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Determination of Fiber Volume in Carbon/Cyanate Ester Composites Using Thermogravimetric Analysis (TGA)

Daniel L. Polis and Marjorie F. Sovinski

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ABSTRACT

The resin content, and by extension the fiber volume, of carbon fiber/cyanate ester composite laminates are measured using thermogravimetric analysis (TGA). Conventional measurement involves acid digestion of the laminate to determine resin content. The mean difference between techniques is 0.03%. In addition to eliminating the hazards and environmental impact of standard acid digestion, the TGA technique allows quantification of errors associated with fiber volume measurements, e.g. incomplete resin removal or fiber degradation. An additional benefit of the TGA technique is a reduction in sample size requirements, allowing the examination of fiber volume changes in complex shapes.

INTRODUCTION

The industry standard for measuring fiber volume of composite specimens involves acid digestion. The drawbacks of the acid digestion technique include that it is an environmentally unfriendly method due to hazardous waste generation, that it poses potential hazards to the operator, and that it is a labor intensive method. This technical memorandum covers the development of a method to measure the fiber volume of carbon fiber based composites using a thermogravimetric analyzer (TGA).

The TGA method eliminates both the operational hazard and the hazardous waste associated with acid digestion, and saves a considerable amount of labor as the TGA can be automated. Additionally, the subjectivity of the test is reduced through the use of a quantitative method for determining the point of complete resin removal. Samples tested using the TGA method are smaller by weight than those required for acid digestion by a factor of 10, allowing easier profiling of the fiber volume of complex shapes. The smaller sample size requirements allow for a tighter confidence interval by increasing the sampling number without consuming more material. This increased fiber volume confidence interval could be important for acceptance of composite materials used for precision structures, since fiber volume has an influence on both the modulus and the coefficient of thermal expansion.

This memorandum demonstrates the applicability of this technique by examining a carbon fiber/cyanate ester system commonly used in space structures. Although this study only examines fiber volume variability over a narrow range associated with normal materials and manufacturing deviations, a good correlation between the two techniques is demonstrated.

EXPERIMENTAL PROCEDURE

Materials

Composite laminates evaluated in this study were from the James Webb Space Telescope's (JWST) Integrated Science Instrument Module (ISIM) development program.

Hexcel Composites supplied pre-impregnated material (prepreg) referred to as M55J/954-6 tape. The M55J is an ultra high modulus PAN based carbon fiber with a tensile modulus 78 Msi and a tensile strength 583 ksi. The 954-6 is a 250°F (121°C) curing cyanate ester resin matrix.

Over the course of the development program, fourteen laminate panels were examined. Two to four samples were removed from each panel, depending on the panel size. Samples for acid digestion and TGA were removed from adjacent locations in an attempt to capture the same local constituent content. Approximately 1 g of specimen was removed for each digestion measurement, while less than 0.050 g of specimen was used for each TGA measurement. Care was taken in the machining of the TGA specimens to avoid surface damage that could bias the results of the small specimens.

Fiber Volume Measurements

As described in ASTM D 3171, the determination of fiber volume requires two measurements: laminate density and fiber weight fraction.[1] Laminate densities were measured in accordance with ASTM D 792.[2] Density was measured only for the acid digestion samples, and it was assumed equivalent for the TGA specimens removed from adjacent locations. The fiber weight fraction was determined via acid digestion and TGA as described in the subsequent sections.

Acid Digestion

Acid digestion was performed using sulfuric acid on a hot plate, as described in Procedure B of ASTM D 3171. This is the baseline technique for fiber weight determination of M55J/954-6 laminates.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed on a TA Instruments 2950 Thermogravimetric Analyzer. Each sample was heated from room temperature to 800°C at a ramp rate of 5°C/min using an air purge. Sample weight is monitored in-situ during the entire run. The balance in the TGA has a resolution of 0.1µg. This is three orders of magnitude better than a standard analytical balance, such as that required for acid digestion.

Initially, a pure resin sample was analyzed using the prescribed ramp rate to ensure that resin could be burned out cleanly. Figure 1 shows the weight percent versus temperature plot and the derivative of this curve.

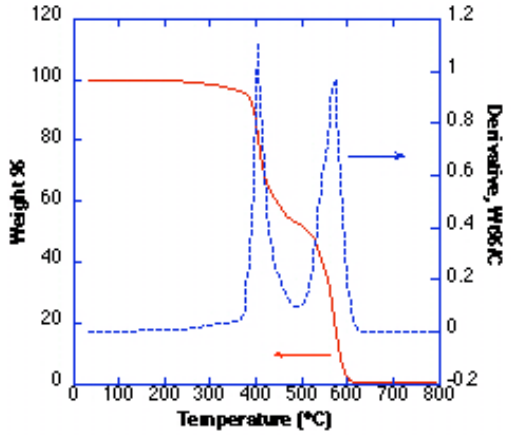

Figure 1. TGA run of 954-6 resin

Figure 1 shows that the resin weight loss plateaus at 0.2% weight, which corresponds to a temperature of ~620°C. This residual weight would correspond to a bias of ~0.17% fiber volume (Vf) if it were consistent in all measurements. ASTM D 3171 states that the residual matrix can be accounted for but should only be considered significant if greater than 0.5%. Therefore, the initial analysis ignores this residual matrix.

RESULTS AND DISCUSSION

A representative plot of weight percent and derivative weight percent as a function of temperature for a composite laminate are given in Figure 2. Although the derivative curve does not show a plateau above ~620°C due to the combustion of the M55J fiber at higher temperatures, it is possible to separate the combustion peaks. Furthermore, a derivative minimum occurs very close to the point at which the plateau was observed in the pure resin, suggesting the weight remaining at that minimum should be representative of the fiber only. Therefore, the second minimum in the derivative signal is used to define the point at which the fiber weight fraction (W_f) is defined.

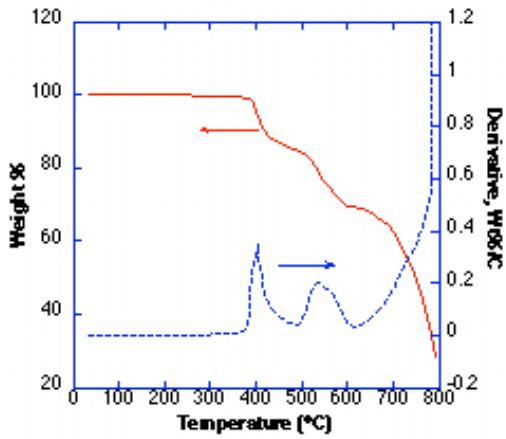

Figure 2. TGA run of M55J/954-6 laminate

This measurement was performed on 39 samples, taken from 14 different panels. Each fiber weight fraction (W_f) measurement was then converted to fiber volume (V_f) as follows:

(1) $$V_f = W_f*(\rho_c/\rho_f)$$

where ρ_c and ρ_f are the densities of the laminate and fiber, respectively. As was mentioned previously, ρ_c was assumed to be equal to the density determined from the paired sample removed for acid digestion and ρ_f = 1.9 g/cc was used for all samples.

Figure 3 shows all of the individual data points and compares V_f (acid digestion) to V_f (TGA). Because all the panels were fabricated at the same nominal fiber volume, the measurement noise is large relative to the data set range, making a regression analysis of limited value. Regardless, the best fit slope was determined by setting the intercept equal to zero. The best fit slope was 0.995, whereas a completely unbiased correlation would have a slope equal to 1.000. The low R value is indicative of a regression analysis spanning only 5.8%, while the average range of V_f from a single panel (acid digestion) is 1.5%, demonstrating that the noise is large relative to the signal.

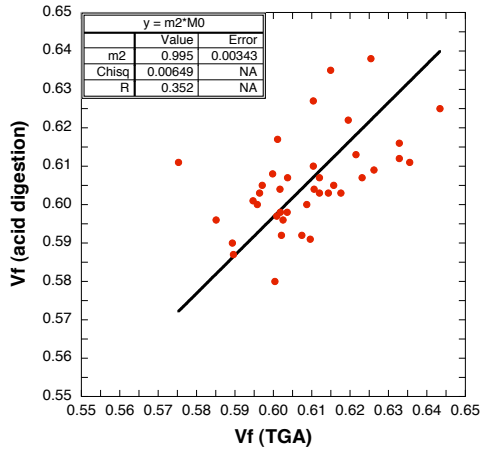

Figure 3. V_f (acid digestion) versus V_f (TGA)

Statistical Analysis

For a more complete statistical analysis, the data was examined using a paired t-test. A t-test would determine if the measurements from the two techniques are statistically different, i.e. if a systematic bias between the techniques exists. This is best illustrated in Figure 4, where a histogram of the differences between the two techniques is shown.

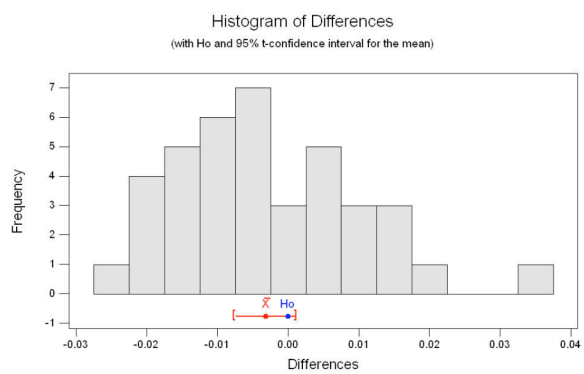

Figure 4. Histogram of V_f differences (Acid digestion - TGA)

The mean difference, V_f (acid digestion) - V_f (TGA), is -0.3% and the bars at the bottom of Figure 4 illustrate the 95% confidence on mean difference (-0.737%, 0.113%). While the difference is relatively small and the confidence band spans zero, the p-value is relatively low (0.14), which suggests this bias is real. A negative bias is consistent with under-digested resin; therefore, a closer look at residual resin is required.

Correction for Residual Resin

Up to this point, the second minimum in the derivative weight loss curve was defined as the point at which the fiber weight fraction (W_f) is determined. However, this leads to some variation in the temperature at which the W_f is determined. For our measurements, the average temperature used to determine fiber weight fraction was 612°C, with a minimum and maximum of 582°C and 623°C, respectively. The assumption that the weight loss had plateaued by this point is therefore invalid. Figure 5

shows a magnified view of the weight loss curve over this temperature range for the pure resin and reveals that if the residual resin was not accounted for, significant errors would occur at temperatures below ~620°C. It should be noted that the residual weight curve for a composite would be ~1/3 of what is shown in Figure 5 at a nominal fiber volume of 60%.

To illustrate this point more fully: with the original assumption of a weight loss plateau at ~620°C, there would be ~2.5 wt% of extra resin assumed to be fiber weight at 585°C. This fiber weight error is then converted to a 2.1% increase if V_f based on a nominal laminate density of 1.6 g/cc and ρ_f = 1.9 g/cc.

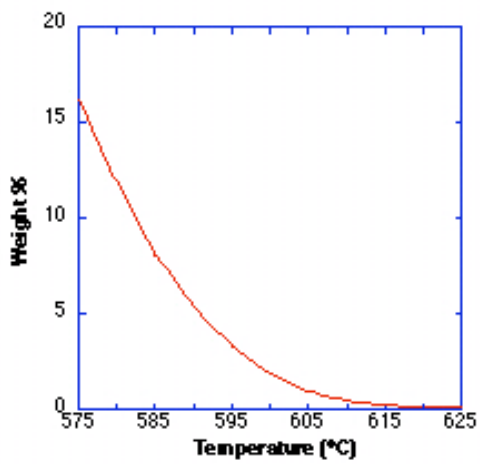

Figure 5. TGA run of 954-6 resin, high temperature residual matrix.

To correct the original W_f determination for incomplete resin removal, the residual matrix weight fraction at the temperature of interest, $RW_m(T)$, is introduced as follows:

(2) $W_f(corrected) = 1 - W_m(corrected)$

where

(3) $W_m(corrected) = W_m(uncorrected)/(1 - RW_m(T))$

Using the W_f (corrected) data for the TGA method, the differences between individual data points from the two techniques is shown in Figure 6. There is no longer a bias, such that the mean difference is approximately zero (-0.01%) with a 95% confidence interval on the mean difference of (-0.41%, 0.39%). This demonstrates that there is no systematic bias in the TGA technique relative to the acid digestion technique.

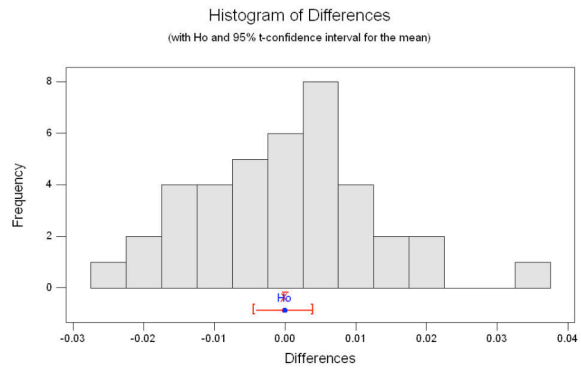

Figure 6. Histogram of V_f differences (Acid digestion - TGA (corrected)).

Although the mean difference in Figure 6 is essentially zero, it is still apparent that individual differences can be large, with a maximum observed difference of 3.6%. This is most likely due to the combination of the actual V_f variability within a panel and the random errors from each technique. The impact of these factors is difficult to isolate, as standards for this type of measurement are not available. However, the two techniques appear to have comparable errors, as is evident from the nearly equivalent standard deviations of 1.23% and 1.27% (acid digestion and TGA, respectively).

Panel-Averaged Data

The relevant manufacturing specification is often the panel-averaged V_f., therefore it is important to examine the panel averaged data. Additionally, sample averaging reduces uncorrelated measurement errors. Figure 7 shows all of the panel-averaged data points, comparing V_f (acid digestion) to V_f (TGA). Again, only the slope was fit in the regression analysis. The best-fit slope is 1.000 and the R = 0.883, suggesting a good correlation with no bias between the two techniques.

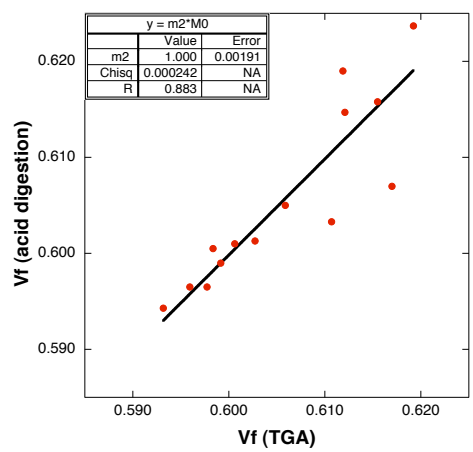

Figure 7. V_f (acid digestion) versus V_f (TGA) for panel averages.

The histogram of differences for the panel averages, shown in Figure 8, reveals that even the maximum differences are less than 1.0%, with the majority of observations falling within 0.3%.

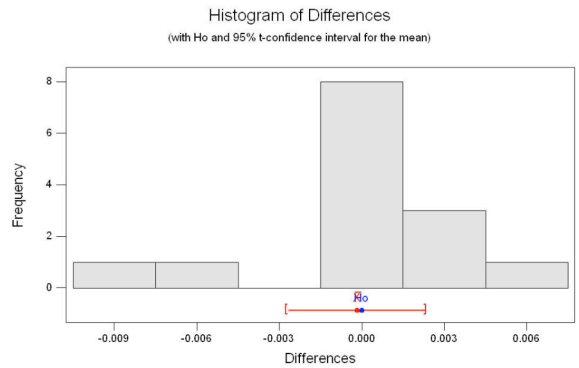

Figure 8. Histogram of V_f differences (Acid digestion - TGA (corrected)), for panel average data.

Improvements in the TGA Method

Two potential areas to reduce measurement uncertainty with the TGA technique are relatively straightforward. The first is a baseline burnout curve on the fiber of interest. Similar to the baseline performed on the pure resin, a baseline measurement would compensate for some initial fiber burnout that occurs prior to the point of fiber weight fraction determination. The second option to reduce uncertainty involves tailoring the ramp rate to allow resin-fiber peak separation, rather than using a straight ramp. Figure 9 illustrates a tailored ramp in which the total cycle time was kept the same as the constant 5°C/min ramp, but the sample was held for ~60 minutes at the two characteristic resin degradation temperatures (400°C and 550°C). Although the same plateau residual weight content is reached as that of the constant ramp rate test (~0.2%), the plateau begins at 551°C instead of the 625°C found with the constant ramp. This temperature reduction may serve to eliminate both matrix and fiber weight compensation.

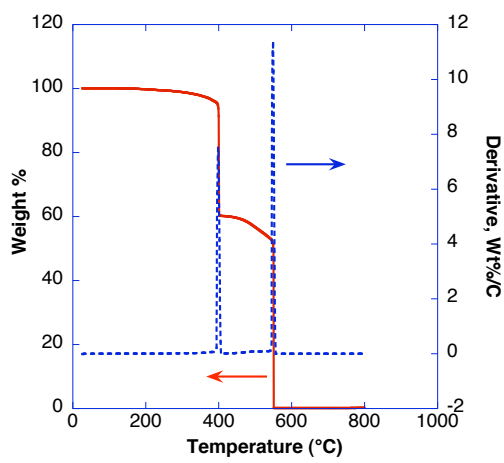

Figure 9. TGA run of 954-6 resin with 60 minute holds at 400 °C and 550 °C.

Impact of Sample Number

The analysis demonstrates the equivalency of the TGA technique relative to the baseline acid digestion technique using less than 1/10 of the sample size. However, testing multiple samples and averaging the results helps reduce random measurement errors, regardless of the technique. The relationship between the standard deviation of individual measurements, σ_x, to the standard deviation of means, $\sigma_{x(n)}$, is given by the central limit theorem (assuming a normal distribution) as follows:

(4) $$\sigma_{x(n)}, = \sigma_x / n^{1/2}$$

where n is the number of samples averaged.[3] Given this relationship, it is expected that the maximum difference between panel-averaged data, V_f (acid digestion) - V_f (TGA), would be dependent on the number of samples that were averaged. Although limited data is available to illustrate this, Figure 10 displays the panel-averaged difference versus the number of samples used in the average (2, 3, or 4 samples). The two largest differences come from panels in which only 2 samples were removed. Only 2 panels were sampled 4 times, but both show panel-averaged measurements that agree within 0.1%.

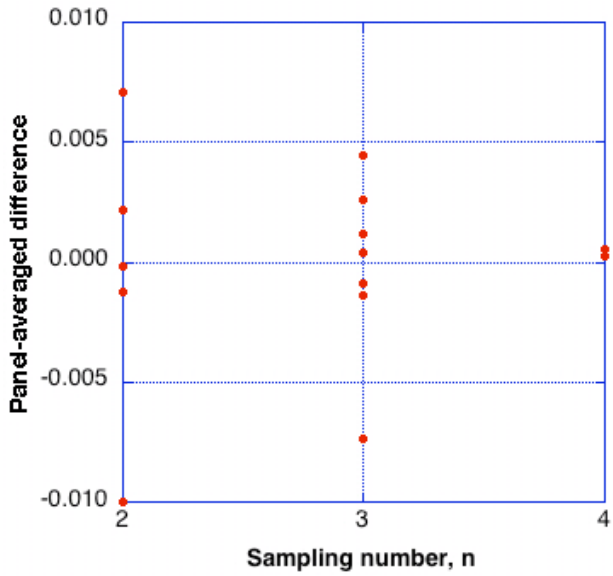

Figure 10. Panel-averaged V_f differences between the two techniques for a given panel versus the number of samples averaged.

While both techniques would benefit from testing a larger number of samples, it is easier to implement on an automated method such as TGA. Additionally, since the TGA sample size is much smaller than the acid digestion sample size, more sampling would not require a significantly higher material consumption.

CONCLUSIONS

The data presented demonstrates that thermogravimetric analysis (TGA) can be used to determine resin content and fiber volume of carbon fiber/cyanate ester composites. Though no standards were available, it is shown that the TGA technique has a good correlation and no bias relative to the baseline technique of acid digestion. The implementation of this technique would reduce hazardous waste, operator hazard, and operator time/cost.

The TGA technique utilizes a small sample size and an automated method, both of which could lead to unique capabilities to characterize composites over complicated profiles and/or with additional accuracy. Although this study focused on one particular fiber/resin system, it is believed that customized thermal profiles could be determined for most aerospace composites. Determining the applicability of this technique in other materials systems requires only small samples of pure resin and fiber. Additionally, for hybrid composites (multiple fiber types in a single laminate) it may be possible to separate fiber peaks, which will eliminate certain assumptions in the calculation of V_f. Due to the nature of hybrid composites, further research would be required to determine the applicability of this technique with a hybrid composite matrix.

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2. ASTM D-792-91, "Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement," ASTM International, 1998.

3. B. Ostle, K. Turner, C. Hicks, and G. McElrath. *Engineering Statistics, The Industrial Experience*. Belmont: Duxbury Press, 1996.

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14. ABSTRACT
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