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Development of a Methodology for Characterizing Reaction Kinetics, Rheology, and In-Situ Compaction of Polyimide Prepregs During Cure

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ABSTRACT

PMR-type polyimide prepregs are challenging to fabricate into high quality composites due to volatiles that are generated and must be removed in-situ during processing. Despite several decades of academic and industrial study, the core challenge of effective and repeatable volatile removal still plagues manufacturers of polyimide composite structures. A method for the *in-situ* characterization of polyimide compaction during composite cure cycles would greatly help in understanding and controlling the process. To this end, the current work was conducted to develop accurate, reliable, and practical characterization techniques of the prepreg rheology, volatile generation, and subsequent volatile removal from the prepreg during composite fabrication. Thermal analysis was used to characterize volatile generation, reaction rates, and rheology. A novel approach was used to measure the thickness of the prepreg *in-situ* during vacuum bag / oven processing using a high-temperature LVDT. Experimental results are presented for the commercially available RM-1100 polyimide/carbon prepreg system, including the reaction rate, rheology, and panel thickness results for a series of heating rates and ply counts. Taken together, the results show the key interrelationships in these coupled phenomena and how that information can be used to select the optimum

temperature of pressure application to minimize the final void content. Two autoclave trials were conducted which demonstrated the ability to reduce void content from 9.5% to 3.1% by using the information and criteria developed by our methodology. Overall the results showed that the methods developed in this study were able to accurately measure polyimide prepreg thickness in-situ during the imidization phase of the cure and were effective in cure cycle optimization.

INTRODUCTION

The difficulty in fabricating composites using PMR-type (Polymerization of Monomeric Reactants) polyimide resin systems and prepregs has been studied for decades. Numerous experimental studies have illustrated the key challenges, which are related to the to the complexity of the different polymerization reactions taking place, as well as the volatiles that are generated and must be removed during the high temperature cure cycle [1-9]. PMR-type polyimide resins cure via a two-stage reaction. The first (at lower temperatures) is a condensation reaction that forms a relatively low molecular weight imide oligomer and the by-products of alcohol and water. This reaction is followed by a higher temperature addition cure crosslinking reaction, which emits only a small amount of undesired volatile by-products. As a result, during the cure cycle polyimide prepregs will emit volatiles from the water and alcohol by-products as well as solvents used in their manufacture. In order to get a fully consolidated, low void volume composite, most of the volatiles must be removed while maintaining a sufficiently low resin viscosity using a properly designed cure cycle.

Accordingly, a typical PMR-type polyimide cure cycle has two distinct steps. The first is the imidization reaction and volatile removal, which is typically done in a vacuum bag under full vacuum but no applied autoclave pressure. The second step is the addition cure and layer consolidation. This step requires increased pressure over atmospheric, typically 180-200 psi in an autoclave. A typical polyimide cure is shown in Figure 1 [10]. The timing of when to apply high pressure is one of the key factors in the process design. Ideally, the autoclave pressure is applied after the volatiles have been removed but prior to the resin reaching a state of high viscosity or gelation. Unfortunately, these two processes can overlap. Due to these complexities, trial and error approaches for determining cure parameters are very costly and time consuming due to the number of trials often required to be successful [11].



Figure 1: Typical PMR-type Polyimide Autoclave Cure Cycle. [10]

Conducting lab scale processing studies for PMR-type polyimides and prepregs, including characterization of the reaction kinetics and rheology of the resin in the prepreg, is complicated by to the volatiles that are generated. These volatiles create

difficulty in performing traditional degree of cure and viscosity measurements via differential scanning calorimeter, infrared spectroscopy, and parallel plate rheology. Furthermore, devolatilization of polyimide prepregs is a function of many variables (such as fiber/fabric geometry, resin content and composition, prepreg aging, etc.) which adds an additional challenge for characterization. Despite this, several studies have been conducted in an attempt to characterize certain aspects of polyimide composite processing including volatile removal and rheological behavior [7, 12-14]. Previous studies of the devolatilization of polyimide prepregs were conducted in a controlled experimental setup that involved rigid, non-perforated top and bottom plates that did not allow for mass transport through thickness of the composite [5, 12]. Unfortunately, these conditions are not representative of vacuum bag and autoclave cure cycles currently used for polyimides. Present industrial practice involves the use of perforated or gas permeable peel plies to allow volatiles to escape through the top surface instead of the sides of the panel [5, 12, 15-18]. In addition, most of the previous studies assumed the distance between the top and bottom caul plates to be constant, not allowing the prepreg to loft and compact. This is also different than that experienced in vacuum bag / autoclave curing practice, where the thickness is free to change under hydrostatic pressure as gas is generated and removed.

The goal of the current study was to develop a practical, field-implementable methodology for the characterization of polyimide prepreg volatile generation, rheology, and compaction during composite fabrication to aid in cure cycle development. This was accomplished by first characterizing the imidization reaction kinetics and prepreg rheology as a function of temperature for various heating cycles using analytical

equipment. Then, a novel approach was used to indirectly quantify the mass transport and removal of the volatiles from the prepreg stack during actual vacuum bag cure. Specifically, a high temperature LVDT was used to make in-situ thickness measurements during vacuum bag / oven cure cycles. The coupled information from these measurements can be used to identify the temperature during the cure cycle when trapped gas is minimized, which is when autoclave pressure should be applied. In future work, we plan to develop models to predict the reaction kinetics, rheology, and composite compaction during cure under *arbitrary* conditions, but using data from a *limited* number of experimental trials. The model predictions can then be used for cure cycle development and optimization, as well as material characterization and quality control for PMR-type polyimide material systems, greatly reducing the number of trial-and-error experiments. The current study establishes the experimental data base and process insight needed in subsequent model development.

EXPERIMENTAL DEVELOPMENT

2.1 Materials

The prepreg used in this study was procured from Renegade Materials Corporation (Springboro, Ohio). The resin system was RM-1100, which is a PMR-type polyimide resin system of proprietary composition. The fibers were T650-35 carbon fiber in an 8 harness satin weave fabric (fiber areal weight of 371 g/m^2). The sizing of the T650-35 fabric was removed in a proprietary process before prepregging. As a strategy to improve material consistency in terms of resin and volatile content, all prepregs were debulked prior to characterization tests as well as the layup process. This allowed for removal of any solvent and moisture. The debulk process consisted of heating 4 ply stacks of prepreg in a vacuum bag to 50°C for 24 hours. Through weight measurements, it was verified that the material resin contained less than 1 wt% volatiles after drying. The final composition of the prepreg after drying was characterized by ASTM D3529, which indicated 56 wt% fibers, 36 wt% resin, and 8 wt% volatiles (these volatiles associated with imidization and crosslinking).

The RM-1100 prepreg resin imidizes through a condensation reaction between diester diacid groups and the diamines upon heating of the prepreg, which creates the low molecular weight imide oligomer and volatile by-products (H₂O, C₂H₅OH). The resin subsequently addition-cures through a crosslinking reaction with the endcap at higher temperature. This is typical for PMR-type polyimides, therefore, this material system can be used to demonstrate the typical challenges with volatile generation and removal during imidization and prior to crosslinking. It is typical for most PMR-type resins to continue to lose some weight even after imidization is complete [10, 19]. Although the crosslinking is an addition cure reaction, the endcap is assumed to emit a small amount of undesirable volatiles due to thermal decomposition. This work focuses on the imidization condensation reaction to form the imide oligomer.

2.2 Analytical Material Characterization Techniques

2.2.1 Reaction Kinetics Characterization

The condensation cure imidization reaction was characterized with thermogravimetric analysis (TGA). The dried RM-1100 prepreg samples were heated from ambient to 400°C using ramp rates of 0.55°C/min, 1.1°C/min, 2.2°C/min, and 4.4°C/min in a TA Instruments Q500 TGA in nitrogen. Specimen size was approximately 10 mg. Specimens were prepared by manually cutting from the prepreg. Three specimens were run for each heating rate. Since the prepreg samples were dried prior to the TGA experiment to remove any solvent, the remaining weight loss was from the cure reactions only. The TGA weight loss data was then used to calculate the Degree of Imidization (DoI) and effective reaction rate at each time during the heating cycle using the following equation:

$$DoI(T) = \frac{w_p(T)}{w_{p,tot}}$$
(1)

where $w_p(T)$ is the cumulative weight *loss* of the prepreg at a given temperature, and $w_{p,tot}$ is the total weight loss from ambient to 275°C, which was determined to be the completion of the imidization reaction for similar polyimide resins through prior study [10]. The goal here was to express DoI as a function of *temperature only* for each of four heating rates (0.55, 1.1, 2.2, and 4.4 °C/min). The reaction rate for imidization, r_1 (sec⁻¹), was calculated at each temperature by taking the derivative of the DoI with respect to time as given in Equation 2.

$$r_I = \frac{d(DoI)}{dt} = \frac{1}{w_{p,tot}} x \frac{dw_p}{dt}$$
(2)

As stated before, PMR-type polyimides continue to lose weight upon further heating after imidization as a result of undesired volatile products from the crosslinking reaction. As a result, the rate will not reach a value of zero after the imidization is complete, and therefore the calculated DoI parameter can exceed a value of 1. It should be understood that the imidization reaction referred to herein contains a contribution from the poorly understood crosslinking reaction. Although imidization and crosslinking are very different reactions, they both indeed contribute to volatile generation during cure.

2.2.2 Prepreg Rheology Characterization

The prepreg rheology was measured with a TA Instruments ARES RDA in torsional braid mode. One ply of the dried prepreg was cut into a 1.5 inch long x 0.5 inch wide rectangle and placed in the torsional clamp within the RDA. The samples were heated at 0.55° C/min, 1.1° C/min, 2.2° C/min, and 4.4° C/min from ambient to 400^{\circ}C. The sample was subjected to oscillating torsion with the following parameters: frequency = 1 Hz and constant strain = 0.006%. Two samples were run at each heating rate. The primary result calculated from this test was the shear storage modulus, G' (dyne/cm²).

Generally this technique yields information about the resin rheology because as the resin softens or hardens, the required torque will decrease or increase, respectively. This qualitative information is relevant for understanding composite compaction because the flow of the resin is a critical parameter. G' as a function of temperature is often used to characterize the resin flowability in a sample of prepreg, which will also be employed in the current study. When autoclave pressure is applied, the resin needs to have sufficient flowability to allow for compaction, while not allowing excess bleed out of the panel. For PMR-type polyimides, the prepreg goes through several different phases during cure. Initially, the prepreg is tacky and pliable. Upon heating, the resin softens and flows until the condensation imidization reaction begins which results in an increase in modulus as molecular weight increases and imide rings are formed. The amount of this increase can span different magnitudes for different polyimides depending on the

chemistry. With continued heating, the imidized resin will soften and flow to allow for compaction with autoclave pressure. At a certain temperature, the crosslinking reaction will begin which results in a second rapid increase in modulus as the resin approaches its gel point temperature. The effective gel point temperature was determined from the RDA data by finding the temperature at which G' increased 25% from its minimum value to the value at the final cure temperature. At the effective gel point temperature, the prepreg loses its ability to sufficiently flow and consolidate to a low void volume composite. Therefore, it represents the maximum temperature before pressure must be applied to the prepreg in order to get proper consolidation in the process cycle.

2.3 Panel layup

The thickness of the composite panel, which is related to the number of plies of prepreg, will have an effect on the mass transport of the volatiles. All panels were prepared using prepregs cut to 6 in. x 6 in. Three prepreg stacking sequences were used to characterize the compaction during cure: [0/90]_{3s}, [0/90]_{6s}, and [0/90]_{20s}. These stacking sequences resulted in 12, 24, and 40-ply composite panels. These were each heated at 0.8°C/min to study the effect of ply count. For thicker PMR-type parts, slow heat rates are typically used in industry. These ply counts and heating rates are representative of typical PMR-type polyimide parts in industry. The total area is not very relevant since the volatile escape upwards through the thickness, not laterally through the sides.

2.4 In-Situ Compaction Measurement and Vacuum Bagging

A technique was developed in this study to accurately and repeatedly measure prepreg stack thickness in-situ while surviving the temperatures required for polyimide autoclave cures (up to 310°C in this study). Fortunately, there are commercially available linear variable displacement transducers (LVDT) that can withstand these temperatures. A high temperature LVDT (model LIN56A) was purchased from RDP Group (Pottstown, PA) for the thickness measurement. Its upper use temperature was 343°C. A frame was built to hold the LVDT above a vacuum bag containing the polyimide prepreg stack. The frame was a built from 2 in. by 2 in. square steel tubing. It was clamped to the side of the tool plate using C-clamps. The LVDT was placed in a metal clamp, adjusted to the correct height, and then tightened with a set screw. A photo of the system is shown in Figure 2. A method was developed to normalize the thickness data in order to isolate the changes in the prepreg stack thickness only, rather than including the dimensional change of the entire setup due to thermal expansion. This process, which involved making measurements on the vacuum bag set up without the prepreg stack, is described in more detail in Magato dissertation [20].

The vacuum bag design used in this study, shown in Figure 3, is a typical bagging arrangement for PMR-type polyimides allowing for volatile release while maintaining no resin bleed into the breathers. This was accomplished by the non-porous PTFE coated glass fabric (Release-Ease® 234 TFNP from Airtech International, Inc.). It allowed volatiles to escape while being non-porous to the resin. There was no lateral bleed of resin due to the non-porous barrier film and sealant dam surrounding the prepreg stack. The entire setup was then placed in a composite curing oven (ASC model OV6X6X6-1000F). The oven was equipped with vacuum and temperature processing controls similar to an autoclave. When curing polyimides, the volatile removal step occurs using vacuum bag pressure only (no over-pressure), even when performed in an autoclave.

After devolatilization, pressurized nitrogen is normally used to pressurize an autoclave and compact the composite, although this was not possible with the oven used in the current study. Nevertheless, the composite curing oven at Maverick Corporation and the LVDT system allowed for study of the cure cycle through devolatilization and gelation under normal conditions. For a complete description of the experimental setup, refer to Magato dissertation [20]. The cure cycle consisted of a 0.8°C/min ramp rate to 300°C, which was chosen as the maximum temperature based on the prepreg manufacturer's recommendation to apply pressure at this temperature. Also per the manufacturer's recommendation, a vacuum pressure of 12.7 cm Hg was used up to 176°C, at which point a minimum vacuum pressure of 63.5 cm Hg was maintained.



Figure 2: Photo of Vacuum Bag and LVDT Sensor in Place.



Figure 2: High-Temperature Bagging Schematic with LVDT Placement.

RESULTS AND DISCUSSION

3.1 Reaction Kinetics Characterization Results for RM-1100

A comparison of the TGA data for the various heating rates is shown in Figure 4. The minor weight loss (< 1%) from ambient to about 80°C was attributed to the residual volatiles that could not be removed through the drying process. The prepreg lost approximately 6-7% weight up to the designated end of imidization at 275°C (this corresponds to 14-16% of the original resin weight). However, it is typical for PMR-type polyimides to experience continual weight loss with increasing temperature beyond the imidization reaction. This is from gaseous by-products generated from the crosslinking reaction and not imidization. Even though the crosslinking reaction is referred to as an addition type, there is actually some non-negligible weight loss attributed to degradation of the endcap [10, 19]. There was very little difference in the weight loss of the prepreg for the different heating ramp rates up to the final cure temperature of 371°C. The prepreg lost an additional 1 wt% from 250 to 371°C, for a total of approximately 7.5 wt% for the entire cure cycle. This represents the total amount that must be removed during an actual vacuum bag cure cycle



Figure 4: TGA Results for RM-1100 Prepreg (Based on Weight of Fibers + Initial Resin).

The results for DoI and effective reaction rate are shown in Figures 5 and 6. The DoI for RM-1100 changed moderately as a result of increasing ramp rate. In other words, RM-1100's reaction kinetics were rate dependent, which is often encountered with multicomponent thermoset resins systems. The DoI was not limited to a maximum value of 1.0 for the purpose of quantifying the additional weight loss measured up to 310°C. The reaction rates peaks (Figure 6) exhibited a steadily increasing height and shift toward higher temperatures as heating rate was increased.



Figure 5: DoI Results for RM-1100.



Figure 6: Effective Reaction Rate Results for RM-1100.

3.2 Rheology Characterization Results

The G' results for RM-1100 are given in Figure 7. The increase in modulus due to the onset of the imidization reaction is seen at approximately 100°C. Also, the softening of the prepreg is at approximately 215°C. The temperature of the material softening will likely have an effect on how the material compacts during processing. The

minimum and maximum G' values shifted to higher temperatures as the heating rate was increased, which is commonly observed in RDA characterization.



Figure 7: Shear Storage Modulus Data for RM-1100 Prepreg.

The results for the gel point temperature for RM-1100 are listed in Table 1. There was an increase in the gel point temperature as a result of increasing ramp rate for the RM-1100. This reflects the rate dependency of the reaction. The general strategy for achieving good compaction is to apply pressure at a temperature that is safely below the gel point temperature, by at least 10-20°C.

Ramp Rate (°C/min)	Gel Point Temperature (°C)
0.55	335
1.1	345
2.2	355
4.4	362

Table 1: Gel Point Temperature for RM-1100.

3.3 Prepreg Compaction Characterization

The measured results for the panel thickness during cure are given in Figures 8 and 9 in terms of change in thickness and total panel thickness, respectively. An overlay of the panel thickness change, effective reaction rate, and G' for the 40 ply panel is shown in Figure 10. The panel thickness increased (or lofted) with increasing reaction rate during the imidization reaction. The panel thickness then decreased sharply once the imide material softened sufficiently, as indicated by the drop in shear storage modulus, thus removing trapped gas from the system. There was also a sudden decrease in panel thickness at 176°C, which corresponded to the increase in vacuum pressure. The "normal" time to apply pressure given the criteria discussed earlier would be at 300°C. In order to investigate the effect of applying autoclave pressure at different temperatures, autoclave trials were performed on 40 ply composite laminates, as presented in the next section.



Figure 8: Panel Thickness Change for Different Ply Counts Using 0.8°C/min Cure Cycle.



Figure 9: RM-1100 Total Panel Thickness for Different Ply Counts Using 0.8°C/min

Cure Cycle.



Figure 10: Panel Thickness Change, Reaction Rate, and G' for RM-1100 for 40-ply panel.

3.4 Autoclave Validation Trials

The final task was to validate our methodology by using the in-situ thickness measurements of the 40-ply panel to select one favorable and one non-favorable temperature for pressure application during subsequent autoclave processing trials. Autoclave trials were performed at Renegade Materials Corporation with a 40-ply RM-1100 laminate using two cure cycles. The goal was to determine the thickness and final void content of thick polyimide composites when pressure was applied at *two different temperatures*. This implies the panel thickness was different at the time of pressure application since one panel had more time to vent volatiles and reach a higher temperature (lower viscosity). Everything was the same for the two panels except the pressure application temperature.

The autoclave cure cycles are given in Table 2. A ramp of 0.8°C/min from ambient to 250°C or 300°C was used, and the same vacuum profile was used as in the previous oven experiments. Upon reaching 250°C or 300°C, 200 psi pressure was

applied, and the panels were heated at 0.8°C/min to 371°C. The panels were held for three hours at 371°C under 200 psi compaction pressure, which is the standard pressure and final cure temperature for RM-1100, followed by cooling to ambient. The panels were evaluated for final composite thickness and fiber and void volume. The fiber and void volumes were measured using ASTM D 3171.

For the first cure cycle, the pressure application temperature was chosen with the expectation that the final composite would have high void content based on the amount of trapped gas at the time pressure was applied. Therefore, the 200 psi pressure was applied at 250°C. At this temperature, the resin had not softened sufficiently to allow compaction of the prepreg before pressure application, resulting in a higher panel thickness. For the second experimental cure cycle, the 200 psi pressure was applied at 300°C, which allowed for further prepreg compaction before the pressure being applied. This cycle was expected to result in a better compacted, lower void volume final composite by allowing more of the gas generated to be removed before the autoclave pressure was applied. For reference, the oven cure data for the 40-ply panel from Figure 9 was replotted in Figure 11 with the temperatures identified where pressure was applied in the autoclave validation trials. The measured panel thickness at the pressure application temperature for cure cycle 1 was 0.814 inches, compared to 0.753 inches for cure cycle 2.

Table 2: Autoclave Cure Cycles

Store #	Cure Cycle 1	Cure Cycle 2
Step #	(expected non favorable)	(expected favorable)
1	25- 250°C @ 0.8°C/min,	25- 300°C @ 0.8°C/min,
	vacuum bag only	vacuum bag only
2	Apply 200 psi autoclave	Apply 200 psi autoclave
Z	pressure at 250°C	pressure at 300°C
2	Continue heating to 371°C at	Continue heating to 371°C at
3	0.8°C/min	0.8°C/min
4	Hold at 371°C and 200 psi	Hold at 371°C and 200 psi
4	for 3 hours	for 3 hours
5	Cool to ambient at	Cool to ambient at
	5.0°C/min, release pressure at	5.0°C/min, release pressure
	140°C	at 140°C



Figure 11: 40 Ply Panel Thickness Result from Oven Cure Cycle, showing the selected temperatures of pressure application for the subsequent autoclave cure cycles.

The measured final thickness for the cured panels are listed in Table 3. As expected, the panel using cure cycle 1 did have higher void content, 9.5%, versus 3.1% for cure cycle 2. The cure cycle 2 panel also had a lower final composite thickness, and therefore lower per ply thickness and higher fiber volume fraction, as expected as well. Photos of the cross section of the 40 ply composite panels are shown in Figures 12 and 13. The high void content is visible throughout the experimental cure cycle 1 panel. The cross section of experimental cure cycle panel 2 appears much better consolidated with only a few visible voids.

	Cure Cycle 1	Cure Cycle 2
Panel Final Thickness (in)	0.620	0.579
Per Ply Thickness, PPT (in)	0.0155	0.0145
Fiber Volume (%)	52.7	56.5
Void Volume (%)	9.5	3.1

Table 3: Autoclave Cured 40-Ply Co	omposite Panel Results
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Figure 12: Cross Section of 40 Ply RM-1100 Final Composite Panel Fabricated with

Experimental Cure Cycle 1, Showing High Void Volume.



Figure 13: Cross Section of 40 Ply RM-1100 Final Composite Panel Fabricated with Experimental Cure Cycle 2, Showing Low Void Volume.

The autoclave trials illustrate how the LVDT measurements from oven cure cycles can be used in autoclave cure cycle development to fabricate low void volume polyimide composites. With this measurement, a temperature for pressure application can be selected that results in minimal gas trapped in the prepreg at the temperature pressure is applied. The criteria for selecting the temperature of pressure application is minimal panel thickness before the gel point temperature is reached. Further trials evaluating temperatures higher than 300°C, ramp hold steps, or both are required in order to truly optimize the cure cycle to find the ideal conditions for minimal void volume in final compacted composite. In this work, only a constant heating ramp was used to demonstrate the methodology for this class of material.

CONCLUSIONS AND RECOMMENDATIONS

Practical methods for the characterization of reaction kinetics, rheology, and composite panel compaction were successfully developed to aid in the development of cure cycles for PMR type polyimide composites. The PMR-type polyimide prepreg used for this study was Renegade Materials Corporation's RM-1100. The results validated the methodology of using in-situ LVDT measurements of the prepreg stack thickness during cure to indicate the amount of trapped gas and, along with analytical rheology results, determine the optimum time to apply autoclave pressure to ensure low porosity. Composite panels were fabricated from RM-1100 using two different temperatures for pressure application, resulting in two different prepreg thicknesses when pressure was applied in the autoclave. The void volumes in the final cured composite were significantly different, 3.1 % vs. 9.5%, when pressure was applied at the predicted ideal temperature vs. a predicted non-ideal temperature. These results confirm that in-situ panel thickness measurements and analytical rheology results are sufficiently accurate to aid in selection of a pressure application temperature that will result in a low void volume polyimide composite panel of realistic thickness and using realistic heating rates.

In a future publication, details of neural network models for the prediction of reaction kinetics, rheology, and composite thickness during cure will be developed and discussed. A predictive model is needed for these measurements in order to reduce the number of trial-and-error experiments for cure cycle optimization. For the current study, the tool, vacuum bag sequence, and vacuum profile were all held constant, and the effects of ply count and heating rates were studied. The same methodology can be used to study the effect of other processing variables in the future. By combining the ability to measure composite thickness for multiple cure cycle variables, further cure cycle optimization could be performed, resulting in further reduction in the final void volume of the composite with minimal trial-and-error.

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