

Curing cycle modification for RTM6 to reduce hydrostatic residual tensile stress in 3D woven composites

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ABSTRACT: Triaxial residual tensile stresses resulting after cooling a 3D woven composite from the curing temperature cause cracking in the resin pockets for weave architectures that have high through-the-thickness constraint. We show how curing cycle modifications can reduce the hydrostatic tensile stress generated by thermal mismatch during cooling of Hexcel RTM6 epoxy resin constrained in a quartz tube which simulates extreme constraint in a composite. The modified curing schedule consists of a high temperature cure to just before the glass transition, a lower temperature hold that takes the resin through the glass transition thereby freezing in the zero stress state, followed by high temperature cure to bring the resin to full conversion. We show that this process is sensitive to heating rates and can reduce the zero stress state of non-toughened RTM6 resin to a temperature similar to a commercial rubber-toughened resin, Cycom PR520. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43373.

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INTRODUCTION

Three-dimensional (3D) woven composites with high through-the-thickness constraint fabricated by resin transfer molding often exhibit resin pocket microcracking. The through-the-thickness constraint generates a significant hydrostatic tensile stress in the resin pockets that is not observed for 2D laminates. These stresses arise from the difference in coefficient of thermal expansion (CTE) between the resin and the carbon fibers (55 ppm/K vs. -0.4 ppm/K in the axial direction) as the composite cools from the curing temperature. This problem has been studied using mesoscale finite element methods and experimental methods in the following references.^{1–10} This article focuses on the measurement and control of hydrostatic tensile stress generated when a curing epoxy resin is constrained from contracting or expanding during curing and during cooling after curing.

While traditional pressure-volume-temperature (PVT) measurement systems can subject the material to a hydrostatic compressive stress, the only way to subject a material to a purely hydrostatic tensile stress is to constrain it in a container that has a different CTE than the material and change the temperature. We constrained the epoxy in a quartz tube and inferred the stresses in the resin from the displacement of the tube wall. A version of this technique was previously reported by Plepys¹¹ and used for Epon 828 epoxy with Jeffamine T-403 curing agent. Plepys¹¹ used strain gages to infer the stress

while we use a custom dilatometer to measure the change in diameter of the tube.

Minimizing the hydrostatic tensile stress will suppress the tendency toward resin pocket microcracking. This can be achieved through the use of fiber architectures with lower through-the-thickness constraint but such an approach does not take full advantage of the property enhancements from the 3D architecture. In this article, we show how the curing time–temperature profile can be modified to lower the hydrostatic tensile stress at a given temperature by control of the rubber-to-glass transition temperature.

EXPERIMENTAL

We subject Hexcel RTM6 epoxy resin to a nearly hydrostatic tensile stress by constraining the resin in a capped, low coefficient of expansion (CTE) fused quartz tube as it cools from the curing temperature.¹² The stress in the resin is generated from the thermal mismatch between the resin and the confining tube as it cools from the curing temperature. The low CTE of the quartz tube is intended to simulate the extreme of process-induced stresses that may occur in the resin pockets of 3D woven composites as well as evaluating failure theories under nearly pure hydrostatic tension.

The tube wall displacements were measured using a high resolution custom dilatometer as shown in Figure 1, see Ref. 13. The stress in the resin was estimated from the tube wall displacements, $2u$,

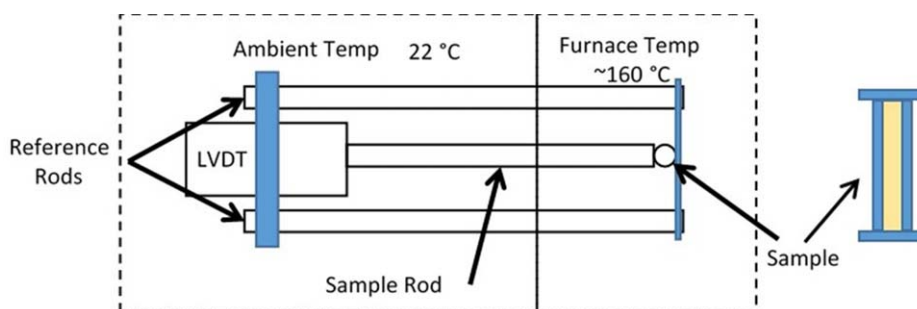


Figure 1. Schematic of dilatometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

referenced to an empty tube subjected to the same temperature cycle using plane strain pressure vessel equations¹⁴:

$$u = \frac{-2\sigma_H(1-\nu^2)r_i^2r_o}{E'(r_o^2-r_i^2)} \quad (1)$$

$$E' = \frac{E}{1-\nu^2}; \quad \nu' = \frac{\nu}{1-\nu}$$

The inner and outer radius are r_i and r_o , respectively, E is the elastic modulus, ν is Poisson's ratio of the quartz, and σ_H is the hydrostatic stress which is positive for hydrostatic tension. The measurement system exhibited less than 25 nm hysteresis for an empty tube subjected to a full thermal cycle. This is equivalent to a hydrostatic resin stress resolution of approximately 0.5 MPa.

The temperature of the quartz tube wall was measured with an Omega C01, low thermal mass, cement-on thermocouple that was glued to the quartz tube. The furnace chamber was approximately 50 mm × 40 mm × 40 mm and was heated using flowing hot air from a heat gun. The temperature was controlled using a PID temperature controller that was carefully tuned to minimize the difference between the command and the feedback temperatures. The thermal time constant of the quartz tube/epoxy system is estimated to be approximately 15 s using a lumped capacitance model assuming a heat transfer coefficient of ~ 200 W/m²·K for air and ~ 6 s assuming the thermocouple accurately measures the surface temperature of the cylinder. There is minimal thermal lag between the temperature of the resin and the outer surface of the quartz tube.

The Hexcel Hexflow RTM6 resin used in this work was purchased by Albany Engineering Composites and stored at -12°C prior to being packed in dry ice for transport to the University of New Hampshire where it was stored at -18°C . The resin was thawed to room temperature, heated to 100°C , degassed for 5–10 min at a vacuum of ~ 10 kPa, and injected into 3 mm inner diameter, 6 mm outer diameter, and ~ 20 mm long quartz tubes. Prior to injection, the tubes were cleaned in several soap solutions, rinsed with distilled water, dried, capped on one end using a small amount of RTM6 resin to attach a square piece of glass, and then stored in ethanol. The final cap was placed on the top of the tube after it was injected with resin. It is not firmly attached until the resin cures.

RESULTS AND DISCUSSION

Concept of Zero Stress Temperature

Figure 2 shows representative stress vs. temperature curves for two different slightly modified, standard cure cycles;

- Room temperature (RT) to 160°C at $5^\circ\text{C}/\text{min}$, hold for 75 min at 160°C , cool to room temperature
- Room temperature to 160°C at $5^\circ\text{C}/\text{min}$, hold for 75 min at 160°C , heat to 180°C at $5^\circ\text{C}/\text{min}$, hold for 120 min, cool to room temperature

(The standard heating/cooling rates are $1^\circ\text{C}/\text{min}$ and we will show this is an important difference.) Note that there is no stress generated during the heating portion.

For the RT- 160°C -RT cycle, a small amount of stress is generated during the hold period which we attribute to curing-induced shrinkage. The stress increases linearly on cooling from 160°C until it drops discontinuously when the resin extensively fractures. We used Eq. 4 from Ref. 15 to estimate that the resin has cured to a $\sim 85\%$ conversion after the 160°C , 75 min hold.

For the RT- 160°C - 180°C -RT cycle, when the resin is heated from 160°C to 180°C , there is initially a linear increase in compressive stress suggesting it is in the glassy state. However, the stress decreases to nearly zero during the 120 min hold at 180°C . The stress increases linearly on cooling from the final post cure temperature until the resin fractures.

We empirically define the zero stress temperature, T_z , as the temperature at which the stress vs. temperature plot intersects the temperature axis for zero stress. The value of T_z is

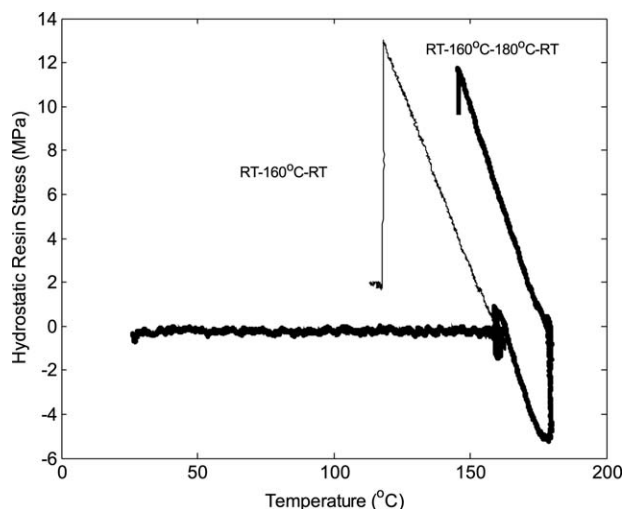


Figure 2. Hydrostatic resin stress vs. temperature for two slightly modified standard cure schedules for RTM6.

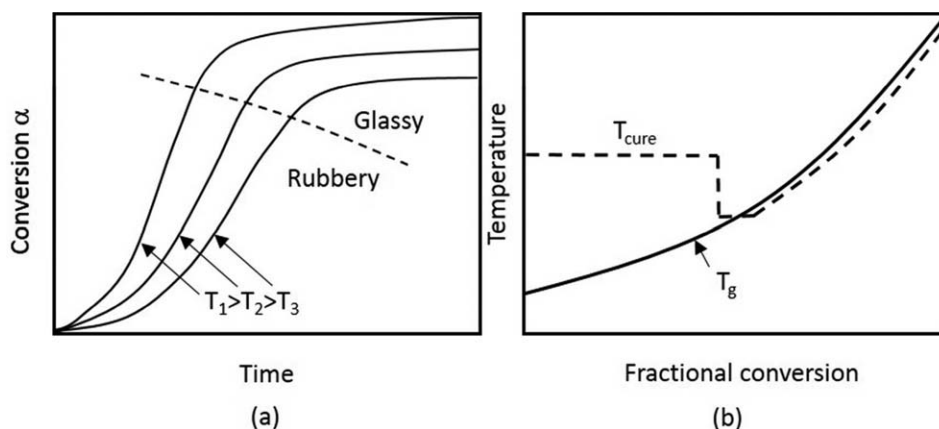


Figure 3. (a) Schematic conversion vs. time and temperature vs. conversion for “typical” epoxy. (b) Schematic dependence of T_g on degree of conversion. The dashed line shows the proposed temperature vs. conversion path to shorten the time to fully cure the resin while going through the rubber-glass transition at a low temperature to achieve a lower zero stress temperature.

approximately 160°C for the curing temperature for the RT-160°C-RT cycle. The value of T_z is approximately 180°C for the RT-160°C-180°C-RT cycle which is also the final curing temperature. The hydrostatic stress linearly increases on cooling from T_z according to $\sigma_H = \beta(T_z - T)$ where $\beta > 0$. While β is related to fundamental parameters, we use it simply as a fitting constant to describe the stress-temperature behavior on cooling. If T_z can be shifted to a lower temperature, T_z' , the thermal mismatch stress at a given temperature can be decreased by $\Delta\sigma_H = \beta(T_z - T_z')$. For the constraining tube, β is a function of the CTE difference between the resin and tube material, the bulk modulus of the resin, and the stiffness of the constraining tube which is a function of the tube modulus and the inner and outer radii.

Figure 2 illustrates that the zero stress temperature can be impacted by processing conditions for a constant tube geometry and CTE difference. This article shows how the curing process can be manipulated to decrease the hydrostatic tensile stress in a finished part. This may prevent resin pocket microcracking and will definitely improve the load carrying capacity and fatigue resistance.

Lowering the Zero Stress Temperature by Controlling the Temperature of the Rubber-to-Glassy Transition

The curing process of epoxide resins with amine linkers has been extensively investigated by a number of groups for over 50 years (see Ref. 16–21 for a brief list of articles that influenced this article). Mooseburger-Will performed two recent studies describing the properties of partially cured RTM6 which are highly relevant to this work.^{17,22} At any given curing temperature, the resin starts out as a liquid where the viscosity increases with curing time until the resin reaches the gel state and has infinite viscosity. The resin in the gel state is proposed to consist of one large interconnected molecular network with the unreacted epoxide and linker molecules in the interstices. At this point, the resin is in the rubbery state and the modulus monotonically increases with time in concert with increasing degree of conversion of the remaining molecules. As this progresses, there is a transition range where the material is said to vitrify going from the rubbery to glassy state. If the material is constrained, the temperature at which it goes through the rubbery-to-

glassy transition is proposed to be the zero stress temperature. This is supported by the experimental measurements described in this article. The modulus increases significantly over this transition range. The continued conversion of the remaining molecules into the network progresses at a diffusion-controlled rate which is at least an order of magnitude slower than the previous reaction-controlled rate. This transition in reaction rate leads to a saturation in the degree of conversion at a given curing temperature as summarized in the schematic of Figure 3(a).

The glass transition temperature, T_g , is approximately equal to the curing temperature when it initially vitrifies but continues to slowly rise to a limiting value with continued conversion. The T_g for RTM6 can be related to the degree of conversion through the following formula¹⁵:

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2)$$

where α is the degree of conversion, $\lambda = 0.453$ is a fit constant, $T_{g0} = -11^\circ\text{C}$ is the glass transition temperature for the monomer and $T_{g\infty} = 206^\circ\text{C}$ is the glass transition temperature for the fully cured monomer. This dependence of T_g on degree of conversion is also summarized in the schematic in Figure 3(b).

Figure 2 illustrated that lowering the curing temperature can result in lower zero stress temperature which thereby lowers the driving force for cracking in the resin pockets. However, this approach has two disadvantages. First, the time to go through the rubbery-to-glassy transition becomes unacceptably long from a processing standpoint (>240 min at 120°C vs. 60 min at 160°C (Hexcel RTM6 Product literature) and the maximum degree of conversion is lower for lower cure temperatures. Lower conversion leads to lower T_g and lower strength.

We propose to solve this problem using the following procedure:

- Partially cure the resin at a higher temperature until it reaches a degree of conversion that is just before the rubbery-to-glassy transition at the lower curing temperature. The goal of this step is to decrease the amount of time to reach a given degree of conversion.

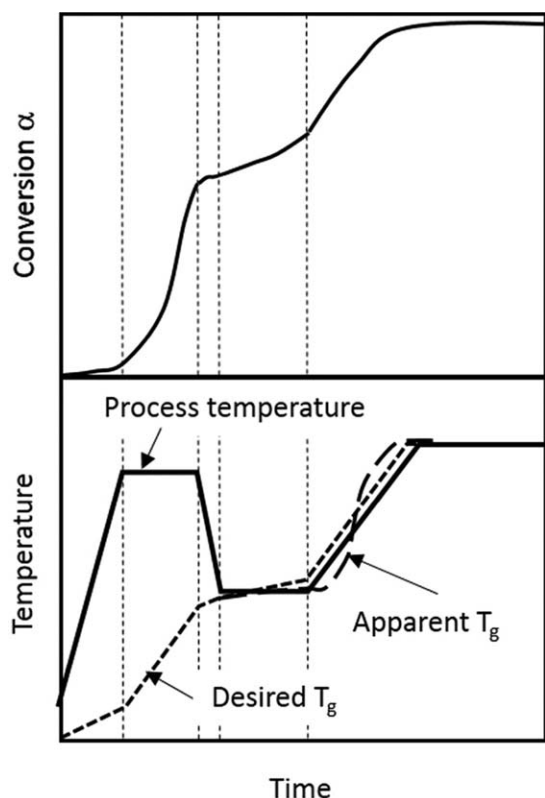


Figure 4. Conversion (upper) and temperature (lower) vs. time for proposed curing schedule. The apparent T_g line schematically shows that we believe our process temperature was above T_g on the initial portion of the second ramp. This provides an explanation for the behavior shown in Figure 8.

- Continue the cure at a significantly lower temperature until it goes through the rubbery-to-glassy transition thereby freezing in the zero stress state at the lower temperature.
- Increase the degree of conversion to nearly 100% (and therefore get the maximum T_g) by raising the temperature to that typically associated with the final standard cure—120 min hold at 180°C.

The proposed process is shown as the dashed line in the schematic of T_{cure} vs. fractional conversion in Figure 3(b).

This final step must be done in such a way so that the heating rate is not so high to cause the resin to revert back to the rubbery state and erase the zero stress state. However, the desire to minimize processing time requires as high a heating rate as possible. We speculate that this transition in conversion rate from the rapid reaction-controlled rate to the slower diffusion-controlled rate occurs gradually over the same range as the rubbery-to-glassy transition. One could expect the conversion to progress at a decreased, but significant, reaction-controlled rate that is well above the diffusion controlled rate if T_{cure} is only slightly below T_g .

Modification of the Curing Schedule to Achieve Low Zero Stress Temperature

The upper schematic in Figure 4 shows the proposed progression of the degree of conversion as a function of time for the process temperature vs. time plot in the lower schematic. The

transitions in conversion rate are correlated to the process temperature changes in the lower schematic. The lower schematic also has the desired (and apparent) transitions in T_g relative to the process temperature. While it was our intention to keep the process temperature below T_g , we did not optimize the process. The “Apparent T_g ” line will be correlated with our observations in Figure 8.

The following quantities must be determined to achieve the goals of the modified process.

1. The maximum cure time at the high temperature (160°C in this case) so that the resin is still in the rubbery state at the lower cure temperature.
2. The time to transition the partially cured resin from the rubbery to glassy state at the lower cure temperature.
3. The maximum heating rate to the final cure temperature so that conversion can continue to progress while staying below the T_g for the evolving degree of conversion

Figure 5 shows the hydrostatic stress as a function of temperature for several different curing times at 160°C. The stress increases immediately on cooling for the standard 75 minute cure. However, the resin can be cooled to 100°C for the 50 min cure before the stress begins to increase. The stress begins to increase at about 60°C for the 40 min cure and never increases for the 30 min cure.

We propose that the temperature at which the stress increases is the T_g for the current degree of conversion. To support this proposal, we show the stress vs. temperature curve for Cycom PR520, a toughened resin in Figure 6. We subjected the resin to the standard cure schedule, 120 min at 180°C, and cooled at 5°C/min. The Cycom product literature states that $T_g = 160^\circ\text{C}$. The stress is slightly compressive with a very small stress-temperature slope for $T > T_g$. It increases linearly with decreasing temperature when $T < T_g$. Therefore, we can assume the slope transition is associated with T_g .

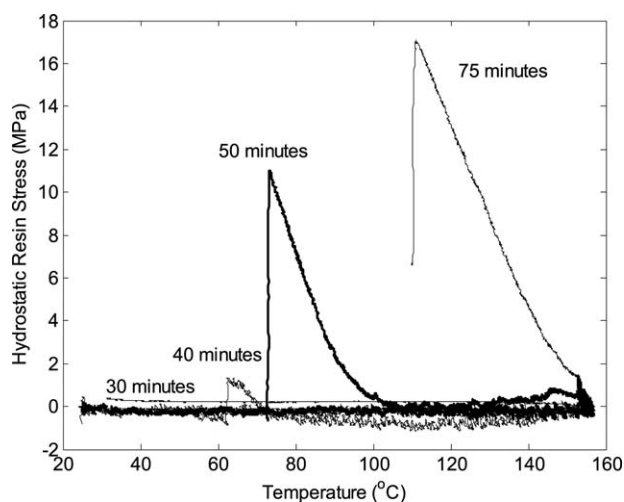


Figure 5. Resin hydrostatic stress vs. temperature for several different cure times at 160°C. The manufacturer’s recommended cure time, 75 min, yields linear, glassy behavior on cooling. The shorter cure times all exhibit a zero stress plateau before the stress linearly increases with further cooling.

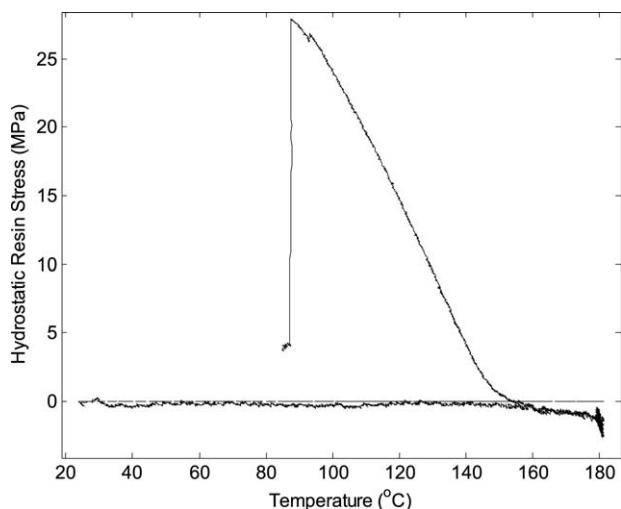


Figure 6. Hydrostatic resin stress vs. temperature for Cycom PR520 rubber-toughened resin subjected to the recommended cure. The zero stress temperature is $\sim 150^{\circ}\text{C}$ for a cure temperature of 180°C . The initial zero stress plateau is attributed to the rubbery domains.

If we assume that the temperature at which the stress increases is the T_g , then using eq. (2), the degree of conversion is ~ 0.5 for the 40 min cure and 0.65 for the 50 min cure. The maximum degree of conversion for the 160°C cure is approximately 0.89. The maximum degree of conversion at 120°C is approximately 0.77. We chose to limit the cure to 30 min at 160°C to ensure that it was in the rubbery state for the low temperature cure. In fact, the resin was likely in the liquid state with a conversion of approximately 0.3–0.4 after 30 min at 160°C based on Karkanis' viscosity-temperature-time data.¹⁵ We could/should have accelerated the process by curing for 50–60 min and still have been in the rubbery state at 120°C . The maximum allowable conversion would have been ~ 0.77 . This could be the subject of future work.

The next step was to determine how long of a hold time at 120°C was necessary to bring the RTM6 resin to the glassy state after the 30 min hold at 160°C . Figure 7 shows the hydrostatic stress on cooling from 120°C for different hold times. The stress does not immediately increase on cooling for the 40 min hold indicating it is in the rubbery state. It does increase on cooling for 60 min holds and longer indicating it is in the glassy state at 120°C and below. We chose a hold time of 50 min at 120°C to minimize the total cycle time.

The final step is to fully cure the material at 180°C . However, this process is complicated by the fact that this is above the T_g for the state of conversion achievable at the low curing temperature ($T_g \sim 120^{\circ}\text{C}$ and the maximum conversion is 0.77). Heating above T_g will shift the material back to the rubbery state and erase the frozen-in zero stress temperature. One solution to this problem is to control the heating rate so that $T < T_g$ as the resin continues to increase the degree of conversion.

Figure 8 compares the hydrostatic stress vs. temperature curve for ramp rates of $0.5^{\circ}\text{C}/\text{min}$, $1^{\circ}\text{C}/\text{min}$, and $5^{\circ}\text{C}/\text{min}$; for samples that had already been subjected to 30 min at 160°C , $5^{\circ}\text{C}/\text{min}$ to 120°C , and 50 min at 120°C . The stress initially stays close to zero as the temperature is increased for the $0.5^{\circ}\text{C}/\text{min}$ ramp

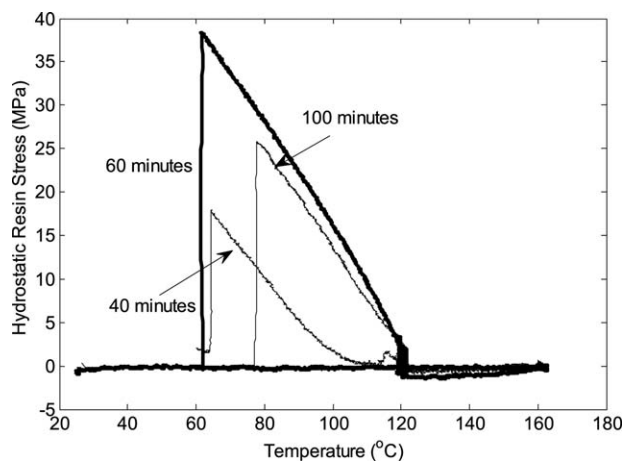


Figure 7. Hydrostatic resin stress vs. temperature for RTM6 resin subjected to a 30 minute hold at 160°C followed by 40, 60, and 100 minute holds at 120°C .

rate. This strongly suggests the resin is in the rubbery state. The resin exhibits a linearly increasing compressive stress for $T_{\text{process}} > 150^{\circ}\text{C}$ which is consistent with the glassy state. Apparently the conversion increased during the ramp to the point where $T_{\text{process}} < T_g$. The compressive stress continues to increase in magnitude until it reaches the 180°C curing temperature and stays stable until the sample is cooled. No relaxation of stress occurs during the 120 min hold at 180°C . This behavior is consistent with the “Apparent T_g ” in the schematic of Figure 4. The fact that the stress is the same for the heating and cooling and goes tensile on further cooling further supports the assertion that the resin is in the glassy state once $T_{\text{process}} > 150^{\circ}\text{C}$. The zero stress temperature is $\sim 150^{\circ}\text{C}$ for the $0.5^{\circ}\text{C}/\text{min}$ rate which is approximately the same as for the Cycom PR520 toughened resin as shown in Figure 9. However, this is roughly a 30°C improvement over the 180°C zero stress temperature for the standard cure as shown in Figure 2. Had we cured for longer at

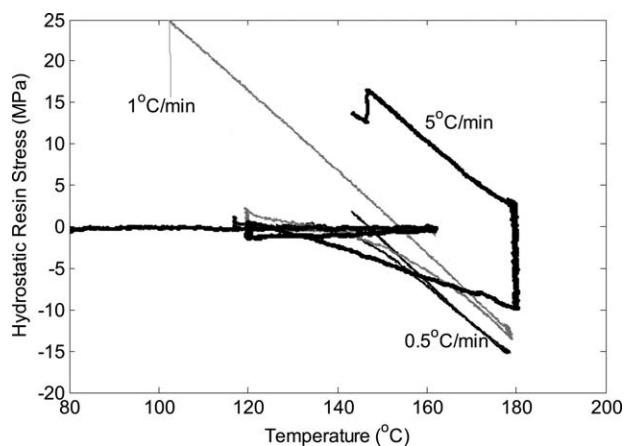


Figure 8. Hydrostatic resin stress vs. temperature for resin subjected to a 30 min cure at 160°C , a 50 min cure at 120°C , and subsequently heated at different temperature ramp rates to 180°C for a 120 min hold to finish the cure. The zero stress state is $\sim 150^{\circ}\text{C}$ for the $0.5^{\circ}\text{C}/\text{min}$ ramp rate and $\sim 200^{\circ}\text{C}$ for the $5^{\circ}\text{C}/\text{min}$ ramp rate.

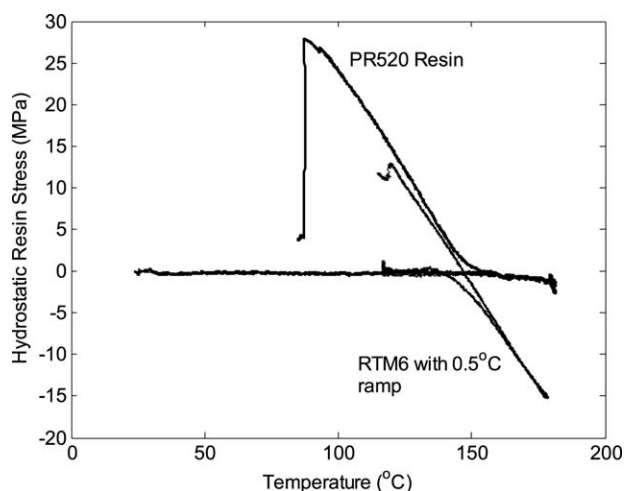


Figure 9. Comparison of hydrostatic resin stress for Cycom PR520 resin and for the RTM6 resin with the modified cure cycle that uses the 0.5°C/min heating rate.

160°C and 120°C, the degree of conversion might be high enough to keep $T_{\text{process}} < T_g$ during the entire ramp from 120°C.

The stress–temperature curves in Figure 8 for faster ramp rates exhibit behavior that is consistent with strain rate effects for rubbery deformation. The compressive stress immediately begins to increase in magnitude on heating for 5°C/min ramp rate. This could suggest that the resin is in the glassy state but the slope of the stress vs. temperature curve for heating is lower than for the cooling curve. We attribute this linear increase in the magnitude of the compressive stress to a strain rate effect – the rubbery network is being strained so rapidly it cannot reach its nearly zero stress state.^{23,24} The proposal that the resin is in the rubbery state is supported by the observation that the stress relaxes significantly during the 180°C temperature hold. It even exhibits a modest tensile hydrostatic stress before cooling which we attribute to curing induced shrinkage. The extrapolated zero stress temperature is ~200°C. The 1°C/min ramp exhibits intermediate behavior with a zero stress temperature of ~160°C.

The time to the end of the 180°C hold for the standard schedule is 355 min. The time to the end of the end of the 180°C was 468 min for the modified cure with the 0.5°C/min ramp rate. The difference in stress at a given temperature during cooling was about 16 MPa. The time to the end of the 180°C was 408 min for the 1°C/min ramp rate resulting in a hydrostatic tensile stress difference of ~13 MPa. If we had been able to modify the cure schedule so that the zero stress temperature was 120°C, the hydrostatic stress reduction would have been ~27 MPa which is approximately equal to the hydrostatic failure stress published for a similar epoxy obtained using a poker chip specimen.^{25,26}

The observation that the hydrostatic tensile and compressive stress in the partially cured resin is negligible after ramping from a hold period until it reaches a specific temperature where the stress increases linearly is difficult to explain. If we assume that the stress increases when the partially cured resin reaches its T_g , the change in slope from zero to a finite value implies a fairly large increase in the bulk modulus at the transition. However, Grassia and

D'Amore²⁷ made PVT measurements that show the bulk modulus only increases by a factor of 1.5–2 when polycarbonate is below T_g . Saraswat *et al.*²⁸ used PVT apparatus to measure the bulk modulus of Epoxy Novolac (EPN 1180) from using Bisphenol-A as a hardener and 1.5% triphenylphosphine (TPP) as catalyst. They also showed that the bulk modulus increases by a factor of 1.5–2 when going through the glass transition but also increases linearly with decreasing temperature. Thus, one would expect that the slope of the stress–temperature curve above the observed transition temperature to be no less than half of that observed below the transition temperature. This is not the case. We do not have an explanation for this behavior and present it as an experimental observation that cannot be attributed to an artifact.

SUMMARY

We used a novel dilatometric technique to demonstrate that curing cycle modifications can significantly decrease the hydrostatic tensile stress in RTM6 resin that is constrained from contracting during cooling from the curing temperature. The curing cycle modifications are based on the resin going through the rubber-to-glass transition at as low a temperature as possible. This was accomplished by an initial higher temperature cure to increase the degree of conversion as rapidly as possible prior to going through the rubber-to-glass transition at the lower curing temperature. We found that the heating from the lower temperature cure to the final finishing cure must be done at a low enough rate to prevent the resin from transitioning back to the rubbery state. The modifications increase the total curing time but to a lesser degree than an extended low temperature cure.

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