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Methods of Fiber and Void Measurement in Graphite/Epoxy Composites

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ABSTRACT: A variety of experimental procedures for measuring composite fiber and void content has been evaluated, including resin removal by sulfuric acid digestion, water takeup, and quantitative microscopy. These techniques were applied to a series of graphite/epoxy laminates; a comparison of the results showed the more convenient resin-removal method to be sufficiently precise unless spatial distributions of the constituents are required, in which case microscopy is indicated.

KEY WORDS: composite materials, epoxy laminates, tests, quantitative analyses, microscopy, graphite composites

The service properties of a fiber-reinforced composite are determined largely by the relative proportion and spatial distribution of the composite's three major constituents: fiber, matrix, and void. Tensile strength and modulus are related directly to fiber volume fraction as predicted by rule-of-mixtures or more elaborate analyses[1].² Voids, generally air bubbles entrapped in the matrix during composite fabrication, have a pervasive effect on composite properties even at a low volume percent: ultimate mechanical properties, especially interlaminar shear strength, are markedly reduced[2,3,4], and resistance to environmental degradation also suffers[5]. Although one generally seeks as low a void content as possible, it has been shown that voids are highly effective in attenuating impact-produced stress waves[6], and in certain applications the designer may be willing to compromise somewhat in other properties if hardness against stress-wave damage is important.

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² The italic numbers in brackets refer to the list of references appended to this paper.

In spite of the importance of fiber and void content in determining composite performance, there exists no general agreement on acceptable experimental methods of measuring these quantities. Measurement of void content at low volume percent is particularly difficult, with some techniques frequently producing anomalous values of negative void content. The available procedures can be placed in one of three categories: gravimetric analyses (density measurement, fiber weighing, etc.), quantitative microscopic examinations of a metallurgically polished interior plane of material, and indirect inference based on the interaction of the material with ultrasonic or other radiation. This paper presents data comparing a variety of methods that fairly well encompass the first two categories; methods based on radiation interaction have not yet proven fruitful for quantitative examinations [4], although ultrasonic attenuation C-scan can be of value for rough qualitative estimates of laminate quality [3].

Data obtained for graphite/epoxy composite are presented here as a means of assessing the various methods, and the conclusions may not be valid if applied indiscriminately to other composite types. For instance, the sulfuric acid used successfully for resin removal in this study is known to attack some glass fibers, and is not able to remove some resins in present use. In the interest of space, most details of the methods used will be omitted from this paper if available elsewhere, and for these the reader is referred to the list of references.

Materials

Samples were drawn from a series of 24-in. by 24-in. graphite/epoxy laminates that had been fabricated to represent a range of fiber modulus, with other materials parameters held constant. Three fiber types were collimated and prepregged commercially in an epoxy-novolac resin; these constituents are listed in Table 1. Prepreg sheets were hand laid up to produce unidirectionally reinforced laminates approximately 1/8 in. thick, and then autoclave-cured at 50 psig. Bleeder cloth was placed at the surfaces to aid gas elimination. The fabrication process was intended to produce laminates having 50 percent fibers by volume and less than 1 percent voids. Plaques of unreinforced resin were also cured to provide a means of measuring matrix properties.

TABLE 1—*Constituents of composite laminates studied.*

| | Constituent Materials | | | |
|---------|-----------------------|--------|----------------|----------------|
| | Source | Type | Modulus (mpsi) | Density (g/cc) |
| Fibers: | 3M | Pluton | 6 | 1.50 |
| | Hercules | HMS | 50 | 1.91 |
| | Celanese | Celion | 70 | 1.96 |
| Resin: | Am. Cyanamid | BP907 | 0.5 | 1.225 |

Figure 1 shows X400 (nominal) micrographs of metallurgically polished sections of the three composite types. Near-nominal constituent fractions were obtained in laminates employing Hercules and Celanese fibers, but those laminates with Pluton fibers contained a significantly higher void content. Regions of excess resin and higher void content were generally found between the original prepreg sheets. The cured laminates were cut into pieces of various sizes for mechanical property studies, and at this time specimens for the present study were taken from scattered locations in the laminate.

Experimental Methods

Density

Composite density was measured for specimens taken from each laminate type by immersion weighing as specified by the ASTM Test for Specific Gravity and Density of Plastics by Displacement (D792). Samples were approximately 1 g in size, and were weighed to five significant figures with an analytical

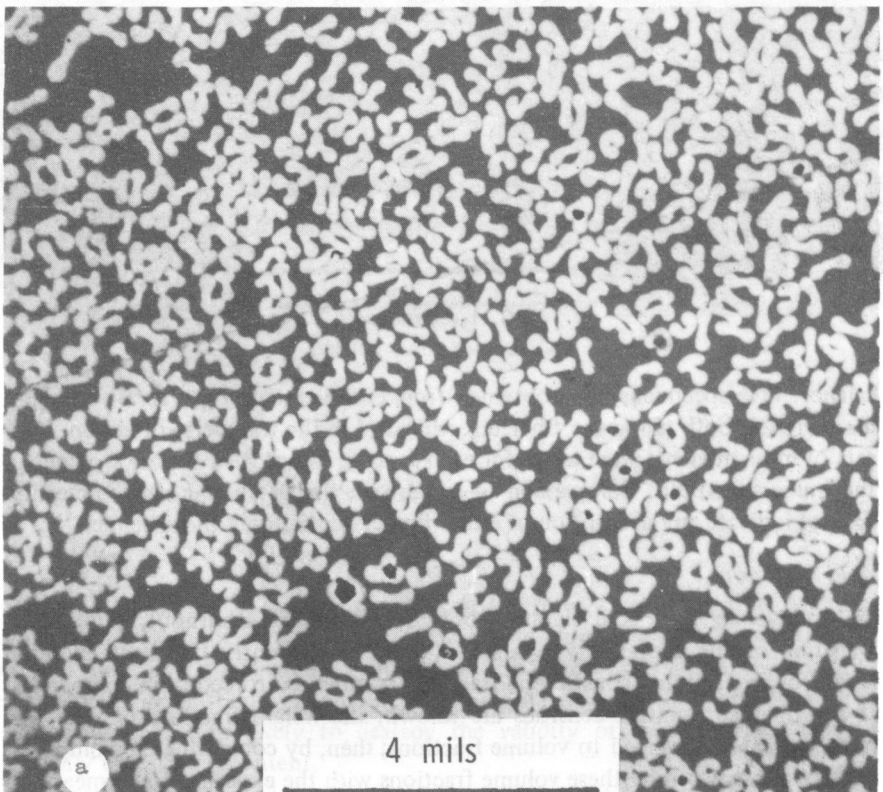


FIG. 1—Micrographs (\approx X400) of graphite/epoxy laminate types studied: (a) Celanese fibers, (b) Hercules fibers, (c) Pluton fibers.

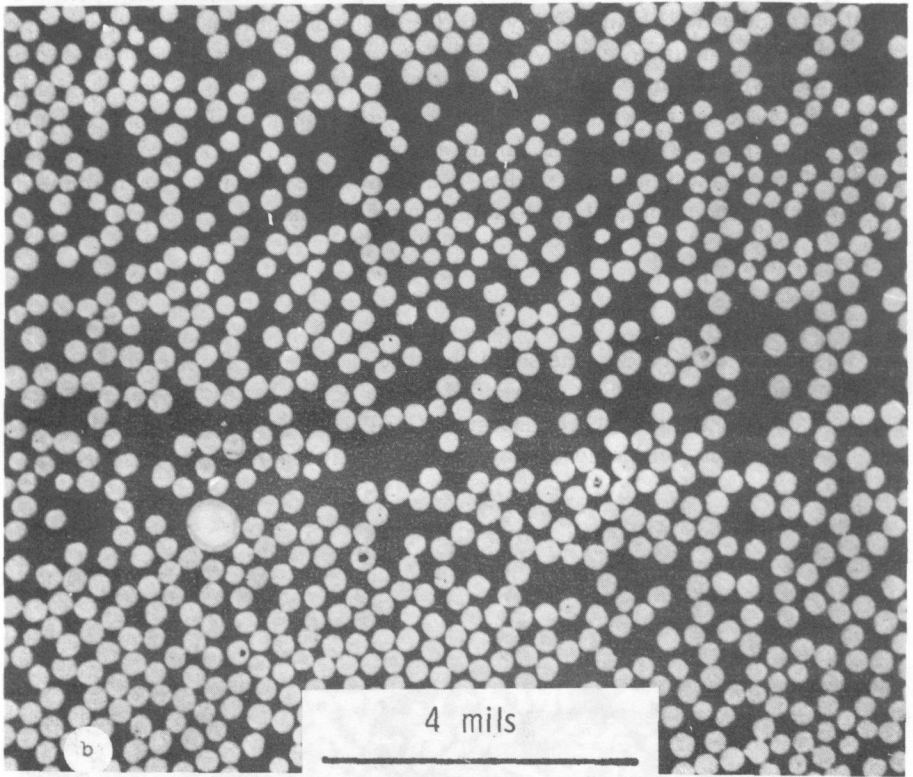


FIG. 1—Continued.

balance. Five specimens were obtained from each laminate type, so as to sample the variation both along the fiber direction and in the transverse direction. Two sets of measurements were taken for each sample, using either water or octane as the immersion fluid. Comparison of weights in air before and after immersion did not indicate any absorption of either immersion fluid by the specimen.

Acid Digestion

Resin removal, by acid digestion or by furnace or TGA burnout, followed by weighing of the supposedly unaffected fibers is currently the most common means of determining constituent fractions in fiber-reinforced resin composites. If the fiber and matrix densities are known, the weight fractions of fiber and matrix can be converted to volume fractions; then, by comparing the composite density as predicted by these volume fractions with the experimentally measured composite density, the volumetric void content can also be inferred by an equation of the form:

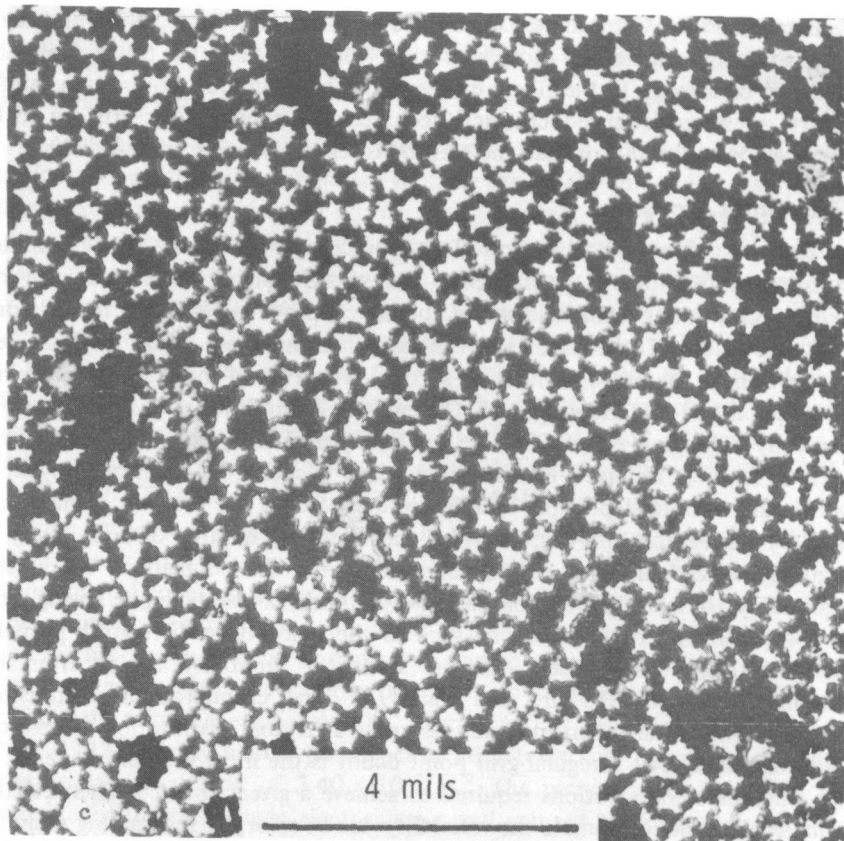


FIG. 1—Continued.

$$\text{Volume \%} = \left[\frac{\rho_r \left(1 - \rho_c \frac{w_f}{w_c \rho_f} \right) - \rho_c \left(1 - \frac{w_f}{w_c} \right)}{\rho_r - \rho_a} \right] \times 100\%$$

where ρ_r , ρ_c , ρ_f , and ρ_a are the densities of the resin, composite, fiber, and air (assumed zero), respectively; and w_c and w_f are the total sample weight and residual fiber weight. Lenoe[7] points out that accurate values for ρ_r and especially ρ_f are difficult to obtain, and that the uncertainties introduced by these values are very likely to destroy the validity of the calculated value, especially at low void content.

The same samples used previously for immersion density tests were subjected to acid digestion testing using fuming sulfuric acid according to a procedure

recommended by Courtaulds Ltd.[8]. Comparison of scanning electron micrographs of virgin fibers and those recovered from acid digestion tests revealed no evidence of damage to the fibers by the acid. The technique requires the careful efforts of an experienced chemical technician if consistent results are to be obtained, but with this proviso the method is relatively quick and efficient.

Quantitative Microscopy

The use of quantitative optical microscopy as a means of determining constituent fractions in petrographic and metallographic structures is over a century old, dating from Delesse's mathematical proof in 1848 that in a uniform rock the volume fractions of the various constituents are equal to their areal proportions as viewed on a random section. (A survey of the early literature has been published by Howard and Cohen[9].) Several variations are possible, generally belonging to one of three types: (a) areal analysis, in which the total area of features observed on the polish plane is counted; (b) lineal analysis, in which the fractional portion of a line intercepted by the features is measured; and (c) point-count analysis, in which the fractional number of a randomly or regularly spaced array of points falling upon the desired features is counted. Variability, or lack of precision, in these methods can be taken as arising from two sources: experimental errors, such as the inability to distinguish properly the constituent boundaries; and the statistical variability arising from the sampling technique. Hilliard and Cahn[10] have calculated these statistical variances for the different methods assuming a random distribution of features, and concluded that a regular-grid point count is the most efficient in terms of the number of observations required to achieve a given variance. Their calculations enable one to estimate the variability due to error, by subtracting away the predicted statistical variance.

A regular 10×10 grid, measuring 2 in. by 2 in., was used for most of the manual microscopy reported here. The desired feature, either fiber or void, was "counted" if it fell on a grid intersection. The grid was overlaid at five nontouching locations on a $500\times$ micrograph measuring 8 in. by 10 in. Five specimens were taken from each laminate type (adjacent to the locations used for the density and acid digestion samples) and metallurgically polished to provide a section perpendicular to the fiber direction; three $500\times$ micrographs were obtained at various locations on each piece. The total actual area observed on each material type was therefore $(2/500)^2 \text{ in.}^2/\text{grid} \times 5 \text{ locations/negative} \times 3 \text{ negatives/piece} \times 5 \text{ pieces/material} = 0.0012 \text{ in.}^2 \text{ per material}$. The corresponding number of grid intersections was $10 \times 10 \times 5 \times 3 \times 5 = 7500$ per material.

Areal analysis was also used for the Hercules fiber content measurement, as the round fiber cross section made such a measurement relatively simple. A mean fiber cross-sectional area was computed by measuring a number of fiber

diameters; then the fractional area of fibers in a given sample subarea could be obtained simply by counting the number of fibers in the subarea.

Image Analysis Microscopy

Manual quantitative microscopy is extremely tedious: more than ten hours of continuous operator time is required to make the 7500 point-count observations described in the foregoing. In recent years, however, the growing number of automatic image analysis systems has provided an interesting alternative. These systems scan an optical image—a photomicrograph or a mounted specimen—with a Vidicon or other optical sensing device, using a television-style raster pattern to develop an array of optical density values corresponding to spatial locations on the sample surface. The instrumentation is tuned to detect an optical density corresponding to a desired constituent, and the resulting array of “picture-point counts” then corresponds to a fine regular-grid point count. Measurements of the three laminate types were made using four different commercial systems: the Quantimet B, Quantimet 720, Bausch & Lomb QMS, and Millipore.

These systems offer great advantage in terms of counting speed, but at some expense of control. The operator has little trouble telling a fiber from a void during manual counting, but variations in optical density or focal plane may lead to experimental errors during automatic instrument operation over which the operator has no knowledge or control (although some systems have automatic focussing and detection accessories that claim to minimize these errors). As an example of counting efficiency, the Quantimet 720 was set for an array of $390 \times 390 = 152\,100$ picture points per location (view) on the sample, the array covering an actual area of 3.40×10^{-5} in.² The picture point count for the desired constituent is made electronically and printed on a teletype, and the microscope stage then moved automatically to another location on the specimen. For each laminate type, 100 locations were scanned on each of five specimens, resulting in an effective 76 050 000 observations over 0.0170 in.² of surface, requiring approximately an hour of instrument time.

Water Takeup

In a recent comprehensive study of the effects of voids in composites, Olster[3] reported that reliable void content data could be obtained in graphite/epoxy systems by weighing specimens at various times during long-term boiling in water, noting that the specimen density increases to some equilibrium value, and calculating a void content assuming that the density increase is due solely to the filling of all void space with water. This technique was used to measure void content in the three graphite/epoxies of the present study, but with anomalous results: in these materials the density rose to a maximum value and decreased monotonically thereafter, not reaching an equilibrium value even after more than 900 h. These results may be due to the resin plaque used for

calibration (unreinforced BP907 epoxy was boiled to measure the water take-up of ostensibly void-free matrix material) being structurally different than the reinforced resin, but further work is necessary to find means of avoiding this problem and of determining for which materials the technique is applicable.

Discussion of Results

As stated earlier, the various analytical procedures were applied to each of five pieces from each laminate type to produce a statistical sample of size $N = 5$, and from these data a mean \bar{x} and a standard deviation s were computed. Tables of Student's t were then used to determine the 95 percent confidence limits for the mean μ of the parent population as

$$\mu = \bar{x} \pm st/\sqrt{N} - 1$$

with $t = 2.776$ for 95 percent confidence and $N = 5$. For the purpose of comparison of the precision of the various methods, graphical displays of the sample mean and the confidence limits are used in addition to tabulated numerical data (Table 2). In the figures, only the ordinate has numerical meaning, and the absence of confidence limits on some values indicates that the limits are smaller than the symbol used to represent that particular method. It should be emphasized that high precision (small confidence limits) in a method, while desirable, does not insure a method's accuracy. However, agreement between several independent methods increases one's confidence that the value is also accurate, that is, that the sample mean is the true mean of the parent population.

Figure 2 displays the results from immersion weight calculations for composite density, and compares octane versus water immersion for the three laminate types. These data show that either fluid is acceptable. The mean values

TABLE 2—Measured constituent fractions and 95 percent confidence limits.

| Quantity | Method | Pluton | | Hercules | | Celanese | |
|-----------------|----------------|--------|--------|----------|--------|----------|--------|
| | | Mean | Limits | Mean | Limits | Mean | Limits |
| Density | Octane | 1.3184 | 0.0026 | 1.5632 | 0.0080 | 1.6042 | 0.0114 |
| | Water | 1.3164 | 0.0013 | 1.5480 | 0.0051 | 1.5903 | 0.0074 |
| Volume Fraction | Point Count | 0.371 | 0.029 | 0.514 | 0.033 | 0.627 | 0.031 |
| | Quantimet 720 | 0.4485 | 0.0987 | 0.445 | 0.040 | 0.538 | 0.040 |
| | Film Reader | n/a | | 0.493 | 0.013 | n/a | |
| | Acid Digestion | 0.5871 | 0.0108 | 0.4714 | 0.0052 | 0.5138 | 0.0094 |
| Void Content | Point Count | 0.0822 | 0.0192 | 0.0055 | 0.0041 | 0.0029 | 0.0010 |
| | Quantimet 720 | 0.0463 | 0.0702 | 0.0023 | 0.0014 | 0.0015 | 0.0007 |
| | Acid Digestion | 0.0571 | 0.0026 | -0.0005 | 0.0007 | 0.0100 | 0.0037 |

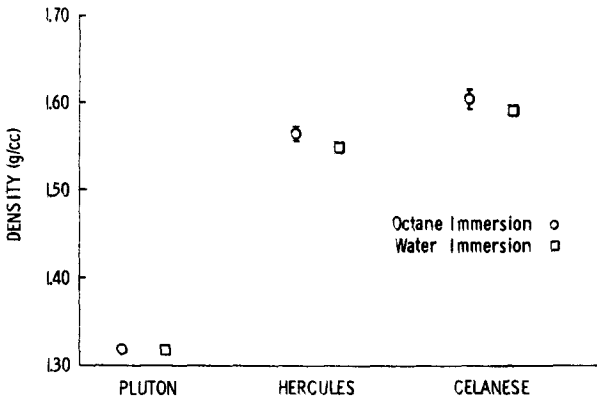


FIG. 2—Comparison of density measurement results.

also agreed with values obtained by placing certain of the specimens in a dioxane-ethylene bromide density gradient column. The small confidence limits of Fig. 2 also indicate that the spatial variability in the laminates is also small, at least on the scale of the approximately 1-g density specimens.

Figures 3 and 4 compare fiber and void content measurements, respectively, obtained for each laminate type by acid digestion, manual point count, and one image analysis system (Quantimet 720). The one case for which areal analysis was used (Hercules laminate fiber content) is also included. The poor precision of the image analysis measurement of Pluton laminate void content is immediately obvious: this is tentatively ascribed to reflection of light from the bottoms of the relatively large Pluton voids that interferes with the grey-level discrimination settings of the instrument. Beyond this, these data do not indicate any particular advantage of one method over the others. It also appears

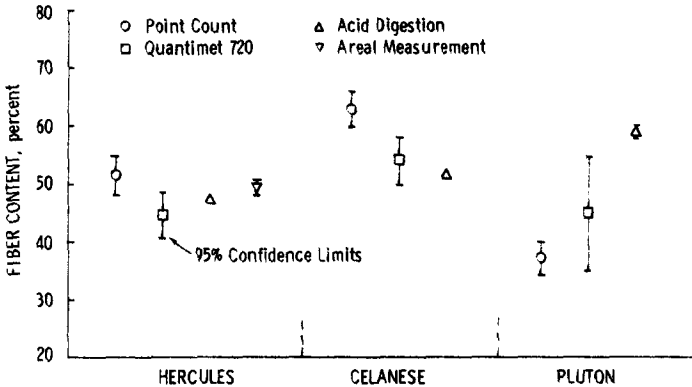


FIG. 3—Comparison of fiber content measurements.

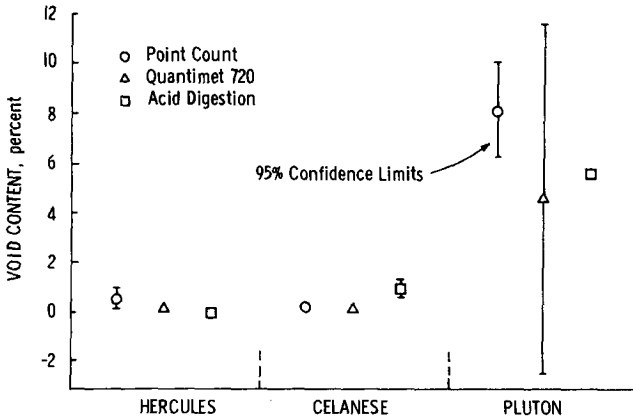


FIG. 4—Comparison of void content measurements.

that utilization of several independent measurement techniques is indicated if confidence in the accuracy of results is required.

Only the Quantimet 720, among the various image analysis systems, was used in the full study of five specimens from each laminate type. The older Quantimet B did not have sufficient discrimination to distinguish voids from matrix, and those data will not be reported here. The Bausch & Lomb QMS and the Millipore instrument were used to measure constituent fractions in one specimen from each laminate, and these data are compared in Figs. 5 and 6 with Quantimet data from the same specimen. (No attempt was made to duplicate exact locations on that specimen, however.) The error bands represent standard

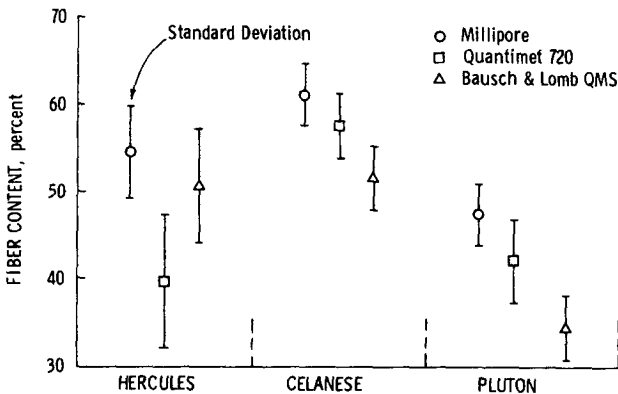


FIG. 5—Comparison of automatic fiber measurement results.

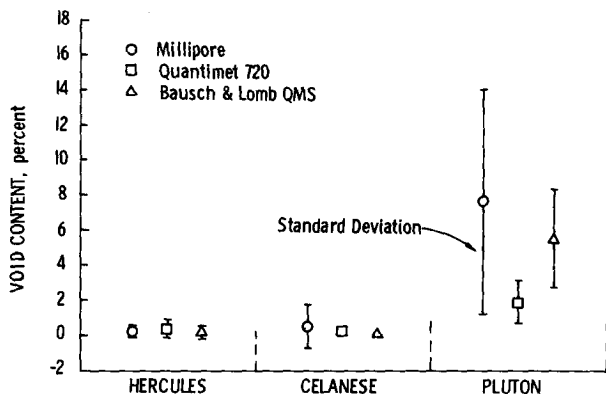


FIG. 6—Comparison of automatic void measurement results.

deviation rather than confidence limits in these two figures. Again, the data do not indicate the superiority of one system over the others. In spite of approximately equal error bands on the fiber measurements, none really agree, and the measurement accuracy is therefore in doubt. The situation is improved for the void measurements on the Hercules and Celanese laminates, although all instruments have trouble detecting the Pluton voids consistently.

In all cases, the variability in the instrumental methods is much larger than that due to statistical sampling, and must be ascribed to experimental errors. Such errors, as mentioned earlier, include counting inconsistencies due to optical ambiguities at the constituent interfaces and variations in grey level within a given constituent over the plane of observation. This is not to say that operator experience with the instrument could not overcome much of this, but at the very least one must say that the technique requires further development before it can be used routinely for measurement of composite constituent fractions.

One compelling advantage of quantitative microscopy is the ability to measure spatial distributions of constituent fractions; these are averaged out in the larger samples used in the resin-removal methods. Figure 7 is a micrograph (approximately $\times 45$) of a Pluton laminate that has been subjected to shock loading, and shock-induced cracks are evident in addition to the high-void regions between the original prepreg sheets. The shock damage analysis in use requires quantitative measures of damage location and amount, and Fig. 8 shows how these data are provided by point count and lineal analysis for the micrograph of Fig. 7. The high-void regions between the prepreg sheets are evident, and the shock crack shows clearly at approximately 0.075 in. (distance is measured in actual inches from the laminate surface). Even here, however, some disagreement between the two methods is seen, most notably at the maxima of the two high-void regions at the right.

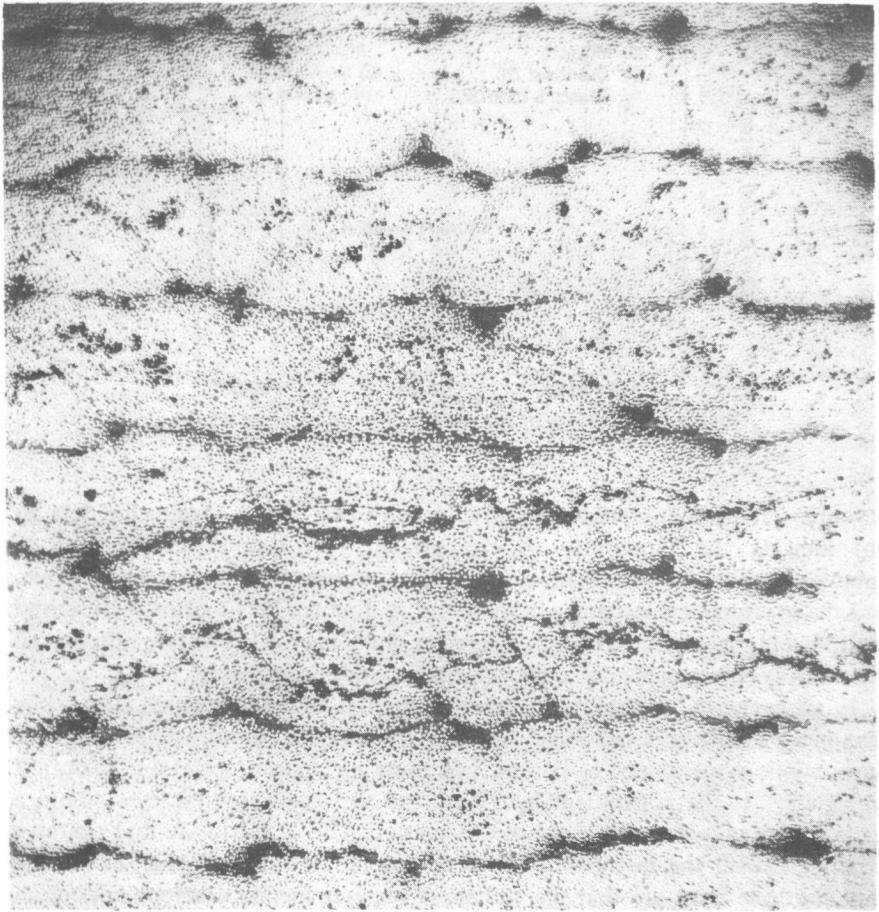


FIG. 7—Micrograph ($\approx \times 45$) of Pluton laminate damaged by shock loading.

Conclusions

Perhaps the conclusion of most practical consequence found here is that the acid digestion technique, despite the uncertainties of the constituent densities, is as reliable as the more complex quantitative microscopy techniques if average values rather than spatial distributions are sufficient. More work is required to develop standardized techniques for quantitative microscopy that reduce the variability arising from experimental errors. Further work is also necessary to extend these conclusions to a wider range of fibers and void contents, and to other composite material types.

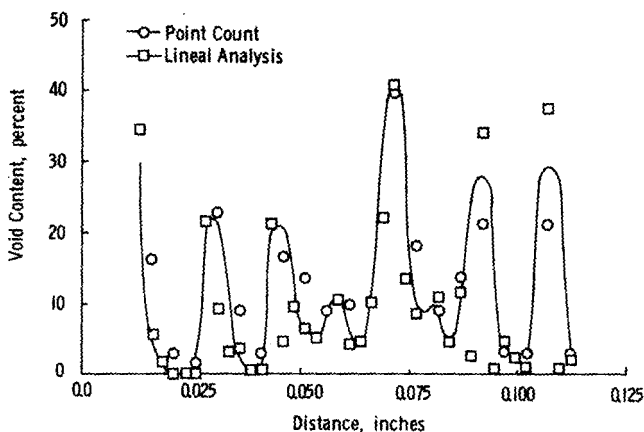


FIG. 8—Quantitative microscopy measurements of shock-damaged Pluton laminate.

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