

REFINED DETERMINATION OF DSC-MEASURED CRYSTALLINITY FOR THERMOPLASTIC COMPOSITE MATERIALS

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Abstract

Differential scanning calorimetry (DSC) is a widely used method for determining the degree of crystallinity of semi-crystalline thermoplastic matrix materials, which is often used as an indicator of part performance. However, the calculation of crystallinity using this method is vulnerable to errors at several stages in the process, including assumptions and oversights when receiving reference values from material manufacturers. In this study, the sensitivity of the calculated degree of crystallinity to the assumed fiber volume fraction is investigated, with manufacturer-provided data compared with in-house measurements. Results show that for the reference CF/LM-PAEK material, the nominal fiber volume fraction of 60% (as reported in the material datasheet) can in fact range from 42.79% to 59.74%, as determined through digital microscopy. Using the fixed nominal value for all measured samples resulted in a relatively high (overestimated) degree of crystallinity ($30.01\% \pm 4.24$), while using measured values for the fiber volume fraction yielded a substantially lower value; $24.76\% \pm 3.50$. A significant improvement in the standard deviation was also observed when the fiber volume fraction is measured rather than assumed, a strong indicator that this approach yields a net improvement for more accurate reporting of the degree of crystallinity.

1. Introduction

The characterization of composite components and thus their performance in or suitability to a particular application is typically assessed using primary and secondary indicators. Primary indicators can be viewed as driven by the specific application. This may include mechanical performance under a particular type of loading (tensile, compressive, shear, etc.) or a resistance to chemical corrosion or gas leakage (permeation) in the context of fluid containers/ vessels for storage. Secondary indicators, on the other hand, are used to explain the observed values of primary indicators. These may include, but are not limited to, the fiber volume fraction, ply thickness, or porosity of a test piece. When considering composite parts manufactured using semi-crystalline thermoplastic matrix materials, the degree of crystallinity is one of the most commonly referenced secondary indicators.

A sample study of 17 peer-reviewed publications showed that almost two thirds (65%) of investigations supported their primary indicator findings with either direct measurements of crystallinity [1 – 9] or references to the range of expected crystallinity in the material [10, 11]. The remaining studies presented findings with other, typically qualitative, secondary indicators [9, 12 – 16]. Of the studies where crystallinity was measured directly, 22% of studies utilized Wide-Angle X-ray Scattering (WAXS) while 89%¹ utilized Differential Scanning Calorimetry (DSC). This value serves to underscore DSC as

¹ One of the observed studies performed both WAXS and DSC measurements, hence the value of 89% rather than the otherwise expected 78%.

a widespread analytical tool. It should be noted that the authors of this work did not include their own publications, in which DSC measurements feature heavily, so as not to bias the observed trends.

DSC enables the calculation of crystallinity, among other thermal characteristics, of thermoplastic composite parts through recordings of the sample enthalpy in response to different temperatures, as will be explained in more detail in the methodology of this work. Suffice it to say here that the popularity of DSC facilities in universities and research institutes can be attributed to the simplistic operation principle, allowing widespread reporting of crystallinity values as previously discussed. However, in contrast to other indicators, particularly primaries such as mechanical failure tests, the interpretation and calculation of crystallinity through DSC is extremely subjective oftentimes poorly documented in literature. Of the aforementioned studies, only one third disclosed the formula used to determine the crystallinity [3, 7, 17]. Given that there are different interpretations of crystallinity, specifically the mass fraction or volume fraction crystallinity [18, 19], this oversight can severely inhibit the comparability of independent studies. Furthermore, even when utilizing the same formulae, assumptions in the input values, particularly those obtained by interpreting the DSC-determined heat flow, can lead to significant deviations in the reported crystallinity.

This work presents a systematic summary of the process used to derive crystallinity values from DSC measurements for semi-crystalline thermoplastic composites. In doing so, the sources of potential errors or oversights are clearly identified, assisting current and future researchers to improve the comparability of their work. Furthermore, the authors will show that investing time to obtain more accurate information on what are currently assumed to be constant values can significantly improve the accuracy of DSC measurements within a given study.

2. Materials and methods

2.1. Fiber-reinforced thermoplastic material

Various carbon fiber-reinforced thermoplastic prepreg tapes were investigated as part of this study. Low-melt polyaryl ether ketone (LM-PAEK) forms the matrix here. The fiber volume fraction of the different tapes varied between 52.28 and 60 vol% and the fiber areal weight between 65.35 and 194 g/m². Also the fiber types and manufacture differed for the tapes. The specific results presented in the results section of this paper are based on a CF/LM-PAEK prepreg tape with a nominal fiber mass fraction of 60%. A typical range of the degree of crystallinity for CF/LM-PAEK is between 20% and 30% [20, 21].

2.2. Characterisation methods

2.2.1. Differential scanning calorimetry

DSC measurements were carried out with a NETZSCH DSC 214 *Polyma* device to analyse the crystallinity of the respective specimens. Circular samples (\varnothing 4 mm and 2.45 mg \pm 0.15) were punched out of the respective tape material and placed in aluminium crucibles. The crucible was sealed with a slide-in lid, with a small hole in the lid allowing gases to escape. In a furnace, integrated into the device, a material sample was exposed to a defined temperature change programme (Figure 1) alongside a reference (empty crucible). Nitrogen was used as purge (40 mL/min) and protective gas (60 mL/min). Temperature sensors were used to record the difference in heat flow between the sample and the reference, which occurs due to transformation, melting and crystallisation processes in the sample.

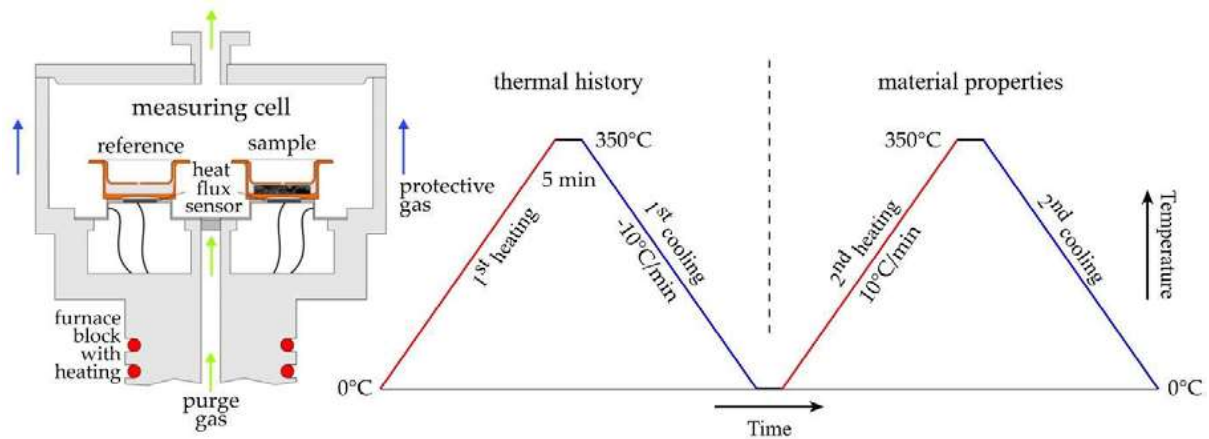


Figure 1. Principle sketch of a DSC measuring cell (left), adapted from [22], and temperature program cycle (right).

The measured heat flow data was imported into the NETZSCH Proteus® Software for evaluation. Figure 3 displays exemplarily the four heat flow curves over temperature corresponding to the dynamic sections of the temperature program for one specimen.

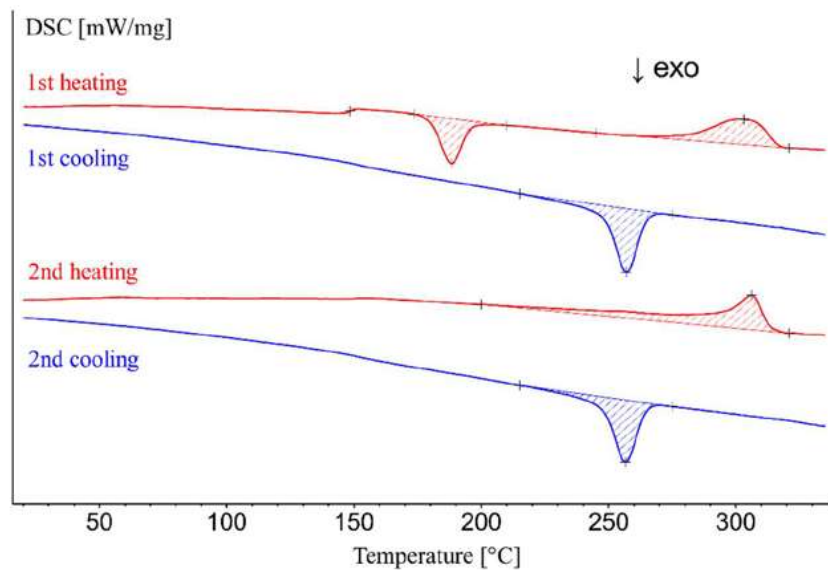


Figure 3. Exemplarily DSC heat flow curves with peak area evaluation.

There are two main topics to be defined influencing the evaluation of the enthalpies: the baseline type and the evaluation borders. Different baseline types are used in the literature, including *spline*, *sigmoidal* and *linear* among others, with measurement standards providing recommendations based on the material behaviour [23]. However, examples of all three are often found for the same material in literature, causing a degree of uncertainty when comparing results. The selection of the boundaries also differs in terms of the temperature range selected.

In internal communications with NETZSCH a linear baseline, extrapolating the baseline from the right (melted area), was suggested for this material type and the borders have been chosen respectively.

The heat flow response is specimen specific and therefore it is important to account for these specific sample properties like for example the fiber volume fraction.

2.2.2. Microscopy

DSC tape samples were analysed as micrographs. After DSC analysis, the crucible lid was carefully removed and the samples were mounted vertically with the fiber orientation perpendicular to the micrograph plane in clear epoxy resin, allowing investigation of the adhesion to the crucible ground. The specimens were then ground with 500 grit SiC paper until the micrograph plane reached the sample centre, followed by a three-step polishing process with 9, 3 and 0.25 μm diamond suspension. The polished specimens were analysed with a Keyence VHX-5000 digital microscope in the bright field at 500x magnification.

A custom python tool was used to assess the local fiber volume fraction for each sample. The image was cropped manually to exclude mounting material and correct warped areas. A binary image (Figure 4) was created using Otsu's threshold and subsequent median filtering from the OpenCV toolbox. Porosity was detected with a custom Max Entropy filter.

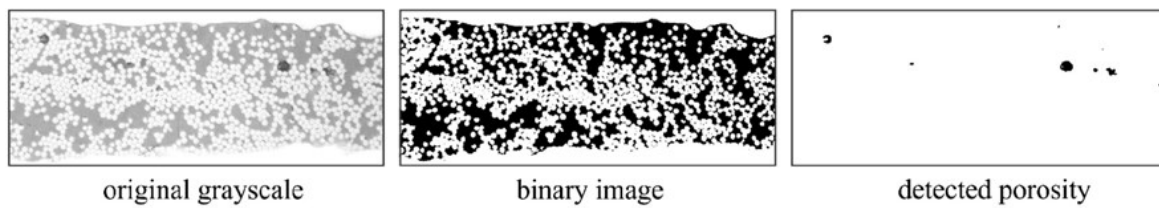


Figure 4. Image processing of micrographs with custom python tool.

The local fiber volume fraction $v_{f,l}$ was then calculated as the total fraction of white pixels corresponding to the fibers and exclusion of the porosity volume.

Additional to the DSC-specimen-related local value, the overall tape mean value $v_{f,m}$ was determined from unprocessed tape samples. Therefore, five image sections from five tape samples were analysed using a similar process.

2.2.3. Crystallinity Calculation

For the crystallinity calculation according to Eq. 1 [24] the fiber volume fraction determined from the microscopic analysis needed to be converted into the fiber mass fraction using Eq. 2

$$X_c = \frac{|\Delta h_m| - |\Delta h_c|}{\Delta h_{ref}(1 - w_f)} * 100 [\%] \quad (1)$$

$$w_f = \frac{v_f * \rho_f}{v_f * \rho_f + (1 - v_f) * \rho_m} \quad (2)$$

with the density of fiber and matrix, $\rho_f = 1.78 \text{ g/cm}^3$ and $\rho_m = 1.3 \text{ g/cm}^3$, respectively (supplied by manufacturer). The calculated degree of crystallinity is in this study the mass-specific degree of crystallinity and does not take into account the differentiation between the density of crystalline and amorphous phase.

Three different values for the fiber mass fraction w_f were considered for the calculation of the degree of crystallinity. Firstly, the nominal fiber mass fraction from the data sheet $w_{f,n}$ was used. Then the tape mean value $w_{f,m}$ of the unprocessed tape samples was selected. Thirdly, the corresponding fiber volume fraction $w_{f,l}$ was used to calculate the degree of crystallinity for each individual DSC sample.

3. Results

Figure 5 displays the distribution of the mass, the local fiber mass fraction and the melting enthalpy of the 18 DSC samples, normalized with the standard deviation and the mean value.

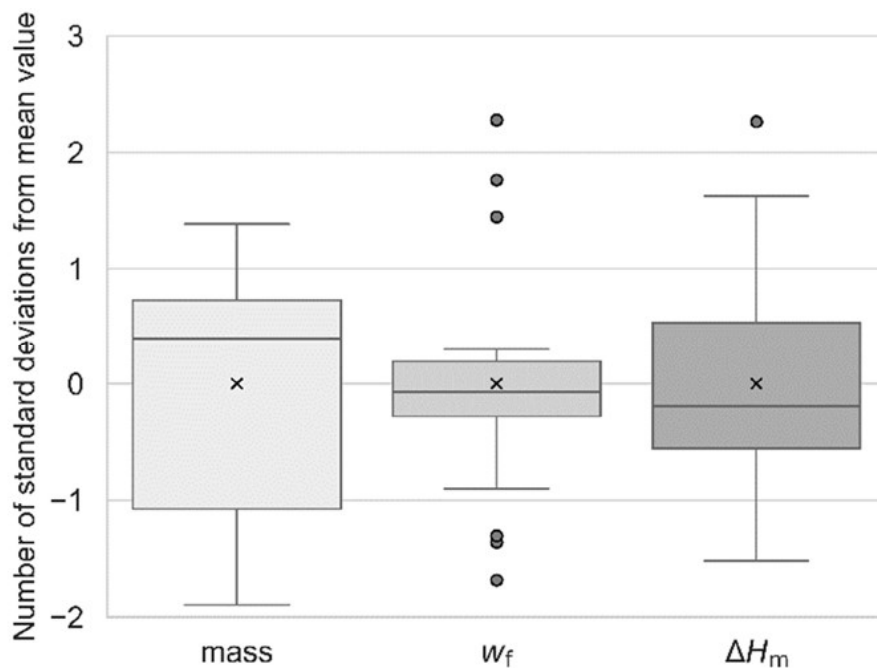


Figure 5. Normalized distribution of sample mass, specimen specific fiber mass fraction and melting enthalpy.

The fiber volume fractions and the corresponding fiber mass fractions are presented in Table 1 together with the calculated degrees of crystallinity X_c following Eq. 1, respectively.

Table 1. Fiber volume and mass fractions and calculated degrees of crystallinity.

		nominal	tape mean	local
Fiber volume fraction v_f	[%]	52.28	43.69	35.33 – 52.01
Fiber mass fraction w_f	[%]	60	51.51	42.79 – 59.74
Degree of crystallinity X_c	[%]	30.01 ± 4.24	24.76 ± 3.50	23.47 ± 3.45

The measured fiber volume fractions (by means of micrograph image processing) are (significantly) lower compared to the nominal value of the material data sheet. This deviation influences the calculated

degrees of crystallinity which are additionally plotted in Figure 6. The median value of the degree of crystallinity decreases with reduced values of the fiber mass fraction. Furthermore the standard deviation reduces for the X_c values calculated with the measured fiber mass fractions.

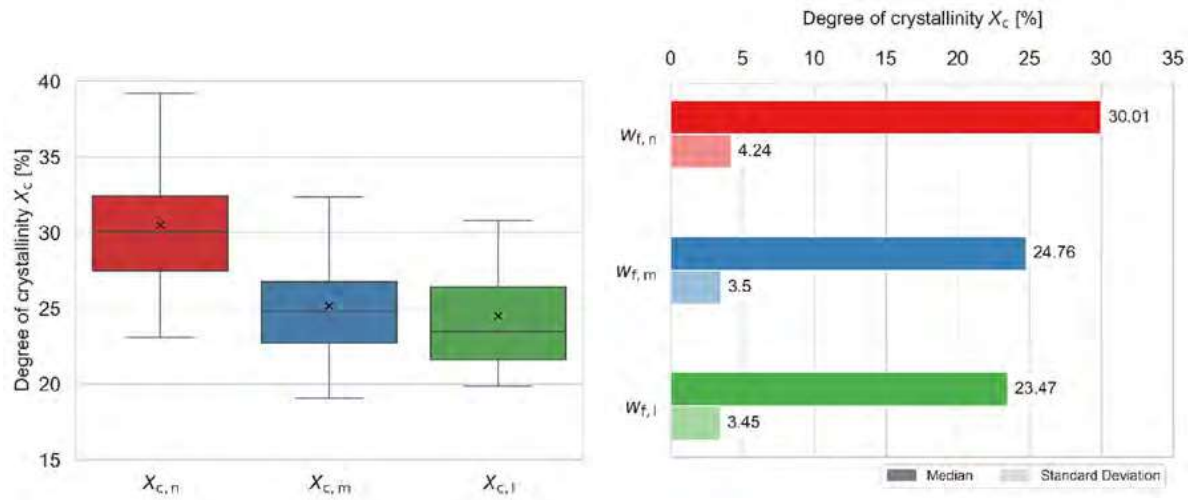


Figure 6. Calculated degrees of crystallinity in dependence on the fiber mass fraction.

Furthermore, the microscopic images of the DSC-samples give some interesting insights. Figure 7 displays four DSC-specimens on the aluminium crucible bottom, after the DSC measurement (left). The cross-section does not show full-surface contact of the tape specimens with the crucible. The larger section on the right reveals local matrix flow where the specimen was in contact to the heated aluminium crucible lid and bottom. The fibers do not show any signs of local displacements.

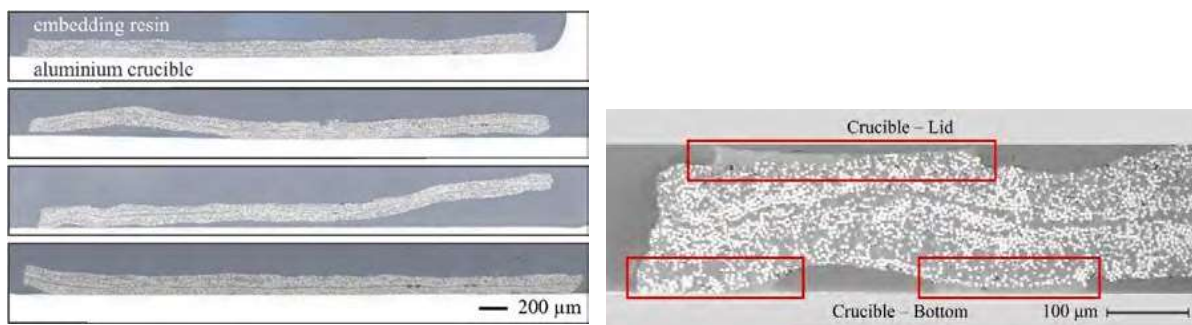


Figure 7. Microsection of four DSC-specimens (left) and of one edge of a DSC-specimen (right) after measurement.

4. Discussion

The degree of crystallinity is overestimated if the nominal fiber mass fraction (data sheet value) is used for the calculation. More realistic degree of crystallinity values in the range of 20 – 30% are achieved for measured tape mean and local w_f values. Also the standard deviation reduces. The very high effort to investigate every DSC sample after measurement via microscopy with regard to the local $w_{f,l}$ is not necessary. The determination of the tape mean value $w_{f,m}$ is a good choice with reasonable effort resulting in realistic X_c values.

The microsections of DSC samples show no full-surface contact between the specimen and the crucible. It is not yet clarified how this influences the heat flow and if the contact can be improved.

5. Conclusion and Outlook

By taking a closer look at the fiber volume fraction using microscopy examinations, it was possible to improve the calculation of the degree of crystallinity. It is recommended to determine the fiber mass fraction tape mean value and use it instead of the nominal data sheet value for the calculation of the degree of crystallinity.

There are still many sources of uncertainties in crystallinity determination which have not yet been explored. The in-depth investigation of the tolerance chain around DSC measurements and evaluations needs to be continued to improve the determination of a reliable value for the degree of crystallinity. In ongoing studies the influence of the nominal and tape mean fiber volume fraction will be investigated for different prepreg tapes. Also the different fiber areal weights will be subject to further investigations.

Acknowledgments

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