W. G. McDonough,[1] *J. P. Dunkers, K. M. Flynn, and D. L. Hunston*

A Test Method to Determine the Fiber and Void Contents of Carbon/Glass Hybrid Composites

ABSTRACT: Hybrid composites are increasingly being used in infrastructure, oil recovery, and aerospace applications. These hybrids generally combine two different types of fibers to reinforce the resin, thereby gaining some of the advantageous properties of both fibers. Typically, carbon and glass are used since this combines the high performance of the carbon with the low cost of the glass. The performance of such materials depends on a number of factors, including the mix ratio of the fibers as well as the fiber and void contents. At present, there is no simple way to determine these features. Although a number of techniques exist for measuring such parameters when only a single reinforcement is present, extension of these methods to hybrids can be difficult. The work here, however, shows that one technique, the burn off test in ASTM D 3171-99, can be extended to characterize carbon/glass hybrids. To verify this procedure, data were obtained for a series of samples with known compositions, and the agreement was excellent. The proposed method has minimal equipment requirements and provides a simple way to obtain important compositional information.

Abbreviations and Notation

TGA thermal gravimetric analysis

W_0 the dry mass of the sample

ρ_r the density of the cured resin

ρ_g the density of the glass fiber

ρ_c the density of the carbon fiber

V_0 the volume of the specimen to be tested

W_{T1} the mass of the sample after the first temperature exposure

W_{T2} the mass of the sample after the first temperature exposure

W_r *the mass of the resin and sizing*

W_g *the mass of the glass fibers*

W_c *the mass of the carbon fibers*

F_{ij} *correction factors*

Introduction

There are great opportunities for the use of composites in applications like infrastructure, oil recovery, and aerospace. To take full advantage of these opportunities, composites must provide good performance at a reasonable price. To achieve this goal, many applications are considering hybrid composites. These systems use two different fibers to reinforce the resin, thereby gaining some of the advantageous properties of both fibers. Typically, carbon and glass are used since

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[1] National Institute of Standards and Technology, Gaithersburg, MD 20899

this mixture combines the high performance of carbon with the low cost of glass. To obtain the best properties with such materials, it is critical that the fibers be mixed in the proper way. Features such as the fiber mix ratio and the fiber and void contents need to be controlled. Unfortunately, there is no simple way to determine these features at present. A number of techniques have been used to characterize composition when a single reinforcement is present, but these methods are usually difficult or impossible to extend to hybrids. One of the important challenges with hybrids is that the fibers are generally mixed at the tow level or even the ply level. As a result, the sample volume that must be used to assure that the composition is typical of that for the full composite is significantly greater for hybrids than it is for a simple composite. The purpose of the work here is to show that one of the current methods, the burn off test in ASTM D 3171-99 [1], can be extended to characterize carbon/glass hybrids.

The current burn off test, which is described in Test Method I-Procedure G of the ASTM standard, applies to composites with a reinforcement such as glass or ceramic that is not affected by high-temperature environments or a reinforcement such as carbon when the temperature can be adequately controlled to minimize degradation of the fiber during burn off. Briefly, it calls for putting the specimens into a preheated muffle furnace at 500°C or lower, depending on the composite system (a temperature at which specimens will not spontaneously ignite).   The specimens are then to be heated to 565°C ± 30°C or another temperature that will burn off the matrix and leave the reinforcement. The maximum time for burn off should be 6 h. The matrix is considered combusted if no matrix/reinforcement blocks exist. Ash and reinforcement should be the only items visible. The sample mass before and after heat treatment is measured and combined with other information to calculate the fiber, resin, and void content of the sample.

We propose to extend this test using a two-step heating procedure. The first heat treatment removes the resin and sizing with minimal effect on the reinforcement. It is similar to what would be done with a carbon composite. After weighing the sample, the specimen is then raised to a higher temperature that burns off the carbon fiber. The key that makes this test possible is that the glass can withstand high temperatures without degradation.

The first section of this paper describes the proposed test method for a general glass/carbon composite. To test this procedure, the paper goes on to examine a specific epoxy/glass/carbon system in a variety of compositions. For these samples, some or all of the compositional data are known and can be compared with the experimental results.

Proposed Procedure

This procedure described below was developed and tested using an epoxy composite reinforced with glass and carbon fibers. Nevertheless, it should be applicable to glass/carbon hybrids with other polymeric matrix resins if the temperatures and times are modified appropriately.

Preliminary Steps

The most important factor in applying the test to a particular system is selecting the appropriate times and temperatures for the heat treatments. The values cited later in the experimental section were found to work well for the epoxy system tested here and are useful starting points, but they may not be optimal for other composite materials. To help select the appropriate test conditions, it is desirable to conduct thermal gravimetric analysis (TGA) experiments on small samples and on the constituents themselves if they are available. This

information can also help in determining the correction factors discussed below if something other than the default values are needed.

Before starting the tests, it is useful to thoroughly dry the specimens by placing the samples in a desiccator and monitoring the mass as a function of time until changes are no longer observed. The error introduced by moisture in the sample is not large but can become important if void content is calculated, since void content is also generally small. The dry mass of the sample is designated W_0.

The sample size tested is also important. It must be large enough to incorporate the characteristic mix of fibers that are present in the composite, and a typical void content if voids fraction is to be determined. This is particularly important for hybrids because the size scale over which variations occur is usually much larger than it is with composites having only a single type of reinforcement.

If you wish to determine volume fractions and void content in addition to mass fractions, some additional data is needed. Densities of cured resin, the glass fiber, and the carbon fiber (designated ρ_r, ρ_G, and ρ_C, respectively) must be measured or estimated from the literature. In addition, the volume of each specimen to be tested, V_0, must be determined.

Before inserting the sample into a crucible (we used porcelain), the crucible should be cleaned, heating to 900°C (or the highest temperature that will be used in the burn off test) in a muffle furnace, cooled to room temperature in a desiccator, and weighed to determine its mass. Each specimen is then weighed and placed into a desiccated crucible.

First Heating Step

The crucibles containing samples are placed into a muffle furnace for the first heating step. The existing standard calls for using a preheated muffle furnace at 500°C or lower, depending on the composite system. After some exposure at 500°C, the temperature is raised to a higher temperature to complete the burn off. The key is that the crucible must not be heated so quickly that ignition or rapid degradation causes parts of the sample to be ejected. On the other hand, very slow heating or too long an exposure at high temperatures may produce degradation of the carbon fibers. For the experiments conducted here, a relatively simple heating procedure was found to work quite well (see next section).

At the completion of the heating process, the crucibles are removed from the muffle furnace and placed in a desiccator for cooling to room temperature. The muffle furnace is left at temperature in preparation for the second heating step. The material remaining in each crucible is often very lightweight, so care must be taken to avoid losing any material during handling. Each crucible with sample is weighed, and the mass of the crucible is subtracted to determine the mass of the specimen after the first temperature exposure, W_{T1}.

Second Heating Step

Once the crucibles have been weighed, they are again placed into the muffle furnace for the second heating step. The temperature is increased to a level that will remove the carbon fiber (generally about 900°C). After an appropriate time, the crucible is removed to see if all of the carbon fiber has been eliminated. If necessary, the crucible can be returned to the muffle furnace so the process can be completed. Once all the carbon is gone, the crucible is removed from the oven and placed in a desiccator until it reaches room temperature. The weight of each crucible and specimen is determined, and the mass of the crucible is subtracted to determine the mass of the sample after exposure to the second temperature, W_{T2}.

Data Analysis

The mass of the resin and sizing (W_r), the glass fibers (W_G), and the carbon fibers (W_C) can then be determined by solving the following three equations in three unknowns.

$$W_o = W_r + W_C + W_G \tag{Eq 1}$$

$$W_{T1} = W_C + W_G \tag{Eq 2}$$

$$W_{T2} = W_G \tag{Eq 3}$$

In the event of incomplete removal of constituents (or removal of more than expected), Eqs 2 and 3 can be modified as follows:

$$W_{T1} = f_{T1,r} W_r + f_{T1,C} W_C + f_{T1,G} W_G \tag{Eq 4}$$

$$W_{T2} = f_{T2,r} W_r + f_{T2,C} W_C + f_{T2,G} W_G \tag{Eq 5}$$

The six correction factors, $f_{i,j}$, account for the fact that the fraction of mass for each component left after a given temperature treatment may not be exactly 0 or 1.

Because glass will not react at high temperatures, it is relatively easy to assure that

$$f_{T2,r} = f_{T2,C} = 0 \quad and \quad f_{T1G} = f_{T2G} = 1 \tag{Eq 6}$$

In selecting the temperature and exposure time for Step 1, the goal is to achieve conditions that come as close as possible to burning off all the resin while leaving all the carbon fiber unaffected so that

$$f_{T1,r} = 0 \quad and \quad f_{T1,C} = 1 \tag{Eq 6}$$

in which case Eqs 0.1, 0.2, and 0.3 are recovered. In the experiments used to develop this test method (see below), these default values worked very well. If these conditions cannot be achieved, it may be possible to calibrate the correction factors to account for the deviation from ideality. To estimate $f_{T1,C}$ from calibration experiments, however, it is recommended that composite sample with known carbon fiber content be used, because our experiments show that fibers in a composite are often more resistant to vaporization than they are when tested without resin.

The mass fractions for the resin and sizing, carbon fiber, and glass fiber are W_r / W_0, W_C / W_0, and W_G / W_0, respectively. The corresponding volume fractions are $W_r / (\rho_r V_0)$, $W_C / (\rho_C V_0)$, and $W_G / (\rho_G V_0)$. The volume fraction of voids is determined by subtracting the volume fraction of all other components from 1. Since this involves subtracting numbers that are almost

equal, careful experimentation is required if this is to be meaningful. For example, accurate measurements of the dimensions for the specimen are essential.

Uncertainties in the determinations outlined above depend on the materials involved, sample size, and how carefully the tests are performed. As a general guideline, however, numbers will be presented later for the particular system tested here.

Experimental Section

To test the proposed procedure, experiments were conducted with a typical epoxy/glass/carbon hybrid formulation. Samples with a variety of glass/carbon fiber ratios were manufactured in-house to obtain specimens with known composition. In addition, some commercially prepared composites were obtained with the same fiber-resin system. For these samples, the carbon fiber / glass fiber ratio was known, but other parameters are not. In both cases, void content is not known so an independent technique, microscopy, was used to determine these values. This section describes the materials and equipment, the development of the temperature cycles for the two heating steps, the manufacture and characterization of the composites, and the experimental uncertainties.

Materials and Equipment [2]

For all samples, the resin used was Epon 862, manufactured from Bisphenol F and epichlorohydrin. The curing agent used was Epi-Cure W, which is composed of mixed isomers of diethyltoluenediamine. The resin/curing agent mass ratio was 100.0/26.4. The carbon fibers were Grafil 34-700 in 12K tows with no twists and the standard sizing. The glass fibers were PPG-1062 with 247 yield, no twist, and the standard sizing. The furnace used was Ney M-525 series II furnace. Masses were measured on an Ohaus Analytical Plus AP 250D balance. Dimensions were measured on a Fowler & NSK MaxCal digital caliper. Thermogravimetric analyses were done on a Perkin-Elmer TGA 7 machine. The microscopy was performed using a Nikon Optihot microscope.

Determination of Heating Steps

To develop an optimized procedure for heating the samples, thermo-gravimetric analysis TGA) was applied to the components. These tests were done in air. Figure 1 shows burn off results for the matrix used in this study. The heating rate to 600°C was 50°C/min, followed by a
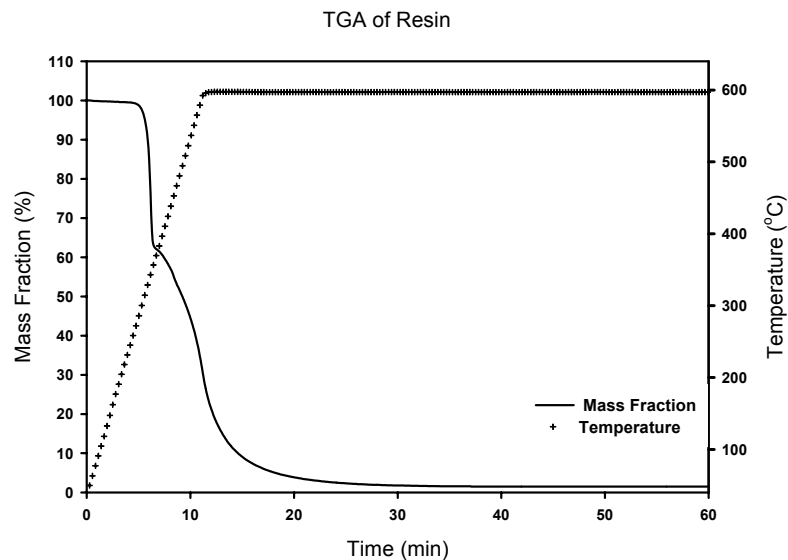

FIG. 1 — *TGA plot of the mass fraction loss of resin at 600°C. Note that the resin was completely burned off after 30 min.*

TGA of Resin

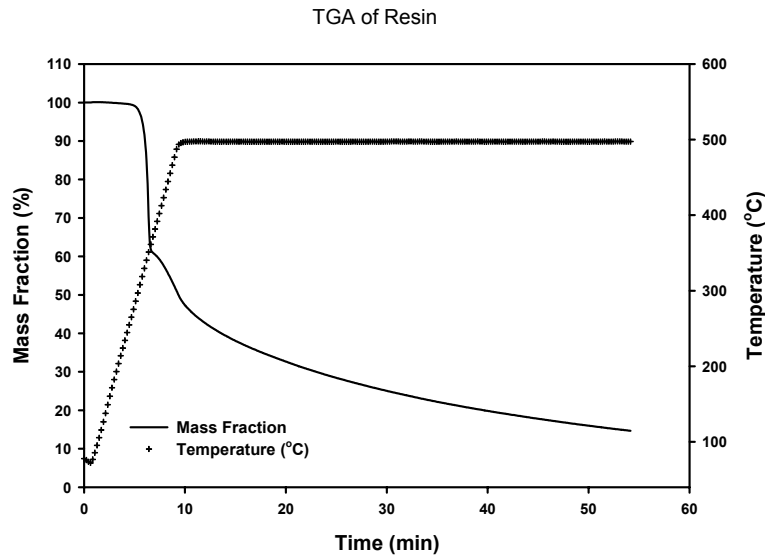

FIG. 2 — *TGA plot of the mass fraction loss of resin at 500℃. Note that the resin was not completely burned off after 55 min.*
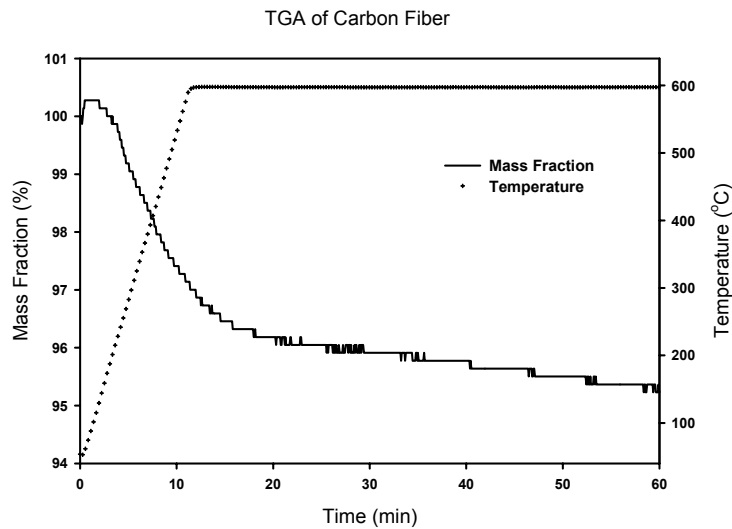
TGA of Carbon Fiber

FIG. 3—*TGA plot of the mass fraction loss of carbon fiber at 600℃.*

hold time at 600°C of 60 min. We can see in the figure that the resin is essentially gone after 25 min. Figure 2 shows the result from bringing the burn off temperature to only 500°C. At this temperature, we clearly have matrix material remaining after 60 min. Thus, for an initial estimate, we selected 600°C as a promising first plateau temperature. Figure 3 shows an

isothermal curve for carbon fiber at 600°C. Here we see a mass loss of around 0.04 mass fraction after 60 min. The mass fraction attributable to sizing is approximately 0.01. The rest of the initial loss might be attributed to removal of moisture, but the downward slope of this curve suggests that some carbon mass was lost as well.   Figure 4 shows the burn off behavior of carbon fibers at 500°C for 30 min followed by a jump to 900°C and a hold for 50 min. We see the small mass loss at 500°C, followed by the complete mass loss at 900°C. From the data presented in these four figures, we concluded that the carbon should be able to survive the first plateau temperature of 600°C, and that the carbon would be removed at a second plateau temperature of 900°C. Note that the TGA runs were done on fibers alone. We can expect less fiber degradation when the fibers are encapsulated in resin. Figure 5 shows the TGA response of glass fibers taken to 900°C, cooled down and recycled to 900°C. The 0.01 mass fraction loss can be attributed to sizing (mass fraction 0.008) and moisture being burned off.
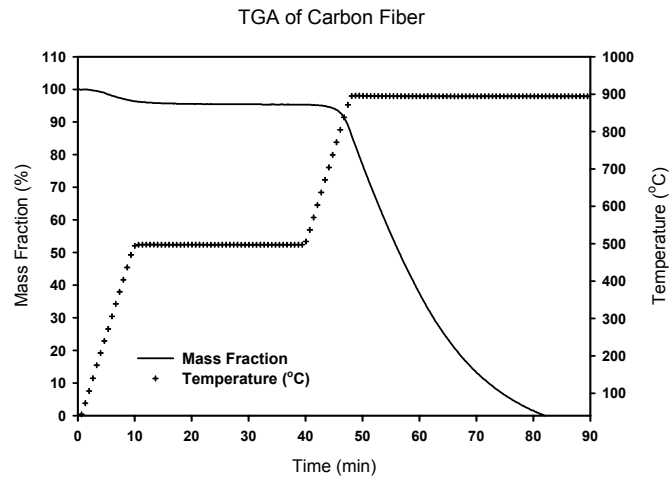
TGA of Carbon Fiber

FIG. 4—*TGA plot of the mass fraction loss of carbon fiber at 500°C and at 900°C. Note that the carbon was burned off at 900°C.*
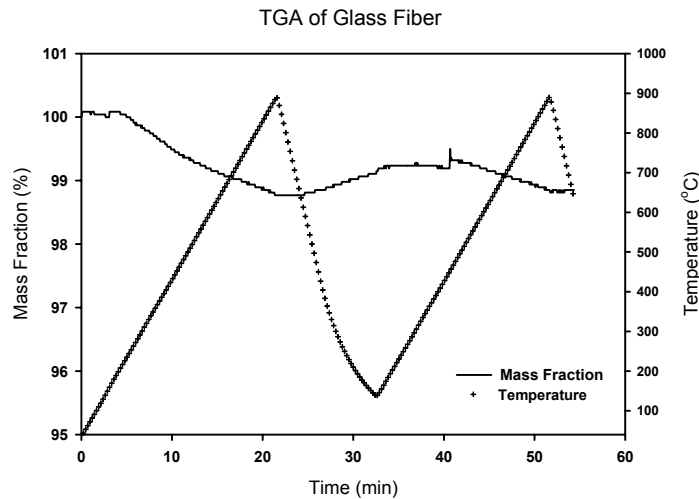
TGA of Glass Fiber

FIG. 5—*TGA plot of the mass fraction loss of glass fiber at 900°C. The increase in mass fraction upon cooling was due to reactive groups grabbing atoms from the air to stabilize themselves.*

Based on the TGA results, we decided that the plateau temperature in the first heating step should be 600°C. If the sample was exposed to this temperature for less than 60 min, we should remove the resin and the sizing on the fibers with minimal effect on the reinforcement. The ASTM standard uses a preheated oven, but we found that with our equipment and samples, we could simply insert the crucibles into the furnace at room temperature and then set the control to 600°C. When the temperature reaches 585°C, usually in around 30 min, the clock was started for the temperature plateau. After 30 min, there should only be reinforcement left in the crucible. It was sometimes useful to extend this time for one or at most two 15 min intervals if any char remained. The time never exceeded 60 min, however, since excessive exposure can reduce the mass of the carbon fiber. After the residue was weighed, the crucible was returned to the furnace at 600°C, and the control was reset to 900°C for the second heating step. When the temperature reached 885°C, the clock was started for the second plateau. All of the carbon fiber was usually removed after 60 min, and in most cases it was gone in 30 min. To confirm this procedure, we ran burn off tests on the base resin, the carbon fibers, and the glass fibers to get a fuller understanding of the responses of the components in the furnace. This defined a general protocol that was tested and further refined by experiments on the full composites.

Sample Manufacturing

By using the materials discussed above, a number of composite samples were prepared for testing. The first set was manufactured in-house at NIST while a second set was prepared by a commercial manufacturer. The first set involved five different compositions based on the number of tows mixed together: all glass tows, three glass tows for each carbon tow (3:1), one glass tow for each carbon tow (1:1), one glass tow for every three carbon tows (1:3), and all carbon tows. The composites were made in custom-built molds containing a cavity nominally 20.0 cm long by 0.8 cm wide by 0.6 cm deep. A hand lay-up process was used. We weighed out carbon tows and glass tows in a predetermined mixture depending on the desired composition. The individual tows were impregnated with resin and partially curing agent at 50°C. We then placed the impregnated tow into the cavity and repeated the process until the cavity was filled. The cover was placed on the mold and clamped in place using C-clamps. The mold assembly was placed into a programmable oven and cured following the schedule specified by the vendor. The oven was heated to 65°C ± 5°C at a rate of 1.5°C/min. This temperature was held 10 h ± 30 min. The oven was then heated to 121°C ± 5°C at a rate of 1.5°C/min. and held at that temperature for 12 h ± 30 min. The oven was allowed to cool slowly, and the samples were removed.

After processing, the specimens were weighed and measured. By knowing the sample dimensions and amount of fibers put in the mold, we could calculate the fiber volume fractions in the specimens. From the known mass of fibers and the weight of the sample, the amount of resin present could be determined. With careful preparation, the samples could be made essentially void free, and this was confirmed by microscopy. This gave us a series of specimens with known compositions to compare with the results from our proposed burn off test. After the samples were molded, they were sectioned into smaller pieces and stored in a desiccator until testing.

The second set of samples was made with the same materials by a commercial manufacturer. Large plates were prepared with two different formulations. In one case, the samples contained 3 glass tows for each carbon tow (3:1), while the other case used one glass tow for every 3 carbon tows (1:3). The manufacturers goal was to obtain a 60 % total fiber volume fraction, but

this could not be guaranteed so only the fiber ration is a known quantity. Small sections of the plate were cut and placed in a desiccator until testing.

Sample Characterization

For the composites made at NIST, the specimens used in the burn off tests weighed around 0.6 g. The corresponding test samples from the commercially made composite weighed 1.4 g. V_0 was calculated by measuring the length, width, and thickness of each specimen. The standard uncertainty in the determination of dimensions was 0.005 cm or less. Typical specimen dimensions for NIST-made composites were 0.6 cm × 0.8 cm × 0.7 cm. Typical specimen dimensions for industrially made specimens were 0.2 cm × 1.9 cm × 1.5 cm. The standard uncertainty in the mass determination was 0.0001 g or less. Values were obtained for the densities of the fibers from the literature [3], and these were consistent with measurements on fiber tows: ρ_G = 2.54 g/cc and ρ_C = 1.77 g/cc. The density of the resin was measured, and is consistent with literature values for epoxy: ρ_r = 1.20 g/cc.

The amount of sizing on the glass and carbon fibers was taken from the supplier data sheets and the procurement specifications. Because the sizing does not add a significant amount to the mass or volume of the composite, the suppliers' data were used without verification. If verification were needed, the amount of sizing on the glass tows could be estimated by a burn off test. For carbon fibers, the sizing content could be determined with a solvent wash.

Although the composition of the samples could be controlled by manufacturing, the void content could not. As a result, it was necessary to independently determine void content. The work here used microscopy for this purpose. Samples were cut, potted, polished, and photographed at high magnification. The pictures were then analyzed with a computer program written using Matlab. The key is that the resolution must be sufficient to see the voids, and yet the area covered must be large enough to obtain results typical of the material as a whole. With hybrids this area can be much larger than with single reinforcement composites because the microstructural variations occur over a larger area. For the in-house fabricated samples, the micrographs indicated that almost no voids were present while the measurements of the commercial composites did show voids. To determine void fraction, 5 to 10 micrographs at a magnification of 50X were analyzed for each sample. Repeated measurements indicated variations in void content of ± 1 %. We suspect that this uncertainty could be reduced by using a larger number of micrographs (larger surface on the specimen), but it provided an adequate measure here since the uncertainty in the determination of void content by the burn off test is also quite significant.

Burn Off Tests

Between 3 to 5 samples at each composition were subjected to burn off tests. One of the objectives in these experiments was to verify/optimize the burn off test conditions, so although most tests used the conditions developed above, a few samples were run with small variations in these conditions. Table 1 lists the test protocol used for each sample. The in-house composites had low fiber volume fractions (between 0.12 and 0.30) while the commercial samples had much higher fiber volume fractions (near 0.60). As a result of this difference, we generally needed 60 min to burn off the carbon fibers in the industrially made specimens during the second heating step.

TABLE 1—*Testing conditions for specimens.*

NIST hybrid 1:1 glass/carbon	
Sample 1	30 min at 600ºC, 30 min at 900ºC
Sample 2	30 min at 600ºC, 30 min at 900ºC
Sample 3	45 min at 600ºC, 30 min at 900ºC
Sample 4	30 min at 600ºC, 90 min at 900ºC
Sample 5	60 min at 515ºC, 30 min at 900ºC
NIST hybrid 3:1 glass/carbon	
Sample 1	40 min at 600ºC, 30 min at 900ºC
Sample 2	30 min at 600ºC, 30 min at 900ºC
Sample 3	45 min at 600ºC, 30 min at 900ºC
Sample 4	45 min at 600ºC, 30 min at 900ºC
NIST hybrid 1:3 glass/carbon	
Sample 1	50 min at 600ºC, 30 min at 900ºC
Sample 2	30 min at 600ºC, 30 min at 900ºC
Sample 3	30 min at 600ºC, 30 min at 900ºC
Sample 4	30 min at 600ºC, 60 min at 900ºC
Industrial Composite	
Sample 1	50 min at 600ºC, 60 min at 900ºC
Sample 2	40 min at 600ºC, 30 min at 900ºC
Sample 3	30 min at 600ºC, 60 min at 900ºC
Industrial Composite	
Sample 1	50 min at 600ºC, 60 min at 900ºC
Sample 2	40 min at 600ºC, 30 min at 900ºC
Sample 3	30 min at 600ºC, 60 min at 900ºC
NIST glass composite	
Sample 1	30 min at 600ºC, 30 min at 900ºC
Sample 2	30 min at 600ºC, 30 min at 900ºC
Sample 3	30 min at 600ºC, 30 min at 900ºC
NIST carbon composite	
Sample 1	30 min at 600ºC
Sample 2	30 min at 600ºC

Statement of Uncertainties

The standard uncertainty associated with the mass measurements was 0.0001 g. The standard uncertainty associated with the dimensions was 0.003 cm. The standard uncertainty associated with the volume of the specimens was 0.002 cm^3. The standard uncertainty associated with the glass volume and carbon volume in the NIST-made composites was 0.002 cm^3. The standard uncertainty associated with the glass volume in the industrial composites was 0.004 cm^3. The standard uncertainty associated with the carbon volume in the industrial composites was 0.009 cm^3. The standard uncertainty in the density for the fibers and resin was estimated to be 0.05 g/cm^3. The combined standard uncertainty for the void volume fraction for the composites was 0.006 cm^3. The combined standard uncertainty for the void volume fraction for

the composites in terms of percentage was approximately 1 %. The standard uncertainty in temperature in the TGA measurements was 2°C.

Results and Discussion

The results obtained here allow us to address three issues. First, the testing protocol can be verified and optimized. Second, the ability of the burn off test to determine resin and fiber contents can be examined. Finally, the sensitivity of the test to void content can be analyzed.

Test Procedure

The processing conditions listed varied somewhat as we tried different plateau temperatures and times. The data for the hybrid resin confirmed what was found in the TGA study (Fig. 1) in that the resin was burned off after 30 min. Sample 2 was kept in the oven 15 min longer, but we have no reason to assume that the resin had not burned off earlier. The carbon tows showed an even greater mass loss at 600°C than that shown in Fig. 3, and both sets of data indicate that we need to minimize the hold time at the first plateau temperature. At 900°C, again we see agreement between the burn off data and the TGA data shown in Fig. 4. The glass tows, both in Table 2 and in Fig. 5, show a similar 0.01 mass fraction loss that we attribute to sizing and moisture. The results from the burn off test for the constituents, combined with the results from the TGA study confirmed our choices of 600°C as the first plateau temperature and 900°C as the second plateau temperature.

TABLE 2—*Results from the burn off tests.*

NIST hybrid 1:1 glass/carbon	expected volume fractions (glass/carbon)	measured volume fractions (glass/carbon)	
Sample 1	0.136/0.08	0.133/0.072	
Sample 2	0.136/0.08	0.14/0.08	
Sample 3	0.136/0.08	0.139/0.075	
Sample 4	0.136/0.08	0.139/0.081	
Sample 5	0.136/0.08	0.139/0.079	
NIST hybrid 3:1 glass/carbon	expected volume fractions (glass/carbon)	measured volume fractions (glass/carbon)	
Sample 1	0.241/0.052	0.246/0.054	
Sample 2	0.241/0.052	0.235/0.051	
Sample 3	0.241/0.052	0.239/0.052	
Sample 4	0.241/0.052	0.241/0.052	
NIST hybrid 1:3 glass/carbon			
Sample 1	0.082/0.155	0.086/0.154	
Sample 2	0.082/0.155	0.080/0.147	
Sample 3	0.082/0.155	0.080/0.148	
Sample 4	0.082/0.155	0.080/0.152	
Industrial composite	expected volume ratios (glass/carbon)	measured volume ratios (glass/carbon)	
Sample 1	37/63	40/60	void volume fraction 0.040
Sample 2	37/63	38/62	void volume fraction 0.044
Sample 3	37/63	38/62	void volume fraction 0.035
Industrial composite	expected volume ratios (glass/carbon)	measured volume ratios (glass/carbon)	
Sample 1	64/36	67/33	void volume fraction 0.036
Sample 2	64/36	66/34	void volume fraction 0.052
Sample 3	64/36	67/33	void volume fraction 0.028
NIST glass composite	expected volume fraction	measured volume fraction	
Sample 1	0.296	0.298	
Sample 2	0.296	0.272	
Sample 3	0.296	0.29	
NIST carbon composite	expected volume fraction	measured volume fraction	
Sample 1	0.125	0.122	
Sample 2	0.125	0.126	

Hybrid resin	
Sample 1	complete mass loss at 600ºC for 30 min
Sample 2	complete mass loss at 600ºC for 45 min
Glass tows	
Sample 1	0.79 % mass fraction loss at 600ºC for 30 min, no change after 60 min at 900ºC
Sample 2	1.0 % mass fraction loss at 600ºC for 45 min, no change after 60 min at 900ºC
Sample 3	1.1 % mass fraction loss at 600ºC for 40 min, no change after 60 min at 900ºC
Carbon tows	
Sample 1	4.1 % mass fraction loss at 600ºC for 30 min, complete mass loss after 30 min at 900ºC
Sample 2	9.6 % mass fraction loss at 600ºC for 45 min, complete mass loss after 30 min at 900ºC
Sample 3	7.2 % mass fraction loss at 600ºC for 45 min, complete mass loss after 30 min at 900ºC

Resin and Fiber Contents

Table 2 shows a comparison between the expected and measured fiber contents for all of the samples. With the in-house prepared composites, the fiber volume fractions are compared. Data for the commercial samples compares the ratios of fiber volume fractions, since that is the quantity that is known. Although some variations are observed, the agreement is very good. Some of the differences can be attributed to uncertainties in the measurements, but a portion of each variation is probably due to inherent differences in the microstructure among the specimens. The glass fibers tend to act as an internal standard since we do not observe any mass loss over the temperatures used for this study. At 900ºC, the glass changes from fiber form to a solidified bead. There is the possibility of "entrapping" some carbon fibers, but we found that even these entrapped fibers were removed eventually. In the NIST specimens, we have a relatively low fiber volume content. This is a limitation of the manual lay-up process in the fabrication of composite specimens. Variations in the industrial composite were probably a function of size of the specimen cut and tested. In other words, care must be taken to be sure that the microstructure of the specimens tested is representative of the microstructure of the entire composite plate.
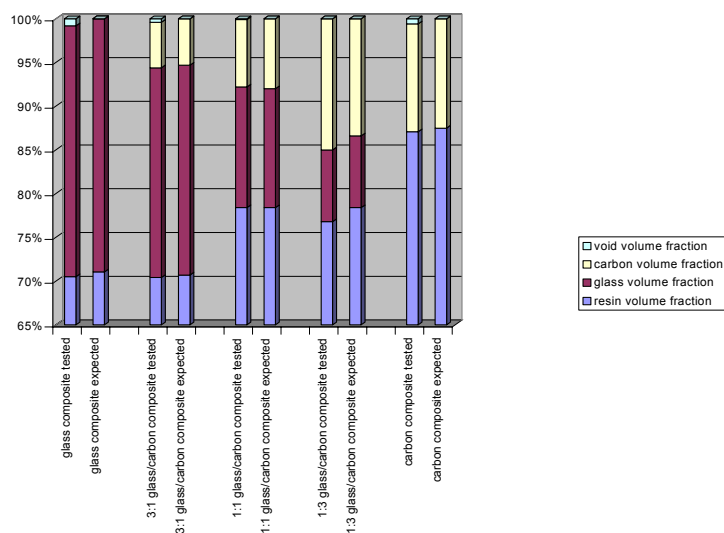

FIG. 6—*Bar chart of the expected and calculated components (volume fractions) of the NIST made composites used in this study.*

The resin volume fraction can be compared only for the in-house specimens, since that is where an expected value is known. To calculate this value, zero void content is assumed based on the microscopic studies. The results are shown in Fig. 6 that compare average compositions for all of the in-house specimens. As with fiber content, the burn off test gave very good results.
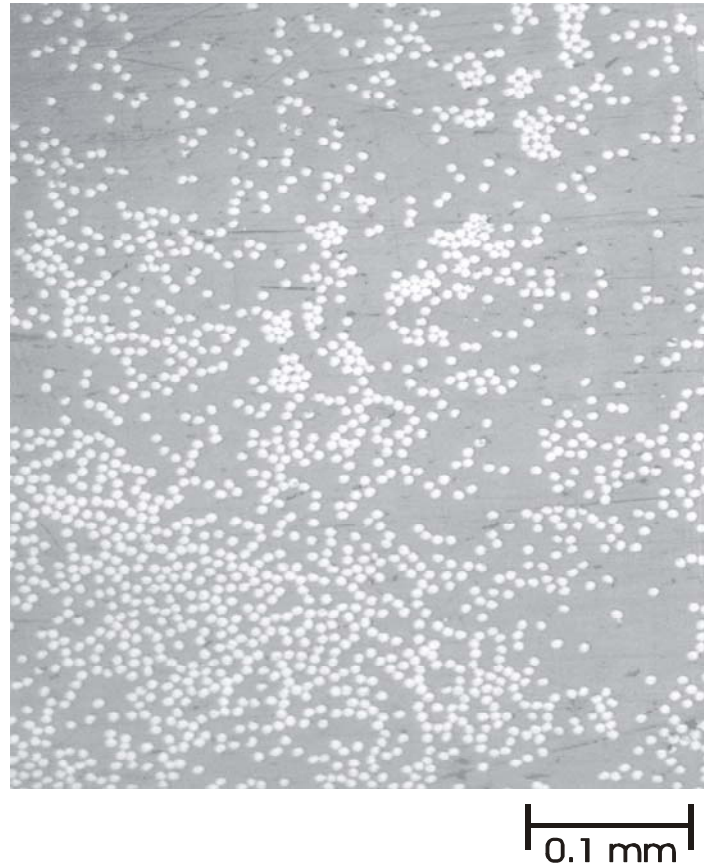

FIG. 7—*Polished surface of a carbon fiber composite made at NIST.*

Void Content

Figure 6 also includes void volume fractions for the composites made at NIST. The expected value is taken as zero based on the microscopy results. This is illustrated in Fig. 7, which shows a typical image of an in-house composite. The data from the burn off tests indicate void contents to be less than 1 %, which is approximately at the level of the uncertainty in the experiment. Consequently, the agreement is very good. For the composites made commercially, a sample microscopy image is shown in Fig. 8. Note that the glass-reinforced region contains more voids that the carbon-reinforced region. This illustrates the importance of coving a large enough surface area to get answers typical of the full composite. For the sample that had the high glass/carbon ratio, the void volume fraction as measured by the burn off test was 3.6 %, compared to a value of 5.6 % determined by microscopy. For the composite that had the low glass/carbon ratio, the void volume fraction obtained from the burn off test was 4.0 % while that estimated from microscopy was 4.9 %. Since each measurement uncertainty for both

experiments is approximately ± 1 %, the results are within experimental error. Consequently, what these data indicate is that the burn off test is an easy method to get a general idea of void content, although the significant uncertainty makes it impossible to distinguish between samples unless the differences in void contents are relatively large.
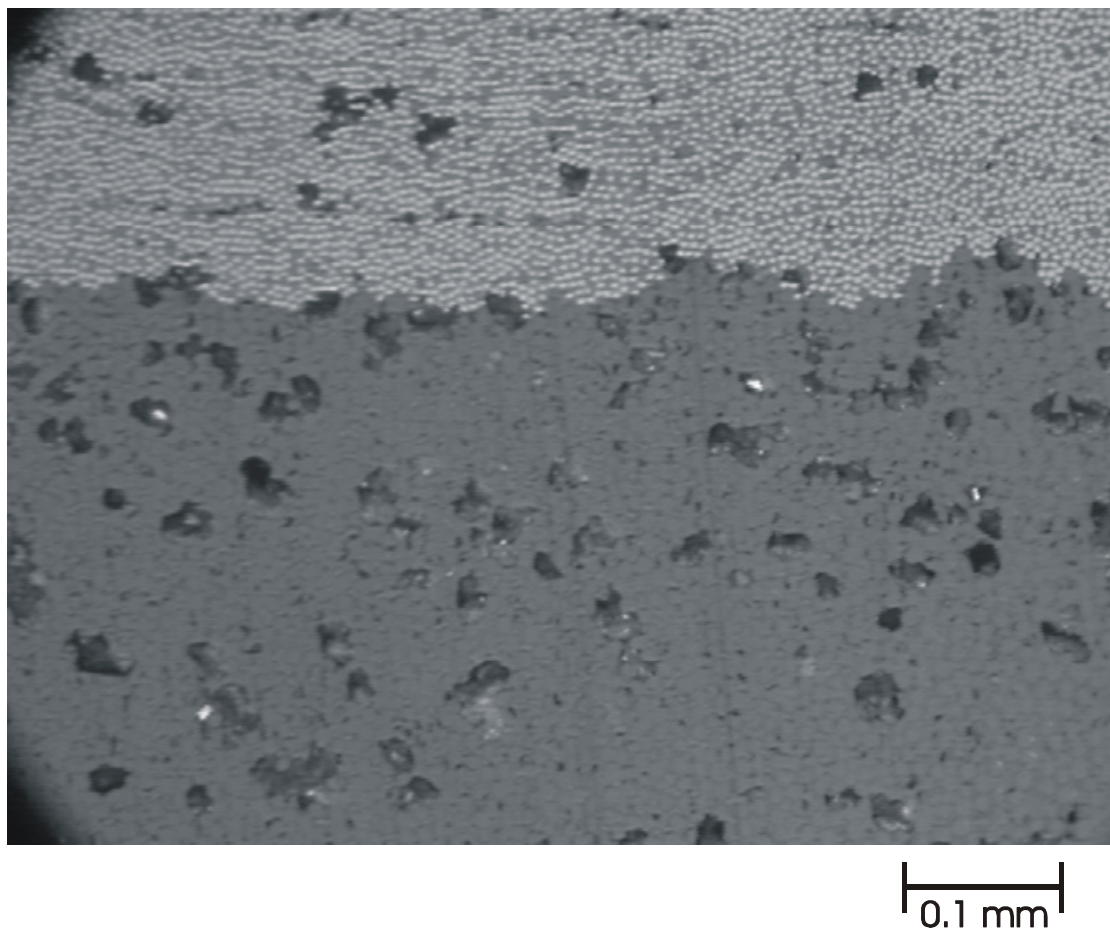

0.1 mm

FIG. 8—*Image of an industrial grade hybrid composite with the carbon fiber section on top and the glass fiber section on the bottom. More voids appeared in the glass section than in the carbon section.*

Conclusions

Based on the data presented in this report, we believe that we have a fast and easy method for determination of the constituent content in glass/carbon hybrid composites using a tow step heating procedure.

By the nature of the burn off test, we probably always get some removal of carbon when burning off the matrix in the first heating step. Nevertheless, when we compared the expected to the measured values of the fiber volume of the carbon fibers, we found that the two values tended to be very close. If we only burn off bare carbon fiber tows, we see a greater loss of carbon mass. Holding the carbon fibers from a composite specimen an extra 30 min at 600°C, we measure a significant amount of mass loss. Thus, we favor limiting the time of exposure at this first plateau temperature.

In the second heating step, we sometimes observed difficulties in removing the carbon at $900^{o}C$. Occasionally, we needed to extend the time at temperature to ensure that the carbon was removed. This removal was verified visually.

As far as voids are concerned, the estimates from the burn off test to date may be on the conservative side. Microscopy may give better results, but this requires measuring a large number of pictures to insure that the surface area covered is sufficient to get a result typical of the bulk material with pictures at the required magnification. This is a very tedious and time-consuming process.

The proposed procedure is a valuable modification to an existing ASTM standard, D 3171.

References

[1] ASTM Standard D 3171-99: Test Methods for Constituent Content of Composite Materials, *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA.

[2] Certain commercial materials and equipment are identified in this study for adequate definition of the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or instruments are necessarily the best available for this purpose.

[3] *Handbook of Composites*, George Lubin, Ed., Van Norstrand Publishing Company, New York, 1982.