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A TGA technique for determining graphite fiber content in epoxy composites[1]

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Abstract

A new technique has been developed to measure the fiber content of graphite fiber-reinforced polymer matrix composites. This new method requires less material and less time than the standard matrix digestion method. With data for the densities of the matrix, fiber, and composite, the method can be used to calculate fiber and void volumes. The new method was verified by comparing results with those obtained by using the standard matrix digestion method.

Keywords: TGA; Epoxy composites; Fiber content

1. Introduction

One of the most fundamental quantities controlling the properties of fiber-reinforced composites is the fiber content. Stiffness, strength, and thermal conductivity, as well as other properties depend mostly on fiber volume fraction and orientation. A quick and accurate method to measure fiber content in composites is useful in quality control of composites in production and in the characterization of new, developmental composites.

The fiber content in graphite fiber composites is usually determined by the acid digestion method [1]. This method requires a sample of at least 0.5 g per replicate and takes several hours to perform. The ignition method used for glass fiber composites is quicker, but is not suitable for graphite fiber composites because ignition also induces weight loss

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of the graphite fiber [2]. The micro technique described in this paper is a modification of the ignition method, which is suitable for graphite fiber composites. The micro scale is made possible by making the measurement in a thermogravimetric analyzer which consists of a furnace with controlled variable temperature and atmosphere around a micro balance. This method has been adapted to graphite fiber composites by selecting an appropriate heating program and, in order to avoid oxidation of the graphite fibers, by using a nitrogen atmosphere instead of air. The results from this micro technique agree with those obtained when using the acid digestion method. A special application of the micro technique to determine the fiber content in two glass and graphite epoxy composites is illustrated.

2. Experimental

The weight loss measurements were performed using a TA Instruments 2950 Thermogravimetric Analyzer (TGA). The specimens were cut from a filament-wound panel of Shell Epon 9405/9470 epoxy reinforced uniaxially with Hercules IM6 graphite fibers. After trying various specimen sizes, we found that a specimen size of approximately 20 mg is most suitable. It is also necessary to cut each specimen into small pieces (about eight pieces for the 20 mg sample). Small pieces facilitate heat transfer and the escape of the volatile products. Since there are resin rich layers on the surface of the specimen, the sampling should be made parallel to the thickness direction of the specimen.

The heating program developed for this composite consists of heating from room temperature to 250°C at a 20°C min^{-1} heating rate, followed by heating at 10°C min^{-1} to 600°C and then kept at 600°C for 40 min. This heating program is designed to achieve a constant residual weight within a fairly short time (40 min) while maintaining a temperature which is not high enough to cause weight loss from the graphite fibers. A typical

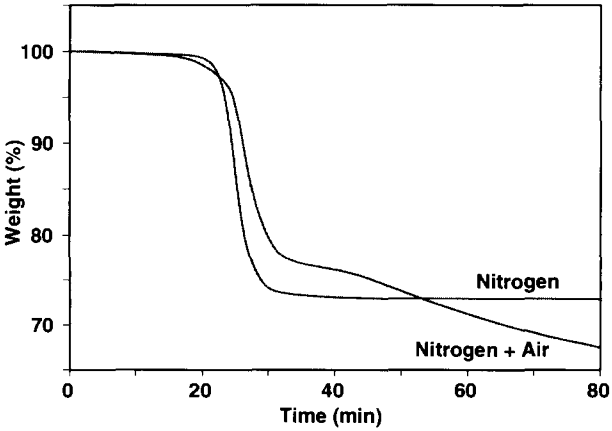

Fig. 1. Weight loss as a function of time for IM6/Epon 9405/9470 graphite/epoxy composite at 600°C in nitrogen (solid line) and in a mixture of nitrogen and air (broken line).

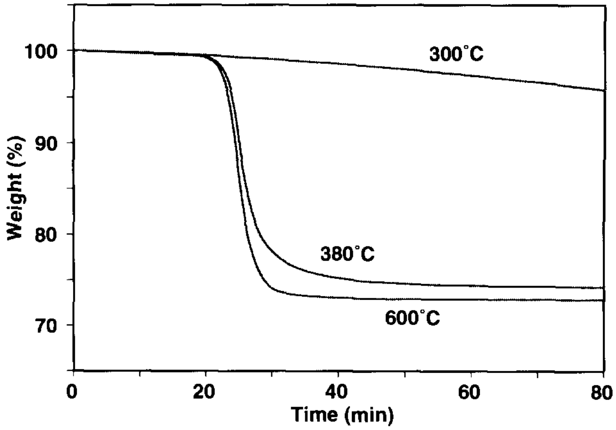

Fig. 2. Weight loss as a function of time for IM6/Epon 9405/9470 graphite/epoxy composite at 300°C (solid line), 380°C (dotted line), and at 600°C (broken line) under nitrogen.

weight loss curve is shown in Fig. 1. If the final temperature of the heating program is too low, a long time is required to achieve the constant residual weight. The thermogram in Fig. 2 shows the slower weight loss achieved at a temperature below 600°C. Too high a temperature may cause weight loss in the fiber, however, the Hercules IM6 showed no weight loss at 600°C. A thermogram of a sample of IM6 fiber tow, as shown in Fig. 3, shows negligible weight loss. The weight loss of 1.1% observed is due to the sizing material and possibly a small amount of moisture. Therefore, we concluded that this heating program did not induce weight loss from the graphite fibers. In this analysis, the weight of the sizing would be included in the weight of the epoxy resin.

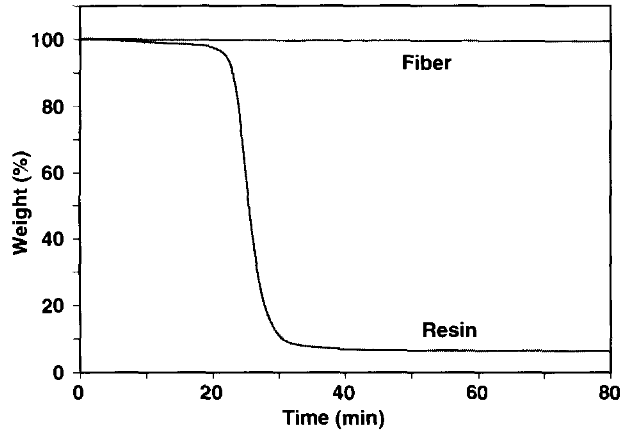

Fig. 3. Weight loss as a function of time for IM6 graphite fiber (solid line) and neat Epon 9405/9470 epoxy resin (broken line) at 600°C under nitrogen.

Uniform sample geometry was found to be essential to obtain reproducible results. Specimens containing large pieces resulted in higher residual weight indicating either incomplete degradation or trapped volatile products.

Another important factor was found to be the complete removal of air from the heating chamber. Air was introduced when the heating chamber was opened to load the sample. The furnace around the balance of the TGA was purged with nitrogen at a flow rate of 80 $cm^3 min^{-1}$. Purging for 5–10 min with nitrogen before the start of the heating program eliminated air from the chamber. The presence of air causes the oxidation of the graphite fibers and the residual weight would be lower than the heating in the absence of air as illustrated in the lower curve in Fig. 1. Under the proper conditions, the resin in a composite specimen is pyrolyzed away, leaving the fibers and a small, but reproducible amount of residue, and the weight of the graphite fiber remains unchanged.

The fiber content of samples of the same composite was also determined by the matrix digestion method [1]. The composites were digested in 70 wt% nitric acid for 4–6 h at its boiling point. A run was performed on the fiber with no resin, and negligible weight change (less than 0.5%) was seen. Prior to acid digestion, the density of each sample was measured by weighing the samples in air and immersed in water, according to the ASTM method D 792 [3]. Samples ranging in weight from 0.7 to 1.2 g were weighed on a balance with 0.0001 g sensitivity. The density of pure epoxy resin, cured under the same conditions as the composite, was also measured. Void contents were calculated according to ASTM D 2734 [4].

3. Results and discussions

3.1. Assumptions

From the weight loss of the composite sample and the percent weight loss of the resin, the original fiber weight percent was calculated, making the following assumptions.

(1) The graphite fibers do not lose weight when subjected to the heating program under nitrogen, and the composite weight loss is due to the degradation of the resin only.

(2) The residual weight of the epoxy resin levels off close to the end of the heating program. This is supported by the thermograms of neat resin in Fig. 2 and of composite in Fig. 1.

(3) The graphite fibers do not affect the degradation kinetics of the epoxy resin and thus the measured weight loss is proportional to the weight fraction of the resin.

3.2. Density determination of composite and resin

The densities of the fiber, epoxy and composite are required for the determinations of the fiber and void contents in the composite. The density of the IM6 graphite fiber was taken from the Hercules product data sheet [5] to be 1.73 g cm^{-3}. The densities of the resin and composite, determined by the immersion method, the fiber content, determined by acid digestion and the void content, calculated from these are listed in Table 1.

Table 1

Density, fiber and void content of 9405/9470 epoxy and 9405/9470 epoxy/IM6 composite, determined by standard methods

Sample	Density/ $(\mathrm{g\ cm^{-3}})$	Fiber weight in % (g)	Theoretical composite density/$(\mathrm{g\ cm^{-3}})$	Void content (%)	Actual fiber volume in %
D-1	1.330	66.21	1.482	10.28	50.89
D-2	1.442	73.95	1.532	5.90	61.64
D-3	1.448	68.19	1.494	3.12	57.07
D-4	1.478	70.50	1.510	2.09	60.23
D-5	1.445	68.47	1.497	3.50	57.26
D-6	1.443	72.56	1.523	5.25	60.53
Average	1.431	70.00	1.506	5.02	57.94
SD	±0.051	±2.90	±0.019	±2.93	±3.91

3.3. Weight percent fiber determination by TGA

In order to determine the fiber weight percent, the percent residue from heating the pure resin under the selected heating program has to be determined. The lower curve of the thermogram in Fig. 3 is a typical weight loss curve when heating pure resin. The percent weight on the level part of the curve is the residual weight after the heating program. The results from four samples have been averaged to give the value of 6.0%. Assume that the residue consists of fiber weight plus resin residue,

$$\begin{aligned} W_{\mathrm{residue}} &= W_{\mathrm{F}} + YW_{\mathrm{R}} \\ &= f_{\mathrm{F}}W_{\mathrm{C}} + Yf_{\mathrm{R}}W_{\mathrm{C}} \\ &= f_{\mathrm{F}}W_{\mathrm{C}} + Y(1 - f_{\mathrm{F}})W_{\mathrm{C}} \end{aligned} \tag{1}$$

where W_{F} is the weight of the fiber, Y is the % residue from heating pure resin, W_{R} is the weight of resin, W_{C} is the weight of composite, f_{F} is the weight % of fiber and f_{R} is the weight % of resin.

Rearranging Eq. (1),

$$f_{\mathrm{F}} = (W_{\mathrm{residue}}/W_{\mathrm{C}} - Y)(1 - Y) \tag{2}$$

The weight percent of fiber in the composite calculated from the weight loss using Eq. (2) on five composite samples is shown in Table 2.

If there were no voids in the composite, the fiber volume percent would be

$$\%\ V_{\mathrm{F}} = \frac{V_{\mathrm{F}}}{V_{\mathrm{C}}} = \frac{V_{\mathrm{F}}}{V_{\mathrm{F}} + V_{\mathrm{R}}} = \frac{W_{\mathrm{F}} / D_{\mathrm{F}}}{(W_{\mathrm{F}} / D_{\mathrm{F}}) + (W_{\mathrm{R}} / D_{\mathrm{R}})} \tag{3}$$

Table 2

Fiber content determination by TGA method

Sample	Sample weight/ mg	Residue in %	Fiber weight in %, f_F (%)	Theoretical composite density/ (g cm^{-3})	Void content in %	Actual fiber volume in %
T-1	20.20	72.82	71.09	1.513	5.45	58.80
T-2	16.12	72.93	71.20	1.514	5.50	58.89
T-3	21.10	73.70	72.02	1.520	5.83	59.57
T-4	16.25	71.09	69.24	1.501	4.70	57.27
T-5	21.55	72.19	70.41	1.509	5.18	58.24
Average		72.55	70.79	1.512	5.33	58.55
SD		±0.97	±1.04	±0.007	±0.42	±0.86

where V_C is the volume of composite, V_F is the volume of fiber, V_R is the volume of resin, D_F is the density of the fiber (1.73 g cm^{-3} from Hercules data sheet) and D_R is the density of the resin (1.431 g cm^{-3} averaged value from Table 1).

The theoretical density of the composite, $D_C{}^\circ$, is the density of the composite in the absence of voids:

$$D_C{}^\circ = \frac{W_C}{V_F + V_R} = \frac{W_C}{(W_F / D_F) + (W_R / D_R)} \tag{4}$$

The theoretical densities of the five samples are listed in Table 2. These values are used to calculate the void content.

3.4. Void content and fiber volume percent

Most composites contain some volume of voids. The void content of a composite may significantly affect some of its mechanical properties [6]. Therefore, the void content is an important parameter in composite characterization.

Let the void content be defined as

$$\text{Void content} = \frac{V_V}{V_C} = \frac{V_C - (V_F + V_R)}{V_C} = \frac{(W_C / D_C) - (W_C / D_C{}^\circ)}{W_C / D_C{}^\circ} = \frac{D_C{}^\circ - D_C}{D_C{}^\circ} \tag{5}$$

where D_C is the theoretical composite density (5th column of Table 2) and D_C is the measured composite density (1.43 g cm^{-3} from Table 1).

The value used for the measured composite density was the average of densities measured by immersion. It was not possible to measure densities of the 20 mg samples used for TGA measurements. The void content values for the five samples calculated from Eq. (5) are listed in the 6th column in Table 2.

The actual fiber volume percent in the composite is the fraction of fiber volume in the total volume of the composite:

$$\text{Fiber volume }\% = \frac{V_F}{V_F + V_R + V_V} = \frac{V_F}{V_C} = \frac{f_F D_C}{D_F} \qquad (6)$$

where f_F is the weight percent of fiber, D_C is the measured density of composite and D_F is the density of the fiber.

The fiber volume percent calculated from the density values and fiber weight fraction using Eq. (6) are also listed in Table 2. The scatter in the results for the five TGA samples is quite small.

The results from both the new micro technique and the acid digestion method agree quite well. Three pieces of important data, the fiber weight percent, the void content, and the actual fiber volume percent obtained using the two methods, are compared in Table 3.

It should be noted that the value for void volume depends on an accurate value for both the theoretical density and actual density of the composite. These two quantities are subtracted in the numerator of Eq. (5), and small errors in either give large errors in the predicted percent void volume. For example, for the IM6/Epon composite studied, a change of 0.01 in the measured density, D_C, would cause a change of 1% in the void volume given by Eq. (5).

The results from both methods are in good agreement. The scatter in both methods probably represents variations in material composition from sample to sample, rather than imprecision in the methods. The samples for the TGA measurements all came from the same 16-ply panel, while those used for the digestion measurements came from several different panels of various thicknesses. The new micro technique using TGA appears to be a reliable method for determining fiber content. The new method requires less material and labor than the matrix digestion technique. If accurate density data are available for the composite, the resin, and the fiber, the method can be used to calculate void content. The void content measured in these samples is typical of filament wound composites and is large enough to cause a significant decrease in mechanical properties The void volumes measured show the necessity of determining the void content of the composite.

3.5. Special application of the micro technique

The micro technique was originally developed to solve a special problem in our laboratory. Two epoxy composites, one with glass fibers and one with graphite fibers, were to be characterized. The resin in both composites was anhydride-cured Epon 826 epoxy. However, the pure resin was not available for characterization. The material quantities were limited so that the conventional digestion method could not be used to determine

Table 3

Average void and fiber content results from TGA and digestion methods

	TGA	Digestion
Fiber weight in %	70.8	70.0
Void volume in %	5.3	5.0
Actual fiber volume in %	58.6	57.9

Table 4

Fiber content determination in glass and graphite Epon 826 epoxy composites

Composite	Residue in air in %	Residue in nitrogen in %	Fiber weight in %	Resin weight in %	Fiber volume in %
Epoxy/glass	70.59	75.30	70.59	29.41	59
Epoxy/graphite	–	68.04	61.95	38.05	58

the fiber content. Therefore, the micro technique was developed. Three series of TGA analysis were performed and their results are:

(1) TGA of epoxy/glass heated in air	70.59% residue
(2) TGA of epoxy/glass heated in nitrogen	75.30% residue
(3) TGA of epoxy/graphite heated in nitrogen	68.04% residue

All the above values are averages from five TGA runs. The initial temperature of 300°C was followed by heating at 5°C min^{-1} to 600°C and then kept at 600°C for 20 min. The residue from the TGA of epoxy/glass heated in air consisted of transparent colorless glass fibers. Therefore, the resin weight was (100–70.59%) or 29.41% by weight. The difference in residual weights between the nitrogen and air TGA was due to the residue of resin heated in nitrogen. The residue from the resin was (75.30 – 70.59)/(100 – 70.59) or 16%. Letting X be the weight of graphite fiber in 100 g of composite, the weight balance is

$$68.04 = X + 0.16(100 - X) = X(1 - 0.16) + 0.16$$

$$X = 61.95 \text{ g or } 61.95\% \text{ by weight in the composite}$$

The results are summarized in Table 4.

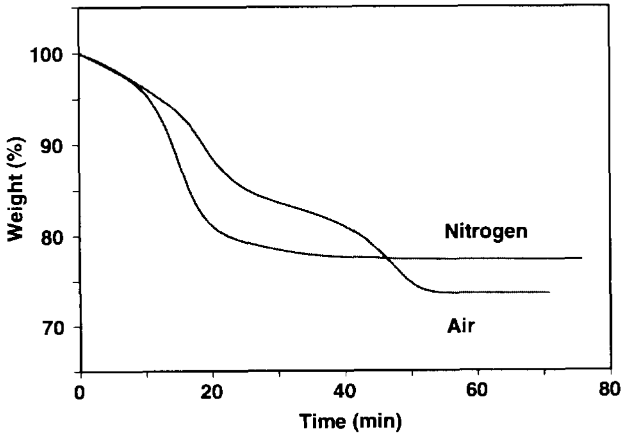

Fig. 4. Weight loss as a function of time of anhydride-cured Epon 826/fiberglass composite at 600°C under air (solid line) and nitrogen (broken line). The difference in the weight loss at long times is due to matrix residue.

The density used for the intermediate modulus graphite fiber was 1.80 g cm^{-3}. The glass fiber density used was 2.5 g cm^{-3}. The resin density used was 1.3 g cm^{-3}. The fiber volume percent calculated from these data are given in the last column of Table 4. The TGA curves of air and nitrogen heating of the epoxy/glass composite are shown in Fig. 4. Both curves level off at the end of the heating program since the glass fibers do not lose weight when heated under air.

4. Conclusions

The reliability of the new micro technique using TGA for fiber and void content analyses of graphite fiber composite has been demonstrated. The proposed method appears to be a quick and accurate method to measure the fiber content in graphite/epoxy composites. For the system investigated, Hercules IM6-reinforced Epon 9405/9470, fiber weight percent measurements were consistent within +1% and agreed to within experimental scatter with measurements made by matrix digestion.

The proposed method requires only a small amount of sample per replicate (20 mg). However, information on the decomposition behavior of the matrix is needed to apply the method with confidence. The applicability of the method to matrix resins other than epoxies still has to be determined.

The method can be used to estimate percent void volume and fiber volume, provided that accurate data are available for the density of the composite being measured and its constituents. The values given by the method for void volume are highly sensitive to errors in the composite density.

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