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THERMOSET POYLMER SCALING EFFECTS IN THE MICROBOND TEST

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Abstract: *The curing performance of two epoxy resin systems has been investigated using the microbond test and FTIR spectroscopy. A novel sample preparation technique involving curing epoxy droplets on thin steel filaments allowed for high-throughput determination of microbond droplet cure state using a conventional benchtop spectrometer. Parity between steel filament and glass fibre microbond samples was confirmed by infrared microspectroscopy. It is shown that cure schedules used in the manufacture of composite parts produced microbond droplets with degrees of cure lower than that of bulk matrix specimens subjected to an identical thermal history. For a commercial resin system, testable microbond droplets could only be produced when a room temperature pre-curing time of at least 2 hours was introduced. It is concluded that microbond testing be supported by some method of droplet cure state characterisation to ensure that interfacial effects are not artefacts of droplet sample preparation.*

Keywords: Glass fibres; Epoxy resin; Interfacial shear strength; Microbond test; Infrared spectroscopy

1. Introduction

Optimisation of the stress-transfer capabilities of the fibre/matrix interface region is critical to composite material mechanical performance. The strength of the interface can be defined in terms of interfacial shear strength (IFSS), which can be characterised by a number of micromechanical methods [1]. Such testing methods can be useful tools in the economical and time-efficient development of fibre treatments and assessment of composite processing parameters by enabling screening and optimisation at the single fibre level without the need to scale up to fabric production, laminate processing, and macromechanical testing [2]. Despite apparent IFSS being strongly influenced by the cure state of the matrix, non-ideal droplet curing behaviour is rarely considered.

Microscale curing effects have been identified as an area for improvement in some of the earliest critical reviews of micromechanical [1] and microbond [3] testing methods. Furthermore, these scaling effects may occur across a wide range of thermosetting matrices including epoxy [4], polyester [5], vinyl ester [6], and acrylic resins [7]. Hypotheses on the cause of reduced droplet (and thin film) cure in the current literature include: evaporation of essential polymerisation components (such as volatile curing agents and styrene); adsorption of curing agent onto the fibre surface; absence of a surrounding mould, droplet surface-to-volume ratio; phase separation during sample preparation; imine group formation; fibre surface moisture; anhydride hydrolysis; surface oxidation; interaction with atmospheric moisture; and reduced autoacceleration.

Such variations in droplet cure state may either make microbond testing impossible (depending on matrix and curing agent selection) or result in apparent IFSS being measured in a material with an undefined system chemistry.

This paper aims to address this fundamental need for a method to directly characterise the cure state of microbond droplet specimens. Previous methods of droplet cure state characterisation have included modified thermomechanical analysis techniques [8] or modelling droplets as thin film specimens [9]. However, a higher throughput solution with less exacting sample preparation requirements is highly desirable. In this paper the microscale curing performance of a commercial epoxy resin designed for wind turbine blade applications and a reference epoxy/tetrafunctional amine system were investigated using novel spectroscopy techniques and the microbond test.

2. Experimental

2.1 Materials

Experiments were carried out using bare (water-sized) E-glass fibres with an average fibre diameter of 17.5 µm from Owens Corning. Two different epoxy resin systems were investigated in this study. One was a multiple-component commercial epoxy/amine system designed for wind turbine blade applications. The other was an experimental system based on a single resin and triethylenetetramine (TETA) curing agent. Resin mixtures were prepared and degassed under vacuum for 10 min to remove entrapped air. Curing cycles consisted of two isothermal stages with intermediate heating rates of 2°C/min and were selected to coincide with curing schedules used in the production of macroscale composite parts. Glass transition temperatures of cured bulk matrix were determined by differential scanning calorimetry (DSC). Details of the epoxy resins used are listed in Table 1.

Table 1: Epoxy resins, curing agents, and temperature schedules used in the investigation

ID	Epoxy Resin	Curing Agent	Cure Schedule	Bulk Tg (°C)
WT1	Epotec YD-535 LV	TH7257	65°C 3.5 h; 75°C 7 h	87
R1	DER332	TETA	60°C 1 h; 120°C 2h	124

2.2 Microbond testing

Microbond testing involves a single fibre being pulled from a restrained droplet of cured matrix while measuring the force required to detach the fibre. IFSS was measured using an in-house designed microbond jig [10]. Successful debonding or instances of droplet plastic deformation were confirmed by in-situ observation of droplet loading using 45x magnification stereo microscopy and a live camera feed.

2.3 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to characterise degree of cure of microbond droplet and bulk matrix specimens subjected to an identical thermal history. FTIR was performed using a 4100 ExoScan spectrometer and a spherical diamond attenuated total reflectance (ATR) interface. An adjustable probe was used to ensure good specimen contact with the FTIR interface. Analysis was performed in the 4000 to 650 cm^{-1} range with a spectral resolution of 8 cm^{-1} and 64 scans per sample. Glass fibres were replaced by steel wire of diameter 50 µm for spectral measurements using a benchtop spectrometer.

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The benchtop FTIR microbond sample preparation methodology and experimental configuration is illustrated in Figure 1.

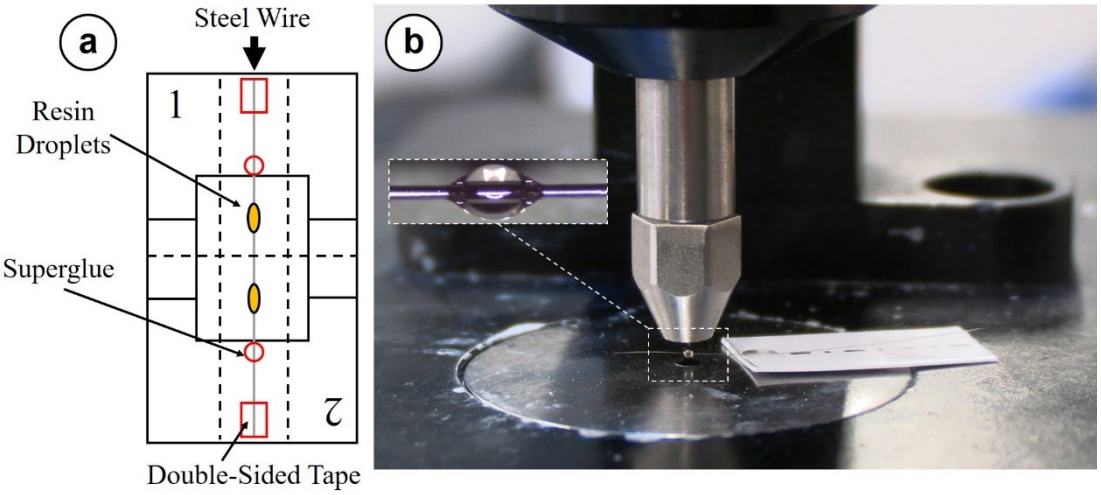

Figure 1: Benchtop FTIR method showing (a) Sample preparation (b) Droplet testing

IR microspectroscopy was performed using a Bruker Hyperion 3000 FTIR microscope equipped with a liquid nitrogen cooled MCT ATR detector in the 4000 to 650 cm^{-1} range with a spectral resolution of 16 cm^{-1} and 32 scans per sample. Glass fibre/epoxy microbond droplet specimens were placed on a glass slide and accurately positioned using a viewing objective and motorised stage.

Degree of monomer conversion was characterised using the reduction of the area of the oxirane group at 915 cm^{-1} against the invariant peak at 1507 cm^{-1} (C=C stretching of the benzene ring) as an internal standard as expressed in Equation 1. Peaks were selected due to stronger relative signal intensities compared to other analytical and reference peaks. Absorbance peak areas were calculated using a baseline integration function between the values of 927–893 cm^{-1} and 1526–1489 cm^{-1}.

$$\alpha = 1 - \frac{(A_{915}/A_{1507})_t}{(A_{915}/A_{1507})_0} \quad (1)$$

3. Results and Discussion

3.1 Microbond testing results

Epoxy resins can be expected to achieve typical apparent IFSS values of 25–35 MPa with unsized glass fibres. Microbond testing of WT1 epoxy resin droplets showed exceedingly low values of apparent IFSS when samples were cured according to the recommended macroscale schedule. As shown in Figure 2(a), in-situ observation during testing showed that the droplets deformed plastically under applied load, indicating incomplete cure. Measurement of IFSS was not possible in such cases and the resulting forces generated during the test can be attributed to frictional effects related to crushing of the droplet and subsequent fibre pull-out from the gel-state matrix. WT1 bulk matrices subjected to identical curing conditions showed T_g of 87°C. Thus, microbond droplets of this epoxy resin should have been capable of producing testable specimens. Conversely, R1 droplets appeared to cure consistently following exposure to immediate elevated temperature heating.

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In-situ observation did not show plastic deformation during the test and an apparent IFSS value of around 38 MPa was measured. As shown in Figure 2(b), successful debonding was confirmed by post-test SEM imaging and the presence of a residual meniscus.

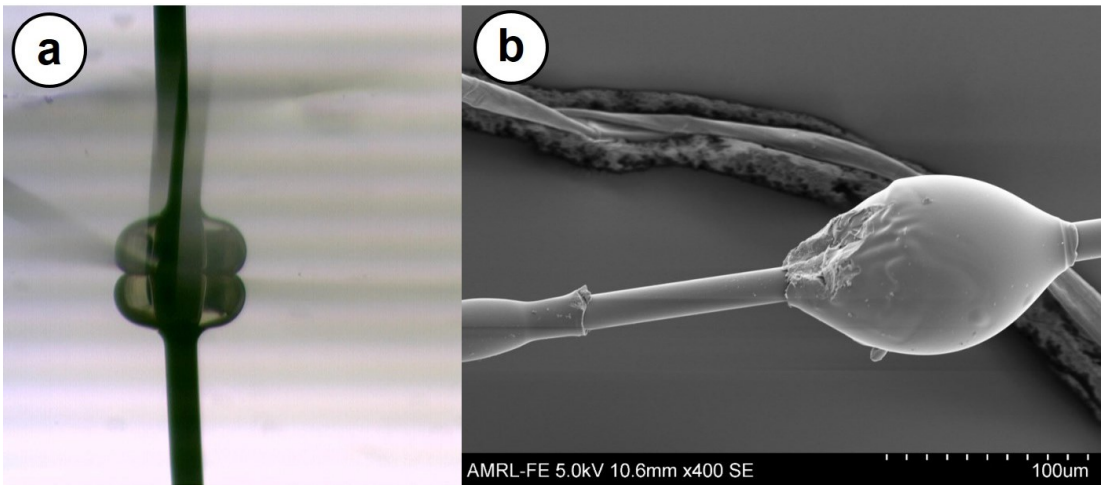

Figure 2: (a) In-situ micrograph of WT1 droplet (b) Post-test SEM of R1 droplet

3.2 Characterisation of microbond droplet cure state

The average mass of individual microbond droplet samples is in the range of 0.5–20 µg. The use of conventional thermal analysis techniques to quantify under-cure was not possible due to insufficient signal to detect T_g or residual exotherm from single droplet specimens. Therefore, droplet spectra collected from microbond specimens cured on thin lengths of 50 µm diameter steel wire were used to study epoxy group conversion. Individual steel filaments were isolated, aligned, and mounted along the vertical axis of a card template using double-sided tape and cyanoacrylate gel superglue before standing for 24 h to fully react. Resins were mixed according to the relevant directions and applied to individual fibres using a thin length of steel wire to produce droplets with embedded lengths of approximately 400 µm. We also performed infrared microspectroscopy on the glass fibre/epoxy microbond droplet specimens used for IFSS measurements to verify that degree of cure values were comparable between glass fibre/epoxy and steel wire/epoxy specimens.

FTIR spectra of WT1 and R1 epoxy microbond droplet specimens cured on glass fibres and steel filaments are shown in Figure 3. A magnified region around the oxirane ring at 915 cm^{-1} is shown in the inset. In all droplet spectra, unreacted epoxy groups are evidenced by increased peak intensities corresponding to vibrations of the oxirane ring at 970, 915, and 760 cm^{-1}. Invariant peaks at 1608 and 1507 cm^{-1} are attributable to C=C and C-C stretching of the benzene ring. The degree of cure of droplets was calculated using Equation 1. Good agreement was shown between spectroscopic methods in that degree of cure values for glass fibre and steel wire epoxy droplets were 0.52 and 0.55, respectively for WT1 specimens. Similarly, degree of cure values for glass fibre and steel wire epoxy droplets were 0.85 and 0.87, respectively for R1 specimens. Accordingly, droplet spectra from resins cured on 50 µm steel filaments were considered comparable models of the cure state of those prepared on unsized glass fibres. This method of sample preparation enables a high-throughput method of droplet cure state assessment by generating sufficient signal strength to allow spectra to be collected from individual droplet specimens.

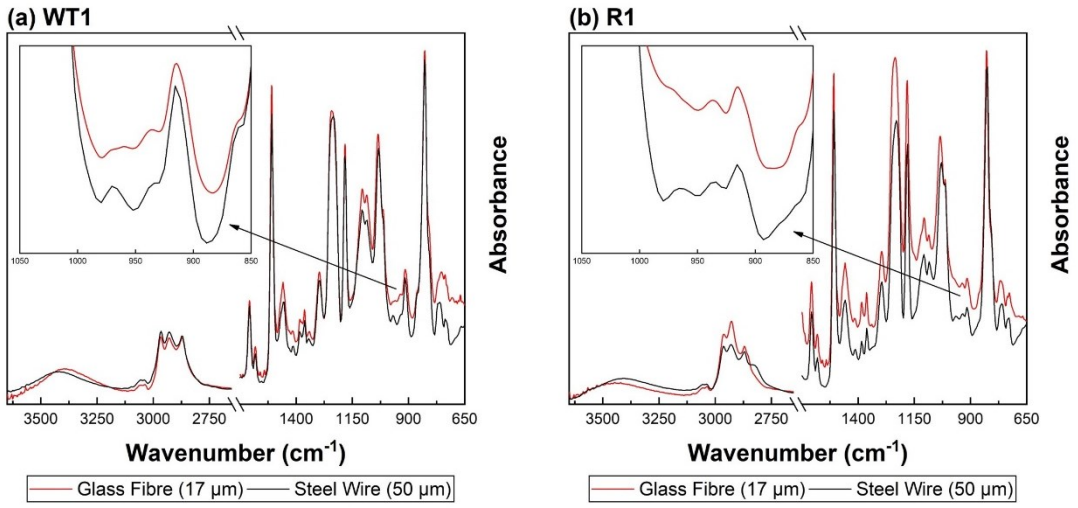

Figure 3: FTIR spectra of epoxy microbond droplets cured on glass fibre and steel wire

3.2 Degree of cure at droplet and bulk matrix scales

FTIR spectra of droplet and bulk matrix specimens subjected to identical thermal histories are shown in Figure 4. Spectra of WT1 microbond samples cured according to the recommended macroscale schedule were commensurate with a non-stoichiometric epoxy/amine network. Unreacted epoxy groups that were not present in comparable bulk matrix spectra were observed. Furthermore, reduced hydroxyl and secondary amine group accumulation (3600–3200 cm^{-1}) and a weaker etherification peak (1100 cm^{-1}) were apparent. The average degree of cure value for these droplet specimens was 0.55. Conversely, cured matrices showed a significantly higher degree of cure values of 0.89. This apparent disparity in curing behaviour may suggest a stoichiometric imbalance due to evaporation of components such as the curing agent. Loss in droplet stoichiometry may have resulted in insufficient amine groups to ensure a strongly cross-linked network structure in the droplet. Poorly cross-linked droplets that show plastic deformation during testing are indicative of a sub-optimal microdroplet T_g. WT1 droplets appeared to have a T_g close to, or below, room temperature and hence do not have a sufficiently high modulus to transmit applied load and enable normal microbond testing to take place.

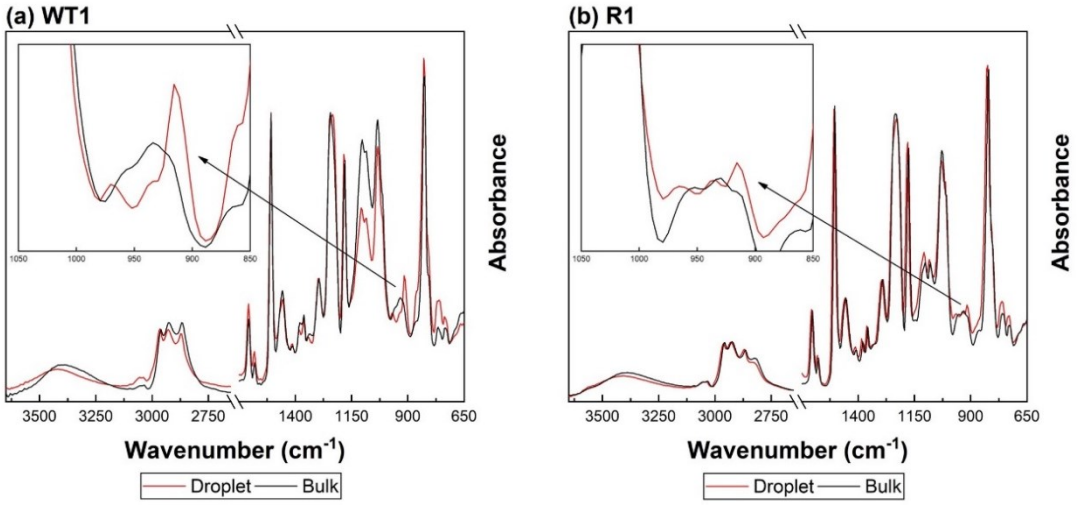

Figure 4: FTIR spectra of microbond droplet and bulk cured matrix specimens

Spectra of R1 microbond droplet specimens were similarly representative of an under-cured matrix formulation, indicated by unreacted epoxy groups at 915 cm^{-1} that were not present in the bulk matrix sample. Degree of epoxy conversion for R1 droplets was 0.87, while comparable bulk specimens reached a conversion of 0.95. These results suggest that the epoxy droplet samples typically associated with the microbond test do not possess material properties comparable to those of bulk matrix specimens, even in cases where good debonding is achieved and reasonable values of apparent IFSS are measured.

It may be suggested that a critical surface-to-volume ratio exists at which some portion of the amine curing agent diffuses to the surface of the droplet and evaporates, despite the fact that vapour pressures for these systems do not indicate particularly high volatility. In any case, spectra of microbond droplet specimens confirmed that the cure state was significantly reduced compared to bulk cured matrices. For a multiple-component commercial resin system, cure state was reduced to the extent that microbond testing was not possible. In a reference epoxy system, droplet degree of cure was lower than that of comparable bulk matrix specimens while remaining sufficiently high to promote good crosslinking and a relatively high droplet T_g.

3.3 Effect of cure cycle modification

Degree of conversion of droplet and bulk matrix specimens subjected to the same range of curing schedules is shown in Figure 5. WT1 droplets cured according to the standard schedule had a degree of cure of 0.55, a value commensurate with a loss of up to 60% of the initial curing agent and a sub-ambient T_g. Droplets that were allowed to pre-cure at room temperature for 2–48 h and partially react prior to curing had degree of cure values between 0.87 and 0.93. Degree of conversion of bulk matrix specimens was not significantly affected by the inclusion of a pre-curing time and in all cases, cured to a higher degree than comparable droplet specimens. For the R1 droplet samples, degree of cure was reduced slightly in the 3–36 h pre-curing range. Degree of conversion was lowest (0.77) following a 36 h pre-cure and was highest when samples were cured immediately (0.87). However, all R1 droplets samples cured to a lower degree than the bulk matrix specimens.

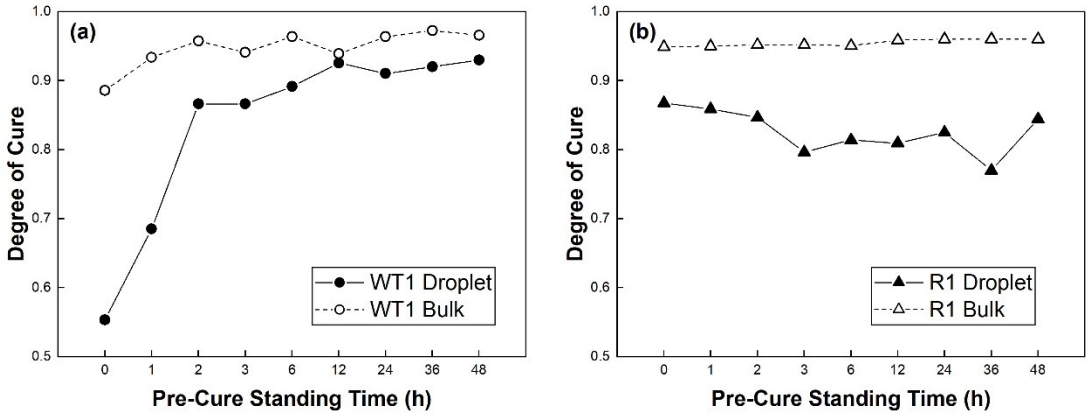

Figure 5: Microbond droplet versus bulk matrix degree of cure

Microbond testing results following the introduction of the same 0–48 h room temperature pre-curing time before the standard curing schedule are shown in Figure 6. The inclusion of a room temperature pre-cure stage had a significant effect on the apparent IFSS of WT1 specimens. Apparent IFSS of R1 samples was entirely independent of pre-cure standing time.

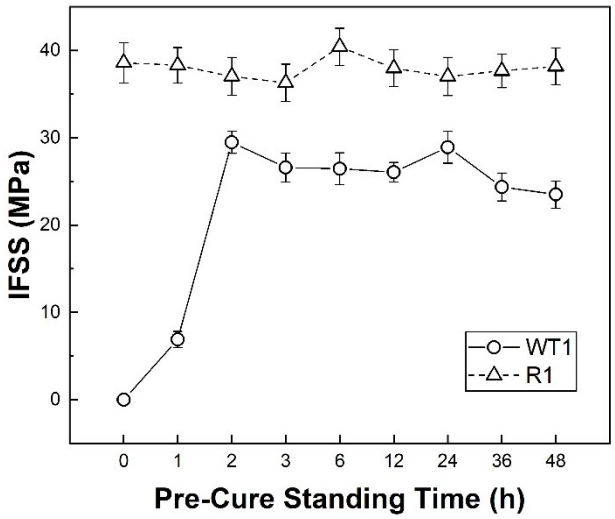

Figure 6: Apparent IFSS versus pre-cure standing time

We report good agreement between micromechanical and spectroscopic methods, in that increased IFSS was measured when droplets had higher degrees of cure. IFSS appeared to show a linear relationship with microdroplet degree of cure up to conversion of approximately 0.8, after which further increases in droplet cure state were not reflected in apparent IFSS. It is possible that an upper threshold IFSS value limited by the adhesion properties and tensile strength of the unsized fibres was reached. Due to the absence of sizing on the fibres, however, it is reasonable to suggest that IFSS was largely dictated by the cure state of the droplet.

The differences in droplet curing behaviour between diamine and tetrafunctional amine cured specimens may be indicative of distinct phenomena that contributes to reduced droplet cure states. For WT1 droplets, diamine curing agent evaporation appeared to result in insufficient amine groups necessary to produce a strongly cross-linked network structure in the droplet. For R1 droplets, cure state may have been lowered by the formation of an imine group or interaction with atmospheric moisture. These phenomena may contribute to depletion of active amine sites available to react with the oxirane ring and reduce droplet degree of cure.

The ability of micromechanical testing methods to inform macroscale materials selection and processing parameters is predicated on an assumption of comparable polymer chemistry and material properties across both scales. The data presented in this study would indicate that this assumption is often invalid for thermoset systems and hence determination of droplet cure state should be considered when employing the microbond test. It should be considered that these data would suggest that even droplets with “ideal” curing behaviour, may in fact have material properties that are inferior to those of the bulk cured matrix and comparable composite part. Interfacial testing methods are often employed to measure the influence of factors such as fibre surface treatments and the application and screening of sizings. Changes in IFSS as the result of such alterations may be masked by the influence of the cure state of the matrix microdroplet. Thus, the route taken in creating microbond samples, and the potential effect of discrepancies in microscale curing and resulting disparity between droplet and bulk matrix material properties, must be carefully considered by all practitioners of the microbond test.

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4. Conclusions

In this paper, the curing performance of two epoxy resin systems was investigated using the microbond test and FTIR spectroscopy techniques. The following conclusions were drawn:

- Droplets cured on thin steel filaments are suitable models of typical glass fibre/epoxy microbond droplet specimens and enable high-throughput determination of microbond droplet cure state using a conventional benchtop spectrometer.
- Cure schedules used in the manufacture of composite parts produced microbond droplets with degrees of cure lower than that of bulk matrix specimens subjected to an identical thermal history.
- For a commercial epoxy resin system, testable microbond droplets could only be produced when a room temperature pre-curing time of at least 2 hours was introduced.

The method proposed in this study is suitable for use with extended range of thermoset polymer matrices. Further work in this area may involve characterisation of the cure states of vinyl ester and polyester droplets by monitoring the depletion of C=C peak intensities associated with the polymerisation of these matrices.

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