Predicting sharkskin instability in extrusion additive manufacturing of reinforced thermoplastics

Vidya Kishore[1,2], Christine Ajinjeru[1,2], Peng Liu[2], John Lindahl[2], Ahmed Hassen[2], Vlastimil Kunc[1,2,3], Chad Duty[1,2]

[1]University of Tennessee, Knoxville
[2]Manufacturing Demonstration Facility, Oak Ridge National Laboratory
[3]Purdue University

Abstract

The development of large scale extrusion additive manufacturing systems such as the Big Area Additive Manufacturing (BAAM) system has enabled faster printing with throughput as high as 50 kg/h and the use of a variety of thermoplastics and composites with filler loading as high as 50%. The combination of high throughput and heavy reinforcements can give rise to a phenomenon known as “sharkskin” instability, which refers to extrudate surface distortions typically in the form of roughness or mattness, and is commonly observed in traditional extrusion processes. The onset of this instability depends upon the viscoelastic properties of the material and processing parameters such as throughput, shear rate, extruder die geometry, and temperature. For printed parts, such instabilities are undesirable and detrimental to mechanical properties. This work examines the effect of process parameters on the rheological properties of BAAM thermoplastics and composites to predict the occurrence of sharkskin during printing.

Introduction

Reducing mechanical anisotropy of the printed parts has been one of the areas of significant interest in extrusion additive manufacturing (AM) of thermoplastics and composites. One of the important criteria for improving strength in the print direction, typically z-direction, is enhancing the extent of bonding between the printed layers (or beads). For most thermoplastics, primary bonding mechanism is based on thermal fusion and polymer interdiffusion across the interface of the beads, which depend on thermal history of the beads as well as contact area between them [1,2]. The extrusion of smooth beads offers more intimate surface-to-surface contact than beads with a macroscopically rough surface (“hairy” or fractured surface), wherein the area of direct contact available for molecular interdiffusion would be much lower. Most of the common materials printed on filament based extrusion platforms have a relatively smooth bead surface, as these systems operate at low to moderate throughput. However, on large scale platforms such as the Big Area Additive Manufacturing (BAAM) systems, where materials with high filler loadings (~50% by weight) are processed with high throughput (~ 50 kg/hr), surface irregularities can appear in the form of mattness or roughness, which is undesirable to achieve good bonding between the printed beads. Although several fiber reinforced thermoplastics have been printed on the BAAM without such irregularities, exploring new materials and processing regimes can give rise to such behavior, depending upon the intrinsic material properties, print platform, and processing conditions.

The irregularities in surface features during extrusion are mainly caused by various polymer melt flow instabilities, a phenomenon commonly observed in traditional extrusion processing of some thermoplastics. The occurrence of such melt flow instabilities in traditional polymer processing have been widely reported in literature over the past six decades and have been known to be one of the factors limiting the processing of various materials to manufacture tubes, rods, sheets and wire coatings [3,4]. These instabilities can be generally categorized in to four stages, depending up on shear stress response of the material at various processing shear rates, as shown in Figure 1 (adapted from [4]).

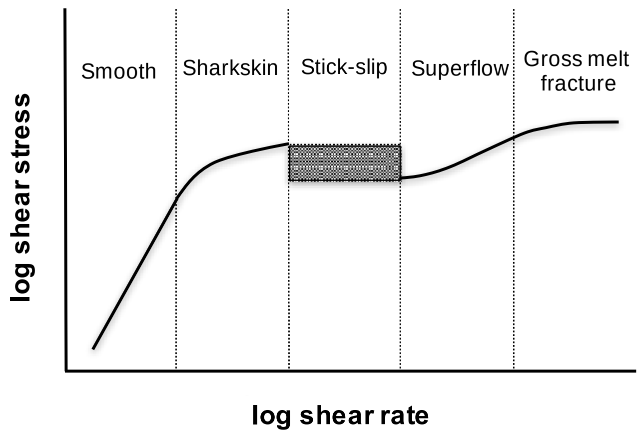

Figure 1. Schematic of a typical flow curve for various instabilities.

During extrusion, when the polymer melt is subjected to sufficiently high stresses as it exits the die, instabilities in the extrudate first occur in the form of surface mattness or roughness, followed by local cracks and distortions in the direction perpendicular to the melt flow, eventually leading to volumetric distortions of the extrudate. As shown in Figure 1, the first appearance of surface-related defect manifests as roughening of the surface, i.e, small-amplitude periodic distortions known as the “sharkskin” effect. Upon further increase in the flow rate, sharkskin increases, eventually leading to pressure oscillations, known as stick-slip instability. With further increase in flow rate, the extrudate become smooth and defect free, a state known as “superflow” and at very high shear rates, distortions lead to gross melt fracture state (volumetric distortions) [3-5].

In several reported works, the occurrence of sharkskin instability has been attributed to a local stress concentration or stress singularity at the die exit and local stick-slip conditions at the die exit. The local stress concentration is understood to occur when the polymer exits the die, where there is an abrupt change in boundary conditions since the layer of the polymer melt close to the die surface accelerates abruptly from almost zero velocity to the average extrusion velocity of the bead. This leads to a sudden increase in tensile stresses on the surface of the polymer that is greater than the tensile stress that the material can withstand. This then leads to surface cracking of the extrudate at the die exit periodically, appearing in the form of sharkskin. The second mechanism (stick-slip condition) is associated with the molecular level interactions between the die wall and the polymer chains close to the wall. Depending up on the surface energies, the polymer chains oscillate between entanglement and disentanglement states due to their reversible coil-stretch transitions. This leads to roughening of the polymer surface as it sticks and slips during flow [4,6,7].

Several factors related to material properties and process conditions can influence the onset and degree of sharkskin instability, typically quantified by the frequency and amplitude of shark skin defects on the extrudate surface. The structure of the polymer matrix being extruded plays an important role in determining the occurrence of these defects, as the structure affects the viscoelastic properties of the polymer. Several studies on polyethylenes have reported that the presence of short or long chain branching lowers the frequency and amplitude of sharkskin defects [4,8]. Sharkskin phenomenon is also lowered by reducing molecular weight of the polymer [8,9]. In terms of process parameters, increasing flow rates (and associated shear rates) increases the amplitude of sharkskin defects. However, an increase in temperature delays the onset of sharkskin to higher flow rates. Die geometry and material also play a role in determining onset of this defect. Increasing length to diameter ratio (L/D) of the die lowers the effect and there is no significant effect of die entry angle on the onset of sharkskin. Typically, in traditional extrusion processing of low temperature materials like polyethylenes, the onset of sharkskin is eliminated using Teflon coated dies or with the use of fluorinated additives, which lower the surface energy at the wall, lowering stick-slip [7,10].

In this work, the authors discuss the observation of sharkskin instability for extrusion of a high temperature semi-crystalline thermoplastic composite on large scale additive manufacturing (AM) test system. The goal of the work is to develop correlations between the rheological properties of the system and the conditions of onset of sharkskin defects. Here, the authors report some preliminary controlled lab scale rheological studies that have been performed to identify conditions for the presence and absence of this instability and to draw broad correlations between rheological properties of the system and the onset of sharkskin defects. This is the first time such observations of sharkskin instabilities have been reported for extrusion AM processing.

Experimental

The preliminary experimental work discussed in this study used three grades of poly(ether ketone ketone) (PEKK), a high performance semi-crystalline thermoplastic material. One of the grades was unreinforced PEKK and the other two were 30 wt.% and 40 wt.% short carbon fiber reinforced grades. Initial extrusion trials were conducted on a BAAM test extruder set-up (Fig. 2) to observe the occurrence of any flow instabilities during extrusion using PEKK with 40 wt.% carbon fibers. The test extruder was located on a separate test stand, but is identical to the extruder used on the BAAM system, with four heating zones and the extruder tip. The nozzle tip temperatures were set to 370 ^{o}C, 380 ^{o}C and 400 ^{o}C for various trials and the screw speeds were set to 100 rpm and 200 rpm for different trials. The nozzle used had an orifice diameter of 7.62 mm (0.3 in).

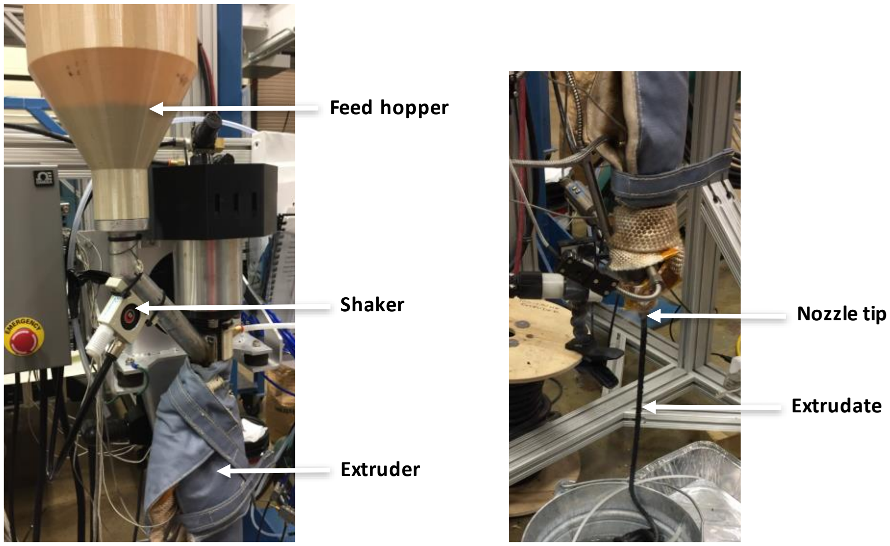

Figure 2. Test extruder set-up.

To replicate the occurrence of shark skin on controlled shear lab scale processes, tests were performed on a Dynisco LCR 7001 capillary rheometer for the three chosen grades of PEKK. Tests were performed in air at a chosen test temperature of 390 ^oC. The capillary die used was made of tungsten carbide with an orifice diameter of 0.75 mm and L/D of 20. Initially, steady shear tests were first performed between 5000 s^{-1} and 5 s^{-1} to obtain the variation of shear stress with shear rate. This was followed by extrusion at constant shear rates of 100 s^{-1}, 250 s^{-1} and 4000 s^{-1} to observe the extrudate surface under each condition.

To correlate results from the capillary rheometry tests with dynamic rheological properties of the material, frequency sweep tests were performed for these materials at 375 ^oC, 390 ^oC and 405 ^oC in air and at 375 ^oC and 390 ^oC in nitrogen using a TA Instruments Discovery Hybrid Rheometer- 2 system with parallel plates fixture.

Results and discussion

Figure 3 shows multiple samples of a PEKK 40 wt.% CF extrudate obtained from tests on the BAAM test extruder at various tip temperature and screw speed conditions. The characteristic sharkskin defect can be observed in the form of periodic irregularities on the surface for all extrusion conditions.

Figure 3. Extrudates obtained at (a) 370 ^{o}C, 200 rpm; (b) 380 ^{o}C, 200 rpm; (c) 400 ^{o}C, 100 rpm; and (d) 400 ^{o}C, 200rpm (The temperatures indicate the set tip temperature).

Controlled experimental trials to extrude the material at the corresponding shear conditions were performed on a LCR 7001 capillary rheometer from Dynisco. Fig. 4-6 represent optical micrographs of the extrudate at three different shear rates for neat PEKK, PEKK with 30 wt.% CF and 40 wt.% CF respectively. For neat PEKK and PEKK with 30 wt.% CF, no sharkskin instability was observed across the three tested shear rates. However, for the 40 wt.% CF reinforced grade, sharkskin defects were observed at the tested shear rates of 250 s^{-1} and 4000 s^{-1}. Plotting the variation of shear stress at various shear rates (shown in Fig. 7 a-c) can help to identify the transition to the "sharkskin" region of the characteristic flow curve shown in Figure 1. As seen in Figure 7 a,b for the neat and 30 wt.% CF reinforced grades, respectively, there is deviation from linear dependence above ~1000 s^{-1}, although no shark skin effect is observed. However, for the 40% CF reinforced grade (Fig. 7c), only a small deviation from linear behavior occurs, and yet shark skin defect is observed. This indicates a difference in the trend observed for these materials when compared to that of polyethylenes which have primarily been the subject of sharkskin studies reported so far.

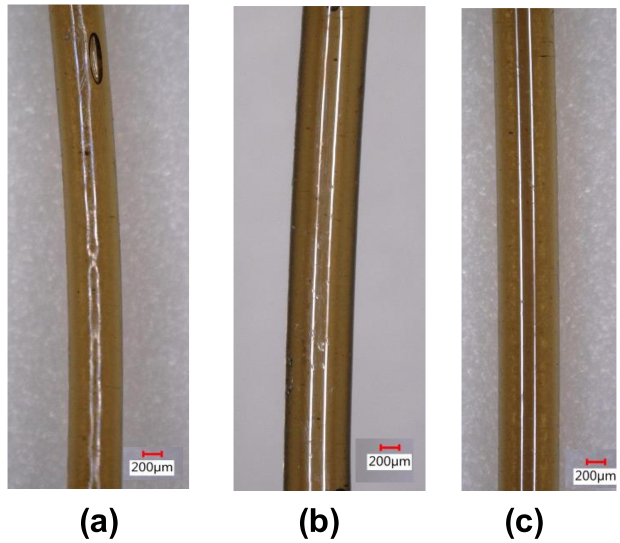

Figure 4. Extrudate from capillary rheometer at 390 °C for neat PEKK at (a) 100 s^{-1}; (b) 250 s^{-1}; and (c) 4000 s^{-1}.

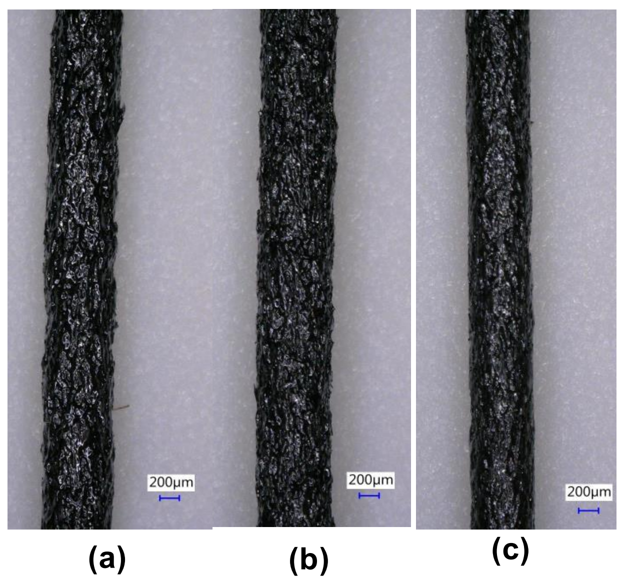

Figure 5. Extrudate from capillary rheometer at 390 °C for PEKK 30 wt.% CF at (a) 100 s^{-1}; (b) 250 s^{-1}; and (c) 4000 s^{-1}.

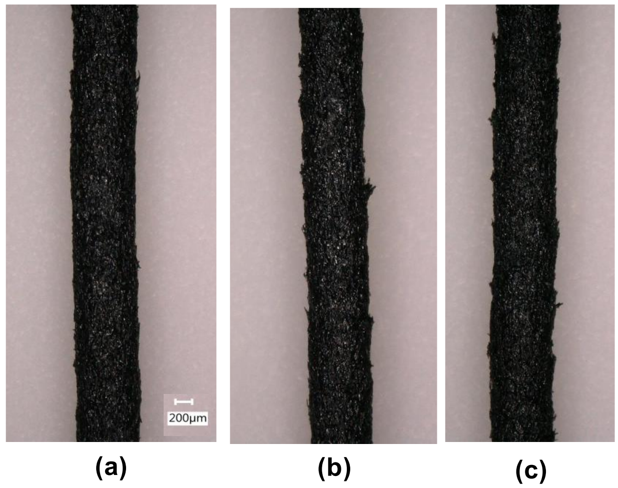

Figure 6. Extrudate from capillary rheometer at 390 °C for PEKK 40 wt.% CF at (a) 100 s^{-1}; (b) 250 s^{-1}; and (c) 4000 s^{-1}.

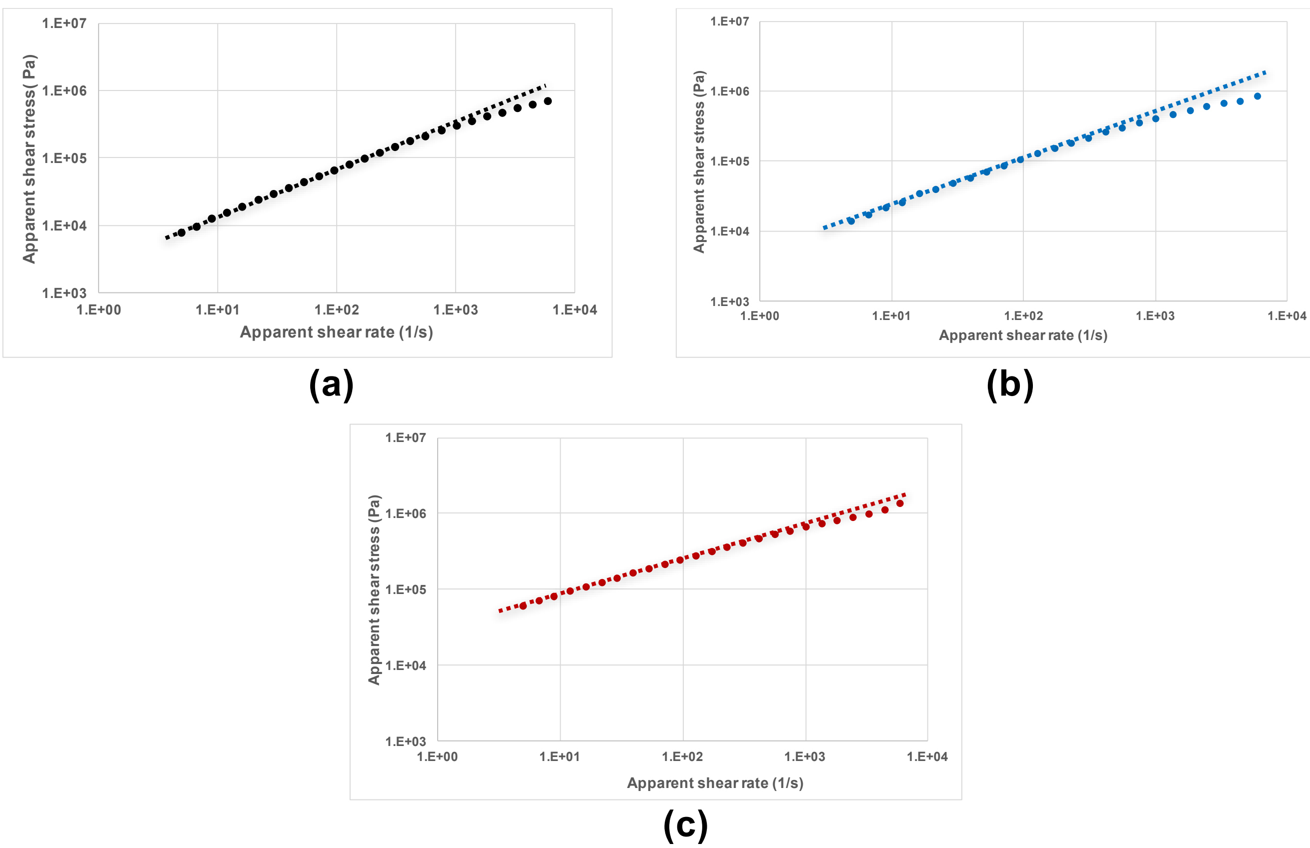

Figure 7. Variation of apparent shear stress with apparent shear rate at 390 °C for (a) Neat PEKK; (b) PEKK with 30 wt.% CF; and (c) PEKK with 40 wt.% CF.

In an attempt to correlate the dynamic rheological properties of the PEKK materials with the onset of sharkskin, frequency sweep tests were conducted at 390 °C in nitrogen to minimize degradation (Fig. 8). It can be observed that for the neat and the 30 wt.% CF grades, the material remains more viscous than elastic (G''>G') at all the tested frequencies (shear rates). However, for the 40 wt.% CF reinforced grade, the crossover frequency (where G'=G") is in the range of 50-100 s^{-1} (observed range from multiple runs), beyond which the dominate material behavior shifts to be more elastic than viscous. The observations made for the extrudate from the capillary rheometer also show the presence of sharkskin defects for this grade at shear rates greater than 100 s^{-1}. This behavior (G'>G") has been observed for the three grades at 375 ^{o}C, 405 ^{o}C as well in air. These preliminary results indicate that the onset of sharkskin defects for PEKK composite materials may correlate to the transition from viscous to more elastic behavior as shear rate increases. This trend may be useful for identifying appropriate processing conditions to avoid sharkskin defects in these materials in future print jobs.

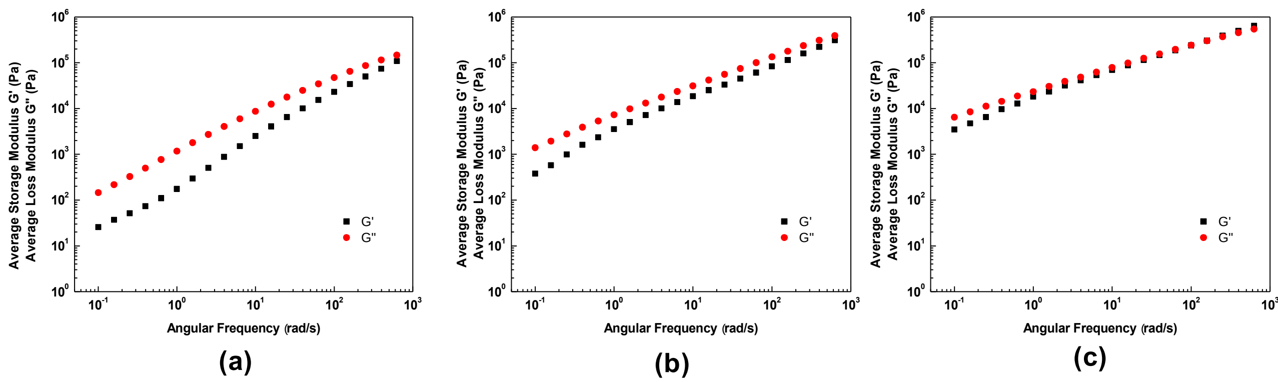

Figure 8. Variation of storage moduli (G') and loss moduli (G") at 390 ^{o}C with frequency in nitrogen for (a) Neat PEKK; (b) PEKK with 30 wt.% CF; and (c) PEKK with 40 wt.% CF.

Conclusions and future work

This work for the first time reports observations of sharkskin instabilities for extrusion additive manufacturing processes for new materials. Test trials were performed on the large scale AM system using carbon fiber reinforced poly(ether ketone ketone) grade and the occurrence of sharkskin instability was observed. Controlled extrusion experiments on a lab scale system was performed using a capillary rheometer and the extrudate surface was observed at different shear rates. No sharkskin defect was observed for neat and PEKK with 30 wt.% CF across a broad range of shear rates (100 s^{-1}- 4000 s^{-1}). However, sharkskin defects were observed at shear rates above 100 s^{-1} for 40% CF PEKK. Preliminary correlations with dynamic rheological properties of these materials indicated the onset of sharkskin may occur at conditions wherein the material transitions from more elastic than viscous behavior (G' > G"). Further studies are needed to better understand and correlate this phenomenon with AM processing conditions and to develop a broad-based criteria to predict the occurrence of sharkskin instabilities in extrusion AM.

Acknowledgments

Research sponsored in part by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. The authors gratefully acknowledge Arkema Inc. for providing the materials used in this study. The authors also thank Ernest Rivera for his assistance with the experimental work.

References

1. Sun, Q., Rizvi, G. M., Bellehumeur, C. T., & Gu, P. (2008). Effect of processing conditions on the bonding quality of FDM polymer filaments. *Rapid Prototyping Journal*, *14*(2), 72-80.
2. N. Turner, B., Strong, R., & A. Gold, S. (2014). A review of melt extrusion additive manufacturing processes: I. Process design and modeling. Rapid Prototyping Journal, 20(3), 192-204
3. Hatzikiriakos, S. G., & Migler, K. B. (Eds.). (2004). Polymer processing instabilities: control and understanding. CRC Press.
4. Agassant, J. F., Arda, D. R., Combeaud, C., Merten, A., Muenstedt, H., Mackley, M. R., & Vergnes, B. (2006). Polymer processing extrusion instabilities and methods for their elimination or minimisation. International Polymer Processing, 21(3), 239-255.
5. Muliawan, E. B., Hatzikiriakos, S. G., & Sentmanat, M. (2005). Melt fracture of linear PE: A critical study in terms of their extensional behaviour. International Polymer Processing, 20(1), 60-67.
6. Aho, J. (2011). Rheological characterization of polymer melts in shear and extension: measurement reliability and data for practical processing. Tampere University of Technology.
7. Miller, E., & Rothstein, J. P. (2004). Control of the sharkskin instability in the extrusion of polymer melts using induced temperature gradients. Rheologica acta, 44(2), 160-173.
8. Allal, A., Lavernhe, A., Vergnes, B., & Marin, G. (2006). Relationships between molecular structure and sharkskin defect for linear polymers. Journal of non-newtonian fluid mechanics, 134(1), 127-135.
9. Pol, H. V., Joshi, Y. M., Tapadia, P. S., Lele, A. K., & Mashelkar, R. A. (2007). A geometrical solution to the sharkskin instability. Industrial & engineering chemistry research, 46(10), 3048-3056.
10. Larson, R. G. (1992). Instabilities in viscoelastic flows. Rheologica Acta, 31(3), 213-263.