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Determination of Thermoplastic Composite Crystallization Process Limits for Dynamic and Isothermal Cooling Processes

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Abstract – **This paper interrogates the relationship between composite laminate consolidation (or thermal forming) cooling process parameters and crystallization kinetics of thermoplastic polymer composite matrix materials. Previously, a trial and error methodology has been utilized to determine the consolidation parameters for the multiple consolidation methods, where each method requires a unique set of parameters. It is proposed that the application of the Avrami Model for crystallization kinetics of semi-crystalline polymers can be applied to determine cooling based process parameters for thermoplastic composite laminate consolidation and thermal forming. To that end, the model was applied and process parameters were proposed for a new PAEK based aerospace structural thermoplastic composite material. Process parameters were proposed for multiple consolidation methods including, continuous compression molding, static press, and shuttle press. Process parameters were also proposed for post-consolidation thermal forming by stamp forming. Based on the time and cost savings associated with the implementation of this methodology, it has been adopted as the standard approach for the determination of cooling based process parameters for all continuous fiber reinforced thermoplastic composite materials used by Boeing.**

Index Terms – Composite, Consolidation, PAEK, Processing, Polymer, Thermoplastic

I. INTRODUCTION

Over the last several years, Boeing has greatly increased its usage of structural thermoplastic composite materials. As the potential design space for thermoplastic composites has grown over time, new materials have been required to be developed to meet the expanding need. Historically, the processing of thermoplastic composite materials was determined by a trial-and-error approach where a process window was generated after multiple iterations[1]. While this process window could be used to create high quality laminates/parts in a stable manner, it may not have been the most optimal cycle possible. For the legacy structural thermoplastic composite material with a poly aryl ether ketone (PAEK) polymer matrix, this iterative approach was used to generate the processing window for three unique processes used for thermoplastic composites: Continuous Compression Molding (CCM)[2], Press Consolidation[3], and Thermal Stamp Forming[4]. However, this iterative approach is both expensive and time consuming. As new materials are developed, a more rapid, cost effective approach to determining the process window is required.

In general, all three of the processing methods mentioned rely on the use of high temperatures and pressures (greater than 350°C and 15 bar) to convert the thermoplastic pre-preg or semi-preg to a consolidated laminate[5]. It is important to note that no chemical reaction is occurring during the processing of these materials, only a compaction and phase change of the polymer. After some time at elevated temperature, the now-consolidated laminates must be cooled. For semi-crystalline polymer materials the cooling step is critical. Cooling controls the percent crystallinity which determines the mechanical performance of the composite. The crystallinity also directly influences any residual stresses in the composite part[6]. To generate crystallinity upon cooling, the three processes utilize both dynamic (non-isothermal) and isothermal cooling. Thus understanding how the two cooling methods impact crystal growth is critical to developing a rapid, low cost methodology to define process conditions for new materials.

One approach to understanding thermoplastic composite crystallization kinetics and processing is to model crystallization behavior at various cooling rates and isothermal hold temperatures[7]. Multiple kinetic models exist, including the Flynn-Waal-Ozawa, Nakamura, and Avrami models[8-11]. The Avrami crystallization kinetic model is the most often selected for polyaryletherketone (PAEK) materials such as polyetheretherketone (PEEK) and PEKK[12-15]. Even with the selection of this model, it was not known if the model could be applied to accurately generate a process window[11]. Specifically, the impact of high pressure on the model's accuracy was not known[11]. But with the potential time and cost savings from the implementation of a correlation model, it was determined that this relationship must be explored.

One of the main factors responsible for the common use of the Avrami Crystallization Kinetics Model is the inclusion of both dynamic and isothermal kinetics models.[16-19] Both models are based on crystallization rates determined by heat flow measurements made using Differential Scanning Calorimetry (DSC). During DSC cooling, the percent crystallinity, α, is measured by monitoring the change in heat flow over time/temperature. When correlated to the time component of the experiment, the following relationship has been established and is the basis for the Avrami crystallization kinetics model[20, 21]:

$$\ln(-\ln(1-\alpha)) = n\ln(t) + \ln(Z) \qquad [1]$$

Where: α = percent crystallinity
t = time
Z = Avrami temperature constant
n = Avrami correction factor

In the case of isothermally cooled processes, Z is directly related to the isothermal hold temperature. For dynamically cooled processes, a correlation factor to correct for cooling rate must be applied:

$$\ln(Z_c) = \frac{\ln(Z)}{|\beta|} \qquad [2]$$

Where: β = cooling rate (°C/time)

The n and Z terms are determined by a plot of $\ln(-\ln(1-\alpha))$ versus $\ln(t)$ where the slope is equal to n and the intercept equal to $\ln(Z)$[13]. These terms are unique for each isothermal hold temperature and cooling ramp rate but the values tend to become more similar at very slow cooling ramp rates of high isothermal temperatures as very slow cooling rates force the slowest crystallization kinetics[22]. To complete the kinetic model, the exponential terms are applied to the crystallization half-time equation shown below in Equation 3[23]. The relationship between half-time and processing for the thermoplastic composites is discussed in this paper.

$$t_{\frac{1}{2}} = \left(\frac{\ln(2)}{Z}\right)^{\frac{1}{n}} \qquad [3]$$

For this work, Differential Scanning Calorimetry was used to generate dynamic and isothermal Avrami crystallization kinetics models for thermoplastic composite consolidation and thermal forming processes. These models were then applied to determine the crystallization half-time and establish robust process windows for all three for a new structural thermoplastic composite material. This model and approach will ultimately reduce the cost and time frame for development and implementation of consolidation/forming processes for new thermoplastic composite materials.

II. Experimental

A. Materials

Unidirectional carbon fiber reinforced thermoplastic composite pre-preg was used as received. The pre-preg material was manufactured to and is in compliance with industry standard requirements. Specifically, the pre-preg utilizes a PAEK polymer matrix with an intermediate modulus carbon fiber. The pre-preg has industry standard resin contents and fiber areal weights for structural aerospace prepreg materials.

B. Dynamic Cooling Differential Scanning Calorimetry

Dynamically cooled differential scanning calorimetry experiments were conducted on thermoplastic unidirectional pre-preg materials to determine crystallization kinetics at various cooling rates. Experiments were completed on a Perkin Elmer DSC 8500 with Helium purge gas. The instrument was calibrated to measure heat flow up to a cooling rate of 750°C/min using Indium and Sapphire standards. (Temperature calibration was completed by the manufacturer.)

For all dynamic experiments, the thermoplastic composite pre-preg samples of approximately 8-15 mg in size were placed in a crimped aluminum sample pan. The sample was heated to 410°C at 10°C/min in the DSC to achieve complete melt. Samples were then cooled at a variable rate to 140°C using the cooled Helium purge gas. The cooling rates targeted were: 5, 10, 20, 30, 40, 50, 60, 80, 100, 150, 250, 350, and 500°C/min. After cooling to 140°C, the samples were heated back to 400°C at 10°C/min to ensure that no cold crystallization was present. (Cold crystallization is defined as any crystallization event that occurs during the heating of the material below the melt temperature.) Transitions were identified and integrated using the standard Perkin Elmer analysis software and Origin 9.0.

C. Isothermal Cooling Differential Scanning Calorimetry

Isothermally cooled differential scanning calorimetry experiments were conducted on the same instrumentation as described for the dynamic cooling experiments. Also as previously described, 8-15 mg samples of thermoplastic composite pre-preg material were placed in a crimped aluminum sample pan. The samples were heated to 410°C at

10°C/min in the DSC to achieve complete melt. Samples were then cooled at 650°C/min to the isothermal hold temperature and held for one hour. After the hold, the samples were cooled to room temperature and then heated to 400°C at 10°C/min to ensure that no cold crystallization was present. Due to the small mass of the samples and instrumental setup, minimal thermal lag was observed between the set point temperature and the sample temperature as measured by the instrumentation, with a maximum differential of 6.95°C between the sample and set point (at a set point of 140°C). Isothermal hold temperatures targeted were: 150, 175, 200, 225, 250, 270, 280, 290, 300, and 325°C. Transitions were then identified and integrated using the standard Perkin Elmer analysis software and Origin 9.0.

III. RESULTS AND DISCUSSION

A. Dynamic Cooling Crystallization Kinetics

Dynamic cooling during thermoplastic composite laminate consolidation is a common process utilized in autoclave consolidation, Continuous Compression Molding and static press consolidation. As such, it is critical to generate a methodology for process parameter development that is applicable to multiple consolidation methods. This approach will prevent excessive trial and error experiments. To that end, we present the application of the Avrami dynamic (non-isothermal) crystallization kinetics model to thermoplastic composite materials and its application to each processing method.

In all three dynamically cooled consolidation methods mentioned above, the cooling rates vary significantly, from less than 1°C/min to in excess of 120°C/min. Because of the wide range of cooling rates that are utilized, a unique experimental methodology was applied to the rate determination study. Specifically, the DSC used for this work is Helium cooled and can achieve cooling rates of up to 650°C/min. It was also critical that we used this method because of the extremely rapid crystallization rate of this specific grade of PAEK. Typical processing conditions can go as fast as 150°C/min in production, but in the future it may be possible that machines can exceed this cooling rate. To that end, it was determined that testing should occur as fast as could be achieved under experimental conditions to ensure optimization to current and future processes.

From the DSC experiments completed, the crystallization onset, crystallization peak, and crystallization end-point temperatures for all cooling rates from 5 to 500°C/min were determined. An overlay plot of the DSC traces is shown in Figure 1, and a plot of crystallization onset, peak, and end-point temperatures is shown in Figure 2. While not specifically stated in the DSC overlay trace plot, there is one significant piece of additional information beyond the temperatures themselves. Upon the reheating of the samples, no cold crystallization of the polymer was observed indicating full crystallinity was achieved (approximately 30%) for all cases. Additionally, the heat of crystallization for the DSC

experiments was on average 15.83 J/g (± 2.86 J/g) for the dynamic cooling across all cooling rates.
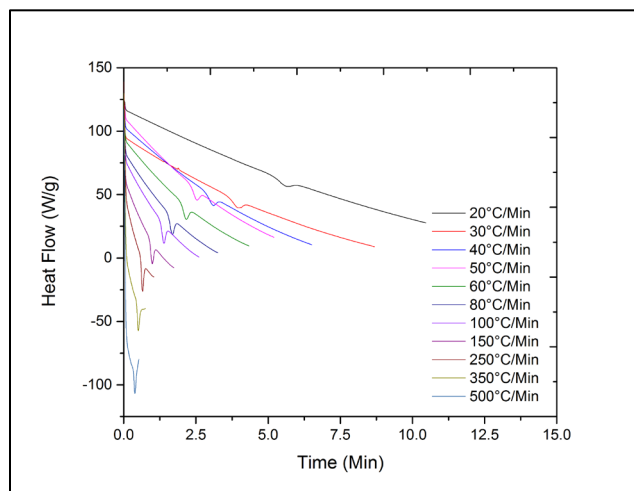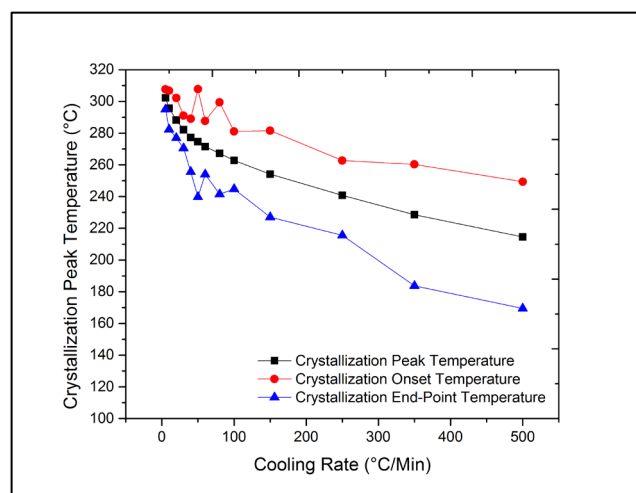

Figure 1. DSC Dynamic Cooling Trace Overlay

Figure 2. Dynamic Crystallization Onset, Peak, and Endpoint Temperatures

From the crystallization peak curves, a plot of percent crystallinity (α) versus temperature or time can be generated (via integration of the crystallization peak and normalization to 100%). The Avrami equation (Equation 1) was applied to the percent crystallinity data. The Avrami kinetic factors for n and Zc for the half-time equation were then calculated from the slope and intercept of a plot of $\ln(t)$ versus $\ln(-\ln(1-\alpha))$, respectively. Avrami kinetic plots are shown in Figure 3. Table 1 shows the calculated values for n and Zc for each ramp rate that were used for the subsequent half-time calculations.
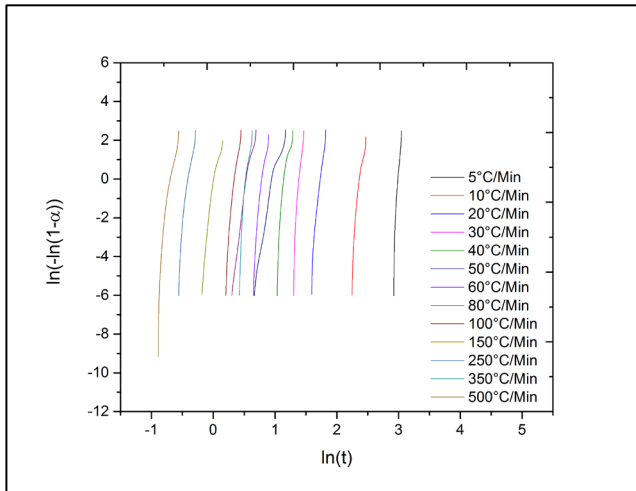
Figure 3. Avrami Dynamic Plot Overlay

Table 1. Avrami Dynamic Cooling Kinetic Factors

Cooling Ramp Rate (°C/min)	n	$\ln(Z_c)$
5	50.545	-151.380
10	28.388	-67.616
20	29.062	-50.496
30	39.120	-54.612
40	24.563	-28.682
50	15.583	-15.431
60	27.865	-22.325
80	21.487	-11.917
100	29.032	-10.255
150	21.053	-0.677
250	24.642	9.734
350	17.294	10.709
500	17.419	15.576

Using the calculated Avrami kinetic parameters for each ramp rate, a crystallization half-time was calculated using Equation 3, where the half-time represents the time required to achieve 50% of the total crystalline content. Half-times for each ramp rate are shown in Figure 4. We observed a slightly different trend than expected for the half-time data. Data generated on other polymer systems typically show a parabolic correlation with cooling ramp rate, not a logarithmic trend as we observed[15]. At very high temperatures this means that crystallization takes a significant amount of time, due to the large amount of thermal energy in the polymer (thermodynamic limited process). At very low temperatures, the polymers typically take longer to crystallize because polymer chain mobility is limited and it takes longer for polymer chains to orient in such a way that they crystallize (kinetic limited process). We attribute the logarithmic behavior of the PAEK polymer to its ability to rapidly crystallize even at cooling rates as fast as 500°C/min. Other semi-crystalline polymers normally will exhibit cold crystallization at such fast cooling rates, where PEEK did not, causing an increase in the crystallization half-time[19].
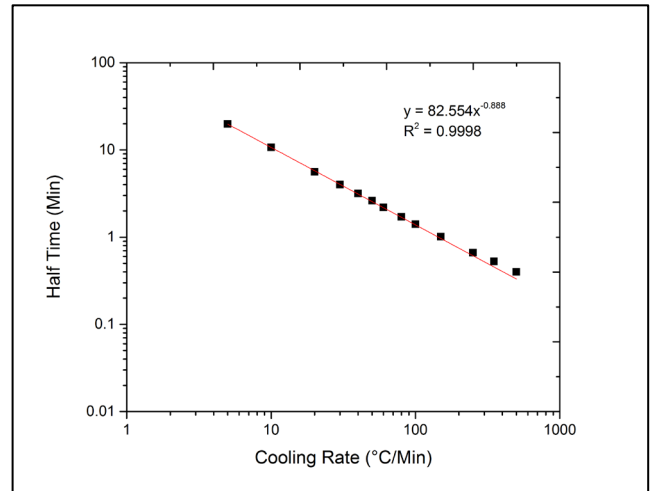

Figure 4. Dynamic Cooling Crystallization Half-Time

The difference between the parabolic and logarithmic trend, is quite advantageous as the kinetics analysis and lack of cold crystallization upon re-heating suggest that at any cooling rate, the PAEK polymer will crystallize completely. However, this does raise a complication, unlike thermoplastic composites based on polyphenylene sulfide (PPS) or PEKK, this PAEK based composite is not cooling rate limited under dynamic conditions[25]. That is to say, either polymer crystallite melting or time for polymer interlaminar diffusion is now the rate limiting step in composite laminate consolidation. By polymer diffusion time becoming the rate limiting step, the process and tool design methodologies used previous for legacy thermoplastic composite materials must be modified to fully realize the potential of the PAEK material. This can be achieved by machine and tooling re-designs where the tool is either hotter and/or longer to account for the differences in matrix interlaminar diffusion where for the legacy materials, a majority of the tool length was designed for more controlled cooling of the matrix which is no longer necessary (Autoclave consolidation is already well understood to be machine limited due to its inability to heat or cool quickly).

So, while PAEK based composites are compatible with PPS/PEKK manufacturing setups, at the current time we will be equipment limited for PAEK composites. Essentially, this means that current possible manufacturing conditions cannot fully utilize the crystallization rate of the material and as consolidation technology develops and improves, the specific grade of PAEK utilized in this composite could make use of these developments where other polymers could not.

B. Isothermal Cooling Crystallization Kinetics

The other method of cooling a consolidated thermoplastic composite laminate is by isothermally holding the tool at a sufficiently low temperature to cause crystallization. This is most commonly done after the laminate is consolidated, during stamp forming to impart some sort of curvature/shape to the laminate. Isothermal crystallization can also be used in a shuttle press consolidation methodology. Also, because the machine setup is simpler, it is often the case that the machines

used have the potential for a much wider array of process conditions than for those that utilize dynamic cooling. Therefore it becomes even more important that a non-trial-and-error methodology is developed for establishing the process window, even in general terms.

In all of the isothermally cooled experiments, the pre-preg samples were heated to 400°C and then cooled as rapidly as possible to the isothermal hold temperatures discussed in the previous section. (The effective rate was around 650°C/min in the DSC utilized in these experiments.) Similar to the dynamically cooled process, the crystallization onset, crystallization peak, and crystallization end-point temperatures were determined from the DSC trace plots. The trace plots can be found in Figure 5 and the peak temperature plots in Figure 6.
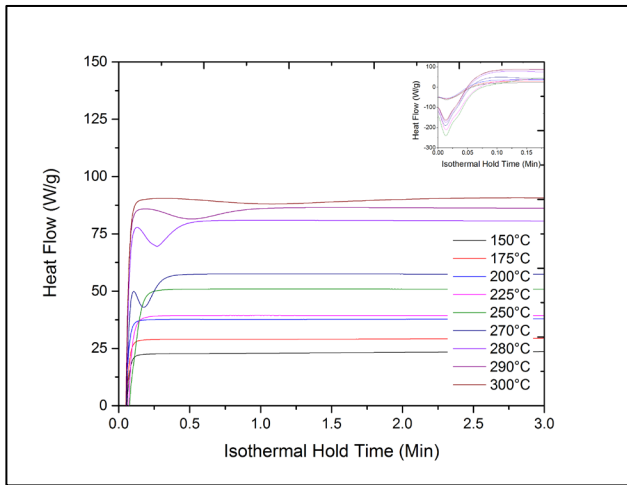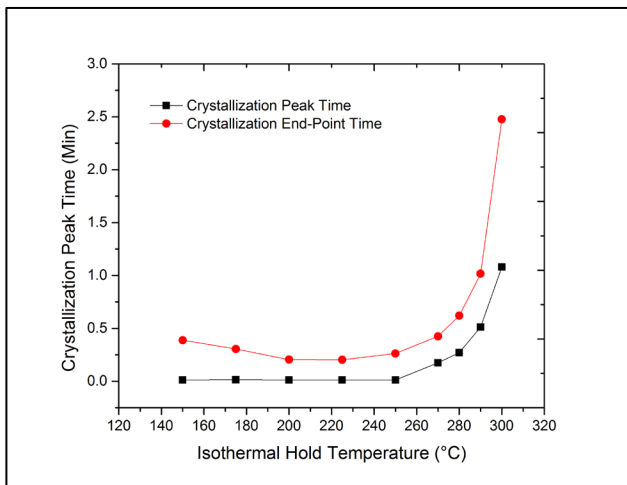

Figure 5. Isothermal Hold Trace Overlay

Figure 6. Isothermal Crystallization Peak and End Times

Also, as with the dynamically cooled experiments, no cold crystallization was observed upon reheating of the sample. The heats of crystallization were all around the anticipated 16 J/g.

The percent crystallinity was calculated as a function of time from the crystallization curves at the various isothermal

hold temperatures and normalized to 100% crystallinity. The Avrami equation was then used to calculate the Avrami kinetic factors from the data for the isothermal cooling approach. Those factors are shown in Table 2 and the Avrami plot is shown in Figure 7.

Table 2. Avrami Isothermal Cooling Kinetic Factors

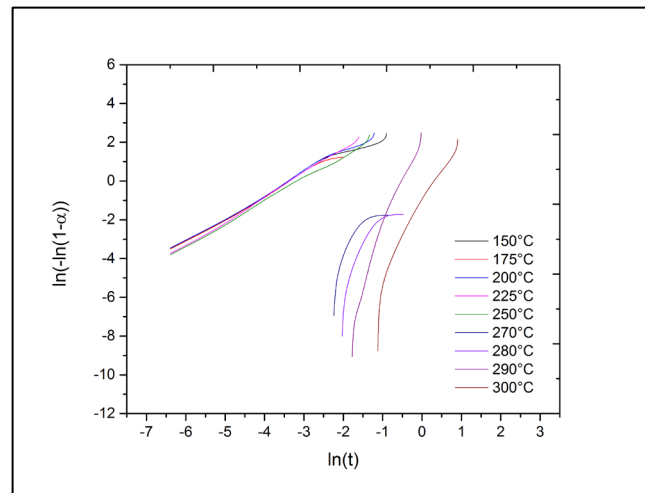| Isothermal Temperature (°C)	n	$\ln(Z)$
150	0.926	3.149
175	1.136	3.769
200	1.073	3.645
225	3.749	-1.711
250	2.170	-0.0771
270	2.649	-1.290
280	1.902	-0.924
290	1.765	-3.379
300	2.079	-3.621

Figure 7. Avrami Isothermal Plot Overlay

Finally, the crystallization half-time was then calculated for each of the isothermal hold temperatures. A plot of the crystallization half-time versus the isothermal hold temperature is shown in Figure 8. The data were more similar to traditionally studied materials than to the results from dynamic cooling for this material. However, it is still rather unique in that at the very low isothermal hold temperatures near the glass transition temperature, the polymer still achieved complete crystallization very rapidly.

This behavior of the polymer is beneficial as it will potentially allow for tooling concepts that utilize materials (such as silicone tooling) that can only survive at lower temperatures and still fabricate parts at a high rate. Expectations must be tempered somewhat because the lower processing temperatures could impact other features such as surface quality and residual stresses. Demonstration parts must be fabricated to verify that the material processed at lower temperatures will meet the other quality criteria.
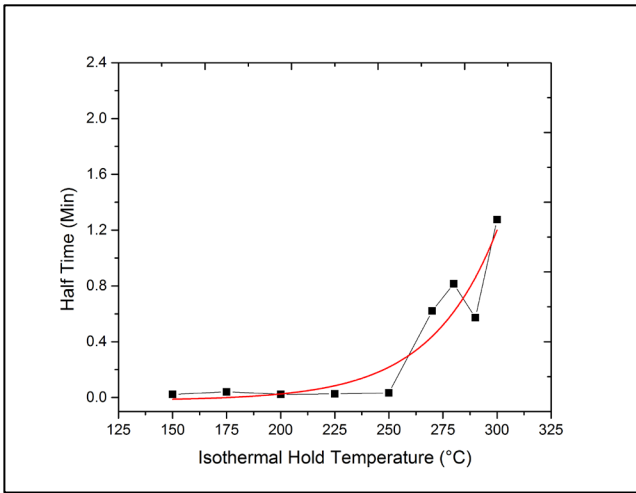
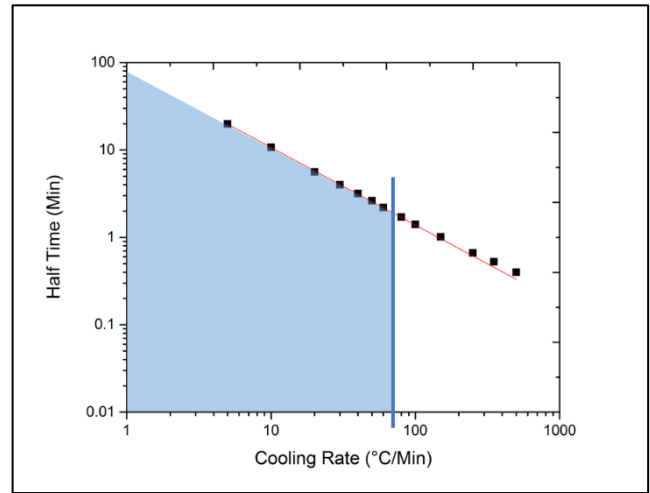Figure 8. Isothermal Cooling Crystallization Half-Time

Figure 9. Dynamic Cooling Process Window

C. Relationship to Process Limits

Based on the crystallization kinetics analysis, process recommendations for both dynamically cooled and isothermally cooled processes can be made. For the dynamically cooled process, a plot of half-time versus cooling rate can be found in Figure 9 (blue area indicates the selected process window). In this case, the plot looks very different than what would normally be expected. Normally, the plot is parabolic in nature as the crystallization requires a long time when cooled very slow (thermodynamically limited) or when cooling very fast (kinetic limited crystallization growth). However, for PAEK polymer crystallizes so rapidly that a linear relationship is observed. This leads to the conclusion that regardless of cooling rate, the PAEK candidate material will always crystallize fully. Thus, from a cooling/crystallization perspective the laminate can be cooled as quickly as is practical for production or for avoidance of residual stresses. (While there is no achievable cooling rate that can cause incomplete crystallization, there may be cooling rates or other machine parameters that cause the laminate to shrink too rapidly such that uniform pressure is not applied across the laminate causing warping or other residual stress effects.)

Figure 9 highlights the rate limiting issues already addressed for the new material. There is no material reason as to why the process window only needs to be below 65°C/min, it is simply that the current dynamically cooled tooling and machinery cannot reliability operate faster than this rate.

For the isothermally cooled processes such as stamp forming or shuttle press consolidation, the half-time curve is more similar to the standard parabolic behavior, but still fairly unique. The plot can be found in Figure 10. In this case, and as expected, crystallization requires longer times as the thermodynamic melt temperature of the polymer is approached (thermodynamic limited). Long crystallization times are also expected for the lowest temperatures, as crystallization becomes kinetically limited by chain mobility. For this PAEK polymer, the expected behavior at low temperatures did not occur. Instead crystallization occurred extremely rapidly at lower temperatures and was complete at every observed hold temperature. (Temperatures lower than 150°C were not tested as they would encroach on the glass transition temperature of the polymer matrix.)
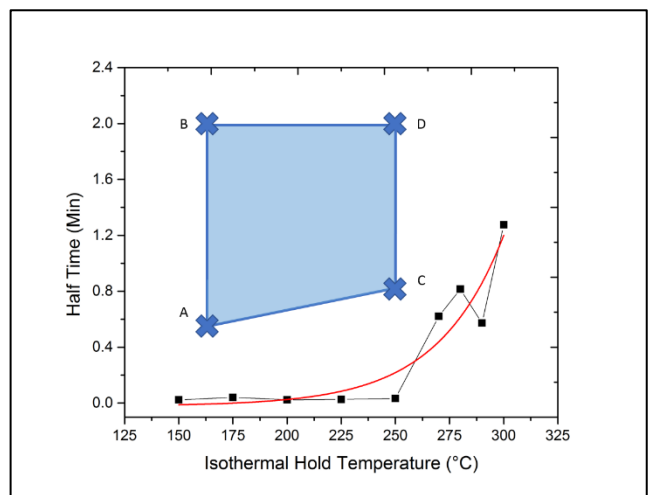

Figure 10. Isothermal Cooling Process Window

From the half-time plot, the recommended process window for tooling isothermal hold temperatures and times has been generated and has been included as a blue overlay on the plot. The specific data points used for the various corners of the window are shown in Table 3. In all cases the minimum process time meets or exceeds twenty half-times meaning that after the process time the laminate has achieved maximum

possible crystallinity. Unlike, the dynamically cooled processes which are tooling limited, that does not apply for the isothermally cooled processes. In this case, there is both an upper and lower thermal limit for the process conditions. The lower limit is determined by the glass transition temperature of the PAEK polymer, the upper limit by the melt temperature. In the middle, are the time constraints required to ensure a margin of safety and eliminate the possibility of a laminate that does not show complete crystallization after processing.

Table 3. Isothermal Process Limits

Condition Designation	Isothermal Temperature (°C)	Half Time (sec)	Process Time (sec)	No. Half Times
A	165	1.5	30	20
B			120	80
C	245	1.8	45	25
D			120	66

IV. CONCLUSIONS

Thermal-based process window limitations were recommended for both dynamically and isothermally cooled processes. These process windows are based solely on the melt and crystallization kinetics of the polymer and must be validated mechanically. However, this methodology eliminates entirely the guess and check methods that were previously. Under the guess and check system, parts would had to be fabricated at multiple tool temperatures and evaluated thermally and mechanically until the process window was determined. By the implementation of this methodology (Avrami kinetic modeling) we can determine the extremes of the process and then optimize, reducing cost and implementation time for all semi-crystalline thermoplastic composite materials. Furthermore, this work demonstrates that for full implementation of this specific PEAK, changes to the tooling concepts of the various consolidation processes is required to more efficiently manage the heat transfer to and from the composite material. Lastly, the methodology developed in this work has been used to provide processing parameters via Continuous Compression Molding, Press Consolidation, and Thermal Stamp Forming.

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