# CRYOMILLING: A CRITICAL STEP FOR ACCURATE DETERMINATION OF DEGREE OF CURE AND RESIN CONTENT IN CARBON FIBRE REINFORCED THERMOSETTING COMPOSITES

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## Abstract

A new specimen preparation method is proposed for thermal analysis to characterise the cure kinetic of thermosetting fibre-reinforced polymers (FRPs). For instance, differential scanning calorimetry (DSC) measurements according to commonly used international standards leads to coefficient of variation up to 23% in enthalpy of reaction and a deviation from the nominal resin content of up to 17% for inhomogeneous materials such as NCF and woven pre-impregnated (prepreg) composites. To address this issue and decrease the coefficient of variation, prepreg fabrics were cryogenically milled to develop a homogeneous powder without altering the chemical reaction in the matrix. The quantitative results showed cryogenic milling decreased the coefficient of variation in enthalpy of reaction to as low as 0.2% and deviation from the nominal resin content of 0.5%.

## Introduction

Due to new environmental challenges, novel materials such as carbon fibre reinforced plastic (CFRP) composites are replacing their metallic counterparts in the transportation industry. Most problems in manufactured CFRP composite parts are related to ineffective optimisation of the curing process. To improve the quality of the CFRP parts, it is essential to precisely control and evaluate the cure process[1].

DSC is one of the most versatile methods that is widely used to monitor the curing of thermosets. The main challenge in evaluating the CFRP cure kinetics or degree of cure is that only the resin contributes to the total heat of reaction, while the carbon fibre generates no chemical reaction and only manipulates the effective weight of the specimen. The degree of cure that is directly influenced by the measured heat flow will be inaccurate for the normalised DSC specimen and more likely will be overestimated. This is not the only adverse effect of the fibres in the DSC specimens. The best specimens for DSC measurement are in a powder form that allows homogeneous contact at the bottom of the pan, and therefore the DSC sensor. The above mentioned variations results in up to ±20% error in the total heat measured per normalised weight specimen. Not only do these variations affect the evaluation of the degree of cure of the final product, but also makes the thermokinetic analysis of such materials impossible (considering the fact that the neat resin is not provided by the manufacturers of prepreg in most cases). For the composite manufacturer to optimise the cure time, an accurate total heat flow of the uncured prepreg is required as a reference to avoid premature moulding or under-cured product. Traditionally for Thermokinetic analysis, DSC specimens are prepared according to ASTM or ISO standards such as ISO 11357 for 5 heating rates and modelled with either ASTM standards or free model system. In this study it has been shown that cryomilling is an excellent pre-step that can be used in the analysis of cure kinetics [2]. Cryomilling is a common technique used in multiple industries where the homogenising of materials is crucial but the chemical characteristics of the materials must stay intact such as nanocomposite and thermoplastics processing [3, 4].

## Experimental procedure

Thermal analysis of epoxy based prepreg CFRP was performed on samples of ~10 mg in sealed aluminium pans with a Mettler Toledo HP-DSC-1 differential scanning calorimetry (DSC) over a temperature range of 30 to 230 °C at a 10 °C/min heating rate under a nitrogen flow. Specimens were prepared both with cryogenic milling and conventional method that is cutting the samples with a scalpel. Both sets were characterised using DSC, DSC/TGA, FTIR, optical and scanning electron microscopy (SEM) to investigate the effect of Cryomilling on the crosslinking and microstructure of prepreg CFRP composites.

### *Materials*

The family of the thermosetting CFRPs studied in this work are commercially available epoxy based prepreg materials. Materials were purchased commercially from various suppliers such as Cytec and Mitsubishi in a prepreg form. They were stored at -20 °C in a freezer and were tested within their expiry date. They are named in this work based on their architecture and nominal carbon fibre content as NCF-50 (EF7312), Woven-40 (368) and unidirectional-30 (368).

*Results and discussion*

Non-isothermal DSC was used to measure the total enthalpy of reaction for the uncured prepreg composites. The total enthalpy of reaction can be calculated by integrating the heat flow as a function of time over the complete exothermic reaction. The resin content can then be calculated from the total heat released in DSC data such that:

$$C_r = \frac{H_c}{H_T}\, x\, 100$$

where $C_r$ is the resin content ranging from 0 (no resin) to 100 (only resin). $H_c$ is the total enthalpy of the reaction for the prepreg composite and $H_T$ corresponds to the total enthalpy of the reaction for the neat resin.

## Results and discussion

The dynamic DSC curves for the epoxy based prepreg with a woven structure were examined for 3 hand-cut, 3cryomilled and neat (extracted from the side of the prepreg rolls) resins and shown in Figure 1. The hand cut and cryomilled traces are comparable to each other with enhanced reproducibility observed with the cryomilled samples.  Similar results were observed with the other two types of prepregs.

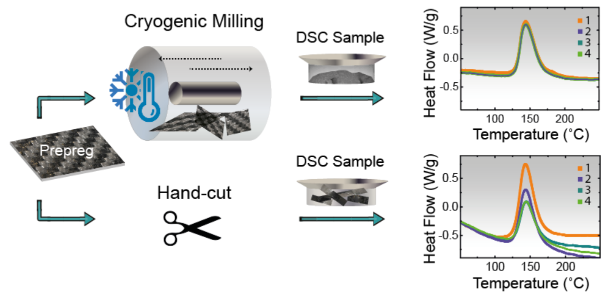


***Figure 1:*** *Schematic illustration of cryomilling process vs hand cut and DSC cure behaviour of woven prepreg.*

From the results shown in Table 1, it is clear that cryogenic milling generates a resin content closer to the nominal value when compared to the conventional hand-cut DSC samples. This is consistent across each of the prepregs. Higher variations can be seen in the prepregs with higher resin content. The highest deviation was measured to be 11.4 % for the biaxial Non-Crimp Fabric (NCF). The standard deviation for all prepreg materials were reported to be below 1% indicative of a highly reproducible process. This can be explained by knowing that the best samples for thermal analysis measurements are in either a liquid or powder form to allow maximum contact for heat transfer during the non-isothermal or isothermal measurements.

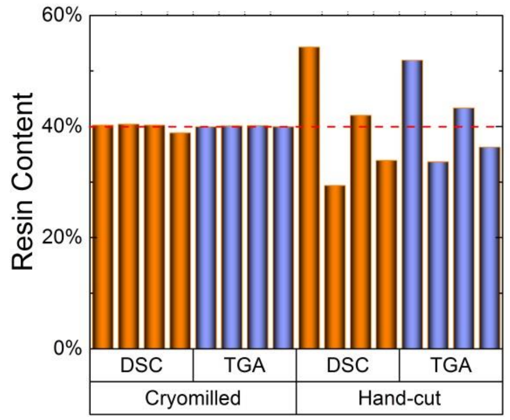


***Figure 2:*** *Resin content measured by DSC and TGA from cryomilling vs hand-cut for woven 40 % prepreg.*

To confirm that the variation in the total enthalpy of the curing is not due to the pre-curing during the handling of the prepreg materials, simultaneous TGA/DSC was performed (Figure 2) and the respective resin contents calculated (Table 1).

| Materials | Measured Resin Content (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cryomilled | | | | | Hand-cut | | | |
| | DSC | SD | TGA | SD | | DSC | SD | TGA | SD |
| 40 % Woven | 40.8 | 0.9 | 40.1 | 0.1 | | 39.9 | 10.9 | 41.3 | 8.2 |

***Table 1:*** *Resin content by combined TGA/DSC measurements for the cryomilled vs the hand-cut samples.*

He et al. has reported that difference in obtained fibre content from TGA analysis is about 1-3 wt % higher than those measured from the processing statistical (PS) method. Furthermore, PS and carbonization in nitrogen (CIN) [5] methods do not show repeatability better than 4.7 wt % [6]. However, these reported values are for cured prepreg materials only. It can be expected that an uncured prepreg has more deviation in the resin content than the cured part because when the resin is at its minimum viscosity it will fill any resin poor areas. Lower standard deviations obtained for the TGA analysis of precured cryomilled samples are achieved when compared to these previously reported values highlighting the enhanced accuracy of the cryomilled method [2]. For thermosetting resins, there is no possibility to use the DSC method for measuring carbon content but again using cryomilling to produce a homogeneous powder ensures reliable dispersion of the fibre for the cured specimen and also improved contact between the DSC sensor and the aluminium.

Table 1 shows that the standard deviation decreased by 100 times for the TGA method. The lower reproducibility of DSC could be due to the less sensitive DSC sensor used in the hybrid equipment and the use of Alumina crucibles.

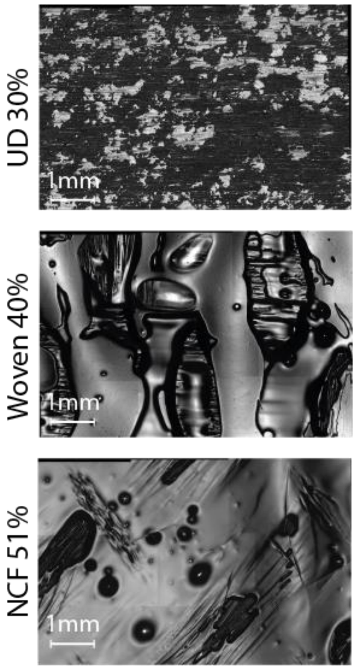


***Figure 3:*** *Optical micrographs of 3 different prepreg systems 5x stitched-images of the prepreg systems.*

To understand the homogenising effect of Cryomilling better, optical microscopy was employed and the optical micrographs are shown in Figure 3. The brighter patches are representative of resin rich areas. It is clear that the UD has a more homogenous structure when compared with the other two prepregs in line with the lower standard deviation shown in Figure 4. The resin poor areas might have been created where the tows are crossing due to differences in height.

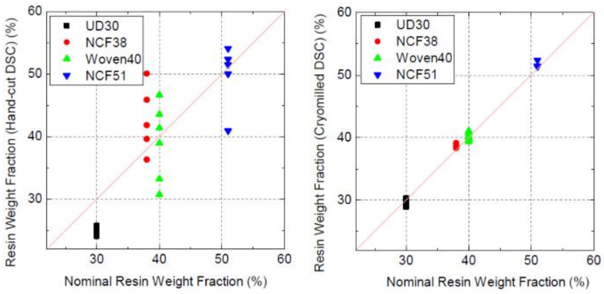


***Figure 4:*** *Four different CFRP uncured prepregs were measured by conventional and cryomilled methods.*

Nominal resin content with the resin content measured by stand-alone DSC is shown in Figure 4 using the conventional Hand-cut preparation method versus the Cryomilling preparation method for four different CFRP uncured prepregs. The faint red line specifies the perfect match.

## Conclusion

By using simultaneous DSC-TGA analysis one can get the accurate degree of cure for each part that is essential for manufacturing. In addition, in the extreme case where it might be impossible to gain such information on the neat resin, this method can be used to reverse engineer the total heat if the fibre-volume is known.

## References

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