

Determination of the Fiber Content in Polymer Composites by Means of X-Ray Absorption Measurements

C. SCHIPP,¹ S. RÖBER,¹ H. G. ZACHMANN,^{1,*} and J. C. SEFERIS²

¹Institut für Technische und Makromolekulare Chemie, University of Hamburg, Germany, and

²Polymeric Composition Laboratory, University of Washington, Seattle, Washington, USA

SYNOPSIS

The X-ray absorption coefficients of carbon fibers, different polymeric matrix materials, and composites were measured and the fiber contents in the composites were calculated from the measured absorption. In addition the fiber content determinations were performed by means of acid digestion of the polymeric matrix and weighing. Good agreement was found between the results obtained by the two different methods. The experimental error in the fiber content measurements was determined as a function of the difference in the absorption coefficient of the matrix material and the fiber.

INTRODUCTION

The fiber content is one of the most important parameters in establishing the composite's strength and stiffness characteristics.¹⁻³ Due to different effects, like bleeding out of fibers in the case of thermosets, the fiber content cannot be completely controlled by processing. Therefore, it is important to have available nondestructive methods for the determination of the amount of fibers present in the composites.

Up to now the most commonly used techniques for determining the fiber content were density measurement or acid digestion of the polymer matrix.^{4,5} In the present paper we want to present a new method based on X-ray absorption measurement. This method is nondestructive and yields good results provided the difference between the absorption coefficients of the fiber and the matrix is sufficiently large.

PRINCIPLE OF MEASUREMENT

When an X-ray beam passes through a sample of thickness d , the intensity I_0 is decreased by absorption to the intensity I given by

$$I = I_0 \exp(-\mu' d) \quad (1)$$

μ' being the linear absorption coefficient. In many cases, a sample of uniform thickness cannot be obtained: in prepregs for example, the fibers lying close to the surface cause considerable surface roughness. In the case of the fibers, the determination of the correct thickness of a sample obtained by winding up the neat fibers as illustrated in Figure 1 is even more problematic. Therefore, the mass absorption coefficient μ , which refers to the mass per unit area of the sample instead to the thickness d , was used in this work. If M is the mass of the laminate which can easily be determined by weighing and A the area, one can write

$$I = I_0 \exp(-M\mu/A) \quad (2)$$

Obviously, $\mu = \mu' Ad/M = \mu'/\rho$, where ρ is the density.

If a sample S consists of two sheets of different matrices having mass absorption coefficients μ_f and μ_m and masses M_f and M_m each covering the same area A [see Fig. 2(a)], the X-ray beam intensity after absorption is given by

$$I = I_0 \exp\left\{-\left[\frac{M_f + M_m}{A}\right] \times [x_f \mu_f + (1 - x_f) \mu_m]\right\}. \quad (3)$$

* To whom correspondence should be addressed.



Figure 1 Schematic illustration of a sample of neat carbon fibers.

In this case, an average absorption coefficient

$$\mu = x_f \mu_f + (1 - x_f) \mu_m$$

is measured if Eq. (1) is applied for the evaluation of the results. Thus, from μ the mass fraction x_f can be determined by means of the equation

$$x_f = (\mu - \mu_m) / (\mu_f - \mu_m) \quad (4)$$

provided μ_f and μ_m are known.

In a composite, the different phases (fibers and matrix) do not form layers. The actual arrangement is more accurately represented by Figure 2(b). If the X-ray beam follows a path as indicated by the straight line k in Figure 2(b), small volumes of phase 1 and phase 2 will alternately be passed. This is also true for all other lines parallel to k . In the case of all such lines, the total fraction of mass 1 will be given by $M_f / (M_f + M_m)$ and that of mass 2 by $M_m / (M_f + M_m)$. Thus, the system is equivalent to a many layer system as indicated in Figure 2(c) which, concerning the calculation of absorption, again is equivalent to the two layer system in Figure 2(a). Of course, this consideration is only correct if the thickness of the prepreg or laminate is large as compared to the fiber diameter, so that the fibers are randomly arranged.

EXPERIMENTAL

The X-ray absorption of the neat matrix materials, prepreps, and laminates was measured on small plates having lateral dimensions 2 cm \times 3 cm and thicknesses varying between 0.3 and 5 mm. A neat

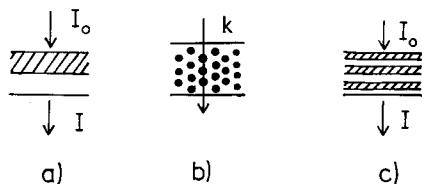


Figure 2 Schematic illustration: (a) a two layer sample; (b) a composite sample; (c) a multilayer sample. (k indicates the path of the beam through the sample)

carbon fiber sample was created by winding the fiber on a frame as indicated in Figure 1.

The X-ray absorption measurements were performed on a goniometer from Siemens (D 500). The wavelength of the X-rays was 1.54 nm (CuK_α radiation). A nickel foil filter and electronic discrimination of the pulse height in the detector were used for monochromatization. The counting rate was about 10,000 counts per second and the counting time was chosen such that approximately 500,000 counts were obtained.

Since the high intensity of the primary beam would damage the detector, the strong 300 reflection from β polypropylene was used for measuring the absorption. A 200 μ thick film of polypropylene (F in Fig. 3) crystallized in the β modification was placed in the sample holder and the scattered intensity I_0 was measured at a scattering angle of $2\theta = 16.9^\circ$, where the 300 reflection appeared. The slit of the detector had the dimensions 12 mm \times 1 mm. Then the sample S (the absorption of which we wanted to determine) was placed in front of the detector and the X-ray intensity was measured again (Fig. 3). This intensity, which will be denoted by I , is smaller than I_0 , because of the absorption by the sample S. The mass absorption coefficient μ of the sample S is then given by

$$\mu = (A/M) \ln(I_0/I). \quad (5)$$

The mass per unit cross surface area was determined by weighing the sample and measuring the dimensions of the surface. The error in the measurement of the absorption coefficient caused by fluctuations in the primary beam intensity as well as by the inaccuracy in the determination of the sample surface dimensions, of the sample weight, and of the scattering X-ray intensity, was estimated to be $\pm 2\%$. In order to increase the accuracy of the experiment, each absorption measurement was performed 16 times and the measured values were averaged. Thus according to the error propagation law, the error in μ was reduced by a factor of $(1/16)^{1/2}$ to $\pm 0.5\%$. In the measurements the location of each sample was

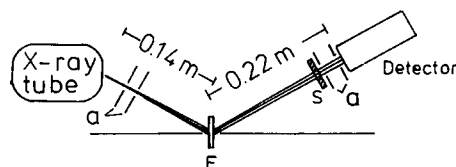


Figure 3 Schematic illustration of the method of the absorption measurement (F indicates the polypropylene foil, a the aperture and S the sample)

Table I Mass Absorption Coefficient μ of Different Materials

Material	Absorption Coefficient [cm ² g ⁻¹]
PET	6.73 ± 0.02
PEEK	5.43 ± 0.02
C-Fiber	5.06 ± 0.04
PET/Prepreg	5.50 ± 0.03
PEEK/Prepreg	5.19 ± 0.03
PEEK/Laminate (±45°)	5.22 ± 0.03

also changed in order to average out local fluctuation of fiber content.

For comparison with the X-ray absorption results, the fiber content in the prepregs and laminates was also determined by matrix digestion and weighing. An approximate 500 mg portion of the composite material was weighed. Afterwards, the matrix was removed by dissolving in concentrated sulfuric acid during 24 h under stirring. After filtration, the remaining carbon fibers were washed three times by fresh concentrated sulfuric acid, then washed by water and finally by methanol before being dried overnight and weighed.

RESULTS

Table I represents the absorption coefficients measured from poly(ethylene terephthalate) (PET) and poly(ether ether ketone) (PEEK), the carbon fibers, and the composites. The values in this table were obtained by averaging of 16 measurements from each sample as described above. While the error in the absorption coefficient of the matrix materials and the composites is ±0.02 and ±0.03 cm²/g, respectively, the error in the absorption coefficient of the carbon fibers as originally measured was much larger, namely 0.09 cm²/g. This could be attributed to the difficulties in obtaining uniform samples due to wrapping of the fibers as shown in Figure 1. A more accurate carbon fiber absorption coefficient value could not be obtained from the literature because, for example, the values listed in the International Tables for X-ray Crystallography⁶ range from 3.83 to 5.56 cm²/g. Therefore in order to obtain a more reliable value, the X-ray absorption of a prepreg with known fiber content was also measured, and the absorption coefficient of the fiber was calculated from the result obtained by this measurement. In this way, the experimental error could be decreased to ±0.03 cm²/g.

Table II Mass Fraction of Carbon Fibers

Sample	By Weight	By X-Ray
PET/Prepreg	77%	73% ± 2%
PEEK/Prepreg	69%	65% ± 10%
PET/Laminate	71%	68% ± 2%
PEEK/Laminate	71%	62% ± 10%

In Table II, the carbon fiber mass fractions calculated from the measured absorption coefficients by means of Eq. (4) are listed and compared to the results obtained by weighing. Good agreement is obtained between the values found by using the different methods. The differences between the two columns in Table II are less than 4% except for the PEEK laminate where a discrepancy of 9% was found. This discrepancy is due to the fact that the difference in the absorption coefficient of PEEK and of the carbon fiber is smaller than that of PET and the carbon fiber.

From this it follows that it is important to calculate the experimental error in the determination of the fiber content x_f by means of the error propagation law. If the errors in x_f , μ_f , μ_m and μ as designated by Δx_f , $\Delta \mu_f$, $\Delta \mu_m$ and $\Delta \mu$, respectively, it follows from Eq. 4.

$$\Delta x_f = \frac{[\Delta \mu^2 + \Delta \mu_m^2 (x_f - 1)^2 + \Delta \mu_f^2 (-x_f)^2]^{1/2}}{|\mu_f - \mu_m|} \quad (6)$$

If, according to Table I, we set $x_f = 0.7$

$$\Delta x_f = \frac{(\Delta \mu^2 + 0.09 \Delta \mu_m^2 + 0.49 \Delta \mu_f^2)^{1/2}}{|\mu_f - \mu_m|} \quad (7)$$

From Table I we find $\Delta \mu = \Delta \mu_f = 0.03$ cm²/g and $\Delta \mu_m = 0.02$ cm²/g, furthermore $|\mu_f - \mu_m| = 1.67$

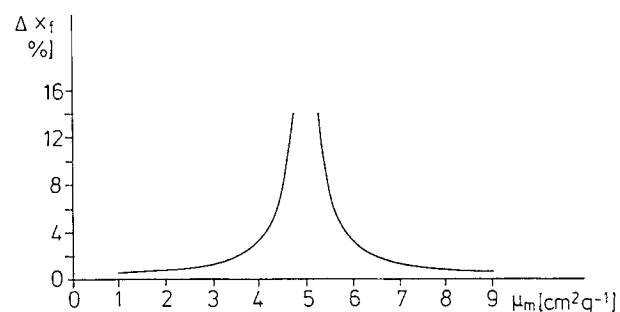


Figure 4 Error in fiber content Δx_f (expressed in % fiber mass) as a function of the mass absorption coefficient of the matrix μ_m . Assumed error in μ_c is 0.5%.

cm^2/g and $0.37 \text{ cm}^2/\text{g}$ for PET and PEEK, respectively. Using these values, the experimental errors shown in Table II were obtained.

Clearly, the experimental error strongly depends on the difference between the absorption coefficient of the matrix material and that of the carbon fiber. If both are the same, the error becomes infinite because the two phases cannot be distinguished anymore. To illustrate this dependence, Δx_f was calculated as a function of μ_m . The result is shown in Figure 4.

In the case of the composites, the discrepancies in the absorption values measured at different locations were considerably larger than in the case of the neat matrix. A variation of about ± 0.10 was found between individual measurements for the composite, while only ± 0.06 was found for the matrix when using the geometrical arrangement and the slit width described in the experimental section. The larger fluctuation in the case of the composite is due to local variations in the fiber content.

DISCUSSION AND CONCLUSIONS

Our results show that X-ray absorption measurements are a suitable technique for the determination of the fiber content in composites. The accuracy of the result depends strongly on the difference in the absorption coefficients between the matrix and the fiber. The experimental error can be kept smaller than 3% if the absorption coefficient is comparatively large as in the case of PET, or even smaller in the case of PPS where $\mu = 60.88 \text{ cm}^2/\text{g}$. The error is larger in the case of PEEK. Measurements on the J1 polymer, a polyamid homopolymer based on bis(paraaminocyclohexyl) methane supplied by DuPont, where $\mu = 4.93 \text{ cm}^2/\text{g}$, seem to be impossible.

A difficult problem in performing the measurements is the determination of the carbon fiber ab-

sorption coefficient. As these coefficients may vary for fibers of different origins, the measurement must be performed on the fiber which is used in the composite. The simple method of preparing a sample by winding the fiber on a frame does not give sufficiently accurate results. A more elaborate technique, like preparing a prepreg with known fiber content, must be applied.

In measuring the absorption coefficient the highest possible accuracy must be achieved by optimizing counting rates and counting times, monitoring the intensity of the primary beam, and by taking the average of several measurements. We believe that by using improved techniques, the error of the experiment can be decreased below the value of 2% achieved in our investigation. As a consequence, matrix materials having absorption coefficients closer to that of the fiber may be included in future investigations.

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