second term is volumetric flow rate in the absence of slippage (slip velocity, $V_s = 0$). Moreover, the apparent shear rate for the round capillary and slit dies are defined as $\dot{\gamma}_{app} = 4Q/\pi R^3$ and $\dot{\gamma}_{app} = 6Q/WH^2$, respectively, where $R$ is the radius of the round capillary die, $W$ is the width (here $W = 5$ mm), and $H$ the height (here $H = 0.5$ mm) of the slit die.

Assuming that the shear-thinning regime of the investigated SBR samples can be simply modeled by a power law behavior (Figure 8), as defined by Equation (2). Then Equation (3) can be integrated and then Rabinowitsch–Weissenberg[4] corrected.
to yield the following formulas\(^{(3,4)}\) for the slip velocity \(V_s^{\text{Capillary}}\) of round capillary die flow

\[
V_s^{\text{Capillary}} = \frac{D}{8} \left( \gamma_{\text{app}} - \frac{4n}{3n+1} \frac{\sigma \lambda}{K} \lambda \right) \tag{4}
\]

and for the slip velocity \(V_s^{\text{Slit}}\) of slit die flow

\[
V_s^{\text{Slit}} = \frac{H}{6} \left( \gamma_{\text{app}} - \frac{3n}{2n+1} \frac{\sigma \lambda}{K} \lambda \right) \tag{5}
\]

Equations (4) and (5) can be used to determine the slip velocity of molten polymers as a function of the wall shear stress. The extrude velocity \(V_{\text{ext}}\) is calculated according to a volume flux balance

\[
V_{\text{ext}} = V_{\text{puton}} \frac{A_{\text{barrel}}}{A_{\text{die}}} \tag{6}
\]

where \(A_{\text{barrel}}\) and \(A_{\text{die}}\) are the cross-sectional areas of the barrel (or reservoir) of the capillary rheometer and the die, respectively. In case of a passive polymer–wall interface (i.e., no chemical interaction between the polymer and solid surface), Brochard-Wyart and de Gennes\(^{(39)}\) proposed an interfacial rheological law in terms of an extrapolation length \(b\), as follows

\[
V_s = b \left[ \frac{dV}{dy} \right]_{y=0} = b \gamma_{\omega} \tag{7}
\]

where \(V_s\) is the slip velocity, \(V\) is the velocity of the fluid, and \(\left[ \frac{dV}{dy} \right]_{y=0}\) is the shear rate, presented by the Dirichlet boundary condition at \(y = 0\), and \(\gamma_{\omega}\) is the wall shear rate.

The custom-built slit die encloses a series of three piezoelectric pressure transducers distributed along the slit die.Palza et al.\(^{(32)}\) suggested to study the flow dynamics along the die land with the cross-correlation of the time-dependent pressure signal from the piezoelectric transducers. Thus, the time-dependent cross-correlation can be computed. The maximum is the so-called cross-correlation time and represents the time that an event needs to travel from \(T_{r1}\) to \(T_{r2}\). Hence, in case of stick-slip instability, the average stick-slip velocity \(V_{\text{Stick} - \text{slip}}\), that is, the average velocity of the stick part and slip part, can be captured by the three transducers during its flow along the die land. The time cross-correlation function is defined by Equation (8)\(^{(40)}\)

\[
\int_{\text{corr}} J (\tau) = \frac{1}{T_{r2} - T_{r1}} \int_{T_{r1}}^{T_{r2}} p_i (t) p_j (t + \tau) \, dt \tag{8}
\]

The subscripts \(i\) and \(j\) represent different transducers. The time-dependent pressure signal from the piezoelectric pressure transducers is first drift baseline corrected with a first-order polynomial, and the mean pressure value is subtracted, \(p(t) = p(t)_{\text{drift corrected} - p_{\text{mean}}}\). Then it is cross-correlated and normalized so the covariance at zero lag are identical 1. For periodic functions, the cross-correlation function is also periodic.\(^{(40)}\) If there is a maximum in the cross-correlation function, then it is highly correlated, therefore the events could be assumed to happen simultaneously. The time where the first maximum occurs is the cross-correlation time, \(\tau_{CC}\). Using the cross-correlation time, which is the time that one pressure oscillation of the stick-slip instability travels from \(T_{r1}\) to \(T_{r2}\), and the known distance between the transducers \(L_{\text{corr}}\), the \(V_{\text{Stick} - \text{slip}}\) can be calculated. Thus, \(V_{\text{Stick} - \text{slip}}\) is obtained by

\[
V_{\text{Stick} - \text{slip}} = \frac{L_{\text{corr}}}{\tau_{CC}} \tag{9}
\]

### 4.3. Modeling of the Spatial and Time Characteristics of Flow Instabilities

The flow instabilities are here characterized based on their spatial characteristic wavelength and their characteristic time periodicity (or frequency) of the surface and volume distortions. Wavelength \(\lambda\) is defined as the average spatial distance between two consecutive similar distortions (Figure 5). The characteristic time periodicity is obtained by three methods. First, identified via offline optical analysis is undertaken on the already collected extrudates at room temperature. Offline optical characteristic time periodicity \(\tau_{\text{Char. off-line}}\) is defined as the ratio of the wavelength \(\lambda\) and the extrude velocity \(V_{\text{ext}}\) (Equation (10))

\[
\tau_{\text{Char. off-line}} = \frac{\lambda}{V_{\text{ext}}} \left( \frac{V_{\text{Char. on-line}}}{\lambda} \right) = \frac{V_{\text{ext}}}{\lambda} \tag{10}
\]

In case of multiple wavelengths, for example, in case of stick-slip, more than one periodicities are obtained. In terms of stick-slip instability, one extrude velocity is assumed, which is obtained by Equation (6), and the characterization takes place in both regions, stick and slip.

Second, online optical characteristic periodicity \(\tau_{\text{Char. on-line}}\) is defined as the time between two consecutive similar events in the space–time diagram (Figure 3c). The advantage of the online optical characteristic periodicity is that it does not use any estimated or assumed value like the extrude velocity. Third, the Fourier transform (FT) analysis of the pressure signal from the piezoelectric transducers, \(\tau_{\text{Char. FT pressure}}\) can also be used to give the characteristic time periodicity.\(^{(8,9,11,23)}\)

The spatial characteristic wavelength \(\lambda\) can be obtained by the proposed model, Equation (11), from Wang et al.\(^{(29)}\) and Barone et al.\(^{(36)}\) For round capillary dies (circular cross-section area), the spatial characteristic wavelength \(\lambda\) of flow instabilities is correlated with the diameter of the die \(D\), the swelled diameter of the extrude \(D'\), instability time periodicity \(\tau_{\text{sp}}\), and the apparent shear rate \(\gamma_{\text{app}}\). The value of the swelled diameter \(D'\), as defined within this study, is the average value from the collected extrudates as obtained by the capillary extrusion dies

\[
\lambda_{\text{Char.}} = \frac{D}{8} \left( \frac{D'}{D} \right)^2 \gamma_{\text{app}} \tau_{\text{sp}} \tag{11}
\]

Equation (11) results from the following condition, \(\lambda = V_{\text{ext}} \tau_{\text{sp}}\). The average extrude velocity is given by the product of extrude velocity and the die swell factor, \(V = V_{\text{extr}} (D)/D'\).\(^{(29)}\) The extrude velocity for round capillary and slit dies is given by
the power law dependency of the shear stress by the shear rate, $f \approx \propto \sigma^2$. Knowing the power law dependency of the shear stress by the shear rate, $\sigma(\dot{\gamma}) = K \dot{\gamma}^n$ (Table 3), this study suggests that

$$f_{\text{Char}} = \frac{1}{r^*} = a \dot{\gamma}_{\text{app}}^{n+0.5}$$

where $a$ is a constant and assumed to be material dependent.

5. Results and Discussion

5.1. 2D SEC-NMR Technique

A new combined method\textsuperscript{[36]} using a low field benchtop NMR (62 MHz, 1.45 Tesla, $^1$H) spectrometer coupled to SEC was used to correlate the molecular weight distribution and the chemical composition of the SBR samples. For the SBRs, the sequence distribution and chemical composition have the dominating influence on the mechanical and physical properties. The latter facilitates the fundamental understanding of structure–property relationships.

The 2D SEC-NMR technique\textsuperscript{[36]} is used to investigate the multimodality with respect to the correlation of molecular weight distribution and chemical composition. Figure 6 illustrates the 2D SEC-NMR contour plots, including the respective normalized 1D NMR spectra and SEC elugram plots. As evident from Figure 6a,b, there are two distinct components, at an elution volume of $\approx 40$ and $\approx 60$ mL, with their resulting $^1$H-NMR resonance groups. According to $^1$H-NMR spectra, the first fraction at an elution volume of $\approx 40$ mL in both Figure 6a,b, it is ascribed to SBR. Additionally, the second fraction at an elution volume of $\approx 60$ mL is identified as low molecular weight hydrocarbon species. As the measurements were performed at nonquantitative NMR conditions, i.e., the free induction decay (FID) acquisition length of the analyte was $\approx 5 \times T_1$, where $T_1$ is the longest longitudinal relaxation time, therefore only semiquantitative comparisons can be made.$^{[60]}$ Comparing the $^1$H-NMR spectra qualitatively between Figure 6a and b, the results indicate that sample A has a higher amount of 1,2 butadiene isomer relative to B ($\delta = 4-6$ ppm). This result is in agreement with the high field $^1$H-NMR results (Table 2). An estimation on the amount of low molecular weight hydrocarbons relative...
to the SBR components within SBR A and B was conducted by performing a 2D integration. It is found, qualitatively, that sample A and B contains about 5% and 6% in weight fraction of the low molecular weight hydrocarbon component, respectively.

5.2. Linear and Nonlinear Rheology

The investigated samples have similar multimodal MWD with relatively similar weight composition of each mode. Specifically,
the MWD (Table 1) of both SBRs have a bimodal behavior. The high molecular weight tail ($M_w \approx 757$ kg mol$^{-1}$ for the SBR A, and $M_w \approx 650$ kg mol$^{-1}$ for the SBR B) and the medium molecular weight component ($M_w \approx 260$ kg mol$^{-1}$ for the SBR A, and $M_w \approx 256$ kg mol$^{-1}$ for the SBR B) have rather similar fractions for both of the polymer samples. The influence of the high molecular weight amount on the linear viscoelasticity needs to be discussed. The study of Wasserman and Graessley[45] has shown that differences of about $\approx 1.2\%$ high molecular weight fraction between two linear polystyrene melts could increase $G'$ almost four times in the terminal flow regime.[45]

The linear viscoelasticity of the two investigated materials has been obtained by oscillatory frequency sweep in a wide range of temperatures ($-45$ to $+120\, ^\circ C$). Figure 7a presents the master curve of $G'$ and $G''$ as a function of angular frequency ($10^{-3}$ to $10^{10}$ rad s$^{-1}$) over 13 decades at reference temperature of $120\, ^\circ C$. None of the two samples have reached the terminal zone where both $G' \propto \omega^2$ and $G'' \propto \omega$. The longest relaxation time of the material $\tau_d$ is the reptation time and can be obtained by the inverse of the existing crossover from $G'$ and $G''$ for polymers with narrow MWD and linear molecular architecture. For complex molecular architectures and broad or bimodal MWDs, different approaches for the determination of the reptation time have been suggested in literature, for example, the double reptation theory.[18] For simplicity within this study, the reptation time is determined by the inverse of the existing crossover from $G'$ and $G''$. Although owing to the multimodality of the samples, the relaxation time is named as the overall relaxation time.

Figure 7. a) Comparison of the master curves of the two investigated samples at reference temperature of $120\, ^\circ C$. Storage and loss moduli as a function of angular frequency; the longest relaxation time of the SBR B is almost double than the SBR A. b) The van Gurp–Palmen plot indicates a different behavior between the two samples below $|G^*| < 3 \times 10^5$ Pa. This difference can be associated with the existence of branches. c,d) Transient nonlinear extensional viscosity for both materials at $120\, ^\circ C$. d) SBR B presents strain hardening at $\varepsilon^\text{dot} = 0.01$ s$^{-1}$ which indicates the existence of low degree branched molecules.
time, because it takes into account the contributions from all the molecular weight components. The SBR B has almost double the relaxation time $\tau_0$ than the SBR A, specifically $\tau_0, \text{SBR B} \approx 1.25 \times 10^{-3}$ s and $\tau_0, \text{SBR A} \approx 6.2 \times 10^{-4}$ s at 120 °C. It is known that the relaxation time depends on the number of entanglements to the third power, $\tau_0, \text{SBR B}/\tau_0, \text{SBR A} = (Z_{\text{SBR B}}/Z_{\text{SBR A}})^3$. Knowing that $G^*_{\infty} = \rho RT / M_\infty = ZpRT / M_\infty$ and the ratio of the plateau modulus values, $G^*_0, \text{SBR B}/G^*_0, \text{SBR A} \approx 1.25$ (Figure 7a).

Then, the difference of the longest relaxation times between the samples is explained by the different number of entanglements, $\tau_1, \text{SBR B}/\tau_1, \text{SBR A} = (Z_{\text{SBR B}}/Z_{\text{SBR A}})^1 = (G^*_0, \text{SBR B}/G^*_0, \text{SBR A})^1 \approx 2$. Moreover, observing the $G'$ over three decades, from $10^{-3}$ to $10^3$ rad s$^{-1}$, of angular frequency and specific at $\omega = 0.0032$ rad s$^{-1}$, the value of $G'$ for the SBR B is about 4.5 times lower than the value of $G'$ for the SBR A. This is explained by the difference in the high molecular weight tail of the MWD (Table 1). To investigate the molecular architecture of the samples, the van Gurp–Palmen plot is presented in Figure 7b. The plot exhibits a difference between the two samples at magnitude of complex moduli below $|G^*| < 3 \times 10^3$ Pa. Both samples at $|G^*| = 10^4$ Pa present a second relaxation process which can be associated with the existence of branches. The phase angle of SBR B has lower values than SBR A at $|G^*| = 10^4$ Pa which implies the existence of higher volume fraction and/or higher molecular weight branches. Usually, nonlinear transient extensional rheology is used to investigate the existence of branches via the strain hardening effect in polymer melts. The Carreau model, $\dot{\gamma} = \dot{\gamma}_0 \left(1 + \frac{\dot{\gamma}}{\dot{\gamma}_0}ight)^{\alpha-1}$, was used to fit the capillary die data and quantify the difference between them. At high shear rates/angular frequencies after $\dot{\gamma} > 1/\tau_0$, longer chains acquire more elastic energy near the wall than shorter ones, which creates forces that lead to segregation of longer chains away from the wall toward the centerline (low shear stress area). Similarly, shorter chains would potentially migrate toward the wall (high shear stress area). Hence, the slippage becomes stronger as the amount of low MW components increases at the wall.

To investigate the processing flow behavior in a controlled way, capillary rheology experiments were carried out with round capillary and slit dies. The raw round capillary die data were further processed by Bagley and Rabinowitsch-Weissenberg corrections using a series of three round capillary dies with length-to-diameter ratios of $L/D = 5, 10, 15$ and $D = 2$ mm at 120 °C. The viscosity data from the round capillary die with $L/D = 15$ are presented in Figure 8. For the slit die with $L/H = 60$, only Rabinowitsch-Weissenberg correction is applied. The $L/H = 60$ allows to neglect exit pressure influence, thus the wall shear stress is directly obtained from pressure values. The empirical relationship Cox-Merz rule has been applied to our data (Figure 8). The Cox-Merz rule implies a universal relation between linear oscillatory shear and the nonlinear steady-state shear. This rule states that the shear rate dependency of the steady-state viscosity $\eta(\dot{\gamma})$ is equal to the magnitude of the complex viscosity $|\eta^{*}(\omega)|$, that is, $\eta(\dot{\gamma}) = |\eta^{*}(\omega)|$, with the numerical values of $\gamma = \omega^{-\nu}$.

The viscosity data of the SBR A and B are presented in Figure 8. Despite the bimodal MWD and the existence of branching molecular architecture Cox-Merz rule applies to fit the shear rates below $\dot{\gamma}_R < 20$ s$^{-1}$. Deviation between the capillary and rotational rheometer data is detected for shear rates/angular frequencies higher than $\dot{\gamma}_W > 30$ s$^{-1}$ (Figure 8). Then, the shear viscosity data from capillary rheology are below the magnitude of the complex viscosity data from oscillatory rheology. The deviation of the Cox-Merz rule for both samples starts at similar shear rate, $\dot{\gamma}_W \approx 20$ s$^{-1}$. This is explained by the bimodal MWD, molecular architecture, and the similar amount of low MW component. According to Inn, the Cox-Merz rule fails at high shear rates/angular frequencies for bimodal MWD as the amount of low MW component increases at the wall. This observation is explained based on the segregation theory. During fast flow ($\dot{\gamma} > 1/\tau_0$), longer chains acquire more elastic energy near the wall than shorter ones, which creates forces that lead to segregation of longer chains away from the wall toward the centerline (low shear stress area). Similar, shorter chains would potentially migrate toward the wall (high shear stress area). Hence, the slippage becomes stronger as the amount of low MW components increases at the wall.

The Carreau model, Equation (1), was used to fit the capillary data and quantify the difference between them. At high shear rates/angular frequencies after $\dot{\gamma}_W > 20$ s$^{-1}$, the shear-thinning behavior happens, it is observed for both viscosities a difference of a factor $= 1.3$. At those high shear rates, the flow is not influenced by MWD. In contrast, between $\dot{\gamma}_W = 0.03$ and $20$ s$^{-1}$, where the MWD has the dominant influence on the flow, the two materials exhibit difference by a factor of $= 2$. In addition, the power law model, Equation (2), was used to fit the shear rate dependent (shear-thinning) viscosity data.
from rotational rheometry at the region where the Cox-Merz rule fails. Thus, material parameters $K$ (consistency index) and $n$ (flow index) were obtained and used for the computation of the slip velocity. The fitting values of the models are listed in Table 3.

Steady-state viscosity curves from slit and round capillary dies are presented in Figure 9. The absolute values of steady-state viscosity are similar between the two geometries for the SBR A (Figure 9a). Although, in Figure 9b, deviation of the steady-state viscosity between the two geometries is detected after $\dot{\gamma}_w > 30 \text{ s}^{-1}$ owing to the onset of stick-slip instability in the slit die for the SBR B sample. During the extrusion of SBR B with two different dies, it was found that this material in the round capillary die presents stick-slip instability within the shear rate range $\dot{\gamma}_w = 30–60 \text{ s}^{-1}$. However, in the slit die the stick-slip instability is observed at $\dot{\gamma}_w = 40–300 \text{ s}^{-1}$ for SBR B sample. Hence, according to experimental observations the stick-slip instability occurs over a wider range of shear rates in the slit die than the round capillary die for the SBR B sample. For this reason, the viscosity data from the slit die have a slight deviation from the round capillary die (Figure 9b).

Figure 10 presents the raw pressure signal from the three piezoelectric pressure transducers of the slit die. The dimensions of the slit die are $L = 30 \text{ mm}$ and $0.5 \times 5 \text{ mm}^2 (H \times W)$ cross-section area. a) SBR A presenting sharkskin and an enlarged part of the pressure profile from Tr1 to depict the pressure oscillations. b) SBR B presenting sharkskin up to $\dot{\gamma}_{\text{app}} = 20 \text{ s}^{-1}$ and afterward stick-slip up to $\dot{\gamma}_{\text{app}} = 200 \text{ s}^{-1}$. 

Figure 9. a) Absolute values of the steady-state viscosity as a function of wall shear rate $\dot{\gamma}_w$ for slit and round capillary dies. Agreement between both geometries is observed for (a) SBR A where only sharkskin instability appears. Deviation between the two geometries occurs for (b) SBR B after $\dot{\gamma}_w > 30 \text{ s}^{-1}$ where the stick-slip instability appears at the slit die between $\dot{\gamma}_w = 40$ and $300 \text{ s}^{-1}$; afterward, gross melt fracture instability occurs. b) The shear rate range of the stick-slip instability for the SBR B material at the round capillary and slit dies is displayed by the shaded areas in the plot.

Figure 10. Profile of pressure signal during capillary extrusion at 120 °C, as detected by the three piezoelectric transducers within the slit die. The dimensions of the slit die are $L = 30 \text{ mm}$ and $0.5 \times 5 \text{ mm}^2 (H \times W)$ cross-section area. a) SBR A presenting sharkskin and an enlarged part of the pressure profile from Tr1 to depict the pressure oscillations. b) SBR B presenting sharkskin up to $\dot{\gamma}_{\text{app}} = 20 \text{ s}^{-1}$ and afterward stick-slip up to $\dot{\gamma}_{\text{app}} = 200 \text{ s}^{-1}$.
200 \text{s}^{-1}, \text{respectively.} \) Selected optical visualizations of the extrudates are given by Figures 11a and 12a. Data are recorded for about 500 s, at each shear rate to capture both types of flow instabilities. In Figure 10a, sharp peaks are observed any time that the shear rate is changed owing to the collection of the extrudates. Because of the inherent detection mechanism of the piezoelectric transducers, absolute values of the pressure signal are not reliable.\cite{32} Nevertheless, the pressure fluctuations at a given shear rate provide the characteristic frequency of the flow instability via the already discussed data analysis.\cite{8,9,23–25}

5.3. Offline and Online Optical Analysis

Using the offline optical analysis techniques, the collected extrudates were investigated at room temperature. In Figure 11a, selected extrudates obtained by the slit die for the SBR A at 120 °C are presented. The extrudates have been investigated by transmission polarization microscopy at \( \dot{\gamma}_{\text{app}} = 30, 50, 70, 100, 200, \) and 500 s\(^{-1}\). Figure 11b presents selected extrudates obtained by the round capillary die for the SBR A as they investigated by incident light microscopy at \( \dot{\gamma}_{\text{app}} = 7, 10, 30, 70, 100, \) and 500 s\(^{-1}\). For the SBR A sample, a stick-slip instability is not presented.

In Figure 12a, selected extrudates with stick-slip instability obtained by the slit die for the SBR B at 120 °C are presented. As mentioned before the stick-slip instability is separated into two regions, stick and slip parts. Both regions at apparent shear rates of \( \dot{\gamma}_{\text{app}} = 30, 50, \) and 70 s\(^{-1}\) are presented. Figure 12b presents selected extrudates obtained by the round capillary die for the SBR B as they investigated by incident light microscopy at \( \dot{\gamma}_{\text{app}} = 7, 10, 30, 50, \) and 70 s\(^{-1}\). Stick-slip instability for the obtained by the round capillary die extrudates has been observed at \( \dot{\gamma}_{\text{app}} = 30 \text{ s}^{-1} \), both regions, stick and slip, are presented separately.

Observing the extrudates obtained by the slit die at Figures 11a and 12a the proposed definitions\cite{8,9,11} of sharkskin and stick-slip met flow instabilities agree with the appearance of the extrudates. However, noticing the extrudates obtained by the round capillary die at Figures 11b and 12b, only the extrudate \( \dot{\gamma}_{\text{app}} = 7 \text{ s}^{-1} \) for the SBR A can be categorized as surface instability, and possibly designated as sharkskin. The rest of the extrudates obtained by the round capillary die can be categorized as volume instability and generally named as melt fracture or spurt.\cite{5,10} For both Figures 11b and 12b, the spatial characteristic wavelength of the flow instability can be identified. Based on the spatial characteristic wavelength of the flow instability, the extrudate distortions can be quantified, regardless of the type of flow instability.

Using the online optical analysis technique during the extrusion of the samples by the slit die, space–time diagrams have been constructed for each shear rate, and the characteristic time periodicity of the flow instabilities is investigated. In Figure 13, space–time diagrams for SBR A at \( \dot{\gamma}_{\text{app}} = 10 \) and 30 s\(^{-1}\) are presented sharkskin instability at 120 °C. In Figure 14, selected space–time diagrams for \( \dot{\gamma}_{\text{app}} = 10 \) and 70 s\(^{-1}\) of the SBR B are presented at 120 °C. In Figure 14a, the sharkskin flow instability is presented at \( \dot{\gamma}_{\text{app}} = 10 \text{ s}^{-1} \), while in Figure 13b the stick-slip instability is captured at \( \dot{\gamma}_{\text{app}} = 70 \text{ s}^{-1} \). For both Figures 13 and 14 at each space–time diagram, a snapshot for a specific region of the extrudate is shown enlarged, and the characteristic time periodicity can be better visualized.

![Figure 11](image11.png)

**Figure 11.** Offline optical analysis of SBR A extruded at 120 °C by a) transmission polarization microscopy and b) incident light microscopy. Extrudates from a) slit die of \( H = 0.5 \text{ mm}, W = 5 \text{ mm}, \) and \( L = 30 \text{ mm} \) and b) round capillary die of \( L/D = 15 \) with \( D = 2 \text{ mm} \). The apparent shear rate \( \dot{\gamma}_{\text{app}} \) is mentioned at each extrudate.

![Figure 12](image12.png)

**Figure 12.** Offline optical analysis of SBR B extruded at 120 °C by a) transmission polarization microscopy and b) incident light microscopy. Extrudates with the stick-slip instability from a) slit die of \( H = 0.5 \text{ mm}, W = 5 \text{ mm}, \) and \( L = 30 \text{ mm} \) in the shear rate range between \( \dot{\gamma}_{\text{app}} = 30 \) and 70 s\(^{-1}\) and b) round capillary die of \( L/D = 15 \) with \( D = 2 \text{ mm} \) at \( \dot{\gamma}_{\text{app}} = 30 \text{ s}^{-1} \). The apparent shear rate \( \dot{\gamma}_{\text{app}} \) is mentioned at each extrudate.
5.4. Slip, Extrudate, and Average Stick-Slip Velocities

Using Equations (4) and (5) slip velocities\(^{[3]}\) are obtained for both geometries (Figure 15). The slip velocity of each material as a function of wall shear stress presents a master curve independent of the die geometry. The investigated samples seem to behave slightly different with SBR A to present higher slip velocities at \(\sigma_W > 5 \times 10^5\) Pa than the SBR B.

Applying the interfacial rheological law\(^{[19]}\) Equation (7), the slip length for both geometries is obtained (Figure 15b). As expected, the slip length in the slit die is approximately three times lower than in the round capillary die. In addition, both materials have similar slip length despite displaying different types of flow instabilities.

The computed values by Equation (9) for the average stick-slip velocity \(V_{\text{stick-slip}}\) for the SBR B material are presented as well (Figure 15a). The cross-correlation time which is obtained by the first maximum of Equation (8) represents the time that a whole pressure oscillation, that is, a stick-slip event, travels from \(T_r\) to \(T_f\) (Figure 16). The duration of the stick-slip is quite large because both contributions are taken into account, that is, the stick part which is the pressure buildup and the slip part which is the rapid pressure drop (Figure 4b).
5.5. Time and Spatial Characteristics of Flow Instabilities

The characteristic frequency (or periodicity) of the flow instability was obtained and compared for both slit and round capillary dies. Especially, the highly pressure-sensitive slit die and the online optical analysis for the slit die were used for both materials. The collected extrudates from the slit and from all round capillary dies \((L/D = 5, 10, 15\) with \(D = 2\) mm) were investigated by offline optical analysis at room temperature. In Figure 17a, the characteristic frequency of the SBR A is presented. All the optical analysis techniques, either online or offline, for the slit and for all the round capillary dies exhibit a linear increase behavior as a function of shear rate within \(\dot{\gamma}_{\text{app}} = 3–700\) s\(^{-1}\). Regarding the highly pressure-sensitive slit die, a “plateau”-like trend is observed within \(\dot{\gamma}_{\text{app}} = 10–300\) s\(^{-1}\). Observing the overall trend of the characteristic frequency, a monotonic linear increase as a function of shear rate in log-log scale can be asserted. Thus, the data are fitted by Equation (15), specifically for the SBR A, \(f_{\text{Char.}} = 2\dot{\gamma}_{\text{app}}^{0.5}\). The overall deviation of each technique from the fitting function is estimated to vary at most by 30%. Higher than 30% deviation from the fitting function is observed at low, \(\dot{\gamma}_{\text{app}} = 10\) and 20 s\(^{-1}\), and one at high, \(\gamma_{\text{app}} = 300\) s\(^{-1}\), shear rates where the respective frequencies are obtained by the highly pressure-sensitive die. The respective frequencies are marked in Figure 17a.

In Figure 17b, the characteristic frequency as a function of apparent shear rate for the SBR B is presented. All the optical analysis techniques, either online or offline, for the slit and for all the round capillary dies exhibit a linear increase tendency as a function of shear rate within \(\dot{\gamma}_{\text{app}} = 3–700\) s\(^{-1}\) described by a power law behavior. Concerning the highly pressure-sensitive slit die, an increased trend is observed as well. Low-frequency components, below \(f_{\text{Char.}} = 5\) Hz, are observed during the stick-slip instability above the \(\dot{\gamma}_{\text{app}} > 30\) s\(^{-1}\) owing to side slip instabilities at the slip part of the extrudate (Figure 4a). Substantial...
low-frequency components, $f_{\text{Char}} = 10^{-2}$ Hz, are observed during the stick-slip instability above the $\gamma_{\text{app}} > 30$ s$^{-1}$ as well. These characteristic frequencies occur from the stick-slip pressure oscillation (Figure 4b).

Analyzing the characteristic frequency, a monotonic linear increase as a function of shear rate was fitted by a power law function such as $f_{\text{Char}} = 1.1\gamma^{0.5}_{\text{app}}$. Similar to SBR A, the deviation of each technique from the fitting function is estimated to vary at most by 30% up to $\gamma_{\text{app}} = 100$ s$^{-1}$. The low-frequency components within $\gamma_{\text{app}} = 50–500$ s$^{-1}$, scale also with the power of 0.5 and differ by a factor of about $\approx 3.13$ from the main fitting function (Figure 17b). This difference occurs owing to inherent variation in extrudate velocity within the stick-slip instability. In addition, above the $\gamma_{\text{app}} > 200$ s$^{-1}$ deviation from the fitting function is presented by the offline optical analyzed data as well. This deviation occurs owing to the difficulties to measure precisely the spatial characteristic wavelength of the distortions in the slip part of the extrudate (Figure 4a).

Knowing the fitting function for the characteristic frequency (or periodicity), the dimension of the die ($D$ for round capillary, $H$ and $W$ for slit) and the swelled diameter $D'$, Equations (11) and (13), can be used to predict the characteristic wavelength of the flow instabilities for round capillary and slit dies. Following the ratio between the extrudates velocities of $V_{\text{extr}} = 3W_{\text{extr}}$, a similar behavior is expected to be found for the spatial characteristic wavelength as well. Assuming that the characteristic time periodicity is material dependent and the swelling factor remains similar between the slit and round capillary geometries, the ratio of the spatial wavelength between the two geometries is given by $\lambda_{\text{Capillary}} = 3\lambda_{\text{Slit}}$ (Figure 18).

From quantitative point of view, for all the investigated round capillary dies ($L/D = 5, 10, 15$ with $D = 2$ mm) the spatial characteristic wavelengths of the instabilities do not deviate much of each other. Especially, observing Figure 18b, it appears that they have similar wavelength in the whole range of the investigated shear rates.

6. Conclusions

Based on the obtained results, the following correlations between the molecular properties, rheological characterization, and extrusion flow are apparent for the investigated SBR samples:

1. SBR B has more or/and higher molecular weight branches than the SBR A. Both samples have about 5% (SBR A) and 6% (SBR B) of low molecular weight hydrocarbons. These two findings explain the differences in the zero shear viscosity and the different flow instabilities.

2. SBR polymers with similar MWD and chemical composition, but different isomer content of the butadiene monomer at the same temperature difference from the $T_g$ disclose different types of flow instabilities during extrusion. At temperatures $T > T_g +100$ °C the influence of the butadiene isomers is neglectable compared to the influence of the topological constraints (entanglements) and molecular architecture (linear, branched).

3. For the slit die (rectangular cross-section area) geometry, the stick-slip instability manifests itself in a broader range of shear rates compared to the round capillary (circular cross-section area) die for the investigated SBR B at 120 °C.

4. The characteristic frequency of the flow instabilities obtained by the highly sensitive slit die, offline and online optical analysis techniques can be fitted by a power law model as a function of shear rate to the power of $0.5$, $f_{\text{Char}} = a\gamma^{0.5}_{\text{app}}$. The overall deviation of each technique from the fitting function is estimated to vary at most by 30%.

5. The qualitative model for the spatial characteristic wavelength, proposed by Wang et al.[29] and Barone et al.[30] for round capillary die, Equation (11), and its modification for slit die, Equation (13), are in agreement with the experimental data obtained from the SBR polymers for both die geometries.
6. Assuming the same range of shear rates for both slit and round capillary dies and given the dimensions of them, the modified version (Equation (13)) of the model proposed by Wang et al.\(^{29}\) and Barone et al.\(^{30}\) predicts the spatial characteristic wavelength from a round capillary to slit die and vice versa.

**Appendix A**

Volumetric flow rate \(Q\) inside the die is given by Equation (A1) and directly after the die exit by Equation (A2)

\[
Q = W \cdot H \cdot V_{\text{ext}}^\text{Slit} \quad (A1)
\]

\[
Q = W' \cdot H' \cdot \langle V \rangle \quad (A2)
\]

Assuming no volume change, Equations (A1) and (A2) can be equated

\[
\langle V \rangle = \left( \frac{W}{W'} \cdot \frac{H}{H'} \right) V_{\text{ext}}^\text{Slit} \quad (A3)
\]

knowing the extrudate velocity for slit die

\[
V_{\text{ext}}^\text{Slit} = \left( \frac{H}{6} \right) \gamma_{\text{app}} \quad (A4)
\]

and then coupling Equations (A3) and (A4), Equation (A5) is derived

\[
\langle V \rangle = \left( \frac{W}{W'} \cdot \frac{H}{H'} \right) \left( \frac{H}{6} \right) \gamma_{\text{app}} \quad (A5)
\]

Defined\(^{29,30}\) the spatial characteristic wavelength as

\[
\lambda = \langle V \rangle \tau^* \quad (A6)
\]

the analytical formula for the spatial characteristic wavelength for the slit die geometry is given by Equation (A7)

\[
\lambda_{\text{Slit}} = \left( \frac{W}{W'} \cdot \frac{H}{H'} \right) \left( \frac{H}{6} \right) \gamma_{\text{app}} \tau^* \quad (A7)
\]

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data available on request from the authors.

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[30] J. R. Barone, N. Plucktavesak, S. Q. Wang, J. Rheol. 1998, 42, 833.
[31] Y. W. Inn, R. J. Fisher, M. T. Shaw, Rheol. Acta 1998, 37, 573.
[32] F. N. Cogswell, J. Non-Newtonian Fluid Mech. 1977, 2, 17.
[33] A. Provenzale, L. Smith, R. Vio, G. Murante, Physica D 1992, 58, 31.
[34] C. S. Dutcher, S. J. Muller, J. Fluid Mech. 2009, 641, 85.
[35] R. Kádár, C. Balan, Eur. J. Mech. B 2012, 31, 158.
[36] C. Botha, J. Höpfner, B. Mayerhöfer, M. Wilhelm, Polym. Chem. 2019, 10, 2230.
[37] D. van Dusschoten, M. Wilhem, Rheol. Acta 2001, 40, 395.
[38] F. A. Morrison, Understanding Rheology, Oxford University Press, Oxford 2001.
[39] F. Brochard-Wyart, P. G. Gennes, Langmuir 1992, 8, 3033.
[40] J. Honerkamp, Stochastic Dynamic Systems: Concepts, Numerical Methods, Data Analysis, Wiley-VCH, New York 1994.
[41] Y. W. Inn, L. Wang, M. T. Shaw, Macromol. Symp. 2000, 158, 65.
[42] J. R. Barone, S. Q. Wang, Paper IR6, SoR 70th Annual Meeting, 1998.

[43] M. Maurice, Rubber Technology, Springer Science + Business Media, Dordrecht, The Netherlands 1999.
[44] H. E. Railsback, N. A. Stumpe, Rubber Age 1975, 27, 101.
[45] S. H. Wasserman, W. W. Graessley, J. Rheol. 1992, 36, 543.
[46] R. R. Ernst, G. Bodenhausen, A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Vol. 14, Clarendon, Oxford 1987.
[47] J. D. Ferry, Viscoelastic Properties of Polymers, 3rd ed., Wiley, New York 1980.
[48] N. J. Inkson, R. S. Graham, T. C. B. McLeish, D. J. Groves, C. M. Fernyhough, Macromolecules 2006, 39, 4217.
[49] M. Abbasi, L. Faust, M. Wilhelm, Adv. Mater. 2019, 31, 1806484.
[50] P. Cox, E. H. Merz, J. Polym. Sci. 1958, 28, 619.
[51] W. F. Busse, Phys. Today 1964, 17, 32.
[52] S. Costa, P. F. Teixeira, J. A. Covas, L. Hilliou, Fluids 2019, 4, 66.
[53] F. J. Stadler, A. Nishioka, J. Stange, K. Koyama, H. Münstedt, Rheol. Acta 2007, 46, 1003.
[54] F. J. Stadler, C. Piel, W. Kaminsky, H. Münstedt, Macromol. Symp. 2006, 236, 209.