Thermoplastic pultrusion's cooling temperature effects on pulling forces and deconsolidation

N. A. ALSINANI[1], L. LABERGE LEBEL,

Advanced Composites and Fibers Structures Laboratory (ACFSlab), High Performance Polymer and Composite Systems (CREPEC), Polytechnique Montreal, 2500 ch Polytechnique, Montreal, Qc, Canada, H3T 1J4
Email: nawaf.alsinani@polymtl.ca, lll@polymtl.ca

Abstract

Surface finish defects and deconsolidation have slowed the commercial use of thermoplastic pultruded products. During the cooling process, the metal-polymer adhesion forces vary with any change in temperature. We have developed an efficient cooling system that is able to accurately control the cooling temperature profile. The aim of this study was to investigate the effects of varying cooling die temperatures on the pulling forces and the deconsolidation behaviour in thermoplastic pultrusion. Carbon/PEI pultruded rods of 4.76 mm in diameter were produced using a multi-die pultrusion system. The fiber volume content of the rods was 56%. Adhesion forces in the cooling die were measured using pulling force data collected by a load-cell in the pultrusion line. To accurately measure the pulling forces that come from metal-polymer adhesion in the cooling die only, the pultruded beams were re-inserted into a single-die pultrusion system. After the re-insertion of the rod, it was reheated to the processing temperature before being cooled in the cooling die. In all experiments, the production speed and the heating die temperature were kept constant. The selected cooling temperatures were $T_g/2$, and T_g and $(T_g + T_p)/2$. Deconsolidation and surface finish quality were characterized using microscopy and surface roughness measurement. High pulling forces were observed when cooling was raised to T_g and higher. Deconsolidation and higher void content were also observed when the cooling temperature was higher than T_g. The proposed state-of-the-art cooling system will create significant new opportunities for the use of thermoplastic pultruded products in many fields.

Keywords: Thermoplastic, cooling, pultrusion, amorphous.

1.0. Background and Requirements

Surface finish defects and impregnation challenges have impeded the commercial use of thermoplastic pultruded products[1]. The multi-die pultrusion process was recently developed to overcome impregnation challenges. In this process, the polymer and reinforcement fibers are pulled together through a number of heated dies in order to liquefy the resin fibers. To fully impregnate the reinforcement fibers, the yarns entering the dies contain additional resin fibers. This process was capable of producing fully impregnated composite rods by blending various materials such as Flax/PLA [2], Flax/PP [3], Carbon/PA [4], Carbon/PEI [5] and/or Carbon/PEEK [6]. A similar four-die pultrusion system was implemented into additive manufacturing technology [7]. The implementation of the four-die pultrusion system lowered the void content in the printed extrudate by more than 80%. These results indicate a high potential of the multi-die pultrusion technology to overcome the impregnation challenges. Yet, the post-impregnation challenges, namely the cooling process, remain unsolved. Contrary to thermoset composites, thermoplastic pultruded composites must cool while being constrained between mold surfaces. Otherwise, they deconsolidate in a porous structure, resulting in composite materials with low mechanical properties [8]. Moreover, thermoplastic polymers tend to adhere to metallic mold surfaces during the cooling process [9]. These post-impregnation problems can result in high pulling forces, poor surface finish quality and deconsolidation thus preventing the commercial use of the pultruded products.

When a thermoplastic polymer is heated, the state of the thermoplastic changes from a glassy state to a viscous flow state, and the microscale adhesion behaviour of the thermoplastic polymer with the metals can vary remarkably. Before reaching a viscous flow state and at temperatures slightly over the glass transition temperature (T_g), it was observed that the contact forces between an amorphous polymer and a metallic surface change. The metal-polymer adhesion forces increase with increasing temperature [9]. This means that when cooling is done in thermoplastic pultrusion, the cooling temperature profile will result in a distribution of metal-polymer adhesion forces over a specific distance. For example, setting the cooling system to be at a temperature close to or above T_g will result in a longer cooling distance where metal-polymer adhesion force values are higher. This will increase the pulling forces and may result in the failure of the pultruded beam. Another detrimental effect of the high metal-polymer adhesion forces is the “sloughing” phenomenon [10]. If these adhesion forces are higher than the pultruded material’s strength, fragments of the pultruded beam will tear out and stick to the die surface. These pieces will plow into the beam’s surface, resulting in an irregular surface finish. In addition to causing poor surface finish, if left unchecked, the sloughing problem may cause massive pulling force leading to major fiber damage. To reiterate, adhesion forces between the polymer and die walls vary during the cooling process between processing temperature (T_p) and T_g. Therefore, the sloughing critical distance (SCD) can be defined as the distance in the pultrusion die where the pultruded material’s temperature is between $\mathrm{T_p}$ and $\mathrm{T_g}$ when it comes into contact with the surface of the cooling die.

According to the literature reviewed, there are very few works on sloughing in thermoplastic pultrusion. Batch *et al.* [10] studied sloughing during thermoset pultrusion. They recommended some practices to reduce the chances of sloughing. These included adding lubricants, polishing the die surface and increasing fiber volume fraction. Any roughness or cracks in the die surface was found to increase the chances of sloughing [10]. Increasing fiber volume fraction decreased the chances of sloughing occurrence as they provide more fibers for the resin next to the wall, thus increasing the surface’s shear strength of the pultruded beam [10]. However, few studies were found that investigates the SCD in thermoplastic composite pultrusion. The main objective of this study was to study the effects of SCD on pulling forces, the surface finish quality and the deconsolidation behavior in pultruded beams.

2.0. Materials and method

2.1. Materials

Table 1 outlines the materials used in this study and their properties. Commingled Carbon/PEI yarns were used to manufacture unidirectional composite rods. The commingled yarns (Concordia fibers) were made of 12K (AS4, Hexcel) carbon fibers and PEI (Ultem, SABIC).

Table 1 Properties of the AS4 and Ultem PEI.

Parameter	Unit	PEI	AS4 carbon fiber
Glass transition (Tg)	°C	217	-
Processing Temperature (Tp)	°C	370-400	-
Solid density [11]	g/cm^3	1.28	1.79
Melt density [12]	g/cm^3	1.21	-
Melt viscosity	Pa.s	[200, 500]	-

2.2. Method

2.2.1. Producing Carbon/PEI rods using pultrusion

Figure 1 shows the schematic for the pultrusion system used in this study. The pultrusion apparatus included a creel, a guide, a preheater, four pultrusion dies, a cooling die, a load-cell and a pulling system. A closed circular thin-walled tube section of 11.4 mm protruded from the last pultrusion die to the cooling die. The tube was placed inside a 3 mm-deep hole at the cooling die's inlet. The fit between the tube and cooling die inlet's hole was a medium running fit (RC5). The resulting tube length exposed to air was 8.4 mm. The thickness of the thin wall was 1.59 mm in order to minimize the thermal interference between the fourth pultrusion die and the cooling die. To have control over the temperature, the cooling die was equipped with two heating cartridges and two air cooling channels. The preheater was a tube wrapped with a cable heater with a length of 300 mm and was 12 mm in diameter. Note that all four pultrusion dies had a conical cavity tapered at $5°$ relative to a horizontal axis, followed by a straight cylindrical cavity. The diameter of each die's cylindrical exit was 5.13, 5.00, 4.90 and 4.76 mm respectively. A white triangle in Figure 1 represents a thermocouple's location in the pultrusion dies. Also, a red circle indicates a heating cartridge's location and a blue circle indicates an air-cooling channel's location.

Each of the 21 bobbins used contained one commingled yarn with a fiber volume fraction (V_f) of 47%. The change in the die's exit area gradually increased the composite V_f to a nominal value of 56%. The 21 yarns produced a filling ratio of 93.1%, 98%, 102% and 106% in the first, second, third and fourth die respectively. Since the filling ratio of the first and the second dies were below 100%, they did not contribute to the impregnation pressure. Instead, the first two dies acted as a contact preheater to help reduce the resin's viscosity. The impregnation system temperature was set at 380℃ and the cooling die temperature was set at 108℃. In both cases, the production speed, controlled by a puller, was kept constant throughout the process at 50 mm/min.

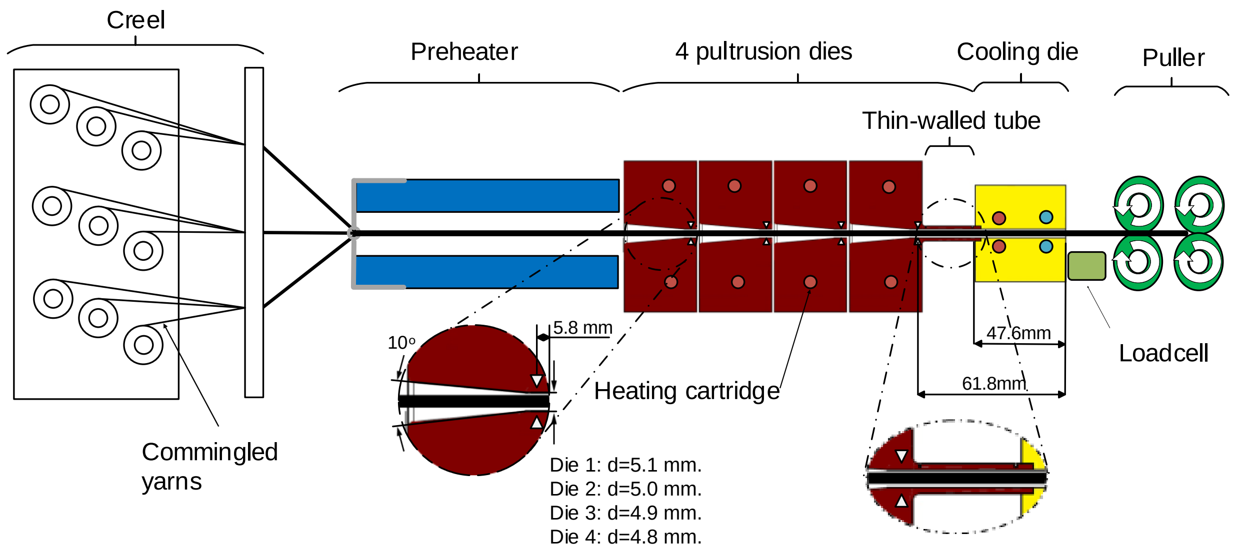

Figure 1 A schematic of the multi-die pultrusion system used in this study. The pultrusion system includes, a creel, a pre-heater, four pultrusion dies, a cooling die, a load-cell and a pulling system. The thin-walled tube is part of the fourth die. The tube protrudes from the fourth die to the cooling die. A white tringle denotes a thermocouple's location in the pultrusion die. A red circle indicates a heating cartridge's location and a blue circle indicates an air cooling channel's location.

2.2.2. Re-heating pultruded beams and pulling force measurement

After producing the pultruded rods using the four-die pultrusion system, a single-die pultrusion system was used to test the cooling die temperature effects on the pulling force. Figure 2 shows the schematic for the single-die system used to test the cooling die temperature effects on the pulling force. This system included the same pre-heater, last pultrusion die including the protruding thin-walled tube, the cooling die, the load cell and pulling system presented in Figure 1. A pre-consolidated rod was inserted with a wire-thermocouple. This rod was heated in the pre-heater before entering the pultrusion die. Then, the rod proceeded through the heating and cooling dies. In order to track temperature inside the rods, a wire-thermocouple was attached to the rod's tip using a digital soldering station (FX888D, Hakko). The thermocouple attachment was done by slightly melting the mid-point of the rod's tip to provide some space and adhesion for the thermocouple.

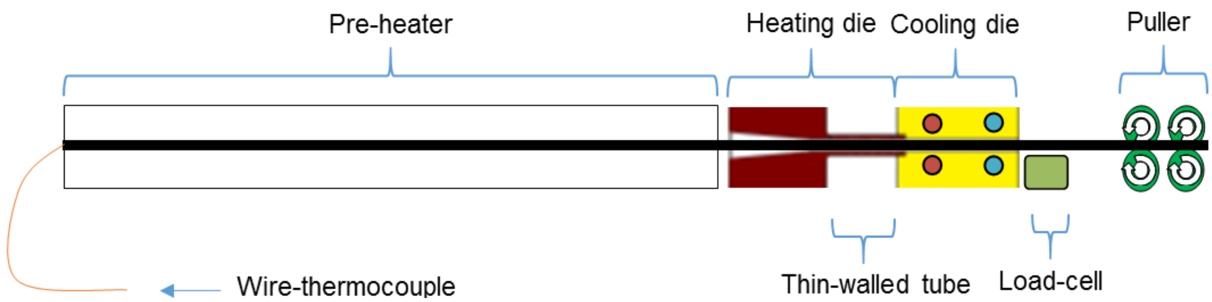

Figure 2 A schematic for the single-die system used to test the cooling die temperature effects on the pulling force. The set up includes a wire-thermocouple, a well-consolidated rod, a pre-heater, a pultrusion die, a thin-walled tube, a cooling die, a load-cell and a puller. A red circle indicates a heating cartridge's location and a blue circle indicates an air cooling channel's location.

Table 2 shows the temperature set points and the production speed used for the single-die test. All experiments were performed three times. Nominal pulling speed was 50 mm/min. The preheater temperature was set at 200 ℃ and the pultrusion die temperature (T_p) was 380 ℃. The selected range of cooling temperature was in relation to T_g. The first selected cooling temperature, 109 $°C$, was T_g/2. The second selected cooling temperature, 216 $°C$, was ~ T_g. The third selected cooling temperature, 300 $°C$, was (T_g + T_p)/2.

Table 2 Pultrusion parameters using different cooling temperatures.

Sample name	Preheater ($°C$)	Pultrusion die ($°C$)	Cooling die ($°C$)	Pulling Speed (mm/min)
PEI-109	200	380	109	50
PEI-216			216	
PEI-300			300	

2.3. Characterization

Five cylindrical samples measuring 0.8mm in length were taken from the reprocessed rods using a precision saw. The cylindrical samples were polished and analyzed under a microscope (Metallovert, Leitz). Photos of 200 X magnification were taken and then stitched to form the whole cross-section of a pultruded rod. The surface finish quality was characterized using a surface roughness characterization machine (Surfcoder-SE700, Kosaka). Nine points, 45° in between each, were taken from each sample along its radius. The sample length was 0.8 mm, the number of samples was 5, the pitch was 0.5 μm and the evaluation length was 4.0 mm.

3.0. Results and discussion

3.1. Sloughing critical distance determination

Figure 3 shows the temperature measurements taken by the wire-thermocouple in the single die reprocessing experiments (see Figure 2). It is important to note only one trial was achieved for each experimental set-point due to frequent loss of the wire-thermocouple. Figure 3 (a) shows the temperature measurement during a PEI-109 experiment. PEI is an amorphous polymer with a $\mathrm{T_g}$ around 216 ℃. T_c was set at 109 ℃. From this temperature-distance plot, the SCD was measured to be 23 mm. The pultruded beam also left the cooling die at a temperature below $\mathrm{T_g}$, which should prevent any potential deconsolidation upon exit. Figure 3 (b) shows the temperature measurement during a PEI-216 experiment. In this experiment, the cooling temperature was set to the $\mathrm{T_g}$ of PEI. Consequently, the pultruded material was cooled slower than the PEI-109. The SCD was measured to be 43.3 mm. However, the pultruded product still left the cooling die with a temperature 10 degrees below $\mathrm{T_g}$. The reason for the discrepancy between the cooling die set point and the exit temperature of the rod might be related to location of the air cooling channels, which were located near the exit. Thus, these channels may have caused the pultruded rods to cool down below set point. Figure 3 (c) shows the temperature measurement during a PEI-300 experiment. In this experiment, the cooling temperature was set to 300. Here the SCD was measured to be longer than 61.8 mm. This result indicates that the SCD extends beyond the cooling die exit. The maximum recorded heating die temperatures were 359.2 ℃, 363.4 ℃ and 377.5 ℃ for PEI-109, PEI-216 and PEI-300 respectively. All temperatures were below the desired T_p. The data collected for the control thermocouples placed within the heating die (see triangles in Figure 1) measured a temperature equal to the desired T_p of 380 ℃. Moreover, PEI-109 had the largest difference between its maximum achieved temperature and T_p. PEI-216 had the second largest difference and finally PEI-300 had the lowest difference. This indicates that the cooling die extracted heat from the rod upstream of the cooling die entrance while the rod was still inside the heating die. This phenomenon is attributed to the high thermal conductivity of the protruding cooling tube as well as the high axial thermal conductivity of the pultruded C/PEI rod.

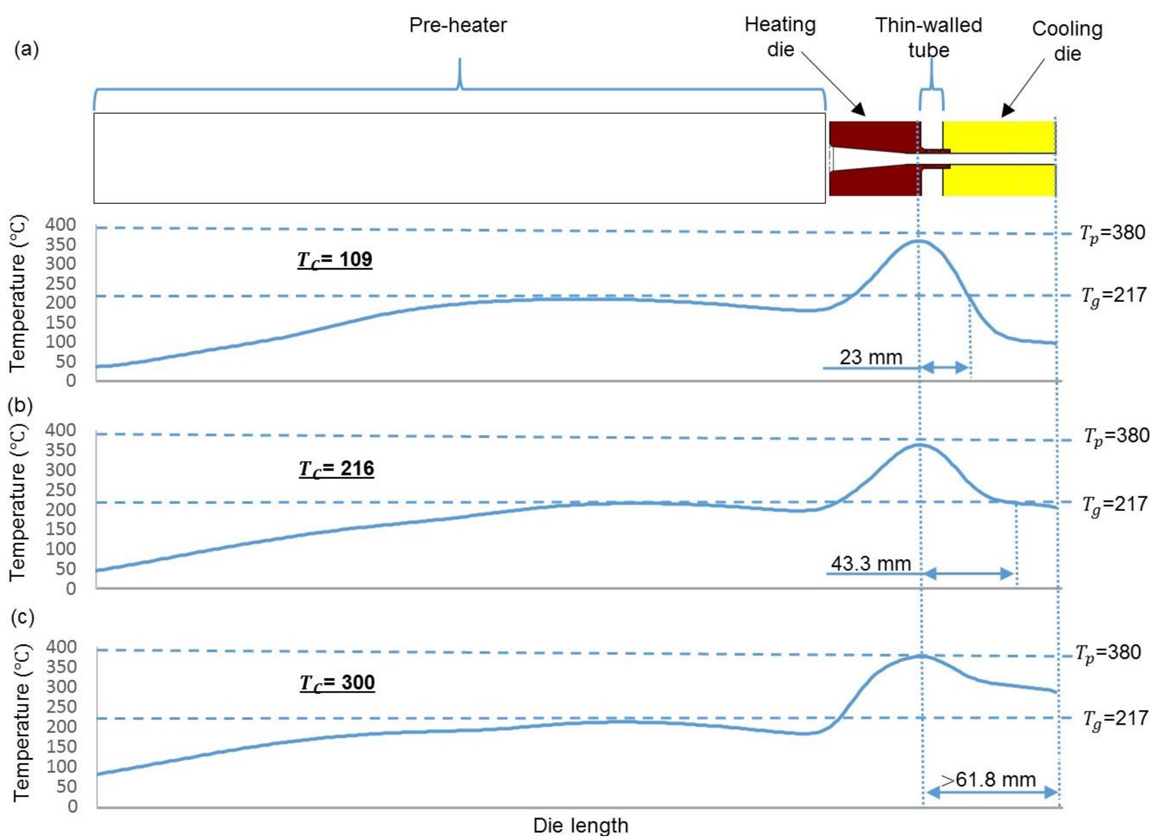

Figure 3 (a) the temperature measurement during a typical PEI-109 experiment. The measure critical sloughing distance was 23 mm. (b) The temperature measurement during a typical PEI-216 experiment. Here the critical sloughing distance was 43.3 mm. (c) The temperature measurement during a typical PEI-300 experiment. The critical sloughing distance was measured to be more than 61.8 mm.

3.2. Deconsolidation behavior after leaving the cooling die

Figure 4 (a) shows the microscopic image of PEI-109 which has a lower SCD than PEI-216. The microscopic image is showing a perfectly circular cross-section, with insignificant void content. Figure 6 (b) shows the microscopic image of PEI-216, where the sloughing critical distance is longer than PEI-109. The microscopic image is showing a circular cross-section with small voids appearing as black spots on the top left to the center of the cross-section. Nevertheless, the void content in this sample is insignificant. For PEI-216, the nearly perfect circular cross-section does not seem to be significantly affected by it slightly higher SCD. Figure 4 (c) shows the microscopic image of PEI-300 which has the longest SCD than the other samples. The microscopic image is showing significant irregularities along the outer surface of the cross-section with more voids appearing as black dots. The SCD of PEI-300 seems to significantly affect the roundness of the cross-section. In addition, more black areas are appearing possibly from thermal deconsolidation.

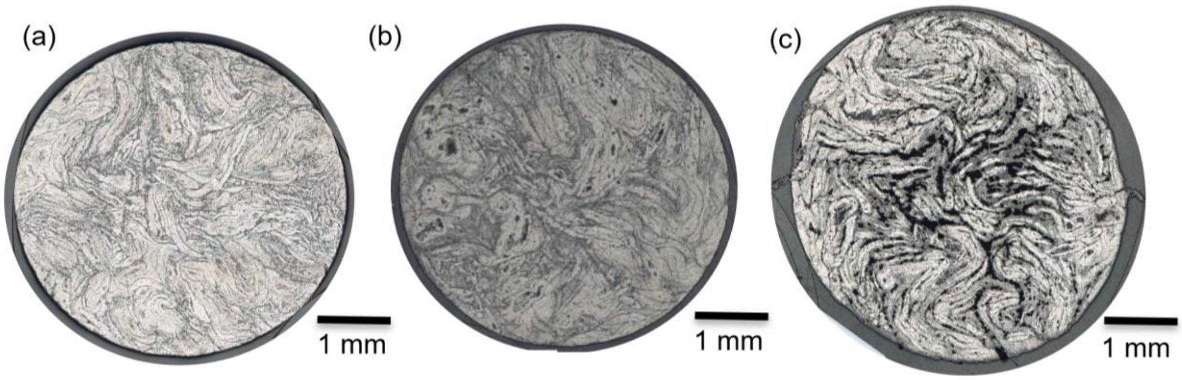

Figure 4 The microscopic images of Carbon/PEI pultruded materials. (a) PEI-109. (b) PEI-216. (c) PEI-300.

3.3. Cooling die temperature's effect on pulling forces

Figure 5 shows the cooling die temperature's effect on pulling forces. The results were presented for the time interval [100 to 400] seconds. PEI-109 experiment had the lowest pulling forces. This is attributed to its lowest SCD being around 23 mm. PEI-216 had significantly higher pulling forces. The longer SCD resulted in a longer metal-polymer adhesion. This has caused the PEI-216 to have higher pulling forces. PEI-300 is showing very similar pulling forces to the PEI-216 at the beginning of the time interval. However, towards the end of the time interval, PEI-300 pulling force is showing an increasing trend. During the PEI-300 experiments, high level of sloughing caused some PEI impregnated carbon fibers to detach from the rod and stick to the cooling die surface. Then, it was observed that carbon fibers started separating from the pultruded material. This incident is typical sloughing. Thus, the increasing trend in the pulling forces was likely caused by this fiber separation (sloughing). Figure 6 shows Image of the cooling die's exit during PEI-300 experiment. The image is showing carbon fibers detaching from the pultruded beam as it leaves the cooling die. PEI is an amorphous polymer. Here, setting cooling temperature above T_g seems to affect the pulling forces significantly as it caused sloughing occurrence.

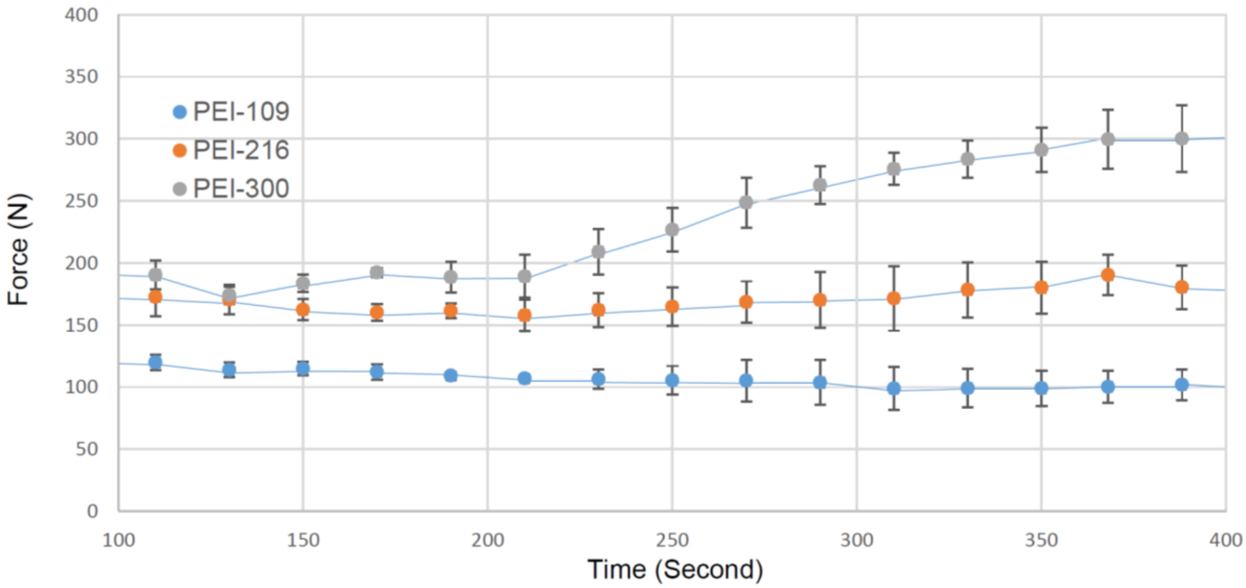

Figure 5 Cooling die temperature's effect on pulling on Carbon/PEI pultruded rods.

Figure 6 Image of the cooling die's exit during PEI-300 experiment. The image is showing dry carbon fibers detaching from the pultruded beam as it leaves the cooling die.

3.4. Surface finish quality

Figure 7 presents the effect of cooling die temperature's on surface finish quality for Carbon/PEI. PEI-109 resulted in rods with RA with $0.72 \pm 0.09\ \boldsymbol{\mu m}$. PEI-216 showed a higher RA of $1.39 \pm 0.11\ \boldsymbol{\mu m}$. PEI-300 is showing the highest RA and highest error bar of $1.99 \pm 0.21\ \boldsymbol{\mu m}$**.**

This high RA value indicates that longer SCD generates rods with lower surface finish quality.

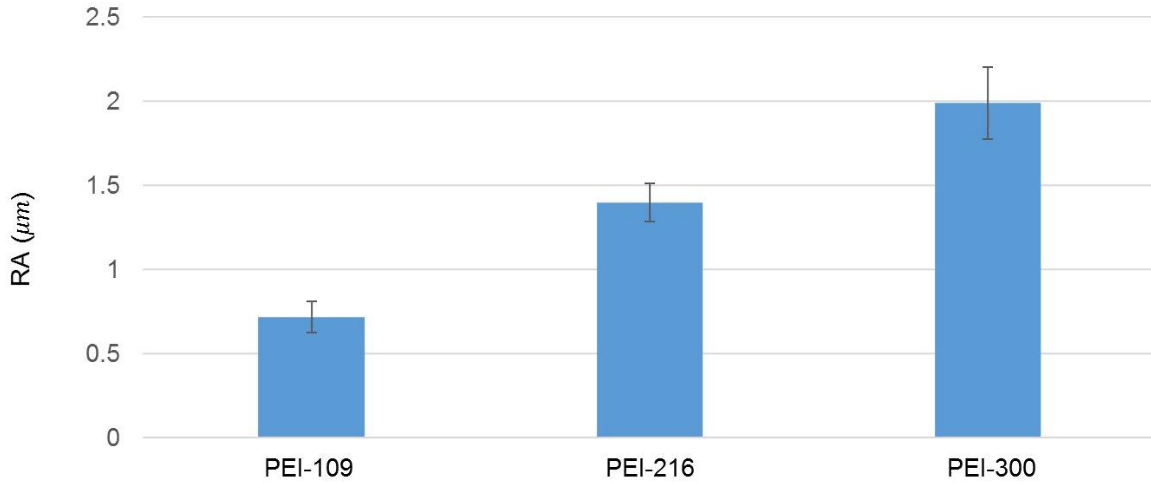

Figure 7 Effect of cooling die temperature's on the RA numbers for Carbon/PEI.

4.0. Summary and Next Steps

The effect of SCD was characterized using surface finish quality, microscopy and pulling forces. This distance varied by changing the cooling die temperature. Microscopic images showed direct correlation between SCD and deconsolidation. Thermal deconsolidation occurred when cooling was set higher than T_g. In addition, a noticeable increase in pulling forces were observed when the cooling temperature was raised above T_g. RA results showed that rods with longer sloughing-critical distance had lower surface finish quality. PEI-109 resulted in rods with RA value of 0.72 $\pm$ 0.09 μm, whereas PEI-300 had the highest RA number. Further work will need to be done to confirm the influence of the SCD on pulling forces and on the pultruded rod's surface finish quality.

Acknowledgements

The authors would like to thank Bombardier Aerospace, Pultrusion Technique, Saudi Arabia's Saline Water Conversion Corporation and Ministry of Education (KSP12014087), NSERC (CRDPJ488387-15) and Prima Quebec (R10-009) for financing this research project. Also, the authors would like to thank Felix Lessard for his help in attaching the wire thermocouples.

Bibliography

[1] K. Chen, M. Jia, S. Hua, and P. Xue, "Optimization of initiator and activator for reactive thermoplastic pultrusion," *Journal of Polymer Research,* vol. 26, p. 40, 2019.

[2] A. Oswald, F. Lapointe, and L. Laberge Lebel, "Multi-die, Vacuum Assisted Pultrusion of Flax/PLA Thermoplastic Biocomposite Rods," in *ECCM17-17th European Conference on Composite Materials*, 2016, pp. 1-8.

[3] N. Alsinani and L. Lebel Laberge, "Effect of length variation of flax/polypropylene pellets produced by multi-die pultrusion on the quality of injection molded product.," presented at the Automotive Composites Conference & Exhibition (ACCE 2018), 2018.

[4] F. Lapointe, A. Oswald, A. Nakai, and L. L. Lebel, "Manufacturing of Carbon/Polyamide Beam by Vacuum Assisted Pultrusion," in *ECCM17-17th European Conference on Composite Materials, Munich*, 2016, pp. 1-9.
[5] M. B. Ghaedsharaf, J-E., Laberge Lebel, L., "THERMOPLASTIC COMPOSITE ROD MANUFACTURING USING BIAXIAL BRAID-TRUSION," presented at the ECCM18 - 18th European Conference on Composite Materials, Athens, Greece., 2018.
[6] F. Lapointe and L. Laberge Lebel, "Fiber damage and impregnation during multi-die vacuum assisted pultrusion of carbon/PEEK hybrid yarns," *Polymer Composites,* 2018.
[7] M. Eichenhofer, J. C. Wong, and P. Ermanni, "Exploiting cyclic softening in continuous lattice fabrication for the additive manufacturing of high performance fibre-reinforced thermoplastic composite materials," *Composites Science and Technology,* vol. 164, pp. 248-259, 2018.
[8] L. Ye, Z.-R. Chen, M. Lu, and M. Hou, "De-consolidation and re-consolidation in CF/PPS thermoplastic matrix composites," *Composites Part A: Applied Science and Manufacturing,* vol. 36, pp. 915-922, 2005.
[9] K.-S. Kim, J.-C. Heo, and K.-W. Kim, "Effects of temperature on the microscale adhesion behavior of thermoplastic polymer film," *Tribology letters,* vol. 38, pp. 97-106, 2010.
[10] G. L. M. Batch, C.W., "Analysis of pressure, pulling force and sloughing in pultrusion," *American Society of Mechanical Engineers, Heat Transfer Division, (Publication) HTD,* vol. 132, pp. 109-112, 1990.
[11] HexTow carbon fiber datasheet. (2015). Available: http://www.hexcel.com/user_area/content_media/raw/AS4_HexTow_DataSheet.pdf
[12] J. S. Yu, M. Lim, and D. M. Kalyon, "Development of density distributions in injection molded amorphous engineering plastics. Part I," *Polymer Engineering & Science,* vol. 31, pp. 145-152, 1991.