STUDY OF OUT-TIME ON THE PROCESSING AND PROPERTIES OF IM7/977-3 COMPOSITES

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ABSTRACT

The capability to manufacture large structures leads to weight savings and reduced risk relative to joining smaller components. However, manufacture of increasingly large composite components is pushing the out-life limits of epoxy/ carbon fiber prepreg. IM7/977-3 is an autoclave processable prepreg material, commonly used in aerospace structures. The out-life limit is reported as 30 days by the manufacturer. The purpose of this work was to evaluate the material processability and composite properties of 977-3 resin and IM7/977-3 prepreg that had been aged at room temperature for up to 60 days. The neat resin was evaluated by differential scanning calorimetry, DSC, to characterize cure behavior of the aged material, as well as any change in activation energy. The rise in the modulus of the uncured prepreg was monitored throughout the 60 days by dynamic mechanical analysis, DMA. Composite panels made of the fresh and aged prepreg material were also characterized by DMA. The overall test results suggested that IM7/977-3 was a robust material that offered quality laminates throughout this aging process when processed by autoclave.

1. INTRODUCTION

The Ares V Cargo Launch vehicle is slated to utilize epoxy/carbon fiber composites in several dry structures; most of which are of substantial size. For example, the rocket interstage is planned to be 10 meters in diameter and 12 meters in height. It has been anticipated that processing these structures could push the out-life limits of most conventional carbon fiber/epoxy prepreg materials.

Many common epoxy systems used in the aerospace industry are composed of a mixture of epoxies, curing agent, and catalyst. Many times the curing agent is an amine, which reacts with the epoxy at room temperature. Consequently, prepreg material is kept frozen to avoid premature advancement of cure. This requirement raises concern for the fabrication of a large part where plies initially placed on a tool would be kept at room temperature until the remainder of the part is laid-up. Cure advancement of the epoxy within those early plies could alter the rheology and cure profile of the material, and result in inhomogeneous cure throughout the laminate.[1] Additionally, loss of tack as the material sits on the tool may lead to voids or debonded areas within the laminate.[2]

In this work, the processability and cure chemistry of IM7/977-3 was investigated with respect to the materials out-time. DSC and DMA were the primary characterization techniques. DSC has been widely used to characterize kinetic parameters of epoxy cure; as well as other resin systems.[3] Values such as activation energy, pre-exponential factor and rate constant can be obtained by either isothermal or dynamic experiments. DMA is an effective technique for prepreg process characterization and in-situ cure monitoring by this method has been used to identify processes such as gelation and vitrification.[4] Two to three ramp rates were used during DMA and DSC analysis and composite processing. This included a 0.28^{o}C (0.5^{o}F) per minute ramp rate, which is slow with respect to the manufacturers recommended ramp rate, but likely representative of the actual rate of temperature change within a large part during autoclave or oven cure.

Throughout the report, some data will be compared to a proprietary Resin X, which has a shorter out-time (21 days) as listed by its manufacturer. While it is not a direct competitor to 977-3; Resin X is an epoxy.

2. MATERIALS AND PROCEDURES

2.1 Materials

IM7/977-3 (145gsm) and 977-3 epoxy resin were purchased from Cytec Industries. Both materials were used within the manufacturers recommended freezer life period.

2.2 Out-time of resin and prepreg

Samples for characterization of out-life by DSC or DMA were prepared by leaving prepreg or resin out of the freezer, at room temperature, but in a plastic Ziploc to avoid potential dust accumulation. Samples were tested by these methods every ten days, up to 60 days out of the freezer. (10 days out, 20 days, 30 days, 40 days, etc.)

A modulated Differential Scanning Calorimeter (DSC/Model No Q1000, TA Instruments) was used to evaluate the cure reaction enthalpy of the epoxy resin, thus the degree of cure advancement. The resin (8-12 mg) was weighed into a crimped aluminum DSC pan. The tests were performed under nitrogen, with the ramp rates including 0.5^{o}C/min, 2^{o}C/min and 4^{o}C/min. Kinetic parameters such as activation energy (Ea) were calculated following ASTM E698-05.

Additional processing characteristics, including modulus, gelation, and vitrification temperatures were obtained by Dynamic Mechanical Analysis (DMA/Model No 2980, TA Instruments). The uncured prepreg was placed in a torsional holder and the experiment was run following the manufacturers cure cycle, with the exception that the ramp rate was either 0.28^{o}C/min (0.5^{o}F/min) or 1.11^{o}C/min (2^{o}F/min).

2.3 Out-time of laminates for autoclave processing

Fresh prepreg plies were laid-up in a quasi-isotropic sequence, as a total of 16 layers in a balanced and symmetric sequence; [0,+45,90,-45]2s. The prepreg stacks were then placed in a plastic Ziploc bag which was left open at room temperature for up to 60 days. Panels were processed in the autoclave every 10 days, at 2 ramp rates, either 0.5^{o}F per minute or 2^{o}F per minute. The cure profile used was:

1. Bag panel and stabilize vacuum pressure at greater than 25 in Hg.
2. Apply 85 psi autoclave pressure and vent vacuum bag to atmosphere when pressure reaches 20 psig.
3. Heat to 177^{o}C (350°F) at a rate of either 0.28 ^{o}C (0.5^{o}F) or 1.11 ^{o}C (2.0^{o}F)
4. Hold at 177^{o}C (350°F) for 360 minutes.
5. Cool to 140°F at a rate of 1.5°F/min.
6. Release pressure.

The bagging sequence used is shown in Figure 1:

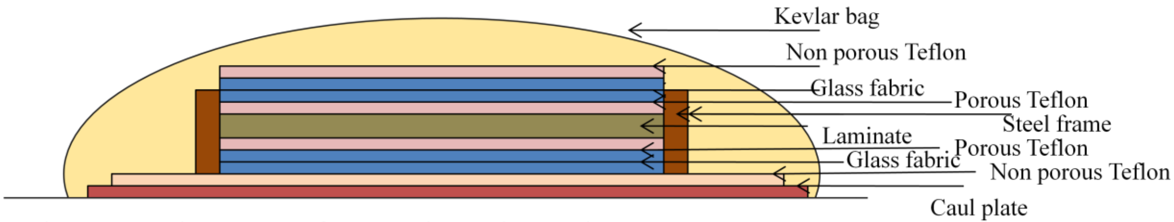


Figure 1: Bagging sequence for composite panel processing.

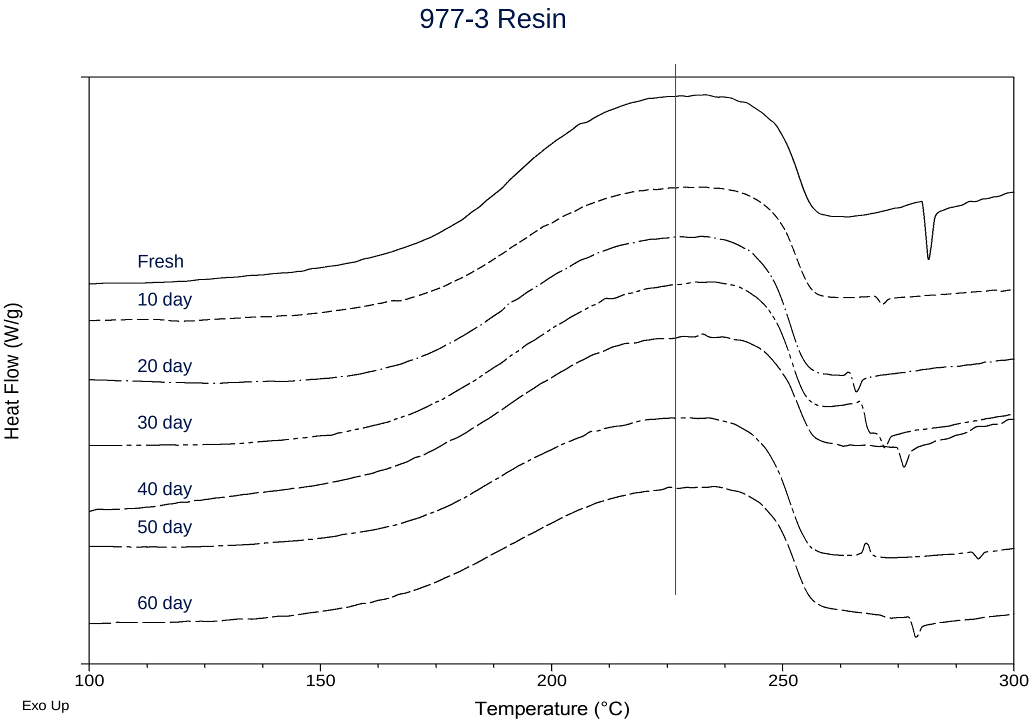
Laminate quality was characterized by C-scan (Ultrapac 1650/Ultrasonics by Physical Acoustic). DMA measurements provided T_g and modulus values of the cured laminate.

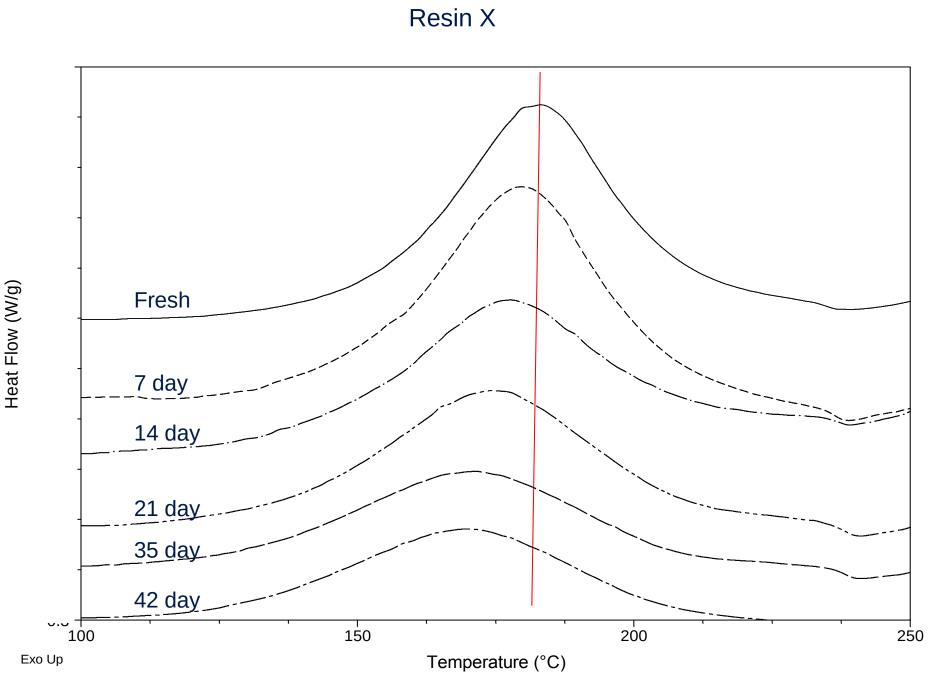
3. RESULTS AND DISCUSSION

The following results describe the cure kinetics and rheology of fresh and aged 977-3 and the resultant mechanical performance of autoclave processed panels.

3.1 DSC

DSC experiments of the 977-3 resin were run at three different heating rates; 0.5 ^{o}C (0.28°F) per min, 2 ^{o}C (1.11°F) per min, and 4^{o}C (2.22°F) per minute. Acquisition of three data points allowed calculation of kinetic parameters including the activation energy of the cure reaction. Additionally, the enthalpy of cure was tracked with respect to resin out-time by integration of the area under the exothermic reaction. Sample DSC curves are shown in Figure 2. There was not a measureable change in the enthalpy of the reaction with out-time, nor in the temperature at which the reaction occurred. This suggests little to no room temperature conversion of the resin well beyond the manufacturer's recommended out-life. Furthermore, the resin maintained a 'gummy' nature for up to 50 days at room temperature, becoming gradually brittle beyond that time. For comparison, the DSC curves of out-lifed Resin X show not only a drop in the enthalpy of cure with aging, but also a reduction in the temperature at which cure occurs. Such a trend is indicative of resin advancement. This is undesirable as cure advancement of the resin prior to processing could lead to poor consolidation, variation in cure within the structure, and variation in mechanical performance.[5]





Figures 2a and 1b: DSC curves of fresh and out-lifed (1a) 977-3 resin and (1b) Resin X.

The measured enthalpy of cure, as determined by the area under the exotherm in the DSC, is plotted in Figure 3 and illustrates the stability of 977-3 resin to room temperature out-time.

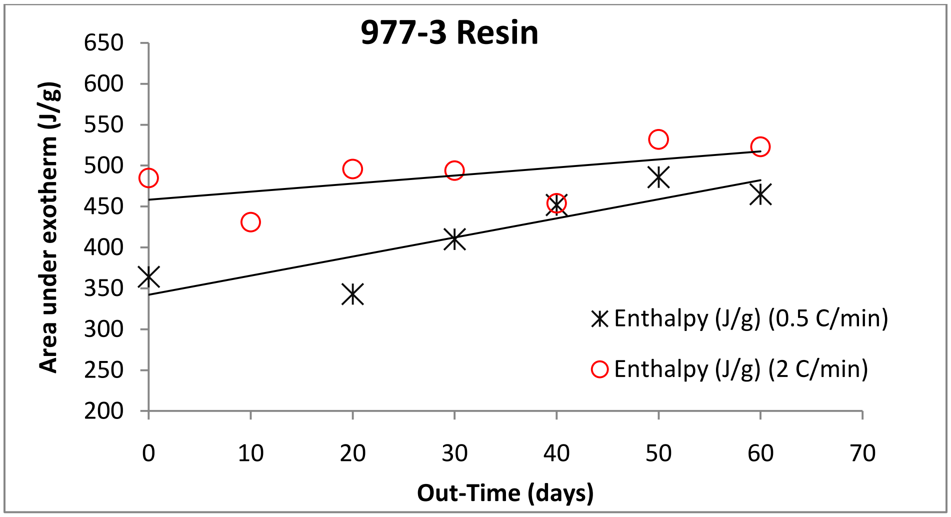


Figure 3: Plot of enthalpy of epoxy cure vs. resin out-time for 977-3 resin.

For clarity within the plot, the data for the 4°C per minute ramp was omitted as it tends to overlap the other datasets. All of the ramp rates show an apparent increase in the area under the epoxy cure exotherm. This may be attributed to moisture absorption into the resin as it was aged. Past work has demonstrated an increase in epoxy reaction rate following prepreg aging in a humidity chamber.[6] However, the influence of moisture absorption on the reactivity of 977-3 resin was not investigated in this study. By comparison, Resin X showed a measureable reduction crosslinking enthalpy with out-time as plotted in Figure 4.

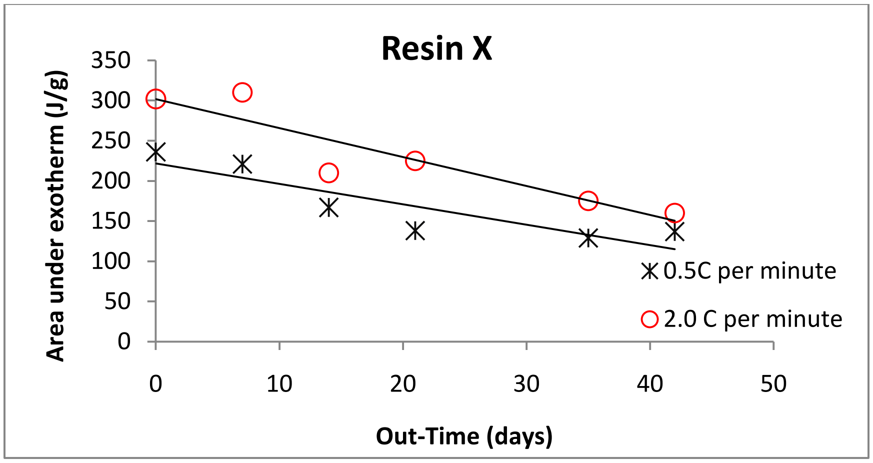


Figure 4: Plot of enthalpy of epoxy cure vs. resin out-time for Resin X.

The cure kinetics of the resin were calculated from dynamic DSC experiments based on the Flynn/Wall/Ozawa method.[7] The calculated Ea was stable over the 60 day out-time as plotted in Figure 5. Stability of the activation energy implies there was limited conversion of the 977-3 resin during the 60 days at room temperature. The fluctuation in the data is likely due to the minimal number of data points collected at each out-time. The Flynn/Wall/Ozawa method described in ASTM E698-05 requires a minimum three DSC scans to construct a plot of log β vs 1/T; where β is the heating rate and T is the temperature of the peak of the reaction exotherm. An Arrhenius relationship is assumed and Ea is derived based on the slope of the curve. The ASTM standard was followed; however, the fluctuation in the activation energy data cannot be explained at this time. Additional ramp rates for each out-time may reduce the scatter.

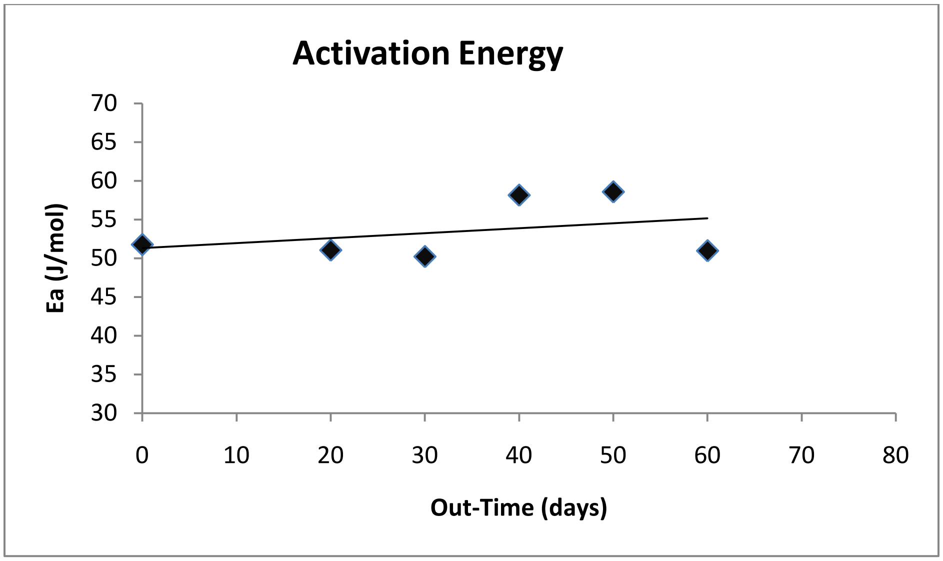


Figure 5: Activation energy of 977-3 resin from 0 to 60 days at room temperature.

3.2 DMA

The temperature profile used in the dynamic mechanical analysis experiments followed the manufacturers recommended cure profile, except the heating rate which was either 0.28 °C (0.5 °F) or 1.11 °C (2 °F) per minute. Therefore, the profile of the DMA experiment included a ramp to 177°C, followed by a 6 hour hold at that cure temperature. Two variables were studied in this experiment including ramp rate and prepreg out-time. Variation of ramp rate did not change the shape of the curve but shifted both storage modulus, E', and tan δ curves with respect to the hold temperature in the cure cycle.

- Figure 6 shows the storage modulus (E') vs. time scan (at the 1.11°C per minute ramp rate) of the fresh and 60 day out, uncured, epoxy prepreg. The plots show a reduction in E' at the onset of the experiment which is related to softening of the matrix on heating from room temperature. The mixture remains at a reduced E' until the hold temperature is reached in the cure profile (135 min, 177°C). At this time, the storage modulus begins to rise. Two peaks occur in the tan δ plot; the first peak maximum occurs at 145 minutes and appears to indicate the onset of gelation, and the second at 200 minutes would be indicative of vitrification.[8]

- There was a considerable reduction in the onset temperature of cure at the slower cure rate, 0.28°C per minute. The temperature scan also shows an early reduction in E' at the onset of the experiment due to softening of the matrix. However, at this ramp rate, the modulus begins to build at 155 °C, which is more than 20 °C earlier than the 1.11 °C/min rate. Tan δ peaks related to gelation and vitrification occur at 163 °C and 177 °C, respectively.

The vitrification peak does not necessarily mark the end of network formation, rather it indicates that the resin glass transition temperature, $T_{g,}$ has reached the cure temperature. As a result, the T_g of the isothermally cured resin will be higher than the cure temperature. It is important to note that the peak associated with vitrification occurs at 177 °C at both ramp rates. The primary difference was that the 0.28 °C per minute ramp led to vitrification at the onset of the isothermal hold, whereas at the faster ramp, vitrification was reached over an hour into the isothermal hold. Effects of the cure rate on the physical properties of a cured composite panel will be addressed later in the paper.

As with DSC, the DMA results showed little variation in prepreg behavior with out-time up to 60 days.

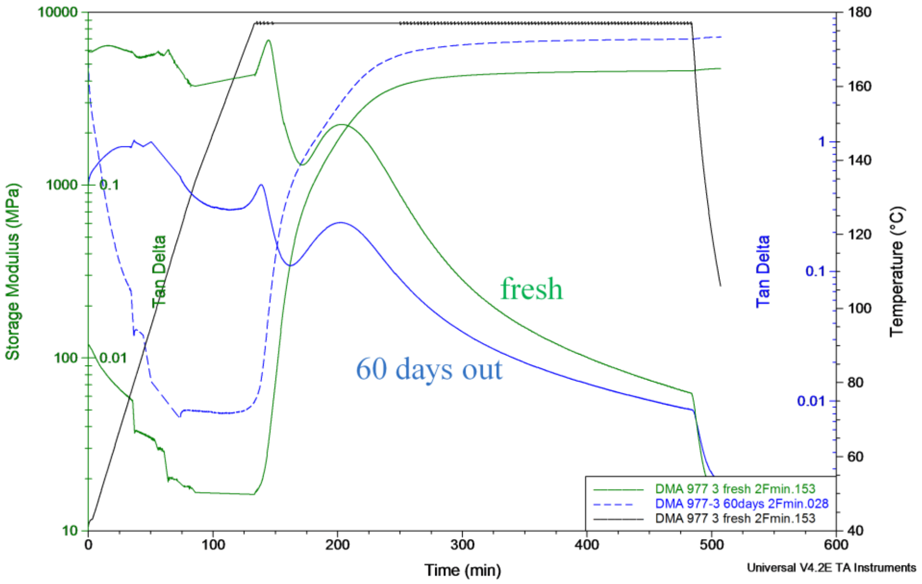


Figure 6: Dynamic Mechanical Analysis plots of IM7/977-3 following 0 and 60 days out-time, following a 1.11 °C/min ramp rate.

3.3 Composite Properties

Quality of the cured laminates was examined by C-scan. The results indicated comparable consolidation between 0 and 60 days; Figures 7 and 8 respectively. Dark black or orange colors from the C-scan are indicative of a well consolidated part. There is obvious panel to panel variation, but no significant changes that would suggest the out-life panel was not consolidated to a level comparable to the fresh prepreg. However, processing differences were observed, including a reduction in resin bleed out as out-time increased as well as an increase in the average thickness of the laminate with out-time; from 1.78 mm with fresh prepreg to 1.93 mm with 60 day aged prepreg. Microscopic imaging and acid digestion experiments will be used to determine void content within the laminates and any contribution of voids to the increase in thickness of the aged specimens.

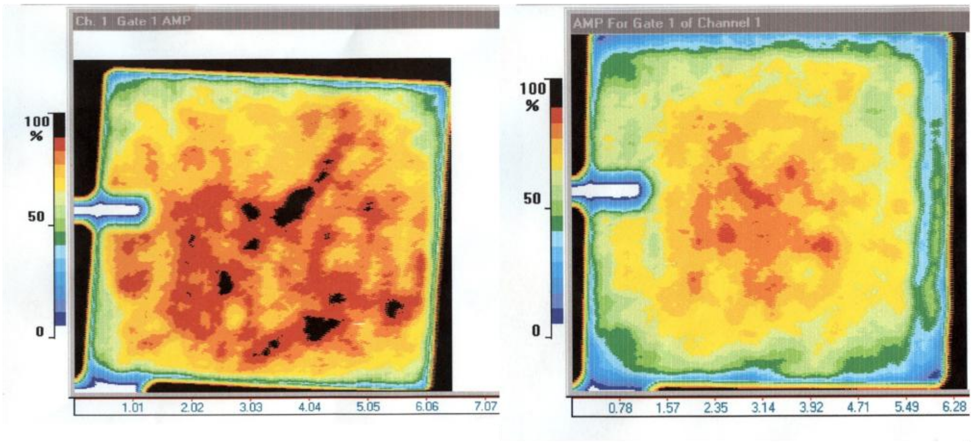


Figure 7: C-scan images of IM7/977-3 laminates processed from fresh prepreg at a 0.28°C (left) and 1.11°C (right) per minute ramp rate.

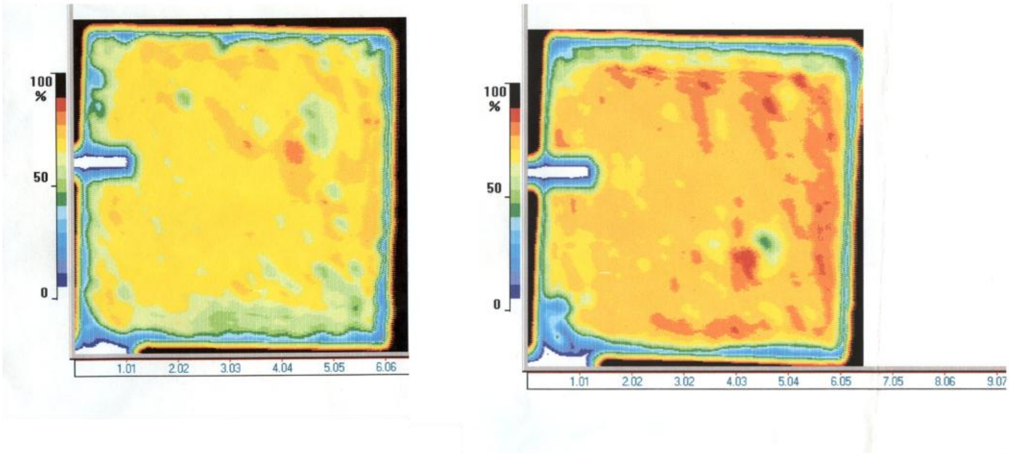


Figure 8: C-scan images of IM7/977-3 laminates processed from 60 day out-time prepreg at a 0.28 °C (left) and 1.11 °C (right) per minute ramp rate.

T_g of the cured composite laminate was characterized by DMA in single cantilever beam mode. The T_g was taken as the intersection of extrapolated tangents of the plateau region and the modulus drop. The data did show a drop of the T_g with out-time. This was more significant when employing the 0.28 °C per minute ramp rate.

T_g of the fresh material was 235 °C and 229 °C following ramp rates of 0.28 °C and 1.11 °C per minute, respectively. The T_g of panels prepared from prepreg with a 60 day out-time had a T_g of 211 °C and 222 °C where the ramp was 0.28 °C and 1.11°C per minute, respectively.

The chemical analysis and flat panel preparation indicate that the prepreg was processable with little change to the laminate T_g. However, these analyses do not account for the prepreg tack, which is critical for laying up complex parts. Qualitative inspection of the prepreg showed a minimal amount of tack remaining at 60 days, and a significant loss of flexibility. Such characterization should be included into future work.

4. CONCLUSIONS

DSC and DMA analyses demonstrated that IM7/977-3 offered minimal cure advancement of the resin when left at room temperature for up to 60 days. DSC showed no change in the enthalpy of the crosslinking reaction with aging, or in the temperature at which the epoxy cure process occurs. DMA also showed similar stability with out-time. The DMA plots did however show a reduction in gelation and vitrification temperatures as the ramp rate was reduced from 1.11 °C to 0.28 °C. This, however, did not influence the T_g of the cured laminate; as there was not a substantial difference in the T_g of the fresh material prepared at the different ramps. Ultrasonic scanning suggests the panels are well consolidated, even following 60 days at room temperature and ambient conditions; however, additional characterization of the laminate quality will be necessary.

5. REFERENCES

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