Investigation of melt flow instabilities in SBR: influence of MWD and microstructure at in situ pressure fluctuations as detected by capillary rheology

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ABSTRACT
During the extrusion process of molten polymers, flow instabilities occur which manifest themselves as distortions on the surface and volume of the extrudates[1]. These phenomena include sharkskin or surface melt fracture, slip-stick or periodic melt fracture and gross melt fracture or large amplitude periodic and/or non-periodic chaotic anomalies[2]. In this study the pattern formation of the melt flow instabilities of pure SBR samples which are produced by solution (anionic) or emulsion polymerization are investigated. Those SBR have different bimodal and broad molecular weight distributions (MWD) and microstructure. This study use a high sensitive in situ mechanical pressure instability detection system[3,4] in polymer processing equipment in combination with offline and online optical analysis. Thus, the characteristic frequency pattern of instabilities as a function of the apparent shear rate is correlated with the influence of the MWD and the microstructure of the material.

INTRODUCTION
The characteristic frequency of the melt fracture and the wall slip behavior of solutions of polymerized bimodal SBR resins, and emulsion polymerized SBR with broad MWD were investigated and compared in this study. Linear oscillatory rheological measurements have been done to obtain the linear rheological parameters as reptation and entanglement time, plateau modulus, zero shear viscosity and the molecular entanglement weight. By comparing the flow curve observed by capillary rheology measurements with the linear viscoelastic (LVE) data, it was observed that the apparent slip increased with content of low molecular weight (M_W) component.[5] It was empirically observed that the onset stress of sharkskin melt fracture was proportional to the plateau modulus. For polyethylene, it was proposed that the distinct separation of the two modes of the bimodal resin, especially the high content of small chains could cause the significant wall slip, and unusual melt fracture behaviors.[5] Based on literature review for the bimodal metallocene PE[6], first reported that the addition of low M_W component drastically increased the melt flow index. Munoz-Escalona et al.[7] found that the bimodal metallocene PE in the capillary flow showed more shear thinning behavior than the unimodal PEs of similar M_W. Hence, lower viscosities in extrusion flow could be obtained with the bimodal resins. In this report upon to those previous studies, we discuss similar outcome for SBR materials and we correlate them with the characteristic frequency pattern of instabilities.

EXPERIMENTAL
The experimental setup is based on a Göttfert Rheotester 2000 capillary rheometer with a slit die 0.2 x 3 x 30 mm^3. The die is equipped with three high sensitivity piezoelectric pressure transducers, see Fig. 1, and has an aspect ratio of W/H = 15, where W and H are

the channel width and height respectively (W = 3 mm, H = 0.2 mm). The transducers are capable to measure up to 2000 bar, at maximum temperature 250 °C with 10^{-5} bar resolution. The three transducers, Tr1-Tr3, are equally distributed along the channel length. The optical analysis is performed online and offline. A visualization system is positioned at the die exit for advanced online image analysis. A Sony 500a camera is placed at ~3.5 cm below the exit, aligned with the extrudate in the x_2 direction and ~20 cm from the extrudate. The lens consist of a Sony optical steady shot 3.5-5.6/16-50 OSS. For the offline optical analysis a Keyence digital microscope VHX 900F is used. The wide range of 1:1 – 2000:1 magnification of the microscope provide high-resolution pictures of the extrudates.

Commercial samples with different molecular weight distribution (MWD), Fig. 2, topologies (i.e. linear, stars) and microstructure (i.e. styrene, vinyl) are presented, see Table 1 and 2.

The oscillatory shear measurements were performed on a TA Instruments ARES-G2 and Scarabaeus RPA *elite* rheometers. Master curve of the SBRs are obtained by ARES-G2 due to the wide temperature range. Dynamic frequency sweep experiments are performed in Scarabaeus RPA *elite* due to closed cavity where prevent the slippage of the sample out of the geometry.

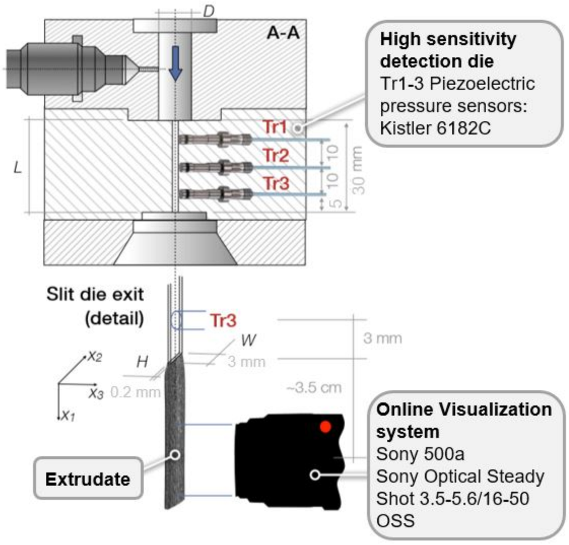

Figure 1. Detailed schematic view of the high sensitive instability detection system. All pictures in this study were performed by this setup[10].

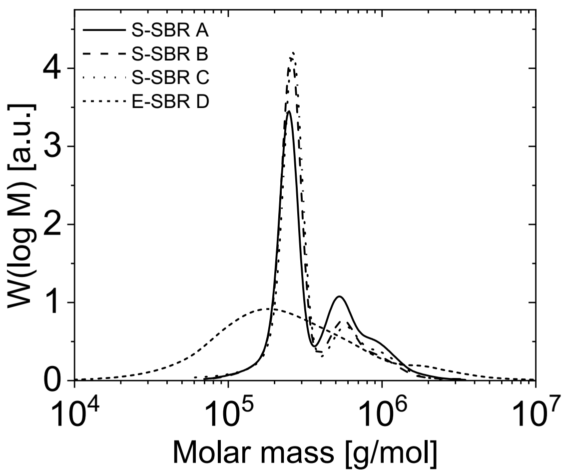

Figure 2. MWD curves of the SBR resins obtained from SEC.

RESULTS AND DISCUSSION

The SEC graphs of the four SBR samples are shown in Fig. 2. There is a distinct separation of the two modes in the bimodal resins. The relative compositions of the two components of the bimodal resins were similar between S-SBR B and S-SBR C, and different from the S-SBR A which has the lowest amount of low M_W content, see Table 1. The topology of the molecules is linear at the low M_W and stars with two (double molecular weight of the linear) and three arms at high M_W. The E-SBR samples displays a broad MWD which is assumed to be a linear molecules. In Table 2, high filed ^{1}H NMR 400 MHz data is presenting the microstructure of the polymer. The interesting point of this study cause from the differences in performance of the melt flow instabilities for the S-SBR which have similar MWD but different microstructure, see Table 2. Using the homebuilt high sensitive slit die[3] the pressure is in situ monitored along the die during the experiment. Fig. 1 is depicting the device which measure the in situ mechanical

Table 1. Molecular weight characterization of the SBR resins.

S-SBR		Weight Fraction	Mn [kg/mol]	M_W [kg/mol]	PDI
A	Bimodal		250.0	400.0	1.46
	Low- M_W	0.343	244.0	248.9	1.02
	High- M_W	0.657	450.0	530.4	1.08
B	Bimodal		287.0	388.0	1.40
	Low- M_W	0.505	251.7	255.6	1.01
	High-M_W	0.495	612.4	648.9	1.05
C	Bimodal		286.0	391.0	1.36
	Low- M_W	0.500	258.0	262.0	1.02
	High- M_W	0.500	688.0	757.0	1.10
E-SBR		**Weight Fraction**	**Mn [kg/mol]**	**M_W [kg/mol]**	**PDI**
D	Unimodal	-	138.0	508.0	3.70

Table 2. Microstructure of SBR resins given by ^{1}H NMR 400 MHz in weight fraction.

S-SBR	Styrene (%)	Butadiene (%)	Vinyl (%)
A	21.1	78.9	62.1
B	15.0	85.0	30.0
C	20.0	80.0	54.0
E-SBR	**Styrene (%)**	**Butadiene (%)**	**Vinyl (%)**
D	43.1	56.9	8.5

pressure signal in three different places. The placement of the piezoelectric transducers happen with respect to measure the actual pressure fluctuation in the entrance, middle, and the exit of the die. Supported by previous studies from Palza et al.[3,12], Kádár et al.[4], and Naue et al.[5], using a similar die was suggested the following. (i) Sharkskin instability caused by the strain localization of the grafted chains and the extensional deformation of them during the change of the velocity profile from Poiseuille to Plug flow at the exit of the die. Due to incompressible flow the indication of sharkskin is more pronounced at the Tr3 but inside the die also. (ii) The relative intensity of the in situ pressure oscillation of the Fourier transformation (FT) analysis of the pressure signal from all transducers record in the same frequency the characteristic pattern of melt flow instability. Both of those statements are also found in this study on the different polymer.

The Fourier transformation signal is subjected to averaging per thirty one point to improve the readability, see Fig. 3. More details regarding the experimental system can be found elsewhere[3]. In Fig. 3, a Fourier spectra from the mechanical pressure at 120 °C at three different shear rates and samples is presented. Characteristic frequency is obtained by distinguishing peak at the FT spectra from all transducers at the same frequency. The error bars are obtained by the peak's broadness while the plotted is the approximate average (gray area) peak, as highlighted in Fig. 3.

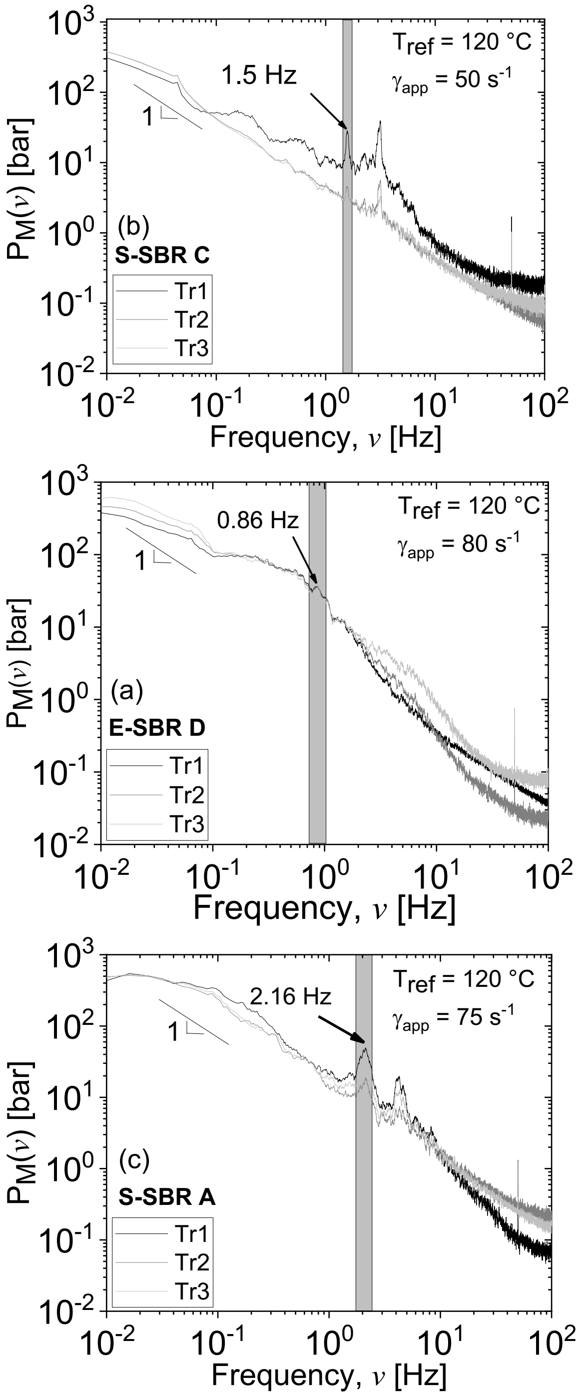

Figure 3. Representative FT spectra of raw data for the sharkskin instability at different shear rates. The FT spectra of all transducers record in the same frequency the characteristic pattern of sharkskin instability.

At high frequencies (~50 Hz) very sharp frequency contributions appear which are material independent and related to the measurement system. For the offline optical analysis of the extrudates solid samples for each shear rate were collected and then digitized using a digital microscopic (Keyence VHX 900F) setup for image analysis. A homemade image analysis software was implemented using MATLAB. In general, the melt flow instabilities appeared as approximately periodic patterns of parallel lines in the images. Provided the images were adjusted so that the lines are vertical, the FT can be used for the analysis. Thus, a FT of each row in the image gives the average number of lines found in this specific row. An average of all rows then gives an estimate of the average number of lines (instabilities) in one image. For detailed description of the algorithmic steps visit Naue et al.[8]. The same protocol is applied in the online optical analysis also. During the extrusion experiment a Sony 500a camera is recording the extrudate at ~3.5 cm after the die exit and ~20 cm far away from it[11].

The onset of instabilities, their development and characteristics are based on steady-state signal of the mechanical pressure data and the corresponding optical (online and offline) analysis. Firstly, the S-SBR A, C and E-SBR D present in a wide range of shear rates, 5 s^{-1} to 10^3 s^{-1}, sharkskin instability. In Fig. 4, is presented the profile of the characteristic frequency of the sharkskin and how this is developed as the shear rates increased. Overall, sharkskin is defined as fast periodic surface distortions with small amplitude[1]. In our study this definition is validate for the S-SBR C at 20 s^{-1}, see Fig. 5(b). In general Fig. 5 is depicting the extrudates from the offline analysis in a wide range of shear rates. None of them present a clear smooth surface or volume distortion, to be characterized as a smooth or gross melt fracture (volume distortion) respectively. Thus, those extrudates present sharkskin instability. Based on that, sharkskin can be defined as a periodic surface instability. Regarding to the speed of instability, fast or slow, is depending on the shear rate and the material. In Fig. 4, the characteristic frequency profile of sharkskin instability is obtained from the pressure FT spectra ($\nu_{pressure}$), offline ($\nu_{offline}$) and online (ν_{online}) optical analysis. It is mentioned that the characteristic frequency profile is developed as power law behavior.

First, a slope of one, on log-log scale, is obtained by the experimental data in all of the samples. That is, as the apparent shear rate increase, the pattern of the sharkskin instability increase as well with the same rate. Secondly, a reduction of the slope to 0,3 is observed. From optical analysis point of view this slope is characterized by the higher frequencies associated with small amplitude on top of lower frequencies associated with higher amplitude instabilities. Characteristic extrudes for that are presented by Fig. 6(c) at 100 s^{-1} and 200 s^{-1} shear rates. Thirdly, in S-SBR A at high shear rates a slope of two is obtained and display an irregular surface pattern.

Stick-slip instability is characterized by two regions with different extrudate surface. Fig. 6(d) is depicting the extrudates of those two regions. With respect to the characteristic frequency profile of the stick-slip instability, the same trend of the power law is observed. Both of those regions present different characteristic frequencies, see Fig. 5. The grey circle symbols represent the stick region, and the black squaresymbols display the slip region. The characteristics frequencies of the stick region are a factor of ten times higher than slip, see Fig. 5. The offline optical analysis is capable to obtain the characteristic pattern for the stick region due to high magnification and focus of the digital microscope. In contrast, online optical analysis is not able to record the stick region by reason of magnification of the camera lens.

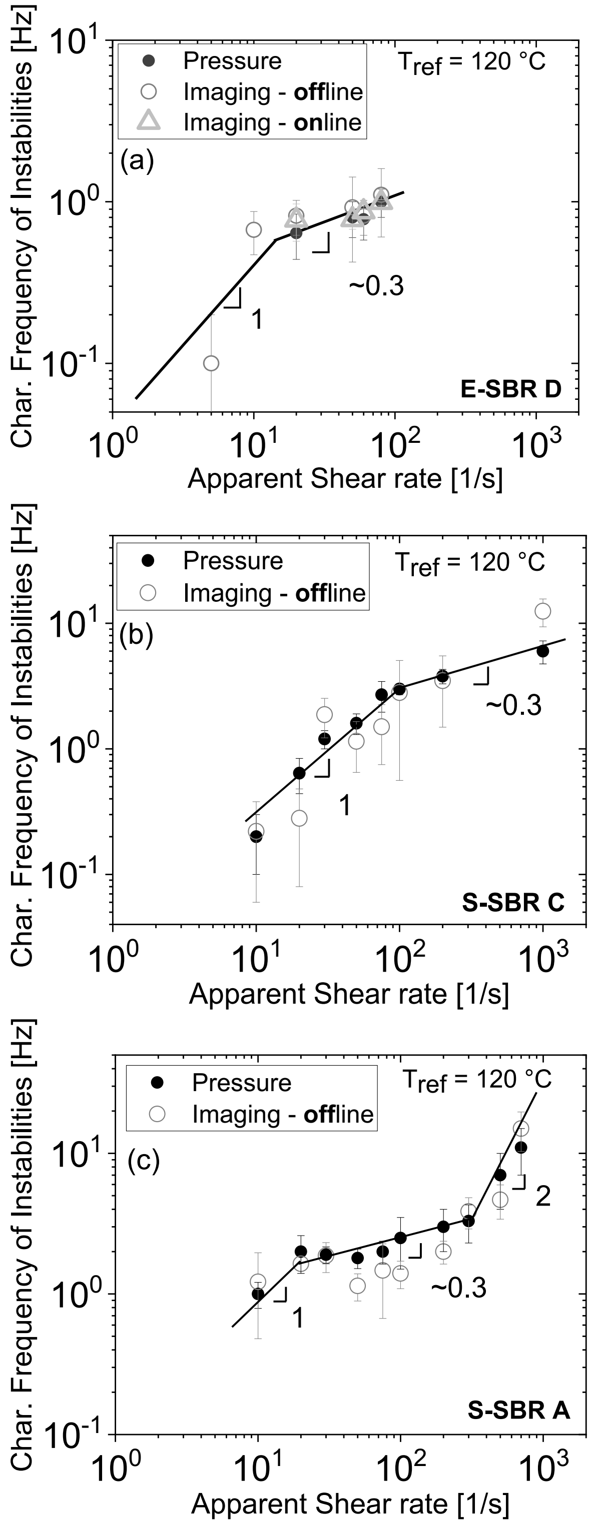

Figure 4. Comparison between the characteristic pattern identified from FT spectra, offline and online optical analysis of the extrudates for sharkskin instability.

Concerning the influence of the MWD in the profile of the characteristic frequency of instabilities is achieved that samples with different MWD present the same power law behavior but in different shear rates. Especially for the bimodal samples, S-SBR A has 34% and S-SBR C, 50% low M_w content. The higher the amount of low M_w content the later the slope of 0,3 appear. That is, the high

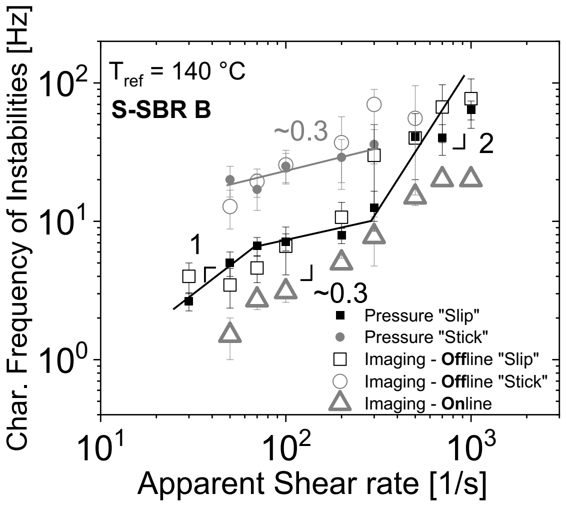

Figure 5. Comparison between the characteristic frequency identified from FT spectra, offline and online optical analysis of the extrudates for stick-slip instability. The grey circle symbols represent the stick and the black square the slip region. See Fig. 6(d).

content of low M_W increase the rate of the slip in higher shear rates.

The difference of the instability type for the samples with the same MWD are based on the different microstructure of them. S-SBR B has 15% styrene and 30% vinyl content rather than S-SBR C has 20% styrene and 54% vinyl content. The higher the amount of the side arms topologies in the macromolecule chain the more dominant the sharkskin instability according to Molenaar and Koopmans[9].

The optical analysis, offline and online, intended to correlate the surface pattern of the extrudates with the characteristic

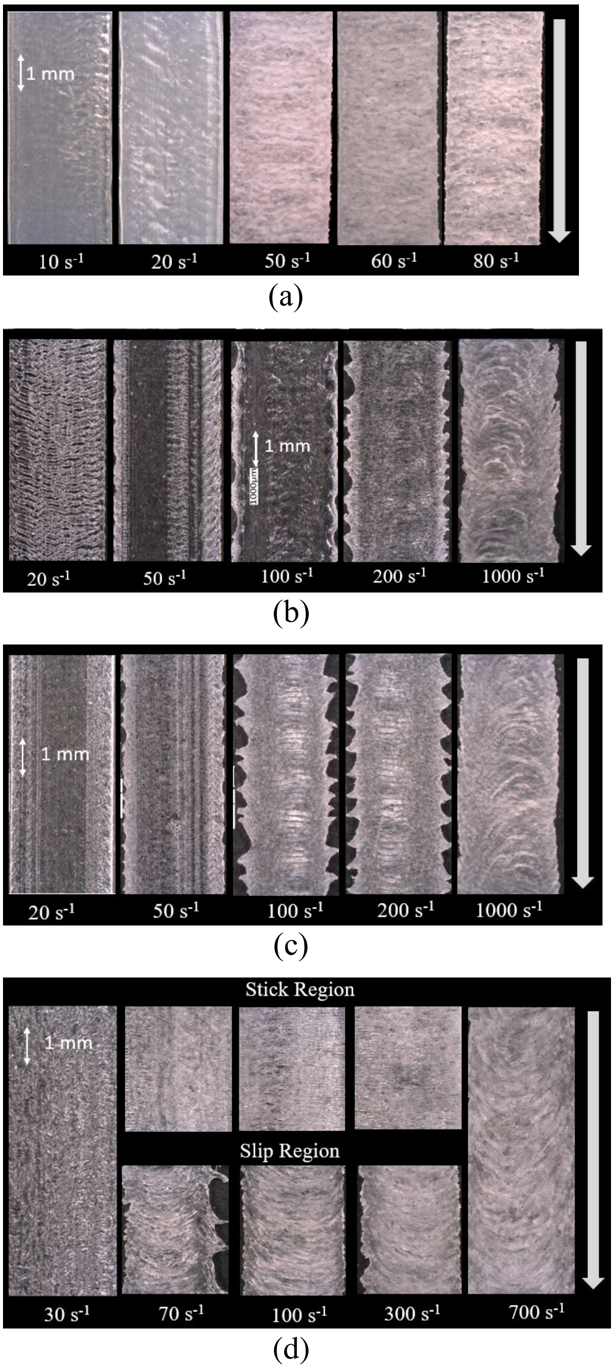

Figure 6. (a) E-SBR D (b) S-SBR C (c) S-SBR A (d) S-SBR B. Offline pictures of extrudates from the slip die, 0.2 x 3 x 30 mm^3. Shear rates of extrudates are displayed and the arrow identify the flow direction.

frequency from the pressure FT spectra during the extrusion. The purpose of this correlation focused on industrial online characterization of extrusion lines via optical analysis and correlations with the material molecular properties. Fig. 7 is presenting the agreement between the $v_{pressure}$ and $v_{offline}$, v_{online} from two different type of instabilities, sharkskin and stick-slip. At Fig. 7(a), the slip characteristic frequency from the pressure FT spectra is matching with the offline and online frequencies. In addition, a slope of one, on log-log scale, describe the agreement between the offline and the frequency from the pressure FT spectra. From the online optical analysis point of view, there is a factor of three deviation from the offline. The interpretation of this deviation is based on two reasons. First, the surface of the sample does not have regular pattern and it is difficult to be captured by the online camera due to focus and magnification limits. Second, the high speed of the slippage is not easily captured by the online video.

Regarding the sharkskin instability, see Fig. 7(b), there is an agreement with the slope of one between the online, offline optical analysis and the characteristic frequency from the pressure FT spectra. This arrangement depends on the surface of the extrudates which have a regulate pattern with easily distinguished grey colour zones.

SUMMARY AND CONCLUSIONS

A combination of a high sensitive slit die with an online and offline optical system for capillary rheometer, capable to in situ detect and analyse melt flow instabilities of SBR, was briefly described in this publication. The combination of the online optical analysis with the capillary rheometry and the correlation of the in situ pressure signal with the surface pattern of the extrudates is a promising online characterization method for extrusion lines. Furthermore, the influence of the MWD and the microstructure of the material to melt flow instabilities is still an open issue. However, correlations via the combination of the high sensitive die and the optical analysis may be a useful tool to overcome the current challenges.

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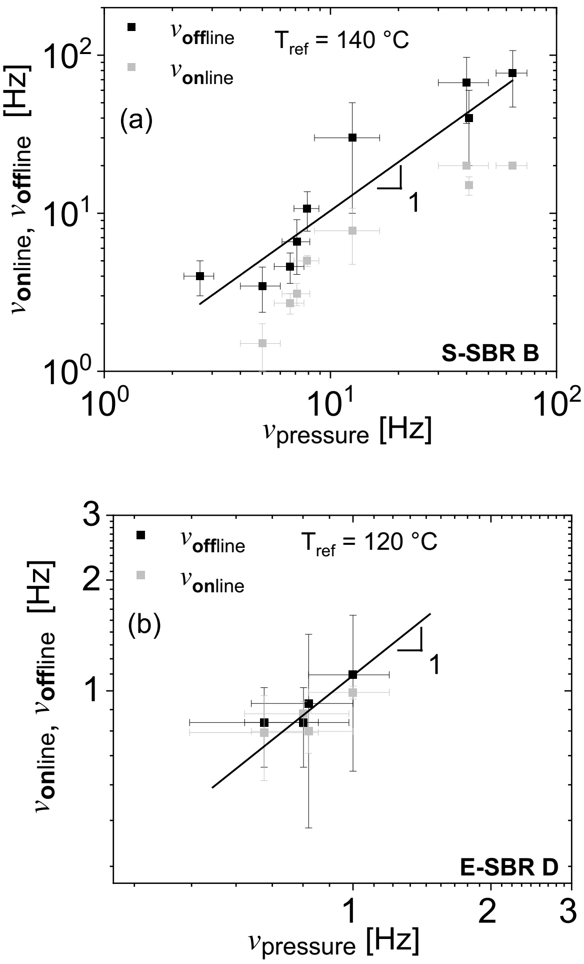

Figure 7. Comparison the characteristic frequency from offline, online analysis with the characteristic frequency from pressure Fourier spectra. (a) S-SBR B at 140 °C with stick-slip and (b) E-SBR D at 120 °C with sharkskin instabilities.

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