



Thermoplastic prepreg with partially polymerized matrix: Material and process development for efficient part manufacturing

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Abstract: Extensive use of thermoplastic composites has been restricted by processing challenges emerging from high melt viscosities. We demonstrate the feasibility of thermoplastic prepreg with partially polymerized poly(methylmethacrylate) (PMMA) matrix and carbon fiber reinforcement. The low viscosity pre-polymer resin allowed part consolidation at low temperature and pressure. The chemical kinetics and rheology of PMMA polymerization were characterized, and an aging study was conducted to assess pre-polymer stability. Prepregs were fabricated using lab-scale methods, and a fabrication map was constructed to determine the optimal extent of polymerization for the prepreg. The prepregs were tested for tack and drape at ambient temperature, and thermoformed for microstructural and chemical analysis. The results show that auto-acceleration drives both the rate of polymerization and viscosity evolution, while refrigeration delays pre-polymer out-time effects. The thermoformed laminates exhibited near-zero porosity. This work establishes material and process development guidelines for reactive thermoplastic prepreg, and highlights potential advantages of the proposed prepreg.

1. INTRODUCTION

Continuous fiber reinforced thermoplastics (CFRTPs) are less technically mature and less widely used than thermoset composites [1]. However, interest in CFRTPs has grown rapidly



across multiple industries, including automotive, aerospace, and sporting goods, because of intrinsic advantages over thermoset counterparts [2–5]. For one, thermoplastics are inherently tougher and less brittle than thermosets, resulting in composites with greater impact resistance [6]. Most CFRTP product forms have unlimited shelf-life, because the matrices are fully polymerized before part consolidation, allowing room temperature storage [7]. Melt processing of thermoplastic composites consists of imposing only physical changes to the matrix (melting and solidifying), rather than time-consuming chemical reactions. Hence, production cycle times for CFRTPs can be much shorter than those for thermoset composites [6,8]. Finally, thermoplastic matrices can be re-processed and re-formed upon heating, which allows CFRTPs to be recycled [9] and welded [8,10,11].

Despite these advantages, melt processing of CFRTP retains one critical challenge. The manufacture of CFRTP structural parts with competitive mechanical and physical properties requires the thermoplastic matrix to possess high molecular weight prior to processing, which increases both the melt viscosity and the melting temperature of the matrix [12–14]. To ensure proper impregnation of fiber beds and void removal, high-performance CFRTP parts must therefore be processed at high pressure and temperature [3,6]. Typically, the processing temperature of CFRTP must exceed the melting (for semi-crystalline polymers) or glass transition (for amorphous polymers) temperatures of the matrix to supply the polymer chains with enough energy for sufficient matrix flow [3,10,15]. Consequently, costly investments in infrastructure and operations are required for CFRTP melt processing [8,16].

Recently, reactive resin transfer molding of CFRTP has been developed as an alternative to melt processing [5,6,17]. During reactive liquid molding, low viscosity polymeric precursor (monomer or prepolymer) is injected into the tool instead of fully polymerized high viscosity thermoplastic melt, thereby facilitating complete saturation of the fiber preform. Subsequently, the precursor is polymerized *in situ* in the mold. This process eliminates the need



for high processing temperature and pressure, because the low viscosity pre-polymer can readily impregnate the fiber bed [6,16]. In addition, the processing temperature of reactive CF RTP processing is typically less than that of melt processing, because the temperature required to polymerize the resin is generally less than the melting temperature of the resulting polymer [6,18]. Engineering thermoplastics with well-developed reactive liquid molding schemes include polyamide 6 [16–19], polyamide 12 [4,14,20,21], poly(butylene terephthalate) [5,13], and poly (methyl methacrylate) (PMMA) [22,23]. However, the thermoplastic species that can be liquid molded are limited by the crucial constraints imposed by the nature of *in situ* polymerization and liquid molding itself [4,5,13].

Here, we investigate and demonstrate the feasibility of reactive processing of CF RTP prepregs. A conventional thermoplastic prepreg includes a fully polymerized matrix prior to part consolidation, whereas resin in a typical thermoset prepreg is B-staged (partially cured) to facilitate prepreg handling and prevent excessive resin flow during part consolidation. Fully polymerized CF RTP prepregs can be stored indefinitely at ambient conditions, but consolidation normally requires high processing temperature and pressure. Moreover, CF RTP prepregs lack tack and drapability at room temperature, both of which are important material characteristics. To address these issues, we fabricated a *thermoplastic prepreg with partially polymerized matrix* by fully impregnating plies of carbon fiber reinforcement with low viscosity monomer (methyl methacrylate, MMA), then polymerizing the resin to an intermediate molecular mass state. The objective of this case study was to create a CF RTP prepreg that not only provides tack and drape at room temperature (for greater conformability), but also facilitates resin flow during consolidation below the final glass transition temperature of the amorphous PMMA thermoplastic matrix. PMMA was used in this study as a technical pathfinder to identify opportunities and challenges associated with reactive processing of thermoplastic prepregs.



First, the chemical kinetics and rheology of neat PMMA polymerization were examined using differential scanning calorimetry (DSC) and rheometry. The aging of PMMA pre-polymer was investigated for three different storage temperatures to gain insights into the effects of out-time accrual and of refrigeration on pre-polymer resin aging. Two-ply PMMA pre-polymer prepreg laminates were fabricated to construct a fabrication map to determine the optimal extent of polymerization and monomer/fabric weight ratio for the prepreg. The prepreps were evaluated for tack and drape at ambient temperature, and thermoformed at low pressure, below the final glass transition temperature of PMMA, for porosity analysis. The chemical composition of the final matrix of the consolidated laminate was analyzed using Fourier-transform infrared spectroscopy (FTIR). To address scale-up challenges, an eight-ply prepreg laminate was produced and thermoformed for microstructural analysis. Finally, a conventional thermoplastic prepreg with fully polymerized matrix was also fabricated to explore matrix flow under various thermoforming conditions and to demonstrate that forming of conventional CF RTP prepreg comprised of the same material is substantially more resource-intensive.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate (MMA) monomer and benzoyl peroxide freeradical initiator (Luperox® A98, Sigma-Aldrich) were acquired. Under ambient conditions, MMA is a colorless transparent liquid with low viscosity (0.53 mPa·s) and 100 °C boiling point [24]. For both polymerization characterization and prepreg laminate fabrication, 3.0 wt% of benzoyl peroxide was dissolved in MMA, and the resulting monomer/initiator mixture was stored under refrigeration (4 °C) to prevent polymerization of the material before application. For the



prepreg reinforcement, a plain weave carbon fiber fabric with an areal weight of 193 g/m² and 3000 fiber/tow count was obtained (part#1530, Fibre Glast).

2.2. Polymerization & resin characterization

2.2.1. Modulated differential scanning calorimetry (MDSC)

The reaction kinetics of PMMA polymerization was characterized using DSC (TA Instruments, Q2000) under nitrogen purge (50 cm³/min). Monomer samples (7–10 mg) were sealed in aluminum hermetic pans with lids and exposed to an isothermal dwell at four different temperatures (60, 70, 80, and 90°C) for prescribed durations (1–4 h). The samples were subsequently heated to 200°C at 2°C/min to measure the remaining heat of polymerization and determine the amount of residual monomer. For the ramping step, sinusoidal temperature modulation of ± 0.5 °C/min was applied over the linear temperature ramp to distinguish reversing and non-reversing heat flow signals. Reversing heat flow is related to heat capacity and rate of temperature change, while non-reversing heat flow depends on kinetic components of the reaction [25–27]. Glass transition is a heating rate dependent transition and can be examined from the reversing heat flow signal, while polymerization is a temperature dependent transition and thus appears in the non-reversing signal [25,27].

2.2.2. Rheometry

The viscosity evolution during PMMA bulk polymerization was measured using a rheometer (TA Instruments, AR2000ex), equipped with a Peltier plate and cone-and-plate fixture (cone angle 2:0:5, cone diameter 40 mm, and truncation 53 μ m). The cone-and-plate geometry, which provides uniform shear rate and high rheological accuracy, was selected because the viscosity profile of PMMA polymerization was expected to span a wide range, from low viscosity monomer to high viscosity polymer. A solvent trap cover was used to suppress evaporation of the highly volatile MMA monomer. To confine enough MMA at the center of the Peltier plate



without leakage, a circular side wall was fabricated with silicone vacuum bag sealant (A-800, General Sealants). For the rheology test, cell temperature was increased from room temperature to 90 °C at approximately 32.5 °C/min (the maximum ramp rate of the rheometer) and held constant for 1 h, under oscillatory shear at 1 Hz frequency and 0.01% strain (within the linear viscoelastic region).

2.2.3. Pre-polymer aging study

PMMA pre-polymer resin samples of known initial degree of monomer conversion were prepared by reacting MMA monomer at 90 °C for 10 min using DSC. The samples were then removed from the DSC and stored at three different temperatures: 25 °C, 4 °C, and –18 °C. For each storage temperature, the samples were aged for 1, 2, 4, 8, 12 h and 1, 2, 7, 14, 28 days. Once aging was complete, each sample was placed back in the DSC and heated to 220 °C at 2 °C/min to determine the extent of additional polymerization accrued during aging. All samples were weighed before and after aging to confirm that no weight loss had occurred. The purpose of this study was to monitor accrual of pre-polymer resin out-time and determine if refrigeration is required to prevent or delay PMMA pre-polymer aging.

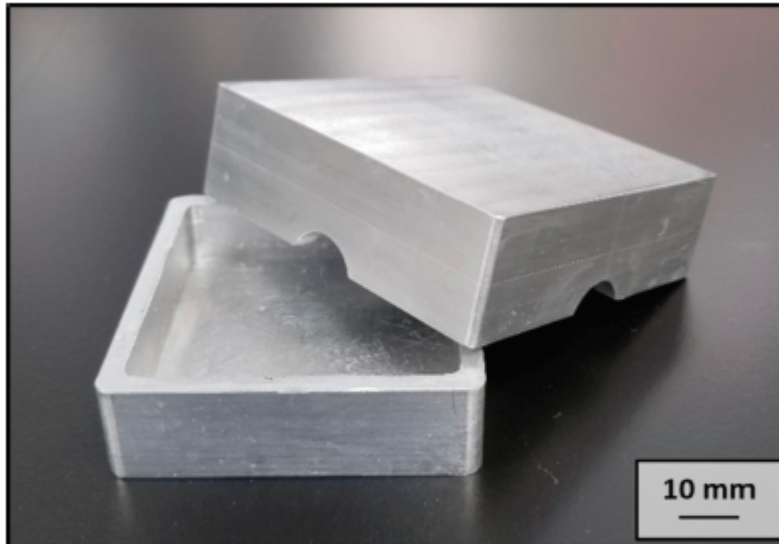
2.3. Prepreg laminate fabrication & characterization

2.3.1. Prepreg laminate fabrication

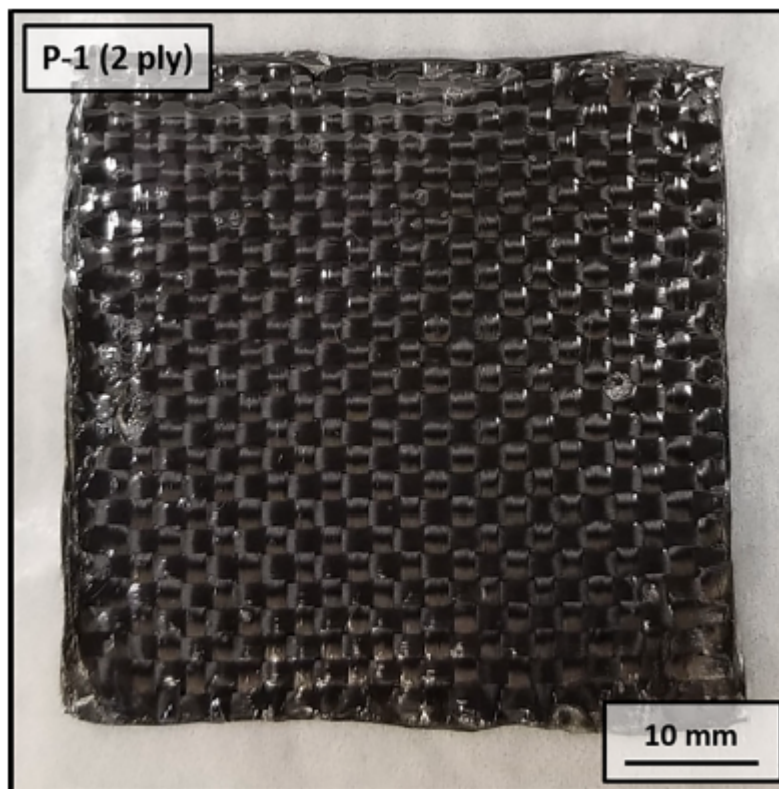
For prepreg fabrication, an aluminum tool (50mm×50 mm) consisting of top cover and bottom container was designed (Figure 1a). The top cover was intended to prevent excessive monomer vaporization at elevated temperature during pre-polymerization. Mold release agent (20–8185, Buehler) was first applied to the tool interior and allowed to dry for 5 min. Then, the mold was preheated to 90 °C using a hot plate, and two plies of carbon fiber fabric were placed in the tool with the bottom side covered by non-perforated release film (A4000, Airtech). For this study, two-ply prepreg laminates were assembled to facilitate handling of thin samples. Once the tool temperature reached 90 °C, a known amount of MMA was injected into the tool using



a pipette, based on initial trials, and the top surface of the fabric was immediately enclosed by another ply of release film. The low viscosity of MMA ensured complete saturation of the fabric, which could be readily observed. Then, the polymerization proceeded for a prescribed amount of time, determined from DSC and rheology analysis, yielding a partially polymerized



(a)



(b)



Figure 1. (a) Aluminum tool for prepreg laminate fabrication (top cover & bottom container), and (b) sample two-ply PMMA pre-polymer prepreg laminate (P-1).

Table 1. Test matrix for two-ply PMMA pre-polymer prepreg laminate fabrication

Sample	Monomer/fabric weight ratio	Polymerization time
1	4.7	15 min
2		16 min
3	5.2	12 min
4		13 min
5		14 min
6		15 min
7		15.5 min
8		16 min
9		16.5 min
10	5.6	15 min
11		15.5 min
12		16 min

prepreg laminate. The test matrix is shown in Table 1. Using similar fabrication methods, an eight-ply prepreg laminate was also fabricated to explore the possibility that the approach could be scaled up. Eight plies of carbon fiber fabric were fully impregnated by MMA, which was partially polymerized to a pre-polymer state. An image of a sample two-ply partially polymerized prepreg (P-1) is shown in Figure 1b. The proposed processing technique can be used to fabricate both single and multi-ply prepregs depending on the end use. For manufacturing parts with simple geometries, a single multi-ply prepreg laminate can be prepared for easy and fast lay-up. Conversely, for complex-shaped parts that cannot be formed from a single thick prepreg laminate, multiple single-ply prepregs can be produced for lay-up.

2.3.2. Prepreg conformability evaluation

Prepreg tack was measured using a rheometer (TA Instruments, AR2000ex) with parallel-plate geometry. A Peltier plate was used as the bottom plate, and a 25mm disposable disk as the top plate. The prepreg samples of various out-times (from 0 to 60 min, in increments of 10 min) were placed on the bottom plate at ambient temperature, and compressed at 0.10 N/mm² load for 10 s to ensure enough contact time between the samples and the top plate. After equilibration, the top plate was pulled away at 0.1 mm/s, and the sample tack was defined, in



first approximation, as the maximum normal pressure measured by the load cell during top plate retraction [28]. For comparison, the tack of toughened epoxy resin prepreg (CYCOM® 5320-1, Solvay) was also measured. The goal of the tack tests was not to determine the absolute values of tack for the prepreg, but to provide a metric for comparing different prepreg embodiments and tracking with out-time.

To assess the drapability, the prepregs were laid up onto 75° sharp corner mold at room temperature. Two prepreg samples with partially polymerized matrix (D-1 and D-2) and one with fully polymerized matrix (F-1) were prepared. D-1 was draped over the mold right after fabrication, while the D-2 was draped after 1 h out-time. The objective of the drape evaluation was to compare the room temperature pliability and drapability of partially polymerized prepreg to that of a fully polymerized one.

2.4. Laminate thermoforming & analysis

The two-ply and eight-ply PMMA pre-polymer prepreg laminates were thermoformed with hydraulic press (Genesis G30, Wabash) at 90°C and 0.38 MPa for 5 min. For microstructural analysis, the center of each laminate was sectioned, encapsulated with epoxy mounting resin, and ground and polished. Images of each cross-section were recorded using a digital stereo microscope (VHX-5000, Keyence).

The chemical composition of the matrix of the thermoformed laminate was investigated with Fourier-transform infrared spectroscopy (FTIR, Thermo Electron, Nicolet 4700). The collected FTIR spectrum of the final matrix was interpreted and compared to PMMA reference IR spectra [29–32] to demonstrate clean polymerization of PMMA resin throughout the prepreg fabrication and thermoforming.

2.5. Fully polymerized prepreg laminate

To fabricate a fully polymerized prepreg laminate for control, two plies of carbon fiber fabric were fully impregnated with MMA, then polymerized *in situ* at 90 °C for 30 min. The prepared



prepreg (F-1) was thermoformed multiple times using a hot press at different temperatures (90, 150, and 200 °C) under 0.38 MPa for 5 min, and once more at 200 °C with tenfold increase in pressure (3.8 MPa) for longer duration (15 min). The processing temperatures were chosen with respect to the final glass transition temperature of PMMA (115 °C) and typical forming

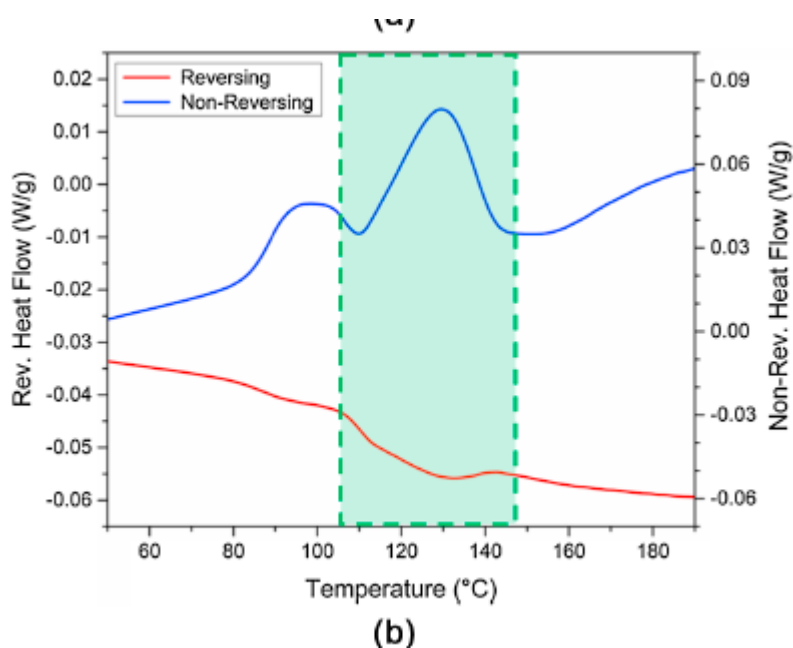
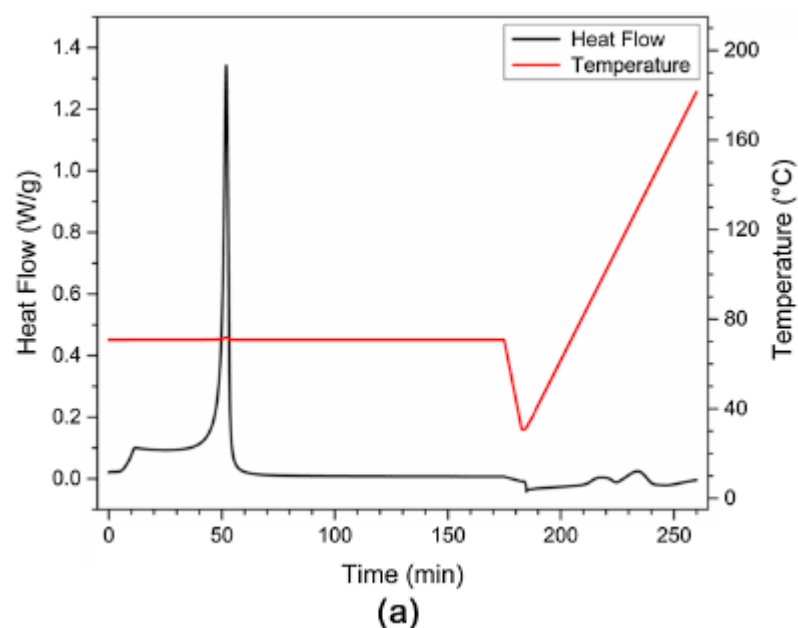


Figure 2. MDSC data showing (a) heat flow & temperature profiles during the isothermal dwell (70 °C) and dynamic ramp steps of MMA free-radical bulk polymerization, and (b) reversing & non-reversing heat flow profiles during the dynamic ramp step. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



temperature of conventional PMMA prepreg (200 °C).

3. RESULTS & DISCUSSION

3.1. Polymerization & resin characterization

3.1.1. Chemical kinetics

Figure 2a shows representative MDSC data of heat flow and temperature profiles during MMA free-radical bulk polymerization at 70 °C. Under the isothermal dwell, MMA polymerization first went through a brief induction period, after which the rate of polymerization slightly decreased until it reached a minimum, as anticipated by the classical free-radical polymerization theory [33,34]. After this local minimum, the polymerization rate deviated from the classical theory by rapidly accelerating and then decelerating until the polymerization attained completion. This auto-acceleration phenomenon is known as the Trommsdorff effect or gel effect [23,34]. As the polymerization progressed, an increase in local resin viscosity led to a rapid drop in termination rate and consequently to a surge in overall polymerization rate [23]. In essence, the produced polymers generated a catalytic effect on the polymerization [33].

During the subsequent dynamic ramp, which was programmed to drive residual monomer to complete polymerization, two overlapping peaks were detected. To identify the peaks, reversing and non-reversing heat flow signals from MDSC were analyzed (Fig. 2b). The glass transition region in the reversing heat flow signal coincided with the second peak of the non-reversing heat flow signal, which was therefore associated with enthalpic relaxation during glass transition. As a result, the first peak corresponded to the heat of residual monomer polymerization.

The DSC data of MMA polymerization were fit to a mathematical kinetics model developed by Jašo et al. [33], which takes into account both classical free-radical polymerization theory and auto-acceleration:



$$X(\tau) = (X_k - a) * (1 - e^{-k_1\tau}) + \frac{a}{1 + e^{-k_2(\tau - \tau_{2max})}} \quad (1)$$

In this model, X (degree of monomer conversion), X_K (final degree of monomer conversion), and τ (time) were obtained from the measured data, while k_1 (reaction rate constant for classical free-radical polymerization), k_2 (rate constant for auto-acceleration reaction), a (fraction of monomer polymerized by auto-acceleration), and τ_{2max} (time at maximum rate of reaction) were calculated using the method of least squares. To calculate the degree of monomer conversion from DSC heat flow data, the following equation was used [33]:

$$X(\tau) = \left(\frac{\int_0^\tau \left(\frac{dH}{d\tau} \right) d\tau}{\int_0^{\tau_k} \left(\frac{dH}{d\tau} \right) d\tau + H_D} \right) \quad (2)$$

where H is the heat evolved during polymerization, τ_k the time at X_K , and H_D the total heat evolved during residual monomer polymerization.

The polymerization temperature of 90°C was of particular interest, being the highest chosen temperature that did not exceed the boiling point of the monomer (100°C at ambient pressure). At this level, the data showed that the final degree of monomer conversion (X_K) was 0.994, and the polymerization essentially ended 19.1 min after the reaction started, when X reached 99% of X_K . Fig. 3a shows the degree of monomer conversion curve and its model fitting for polymerization conducted at 90°C. The values of the calculated fitting parameters are shown in Table 2. Although not presented here, the model yielded similar quality of fit with experimental data at all four polymerization temperatures when appropriate parameters (k_1 , k_2 , a , and τ_{2max}) were determined. Both reaction rate constants, k_1 and k_2 , exhibited strong Arrhenius temperature dependence, where the coefficients of determination (R^2) for the Arrhenius linear regressions were 0.99 and 0.98 respectively.

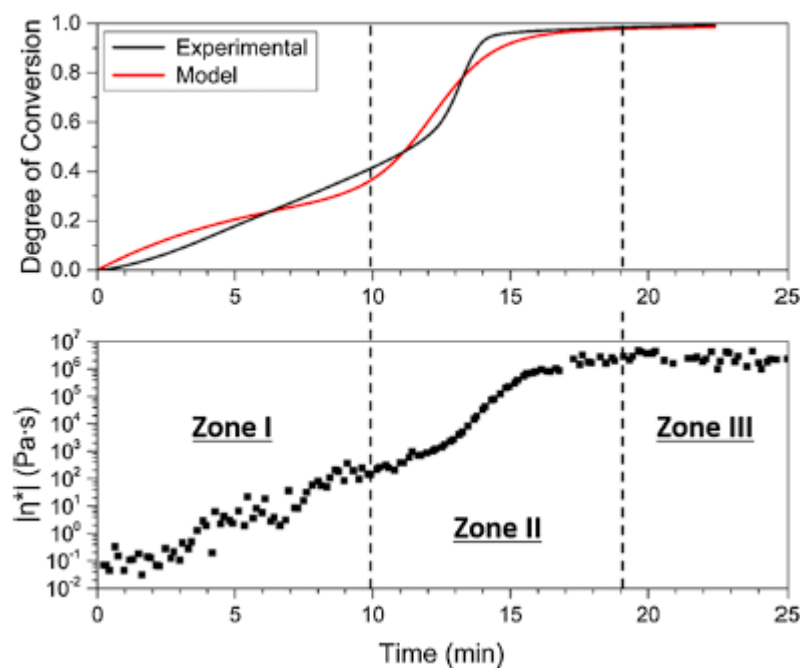


Figure 3. (a) Measured degree of monomer conversion profile and mathematical kinetics model fitting, and (b) viscosity profile of MMA polymerization at 90 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2. Values of the fitting parameters & derivatives for MMA polymerization at 90°C

k_1 (min ⁻¹)	k_2 (min ⁻¹)	a (-)	$X_k - a$ (-)	$\tau_{2\max}$ (min)	Auto-Accel. Onset (min)
0.167	0.911	0.632	0.362	12.2	9.9

3.1.2. Rheology

The viscosity profile for PMMA polymerization at 90 °C was divided into three sections (Figure 3b). The first section (Zone I) corresponded to the first ten minutes of the polymerization, as the initial resin viscosity (~ 0.01 Pa·s) increased linearly on a semi-log scale. In Zone II, which represented the next ten minutes of the reaction, the resin viscosity evolved in a sigmoidal shape. During this phase, the viscosity increased sharply within a short period, driven by the steep rise in the rate of polymerization. In the last region (Zone III), the viscosity curve reached a plateau near 10^6 Pa·s, marking the end of polymerization.

Based on the model fitting using 90°C polymerization DSC data, the onset of auto-acceleration occurred at 9.9 min, which coincided with the viscosity phase transition from Zone



I to Zone II. The correlation indicated that Zone I represented the classical free-radical polymerization phase, while Zone II corresponded to the auto-acceleration reaction step. Moreover, the DSC analysis showed that MMA polymerization was complete at 19.1 min, when the viscosity curve became flat. In short, the degree of monomer conversion and viscosity evolution profiles exhibited similar shapes and trends, especially with respect to the auto-acceleration phenomenon. The similarity indicates that it would be possible to model evolution of PMMA resin viscosity as a function of degree of conversion as well as temperature, analogous to some well-established thermoset cure viscosity models (*e.g.*, Castro-Macosko model [35]).

3.1.3. Pre-Polymer aging study

The degree of monomer conversion of pre-polymer resin samples polymerized at 90°C for 10 min was 0.42. From this state, the samples were aged at room temperature or refrigerated conditions (4 °C or –18 °C) for periods up to 4 weeks. Finally, the aged samples were heated to 220 °C in the DSC to determine the extent of additional polymerization accrued during aging, which was calculated using the following equation:

$$X_{\text{aged}}(\text{fraction of aged resin}) = \frac{H_{r,\text{reference}}(\text{J/g}) - H_{r,\text{aged}}(\text{J/g})}{H_{r,\text{total}}(\text{J/g})} \quad (3)$$

The heat of reaction of the aged pre-polymer resin ($H_{r,\text{aged}}$) was subtracted from that of the unaged reference pre-polymer resin ($H_{r,\text{reference}}$), for which the initial degree of conversion was 0.42 ($H_{r,\text{reference}}$ equal to $0.58 \times H_{r,\text{total}}$). The subtracted value was divided by the total heat of polymerization of PMMA ($H_{r,\text{total}}$) to determine X_{Aged} . The underlying assumption here was that the degree of conversion was expected to increase as a function of aging time. The data obtained during the aging study are shown in Fig. 4.

The resin samples stored at ambient temperature exhibited rapid aging. The degree of monomer conversion reached 0.86 after 1 day, advancing toward 0.91 and 0.93 after 1 and 4 weeks of



aging respectively, leaving little room for further polymerization. In contrast, the samples stored at -18°C (or 0°F , the recommended storage temperature for typical thermoset prepregs) showed much slower aging. The degree of conversion remained below 0.48 after 1 week and 0.57 after 4 weeks, indicating that less than 15% of the pre-polymer resin aged at this temperature. Storing at 4°C seemed to delay polymerization for the first few days, but the degrees of conversion after 1 week eventually approached those of the samples stored at room temperature. The results of the aging study demonstrate that refrigeration at -18°C effectively delays out-time accrual of PMMA pre-polymer resin, but also indicate that this case study material is not as shelf-stable as commercial fully polymerized CFRTP prepregs.

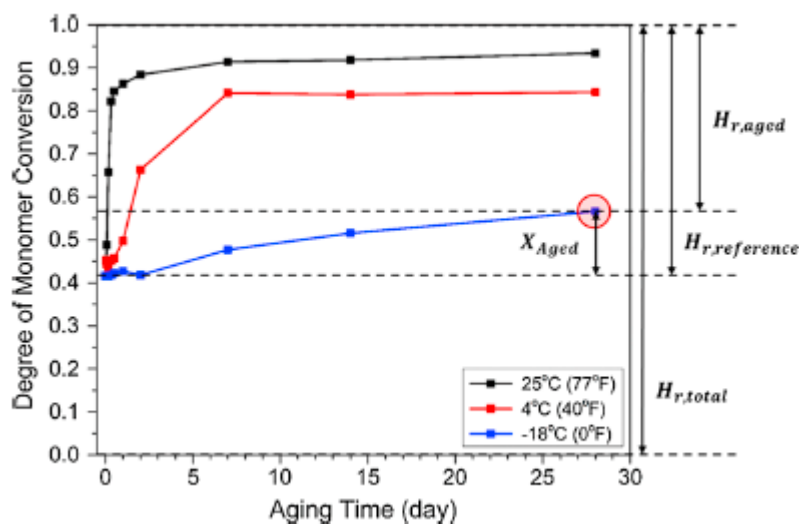


Figure 4. Degree of monomer conversion profiles as a function of aging time for three different storage temperatures, with sample X_{Aged} calculation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Prepreg laminate fabrication & characterization

3.2.1. Prepreg laminate fabrication

After examining polymerization kinetics and pre-polymer aging, prepreg laminates with partially polymerized matrix were fabricated using lab-scale methods. One technical challenge arose during fabrication: control of pre-polymer resin content through selection of an appropriate monomer/fabric weight ratio and pre-polymerization time (in the presence of

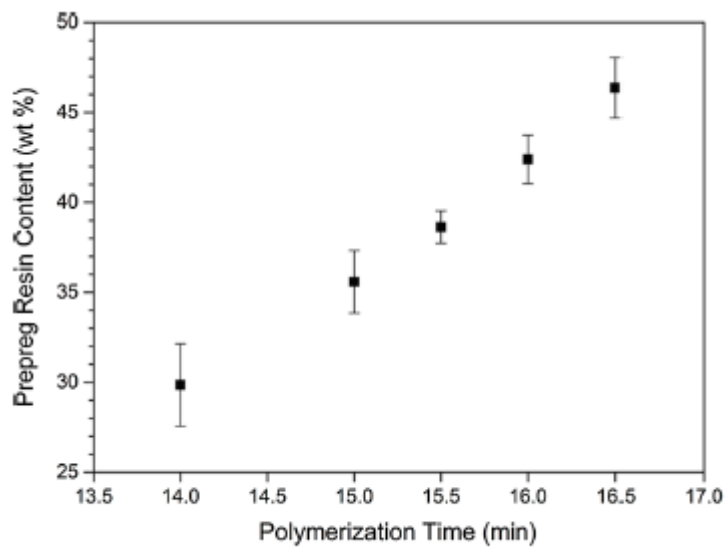


monomer vaporization and bleed). Applying the insights gained from analysis of the chemical kinetics and rheology, we predicted that polymerizing the resin to the onset of auto-acceleration would yield an extent of polymerization acceptable for initial prepreg fabrication trials. This point, obtained from model fitting with DSC data, served as an acceleration onset for both degree of monomer conversion and resin viscosity. When early fabrication attempts near the onset did not produce sufficient conversion and resin viscosity for the model prepreg, the pre-polymerization time was gradually advanced for subsequent trials. The kinetics and rheology analysis permitted analytical prediction of the pre-polymerization time for prepreg fabrication at 90 °C, as well as at other reaction temperatures. For instance, at 80 °C, the polymerization kinetics model indicated that the onset of auto-acceleration occurred at 24.1 min, and hence that initial prepreg fabrication trials should be conducted after 24.1 min of prepolymerization.

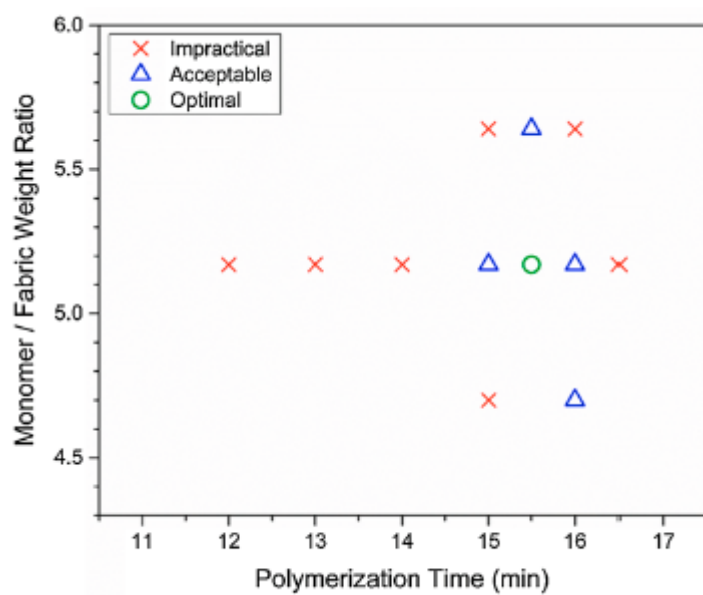
Figure 5a shows the final resin contents of two-ply prepreg laminates with varying polymerization times at 90 °C, where the monomer/fabric ratio was 5.2, a value determined from initial trials. With increasing reaction time, the degree of conversion and resin viscosity increased as well, leading to greater amounts of resin retained on the prepreg. Based on the target resin content for the proposed prepreg, which was 38–42 wt%, an experimental prepreg fabrication map at 90 °C was constructed (Fig. 5b) to determine the optimal resin polymerization time and monomer/fabric weight ratio for the two-ply prepreg laminate. On the map, the samples on the red points were deemed impractical because they resulted in either too little or too much resin. Samples on the blue triangles were acceptable, and a single optimal fabrication point was eventually determined, represented by the green circle near the center. At this point, the monomer/fabric weight ratio was 5.2, and the polymerization time was 15.5 min. Higher or lower weight ratios resulted in excess or insufficient resin, respectively. When the reaction time was less than 15 min, the resin viscosity was unacceptably low, and too much



resin was lost while handling the prepreg. For reaction times exceeding 16 min, the prepolymer resin was excessively converted, reducing the benefits of reactive processing.



(a)



(b)

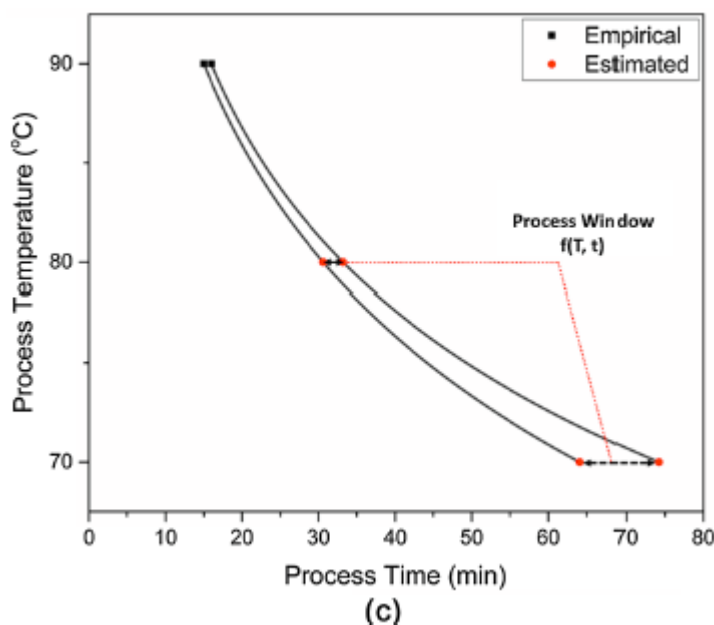


Figure 5. (a) Final resin contents of two-ply prepreg laminates with varying polymerization times at 90°C, (b) experimental prepreg fabrication map at 90°C for two-ply prepreg laminate, and (c) temperature and time dependent prepreg process map, showing empirical (90°C) and estimated (70 & 80°C) process windows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The chemical kinetics model (Eq. (1)) can be used to predict degree of monomer conversion (X) as a function of reaction time at a given polymerization temperature. Using this model and prepreg fabrication trial results at 90°C (Figure 5b), approximate process time windows at other reaction temperatures can be predicted as well. At 80°C, for instance, the time required to achieve the same degree of conversion obtained at 90°C during 15 and 16 min of reaction is expected to be between 30 and 33 min. Under the assumption that the ideal initial monomer/fabric weight ratio of 5.2 does not vary greatly with respect to temperature, a prepreg process map that depends both on temperature and time was constructed to show empirical (90°C) and estimated (70 & 80°C) fabrication time windows (Figure 5c). These results, along with the onset of auto-acceleration data, can provide reasonable time frames for initial prepreg fabrication trials at different temperatures. The optimal processing time span widens with decreasing polymerization temperature as X increases more slowly. Therefore, degree of conversion and thus viscosity of pre-polymer resin can be more precisely controlled at lower



temperatures. On the other hand, as reaction temperature rises, the required polymerization time becomes much shorter, while controlling X becomes significantly more challenging.

The methodology employed here for material characterization and process development of PMMA pre-polymer prepreg, can similarly be applied to design other reactive CFRTTP prepregs (Figure 6). For a given prepreg system, kinetics and viscosity evolution models for thermoplastic polymerization can be used to predict an extent of polymerization acceptable for initial prepreg fabrication trials, and to establish a pre-polymerization temperature profile for materials that require complex reaction schemes. Finally, a prepreg fabrication map can be constructed to identify suitable fabrication conditions for the prepreg.

3.2.2. Prepreg tack characterization

To evaluate tack, we investigated the normal force required to detach the top plate of the rheometer from the prepreg sample at ambient temperature. Tack tests yielded force-per-area peaks (Fig. 7a), where the normal pressure returned to zero level within 1–2 s at the given retraction speed. The evolution of normal force indicated that the prepreg failed adhesively [28]. On the other hand, epoxy prepreg (CYCOM® 5320-1) exhibited more of a cohesive failure, where the normal pressure decreased gradually over a longer period upon hitting the apex. The maximum pressure measured during the top plate retraction, plotted against out-time, is shown in Fig. 7b. With increasing out-time, the maximum pressure or sample tack decreased linearly, and the fabricated prepreg completely lost tack after 1 h of ambient exposure. The goal of tack characterization was to verify that the prepreg possessed tack after fabrication, and to assess the evolution of tack with increasing out-time. The results showed that the prepreg exhibited tack at room temperature, which could potentially improve handling of the prepreg during laminate lay-up, but that for the current embodiment, the evolution of the PMMA pre-polymer resin was rapid.

3.2.3. Prepreg drape characterization



The lay-up of the preregs with partially polymerized matrix (D-1 and D-2) was straightforward, because the samples were highly pliable and shearable under ambient condition (Fig. 8a). Still, D-2, the laminate with longer ambient exposure, exhibited reduced flexibility, indicating that the sample stiffness increased with advancing out-time. The same sample also lost most of its tack after 1 h of out-time (Fig. 7b), but applying a small amount of liquid MMA to the prepreg surface restored sample tack to sustain adhesion to the mold surface. In contrast, F-1, in which the matrix was fully polymerized, was rigid at room temperature, and was impossible to drape onto the corner mold without pre-heating (Fig. 8b). The results of the comparative analysis demonstrate that, unlike conventional thermoplastic prepreg, partially polymerized prepreg is pliable and can be readily draped onto complex geometries under ambient conditions. While the drape evaluation was qualitative in nature, the results were sufficiently different to indicate that partially polymerized thermoplastic prepreg offers handleability advantages.

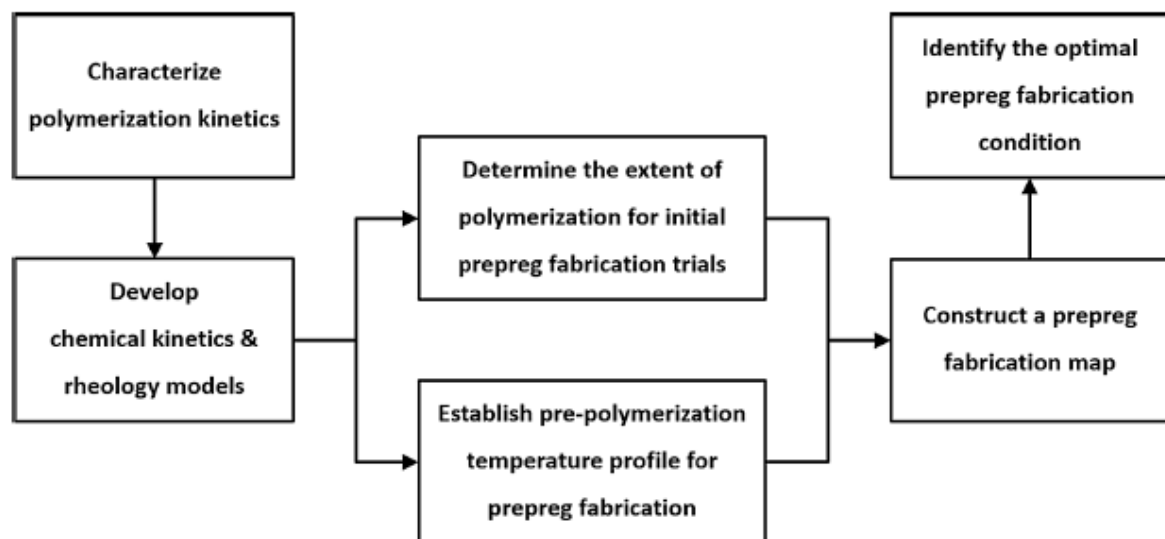
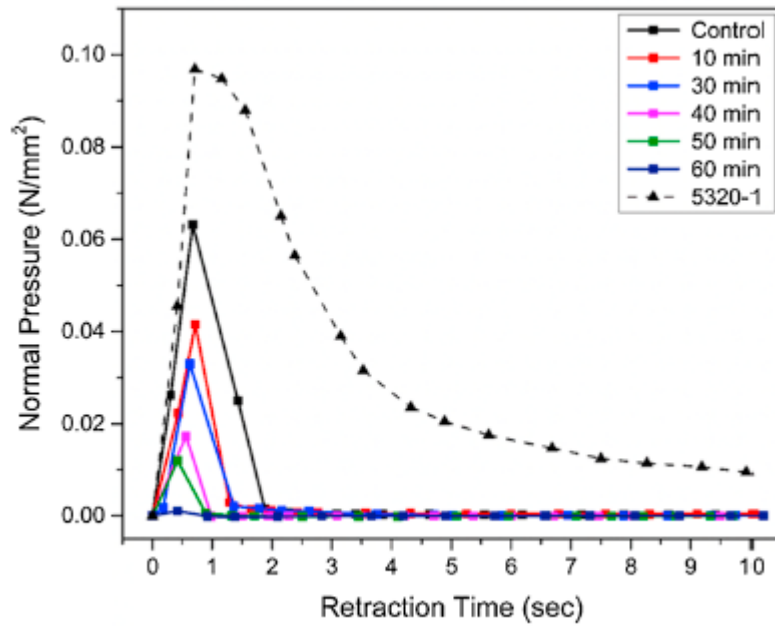
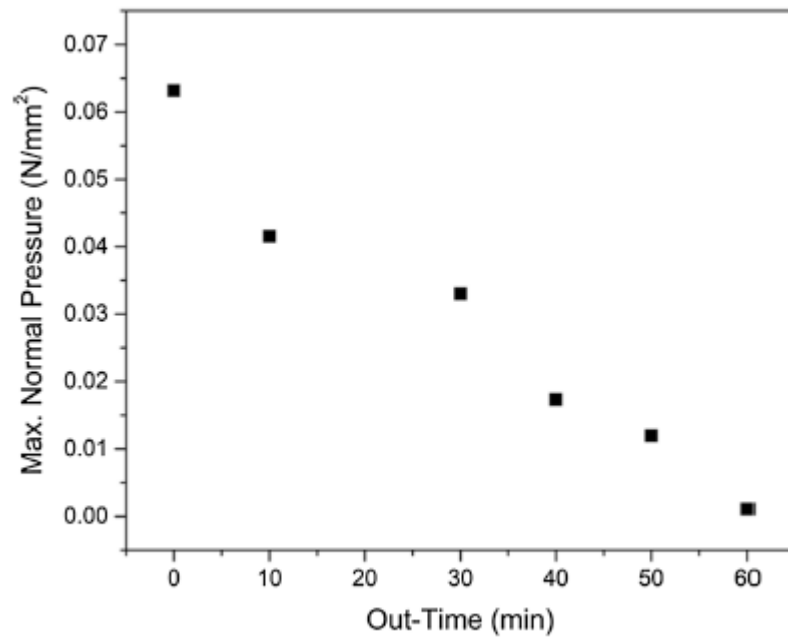


Fig. 6. Methodology of material and process development for the design of reactive CF RTP prepreg.



(a)



(b)

Fig. 7. (a) Normal pressure against the top plate retraction time for prepregs with varying out-times, and (b) maximum force required to detach the top plate, or the sample tack. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Laminate thermoforming & analysis

3.3.1. Microstructural analysis

The prepregs with partially polymerized matrix were thermoformed



at 90 °C and 0.38 MPa for 5 min. The processing temperature (90°C) was lower than the typical forming temperature of conventional PMMA prepreg, which is near 200 °C [36,37], and was even below the glass transition temperature of fully polymerized PMMA, which is 115 °C. Here, the applied pressure of 0.38 MPa was the minimum applicable pressure of the hydraulic press, but remained well below the recommended thermoforming pressure for commercial PMMA prepreg (0.5–2.0 MPa [37]).

Cross-sectional images of the thermoformed two-ply laminate (P-1) are shown in Fig. 9a. The micrographs demonstrate that the laminate is essentially void-free. During prepreg fabrication, the fiber bed was completely impregnated with pre-polymer matrix, because low viscosity monomer fully saturated both macro- and micro-pores in the dual scale fabric, and afterward polymerized *in situ*. Moreover, the prepolymer matrix, with melt viscosity much lower than that of completely polymerized polymer, enhanced resin flow during consolidation, even at low temperature and pressure. Hence, the resin effectively impregnated all dry fiber tows, leaving no resin-deprived regions.

The free-radical bulk polymerization of PMMA is highly exothermic—the heat of polymerization is nearly three times greater than that of epoxy resin [23]. This high reaction exotherm, combined with the auto-acceleration effect, can lead to thermal runaway and increase the reaction temperature above the boiling point of MMA [6]. Thus, reactive processing of PMMA at high temperature can result in porosity in the final part due to monomer vaporization during polymerization [6,23]. However, for fabrication of the PMMA pre-polymer prepreg, where the polymerization temporarily ceases at an intermediate stage before the reaction temperature rises sharply, the number of bubbles entrapped in the matrix is greatly reduced. If the prepreg contains porosity, the low viscosity of the pre-polymer allows removal of gas induced voids during part consolidation by in-plane resin bleed-out, even under low

pressure. Within the test samples, nearly all bubbles were situated at laminate edges, which are typically trimmed.

To verify validity of these results for thicker parts, the eight-ply prepreg laminate (TH-1) was thermoformed under identical forming conditions (90°C and 0.38 MPa for 5 min). Cross-sectional images in Fig. 9b show that this thicker laminate is also free of resin-deprived regions or entrapped bubbles, indicating complete fiber bed saturation and void removal.

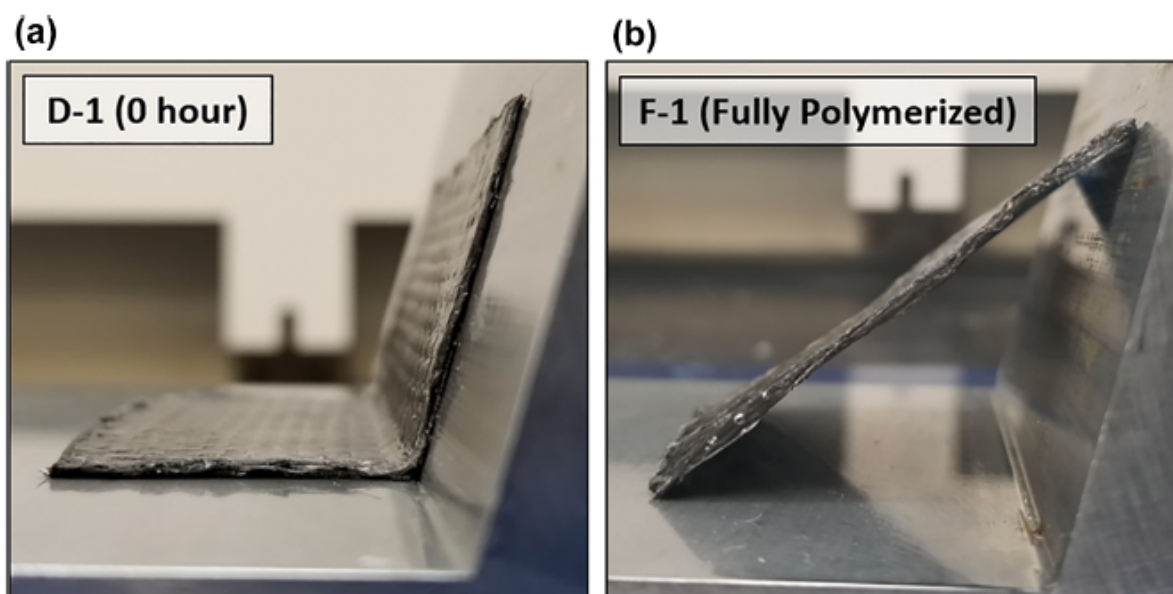
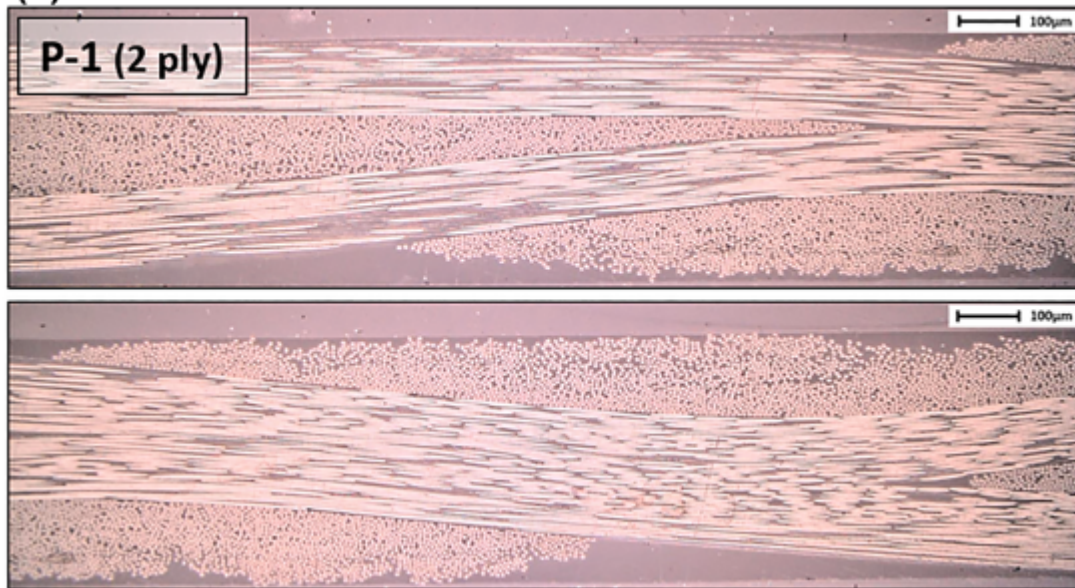


Fig. 8. (a) Partially polymerized thermoplastic prepreg draped onto 75° corner mold right after fabrication, and (b) conventional thermoplastic prepreg with fully polymerized matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3.2. Chemical composition analysis

The chemical composition of the thermoformed PMMA matrix was analyzed using FTIR to confirm that the interrupted polymerization process did not cause adverse effects. The absorbance spectrum collected from the final matrix, shown in Fig. 10, exhibited bands characteristic of PMMA. Some example bands include methyl C-H stretch at 2993 & 2949 cm^{-1} , C=O stretch at 1722 cm^{-1} , methylene C-H bend at 1479 cm^{-1} , methyl C-H bend at 1435 & 1387 cm^{-1} , and C-O-C stretch at 1190 & 1142 cm^{-1} . In addition, the absence of C=C stretch near 1620–1680 cm^{-1} and alkenyl C-H stretch at 3000–3150 cm^{-1} — two characteristic

(a)



(b)

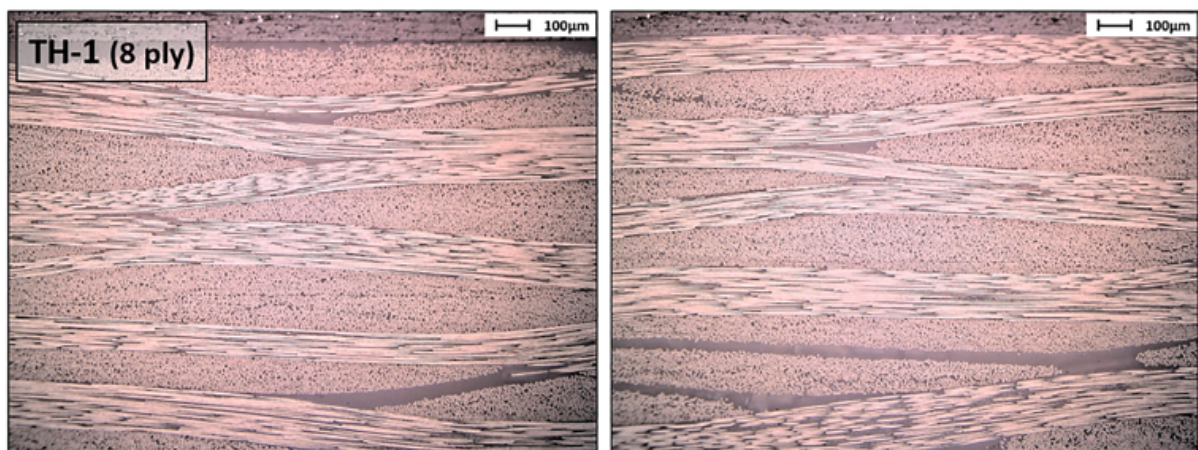


Figure 9. Cross-sectional micrographs of thermoformed (a) 2-ply (P-1) and (b) 8-ply (TH-1) laminates, free of voids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

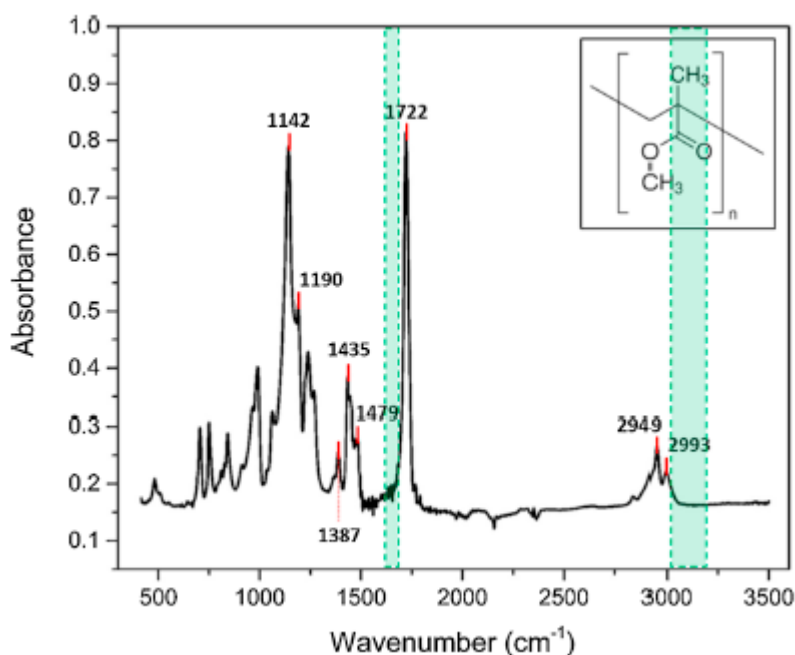


Figure 10. FTIR absorbance spectrum collected from the final thermoformed PMMA matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

bands of the monomer, methyl methacrylate—indicate that the matrix resin underwent complete and clean PMMA polymerization.

3.3.3. Fully polymerized prepreg laminate

A conventional PMMA prepreg with fully polymerized matrix was fabricated to examine matrix flow under selected thermoforming conditions. Sample (F-1) was not fabricated using the standard industrial manufacturing protocol of CF RTP. Rather, it was intentionally fabricated to produce high porosity to better observe matrix flows at different temperatures. Again, the final glass transition and forming temperatures of PMMA were 115 and 200°C, while the pre-polymer prepreg was thermoformable at 90 °C.

Figure 11 shows images of sample F-1 before and after multiple thermoforming under various conditions. When thermoformed at 90°C, the fully polymerized prepreg exhibited no matrix flow. At 150°C, which is greater than T_g but less than $T_{forming}$, minimal matrix bleed-out was observed at laminate edges, which drove some of the entrapped bubbles out. Full matrix flow was observed at 200°C and 3.8 MPa, conditions that were much more resource-intensive



than those used to form the pre-polymer prepregs. The purpose of this comparative analysis was to demonstrate that, unlike partially polymerized prepreg, conventional thermoplastic prepreg must be heated well above the melting or glass transition temperature of the matrix to achieve sufficient flow, and become flexible and thermoformable.

In this work, laminates of relatively small lab-scale size (0.003m^2 area) were manufactured to demonstrate the feasibility of partially polymerized thermoplastic prepreg. Consolidating parts with greater inplane dimensions may require more energy-intensive processing conditions for effective removal of voids near the laminate center if the principal void removal mechanism remains in-plane resin bleed-out. Conversely, if consolidation phenomena (flow and compaction) can be designed to favor some fluid pressure retention during molding, voids can potentially be suppressed by conventional application of pressure. Generally, the low viscosity of pre-polymer resin will allow part consolidation under

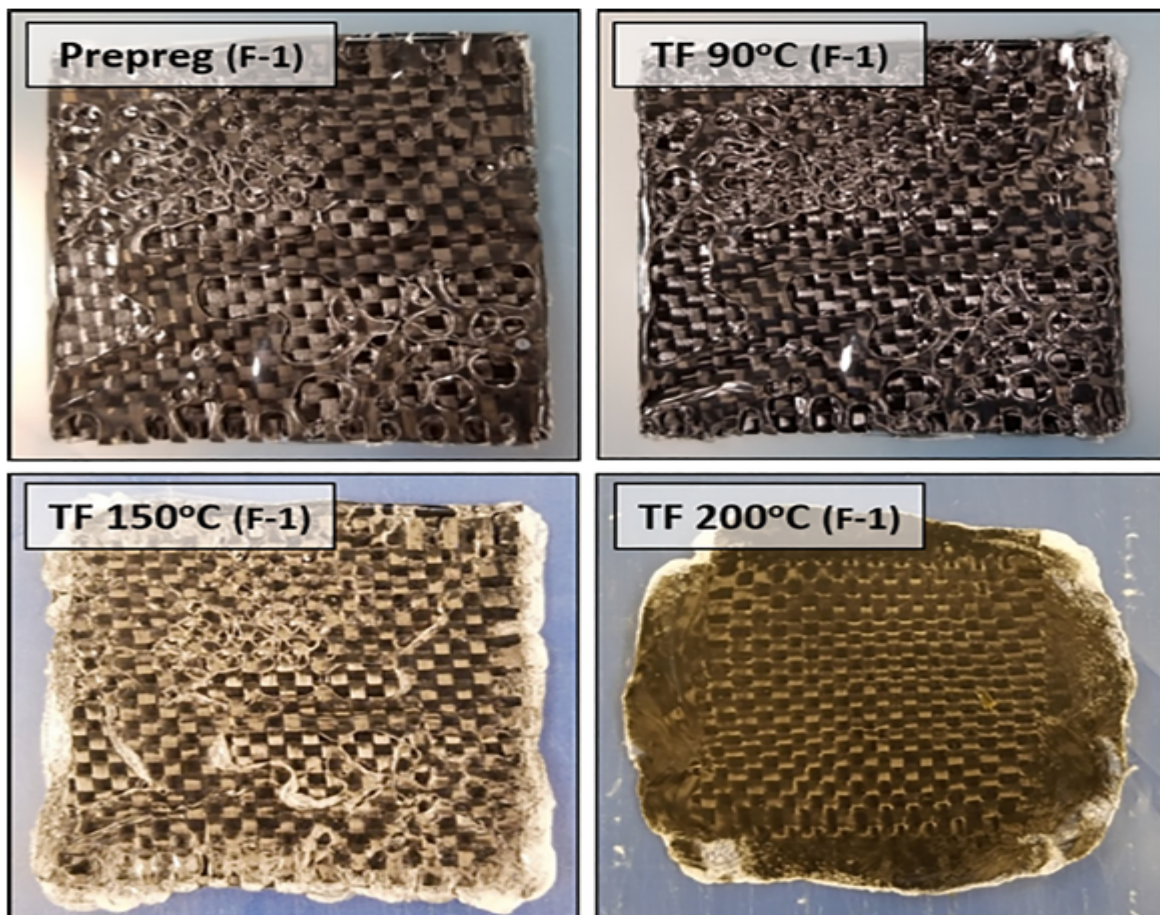




Figure 11. Conventional PMMA prepreg with fully polymerized matrix, before and after thermoforming at different temperatures—90, 150, and 200 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

moderate processing temperature and pressure, well below those required for producing laminates from fully polymerized prepreg of comparable size.

4. CONCLUSIONS

The chemical kinetics and rheology of PMMA polymerization were analyzed to design thermoplastic prepreg laminate with partially polymerized matrix. The auto-acceleration phenomenon from the Trommsdorff effect governed the rate of polymerization and viscosity evolutions of PMMA free-radical polymerization. Aging tests demonstrated that refrigerated storage of PMMA pre-polymer delays conversion due to out-time. Prepreg laminates were fabricated using lab-scale methods, and a fabrication map was constructed for two-ply prepreg laminates to determine the optimal extent of polymerization. The prepreps were characterized for tack and drape at room temperature, and then thermoformed below the final glass transition temperature of PMMA for microstructural and chemical analysis. Both two- and eight ply laminates showed no sign of porosity.

The objective of this case study was to establish material characterization and process development guidelines for reactive processing of CFRTP prepreg, and to demonstrate potential advantages of thermoplastic prepreg with a partially polymerized matrix. Conventional thermoplastic prepreg generally features a fully polymerized matrix with high melt viscosity, and processing requires high pressure and temperature to ensure proper fiber bed impregnation and void removal. On the other hand, the prototype prepreg laminate described here consists of multiple plies of fabric fully impregnated with a pre-polymer matrix, for which the melt viscosity is much less than that of the fully polymerized material. The pre-polymer matrix facilitates resin flow during part consolidation even at low temperature and pressure. Therefore, any voids created throughout part processing are readily eliminated, with



no visible flow- or gas-induced voids remaining in the final consolidated laminate. Moreover, the pre-polymer resin also provides tack and drape, which can accommodate prepreg conformability.

In this study, we focused on material characterization and process development for the most basic MMA polymerization case to determine the feasibility of partially polymerized thermoplastic prepreg. However, varying initiator weight content or mixing additional ingredients such as PMMA polymer or comonomers into the monomer/initiator mixture can significantly alter reaction kinetics and ultimately final degree of polymerization, both of which can affect consolidation phenomena and mechanical properties of fabricated parts. Flow, compaction, and (after gelation) residual stress formation can also influence process-induced deformation, which were not studied here but can affect the shape conformity of a part. Further work will be required to examine the effects of various reactant components on polymerization kinetics and part properties, and to address other processing challenges identified during this study. For example, storage of thermoplastic pre-polymer prepreg requires refrigeration to delay out-time, similar to thermoset prepreg. In addition, the duration of tack and drape of the model PMMA prepreg, while superior to that of conventional CFRTP prepreg, which possesses neither tack nor drape, may be insufficient for complex part fabrication. These limitations can be addressed, in principle, by adopting alternative aerospace-grade thermoplastic matrices with higher melting temperatures, such as polyetheretherketone (PEEK), polyetherimide (PEI), or polycarbonate (PC). Such polymers are expected to extend out-life, as well as tack and drape lives to more practical levels.

Overall, this work describes a pathway to reduce major processing challenges associated with CFRTPs, including the handleability of thermoplastic prepreps, and the thermal and pressure conditions required for part consolidation. Composites manufacturing is undergoing a gradual shift from legacy methods (*e.g.*, autoclave cure of thermoset prepreps) to



processes and materials that enable simpler and more cost-effective fabrication of structural parts. This pathfinder study indicates that partially polymerized thermoplastic prepregs may offer a viable solution toward such advances in CFRTPs.

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