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Introducing Cryomilling for Reliable Determination of Resin Content and Degree of Cure in Structural Carbon Fibre Reinforced Thermoset Composites

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Abstract

A novel material preparation method is presented that facilitates accurate measurement of the degree of cure and resin content within carbon fibre reinforced polymer composites (CFRPs). When using conventional specimen preparation for standard thermal analysis, it is demonstrated that the experimentally-obtained enthalpy of reaction and resin content varies significantly between analyses. Measurement uncertainties arise because small specimen volumes are extracted from materials that exhibit both macroscopic inhomogeneity and physical discontinuities. To address this issue, representative sample volumes of aligned CFRPs were first cryogenically milled to develop a homogeneous powder before smaller specimens were extracted. The variation in obtained enthalpy of reaction between analyses was reduced from 23% (for conventional specimen extraction) to 1% following cryomilling. The accuracy in measurement of degree of cure for the compression moulding parts was improved 7 times. Further, subsequent FTIR analysis proved that cryomilling did not affect the final chemical structure of the cured material.

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Keywords

A. Carbon fibre, A. Thermosetting resin, D. Thermal Analysis, E. Powder processing

1 Introduction

Aligned carbon fibre reinforced polymer (CFRP) prepreg systems are currently being investigated for use in high volume light weight automotive structural applications due to their excellent mass normalised mechanical performance [1, 2]. The latest generation of CFRPs are ideally suited to high volume manufacturing within the transport industry, supporting short cycle times, through low viscosity/rapid curing polymer matrices, and possessing high mass-specific strength, stiffness, and durability [3, 4]. Whilst the aligned carbon fibre reinforcement phase plays a crucial role in structural performance [5, 6], material processability and quality of the final part are strongly linked to the thermo-chemical properties of the matrix [7, 8]. For CFRPs to achieve widespread adoption within high production volume environments such as the automotive industry it is essential to be able to evaluate the quality of the material reliably, simply and rapidly, both for design purposes and to optimise manufacturing parameters [9]. Serious defects in manufactured CFRP composite parts can be related to ineffective optimisation of the curing process therefore to ensure the quality of CFRP parts, it is essential to precisely evaluate and control the cure process. In the case of thermosetting CFRPs this is achieved by fully understanding the complex reactions (cure state) that occur; taking into account the low thermal conductivity of the resin and also the highly exothermic nature of the process [10].

Epoxy resins are part of the family of thermosetting polymers with 3D networks. They are made by chemical reaction or curing between monomers and show excellent chemical and thermal resistance [11, 12]. The chemical reaction that leads to the formation of the 3D polymer network is one of the key characteristics of these systems

[13]. Differential scanning calorimetry (DSC) is commonly used to monitor the curing of thermosets [14] and can be utilised in the evaluation of resin cure kinetics or to quantify degree of cure within an already formulated prepreg material system. The presence of an indeterminate fibre fraction within the specimen under investigation is a source of error in that the mass of the matrix is not precisely known (only assumed). This can lead to errors in the determination of the heat of reaction. The resin/fibre fractions obtained from as-received prepreg are generally indeterminate by DSC because the prepreg material system exhibits inhomogeneity on a macroscopic scale and a typical DSC specimen is of the order of 5-10 mg. Evaluating the degree of cure by measured heat flow is therefore inaccurate as only the resin fraction contributes to the total heat of reaction; the carbon fibre is unreactive and only contributes to the mass of the specimen.

This is potentially not the only adverse effect of the fibres present in DSC specimens on the accurate evaluation of cure kinetics. Thermal properties of thermosetting CFRP composites depend on the volume and architecture of constituent materials. For example it has been shown that heat capacity, thermal conductivity and diffusivity appear to be influenced by the fibre volume fraction and filament count in the composite parts [15]. This can be attributed to carbon fibres having higher thermal conductivity than the matrix phase. This characteristic macroscopic inhomogeneity can result in greater uncertainties of measurement in the weight-normalised total heat flow.

Further, to meet the demands for high volume, economically viable automotive structures; aligned large tow textiles such as non-crimp CFRP prepregs have been increasing in popularity, which produces greater macroscopic inhomogeneities.

Not only do these volumetric variations prevent accurate evaluation of the degree of cure, but they also make the fundamental thermo-kinetic analysis of such materials impossible considering that the constituent prepreg resin is not generally available from manufacturers. For the composite processor to optimise the cure time, an accurate

total heat flow from the uncured prepreg throughout cure is required as a reference. This enables the implementation of an ideal manufacturing cycle curing time, avoiding both premature de-moulding (with an under-cured product with a correspondingly reduced glass transition temperature (T_g) or excessive cure times that unnecessarily tie-up high investment production equipment with no increased product performance. Traditionally, to measure chemical reactions, such as crosslinking, and degree of cure in thermosets, DSC specimens are prepared according to ASTM or ISO standards (ISO 11357-1) [16]. The conventional DSC preparation methods assume homogeneous distribution of the fibre and resin. Currently, there is no method to accurately measure the resin content via normalisation of the heat flow of the exothermic peak in thermosetting composites. There are many methods to measure the carbon fibre content in CFRPs such as ASTM D3171 (acid digestion and air burn-off), processing statistical method (PS), optical microscopy, carbonisation-in-nitrogen (CIN) and thermogravimetric analysis (TGA) [5, 17-19]. He et al. has compared some of these methods and concluded that PS and CIN showed higher reproducibility when compared to optical microscopy and TGA [20]. Optical microscopy and PS methods are not viable options to measure the resin content in a commercial uncured prepreg and acid digestion and CIN do not use comparable sample sizes to those used in DSC measurements (~10 mg). TGA is the closest option for such analysis and has been suggested as an effective method for measuring the fibre content [5, 21]. However, it has been reported recently that TGA has large random errors and a low confidence level, due to small sampling sizes and therefore multiple repeats are required [20]. The same principle applies when sampling only 10 mg of the prepreg for DSC analysis. To reduce the random errors, simultaneous TGA/DSC can be utilised for measuring carbon content on the assumption that the resin fraction undergoes total carbonisation while the carbon fibre stays intact, thus determining the resin fraction via relative weight loss (RWL). However, experiments featuring complete combustion of the neat

constituent resin will also need to be performed to determine the carbon residue fraction produced by the resin under pyrolytic conditions.

When homogenising CFRP composites prior to analysis, a method that does not alter the chemical reaction of the epoxy resin is required. One such method is cryogenic milling (cryomilling), a well-established technique already used in the pharmaceutical industry and thermoplastic polymer/nanocomposite processing where the homogenisation of materials without changing the chemical characteristics is essential [22-25].

In this study, cryomilling has been utilised for the first time in DSC and TGA analysis to achieve more reliable reaction enthalpies and resin contents in thermosetting CFRP composites. Subsequent FTIR analysis was utilised to investigate the effect of the cryomilling process on the final chemical structure of the cured material.

2 Experimental Procedure

Specimens were prepared both by conventional means - manually extracting the DSC and TGA specimens with scissors or a scalpel - and also via cryogenic milling. Both sets of specimens were characterised using DSC and DSC/TGA to obtain cure enthalpy data and relative weight loss data (RWL), and FTIR, optical and scanning electron microscopy (SEM) to investigate the effect of cryomilling on the crosslinking and microstructure of prepreg CFRP composites. Additionally, specimens for degree of cure analysis via DSC were extracted from compression moulded plaques using conventional methods (by hand) and cryogenic milling.

2.1 Materials

Three commercially available bisphenol-A epoxy-based CFRP structural prepreg materials manufactured using continuous aligned carbon fibres arranged into different

reinforcement architectures were obtained from two suppliers Cytec and Mitsubishi. All materials are candidates for research related to high volume automotive manufacturing applications. Their designations in this study are based on their reinforcement fibre architecture: namely *NCF* (non-crimp fabric, biaxial stich-bonded), *Woven* and *UD (unidirectional)*. *Woven* and *UD* prepregs were prepared with the same resin system (368). The *NCF* prepreg (with resin system EF7312) featured the largest-scale inhomogeneity, and was based on a 50K tow that was spread and stitched through-thickness prior to impregnation, creating a biaxial ±45° NCF fabric. The resultant prepreg areal weight was 600 gsm at 51 resin wt %. The *Woven* prepreg was intermediate in terms of inhomogeneity scale, being based on a balanced fabric woven from 12K tows with a resultant areal weight of 400 gsm at 40 resin wt %. Finally, the *UD* prepreg possessed inhomogeneity on the smallest scale, based on fully spread 12K tows giving a prepreg areal weight of 250 gsm at 30 resin wt %. Material details are summarised in Table 1.

All materials were stored at -20 °C in a freezer and were tested within their expiry date.

2.1 Procedure

In order to observe the prepreg macro-structure, optical microscopy (Axioskop Zeiss) and scanning electron microscopy (Carl Zeiss SEM) were utilised prior to sample/specimen extraction.

To enable the determination of prepreg specimen resin fractions via non-isothermal DSC, a datum value for the total heat released in the exothermal curing reaction of the resin system is first required. This is typically achieved by performing non-isothermal DSC on the constituent prepregging ('neat') resin alone. Samples of unfilled resin were not available from the manufacturers; instead it was possible to obtain a sample for

both resin systems from the excess resin bleed present at the sides of the rolls of the *NCF* and *Woven* materials.

A pair of composite cutting shears were utilised during conventional specimen extraction and were designated 'hand-cut'.

2.2 Compression moulding

An industry standard prepreg compression moulding process was used to manufacture flat plaques of each of the candidate prepregs studied in this work. A flat plaque mould (550 x 550 mm) was mounted in a multi-functional instrumented industrial 1700 tonnes Engel V-Duo press. The manufacturing process is explained in further detail in [26]. The moulding parameters were as recommended by the prepreg manufacturers (reported in Table 1).

2.3 Cryo-milling process

The uncured prepreg composite was cut into 3-4 cm^2 pieces and weighed to achieve a total sample of 10±1 g. A freezer/mill (model 6850 from SPEX CertiPrep Group) was used to pulverize samples at cryogenic temperatures. The 10 g prepreg samples were placed in a sealed centre cylinder made of polycarbonate with a steel shuttle bar that grinds materials in liquid nitrogen by magnetically induced impaction. During milling the vial is enclosed, ensuring that the integrity of the sample (e.g. the initial resin content) is maintained. The Spex freezer/mill has the advantage of using liquid nitrogen for cooling to ensure optimum sample brittleness and avoid any heat damage due to friction. The milling cycle was a 5 min precool followed by 10 min run at 15 cps and 1 min after cool. This method multiplies the sampling volume 1,000 times before homogenisation and specimen extraction, therefore increasing the accuracy and precision in the fibre-resin ratio for each DSC specimen (specimens designated

'cryomilled'). Figure 1 shows a schematic illustrating the cryogenic milling and conventional hand-cut preparation methods.

Figure 1

2.4 DSC and TGA/DSC measurements

Thermal polymerisation of the prepreg materials and neat constituent resin specimens was performed via non-isothermal DSC using ~10 mg specimens in sealed aluminium pans under a nitrogen gas flow. A Mettler Toledo HP-DSC-1 differential scanning calorimeter was used over a temperature range of 30 to 230 °C, with a heating rate of 10 °C/min. The DSC was calibrated for enthalpy and temperature using high purity indium and zinc standards.

Simultaneous TGA/DSC was carried out using a Mettler Toledo TGA/DSC-1 in open alumina crucibles using a heating rate of 10 °C/min from 30 to 1000 °C. TGA/DSC experiments were carried out under a nitrogen flow of 50 ml/min to create an inert atmosphere and avoid oxidation. TGA/DSC enabled determination of the resin content in each specimen via the enthalpy of reaction (non-isothermal DSC) and also carbon fibre content following carbonisation (RWL analysis using TGA). The resin content determined by TGA/DSC is unaffected by degree of cure and therefore constitutes as a baseline against which the resin content results obtained via enthalpy of cure can be compared. By comparing the two results for resin content obtained via TGA/DSC, it is possible to understand the current degree of cure in the prepreg material and ensure that pre-curing of the resin does not affect the resin content obtained via enthalpy of cure.

The total enthalpy of reaction was calculated in the range of 80 to 220 °C and the relative weight loss calculated at 600 °C. The carbonisation residue was measured at

600 °C as this temperature threshold has been reported as optimal in effectively carbonising the resin with minimum decomposition of the carbon fibre [19, 20].

2.5 Treatment of data

The total enthalpy of reaction can be calculated by integrating the heat flow in a DSC curve as a function of time over the complete exothermic reaction. The resin content can then be calculated from the total heat released such that:

$$C_r = \frac{H_c}{H_T} \times 100 \quad (1)$$

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.

The resin content in the TGA/DSC samples was calculated using the following formulae with the obtained RWL data:

$$RWL_{\,neat\ resin} = \left(\frac{W_{residue\ R}}{W_{0\ R}}\right) \times 100 \quad (2)$$

$$RWL_{\,prepreg} = \left(\frac{W_{residue\ P}}{W_{0\ P}}\right) \times 100 \quad (3)$$

$$Resin\ Content_{\,prepreg}(wt\%) = \left(\frac{RWL_{\,prepreg}}{RWL_{\,neat\ resin}}\right) \times 100 \quad (4)$$

The degree of cure (α) of the moulded thermosetting prepreg parts can be obtained by measuring the heat generated during the cure of the prepreg using non isothermal DSC such that

$$\alpha\ (\%) = \frac{H_c - H_{part}}{H_c} \times 100\,, \quad (5)$$

where H_c is the total enthalpy of the reaction for the uncured prepreg composite and H_{part} is the total enthalpy of the reaction for the moulded (cured) prepreg composite part. Assuming independent variables, a common variance formula was used to calculate the standard deviation in the degree of cure of the parts as follows:

$$\sigma_{\alpha}(\%) = \sqrt{\left(\frac{\partial \alpha}{\partial H_c}\right)^2 {\sigma_{H_c}}^2 + \left(\frac{\partial \alpha}{\partial H_{part}}\right)^2 {\sigma_{H_{part}}}^2} \quad (6)$$

hence:

$$\sigma_{\alpha}(\%) = 100 \times \sqrt{\left(\frac{H_{part}}{{H_c}^2}\right)^2 {\sigma_{H_c}}^2 + \left(\frac{1}{H_c}\right)^2 {\sigma_{H_{part}}}^2} \,. \quad (7)$$

2.6 FTIR

The temperature-dependent attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of cryomilled and hand-cut uncured prepreg materials were measured with a Golden Gate™ high temperature heated diamond ATR top plate using a Bruker Tensor 27 instrument. Specimens were placed directly (without further preparation) onto the diamond and 20 scans were collected at 4 cm^{-1} resolution and averaged. The heating rate was 10 °C/min over the temperature range of 30 to 230 °C.

3 Results and discussion

3.1 DSC cure characterisation

The non-isothermal DSC curves for the *Woven* specimens are shown in Figure 2. The hand-cut and cryomilled specimen traces are similar to each other in form, with enhanced reproducibility observed with the cryomilled samples. Similar results were observed with the other two prepregs. The mean and standard deviation of the total heat of reaction and the calculated prepreg resin weights are reported and compared to the manufacturer's nominal values in Table 2.

Figure 2

Figure 3 illustrates the values reported in Table 2 for resin content in weight percentage (wt %) using Equation 1. It is clear that the *NCF*, *Woven* and *UD* specimens extracted via cryomilling yield an average resin content closer to the

nominal value as compared to the conventional hand-cut method. The measurement uncertainty was much greater for the hand-cut specimens, with the highest deviation observed with *NCF* (± 11.83 %). The standard deviations in the cryomilled specimen measurements ranged from being a factor of approximately 10x smaller (*UD*) to 20x smaller (*NCF*).

Figure 3

In order to understand the sampling difficulties presented by the macro-structural features of the prepregs and their reinforcement architectures and in an attempt to contextualise the homogenising effect of the cryomilling procedure, optical and SEM micrographs were taken of the material surfaces as received and after cryomilling (SEM only).

Figure 4

The micrographs are shown in Figure 4. Optical micrographs of the as-received material (stitched, 5x magnification) are presented in the left-hand column. The brighter patches are indicative of resin rich areas. It is obvious that the *UD* prepreg has a more homogenous macrostructure when compared with the other two prepregs; there are relatively large (~1mm-scale) variations in resin visible on the *Woven* and *NCF* material surfaces. Looking at the 250x SEM micrographs of the as-received prepreg material surface (Figure 4, middle column) it can be seen that the variations in *UD* are on the scale of ~100 µm whereas the dry (unwetted) filament tow regions in *Woven* and *NCF* exceed the width of the whole micrograph (~1mm total). The discrete macrostructure of the fabric architecture in the 50K *NCF* and 12K *Woven* materials presents a greater challenge to uniform wetting during prepregging than the spread tow architecture of the *UD* material. Indeed, this is borne out in the lower standard deviation for the calculated resin content for the hand-cut specimens as shown in Figure 3.

Comparison of the 250x SEM images of the cryomilled prepregs (right-hand column) reveals that the length of the fibre in the prepared *UD* samples is greater than that of

the other prepregs. Interestingly, although variations in the fibre length are observed following cryomilling this difference is not reflected in the DSC and TGA/DSC results, with greater deviations observed when analysing the hand-cut samples. Further to this, despite the *UD* micrograph demonstrating the greatest variation in fibre length, the same sample exhibited the smallest standard deviation in the resin content analyses (Figure 3), with calculated resin content closely corresponding to that of the nominal value.

3.2 TGA/DSC characterisation

Simultaneous TGA/DSC was performed on the *Woven* material (Figure 5) and the respective resin contents calculated.

In Figure 5, the top panels show the non-isothermal DSC measurements and bottom panels show the TGA relative weight loss. This data proves that any variations in the earlier non-isothermal DSC resin content results are not due to variations in the degree of cure in the prepreg (e.g. due to mishandling) as the TGA analyses show corresponding variations in the residual char. This confirms that the fibre content varies significantly for the hand-cut DSC specimen preparation method. Further clarification is shown in Table 3 where greater precision and accuracy are obtained following cryomilling as compared to the hand-cut procedure. In addition, a better agreement is found between the DSC and TGA results for the cryomilled specimens.

Figure 5

The data shown in Figure 6 (a) (and also Figure 5 (a) & (c)) is for hand-cut specimens chosen from the highlighted areas indicated in the photograph in Figure 6 (b). A significant variation in resin content within a few mm^2 of the prepreg can be seen. Figure 6 illustrates that the architecture of the prepreg and the location of specimen extraction has a direct correlation with deviations in the measurement. Furthermore,

the similarity between the DSC and TGA analysis of the cryomilled material (40.8 versus 40.1 wt %) suggests that deviations in the calculated resin content (via total enthalpy of curing) are solely a result of the variation in the resin content.

Figure 6

It has been reported previously that variation in calculated fibre content of cured prepreg materials from TGA analysis is 1-3 wt % higher than those measured from the PS method [20]. Additionally, PS and CIN methods show poor repeatability in excess of 4.7 wt %. It can be assumed that an uncured prepreg has more variation in the resin content than the cured part as when the resin reaches minimum viscosity during processing, it will wet-out resin starved regions. The standard deviations obtained for the TGA analysis of *Woven* cryomilled specimens are significantly smaller than these previously reported values, highlighting the enhanced accuracy possible via cryomilled specimen preparation. Specifically, the standard deviations are less than 1 wt % for DSC and 0.1 wt % for TGA (Table 3). Using specimens extracted from larger cryomilled samples ensures homogenous dispersion of the fibre for the cured specimen and also better contact between the alumina pan and the DSC sensor.

The reproducibility in the enthalpy calculated by DSC with the TGA/DSC was found to be lower than the previously discussed results from the stand-alone DSC for both the cryomilled and hand-cut samples (Table 2). This was attributed to the lower sensitivity of the DSC sensor used in this equipment with a standard deviation of less than 5% reported by the manufacturer. In addition, the stand-alone DSC (resolution 0.04 μW) produces a 2500-time more accurate heat flow signal compared to the TGA/DSC (resolution 100 μW). Using alumina pans in the TGA/DSC could also contribute to the higher standard deviation reported in Table 3 since aluminium has a conductivity of about 237 W/°Km while alumina has thermal conductivity of around 18 W/°Km.

3.3 Degree of cure of the compression moulded parts

The degree of cure for each moulded part was established via DSC from hand-cut and cryomilled samples using Equation 5 (3 repeat analyses). Table 4 shows the degree of cure calculated from the reference values (total heat enthalpy) reported in Table 2 for each method of preparation.

Figure 7 illustrates the mean degree of cure (σ_α, calculated using Equation 7) for the moulded flat plaques for varying DSC sample preparation. As is evident from Figure 7 and Table 4, the cryomilling step reduces the standard deviation in degree of cure reported for all prepregs. Introducing cryomilling step reduced the uncertainty in the degree of cure by 7 times when compared to the hand-cut method for the *Woven*. Another advantage of using cryomilling before and after curing is that the part quality can be evaluated without knowing the fibre content. Furthermore, by using larger sampling size of 5000 mg instead of 10 mg, this method can be used to measure the degree of cure of thick structural parts.

It was evident from Sections 3.1 and 3.2 that cryomilling process does not alter the total enthalpy of the curing reaction for the prepreg composite. Furthermore, to ensure that the slightly higher degrees of cure reported for cryomilled samples in Figure 7 are not as a result of higher fibre content in the specimens, TGA/DSC was performed on the cryomilled samples of cured flat plaques made of *Woven* and *NCF*. The following values for the resin content of 40.1 ± 0.2 wt % and 50.5 ± 0.5 wt % were measured using Equation 4 for *Woven* and *NCF*, respectively. However, simultaneous TGA/DSC was not deemed to be suitable technique to detect the total enthalpy of curing reaction for these plaques, as no exothermic peak was observed. This was considered to be due to the reduced sensitivity of the DSC sensor in the hybrid equipment; the resolution of heat flow measurements in the dedicated DSC sensor (0.04 µW) is 2500 times higher than that of the hybrid TGA/DSC (100 µW).

Figure 7

3.4 FTIR analysis

FTIR analysis was used to obtain spectra and enable comparisons between the chemical structure of the hand-cut and cryomilled *Woven* samples pre- and post-curing (Figure 8). As the exact composition of the material is not specified by the manufacturer, complete identification of the IR spectra could not be performed. However, salient peaks typically found in epoxy resins are those at 800, 915 and 1250 cm^{-1} which correspond to the C-O and C-O-C groups in the ethylene oxide ring and the C-O ether group, respectively [27]. Prior to curing a greater absorbance was found over the entire hand-cut spectrum compared to the cryomilled sample due to concentration effects. In addition more defined peaks were observed at 1650 and 3400 cm^{-1} in the cryomilled samples. These are likely to correspond to the hardener or other additives and suggest the cryomilling results in phase separation or exposure of these materials to the surface. On heating, the peaks at 800, 915 and 1250 cm^{-1} reduce in both samples corresponding to the opening of the epoxy ring during the curing reaction. Most importantly, following curing the spectra of the two prepregs were identical showing cryomilling to have no effect on the final chemical structure of the material.

Figure 8

4 Conclusions

It is shown that whilst conventional sample preparation results in highly uncontrolled variation of the resin content, cryogenic milling is effective at homogenising samples of structural CFRP thermosetting prepreg composites prior to thermal analysis. This homogenisation is accomplished with no alteration to the cross-linking of the polymer,

and therefore the total heat enthalpy or chemical composition of the cured material.

Moreover, cryogenic milling of thermosetting prepregs produces a homogeneous powder that can be handled easily during specimen preparation as a means for thermal analysis such as DSC and TGA. When compared to conventional sample preparation methods, sampling via cryomilling results in an approximate 100 times reduction in the uncertainty of calculated resin content results for TGA experiments and 10 times reduction when using simultaneous DSC/TGA. It has been shown that sample preparation via cryomilling enables the carbon fibre content to be measured by TGA with lower uncertainty than conventional sample preparation. The main drawback mentioned in the literature when using the TGA method for carbon fibre content measurement was the small specimen volume being non-representative and failing to adequately describe macrostructural inhomogeneity of the carbon fibre reinforced composites [19, 20]. Thus cryogenic milling is proven as an excellent complementary preparation technique, reducing random errors and increasing confidence levels in obtained results, whilst still enabling the benefits of the use of TGA as an environmentally-friendly technique for resin content measurements of cured and uncured carbon fibre composites (as opposed to acid digestion).

When applying the cryomilling sample preparation technique to cured, industrially processed prepreg laminates in order to determine the degree of cure by conventional DSC - a widely-used indicator of final part quality - reductions in the uncertainty of measurement were observed for all candidate structural prepreg materials as compared to the results obtained for analyses of hand-cut samples. Indeed, for the mean degree of cure for the *Woven* prepreg material, a seven-fold reduction in measurement uncertainty was observed. This further indicates the suitability of the cryomilling preparation technique for the homogenisation of cured structural composite samples possessing a large degree of macro-scale inhomogeneity.

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Figure Captions

Figure 1 Schematic comparison between the cryomilling and hand-cut sample preparation. (For a colour version of this Figure, please refer to the online version of this article.)

Figure 2 Non-isothermal DSC cure behaviour of the *Woven* prepreg. The experimental data shown for (a) three hand-cut samples, (b) three cryomilled samples, and (c) the neat resin. (For a colour version of this Figure, please refer to the online version of this article.)

Figure 3 Comparison between resin content measured from non-isothermal DSC from Cryomilling and Hand-cut for 3 various CFRP prepreg systems. (For a colour version of this Figure, please refer to the online version of this article.)

Figure 4 Micrographs of the 3 prepreg systems (optical microscopy and scanning electron microscopy) comparing microstructures of hand-cut and cryomilled samples.

Figure 5 TGA-DSC results of the *Woven* material from 30 to 1,000 °C at 10 °C/min heating rate. Top: DSC results (a) Hand-cut and (b) Cryomilled; Bottom: simultaneous TGA analysis (a) Hand-cut and (b) Cryomilled. (For the interpretation of the reference to colour in the legend, refer to the web version of this article.)

Figure 6 (a) Comparison between resin content measured by DSC and TGA from Cryomilling and Hand-cut for *Woven* (b) Image of *Woven* sample surface. Data marked with arrows in (a) are taken from the areas highlighted in (b). (For interpretation of references to colour in this Figure, refer to the web version of this article.)

Figure 7 Evaluation of α degree of cure (%) measured from non-isothermal DSC prepared by Cryomilling versus Hand-cut for 3 different moulded CFRP prepreg parts. (For a colour version of this Figure, please refer to the online version of this article.)

Figure 8 FTIR analysis of Hand-cut and Cryomilled *Woven* pre and post curing. (For a colour version of this Figure, please refer to the online version of this article.)

Figure 9-comment Nominal resin content with the resin content measured by stand-alone DSC and stand-alone TGA using the conventional Hand-cut preparation method (a & b) versus the Cryomilling preparation method (c & d) for 4 different CFRP uncured prepregs. The red line indicates the perfect match.

Table 1

Prepreg material details.

Material designation	Nominal resin wt %	Reinforcement filament count	Prepreg areal weight (gsm)	Compression Moulding Cure cycle	Glass Transition (T_g)
NCF	51	50K (spread and stitched)	600	3 minutes at 150°C	145°C
Woven	40	12K	400	5 minutes at 140°C	136°C
UD	30	12K (spread)	250	5 minutes at 140°C	136°C

Table 2

The resin content (wt %) and enthalpy of reaction results (measured from non-isothermal DSC) for CFRP prepreg composite specimens.

Material	Nominal resin content (wt %)	Resin Content from Cryomilled DSC (wt %)	Resin content from Hand-cut DSC (wt %)	H_c from Cryomilled DSC (J/g)	H_c from Hand-cut DSC (J/g)
NCF	51	51.74 ± 0.57	52.33 ± 11.83	205.98 ± 2.28	208.33 ± 47.08
Woven	40	40.43 ± 0.77	37.84 ± 4.20	150.81 ± 2.86	141.33 ± 15.70
UD	30	29.80 ± 0.34	23.98 ± 2.36	111.18 ± 1.26	89.46 ± 8.81

Table 3

Calculated resin content results (combined TGA/DSC) for *Woven* material

Nominal resin content (wt %)	Estimated Resin Content (wt %)			
	Cryomilled		Hand-cut	
	DSC	TGA	DSC	TGA
40.0	40.8 ± 0.9	40.1 ± 0.1	39.9 ± 10.9	41.3 ± 8.2

Table 4

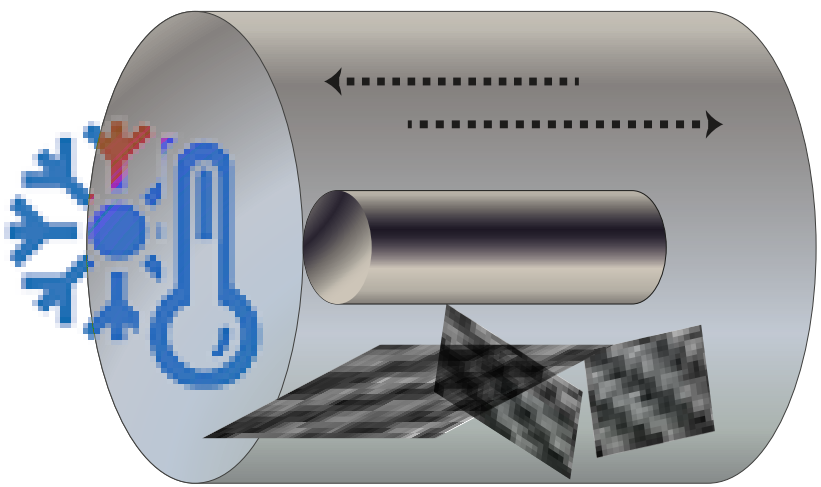
The degree of cure ($\boldsymbol{\alpha}$) and enthalpy of reaction for moulded CFRP prepreg composite parts ($\boldsymbol{H_{part}}$) results measured from non-isothermal DSC.

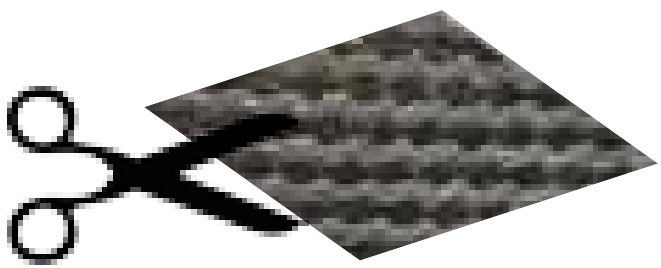
Materials	Nominal resin (wt %)	DSC Prep Method	$\boldsymbol{H_{part}}$ (J/g)	$\boldsymbol{\sigma_{H_c}}$ (J/g)	$\boldsymbol{H_c}$ (J/g)	$\boldsymbol{\sigma_{H_{part}}}$ (J/g)	$\boldsymbol{\alpha}$ (Degree of Cure) (%)	$\boldsymbol{\sigma_{\alpha}}$ (%)
NCF	51	Cryomilled	6.27	0.56	205.98	2.28	96.96	0.28
		Hand-cut	7.00	1.58	208.33	47.08	96.64	1.07
Woven	40	Cryomilled	1.53	0.32	150.81	2.86	98.99	0.22
		Hand-cut	2.41	2.13	141.33	15.70	98.22	1.52
UD	30	Cryomilled	4.83	0.70	111.18	1.26	95.66	0.29
		Hand-cut	5.14	1.17	89.46	8.81	94.25	1.43

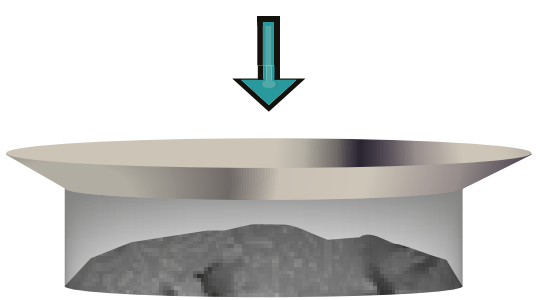
Prepreg *Woven*

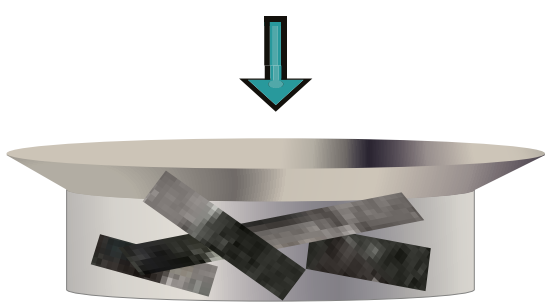
Cryogenic Milling

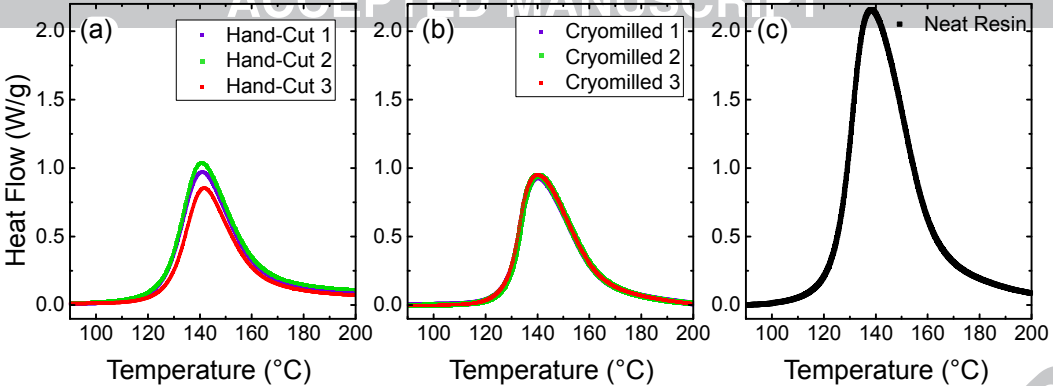
Hand-cut

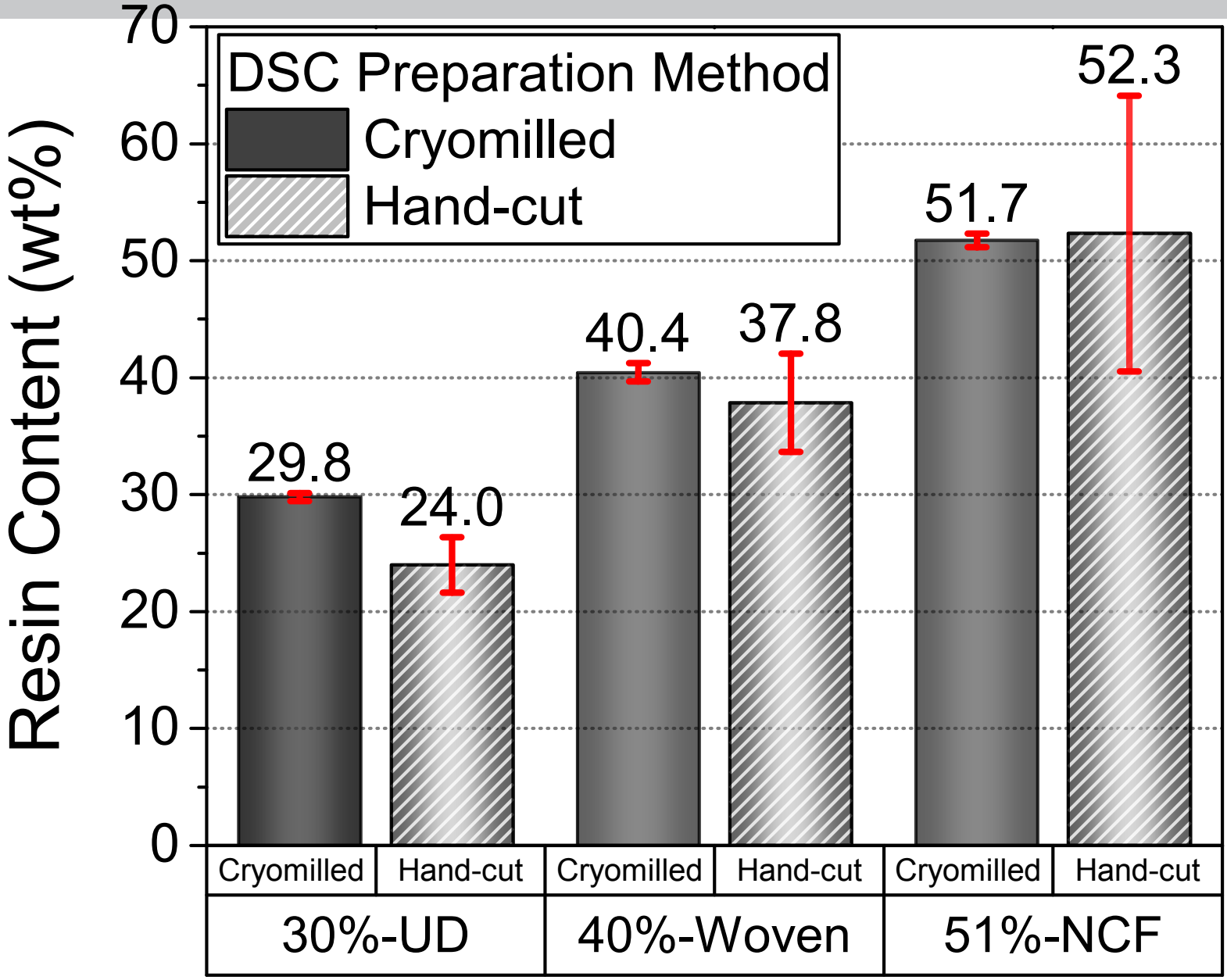


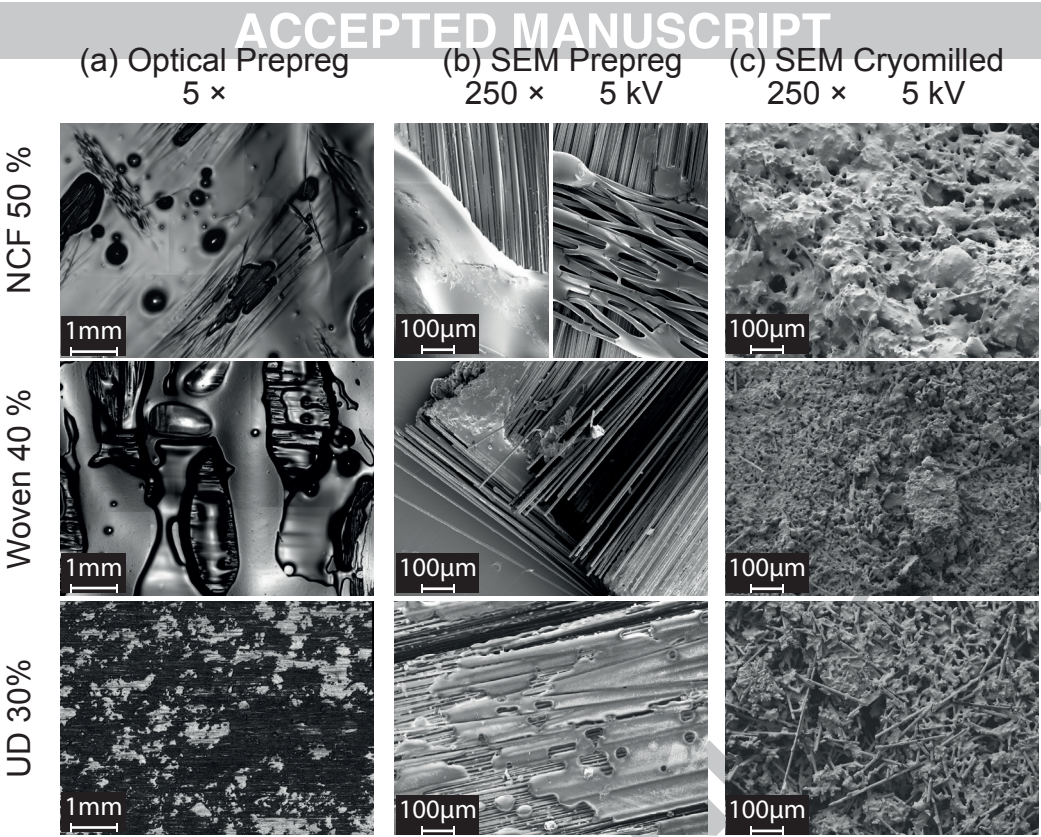


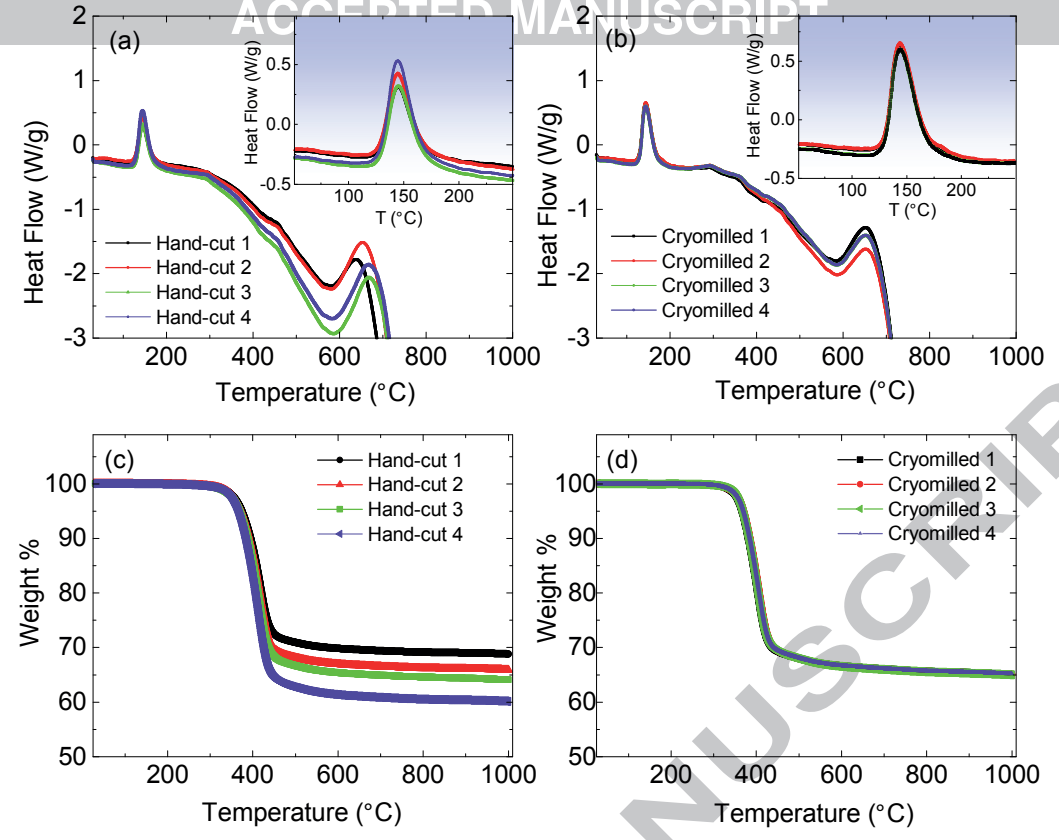


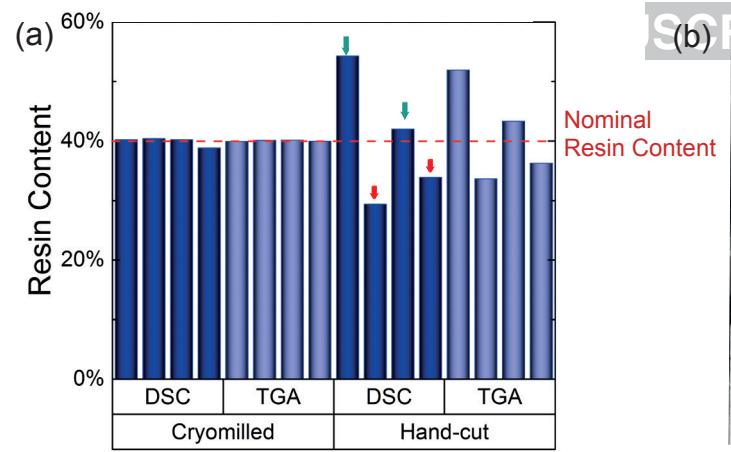


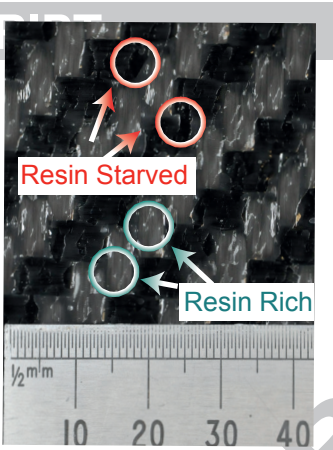


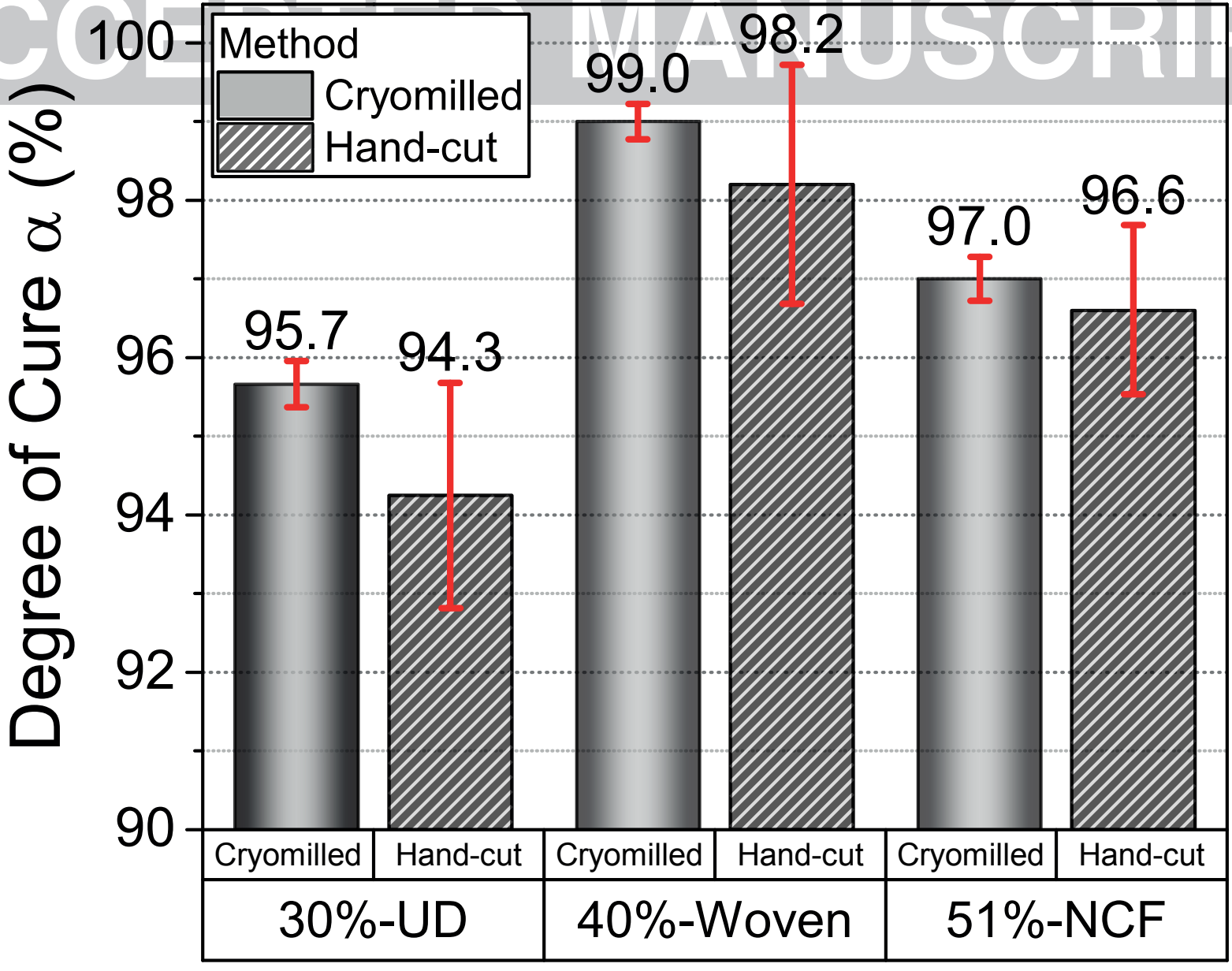


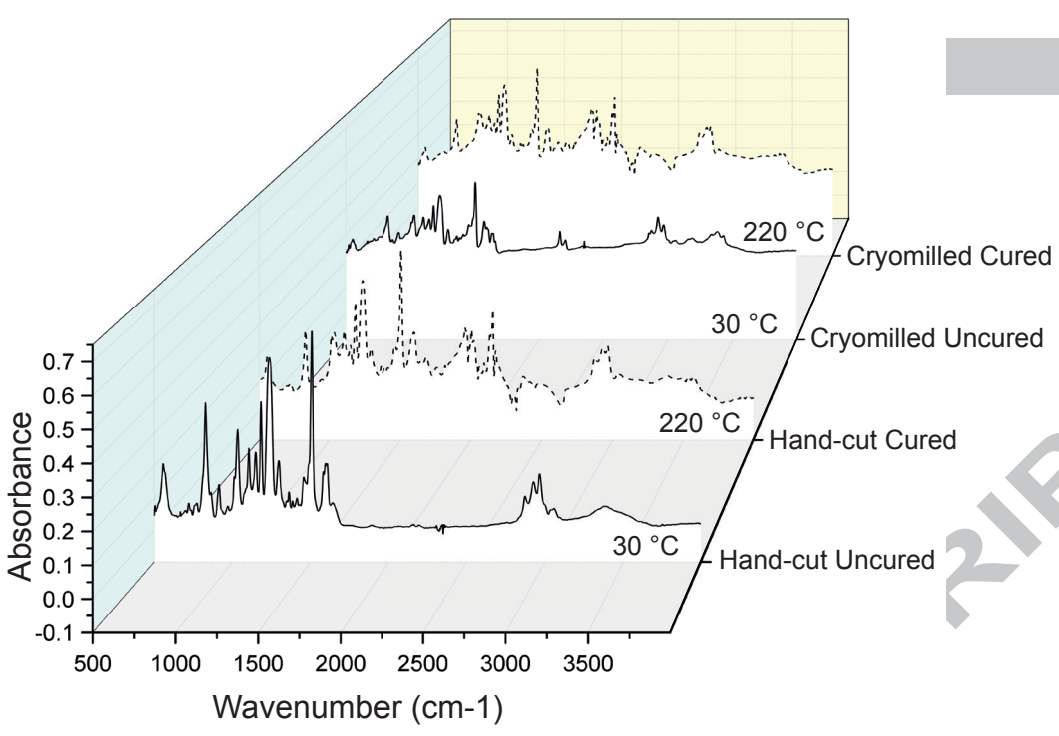





(a)
60%
40%
20%
0%
Resin Content
Nominal
Resin Content
DSC
TGA
DSC
TGA
Cryomilled
Hand-cut


(b)
Resin Starved
Resin Rich
½m/m
10
20
30
40




220 °C
Cryomilled Cured
30 °C
Cryomilled Uncured
220 °C
Hand-cut Cured
30 °C
Hand-cut Uncured
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
500
1000
1500
2000
2500
3000
3500
Wavenumber (cm-1)