

Investigation of the Effect of Cooling Rates on the Mechanical Behavior of Thermoformed Continuous Fiber Reinforced Semi-Crystalline Thermoplastic Composites

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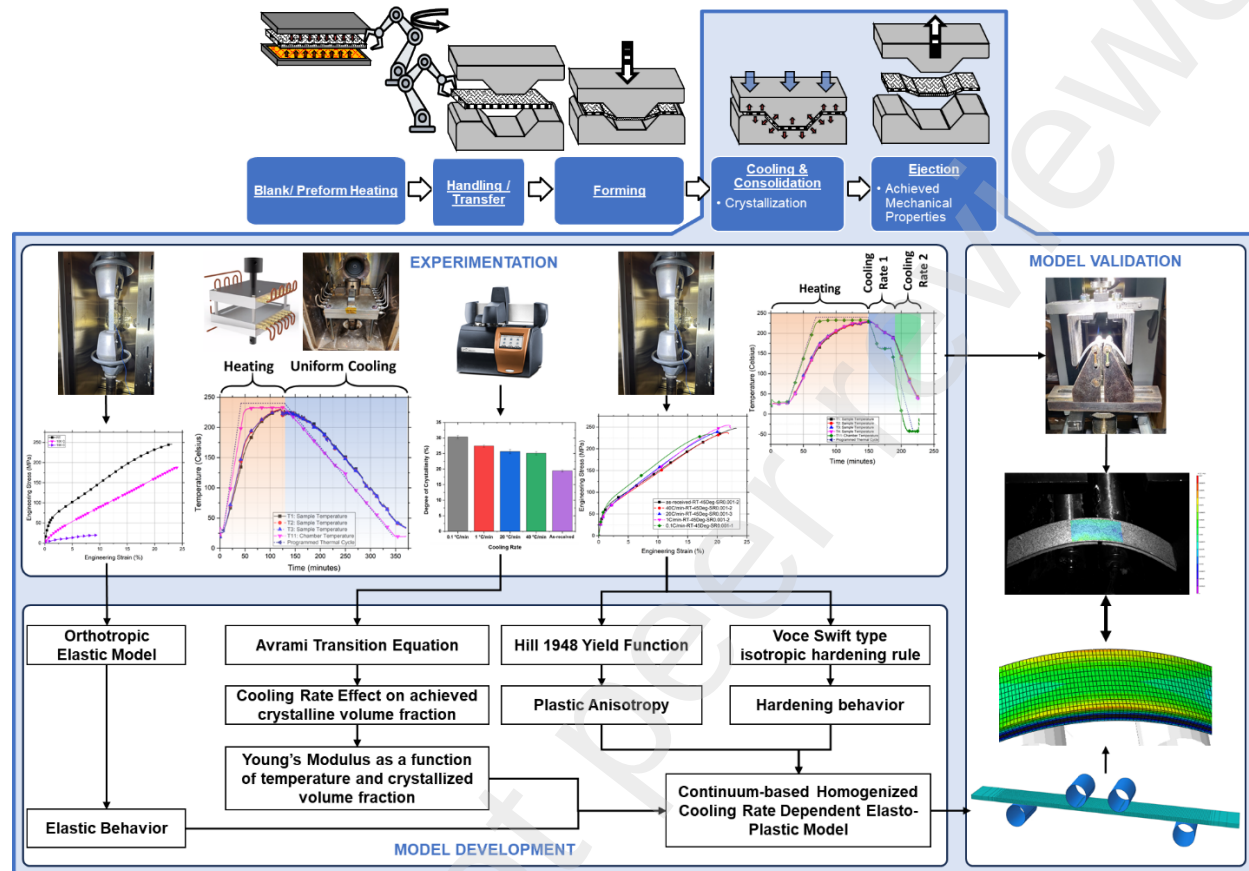
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Abstract

Thermoforming subjects the semi-crystalline thermoplastic composite to varying cooling rates, resulting in variations in microstructure and mechanical properties, subsequently influencing mechanical performance. Modeling this relationship can help develop predictive capabilities that help optimize thermoforming process parameters to maximize part performance. This study investigates the relationship between cooling rates and the degree of crystallinity achieved for 2x2 twill weave bidirectional continuous carbon fiber reinforced polyamide 6. The composite panels were re-consolidated in a flat tool capable of implementing a broad range of cooling rates. Differential scanning calorimetry samples prepared from these panels were evaluated to quantify the cooling rate dependent achieved degree of crystallinity. Coupons were prepared from the flat panels and tested under uniaxial tensile loading to establish the correlation between the degree of crystallinity and mechanical properties. With decrease in cooling rate from 40 °C/min to 0.1 °C/min, an increase in degree of crystallinity (+ 21 %), Young's modulus (+ 40 %) and yield strength (+12 %) was observed for the +45°/-45° orientation coupons. This relationship was analytically modeled as a function of temperature and cooling rate. An orthotropic linear elastic material model was coupled with an anisotropic yield function to account for anisotropy resulting from the orientation of the reinforcement fibers within the thermoformed part. The homogenization-based constitutive modeling approach, which incorporates the effect of cooling rates, provides a computationally efficient and accurate prediction of mechanical behavior. The model was validated via four-point bending tests, to emulate a complex loading condition, on coupons subject to non-constant cooling rates.

Keywords: Semi-crystalline thermoplastic composites, thermoforming, process-structure-property relationships, continuum modeling, elasto-plastic properties, plastic anisotropy, CAE chain

Graphical Abstract



Highlights

- Cooling rates demonstrated to affect crystallinity in semi-crystalline thermoplastics.
- Avrami transition used to model cooling rate dependent degree of crystallinity.
- The degree of crystallinity influences the mechanical behavior of the thermoplastic composite including elastic modulus, yield stress, and hardening.
- A homogenized constitutive model demonstrated to efficiently capture the influence of cooling rate on crystallinity evolution and subsequent anisotropic elasto-plastic behavior in four-point bending tests.
- Cooling rate effects pronounced for loads in directions transverse to continuous fiber orientation where the behavior of semi-crystalline polymer matrix dominates.

1. Introduction

There has been an increasing interest in thermoforming of continuous fiber-reinforced thermoplastic (CoFRTP) composites to make structural components for automotive[1,2], aerospace[3,4], and marine applications[5,6]. Unlike thermosets, thermoplastic composites offer added potential for repair, recycling[7], and remolding[8]. Thermoforming of CoFRTP composites is suitable to sustainably manufacture lightweight, high-performance components for aerospace[9], automotive[10,11], wind energy[12], and hydrogen storage[13]. Semi-crystalline thermoplastics exhibit improved stiffness, strength and good toughness due to strong intermolecular forces, as well as better chemical resistance due to the presence of ordered crystalline structures[14].

Thermoplastics have traditionally been extensively used for non-structural and semi-structural components for electronics, automotive [[15,16] and marine [17] applications. However, in many of these applications we find little use of fiber reinforcements, with random chopped fiber reinforcements being the most widely used in injection molded or compression molded thermoplastic parts [4]. Today, however, there is noticeable interest in adopting continuous fiber reinforcements to facilitate the proliferation of fiber reinforced composites for structural applications [18,19]. Thus, thermoforming has taken center-stage, as it is one of the few feasible fast-cycle thermoplastic manufacturing processes compatible with continuous fiber reinforcements[20]. It also presents the possibility of retaining and using existing steel stamping infrastructure for mass production [21,22]. Several investigations and demonstrations have been conducted over the past few years, showcasing the ability to produce cost-effective structural automotive parts from thermoformed CoFRTP composites [2,23]. These parts are reprocessable [24], repairable, and recyclable [25,26] in comparison to conventional thermoset composite structures, making thermoformed CoFRTP composite parts suitable to meet sustainability requirements [27–29].

The thermoforming process, most commonly used for CoFRTP blanks, can be broken down into five discrete process steps. First, the blank is mounted on a frame or shuttle and transferred to a heater, typically utilizing high-power infrared [30,31], to rapidly heat the blank above the melt temperature of the thermoplastic matrix. This makes the blank pliable, but also results in deconsolidation and the formation of voids [32]. At this point, the heated blank is transferred rapidly to a mold to prevent heat loss. A male and female mold, maintained at a controlled temperature, closes around the heated pliable blank, draping the continuous fiber tows over the geometrical contours of the mold. At the same time, the fiber weave and molten matrix undergo compaction and transverse flow [20–25], redistributing the matrix and distorting the fibers at the tow level, thereby creating localized deviations in fiber orientation and gradients in the fiber volume fraction. This forming step is followed by consolidation and cooling [33] where the pressure over the formed blank is maintained and the formed part is cooled to near-room temperature. Viscous flow of the molten thermoplastic matrix continues at this stage, along with distortion of fiber tows, followed by a phase change of the matrix from a molten state to a solid state [34], resulting in the evolution of residual stresses [35]. For semi-crystalline thermoplastic composites, crystallization also occurs based on the cooling dynamics [36–38]. Cooling is performed within the mold itself to near-room temperatures, ensuring the thermoformed part does not warp or distort excessively. After cooling, the part is ejected from the mold, where any interface stresses between the part and mold surface are released, resulting in spring-in or warpage [39]. The process and the complex interactions occurring at each step are illustrated in Figure 1.

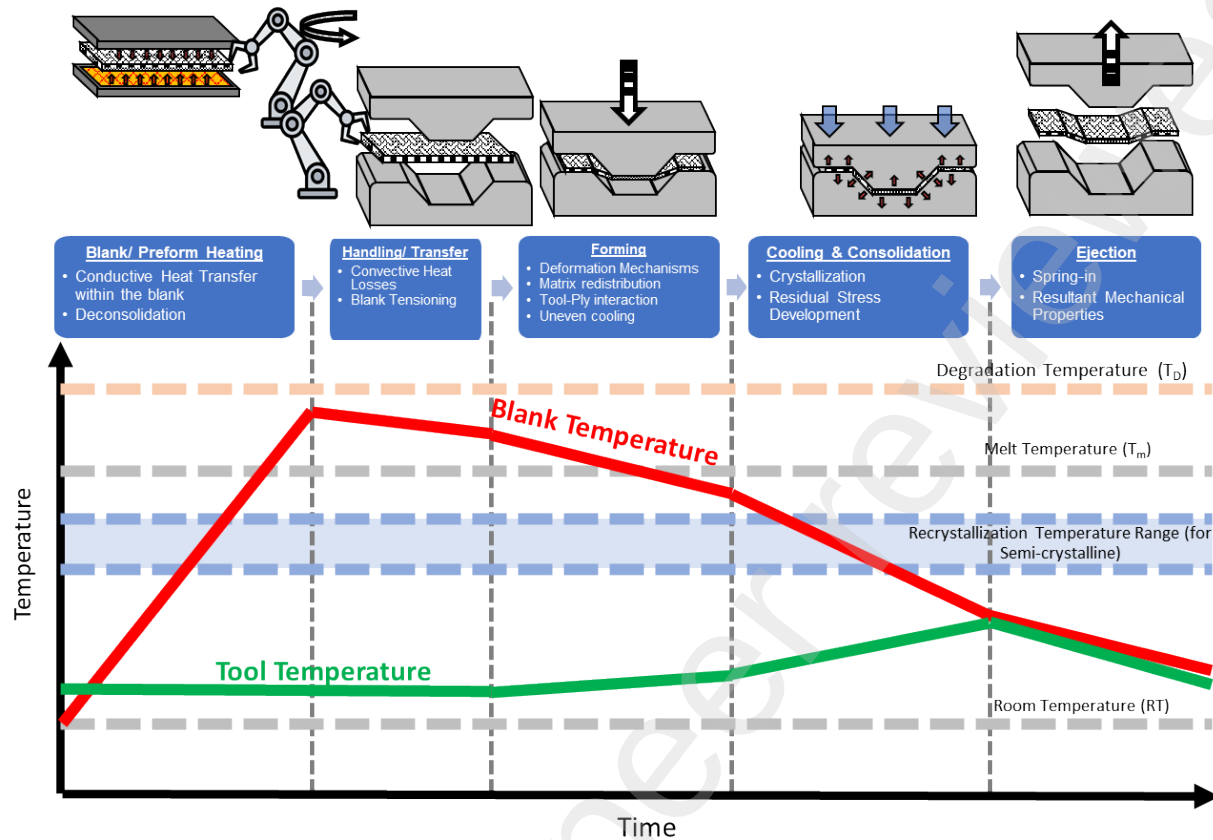


Figure 1. Thermoforming of semi-crystalline thermoplastic composites.

For semi-crystalline thermoplastic composites, the spring-in and resulting properties are significantly influenced by the interactions between process parameters and intrinsic material behavioral tendencies. Chief among them is the impact of cooling rates on the evolution of crystallinity and, subsequently, on residual stresses and mechanical properties. They influence the mechanical performance of the thermoformed component, with variation in process parameters resulting in varied behavior, despite having consistent material composition.

Lee et al. [40] experimentally investigated the effect of varying cooling rates of 1 °C/min, 10 °C/min, and 20 °C/min on the crystallinity and corresponding tensile strength, Mode 1 fracture toughness, Mode 2 fracture toughness, mixed mode bending, and interlaminar shear strength for glass fiber–polypropylene (GF-PP). It was observed that with increasing cooling rates, the largest spherulite crystal size decreased, the β -crystal phase (the hexagonal crystal form) of PP increased, and the α -crystal phase (the monoclinic crystal form) decreased, which are key factors influencing the properties of the PP matrix. Furthermore, with increasing cooling rates, it was observed that both mode 1 and mode 2 fracture toughness improved, and the strain energy released in mixed modes increased. This was attributed to smaller spherulite size, resulting in improved adhesion within the PP matrix. Zhang et al. [41] observed a similar effect of faster cooling rates being associated with lower crystallinity and smaller crystals for carbon fiber–poly aryl ether ketone (CF-PAEK), a high-performance semi-crystalline thermoplastic, thereby improving interfacial shear strength by ~15 %, enhancing matrix ductility and reducing impact damage area by ~75 %, increasing indentation depth by 25 % and marginally increasing absorbed energy.

Um et al. [42] investigated the effect of cooling rates, comparing 100 °C/min and 0.2 °C/min, on the mechanical behavior of carbon fiber-polyethylene terephthalate (CF-PET). The slower cooling rate resulted in the degree of crystallinity (χ_c) increasing from ~ 10 % to ~ 50 %, resulting in 11.6 times improvement in in-plane shear strength, a 3.78 times improvement in shear modulus as compared to a predominantly amorphous equivalent material. Oshima et al. [43] investigated the effect of varying cooling rates, between 1 °C/min, 5 °C/min, and 10 °C/min, on polyphenylene sulfide (PPS) and CF-PPS. Presence of CF led to an increase in the relative χ_c from ~27 % to ~32 % for the slow cooling rate of 1 °C/min, and from ~26 % to 29% for 5 °C/min, but the same trend was not evident for the fast-cooling rate of 10 °C/min. Comparing between 1°C/min and 5 °C/min cooling rate, ~3 % increase in degree of crystallinity was observed for pure PPS polymer, while an increase of more than 10 % was observed for CF-PPS.

Several prior studies have experimentally studied the effect of cooling rate on the crystallinity and mechanical properties of semi-crystalline polymer composites, and developed analytical models accounting for time and temperature effects of crystallization [44–50]. Yang et al. [44] and Sun et al. [50] applied modified Avrami and Ozawa–Avrami equations to glass fiber-reinforced PEEK composites to quantify the influence of cooling rate on non-isothermal crystallization kinetics. Dai et al. [45] also employed the modified Avrami-type equation to correlate cooling rates with non-isothermal crystallization and to analyze the mechanical properties of carbon fiber-reinforced polyether ether ketone (CF/PEEK) composites. Shen et al. [46] developed a computational model to predict the degree of crystallization and residual stress evolution in the selective laser sintering process, incorporating temperature- and time-dependent constitutive behavior of polymers. Pourali et al. [48] used crystallization rate equations to model phase transformation in polyamides, demonstrating that the Avrami equation effectively predicts crystallization kinetics under different cooling rates. Similarly, Kulkarni et al. [49] incorporated crystallization kinetics into their thermoforming simulations, revealing that slower cooling follows a diffusion-controlled crystallization mechanism, leading to higher degree of crystallinity and increased stiffness.

The effect of cooling rates on crystallization, coupled with thermal expansion or contraction of the constituents of the composite, influences the residual stresses induced within the thermoformed component. This influences the spring-in and warpage of the component as well as its mechanical behavior under complex loading conditions. Samy et al. [51] conducted finite element analysis to numerically investigate the impact of process conditions on residual stress and warpage of 3D printed semi-crystalline polymers, demonstrating increased residual stress due to non-uniform crystallization. Jeronimidis et al. [52] investigated the evolution of residual stresses as a function of varying the cooling rate by comparing experimental results from uniaxial tensile and 4-point bending tests against analytical calculations based on classical laminate theory, which took into account the elastic properties and coefficients of thermal expansion (CTE) of an individual lamina. Good agreement was observed with various shapes and residual stress measurement methods, and the analytical prediction based on classical laminate theory and accounting for temperature dependence of CTE and elastic properties. The paper also emphasized the need to incorporate stress relaxation effects, especially at the onset of cooling up to the glass transition temperature (T_g), to avoid overestimating residual stresses. Following initial work by Chapman et al. [53] focused on macroscopic modeling of in-plane residual stresses for CF-PEEK unidirectional laminates using a transient finite difference heat transfer analysis coupled to crystallization kinetics, several other studies have been undertaken to predict residual stresses at micro-scale [47] as well as macro-scale [54] in various fiber reinforced semi-crystalline thermoplastic composites.

In addition to residual stresses, fiber reorientation and defects also influence the mechanical behavior of the thermoformed component. Aridhi et al. [55] presented an analytical modeling approach to capture fiber reorientation during the forming step, based on a rate constitutive equation applied to a simple orthotropic elastic model used for the subsequent prediction of structural performance. The effort, however, is limited to investigating fiber reorientation and does not account for various other interactions for the thermoplastic matrix, like the effect of cooling rate on the evolution of mechanical properties. Similar investigations were conducted to investigate draping behavior, specifically in-plane shear or intra-ply shear, for CF-PA6 cross-ply laminates by Zomer et al. [56], with a focus on capturing the effect of temperature and strain rates.

Limaye et al. [57] investigated the relationship between thermoforming process parameters such as draping, shear of fiber weave and cooling rate on the defects and residual stresses that influence mechanical performance and warpage through a comprehensive end-to-end analysis and experimental validation. Investigation was undertaken at the coupon level to building material data cards, followed by thermoforming simulation and experimental thermoforming trials for a 2.5-dimension component with controlled cooling rates. Macroscopic residual stress predictions arising from anisotropy at the individual ply level, leading to shrinkage [53,58], were determined through a cooling simulation. Residual stresses, fiber reorientation arising out of draping of the 2x2 twill weave of continuous fiber plies, and thickness variation were mapped onto a 3D FE model using a combination of an inbuilt “Result Mapper” tool in Hyperworks and a custom MATLAB script. Subsequently, a coupled analysis of a quasi-static 3-point bend test and dynamic impact test was performed and validated through comparison with experimental test results. In this case as well, the effects of crystallinity at the micro-scale on the fiber matrix interface, and at the macro-scale on the temperature-dependent elastic properties were not addressed. This is critical, especially to develop a better understanding of the thermoforming of semi-crystalline thermoplastic composites, and subsequently enable optimization of process parameters to tune the resulting mechanical properties for the manufactured component.

This study aims to build on existing understanding of the behavior of semi-crystalline thermoplastic composites by capturing the effect of non-constant cooling rates on crystallization and subsequent evolution of elastic modulus and mechanical properties. The analytical model incorporates plastic anisotropy and hardening effects with a continuum-based orthotropic elastic model to predict elasto-plastic response. This enables prediction of not only elastic behavior but also behavior at yield. This is a new and novel contribution to the field, to the best of the authors’ knowledge. By experimentally quantifying the effect of cooling rates on χ_c within the CoFRTP composites, and linking to variation in temperature-dependent elastic properties and CTEs used to predict residual stresses, it is possible to model the mechanical response under complex loading conditions more accurately. Thus, an analytical link is established between cooling rates, crystallization, mechanical property evolution, and prediction of mechanical response.

This study is organized as follows: section 2 provides the approach formulated to utilize minimal experimentation to develop and validate the analytical model developed to predict elastic and yield response of semi-crystalline thermoplastics. Section 3 provides details on the material selection and experimental characterization of as-received material from the supplier. It also describes the experimental setups and methodology utilized, parameters for manufacturing of samples, apparatus and method for preparation of coupons, thermomechanical characterization and testing. The results from these experimental tests are presented and discussed in section 4. Section 5 describes the model development process utilizing the experimental results and puts the model development effort in context of existing materials modeling

theory. Section 6 presents the verification and validation simulation performed to demonstrate the predictive capability of the model by comparing simulation outputs with experimental results from four-point bending tests. Section 7 presents the key takeaways and conclusions drawn from this study and discusses future investigations as a follow up to this study.

2. Approach

The approach to achieve the objectives of this study comprises of three steps: experimental characterization, data analysis and model calibration and lastly, model prediction and validation. The first step involves tensile testing to capture effects of fiber ply orientation and varying temperature. The experimental response is utilized to calibrate an orthotropic linear elastic material model.

The as-received thermoplastic composite material is subsequently heated to a processing temperature beyond the melt temperature of the PA6 matrix, followed by cooling to near room temperature, with constant cooling rates varying from 0.1 °C/min to 40 °C/min. Differential Scanning Calorimetry (DSC) was performed on samples prepared from panels subject to each distinct and near-constant cooling rate to determine the achieved χ_c . Tensile coupons prepared from these flat panels were tested to evaluate the effect of the achieved χ_c on mechanical behavior, including Young's Modulus, yield stress, and hardening. These experimental results were used to calibrate the Avrami transition model used to determine the evolving χ_c as a function of instantaneous temperature and rate of change in temperature. Finally, Young's Modulus and yield stress was modeled as a function of this χ_c and temperature.

Finally, non-constant cooling rates representative of the dynamic conditions experienced during thermoforming, were implemented for a final set of flat panels. Coupons for the four-point bending test were prepared from these panels in both 0/90° and +45°/-45° orientations. The force versus displacement response as well as the strain distributions along the face of the coupon experiencing tension, were measured for validation of simulation results. The developed and calibrated analytical model was used to perform four-point bending simulations, with the simulation response being compared with experimental behavior. Thus, the developed model was validated for a complex loading condition, where the mechanical properties were predicted for previously unexplored cooling rates. The approach has been summarized in Figure 2.

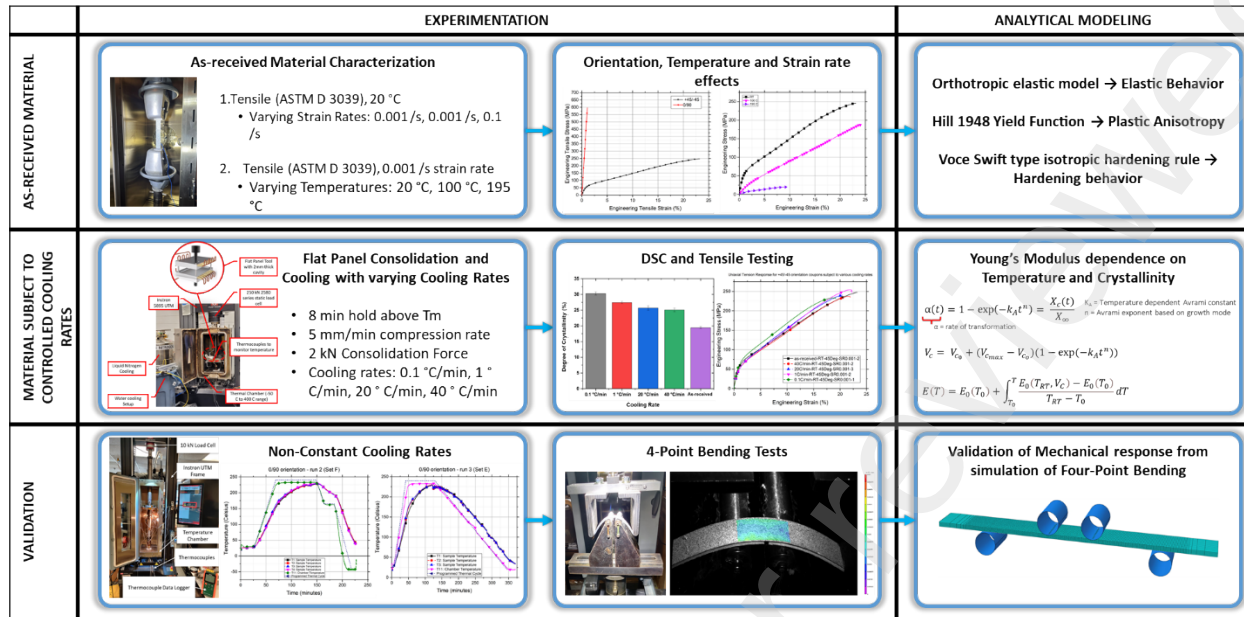


Figure 2. Approach for experimentation and analytical model development for this study.

3. Experimental Materials and Methodology

The fiber reinforced thermoplastic material used for this study is the commercially available Tepex® Dyalite 202-C200 (8) / 45 % nature Typ B supplied by Lanxess (now Envalior, Düsseldorf, Germany), a 2x2 twill weave bidirectional continuous carbon fiber reinforced PA6 laminate with eight (no notable color additives or pigments added to the PA6 matrix), with a fiber content of 45 % (by weight). The bidirectional continuous fiber reinforcements are oriented in the 0°/90° direction with respect to the warp and weft direction. Thus, the in-plane properties are assumed to be equivalent in both warp and weft directions, considering the bidirectional weave and balanced ply stack-up. The average thickness of the pre-consolidated laminate panels, as received from the manufacturer was measured to be 2 mm ± 0.2 mm. The material is as shown in Figure A. 1 in Appendix A.

3.1. Experimental Characterization of As-Received Material

Thermal and physical characterization of the CF-PA6 material was performed to identify key temperature points such as glass transition temperature (T_g), recrystallization temperature (T_{rc}), melt temperature (T_m) as well as degradation onset temperature (T_{deg}). Thermogravimetric analysis (TGA) was performed on the TA Instruments TGA2500 (New Castle, Delaware, USA), where the as-received CF-PA6 material was subjected to a heating ramp at 20 °C/min from room temperature (25 °C) to 800 °C in an inert nitrogen environment. Approximately 8 mg -10 mg of sample CF-PA6 composite material was utilized for these TGA experiments.

Differential scanning calorimetry (DSC) experiments were performed to quantify the T_g , T_{rc} , T_m and enthalpy of crystallization and enthalpy of melting. The TA Instruments DSC 250 (New Castle, Delaware, USA) was utilized for this purpose. A standard heat-cool-heat procedure was utilized over a temperature range of 30 °C to 250 °C with a ramp rate of 10 °C/min. Degree of crystallinity (χ_c) was determined from DSC runs using Equation 1.

$$\text{Degree of crystallinity (\%)} \chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^0} \times \frac{100}{W} \quad \text{Equation 1}$$

where,

W = mass fraction of PA6 in the composite sample used for DSC

ΔH_m = apparent melt enthalpy

ΔH_{cc} = enthalpy of cold crystallization

ΔH^0 = melt enthalpy for 100% crystal PA6 = 230 J/g [59]

Thermal expansion is considered in most thermomechanical analyses as it affects the thermal strain due to temperature changes. The temperature-dependent coefficients of thermal expansion (CTE) for CF-PA6 were measured using TA Instruments TMA 450 (New Castle, Delaware, USA) for thermomechanical analysis (TMA). The samples prepared for TMA were approximately 9.85 mm (3/8") x 9.85 mm (3/8") x 2 mm (length x width x thickness) in dimensions and the change in dimensions was measured between the temperature range of 25 °C to 200 °C respectively. The TMA experiments were performed at varying temperature ramp rates of 10 °C/min and 15 °C/min respectively, under an inert nitrogen atmosphere.

Thermoplastic composites are anisotropic and their behavior is highly influenced by temperature, and strain rates. Mechanical properties of CFRTP vary depending on the direction of the applied load due to reinforcing fibers alignment and orientation within the polymer matrix. Decreased strength and stiffness at high temperatures can significantly impact CFRTP structural integrity and load-bearing capabilities. To investigate the anisotropic properties of the CF-PA6 pre-consolidated sheets in as-received condition, coupons were fabricated in 0°/90° and diagonal +45°/-45° orientations considering the tetragonal symmetry associated with the bidirectional weave. Tensile tests were performed, in accordance with ASTM D 3039, at room temperature with a strain rate of 0.001/s. At least three coupons were tested for each orientation. In addition to tensile tests at room temperature ($T = 20$ °C), tensile tests at elevated temperatures (100°C and 195°C) were also conducted. These temperatures are above T_g and below T_m of the PA6 matrix. For each set of test conditions, at least three coupons were tested.

3.2. Manufacturing with Controlled Cooling Rates

To investigate the effect of cooling rates at the coupon level, as-received CF-PA6 panels (with 45 % mass fraction) of dimensions 150 mm (6") x 250 mm (10") were placed between a flat mold for re-consolidation and cooling. The as-received CF-PA6 panels were heated up to a processing temperature of 215 °C, followed by re-consolidation, where a 2kN consolidation force was applied over the heated CF-

PA6 panel for 8 minutes. Following re-consolidation, cooling was conducted at four distinct rates: 0.1 °C/min, 1 °C/min, 20 °C/min, and 40 °C/min. The flat panel setup consists of top and bottom flat tools with a 2 mm thick cavity, placed inside a temperature chamber, as illustrated in Figure 3. All flat panel re-consolidations were carried out on the Instron 5985 universal testing machine (Norwood, Massachusetts, USA) with a temperature chamber and a 250 kN 2580 series static load cell. The speed of the top tool closure is 5 mm/min. The experiment is force-controlled, and displacement is dynamic to maintain 2 kN consolidation force, thereby achieving constant pressure. Following re-consolidation at constant pressure and temperature, cooling was conducted at four distinct near-constant rates (up until below the T_g of PA6), as illustrated in Table 1.

Table 1: Uniform cooling rates achieved utilizing various cooling strategies with the flat panel consolidation tool setup

Approximate constant cooling rate	Setup Description
0.1 °C/min	the temperature chamber remained closed during the cooling (preventing natural convective heat transfer)
1 °C/min	the door of the temperature chamber was open (natural convective heat transfer aided faster cooling)
20 °C/min	cooling the tool with the aid of room-temperature water running through cooling channels (forced convective heat transfer aided faster cooling)
40 °C/min	cooling the tool with the aid of liquid nitrogen running through cooling channels (forced convective heat transfer using better cooling medium)

K-type thermocouples, with an operating range of -50 °C to 450 °C were placed on the top and bottom halves of the tool as well as in contact with the material, and the interior of the thermal chamber. The setup, comprising of the tool, the thermoplastic composite material and the interior of the thermal chamber, was heated to a temperature above the melt temperature (T_m) of the PA6 matrix. Figure 3b illustrates the thermal cycle the composite blank is subjected to, based on the data recorded by the thermocouples in contact with the material.

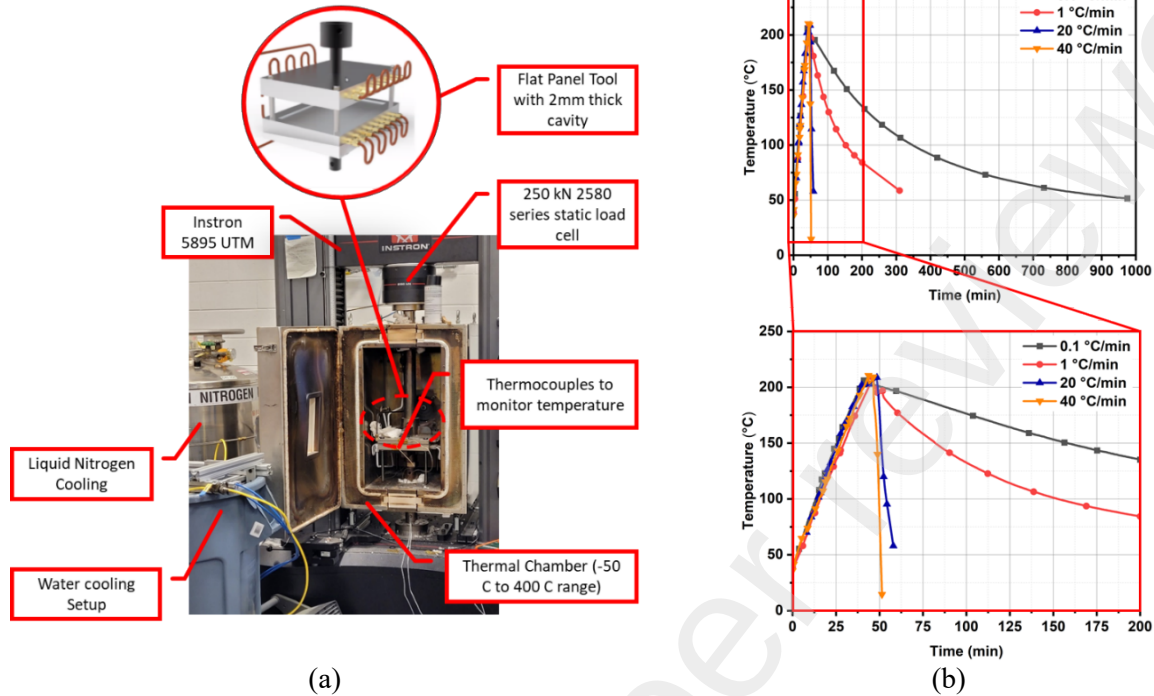


Figure 3. (a) Experimental setup for flat panel consolidation and variable rate cooling of 2 mm thick CF-PA6 panels; (b) Temperature (°C) versus Time (min) for flat panel consolidation with different constant cooling rates implemented.

3.3. Characterization of effect of cooling rates on CF-PA6 material properties

Following the re-consolidation and cooling of the CF-PA6 sheets, coupons were cut using waterjet for mechanical testing and DSC coupons were prepared from sheets subjected to a distinct cooling rate. Precautions were taken to initiate the waterjet cut away from the area of interest to avoid delaminations from being induced in the coupons used for mechanical testing. Again, DSC experiments were performed using the DSC 250 (New Castle, Delaware, USA). Uniaxial tensile testing per ASTM D 3039 was performed on coupons cut in the 0°/90° and +45°/-45° orientations from these panels subjected to different cooling rates. The results were compared with mechanical test results of as-received CF-PA6 panels. These would help capture the effect of cooling rates on mechanical and viscoelastic properties of CF-PA6 composites.

3.4. Manufacturing of samples with non-constant cooling rates

Following the development and calibration of the analytical model, validation experiments were performed. Non-constant cooling rates were implemented on 150 mm x 150 mm square panels, for both 0°/90° and +45°/-45° orientations. The setup to prepare flat panels with non-constant cooling rates consisted of a compression plate setup on a 10 kN capacity Instron 68TM-10 (Norwood, Massachusetts, USA) servoelectric universal testing machine (UTM) with a temperature chamber 3119-615 (Buckinghamshire, England) capable of implementing programmed heating and cooling with controlled and repeatable rates.

The temperature chamber can induce heating or cooling rates of up to 15 °C/min within an operating temperature range of -50 °C to 450 °C. K-type thermocouples coupled with a datalogger were used to monitor and log the material temperature, heating rates, and cooling rates. This was necessary owing to large volume of the temperature chamber causing a temperature lag, and reduction in heating and cooling rates for the material as compared to the set chamber temperature. The temperature chamber has its own internal PID controller with fast-cooling capability using liquid nitrogen. The setup is as illustrated in Figure 4. Again, these trials were force-controlled, with a constant consolidation force of 2 kN being applied, consistent with the previous experiments where different constant cooling rates were implemented. The experimental parameters are summarized in Table 2, with thermal cycles illustrated in Figure A. 5 and Figure A. 6 in Appendix A.

Table 2: Validation runs for flat panel consolidation with constant and non-constant cooling rates

	Orientation	Cooling Profile	Cooling initiation Temperature Setpoint	Intermediate Temperature Setpoint	Cooling end temperature Setpoint
Run 1 - G	0°/90°	0.5 °C/min, 3.5 °C/min	230 °C	200 °C	~40 °C
Run 2 – F		1.1 °C/min, 4.2 °C/min		195 °C	
Run 3 – E		0.6 °C/min, 1 °C/min		180 °C	
Run 4 – B		0.2 °C/ min		-	
Run 1 – A	+45°/-45°	0.5 °C/min, 3.9 °C/min	230 °C	200 °C	~40 °C
Run 2 – C		1.3 °C/min, 4.1 °C/min		195 °C	
Run 3 – D		0.6 °C/min, 1 °C/min		180 °C	

The programmed thermal cycle for the thermal chamber, and the temperature measured using the thermocouple in contact with the thermoplastic composite panel were significantly different, as illustrated in Figure A. 5 and Figure A. 6 in Appendix A, due to two reasons. Firstly, the thermocouple feeding sensor data for the feedback loop of the PID control of the thermal chamber was in contact with the air inside the chamber. Secondly, the difference can be attributed to the large volume of the thermal chamber as well as the mass and heat capacity of the steel compression fixture used to apply consolidation pressure, resulting in a significant lag between the material temperature and the temperature of the air inside the thermal chamber. The programmed cycles were designed iteratively while taking these considerations into account.

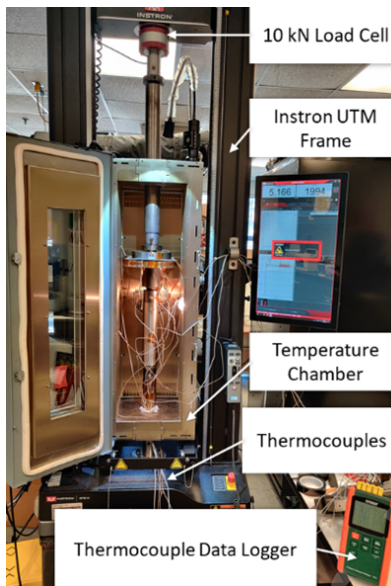


Figure 4. Flat panel consolidation and non-constant cooling setup with automated cooling rate control.

3.5. Four-Point Bending Tests for Model Validation

Four-point bending test coupons with dimensions of 127 mm length, 12.7 mm width, and 2 mm average thickness were prepared from each panel, using a water cooled, diamond-blade slot grinder to avoid delamination or friction heat effects on the thermoplastic matrix. Five coupons were prepared for each cooling rate condition, and subjected to four-point bending test to ensure that the results were repeatable and statistically representative. A 3-dimension digital image correlation (3D DIC) setup by Correlated Solutions (Irmo, South Carolina, USA) with two 5 MP cameras was utilized to gather strain distribution data on the side experiencing tension to help validate strain distribution predictions from simulations, as illustrated in Figure 5. Sampling frequency for image capture varied based on the total duration of the tests, which in turn depended on the orientation, with $+45^{\circ}/-45^{\circ}$ coupons having a sampling frequency of 1 Hz, and $0^{\circ}/90^{\circ}$ coupons with a sampling frequency of 5 Hz.

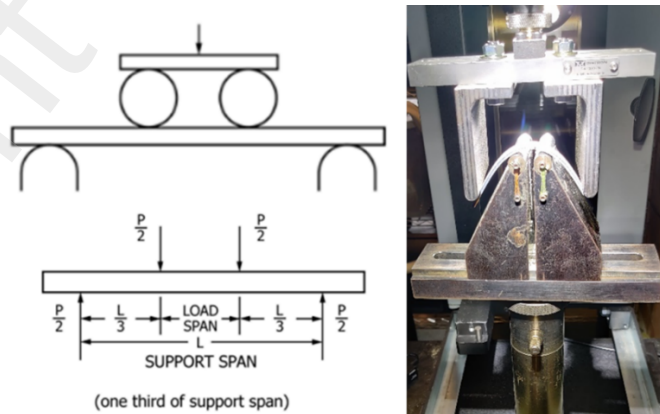


Figure 5. Four-point bending test setup (left) as illustrated in ASTM D6272; (right) modified 4-point bending test setup for extended deflection and strain measurement with 3D DIC.

The bending test setup was based on guidelines provided in ASTM D 6272. The support span (L in Figure 5) was 80 mm, Figure 5 in accordance with the standard recommended 40:1 span-to-thickness ratio. Unlike the standard-recommended loading nose span ($L/3 = 26.67$ mm or $L/2 = 40$ mm), a reduced loading nose span of 20 mm was considered to ensure sufficient clearance between supports and nose for deflections beyond 5 % strain. Consequently, compared to the standard 40 mm loading nose span, the smaller nose span results in lower curvature at the same displacement, leading to a lower measured load. The diameters of the supports and the loading nose were measured to be ~9.8 mm. Typically, the four-point bending tests are stopped at 5 % strain, to determine elastic flexural modulus and strength. However, for the purpose of model validation up to the yield point, the tests were extended well beyond this point. The crosshead rate was determined based on recommendations in ASTM D 790, given by Equation 2 , to be 5.33 mm/min.

$$R = \frac{0.167 Z L_s^2}{d} = 5.33 \text{ mm/min} \quad \text{Equation 2}$$

where,

L_s = support span (mm) = 80 mm

Z = rate of straining outer fibers (mm/mm.min) = 0.01 mm/mm. min

d = depth of beam = 2 mm

4. Experimental Results and Discussion

4.1. Thermal Characterization of as-received composite material

The TGA results are as illustrated in Figure 6 (a). The curve for mass loss shows two distinct cliffs and plateaus. The first sharp drop occurs at 450 °C and is indicative of the PA6 undergoing degradation, accounting for almost 50 % mass loss, indicative of the approximate fiber mass fraction specified by the supplier. The second plateau occurs due to the thermal stability of carbon fibers, which start to degrade at approximately 675 °C, represented by a second sharp drop off in the mass. Thus, we can conclude that the initial mass loss is representative of purely the PA6 matrix, and can be utilized to identify the degradation onset temperature. As summarized in Table 3, the PA6 matrix experiences major mass loss indicative of degradation at temperatures well above 300 °C. Based on this information, the temperature parameters for DSC and TMA were suitably selected to be below 250 °C. This also helps identify the processing temperature limits for subsequent thermal characterization, as well as for forming and consolidation trials where varying cooling rates are proposed to be implemented.

The DSC results, based on the test parameters described in section 3.1 are as illustrated in Figure 6 (b). Based on the normalized heat flow during heating ramps, the matrix melt temperature was determined to be $T_m = 215$ °C and recrystallization temperature to be $T_{rc} = 187.5$ °C. No clear glass transition temperature point is noticeable, typically represented by a gradual cliff in the normalized heat flow. This can be attributed to the fact that the DSC sample is a composite with ~45 % mass fraction comprising of carbon fibers which are extremely stable. Their presence in a substantial amount results in flattening of the DSC curve, making it difficult to identify the correct trend representing T_g of the thermoplastic matrix.

Based on the area under the curve for the peak associated with enthalpy of melt, the χ_c of the as-received CF-PA6 was calculated to be $\sim 19.44 \pm 0.33 \%$.

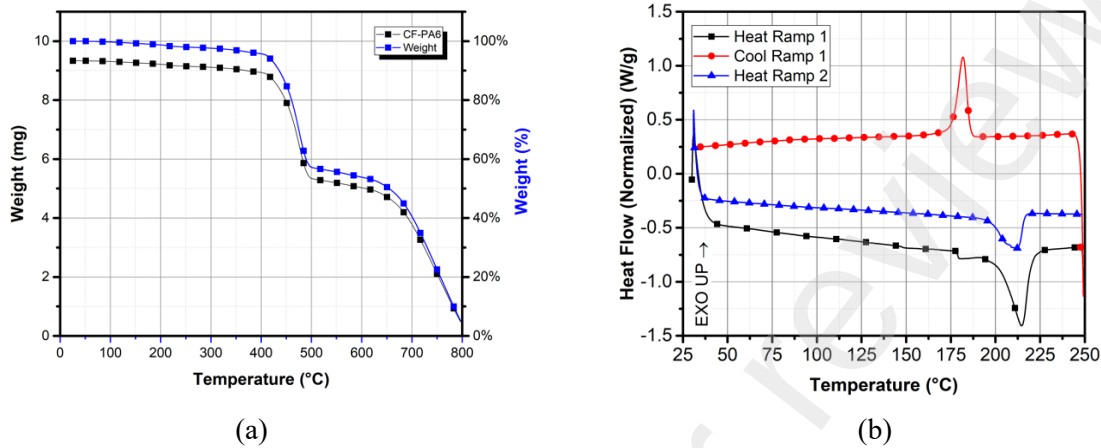


Figure 6. (a) TGA plot for mass (mg) and mass remaining (%) for the CF-PA6 composite with increasing temperature (°C) ; (b) Characterization of CF-PA6 composite within DSC to evaluate enthalpy of crystallization and crystallization onset temperature

Table 3. Temperatures corresponding to 1 %, 3 % and 5% mass loss – as determined through TGA

Weight Loss (%)	Temperature (°C)
1.0 %	177.7 °C
3.0 %	347.38 °C
5.0 %	411.96 °C

TMA was performed on as-received material as well, with the temperature and temperature ramp rate dependency of the thermal expansion of the CF-PA6 composite laminate summarized in Figure 7. For thermoforming a prepreg laminate, the through-thickness CTE is critical as it influences the thickness of the manufactured component during cooling, thereby dictating part thickness, dimensional tolerance and mechanical performance. The CTE in the longitudinal and transverse direction for this 2x2 bidirectional twill weave composite laminate is expected to be equal as all eight plies are stacked in the $0^\circ/90^\circ$ orientation with respect to the warp direction (machine direction). The values for average CTE in both the warp and weft directions for this material and laminate configuration are reported in literature to be $1.54 \text{ e-}6/^\circ\text{C}$ below T_g and $1.86 \text{ e-}6/^\circ\text{C}$ above T_g [57]. The through-thickness CTE was evaluated and the effect of different temperature ramp rates was studied.

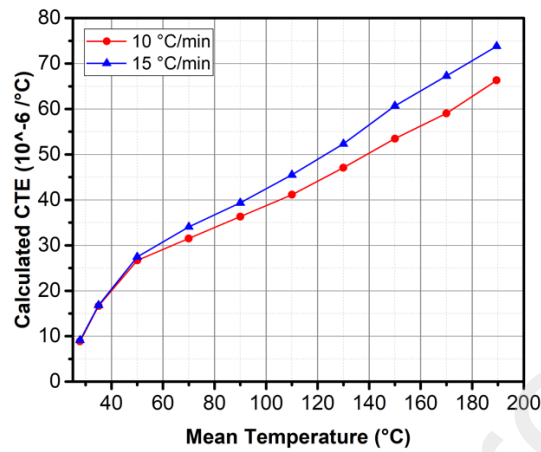


Figure 7. Calculated CTE versus mean temperature determined based on dimensional change measured using TMA.

As illustrated in Figure 7, the temperature ramp rate has a significant effect on the CTE. It is observed that 10 °C/min and 15 °C/min ramp rates exhibit similar trends, with near overlapping CTE values up until the T_g of PA6 reported in literature, and exhibit an increasing trend beyond that temperature point. However, since, this is a measurement of through- thickness CTE of a woven laminate, deconsolidation of the pre-consolidated sheet also contributes to the increasing CTE. Hence, absolute values of CTE may not be utilized for model development, however, the comparative trends exhibited over the broad temperature range are worth reporting. Increase in the temperature ramp rate results in a higher CTE being reported over the temperature range between T_g and T_m .

4.2. Mechanical Characterization of as-received composite material

Figure 8a illustrates that the averaged engineering stress-strain response (determined based on experimental data illustrated in Figure A. 2) in the 0°/90° orientation and +45°/-45° under uniaxial tension. The Young's modulus and tensile strength for 0°/90° orientation coupons are significantly higher than those of +45°/-45° orientation coupons due to high stiffness of the carbon fiber oriented in the direction of tensile load application. The strain at failure for the 0°/90° orientation coupons is, however, significantly lower as fiber are relatively inelastic, with the 0°/90° orientation coupons exhibiting an extremely linear curve up until failure. Furthermore, the coupons in the 0°/90° orientation also exhibit fracture at the end of the elastic deformation, with no pronounced yield point. In contrast, the diagonal +45°/-45° directions exhibit a yield point as well as significant plastic deformation due to the rotation of the carbon fibers and the plastic deformation of the matrix PA6. This results in relatively low stiffness and a much greater total elongation behavior, consistent with reported observations in literature [60].

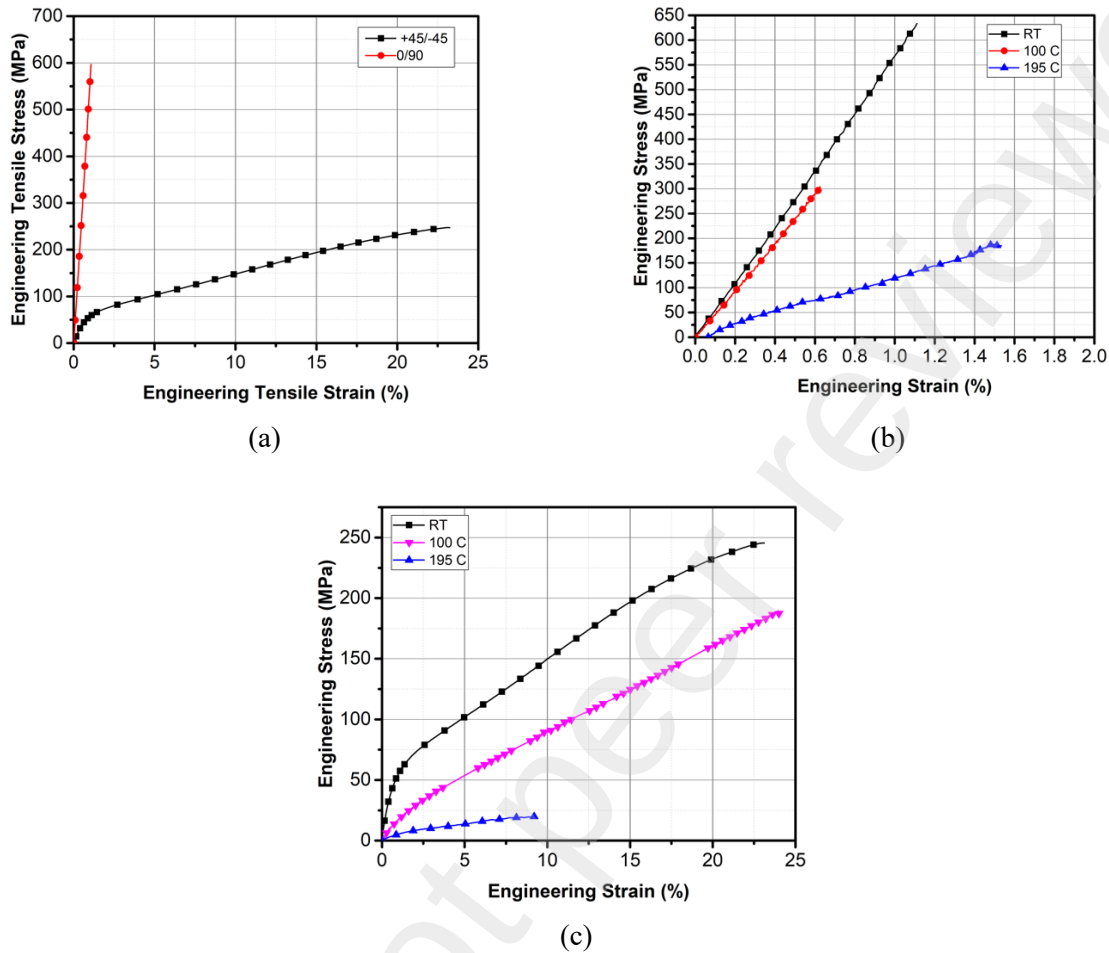


Figure 8. (a) Average engineering stress-strain curves for CF-PA6 coupons under uniaxial tension (Room Temperature, 0.001/s strain rate) comparing 0°/90° and +45°/-45° orientations; (b) Average engineering stress-strain curves at varying temperatures for CF-PA6 for 0°/90° fiber orientation; (c) Average engineering stress-strain curves at varying temperatures for CF-PA6 for +45°/-45° fiber orientation.

For uniaxial tensile at elevated temperatures, additional tests were performed at 100 °C and 195 °C, while keeping a constant strain rate on 0.001 /s. It was observed that the Young's modulus for both 0°/90° and +45°/-45° orientation decreased, as illustrated by the average engineering stress -strain response in Figure 8b and Figure 8c, respectively (determined based on experimental data illustrated in Figure A. 3). The averaged engineering-stress-strain response for the 0°/90° orientation as well as +45°/-45° orientation coupons at elevated temperature was similar in nature to the one at room temperature, in that the stress-strain curve was relatively linear with an abrupt failure point. The test at 100 °C exhibited a slight reduction in stiffness owing to the PA6 matrix being heated to a temperature beyond its T_g . However, there was a drastic change in stiffness for uniaxial tensile tests conducted at 195 °C, attributed to the viscous response and matrix squeeze out, resulting in a lower shear limit as well as slip at the grips. Calibrated mechanical properties, including Young's modulus (E) and Poisson's ratios (ν) measured in the plane of the coupons are summarized in Table 4.

Table 4. Averaged mechanical properties for CF-PA6 at different strain rates and temperatures.

Direction	Strain rate	Temperature (T)	E (GPa)	Poisson's ratio (ν)
0°/90° dir.	$\dot{\epsilon} = 0.001/s$	20 °C (RT)	$E_x = 51.185 \pm 2.332$	$\nu_{xy} = 0.03349 \pm 0.01634$
	$\dot{\epsilon} = 0.001/s$	100 °C	$E_x = 47.987 \pm 2.371$	$\nu_{xy} = 0.0275 \pm 0.0446$
	$\dot{\epsilon} = 0.001/s$	195 °C	$E_x = 13.292 \pm 1.522$	$\nu_{xy} = 0.1300 \pm 0.0682$
$\pm 45^\circ$ dir.	$\dot{\epsilon} = 0.001/s$	20 °C (RT)	$E_{45} = 5.241 \pm 0.247$	$\nu_{12(45)} = 0.8345 \pm 0.046$
	$\dot{\epsilon} = 0.001/s$	100 °C	$E_{45} = 1.449 \pm 0.078$	$\nu_{12(45)} = 0.9446 \pm 0.037$
	$\dot{\epsilon} = 0.001/s$	195 °C	$E_{45} = 0.603 \pm 0.133$	$\nu_{12(45)} = 0.9955 \pm 0.0540$

Note: $E_x = E_y$ is assumed, since the thermoplastic composite laminate consists of 8 layers with the bidirectional woven continuous fibers oriented in the 0°/90° directions. E_{45} = modulus in the direction of load application which is +45°/-45° degrees with respect to the fiber orientations.

4.3. Effect of cooling rates on CF-PA6 material properties

Properties in the +45° /-45° fiber orientation are more dependent on the matrix properties, and hence, DSC and uniaxial tensile tests in the +45° /-45° fiber orientation were performed to investigate the effects of cooling rates on the microstructure and properties dominated by the polymer matrix. This helped experimentally relate effects of cooling rates on mechanical behavior. Following re-consolidation, the χ_c was found to be the highest at 30.28 % for the slowest cooling rate of 0.1 °C/min. As illustrated in Figure 9a, χ_c exhibited an inverse relationship with the cooling rate, with achieved χ_c reducing as cooling rate was increased.

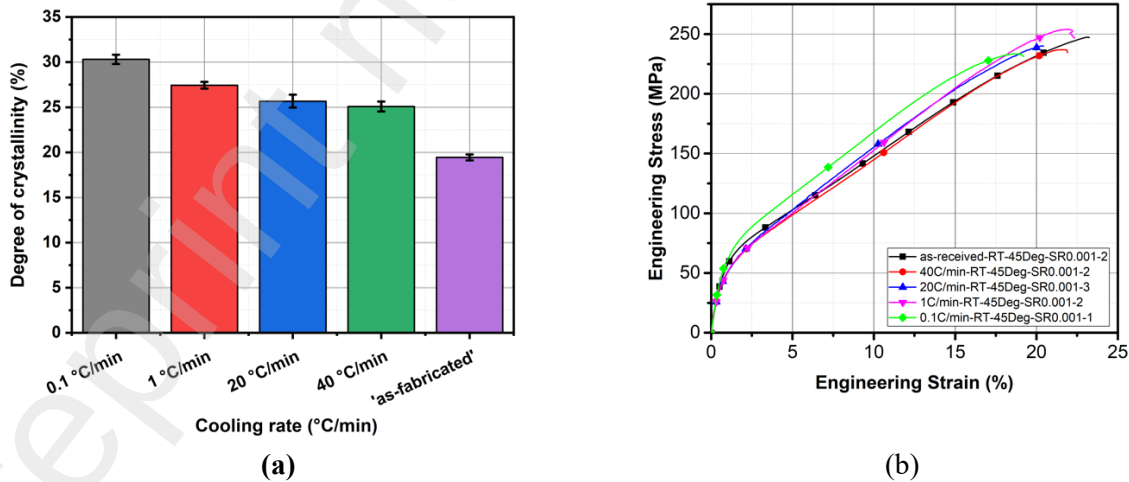


Figure 9. (a) Experimentally determined degree of crystallinity χ_c for PA6 matrix for varying cooling rates and “as-received” CF-PA6 material from supplier; (b) Average Engineering stress-strain curves subject to various cooling rates compared to ‘as-received’ material coupons for +45°/-45° orientation coupons.

During cooling, the polymer undergoes a phase transition from a molten state to a solid state. This transition involves the formation of crystalline regions due to polymer chains interacting with adjacent chains and aligning in an ordered structure due to intermolecular forces. A faster cooling rate limits the time available for nucleation and chain alignment to form an ordered structure, resulting in the lower degree of crystallinity. On the other hand, a slower cooling rate allows time for more extensive chain alignment, nucleation, and crystal growth, leading to a higher χ_c [40,41]. Also, applying pressure during consolidation can enhance the crystallinity of the matrix material. Pressure can promote packing and alignment of polymer chains, which is favorable for forming crystalline regions. This explains the change in achieved χ_c between 'as-received' material compared to the material subject to 40 °C/min cooling rate and a consolidation force of 2 kN.

Moreover, the relationship between stiffness and strength is directly tied to crystallinity, where higher levels of crystallinity correspond to increased stiffness. Figure 9b shows the stress-strain curves of the +45°/-45° orientation CF-PA6 coupons subjected to different constant cooling rates. It can be observed that tensile strength increases with decreasing cooling rates. In contrast, the uniform elongation limit decreased with slower cooling rates. A similar tendency for the effect of cooling rate on tensile properties was observed in several previous studies as discussed in section 1. As the cooling rate decreases, the resulting increase in crystallinity contributes to the improved mechanical properties. Also, the change in cooling rate affects the interaction between the polymer matrix and the carbon fibers. A well-controlled cooling rate can improve the adhesion between the matrix and the fibers, leading to better load transfer and enhanced tensile properties.

All determined mechanical properties, including Young's modulus (E), initial yield stress (YS), ultimate tensile strength (UTS), and Poisson's ratio (ν), are summarized in Table 5 for different cooling rates. Poisson's ratio was calculated based on the principal strains in the longitudinal extension and lateral directions for coupons in the +45°/-45° orientation. Negligible change was observed for UTS and Poisson's ratio for coupons in the +45°/-45° orientation. Change in mechanical properties of corresponding 0°/90° orientation specimens were negligible as presence of continuous fibers predominantly dictated the mechanical properties in that direction. Similar trends are observed for the other intermediate cooling rates of 1 °C/min and 20 °C/min when compared to 0.1 °C/min, and have been quantified in Table 5. Comparing the mechanical properties +45°/-45° orientation specimens for the baseline 40 °C/min with 20 °C/min, a ~6.5 % increase in Young's modulus and a marginal decrease of ~4.7 % in yield strength was observed. Comparing the mechanical properties +45°/-45° orientation specimens for the baseline 40 °C/min with 1 °C/min, a ~7 % increase in Young's modulus and a marginal increase of ~1.5 % in yield strength was observed. As cooling rate decreased from 40 °C/min to 0.1 °C/min, a 21.07 % increase in achieved degree of crystallinity (χ_c) was observed. This ~20 % change in χ_c translated to ~40 % increase in Young's Modulus and an ~12 % increase in yield strength for the +45°/-45° orientation specimens made from panels subjected to these cooling rates.

Table 5: Implications of reducing cooling rate on achieved degree of crystallinity and mechanical properties in the +45°/-45° orientation

Cooling rate (°C/min)	degree of crystallinity (χ_c)		Young's Modulus (E)		Yield Strength (YS)		UTS	Poisson's ratio (ν)
	%	% Change	GPa	% Change	MPa	% Change	(MPa)	-
40	25.01	Baseline cooling rate	4.24	Baseline cooling rate	66.51	Baseline cooling rate	290.18	0.89
20	25.62	+ 2.44	4.52	+ 6.73	63.37	-4.72	290.97	0.84
1	27.40	+ 9.56	4.55	+7.29	67.53	+1.53	303.99	0.82
0.1	30.28	+ 21.07	5.95	+40.43	74.38	+11.83	298.34	0.88

4.4. Experimental Flexural Response for Model Validation

The key results from the four-point bending test required for comparison against the simulation outputs as part of the analytical model validation include the area strain map extracted using 3D DIC for the side experiencing tension as well as validation of the simulated force versus displacement response with the force versus displacement curves obtained through experimental testing. Figure 10a and Figure 10b illustrates the plots for force versus displacement measured at the crosshead of the Instron UTM for 0°/90° coupons and +45°/-45° coupons.

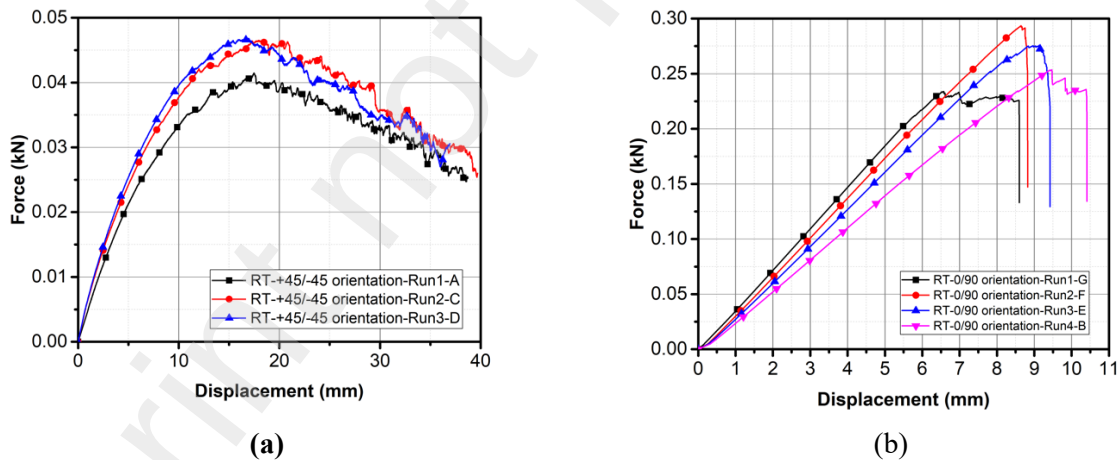


Figure 10. (a) Average crosshead force versus displacement response for +45°/-45° orientation 4-point bending test coupons; (b) Average crosshead force versus displacement response for 0°/90° orientation 4-point bending test coupons.

It can be observed by comparing the force versus displacement response in 4-point bending tests from Figure 10a and Figure 10b, that the 0°/90° degree orientation coupons exhibit much higher stiffness (higher force to yield and lower displacement) compared to the +45°/-45° orientation coupons owing to the continuous carbon fiber reinforcements aligned in the direction of tension and compression experienced

during the bending of the coupon. The force vs displacement response of the $+45^{\circ}/-45^{\circ}$ orientation coupons is dominated by the matrix properties which in turn are greatly influenced by the cooling rate. It is also worth noting that despite the non-constant cooling rates implemented on panels these coupons are made from, the cooling rate experienced around the vicinity of T_{rc} is the most relevant in dictating the achieved degree of crystallinity and subsequent mechanical properties. This is evident from Figure 10a, where set-A experienced a lower initial cooling rate but a higher cooling rate of $3.9^{\circ}\text{C}/\text{min}$ as compared to set-C (subject to $1.3^{\circ}\text{C}/\text{min}$ cooling rate in the vicinity of T_{rc}) or set-D (subject to $1.3^{\circ}\text{C}/\text{min}$ cooling rate in the vicinity of T_{rc}). Thus, it exhibits a less stiff response compared to set-C or D of the $+45^{\circ}/-45^{\circ}$ orientation coupons. Thus, the intermediate temperature setpoint, at which there is a transition in average cooling rate experienced by the panel, is also of relevance in dictating the achieved mechanical properties for thermoformed semi-crystalline thermoplastic composite components. This also explains the slight difference between the higher stiffness exhibited by set-D (which experiences a cooling rate of $0.6^{\circ}\text{C}/\text{min}$ through the recrystallization temperature point of 187.5°C) compared to set-C (which experienced a comparatively higher cooling rate of $4.1^{\circ}\text{C}/\text{min}$ around the same temperature point).

5. Constitutive Model Development

Understanding the cooling rate effects on crystallization and mechanical performance will help build a robust model for the thermoforming process involving semi-crystalline thermoplastic matrices. The cooling rate affects mechanical properties and residual stresses in the formed part, which affects its mechanical performance. Building a comprehensive numerical framework that fully captures cooling rate effects on the structural performance of thermoplastic composites and encompasses all critical process steps is essential for evaluating performance of thermoformed CF-PA6 composite components and optimizing the thermoforming process. Modeling of these causalities in the form of a digital life-cycle or CAE chain for CF-PA6 is critical in predicting process effects on achieved mechanical performance..

5.1. Material Model Development

To predict the complex behavior of the CF-PA6 composite under various thermomechanical conditions, a continuum-scale homogenized constitutive model was employed. Rather than modeling the individual mechanical behaviors of the polymer matrix and reinforcement fibers, the homogenization modeling approach was adopted for thermoforming simulations due to their computational efficiency and suitability for capturing macroscopic behavior. The homogenization model captures material anisotropy due to presence of continuous fiber reinforcement and as well as temperature-dependent behavior of the thermoplastic matrix. By incorporating these factors, the model accurately represents the material's response to thermal and mechanical loads. For the elastic behavior, the orthotropic linear elasticity model, with temperature dependency of the elastic coefficients, was employed. The corresponding compliance matrix is presented in Equation 3.

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \gamma_{xy} \\ \gamma_{yz} \\ \gamma_{zx} \end{pmatrix} = \begin{pmatrix} \frac{1}{E_x} & -\nu_{yx} & -\nu_{zx} & 0 & 0 & 0 \\ -\nu_{xy} & \frac{1}{E_y} & -\nu_{zy} & 0 & 0 & 0 \\ \frac{-\nu_{xz}}{E_x} & \frac{-\nu_{yz}}{E_y} & \frac{1}{E_z} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{pmatrix} \begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{pmatrix} = \begin{pmatrix} \frac{1}{E_x} & -\nu_{xy} & -\nu_{zx} & 0 & 0 & 0 \\ -\nu_{yx} & \frac{1}{E_y} & -\nu_{zy} & 0 & 0 & 0 \\ \frac{-\nu_{xz}}{E_x} & \frac{-\nu_{yz}}{E_y} & \frac{1}{E_z} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{2(1+\nu_{dd})}{E_{dd}} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{55} \end{pmatrix} \begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{pmatrix} \quad \text{Equation 3}$$

Here, x and y correspond to the 0° and 90° directions, respectively, which align with the reinforcement carbon fiber orientations, while z denotes the sheet thickness direction. E_x , E_y , E_z and E_{dd} represent the Young's moduli measured through uniaxial tension tests along the x , y , z and the diagonal $+45^\circ/-45^\circ$ directions, respectively. The Poisson's ratios ν_{xy} and ν_{xz} are obtained from the uniaxial tension test in the x direction, representing the ratio of normal elastic strain in the width and thickness directions, respectively, to the normal elastic strain in the tensile loading direction. Similarly, ν_{yx} and ν_{yz} are from uniaxial tension tests in the y direction, and ν_{zx} and ν_{zy} are from uniaxial tension tests in the z direction, describing the corresponding elastic strain ratios. ν_{dd} represents the ratio of normal elastic strain in the width direction to that in the loading direction during uniaxial tension along the diagonal ($+45^\circ/-45^\circ$) direction.

This integrated approach enables a comprehensive simulation of the material's behavior during the thermoforming process, capturing the effects of temperature on both the elastic and plastic responses of the material. Considering the tetragonal symmetry associated with the bidirectional weave, the number of independent coefficients in the orthotropic elasticity model is further reduced to six ($E_x = E_y$, $\nu_{xy} = \nu_{yx}$, $\nu_{xz} = \nu_{yz}$, $\nu_{zx} = \nu_{zy}$, $S_{55} = S_{66}$). To further simplify the linear elasticity model, the following conditions were considered:

- 1) Under uniaxial tension in X-direction, the elastic volumetric strain is positive: $\varepsilon_{xx}^e + \varepsilon_{yy}^e + \varepsilon_{zz}^e > 0$, which implies $\nu_{xy} + \nu_{xz} < 1$.
- 2) For uniaxial tension in X- or Y-direction, due to tetragonal symmetry, the Poisson's ratios are equal: $\nu_{xy} = \nu_{xz}$.
- 3) Given that the elastic modulus measured in the thickness direction, E_z is lower than that in the $+45^\circ/-45^\circ$ direction, E_{45} , due to the relatively weak interlayer bonding between prepreg layers, it is assumed that $E_z \leq E_{45} < E_x$. Since Young's modulus in the thickness direction, E_z , is less important in most sheet deformations, which are combinations of planar deformation and bending, it is assumed $E_z = E_{45}$.
- 4) From the tetragonal symmetry, $S_{55} = S_{66}$. It is further simplified by assuming that all the shear compliance terms are considered equal: $S_{44} = S_{55} = S_{66}$.

Based on the elastic moduli and Poisson's ratios obtained from uniaxial tensile tests on the as-received CF-PA6 composite sheets (summarized in Table 4) and the simplifying assumptions outlined above, the temperature-dependent elastic compliance and stiffness matrices were determined and the components of the elastic stiffness matrix are as presented in Table 6.

Table 6. Elastic stiffness matrix coefficients for different temperatures (unit: GPa).

Temperature	$C_{11} = C_{22}$	C_{12}	$C_{13} = C_{23}$	C_{33}	$C_{44} = C_{55} = C_{66}$
20 °C (RT)	51.249	1.7224	0.1816	5.2422	1.4285
100 °C	48.025	1.3218	0.0410	1.4491	0.3726
195 °C	14.161	2.0150	0.0994	0.6042	1.511

To capture plastic anisotropy, the Hill 1948 yield function shown in Equation 4, which accounts for temperature variations, is implemented.

$$f(\sigma) = \bar{\sigma} = F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx})^2 + H(\sigma_{xx} - \sigma_{yy})^2 + L\sigma_{yz}^2 + M\sigma_{zx}^2 + N\sigma_{xy}^2 \quad \text{Equation 4}$$

$$\bar{\sigma}(\bar{\epsilon}) = K_1 (K_2 + \bar{\epsilon})^{K_3} + K_4 (1 - \exp^{-K_5 \bar{\epsilon}}) \quad \text{Equation 5}$$

Here, $\bar{\sigma}$ is the effective stress, F , G , H , and N are anisotropic coefficients. Based on the limited experimental data available, the following assumptions were made to obtain these anisotropic coefficients:

- 1) Considering the tetragonal symmetry, the anisotropy coefficients are further simplified: $F=G$.
- 2) The yield stress under balanced biaxial tension was assumed to be equal to the yield stress obtained under uniaxial tension in the $0^\circ/90^\circ$ directions.
- 3) Taking the uniaxial tension in the $0^\circ/90^\circ$ direction as the reference state, the condition, $G+H=1$ was imposed.

Furthermore, since the model was intended to be validated using force-displacement curves from four-point bending tests, the anisotropic coefficients of the Hill 1948 function were calibrated based on the measured yield stresses [61]. Additionally, since the yield stress under the balanced biaxial loading was assumed to be equal to the yield stress in the reference state, the resulting coefficients are $F=G=H=0.5$. The temperature-dependent sets of anisotropic coefficients for the Hill (1948) yield function are summarized in Table 7.

Table 7. Hill 1948 anisotropic coefficients for different temperatures.

Temperature	$F=G=H$	$L=M=N$
20 °C (RT)	0.5	128.46
100 °C	0.5	109.47
195 °C	0.5	987.53

The hardening behavior was modeled using the combined Voce-Swift type isotropic hardening rule described in Equation 5. Here, $\bar{\epsilon}$ denotes the equivalent plastic strain conjugate to the Hill 48 yield function, and K_1 , K_2 , K_3 , K_4 and K_5 are hardening coefficients. Since the $0^\circ/90^\circ$ direction is aligned with the reinforcement carbon fibers, the stress–strain curve exhibits immediate fracture following the elastic region, making it unsuitable for characterizing hardening behavior. Therefore, the hardening coefficients were determined based on the stress-strain curve in the $+45^\circ/-45^\circ$ direction, which include sufficient hardening behavior. The calibrated temperature-dependent hardening coefficients for room temperature conditions are summarized in Table 8.

Table 8. Temperature-dependent hardening coefficients for room temperature conditions.

Temperature	K_1 (MPa)	K_2	K_3	K_4 (MPa)	K_5
20 °C (RT)	465.11	0.9995	0.0301	41917	2.669

The calculated stress-strain curves at room temperature in the $0^\circ/90^\circ$ and $+45^\circ/-45^\circ$ directions, obtained from uniaxial tensile FE simulations using the calibrated homogenization constitutive model, are compared with experimental results in Figure 11. It is worth noting that in the four-point bending test used for model validation in section 6, the region between the two loading noses experiences deformation close to pure bending. As a result, the normal stress in the Z-direction (σ_{zz}) and the shear stresses are negligible. Therefore, the simplifications introduced in the linear orthotropic elasticity model, as well as the use of the Hill (1948) yield function under the plane stress assumption, do not significantly affect the accuracy of the simulation results.

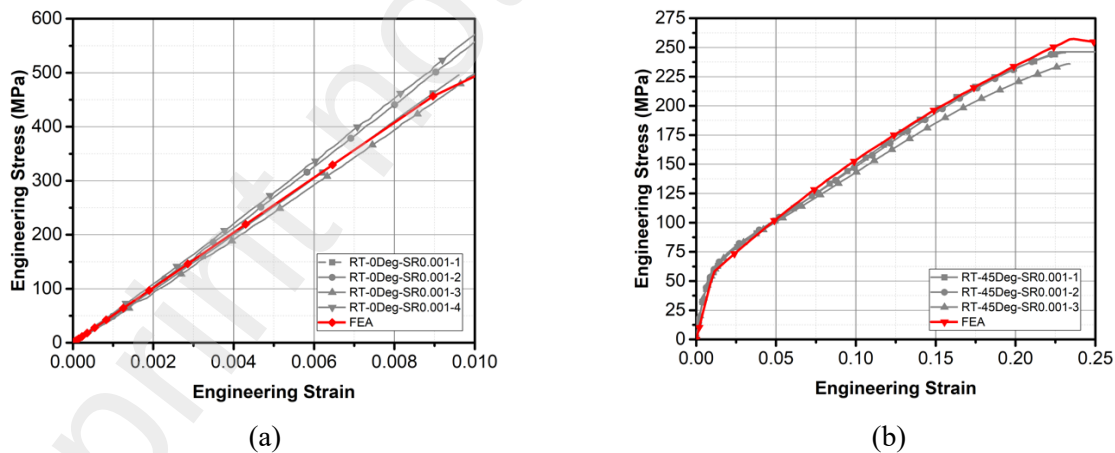


Figure 11. Comparison of the stress–strain curves at room temperature obtained from uniaxial tension FE simulations and experimental results for (a) $0^\circ/90^\circ$ orientation; (b) $+45^\circ/-45^\circ$ orientation.

5.2. Modeling Effect of Cooling Rates

To ensure the model accurately captures the effects of cooling rates, the Avrami transition [62] was implemented. Avrami transition is based on the Avrami equation, describing phase changes, and was integrated into the homogenization model using Equation 6 and the crystallized volume fraction as a function of time is as shown in Figure 12.

$$V_c = V_{c_0} + (V_{c_{\max}} - V_{c_0})(1 - \exp^{-Kt^n}) \quad \text{Equation 6}$$

where

- V_c is the relative crystallized volumetric transformed fraction,
- $V_{c_0} = 0.2308$ is the initial crystallized volumetric fraction,
- $V_{c_{\max}} = 0.51$ is the maximum possible crystallized volumetric fraction for PA6 [62],
- $K=0.0399$ is the Avrami rate constant,
- $n=0.2205$ is the Avrami exponent.

These parameters were determined based on the experimentally measured degrees of crystallinity for four cooling rates summarized in Table 5 . The temperature range over which amorphous polymer chains transition into an ordered crystalline structure was assumed to lie between 186.34 °C and 171.95 °C. This range corresponds to the region of rapid change in heat flow observed in Figure 6 (b) and is consistent with the crystallization temperature (T_c) of CF-PA6 reported in the literature [63–66], which is within the range of 170-196 °C, with the presence of fiber acting as a nucleating agent and allowing crystallization onset at a slightly higher temperature.

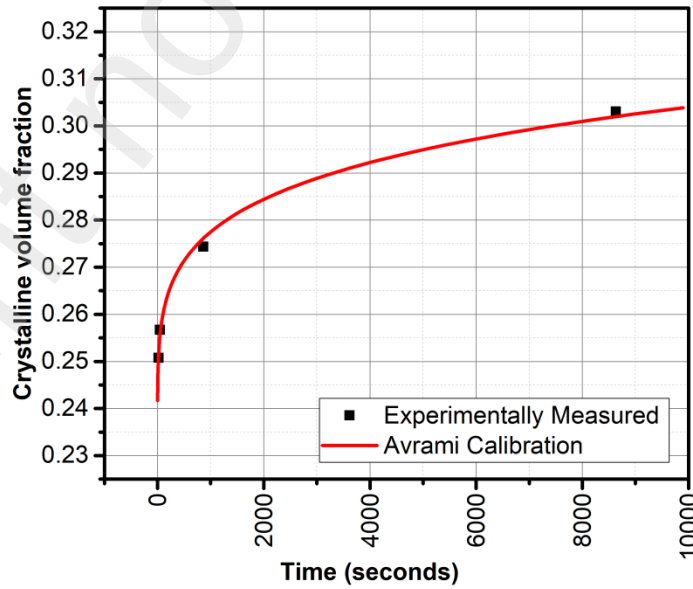


Figure 12: Crystallized volume fraction as a function of time

The Avrami transition is incorporated to capture temperature and crystallinity dependence in Mechanical properties, including Young's modulus and yield stress, during crystallization (from 186.34 °C to 171.95 °C). For example, Young's modulus and yield stress in the diagonal direction (E_{dd} and YS) is modeled as a function of purely temperature during cooling up to crystallization. After the recrystallization point is reached, the Young's modulus is subsequently modeled as a function of temperature and crystallinity as presented in Equation 7.

$$E(T) = E_0(T_0) + \int_{T_0}^T \frac{E_0(T_{RT}, V_C) - E_0(T_0)}{T_{RT} - T_0} dT \quad \text{Equation 7}$$

Here, T_{RT} denotes room temperature, T_0 is the temperature at which an ordered crystalline structure forms (171.95 °C), $E_0(T_{RT}, V_C)$ represents the measured Young's modulus at room temperature as a function of the χ_c as summarized in Table 5, and $E_0(T_0)$ denotes the Young's modulus at T_0 obtained by linear interpolation between values measured at 195 °C and 100 °C. For example, the interpolated value of E_x at T_0 is 21.71 GPa.

Similarly, the yield stress is modeled as:

$$YS(T) = YS_0(T_0) + \int_{T_0}^T \frac{YS_0(T_{RT}, V_C) - YS_0(T_0)}{T_{RT} - T_0} dT \quad \text{Equation 8}$$

Here, $YS_0(T_{RT}, V_C)$ represents the measured initial yield stress at room temperature as a function of the χ_c as summarized in Table 5, and $YS_0(T_0)$ denotes the yield stress at T_0 obtained by linear interpolation between values measured at 195 °C and 100 °C. The following assumptions were made to determine Young's Modulus and yield stress, accounting for crystallization that occurs during monotonous cooling:

- 1) The properties in 0°/90° directions (corresponding to the reinforcement fiber orientation) are assumed to be unaffected by the thermal history.
- 2) The effect of the cooling rate is the most significant in the +45°/-45° direction since the influence of the PA6 matrix is dominant.
- 3) Temperature decreases unidirectionally from an elevated temperature to room temperature.
- 4) The hardening curve is assumed to be proportional to the yield stress.

6. Model validation

6.1. Cooling analysis

Based on the cooling rates summarized in Table 2, the evolution of crystallinity under each cooling condition was calculated using Equation 6. Subsequently, the Young's moduli and initial yield stresses were determined using Equation 7 based on the calculated crystallinity for each cooling condition. The

resulting crystallinity, elastic stiffness coefficients, initial yield stresses (Y_S) in the $+45^\circ/-45^\circ$ direction, and Hill 1948 anisotropic coefficient, N , at room temperature are summarized in Table 9. In the case of the slowest (constant) cooling rate, $0.2^\circ\text{C}/\text{min}$ corresponding to Run 4 (B), the highest crystallinity of 29.31 % was calculated, resulting in the highest elastic coefficients and initial yield stress. In contrast, the fastest (non-constant) cooling conditions, represented by Run 2 (F) and Run 2 (C), predicted the lowest crystallinity of 26.46 % and 26.48 %, respectively, and consequently estimated the lowest elastic coefficients and initial yield stresses.

Table 9: Crystallinity, elastic stiffness coefficients, and Hill 1948 anisotropic coefficient, N , at room temperature after each cooling condition.

	Thickness (mm)	Degree of Crystallinity χ_c (%)	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	Y_S (MPa)	N
Run 1 - G	1.95±0.05	26.59	51.249	1.722	0.162	4.665	1.271	67.074	128.29
Run 2 - F	1.93±0.03	26.46	51.249	1.722	0.160	4.625	1.260	66.841	129.19
Run 3 - E	1.87±0.03	27.61	51.249	1.722	0.173	4.980	1.357	68.910	121.52
Run 4 - B	1.71±0.05	29.31	51.249	1.723	0.191	5.506	1.500	71.965	111.38
Run 1 - A	1.94±0.07	26.51	51.248	1.722	0.161	4.642	1.265	66.935	128.82
Run 2 - C	2.02±0.04	26.48	51.248	1.722	0.161	4.631	1.262	66.872	129.07
Run 3 - D	2.01±0.04	27.61	51.249	1.722	0.173	4.980	1.357	68.910	121.52

6.2. Four-point bending simulation

An FE model for the four-point bending simulation was developed using ABAQUS/Standard as illustrated in Figure 13. The supports and loading nose were modeled as analytical rigid bodies. The CF-PA6 composite coupon was modeled using 8-node solid elements (C3D8R), with eight elements assigned through the thickness direction. Along the length and width directions, elements with a size of 0.5 mm were employed. To improve computational efficiency, coarser elements were assigned to the ends of the CF-PA6 coupon where no contact with the supports occurs.

Penalty-based surface-to-surface contact interactions were defined between the tools and the CF-PA6 coupon, with the friction coefficient assumed to be 0.1. Quasi-static conditions were maintained during the simulation by applying a displacement boundary condition to the loading noses at a rate of 5.33 mm/min, consistent with the experimental setup. The two supports were fully constrained by fixing all degrees of freedom. The material model described in section 5.1 and section 5.2 was employed, with the coefficients summarized in Table 6, Table 7, Table 8 and Table 9.

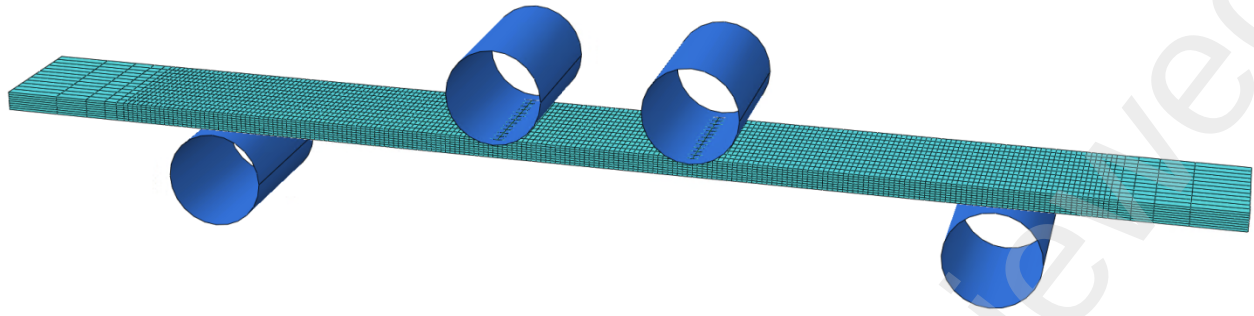


Figure 13. Finite Element model for 4-point bending test on ABAQUS for validation.

It is worth noting that, in the four-point bending test, when the coupon's width-to-thickness ratio is sufficiently large, the central region of the coupon is subjected to the plane strain tension/compression states, while the edges experience the uniaxial tension/compression conditions. Since the homogenization model was calibrated using uniaxial tension tests along the $0^\circ/90^\circ$ and $+45^\circ/-45^\circ$ directions, the four-point bending test is well suited for validating the material response under the dominant plane strain conditions, which were not used in the calibration.

6.3. Model Validation – Results and Discussion

The curves of the loading forces at the supports as a function of the loading nose displacement predicted by the FE simulation are compared with experimental results for coupons oriented in the $0^\circ/90^\circ$ direction and in the $+45^\circ/-45^\circ$ direction, as shown in Figure 14 and Figure 15, respectively. The simulation results exhibit a relatively linear load-displacement response for the $0^\circ/90^\circ$ coupons, while the $+45^\circ/-45^\circ$ coupons show more gradual saturation and softening, which is in good agreement with the experimental observations.

For the $0^\circ/90^\circ$ coupons, the load-displacement curves predicted by the simulation remain linear up to displacements of approximately 6 mm - 7 mm, which is close to the fracture point observed in the experiments. Beyond this point, the curves exhibit a gradual bending due to the onset of plastic deformation. Notably, for coupons with thinner cross-sections or lower crystallinity (and therefore lower elastic moduli), a greater range of elastic deformation is observed before yielding. Since a damage model was not employed in this study, the simulation was extended up to a displacement of 10 mm. At this stage, the maximum equivalent plastic strain on the top and bottom surfaces of the coupons was found to be approximately 0.013 – 0.015. This indicates that, in the displacement range between 7 mm and 10 mm, the $0^\circ/90^\circ$ coupons experienced only minimal plastic deformation.

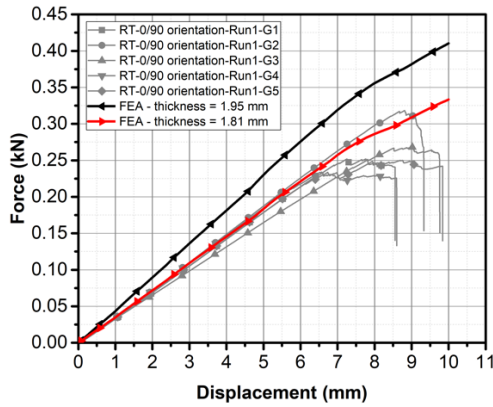
In contrast, the $+45^\circ/-45^\circ$ coupons, which have a relatively lower elastic modulus, demonstrate pure elastic behavior over a broader displacement range of approximately 7 mm - 8 mm. Subsequently, due to a longer hardening regime compared to the $0^\circ/90^\circ$ coupons, their load-displacement curves show a more gradual curvature, extending to displacements beyond 25 mm. At a displacement of 25 mm, the maximum equivalent plastic strain was approximately 0.0023 – 0.0028. It is worth noting that since the anisotropic yield function was defined with uniaxial tension along the $0^\circ/90^\circ$ direction as the reference state, the range of the maximum equivalent plastic strain corresponds to normal plastic strain of approximately 0.018 – 0.025, and total true strains of about 0.035 – 0.044. It can be seen that the initial hardening behavior, as

illustrated in Figure 11(b), significantly influences the prediction accuracy of the four-point bending simulations. Across all cooling rate conditions, the simulations tend to slightly overpredict the loading force compared to the experiments. Several factors were investigated to identify possible causes of the load overprediction observed in the FE simulations. Effects of the friction coefficient, the normalized balanced biaxial stress, and the tool radius were evaluated. However, these parameters did not have a significant effect on the predicted loading force. One of the possible reasons of the overprediction in the FE simulations is the influence of coupon thickness variation. As summarized in Table 9, the CF-PA6 composite coupons used in the four-point bending tests exhibited relatively large thickness variations. This variability can be observed in the substantial scatter of the measured load forces among the five force-displacement curves for each cooling rate condition, as illustrated by the black solid/dotted lines in Figure 14 and Figure 15.

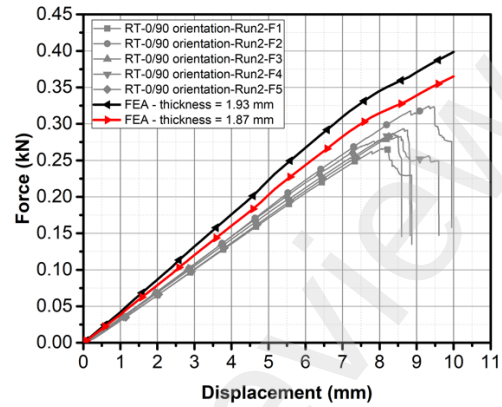
To evaluate the effect of coupon thickness, in addition to the average coupon thickness for each cooling rate condition (red solid lines in Figure 14 and Figure 15), minimum measured thickness was additionally considered for the four-point bending FE simulations (blue solid lines in Figure 14 and Figure 15). Compared to the simulation results with the average thickness, the predicted load force was significantly reduced and became much closer to the experimental results when the minimum thickness was considered. Across all cooling rate conditions, the FE simulations based on the average thickness consistently overpredicted the load force by approximately 20 % compared to the experiments, while those using the minimum thickness closely matched the experimental force-displacement curves with the highest forces. This demonstrates that, despite the variation in coupon thickness, the developed model provides consistent predictive accuracy across multiple constant and non-constant cooling rate conditions.

The other possible reason of the overprediction in the FE simulations is asymmetry between tension and compression in the CF-PA6. Fiber-reinforced composites generally exhibit significantly lower yield stress and hardening behavior under compression than under tension, which may explain the lower loading force measured in experimental four-point bending tests. In particular, for the $0^\circ/90^\circ$ coupons, where the carbon fiber orientations dominate, this asymmetry is expected to be more pronounced.

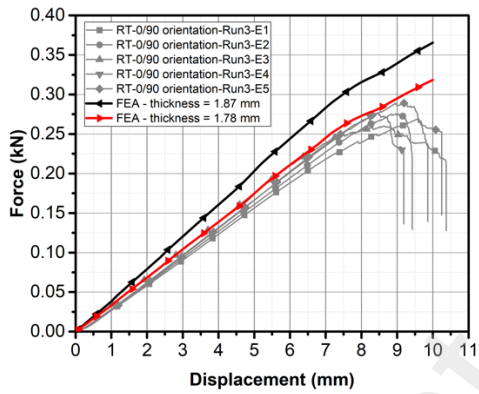
For the $+45^\circ/-45^\circ$ coupons, in which the PA6 matrix behavior is more dominant, and the rotation of the reinforcement carbon fibers is relatively limited within the elastic region, the asymmetry between tension and compression is minimal within the elastic deformation regime up to approximately 7 mm - 8 mm of displacement. In this range, the predicted force-displacement curves for both the average and minimum thickness cases agree reasonably well with the experimental data. However, beyond the onset of plastic deformation, the simulations overpredict the loading force compared to the experiments. It can be inferred that incorporating an asymmetric yield function [67] for the fiber reinforced composite would further decrease the predicted load force, potentially improving the simulation accuracy. However, in this study, the uniaxial compression behavior could not be characterized experimentally due to equipment limitations, such as the absence of an anti-buckling device.



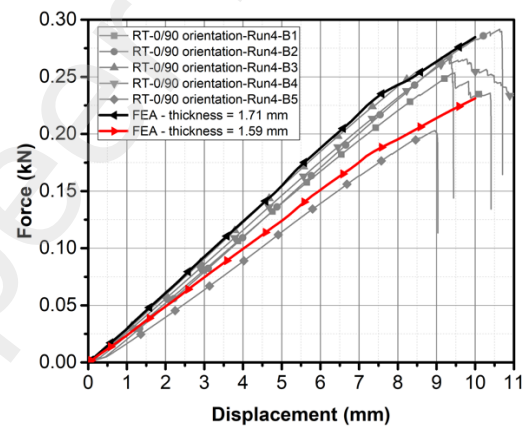
(a)



(b)

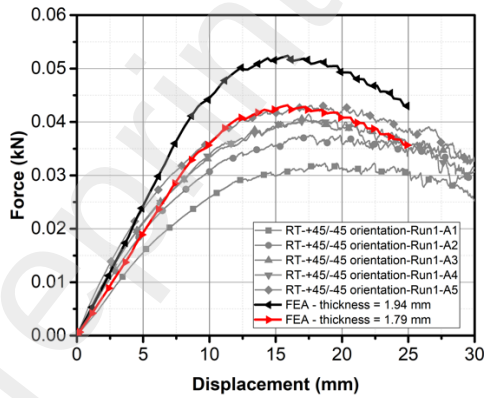


(c)

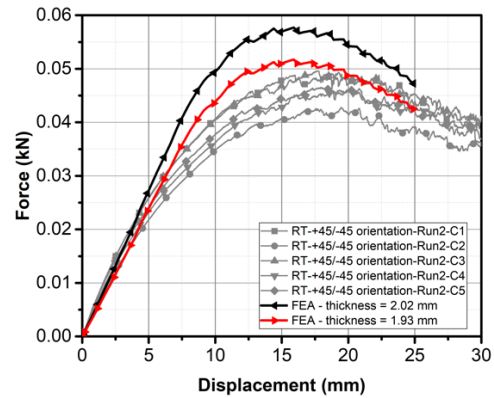


(d)

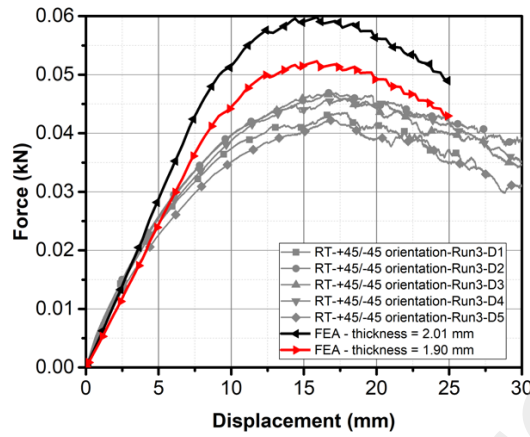
Figure 14. Comparison of load–displacement curves obtained from FE simulations and experiments for samples oriented in the $0^\circ/90^\circ$ orientation: (a) Run 1 (G), (b) Run 2 (F), (c) Run 3 (E), and (d) Run 4 (B).



(a)



(b)



(c)

Figure 15. Comparison of load–displacement curves obtained from FE simulations and experiments for samples oriented in the +45°/-45° direction: (a) Run 1 (set A), (b) Run 2 (set C), (c) and Run 3 (set D).

The distribution of maximum principal strain during the four-point bending test is compared between the experiments and the FE simulations in Figure 16 and Figure 17 for the 0°/90° and +45°/-45° direction coupons, respectively. For a consistent comparison, the strain color indices in the experimental and simulation results were matched as closely as possible. For the comparison, among the 0°/90° direction coupons, Run 2-F (with the fastest cooling rate and the lowest χ_c of 26.45 %) and Run 4-B (with the slowest cooling rate and the highest χ_c of 29.31 %) were selected. The distribution of maximum principal strain was compared at a displacement of approximately 7.2 mm, where the linearity of the force–displacement curve begins to deviate. It is shown that the distribution of maximum principal strain predicted by the simulation shows excellent agreement with the experimental observations. Due to the relatively smaller thickness of the Run 4-B coupon (1.71 mm) compared to the Run 2-F coupon (1.93 mm), its maximum principal strain was found to be distributed at comparatively lower levels.

As for the +45°/-45° direction coupons, Run 2-C and Run 3-D were selected for comparison, with nearly identical average thicknesses of 2.02 mm and 2.01 mm, respectively. But their respective degree of crystallinity χ_c are slightly different (26.48 % and 27.61 %, respectively) due to differences in cooling rates. The distribution of maximum principal strain was evaluated at a displacement of 17.6 mm, corresponding to the maximum applied load in both experiments and simulations. The predicted strain distribution shows very good agreement with the experimental results. In both the experiments and the simulations, the distribution of maximum principal strain is non-uniform across coupon width due to the relatively large deformation associated with the high curvature. This non-uniform strain distribution can be explained by the stress state transition from the uniaxial tension/compression near the coupon edges to the plane strain tension/compression condition in other regions of the coupon.

During the four-point bending test, the top surface of the coupon exhibits positive normal strain in the longitudinal direction, whereas the bottom surface, which is not visible, experiences negative normal strain. Due to the interlayer constraints, the coupon is subjected to a state close to the plane strain tension/compression state during the test. However, as contraction of the upper layers (under longitudinal tension) and expansion of the lower layers (under longitudinal compression) accumulate, the coupon undergoes not only bending about the axis parallel to the width coupon direction but also bending about the

axis parallel to the longitudinal coupon direction. This additional curvature (upward lifting of the coupon's top-surface edges), driven by the accumulation of varying width-direction strains across the thickness under relatively large plastic deformation, is more clearly observed in the $+45^\circ/-45^\circ$ direction coupons as shown in Figure 17.

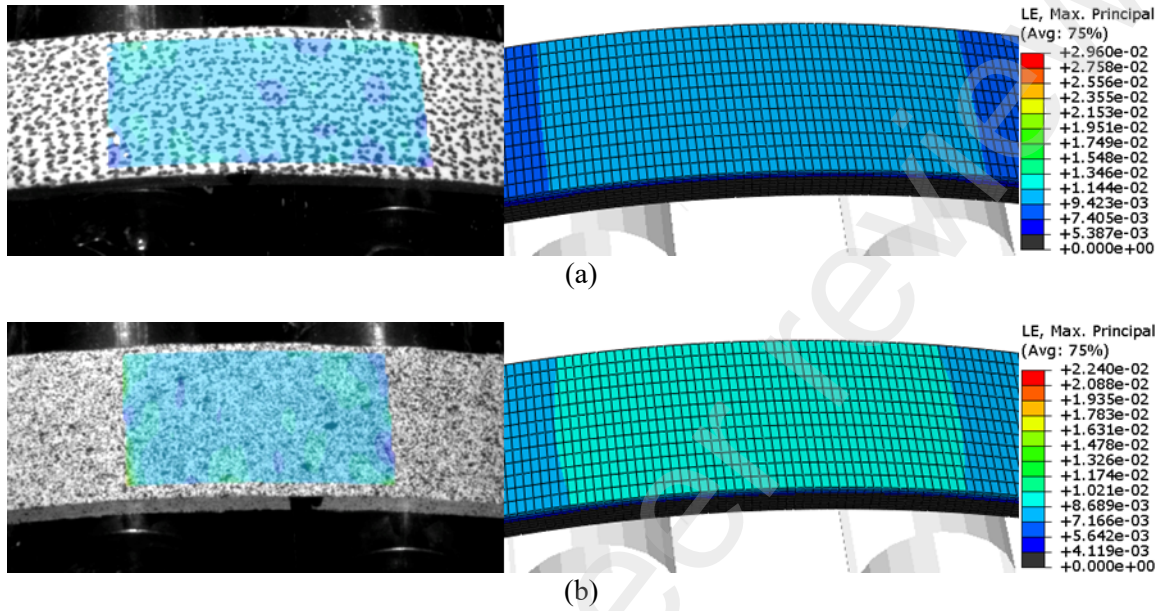


Figure 16. Comparison of the distribution of maximum principal strain at a displacement of 7.2 mm during the four-point bending test between the experiments (left) and the FE simulations (right) for the $0^\circ/90^\circ$ direction samples: (a) Run 2-F and (b) Run 4-B.

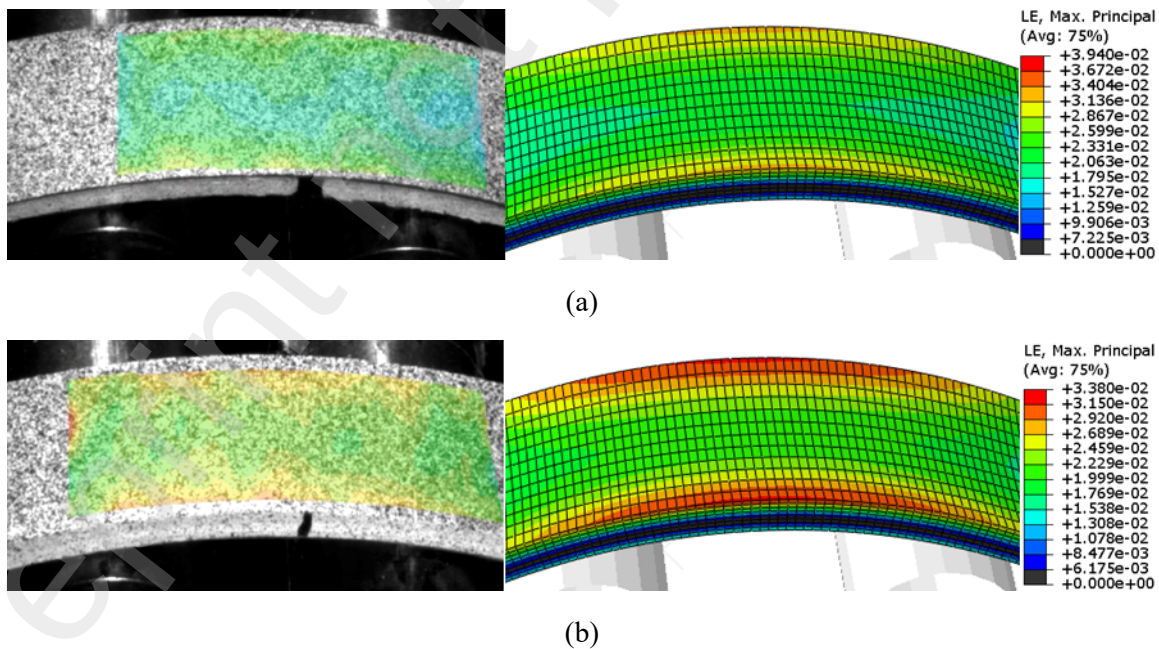


Figure 17. Comparison of the distribution of maximum principal strain at a displacement of 17.6 mm during the four-point bending test between the experiments (left) and the FE simulations (right) for the +45°/-45° direction samples: (a) Run 2-C and (b) Run 3-D.

7. Conclusion

This study is focused on developing an anisotropic thermomechanical model that incorporates the effect of cooling rate on mechanical behavior. In the proposed methodology, initial material characterization involved analyzing coupon-level properties of 'as-fabricated' CF-PA6 composite to explore anisotropy and temperature dependencies. Subsequently, further material characterization was carried out to examine the impact of varying cooling rates on degree of crystallinity χ_c and mechanical properties of the CF-PA6 composite. It was observed that decrease in the cooling rate resulted in increase in the degree of crystallinity and consequently the Young's modulus and yield strength for the +45°/-45° orientation coupons since the matrix response plays a crucial role for that orientation. However, the increase in degree of crystallinity (~21 %) and increase in Young's modulus (~40 %) and yield strength (~12 %) was not linearly proportional. Poisson's ratio and ultimate tensile strength exhibited no significant change.

Based on the characterized mechanical properties, a phenomenological anisotropic thermomechanical model was calibrated. Then, the Avrami transition was implemented to capture the cooling rate effects on material properties. It was assumed that thermal history does not affect the properties in 0°/90° orientation (fiber directions) while the cooling rate effect is the most significant in the +45°/-45° orientation since the influence of the PA6 matrix is dominant. Finally, the calibrated homogenization-based constitutive model, which accounts for the effects of cooling rate, resulting crystallinity, and temperature dependence, was validated by conducting four-point bending tests. The simulation results showed good agreement with the experimental force-displacement curves and principal strain distributions across coupons exhibiting various thicknesses and crystallinity levels induced by different cooling rates, thereby demonstrating the reliability of the proposed model.

It is also worth noting that the cooling rate experienced in the vicinity of T_{rc} is of high importance and can vary based on the temperature field in the heated FRTPC blank during forming and the temperature of the tool before and during forming. This cooling rate can vary significantly based on process conditions and is thus of consequence when aimed to establish the effect on microstructure and subsequent mechanical properties. From this study, we can conclude that cooling rate effects are prominent for complex loading conditions where fibers are not aligned with the loading direction. This is evident from the significant difference observed in the mechanical response of coupons oriented at +45°/-45°, subject to various cooling rates in both uniaxial tensile and 4-point bending tests. The findings from this study are relevant in identifying optimal thermoforming process parameters. A slow cooling rate up until the formed part cools to below T_{rc} , followed by a fast- or super-fast cooling rate, can help improve mechanical properties while ensuring fast cycle times. Thus, the mechanical performance of thermoformed fiber-reinforced semi-crystalline thermoplastic composite components can be improved under complex and varied loading conditions.

Future research will focus on extending the constitutive model by introducing an asymmetric yield function to account for the tension-compression asymmetry of fiber-reinforced composites, as well as

incorporating strain rate- and time-dependent mechanical behavior. These enhancements will enable the application of the computational modeling framework to the thermoforming analysis of parts with more complex geometries and general thermal histories.

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Appendix A

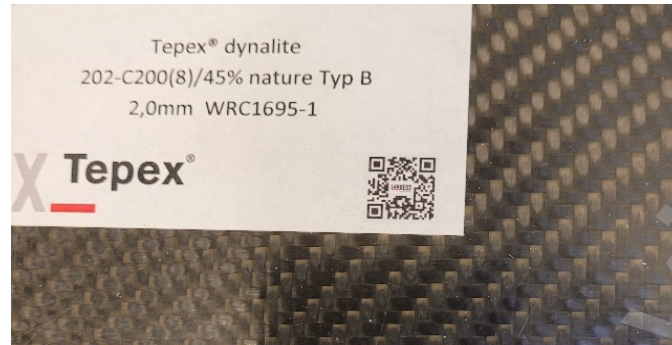


Figure A. 1. Bidirectional 2x2 twill weave continuous CF-PA6 laminate used for this study

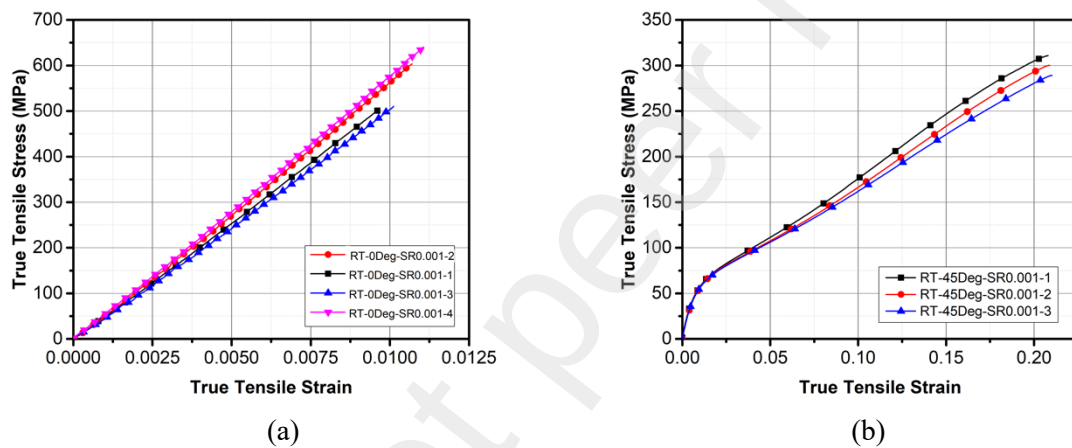


Figure A. 2. Stress-strain curves for CF-PA6 coupons under uniaxial tension (RT, 0.001/s strain rate) obtained using 3D DIC for (a) 0°/90° and; (b) +45°/-45° orientations utilized for calculation of averaged engineering stress -strain curves reported in Figure 8.

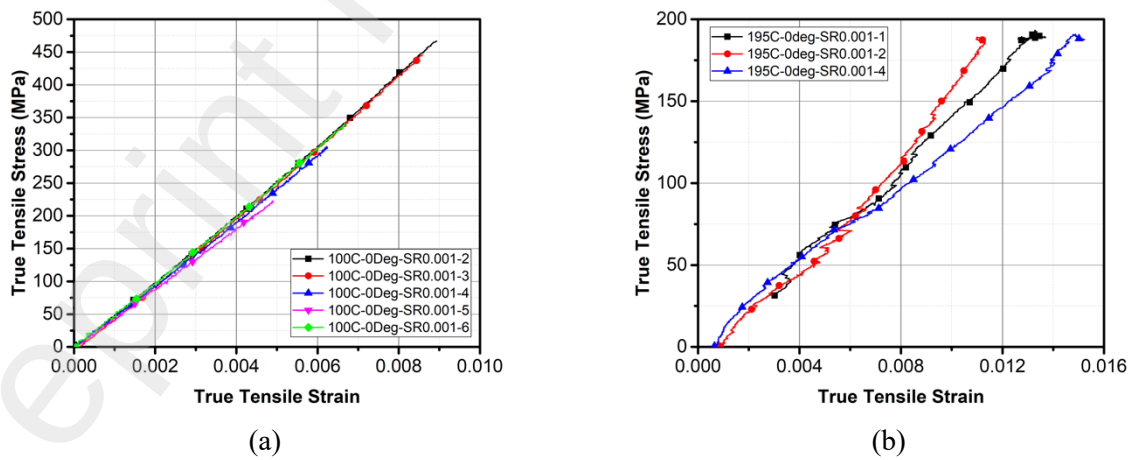


Figure A. 3. Stress-strain curves for CF-PA6 coupons under uniaxial tension (varying temperature, 0.001/s strain rate) obtained using 3D DIC for 0°/90° orientation for (a) 100 °C and (b) 195 °C, utilized for calculation of averaged engineering stress -strain curves reported in Figure 8b.

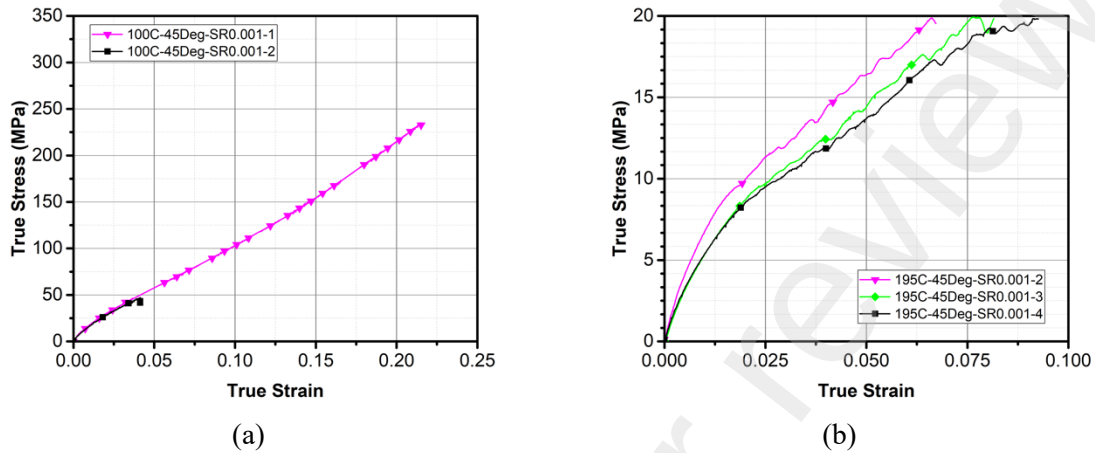
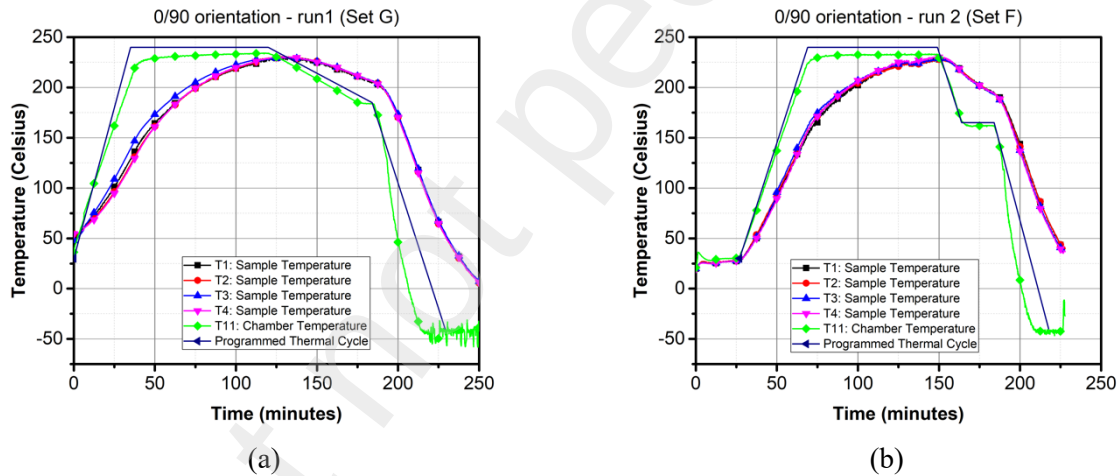
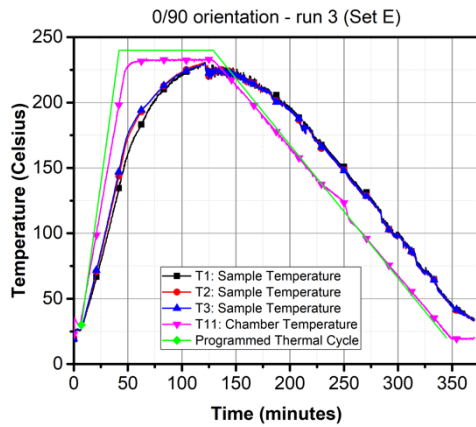
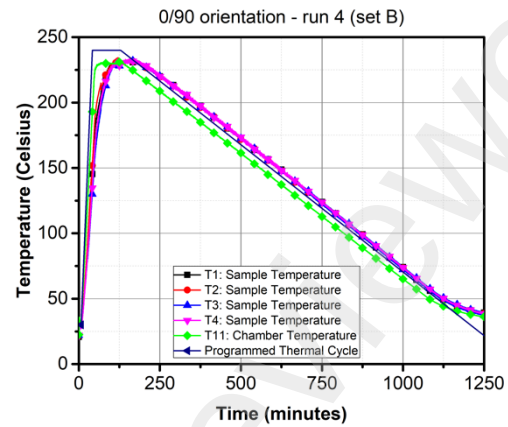


Figure A. 4. Stress-strain curves for CF-PA6 coupons under uniaxial tension (varying temperature, 0.001/s strain rate) obtained using 3D DIC for +45°/-45° orientation for (a) 100 °C and (b) 195 °C, utilized for calculation of averaged engineering stress - strain curves reported in Figure 8c.



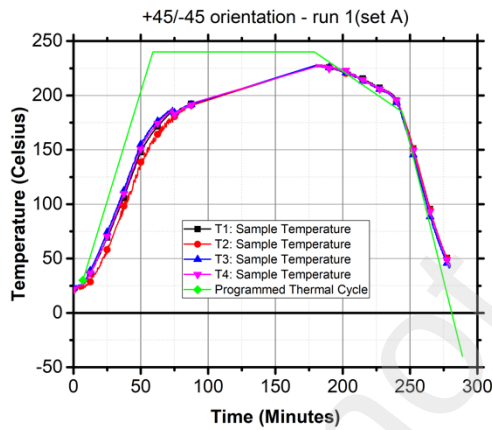


(c)

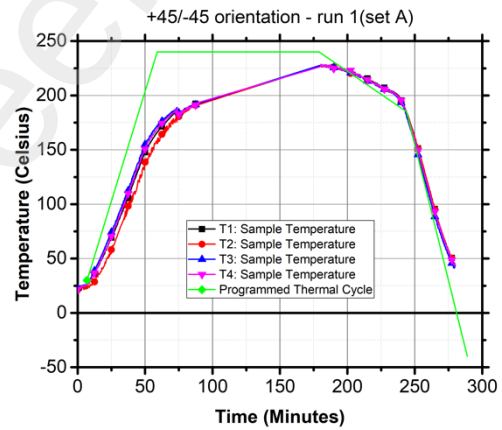


(d)

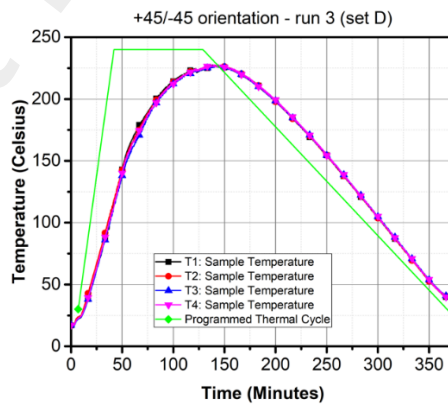
Figure A. 5. Thermal cycles with non-constant cooling rates for (a) run 1 (set G) with $0^\circ/90^\circ$ orientation; (b) run 2 (set F) with $0^\circ/90^\circ$ orientation; (c) run 3 (set E) with $0^\circ/90^\circ$ orientation and (d) run 4 (set B) with $0^\circ/90^\circ$ orientation, as summarized in Table 2.



(a)



(b)



(c)

Figure A. 6. Thermal cycles with non-constant cooling rates for (a) run 1 (set A) with $+45^\circ/-45^\circ$ orientation; (b) run 2 (set C) with $+45^\circ/-45^\circ$ orientation; (c) run 3 (set D) with $+45^\circ/-45^\circ$ orientation, as summarized in Table 2.

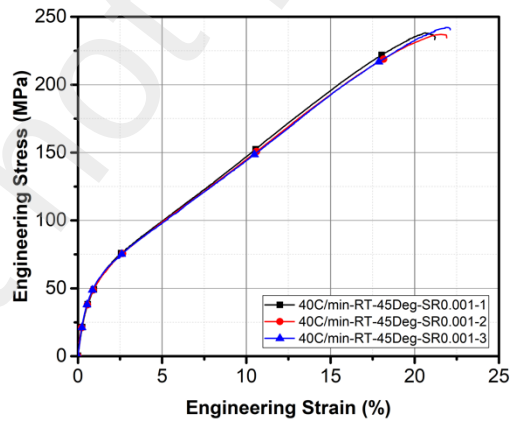
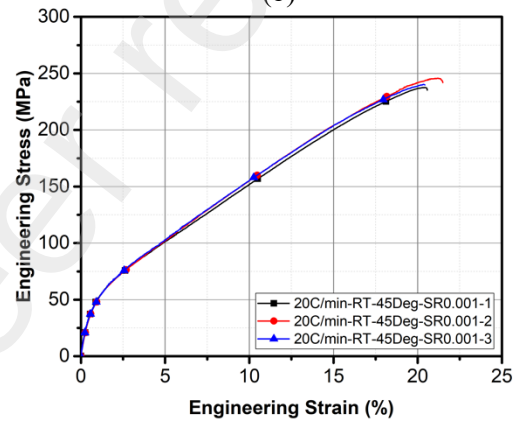
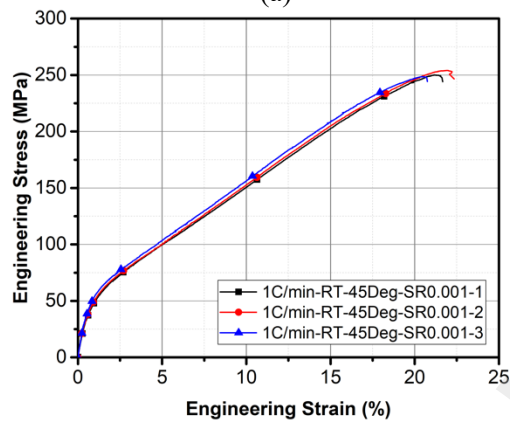
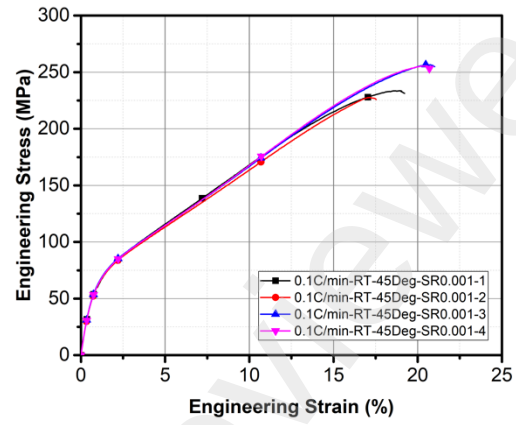
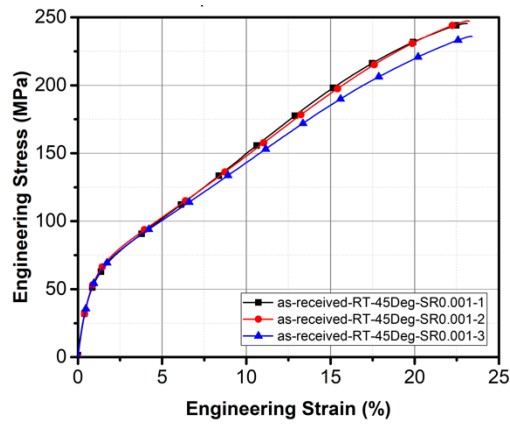
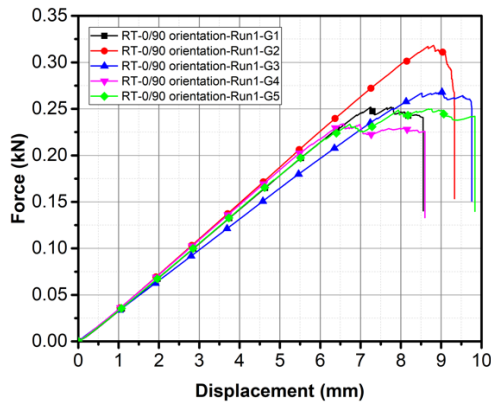
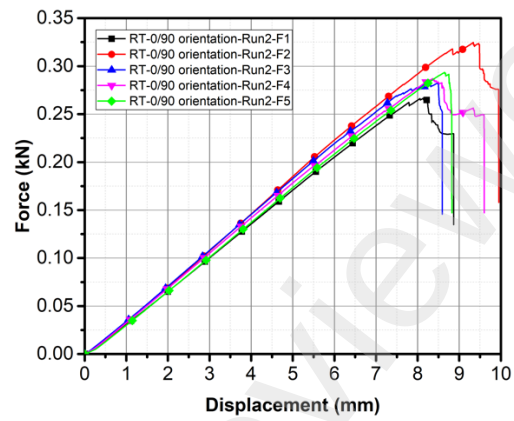


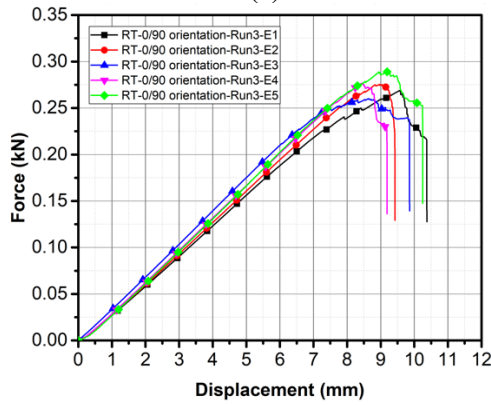
Figure A. 7. Engineering stress-strain curves for CF-PA6 coupons under uniaxial tension (room temperature, 0.001/s strain rate) obtained using 3D DIC for +45°/-45° orientation for (a) as-received; (b) 0.1 °C/min cooling rate; (c) 1 °C/min cooling rate; (d) 20 °C/min cooling rate and (e) 40 °C/min cooling rate, utilized for calculation of averaged engineering stress -strain curves reported in Figure 9b.



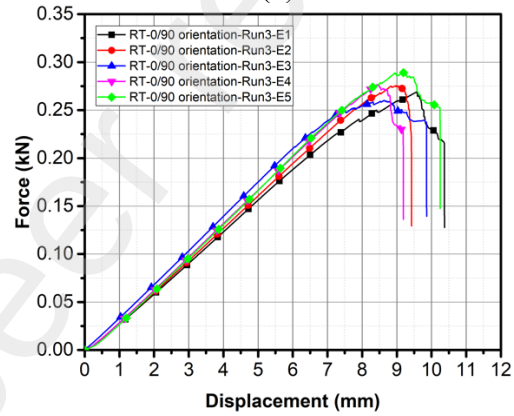
(a)



(b)

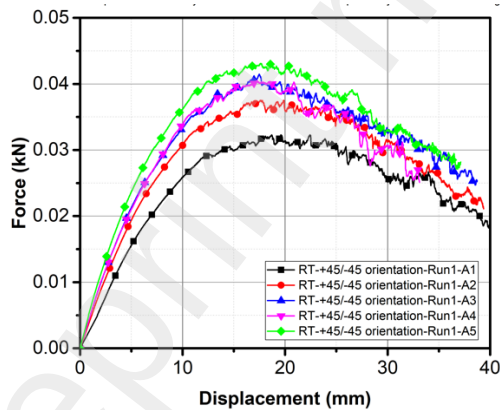


(c)

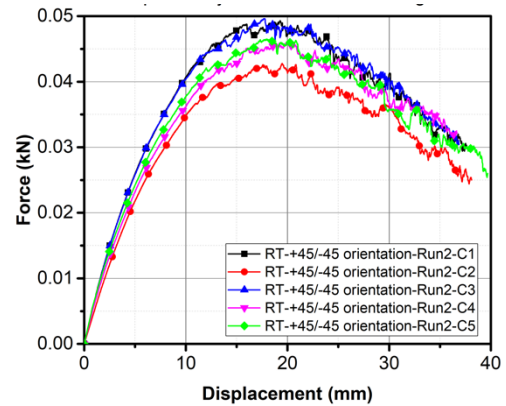


(d)

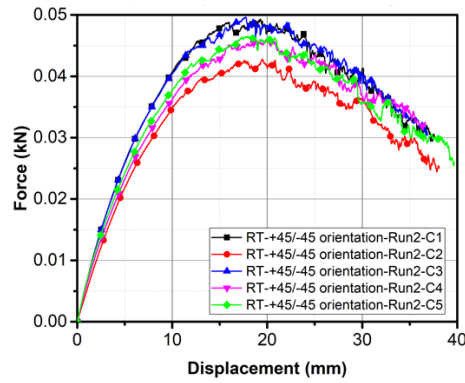
Figure A. 8. Force versus displacement curves representing the flexural response of coupons subject to 4-point bending test for (a) $0^\circ/90^\circ$ samples subject to run 1 thermal cycle; (b) $0^\circ/90^\circ$ samples subject to run 2 thermal cycle, (c) $0^\circ/90^\circ$ samples subject to run 3 thermal cycle, (d) $0^\circ/90^\circ$ samples subject to run 4 thermal cycle, as shown in Table 2 and Figure A. 5.



(a)



(b)



(c)

Figure A. 9. Force versus displacement curves representing the flexural response of coupons subject to 4-point bending test for (a) +45°/-45° samples subject to run 1 thermal cycle; (b) +45°/-45° samples subject to run 2 thermal cycle, (c) +45°/-45° samples subject to run 3 thermal cycle, (d) +45°/-45° samples subject to run 4 thermal cycle, as shown in Table 2 and Figure A. 6.