# Estimation of Crystallinity in a Model Thermoplastic Composite

## INTRODUCTION

Thermoplastic resin composites show considerable promise for structural applications. Some of the advantages of such materials compared to current thermoset resin composites are ease of formability, processability, damage repair, and bonding as well as good environmental resistance and re-processing capability.[1-3] For thermoplastic resin matrices capable of some degree of crystallization there is the promise of increased toughness, reduced moisture degradation, and the chemical resistance required for use in aerospace structures.[4] These properties, especially solvent resistance, are thought to be due to and vary with the crystallinity of the semicrystalline resin.

To aid the development of a characterization methodology for future polymers as tough composite matrix materials with at least known and hopefully controlled crystallinity, a model composite system based upon poly(ethylene terephthalate) (PET) has been studied. Since PET, a semicrystalline polyester, is one of the best characterized polymers, use can be made of the many crystallinity studies which have been made in the past[5-10] as an aid in the subsequent analysis. The present report is concerned with a determination of whether or not an estimation of crystallinity may be obtained by study of the wide angle x-ray scattering (WAXS) of PET in the presence of the carbonaceous fibrous reinforcement, with the simulation made reasonable by keeping the resin content and the crystallinity low.

## EXPERIMENTAL

The prepreg of the polyester composite system was fabricated by wrapping 2 mil commercial PET film on a drum and winding continuous carbonaceous filament upon it. The film surface had been treated with hexafluoroisopropanol, which slightly dissolves the PET and tacks the fiber into the resin. Eight 6 × 6 in. sheets of this prepreg were interspersed with eight 6 × 6 in. sheets of the 2 mil PET film. This assembly was wrapped in commercial polyimide film and stacked in a 6 × 6 in. steel mold. This mold was placed in a press, heated to 290°C, and 100 psi pressure was applied for 10 min. The press platens were then cooled rapidly with water and the assembly removed from the press when its temperature was approximately 150°C. Ultrasonic acoustic tests (c-scans) of the (0°)$_8$ panel were fair to good although some poor fiber wetting was evident. This was probably due to the large squeeze out of the PET polymer which resulted in low percent resin (24.5%, w/w, calcd).

In preparation for an isothermal annealing sequence to produce a range of specimens which vary in crystallinity, coupon specimens, cut from the above prepared composite, were heated between aluminum blocks to approximately 290°C in a vacuum oven. When thoroughly melted, these coupons were rapidly quenched in ice water to produce the quenched melt specimens needed for the annealing procedure. X-ray diffraction analysis confirmed that the specimens were amorphous. Amorphous coupons of PET resin were also prepared and were paired with composite coupons for the purpose of obtaining diffraction patterns of the resin, unobscured by the presence of the carbonaceous reinforcement. Pairs of composite and resin coupons were annealed for 72 h at 97, 105, 111, 119, and 128°C to produce a range of low crystallinities (≤ 25%). These temperatures are much lower than those required to produce high levels of crystalline order, the maximum crystallinity being produced in the temperature range 225–245°C.[5-7] The effects of the annealings were monitored by X-ray diffraction, using an automated powder diffractometer (APD) equipped with a copper X-ray tube and a graphite monochromator for most of the analysis. Some data were taken with a separate manual diffractometer, similarly equipped.

## RESULTS AND DISCUSSION

The relative intensities versus diffraction angle for PET coupons annealed for 72 h at temperatures from 97 to 128°C are compared with an unannealed, and thus amorphous, coupon in Figure 1. An increase in detail with increase in annealing temperature, implying an increase in crystalline order, is observed in this figure. A similar comparison for the PET/carbonaceous reinforcement composites, presented in Figure 2, does not present a clear trend although increasing complexity does appear to be developing in the 16–18° ($2\theta$) interval. These diffractograms were taken with the APD operated at 45 kV and 40 ma, using 1 s counting at every 0.01° over the $2\theta$ range.

Comparison of the diffractogram of the most crystalline specimen in Figure 1, the 128°C coupon, with that of a sample of the carbonaceous reinforcement is shown in Figure 3. The broad carbonaceous diffraction peak, centered around 26 ° ($2\theta$) is seen to be in the position to obscure the dominant PET reflections (as shown in Fig. 2) and thus make impossible a crystallinity determination scheme based upon an index[11] or absolute[12,13] procedure. The uncombined carbonaceous reinforcement diffractogram, however, is relatively flat in the region of the (010) and (0$\bar{1}$1) reflections which are reported[14] to occur at 17.65° (5.05 Å) and 16.10° (5.51 Å), respectively.

There have been observations of the orderly change of crystallinity,[5,7,15] the orderly change of certain $d$-spacings,[15] and the stepwise change in crystalline perfection (as demonstrated by development of additional crystallographic reflections[5,16]) with isothermal annealing of amorphous PET. The goal of the present research and, indeed, the choice of the matrix material was, in part, based upon utilizing past crystallinity studies to obtain an estimate of crystallinity from partial data, that is, WAXS information, partially obscured by the presence of the carbonaceous fiber. Unfortunately, the WAXS information which varies in an orderly manner, like crystallinity, and which could thus be correlated to crystallinity was unattainable from the composite. What was attainable, the presence of (010) and (0$\bar{1}$1) reflections, can, however, be correlated with crystallinity through their mutual change with temperature only in a discontinuous fashion, producing an estimate of crystallinity range.

One study reports[5] the development of ($hk0$) reflections, indicative of two-dimensional order around the polymer chains,[16] with the annealing of PET at temperatures varying from 90 to 140°C. This annealing temperature range is above the glass transition temperature of PET. It is only with the annealing at 160°C and above that reflections involving the $l$-index became apparent, indicating development of order along the chain direction. Thus, both (010) and
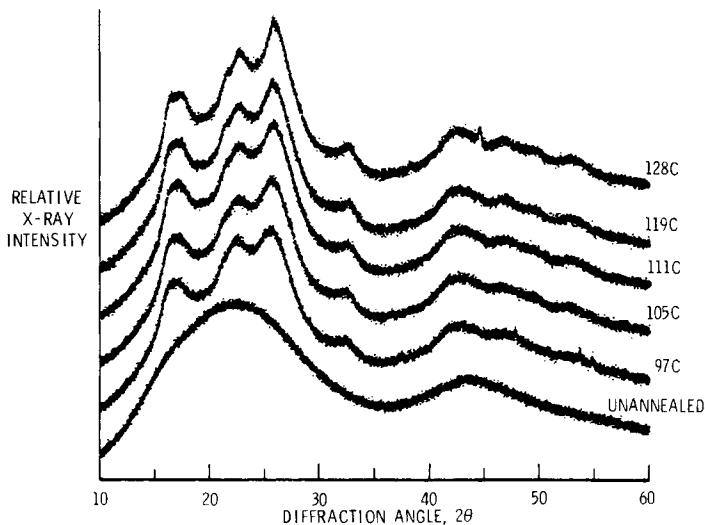


Fig. 1.   Relative X-ray intensity vs. diffraction angle for neat resin coupons annealed for 72 h at various temperatures.
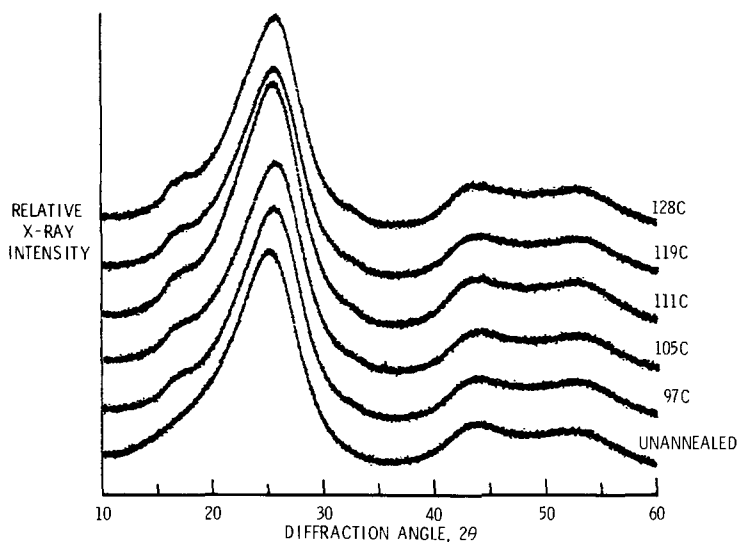
Fig. 2.    Relative X-ray intensity vs. diffraction angle for PET/carbonaceous reinforcement composite coupons annealed for 72 h at various temperatures.

(0Ī1) reflections should be present for higher crystallinity specimens while only the (010) reflection is to be expected for the low crystallinity specimens of this study.

The interplanar spacings of the specimens of Figures 1 and 2 were determined by a peak search routine[17] on the APD data file which have been accumulated for these specimens on hard disk. This routine utilizes a second derivative algorithm to locate the peaks. The interplanar spacings of the peaks found in the angular range 16–18° (2θ) for neat resin and composite specimens are compared on Figure 4. Also, shown on this figure, as a stippled bar varying with temperature, are the previously reported (010) and (0Ī1) reflections along with their low temperature protoreflection.[5] For those specimens (both neat and composite) annealed below 119°C one reflection is found. This reflection is in the range 5.3–5.4 Å and in keeping with the previously reported protoreflection.[5] However, the data for the temperature range 119–128°C seems to show development of a true (010) reflection at a lower temperature than reported earlier. The attainment of 3-dimensional order for the neat resin coupon is suggested for the 128°C annealing.
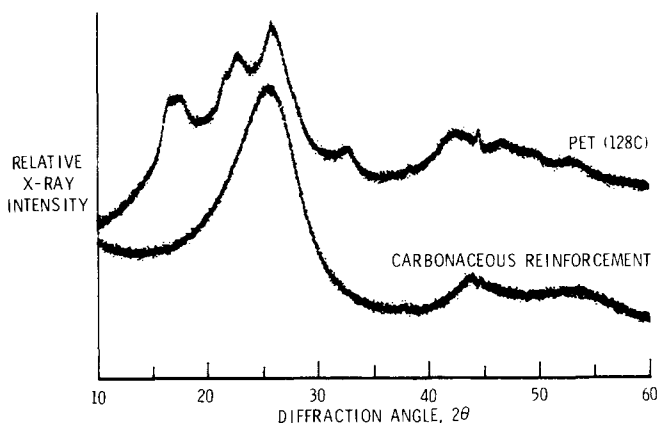


Fig. 3.    Relative X-ray intensity vs. diffraction angle for crystalline PET and carbonaceous reinforcement.
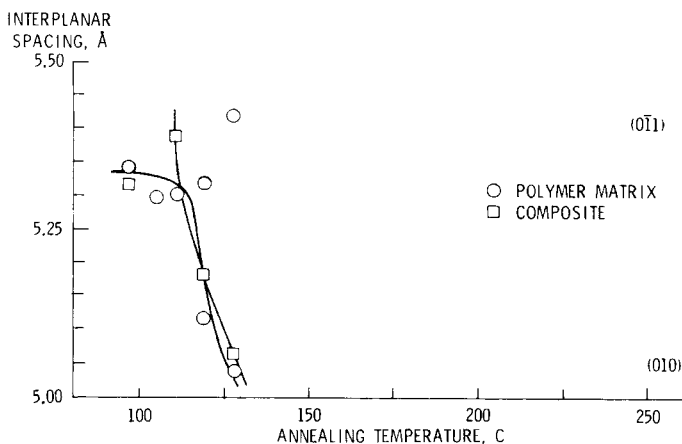
Fig. 4.   Comparison of interplanar spacings measured as a function of temperature for PET matrix resin and composite specimens.

The suggestion of 3-dimensional order for the 128°C coupons was tested by acquiring 100-s counts every 0.1° in the range $2\theta = 14$–$20°$, with a manual diffractometer. Two peaks were resolved from each data set by a multipoint fit to a system of nonlinear equations, solved in the least-squares sense utilizing Levenberg–Marquardt and Gauss algorithms.[18] In this resolution, which separates the crystalline scatter from the background, the peaks were described by a linear combination of Gaussian and Cauchy functions.[19] Interplanar spacings, corresponding to those reflections designated as (010) and (0$\bar{1}$1), respectively, were extracted by this procedure for the polymer matrix, 5.12 and 5.44 Å, and for the composite coupon, 5.06 and 5.39 Å. The peak search routine produced 5.04 and 5.42 Å for the polymer matrix and 5.06 for the composite.

The crystallinities associated with 72 h annealings of PET film have been reported elsewhere.[7] The values of the integral index (based upon the most crystalline available specimen being designated 100%) were reported for temperatures of 80, 100, 120, and 150°C to be, respectively, 7.7, 36.5, 41.6, and 60.9%. Maximum crystallinity for PET, based upon absolute methods,[12,13] as opposed to the index procedure,[11] have been reported to be as high as 63 [10] or 66 [9] or as low as 34–44%.[8] If an intermediate value of 49 [5] is taken as maximum and the integral index values redefined upon this basis, values of percentage crystallinity interpolated for the temperatures 97, 105, 111, 119, and 128°C would be, respectively, 16, 19, 19, 20, and 23%.

Measurement of the interplanar spacings in the angular range $2\theta = 16$–$18°$, using WAXS, for PET/carbonaceous reinforcement composite yields the following crystallinity estimation by comparison of the WAXS reflections attainable with crystallinity estimates appropriate[7] for the annealing conditions:

| WAXS Reflections | Crystallinity |
|---|---|
| No peaks | < 16 |
| 1 peak ($d = 5.1$–$5.4$ Å) | ~ 20 |
| 2 peaks | ≥ 23 |

## CONCLUDING REMARKS

Estimations of crystallinity have been made on PET/carbonaceous filament composite with resin content of about 25% w/w. This is much less than the resin content of what would constitute a structural composite laminate and represents a severe test of an analytical scheme. Crystallinities as low as 16% have been estimated by determination of the interplanar spacings of PET with WAXS in the angular range, $2\theta = 16$–$18°$, with the diffraction pattern of the carbonaceous reinforcement dominating to the extent of masking the major reflections of the resin. In general, neat resin and composite yield the same reflections in the angular range

and thus similar estimates of crystallinity, suggesting nonparticipation of the fiber in the attainable level of crystalline order for long term annealings and that measurements may be made on the composite alone rather than requiring extraneous neat resin coupons or samples of flash.

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