

# Evaluation of Cyanate Ester Prepreg Material Exposed to Uncontrolled Thermal Conditions During Storage

20 September 2009

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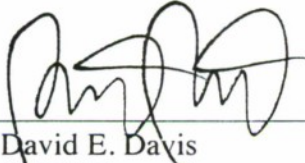
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## 1. Introduction

A contractor recently realized that freezers used for the storage of multiple lots of YLA's RS3C/M50J polycyanurate prepreg had experienced a malfunction that had not been identified for several years. This prepreg material is used to make composite for critical space hardware. The material is to always be maintained at 0°F or lower. However, the freezer had been running at approximately 10–20°F above specified requirements with some excursions as high as 60°F for extended periods of time. The freezer storage thermal data was being recorded, but not assessed by contractor personnel. The higher-than-expected storage temperatures may affect the materials in several ways. If the temperature increases during storage, the degree of polymerization will advance, and thus the molecular weight of the polymer will increase. This increase in molecular weight translates into an increase in viscosity of the polymer that will prevent proper consolidation of the composite during processing. Improper consolidation creates increases in porosity, which, in turn, reduces mechanical performance of matrix-dominated properties. In addition, cyanate ester resins are extremely susceptible to hydrolysis during storage and/or cure. A small degree of absorbed moisture can cause hydrolysis of the cyanate monomer and prevent the primary crosslinking reaction of the network. Typically, this will form carbamates and thus affect the polymerization mechanism, which may result in a degradation of both mechanical and thermal performance, as shown in Figure 1. All materials stored in these freezers have been quarantined awaiting suitable testing.

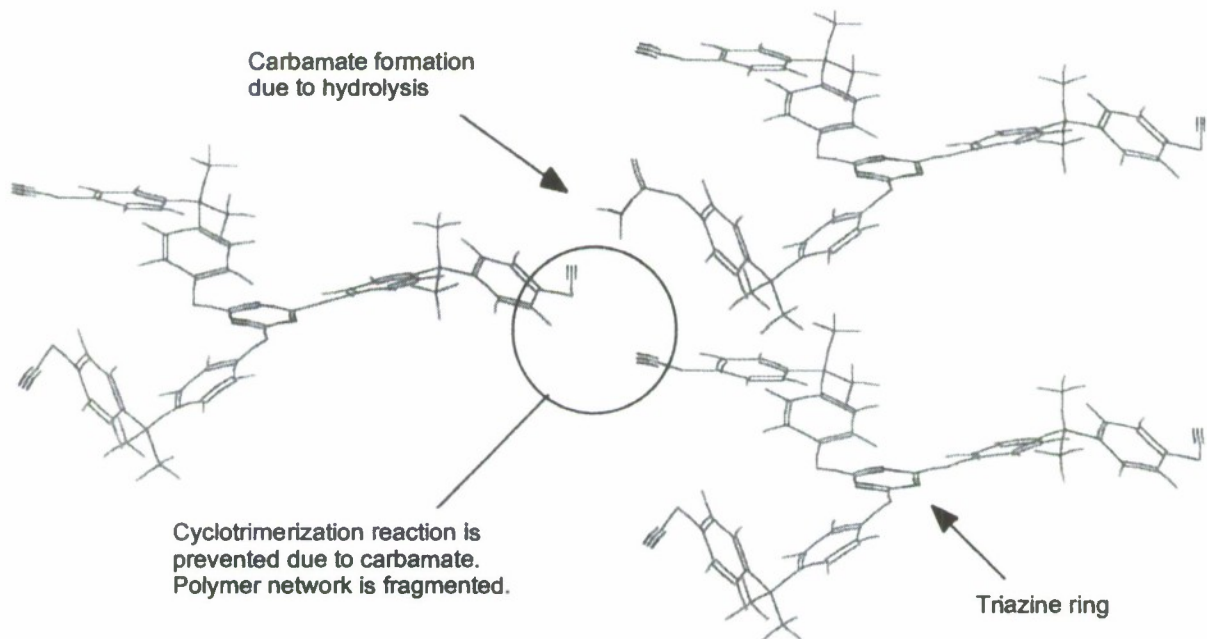


Figure 1. Chemical diagram showing how potential carbamate formation of cyanate ester can prevent cyclotrimerization of the polymer network.

The contractor has proposed that gelation tests be performed on these rolls to verify whether any changes can be identified. A slower gelation time will indicate a more aged system, and indirect correlations can be made with the rheological profile of this system. However, we believe that due to the inherent inaccuracies of gelation tests by the route the subcontractor has proposed, these tests are not sensitive enough to detect changes within the resin. In addition, these tests would not provide any information relative to whether hydrolysis of the network has occurred.

Glass transition temperature (T<sub>g</sub>) measurements by dynamic mechanical analysis (DMA) have been shown to be the best quality control technique to determine whether issues due to hydrolysis have occurred for cyanate-ester composites.\* We have proposed to perform DMA testing of composites manufactured using prepreg material from the affected rolls. The parts will be vacuum bagged and cured by the contractor using the same cure schedule and ovens that are used for the actual hardware. In addition, Tencate, Inc. (resin formulator) has provided prepreg material to the contractor from two additional batches that have been stored properly at the supplier site. This material will also be used to manufacture laminates by the same process and effectively used as the control specimens. The T<sub>g</sub> and loss modulus curve will be used to compare the unaffected prepreg material to the control. In addition, secondary post-treatment methods that were developed at Aerospace as quality control screening techniques will be used to further evaluate the thermal degradation behavior of the composites. This will allow us to more accurately assess what effect subsequent thermal cycling and/or thermal exposure will have on the composite parts using DMA.

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\* R. J. Zaldivar, "Lessons Learned in the Processing of Polycyanurate Resin Composites," TR-98(8565)-8, Technical Report, The Aerospace Corporation, Feb. 2002

## 2. Experimental

### 2.1 Composite Manufacture

Ten plies of Tencate M50J/RS3C resin were used in the manufacture of all composites investigated in this study. Unidirectional plies (12 in. x 12 in.) were taken from each affected roll and stacked, vacuum bagged, and cured. A standard cure schedule was used for the processing of all composites. The heat-up rate was 1°C/min up to 177°C for 2 hours. An autoclave pressure of 100 psi was maintained during processing. The control specimen was manufactured and cured in an identical manner by the contractor.

### 2.2 Dynamic Mechanical Analysis (DMA)

#### 2.2.1 DMA Single-Point Test After Processing

Dynamic mechanical analysis was performed on all composite laminates to evaluate the effect of improper storage on the T<sub>g</sub>. The specimen configuration used for testing was 0.5 in. x 1.0 in. x 0.1 in. A TA Instruments DMA Analyzer was used for all testing. The samples were tested in a single cantilever mode at a frequency of 1 Hz and a maximum displacement of 20 μm. The samples were scanned from room temperature to 300°C at a heat-up rate of 5°C/min. The glass transition temperature (T<sub>g</sub>) was identified as the maximum in loss modulus profile curve. Ten runs were performed on each of the control laminates.

#### 2.2.2 DMA Post-Treatment Test

Segments (2.0 in. x 2.0 in.) for each of the cured laminates were further post-treated at 193°C for 148 h. DMA testing was performed on portions of the 2 in. x 2 in. composite specimens at various intervals. The intervals were 50, 100, and 150 h. The T<sub>g</sub>'s were measured and compared to their initial T<sub>g</sub>. A decrease in T<sub>g</sub> indicates thermal degradation due to carbamate formation. No decreases in T<sub>g</sub> indicates that the resin material has negligible carbamate formation.

### 2.3 Optical Microscopy

Composite cross-sections were epoxy mounted and sanded using 250, 400, and 600 grit paper. The samples were then polished using 6 μm and 1 μm diamond paste. The polished specimens were then analyzed using a Keyence optical microscope to evaluate consolidation of the composite parts.

### 3. Results and Discussion

All of the unidirectional composite specimens were manufactured and provided to Aerospace for analysis. A DMA scan similar to that shown in Figure 2 was performed for each segment of the samples. The compilation of scans shown in Figure 2 shows how the loss modulus peak shifts to lower temperature with increased carbamate formation. The loss modulus peak identifies the T<sub>g</sub> of the composite material. The loss modulus peak temperature as well as the area under the curve indicate the degree of hydrolysis the composite has undergone during cure. The two control specimens, Lot FB14k637-2A and Lot FBI4k686-23-2A, were analyzed using dynamic mechanical analysis. Ten singular tests were performed from segments of each 12 in. x 12 in. panel to verify reproducibility. The values for the T<sub>g</sub>'s were obtained by identifying the peak of the loss modulus curve.

Table 1 shows the T<sub>g</sub> values for both of these control panels. The T<sub>g</sub> is a function of the degree of cure the specimen has undergone. The cure schedule performed on these composites typically yields a T<sub>g</sub> of approximately 195°C when no negligible hydrolysis has occurred. As shown in Table 1, both laminates indicate that a minimal degree of carbamate formation has occurred. The average T<sub>g</sub>'s for both control specimens ( 3-2a and 23-2A ) is approximately 190°C.

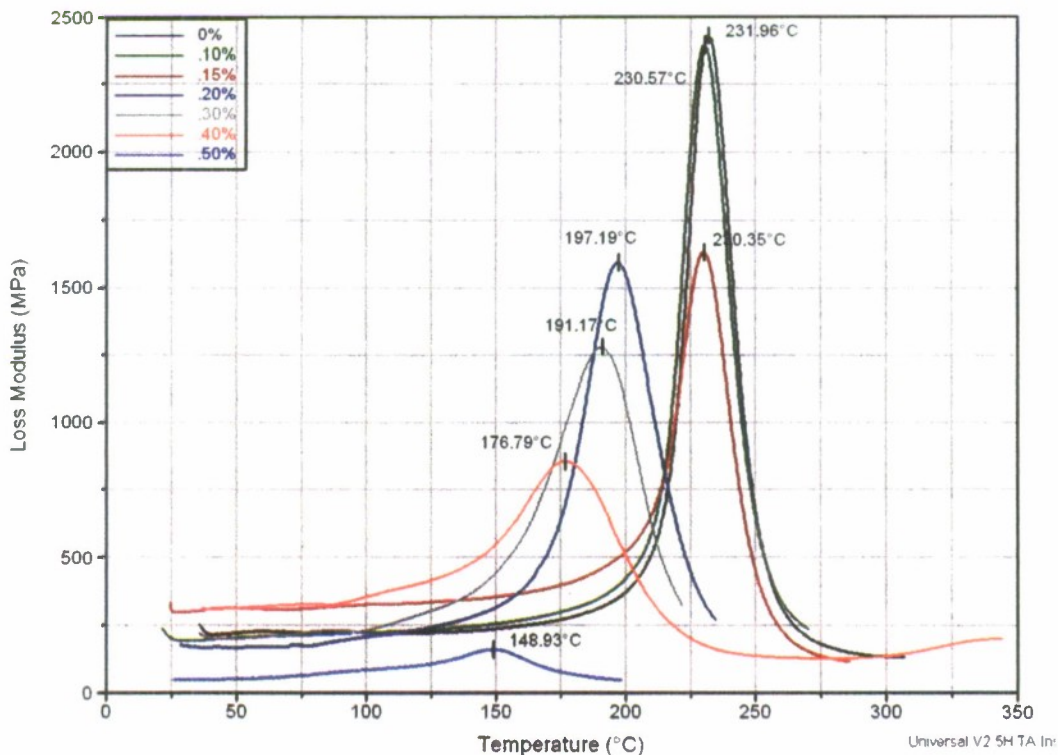


Figure 2. Typical loss modulus scan as a function of carbamate formation for an RS3C Polycyanurate resin.

Table 1. Tg's for the Polycyanurate Control Composites Investigated in This Study

Sample ID	Glass Transition Temperature, Tg, (°C)									
	segment	1	2	3	4	5	6	7	8	9
-3-2A		192.6	192.5	192.6	192.7	191.1	190.6	190.2	190.1	192.6
-23-2A		190.6	190.6	190.1	189.7	189.4	190.9	190.2	188.9	190.2

However, being that the Tg drop is so small, it is difficult to assess with just one Tg measurement whether further thermal cycling or elevated post-cures will cause progressive degradation. Carbamates have been shown to catalyze the polymerization reaction; thus, the small variation observed in the Tg measured and shown in Table 1 may be a result of a higher conversion rate for the hydrolyzed sample and may account for the Tg's having such a negligible variation at these relatively low cure temperatures. Optical micrographs of the composite cross-section exhibited good consolidation with no evidence of microcracking or excessive porosity, as shown in Figure 3. Increased porosity and microcracking are a result of carbamate decomposition during cure.

As previously discussed, heat treatments are often necessary after cure to determine whether subsequent thermal cycling will cause thermal degradation. The amount of carbamate formation is not sufficient to show a decrease in Tg after cure, yet with added post treatments, the thermal degradation will be evident. Figure 4 shows an example of a composite that was post-treated isothermally after cure. One portion of the laminate had moisture contamination while the other side did not. However, the degree of carbamate formations was so small after cure that, as can be seen from the plot, the Tg is the same for both laminates. A single-point Tg measurement after cure would not have been sufficient to identify further thermal degradation. As shown in Figure 3, the portion of the laminate that was adjacent the mandrel and formed carbamates during cure on the outer laminates shows a progressive degradation with post-treatment. The portions of the laminate with no moisture or carbamate formation actually show only a slight increase in Tg, which is due to additional cure caused by the higher thermal post-cure temperature.

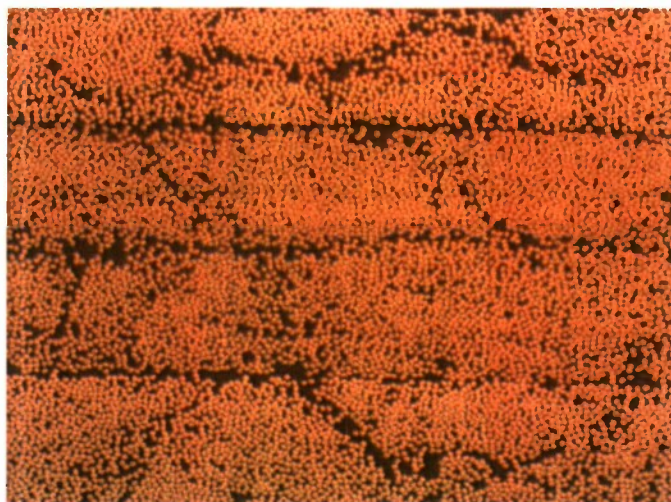


Figure 3. Optical micrograph showing the composite cross-section of a typical composite investigated in this study. There does not appear to be an evidence of microcracking and/or excessive porosity.

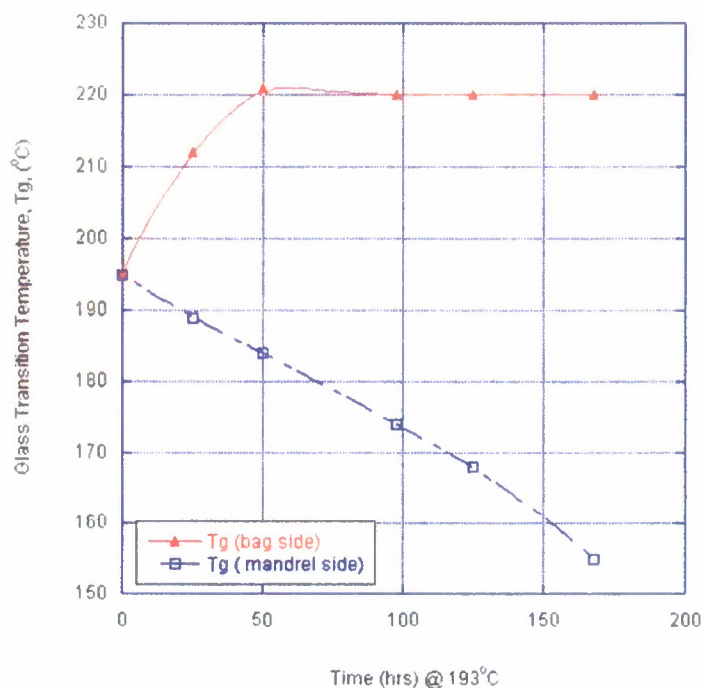


Figure 4. The Effect of an isothermal post heat-treatment on the Tg of a composite processed on a composite mandrel. Red line denotes Tg of the bag side ( no moisture) portion and the blue line denotes the mandrel side (moisture).

Table 2 shows the measured Tg values for three lots of prepreg rolls investigated in this study. The average Tg values for the control samples provided by the supplier are also provided. As shown, the average Tg values for the cured composites are fairly similar and consistent with composites that are well cured. No indications of hydrolysis are evident from the values of the Tg reported. The Tg values are also provided after 24-h and 113-h isothermal holds at 193°C for all five of the prepreg lots. Previous work has shown that a single-point DMA measurement after initial cure is not sufficient to predict whether degradation will occur with subsequent thermal exposure. An isothermal hold is necessary to more closely evaluate the potential for progressive degradation. Table 2 shows that the three lots of material under investigation show no degradation in Tg with subsequent heat treatment. Therefore, composites fabricated from this material would be expected to be free of any potential degradation due to the freezer issue. The prepreg lots in questions were stored in heat-sealed aluminum bags that have helped minimize any potential for degradation.

However, it was quite surprising to observe the behavior shown in Table 2 for the two composite specimens that were planned to be used as control specimens. As shown, upon subsequent isothermal treatment, both of the composites fabricated from this material that was shown, stored at the prepreg supplier show progressive Tg degradation as a function of time. Thus, this material would be highly susceptible to thermal and mechanical degradation as a function of thermal cycling.

Table 2. Tg Values as a Function of Isothermal Hold temperature. Carbamate contaminated specimens typically show a decrease in Tg with time.

Specimen	Tg (°C) (standard cure)	Tg (°C) (193°C @ 24 h)	Tg (°C) (193°C @ 113 h)
FB15K894/8 444460-1-8/8	192.5	233.8	236.5
FBK15K916/8 444460-3-8/15	191.6	230.7	233.4
FB15K916/9 44460-3-9/15	195.7	234.3	235.3
3-2a (control)	191	208	197
23-2a (control)	190	220	212

#### 4. Conclusions

1. Cyanate ester prepreg material not properly stored in proper refrigeration can be affected by hydrolysis, which subsequently can affect mechanical and thermal properties of the cured composite.
2. A single DMA test measuring the T<sub>g</sub> of an affected composite is not sufficient to evaluate carbamate formation due to hydrolysis when the variations in T<sub>g</sub> are small between the control specimens and the affected material. A secondary post thermal heat-treatment is necessary to fully evaluate whether the resultant composite will exhibit progressive thermal degradations during thermal cycling.
3. The prepreg lots investigated in this study exhibited no signs of hydrolysis after cure. Composites parts subjected to post-treatment indicated an increase in T<sub>g</sub> due to additional cure with no progressive thermal degradation. Therefore, the affected prepreg material should not be expected to degrade with further thermal cycling. Optical microscopy and subsequent mechanical testing of the laminates further verify that the flow characteristics of the aged resin material were acceptable for the chosen cure profile, and therefore the prepreg material can be exonerated for fabrication of hardware.

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