

An overview of some scaling issues in the sample preparation and data interpretation of the microbond test for fibre-matrix interface characterisation

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ABSTRACT

The microbond test has been widely adopted by researchers seeking to characterise the fibre-matrix interface in polymer composites. This test requires the preparation of polymer droplets with a mass as little as 20 ng. This brings with it the possibility of scaling issues causing unanticipated significant differences to the properties and performance of these droplets in comparison to macroscale samples. This paper reviews a number of these potential scaling issues in a range of polymer systems which users of the microbond test should be aware of. Some of these phenomena can affect the magnitude of the test results obtained much more than the fibre-matrix interface effects which the test is used to detect. It is concluded that in many cases the structure and properties of the polymer in such microdroplets is not representative of the same polymer, with the same thermal and environmental exposure history, prepared on the macroscale.

1. Introduction

Over the last fifty years a number of experimental techniques have been developed to assess fibre-matrix interface stress transfer capability. In general these techniques can be classified into two categories depending on the nature of samples used and the scale of testing: on a microscopic scale, microcomposites often involving a single fibre are employed to provide direct measurements of interface properties. In contrast, bulk composite specimens are usually used to measure the interlaminar/intralaminar properties, from which the fibre-matrix interface properties are inferred [1–5]. Unfortunately macroscopic scale interface sensitive composite tests can only give qualitative comparative information about the state of the fibre-matrix interface. Those who require a quantitative characterisation of interface performance will normally resort to employing one of the micromechanical tests.

The test methods in this category include the single fibre pull-out test, microbond test (MBT), single fibre fragmentation test (SFFT) and single fibre push-out test. In these tests, the bond quality at fibre-matrix interface is measured in terms of the interfacial fracture toughness, or the interfacial shear strength (IFSS). Of these tests the MBT and the SFFT are probably the most commonly employed and both have a long list of advantages and disadvantages, of the equipment setup, the sample

preparation, and the data analysis, which must be taken into consideration when deciding which to employ for any specific situation [6,7]. For over a decade our research group has been investigating the use of the MBT in the interface characterisation of many different fibre-matrix systems and we have become aware of a wide range of issues related to this test which are not widely discussed in the literature. This paper reviews some of these important challenges which we believe those wishing to use the MBT should be made aware of. It is not our intention here to imply that the MBT should not be used for interface characterisation. Rather that new or inexperienced users of the test should be aware that the simplicity of the idea of the test should not blind the user to the complexities involved, and in particular that the results from the test must be interpreted in terms of the state of the polymer microdroplet produced during the sample preparation. We have found that it is often the case that the state and structure of these microdroplets are not the same as those of a bulk polymer sample.

2. The scale of the microbond test sample

The microbond (microdebond) was first reported by Miller in 1987 followed by a series of papers covering method development and operation [8–12]. The test is basically a modification of the single fibre pullout test which had already been used extensively to characterise the

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interface strength in fibre reinforced composites and reinforced concrete. From a fibre reinforced composite viewpoint there were a number of challenges of the fibre pullout test which the microbond test addressed. In fibre-matrix systems with high levels of adhesion, or using low diameter and/or low strength fibres, the embedded length required for a successful pullout test becomes very small. This results in a challenge in manufacturing reproducible samples which the microbond test addresses to some degree.

Nowadays the concept of the microbond test is well known to those researchers active in the field of composite interfaces. It requires a method for preparation of appropriate samples consisting of a single fibre embedded in one (or more) polymer microdroplets [6,8]. It also requires a test setup which requires a system to restrain the polymer droplet while the fibre is pulled at a constant rate with measurement of the resultant force. There are a number of configurations which have been investigated for the droplet restraint [5,6,8,13–18]. However, the most common method, which is shown schematically in Fig. 1, consists of a pair of parallel aligned blades whose separation can be controlled to sub-micron level [6,19]. The configuration of the test setup for the microbond has been extensively investigated both experimentally and using modelling techniques [12,20–24] and is not the primary focus of this report. As illustrated in Fig. 1 the dimensions of each droplet must be measured, normally using optical microscopy. Ideally each single fibre diameter should also be measured, in particular for glass fibres and natural fibres where significant fibre to fibre variation in fibre diameter is common. The embedded fibre is pulled while the polymer droplet is restrained by the shearing blades until the droplet debonds. A peak force value (F_{max}) will be recorded and divided by the interfacial embedded area (A_e) to obtain a value for the apparent IFSS for each sample.

Notwithstanding the popularity of the microbond test to characterise IFSS, there are currently no accepted standards for the design of a microbond test setup or for the experimental procedure employed for sample preparation and test conditions. Nevertheless, considerable effort has been expended on experimental and modelling studies of the test rig design and testing conditions. However, it appears that few have apparently considered the possible effects of sample preparation on the microscale and, more often than not, assume that the properties of a microbond droplet are essentially equivalent to those of a macroscale sample. It is worth noting here that, despite the name “microbond” test, the weight of material in these “microdroplets” extends down well into the nanogram range, especially for droplet on fine fibres such as carbon fibres. This fact is illustrated in Fig. 2 which shows the weight of polymer (density = 1) in ellipsoidal droplets ($L/D = 1.2$) on fibres of diameter 17 μm (typical for glass) and 7 μm (typical for carbon). It can be seen that

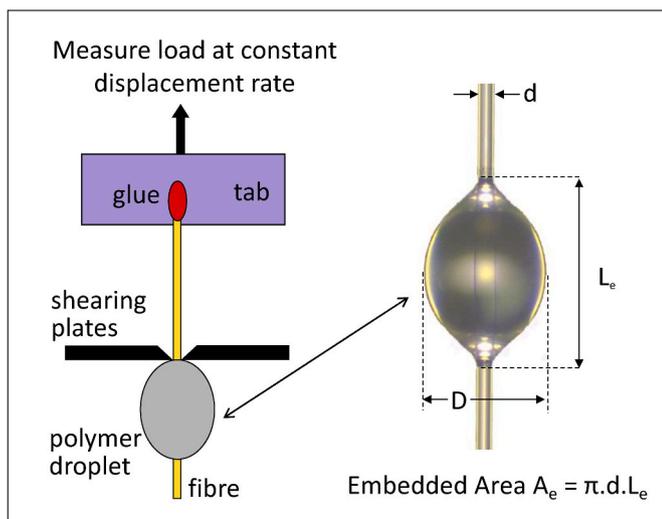


Fig. 1. Schematic diagram of a microbond test setup [6,19].

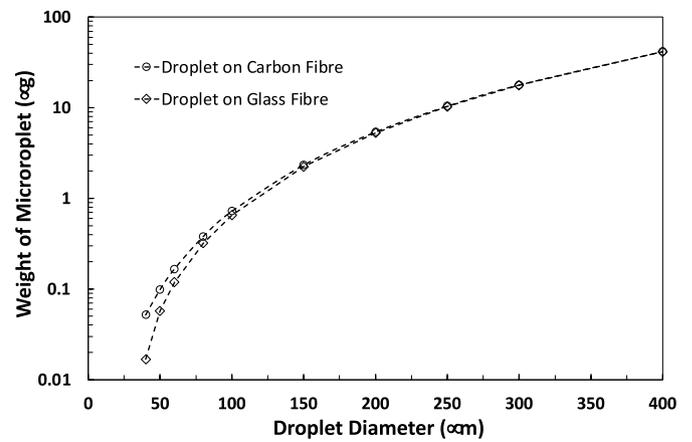


Fig. 2. Weight of polymer in a microdroplet.

for the smallest polymer droplets of 40–50 μm diameter (which were certainly present in Millers first paper) the weight of polymer required is in the 20–80 ng range. Hence one could argue that this is actually a nanoscale testing method. As most experimentalists will be aware the successful use of any characterisation method is highly dependent on being able to prepare a test sample which actually exhibits the properties that it is assumed to possess. However, when one views the test as a nanoscale test there are a number of potential issues which can be raised.

It is clear that the successful application of the microbond test consequently requires well controlled methods for preparing samples on the required micro/nano-scale. As previously mentioned there are no accepted standards for the design of a microbond test setup although the majority will be similar to that described in Fig. 1. There is much greater variation in the sample preparation procedures described in the literature since each fibre-polymer combination will have its individual challenges. Nevertheless, Fig. 3A and B shows some typical sample preparation routes for thermoset and thermoplastic polymer samples. The basic procedure, shown in Fig. 3A, for preparing thermoset samples is very common and has not changed significantly from that described in the seminal papers on the microbond test [8,9]. Isolated single fibres are mounted on a support, commonly the card windows typically used in single fibre tensile testing, using double-sided sticky tape and then firmly secured with glue (often quick-setting cyanoacrylate) on either side of the window. A small amount of the thermoset resin is prepared and then droplets of the resin are applied to the test fibre. This is often done using another mounted fine fibre such as a carbon fibre or steel fibre. After applying the cure schedule appropriate to the resin system the card support can be cut away (as indicated) to supply two samples ready for testing. One frequently observed phenomenon is that the applied liquid resin drop may well break up to form multiple droplets at the point of application (see Fig. 4). This can complicate the post-debond analysis of sliding friction as these multiple droplets can interfere with each other if the test is continued past the first debonding peak.

Due to the relatively high viscosity of molten thermoplastic polymers the above method is generally not suited to producing testable microbond specimens. Where feasible it may be possible to adapt the thermoset method using a solution of thermoplastic polymer. However, such a procedure adds additional questions about the relevance of the test specimen to bulk thermoplastic composites which have usually been melt processed. The sample preparation method shown in Fig. 3B is one which may be used with a wide range of thermoplastic. It involves first pulling a fine thread of the test polymer from a molten pellet (which may be placed on a glass slide on a hotplate). The test fibre is once again mounted with glue on to an appropriate support, which must be resistant to the required processing temperature of the thermoplastic polymer to be tested, Fig. 3B shows a steel washer as support but other

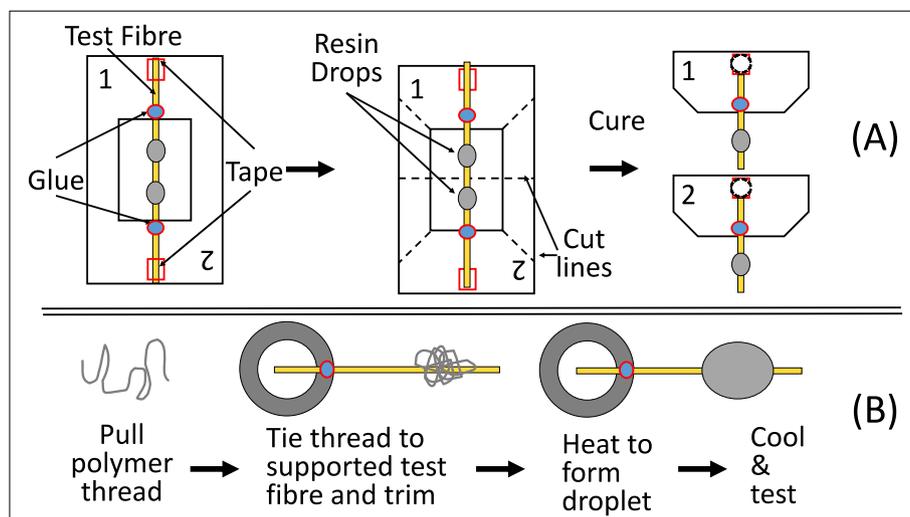


Fig. 3. Schematic of microbond test sample preparation method for A) thermosets and B) thermoplastics.

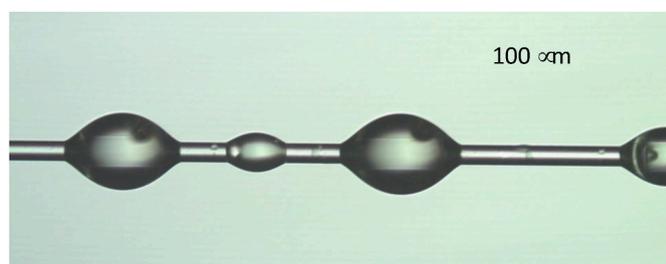


Fig. 4. Image of multiple epoxy droplets formed on a single glass fibre.

methods are possible. The required mass of polymer thread is then carefully tied around the test fibre and trimmed off as necessary. This assembly can then be heated to the required processing temperature and the molten polymer thread can then form a microdroplet. The droplet formation time varies with the polymer type, molecular weight and the applied temperature. The heating (and cooling) step can best be performed under an inert atmosphere to prevent thermo-oxidative degradation.

This scaling issue is central to the discussion that follows, both on potential and actual observed issues with microbond sample preparation. It is also useful for the reader to be aware that the analysis that follows makes use of the published observations [15,19,25,26] that microbond test results are directly related to the testing temperature relative to the glass transition temperature (T_g) of the polymer in the microdroplet. This temperature difference and the resultant effects on the modulus of the droplet polymer material can often dominate the results irrespective of the actual “adhesion” between the fibre and polymer. This effect has been confirmed with investigations of the change in IFSS of both (unsized) GF-polypropylene and (aminosilane sized) GF-epoxy as a function of test temperature [15,25]. Most important to the understanding of many of the results discussed in this paper are the published results on changes in the microbond IFSS of GF-epoxy where the test temperature was kept constant and droplet T_g was changed by changing the epoxy to curing agent ratio [19,25]. Some of the results from these investigations are summarised in Fig. 5 which shows the normalised IFSS versus the normalised polymer modulus [15, 25]. It can be seen that the normalised IFSS results for these diverse polymers all fall on the same trendline when considered in terms of the polymer normalised modulus (at test temperature).

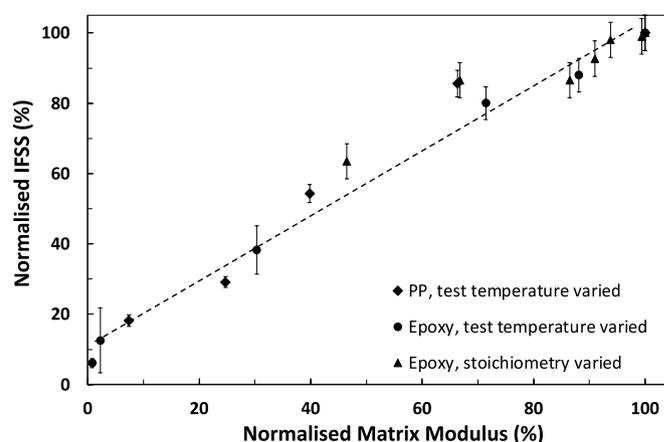


Fig. 5. Dependence of normalised microbond IFSS on normalised droplet modulus [15,24].

3. Some issues with thermoplastic droplet sample preparation

3.1. Polymer degradation effects

The microbond test was originally developed using low viscosity thermosetting resins which could form microdroplets on fibres with relative ease. One of the main challenges when using thermoplastic polymers in the microbond test is the relatively high viscosities of thermoplastic melts. Formation of droplets require high temperatures – certainly above melting temperature and often much higher than normal processing temperatures to enable low enough viscosity to be achieved such that a droplet will form within a reasonable timescale. These high processing temperatures combine with the high surface to volume ratio of the microdroplets and the very short distances involved for the diffusion of reactants such as oxygen to challenge the thermal stability of the polymer. Some polymers are more sensitive than others to thermo-oxidative degradation. Polypropylene (PP) is a thermoplastic composite matrix which is much investigated in terms of its adhesion to reinforcing fibres due to the relatively low level of fibre-PP interaction resulting from the apolar nature of PP. Stabilised commercial PP products are highly robust in terms of their processability. However pure PP is highly susceptible to thermo-oxidative degradation and it has only been through the development of excellent stabilisation packages that PP has been able to achieve its high level of success in the polymer and

polymer composite marketplace. However these stabilisation packages are developed for use in large scale processing. Yang et al. – researched the issue of PP stability and found that the thermal history of PP during microbond sample preparation is critical to obtaining meaningful IFSS results [27].

Their results for microbond peak load versus embedded area are shown in Fig. 6 for GF-PP samples where the droplet preparation has taken place under nitrogen or under air (for 4 and 6 min). It can be clearly seen that the apparent IFSS for this GF-PP combination is significantly affected by the thermal load (temperature and time) and the atmosphere (air or nitrogen) in terms of thermal-oxidative degradation in PP matrix. Without degradation of the PP microdroplet the measured average IFSS is over twice the magnitude obtained from degraded PP samples, giving a value of approximately 8 MPa. Fig. 7 shows SEM micrographs of PP microdroplets prepared under air and nitrogen where the glass fibre had no surface coating which could induce any unexpected issues. The droplet prepared under air shows a mainly featureless surface which might be typical for an amorphous, thermally degraded, PP whereas the droplet prepared under nitrogen clearly shows a “normal” spherulitic structure.

Yang et al. also presented results on the hot-stage microscopy observation of the degradation of PP microdroplets during their processing [27]. It was noted that the PP droplet diameter decreased immediately the processing temperature of 220 °C was reached and that smaller droplets degraded faster than larger ones. No oxidation induction time was observed in these samples despite the fact that the PP was a standard commercial product containing a full anti-oxidant package. Hence the strategy of simply minimising processing time in air does not deliver a PP droplet which is representative of bulk PP and consequently PP microdroplets must be prepared under an inert atmosphere if useful representative data are to be obtained on the IFSS in PP composites. Clearly this means that any data published on PP IFSS obtained using microbond testing where samples were prepared under air must be treated as questionable. In more general terms the experimentalist must ask themselves if the method used to prepare a thermoplastic polymer microdroplet changes the material in the droplet significantly. This question will certainly become more relevant for researchers wishing to use the microbond test with engineering plastic, such as PES and PEEK, which require processing temperatures well above 300 °C.

3.2. Spherulite number and boundaries

Another interesting example of potential scaling issues can also be found in PP microdroplets. The IFSS value obtained from the microbond test is highly dependent on the droplet modulus-temperature relationship. The modulus of semicrystalline thermoplastics such as PP is

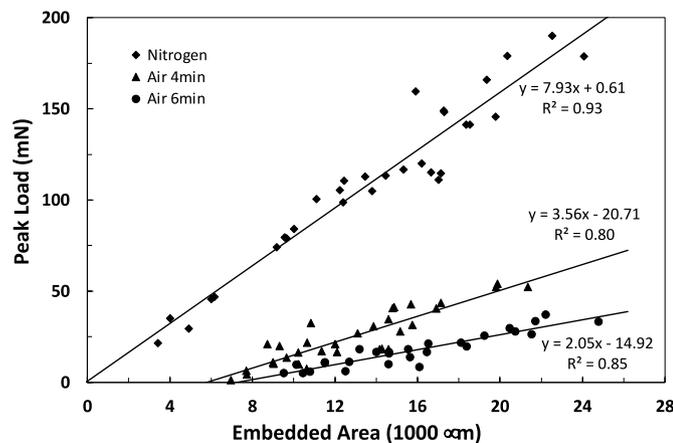


Fig. 6. Microbond test results for GF-PP sample prepared under air and nitrogen [27].

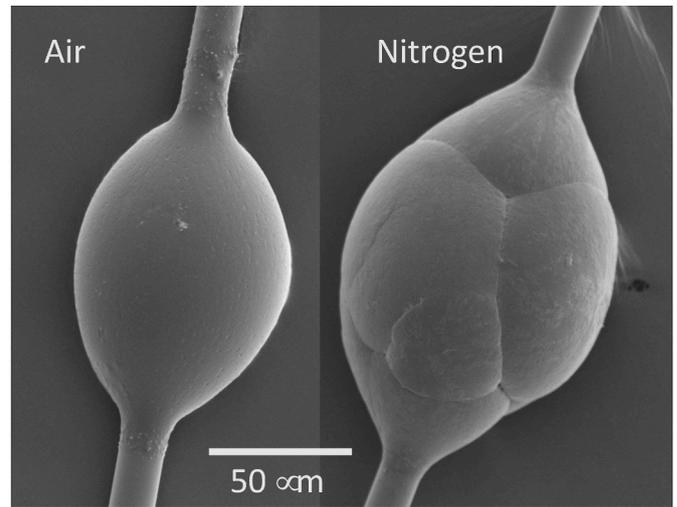


Fig. 7. SEM micrographs of PP microdroplets prepared under air and nitrogen atmosphere.

dependent on the polymer semicrystalline morphology. The thermal degradation example given above is a case in point where the absence or lowering of the droplet crystallinity leads to low modulus and low IFSS [27]. The crystalline structure of these polymers depends on nucleation density and values for PP typical nucleation density ranges from 10^{12} to 10^{14} nuclei per cubic metre [28,29]. Initially that appears to be a large number but when taken in combination with the nanovolumes of some microbond droplets it is possible to find a range of polymer droplet sizes which theoretically contain no heterogeneous nucleation sites. This is illustrated in Fig. 8 which shows the theoretical number of nuclei present in PP droplets obtained by multiplying the above nucleation density range by the range of polymer droplet volumes used Fig. 2. It can clearly be seen that the theoretical number of nuclei in the smallest droplets can fall below one. Since there cannot be fractional nuclei this means that some of the smallest droplets would have no nuclei and hence would be totally amorphous with drastically different mechanical performance from bulk semi-crystalline PP.

Fig. 9 shows SEM micrographs of some PP droplets where the spherulitic morphology is visible. Although there are spherulites present in all the droplets, it can be seen that the smaller droplets actually contain very few spherulites. The number of spherulites per droplet was estimated from a number of such SEM micrographs and the results are also plotted in Fig. 8. Given the potential errors in estimating the content of a 3D droplet from a 2D image the experimental data appear to follow the theoretical trends quite well with both PP polymers appearing to

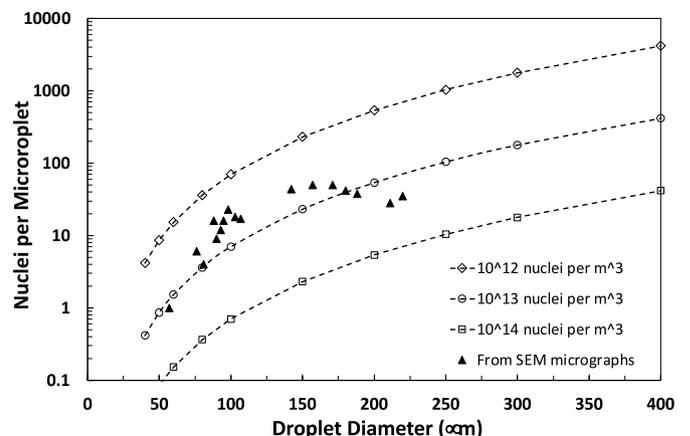


Fig. 8. Possible range of number of nuclei in a PP microdroplet.

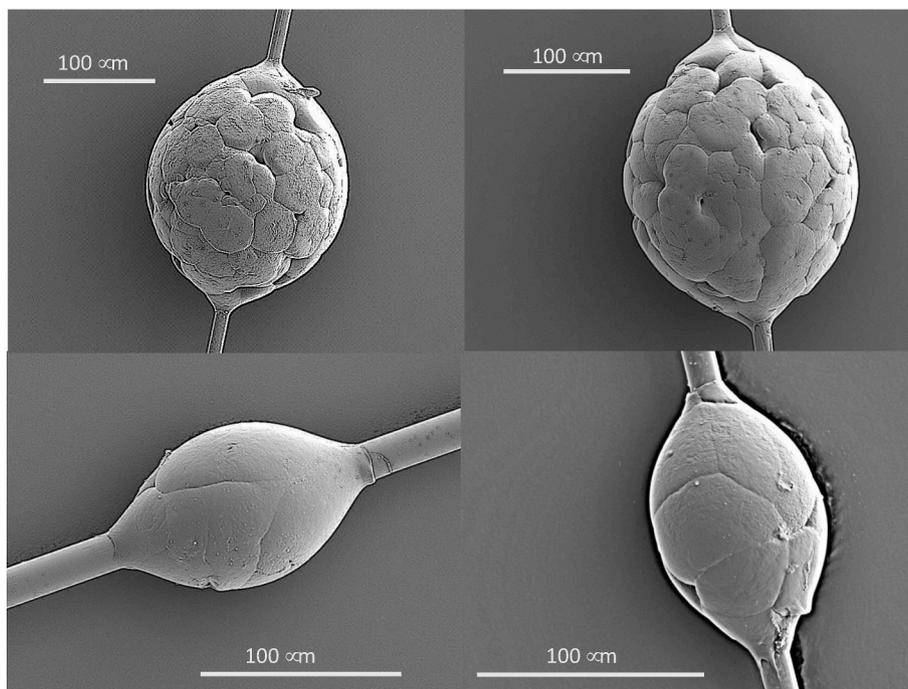


Fig. 9. SEM micrographs showing spherulitic structure of PP microdroplets.

have a nucleation density of around 10^{13} m^{-3} . It is a relevant question at this point to ask whether a PP microdroplet containing only a few nuclei would exhibit the same properties as a macroscopic sample of the same polymer.

3.3. Droplet morphology

The micrographs in Figs. 7 and 9 also reveal another potential issue related to semi-crystalline structure of thermoplastic microdroplets. It is well known to those who have engaged in hot-stage microscopy studies of the crystallisation of thermoplastics that the shrinkage of the polymer during crystallisation can lead to obvious boundaries between spherulites which often contain air sucked into the boundary due to shrinkage in the final stages of crystallisation and cooling. This effect can be clearly seen in the SEM images in Fig. 9. A consequence of this phenomenon is that the surface of the droplet is not smooth and continuous in the manner in which it is always visualized in the diagrams of the microbond test. This is also the case for the many publications which have reported computer modelling of the stress distributions in the microbond test. Furthermore, in most modelling of the microbond test it is assumed that the polymer droplet is homogeneous. However, it is clear from Figs. 7 and 9 that the PP droplets in the images contain “spherulites” and phase boundaries of the same order of magnitude of dimension

as the droplets themselves. The possible effects of this heterogeneous droplet internal structure, and of the rough and pitted microdroplet surface, on the results of the test remain unexplored at this time, but clearly questions about crack initiation and stress concentrations can be posed here.

The presence of a non-uniform surface on microdroplet surfaces is not limited to thermoplastic polymer droplets. Thomason et al. used the microbond test to investigate the relationship of chemical and physical parameters in the micromechanical characterisation of the apparent interfacial strength in glass fibre epoxy systems [25]. They presented evidence that microdroplets are often deformed by residual stresses generated during the cure of the droplet (see Fig. 10). Fig. 11 shows a range of microdroplet deformations which they observed. These range from numerous small pitted craters on the droplet surface to massive deformations of droplet shape. As part of the measurement of IFSS using the microbond test the droplet dimensions are measured using optical microscopy. During this procedure obvious non-symmetric droplet samples are usually eliminated from being tested. However, Thomason et al. noted that these droplet deformations are not clearly visible in optical microscopy – unless you are specifically searching for them [25]. Depending on the plane of observation in the microscope, many of the deformations shown in the SEM micrographs in Fig. 11 might not be picked up in optical microscopy. Furthermore the smaller pitting of the droplet

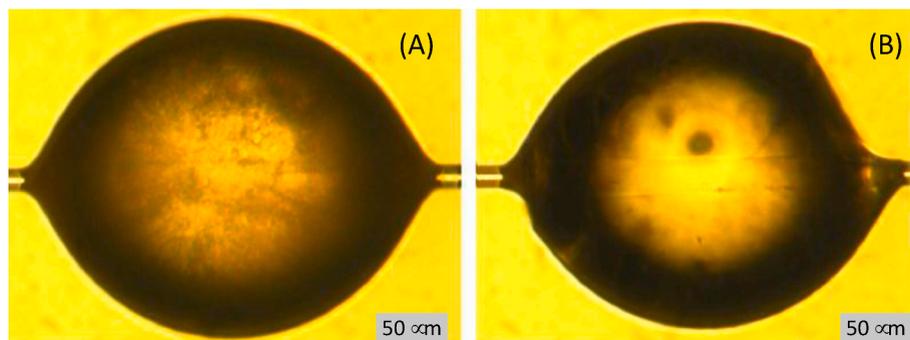


Fig. 10. Optical micrographs of epoxy droplet on glass fibre. (a) Before cure. (b) After cure [25].

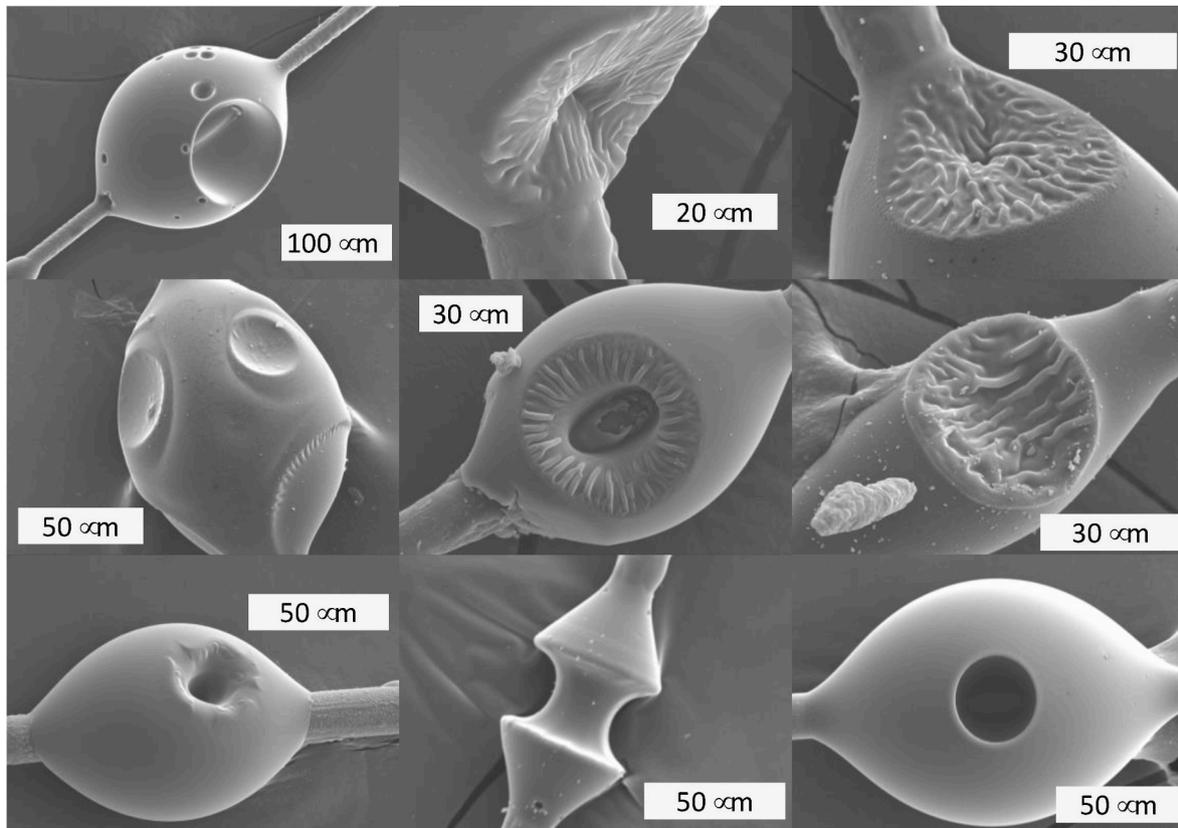


Fig. 11. SEM micrographs showing various deformations of cured epoxy microbond samples [25].

surface would probably also not be observed during the optical microscopy examination. Since SEM observation of every microdroplet to be tested is impractical, and would very likely alter the response of the sample in the microbond test, it seems likely that many tested thermoset microdroplets are also not uniform and smoothly surfaced. The effect that these imperfections in droplet shape may have on the result of a microbond test remains unknown at this time.

3.4. Moisture absorption

An important modifier of polymer performance is the absorption of moisture which is generally acknowledged to lower the T_g and modulus of many common polymers. Polyamide (PA) is an important engineering polymer used in the thermoplastic composites. It is well known that PA absorbs relatively large amounts of moisture and that this significantly lowers the T_g and mechanical performance of the polymer [18,30]. Not only does PA absorb large amounts of moisture but the process is rapid in comparison to many other polymers. Given the very small scale of the microbond test droplets this means that questions must be asked about the moisture content and T_g of polymer microdroplets which are prepared, stored and tested in the presence of a humid atmosphere (which is mostly the case). The following discussion focusses on the important case of PA, however nearly all polymers absorb moisture to some degree and hence the conclusion may well be generalised in proportion to the moisture sensitivity and T_g of any particular polymer type.

The theoretical treatment of moisture absorption in polymers due to Fickian diffusion is well established and the background equations will not be derived here. In terms of what may be happening in a polymer microdroplet we refer to Equation (1) for the time dependent water uptake $M(t)$, as a fraction of the final equilibrium of M_{e_c} in an infinite parallel sided slab of thickness (a) made of a polymer with diffusion coefficient (D) [31].

$$\frac{M(t)}{M_e} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- (2n+1)^2 (D\pi^2 t / a^2) \right] \quad (1)$$

An analogous derivation will also supply the more useful Equation (2) for diffusion into a spherical particle radius (a) [31].

$$\frac{M(t)}{M_e} = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp \left(- Dn^2 \pi^2 t / a^2 \right) \quad (2)$$

The average moisture uptake predicted for a 100 μm thick infinite slab and for spheres of 100 μm and 200 μm diameter for a typical room temperature, 50% RH, PA diffusion coefficient value of $0.4 \times 10^{-12} \text{ m}^2/\text{s}$ are shown in Fig. 12. It is noted here that this is actually falling into another potential scaling issue trap by using a value based on

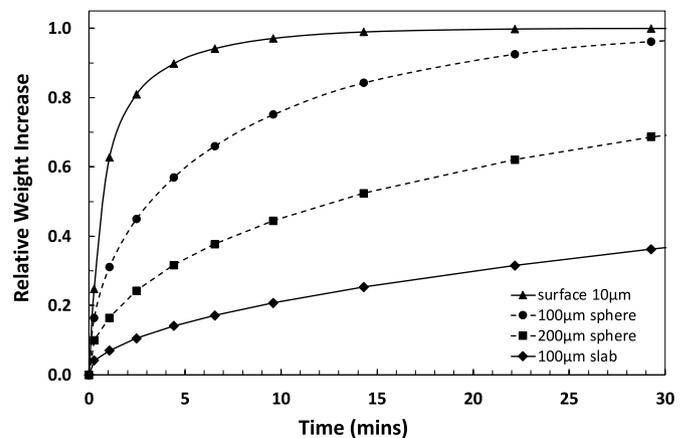


Fig. 12. Water concentration profile in various polyamide shapes ($D = 0.4 \times 10^{-12} \text{ m}^2/\text{s}$).

macroscopic samples. However, no values of D are currently available for microdroplets which may for example have a different crystalline microstructure and hence have a different moisture absorption profile. Comparing the results for a flat slab and a sphere it can be seen that moisture uptake is much more rapid for a sphere. It seems reasonable to propose that the moisture uptake profile for a microbond droplet will be much closer to that of a sphere than of an infinite slab. It can be observed that within 15 min the average moisture content of a 100 μm sphere is above 80% of the final equilibrium value. The actual time that any particular droplet will be exposed to a laboratory atmosphere during testing will vary from measurement to measurement and operator to operator. However, we consider 15 min to be a rough minimum time required to mount and test a single microbond sample. Of course this also assumes that all samples are being stored in a dry atmosphere prior to testing. We suggest that this is probably very rarely the case and it is more likely that the full set (anywhere between 10 and 50 individual samples) of any particular microbond samples will be sitting in the laboratory atmosphere awaiting individual mounting and testing. Consequently, unless extreme precautions are taken, it seems likely that most individual microbond samples are tested at a point where they contain a completely undefined moisture content. Up to this point we are considering the average moisture content of the droplets. However, Fig. 10 also shows the moisture concentration in the surface 10 μm layer of a 100 μm diameter sphere and this deviates strongly from the average values. Clearly the moisture concentration distribution within a PA microbond droplet can also vary enormously within the first 30 min of exposure to a humid atmosphere. Hence the moisture content profile within individual microbond droplets and from droplet to droplet is a complex function of droplet polymer, droplet dimensions, laboratory atmosphere and exposure time.

The consequences of this problem for the outcome of a microbond measurement can be very significant for moisture sensitive polymers such as PA whose T_g will drop from above to below room temperature when going from dry to saturated [30] along with the associated large drop in polymer modulus. In one of the few available papers exploring this issue Downes and Thomason built a microbond test into a dynamic mechanical analyser fitted with a temperature controlled humidity chamber [18]. They presented results on PA6 microbond measurements with steel and glass fibres.

Samples were tested at different humidities after equilibration for 1 h at the chosen RH value. Average IFSS values dropped from 25 MPa to 12 MPa when the humidity level was changed from low to high (RH 0%–90%) which would change the PA T_g (of a macroscopic sample) from approximately 70 $^{\circ}\text{C}$ down to 5 $^{\circ}\text{C}$. Although the case presented here for PA illustrates an extreme example it must be considered that most polymers will absorb some degree of moisture which may contribute to variability in the measurement of IFSS using micromechanical test specimens. However, when dealing with moisture sensitive polymers such as PA it is clearly essential to consider the environmental control of the test specimens and to understand the state of the moisture content profile of the microdroplets under test.

4. Some issues with thermoset droplet sample preparation

4.1. Mixing

One of the potential scaling issues in the preparation of thermoset polymer microbond samples is the question of obtaining homogeneous mixing of components on the microdroplet scale. In general microbond sample preparation requires the mixing of relatively small batches (1–2 g) of polymer which are sufficient for many hundred droplets. The components of thermosetting resins are often mixed at relatively high viscosity and often contain low concentration of critical components, typically around 10:1 ratio of epoxy to curing agent and 1–2% catalysts in some epoxy and vinyl ester systems. The sample preparation method has to strike a balance between the competing requirements of.

- using vigorous mixing to obtain a homogeneous mix on sub-microgram scale
- needing to mix gently to minimise air entrapment
- minimising use of vacuum to remove entrapped air due to loss of volatile components and increased time of reaction prior to application
- limitations on the temperature-time profile of mixing due to the reactivity of the system
- the sensitivity of some thermoset components and reactions to moisture, oxygen, and other unknown contaminants

The scale of the work required to systematically investigate all of these parameters across the wide range of available thermosetting systems is enormous and consequently little evidenced in the available literature on microbond testing. Although not every system will be sensitive all of these issues in the microbond test, many will be affected by some of them, and the lack of systematic investigation and publication on the effects of these parameters on the results of microbond testing is troubling.

4.2. Issues with epoxy thermoset samples

While the use of the microbond test to characterise the adhesion between various fibre and thermosetting polymers has been widely reported in the literature, only a very small proportion of authors have commented on the difference in the behaviour of matrix materials at the microscale and the implications this holds for the applicability of the test. Interestingly, only shortly after the much cited seminal paper on microbond testing from Miller et al. [8], a rarely cited paper by Haaksma and Cehelnik [20] listed the observation of a number of issues with sample preparation of microdroplets which would seem to point towards some scaling issues with the polymerisation of thermosetting resins on this scale. The authors reported that it was “impossible to obtain an interfacial shear strength value” when using the same cure cycle conditions used to prepare single fibre fragmentation test specimens. DGEBA/m-PDA epoxy droplets did not cure on carbon, glass or aramid fibres, indicating microscale curing performance was independent of the fibre used. Examination of droplets using FTIR showed spectra corresponding to the presence of unreacted resin and complete loss of curing agent which was attributed to curing agent evaporation. Rao and Drzal examined the curing performance of the same epoxy system in both microdroplets and thin films. They also concluded that evaporation of curing agent could lead to issues with the microbond test samples and concluded that “extreme care must be taken to ensure careful measurement of mechanical properties of small dimension samples of any system where a volatile curing agent is used” [32].

Zinck et al. reported that the physical and mechanical properties of microdroplets may differ significantly from the bulk matrix material, citing that epoxy droplets were especially vulnerable to this issue due to deviations in stoichiometry arising from diffusion/vaporisation of the curing agent, surface oxidation and potential hydrolysis of hardener during the early stages of the cure [33,34]. Zinck and Gérard later reported that extrapolation of microscale results to macroscopic behaviour must be considered with a great deal of caution due to polymeric microdroplets exhibiting properties different to that of the bulk matrix [35]. Losses in stoichiometry due to specific droplet geometry of microdroplets based on DGEBA epoxy resin cured with both aliphatic and aromatic amines and anhydrides were cited. A comparison of the plasticisation of microscale versus bulk specimens using thin films as models of microcomposites revealed that T_g values were some 50 $^{\circ}\text{C}$ below that of bulk matrices.

Bryce and Thomason investigated the state of cure in microdroplet samples with different epoxy resin systems and a range of different fibres [36–38]. Two commercial diamine-cured epoxy systems did not produce testable droplets when prepared using the normal recommended cure schedule. Cured droplets suitable for microbond testing could be only

formed after significant modification of the recommended macroscale curing schedule. It was not possible to accurately measure the IFSS of samples cured immediately at elevated temperature due to plastic deformation of the samples during microbond testing (see Fig. 13 a&b). However, the inclusion of a room temperature (RT) pre-cure stage had a profound effect on the apparent IFSS of both these two resins. Fig. 14 shows that an initial RT standing time of 2 h was sufficient to ensure good curing and a measurable IFSS value. Further increases in RT standing times of up to 48 h showed no further significant changes in the microbond IFSS values. The improvement in curing performance observed with a RT standing time was attributed to comonomers reacting at low temperature which prevented vaporisation of the curing agent. Conversely, the curing performance of epoxy droplets cured with tetrafunctional triethylenetetramine (TETA) was entirely independent of pre-cure standing time and microdroplets cured consistently across the range of schedules investigated. It was suggested that the higher IFSS values observed for the TETA cured system could be due to the higher T_g values of the droplets.

Bryce has also shown that curing epoxy droplets under inert atmosphere resulted in no significant differences in the values of IFSS obtained in these systems [37]. He further showed that the curing performance of both commercial difunctional amine systems was independent of the type of fibre used. Microbond samples subjected to the same immediate elevated temperature curing schedule failed to cure whether applied to glass, carbon, and steel wire filaments [37]. It was noted that the main components of the curing agent package of these commercial systems was IPD and PPD. Microbond samples were also prepared with DER 332 DGEBA epoxy resin cured with stoichiometric amounts of only IPD or only PPD curing agents. These microbond samples also failed to cure when exposed to immediate elevated temperature curing. However, these samples also appeared to cure well after being allowed to stand and partially react before post-curing [37]. Further investigation revealed that curing microdroplets with amines with a higher number of reactive hydrogen atoms and increased functionality (TETA = 6, TEPA = 7) appeared to play a role in the ability of microbond samples to cure to a high degree and retard the effects of curing agent evaporation (see Table 1) [37,38].

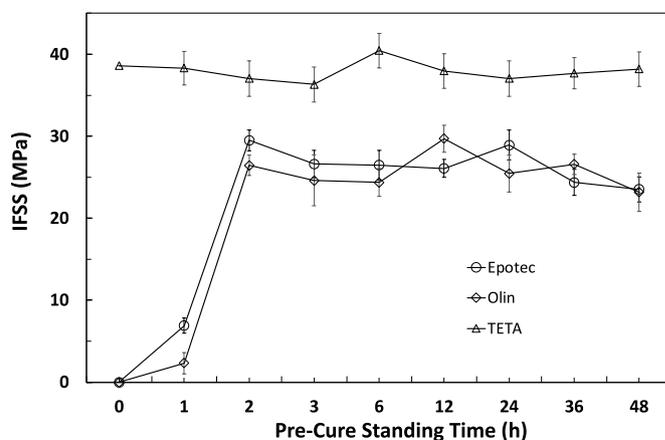


Fig. 14. Relationship between apparent IFSS and pre-cure standing time [38].

Bryce and Thomason further developed a combination of FTIR and thermal analysis techniques to show the cure state of their epoxy microdroplets was consistently lower than that of bulk matrix specimens subjected to the same temperature schedule [36–38]. Good correlation was shown between microbond test results and spectroscopic methods in that an increase in interfacial shear strength was associated with spectra indicating droplets were closer to the stoichiometric ratio (so less loss of curing agent) and had both higher degrees of cure and glass transition temperatures. Fig. 15 shows the much lower degree of cure (conversion) of the epoxy in a microdroplet compared to a bulk polymer sample when using the recommended cure schedule starting immediately at elevated temperature. Fig. 15 also shows the close correlation between microbond IFSS and droplet degree of cure of one of the epoxy systems shown in Fig. 14 which exhibited untestable “soft droplets” when subjected to the recommended bulk polymer curing schedule. Testable droplets were only obtained with this system by allowing an initial cure (or standing time) of 2 h at room temperature. The authors concluded that the values of apparent IFSS obtained from thermoset droplets are strongly influenced by the cure state of the matrix and may

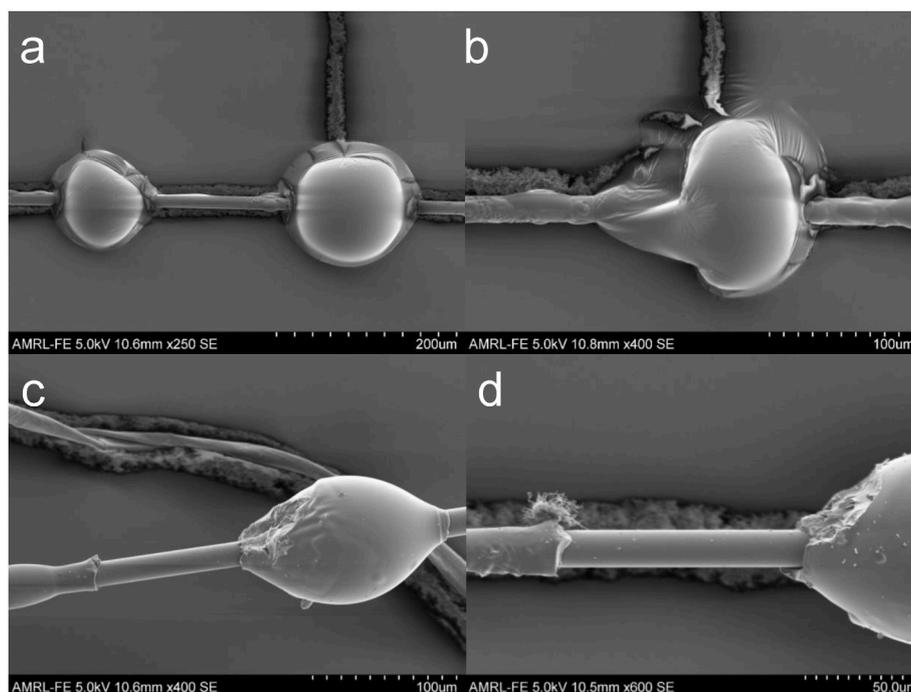


Fig. 13. SEM micrographs of poorly reacted, plastically deformed, (a–b) droplets which had no initial standing time and well reacted, successfully debonded, (c–d) droplets which did have a standing time before elevated temperature curing [37,38].

Table 1
Summary of epoxy curing agent chemistry and microbond curing performance [37].

Amine	Functionality	Ratio (phr)	Vapour Pressure (Pa)	Standard Schedule	Cure With Standing Time
Epotec	4	35.0	100 (@20 °C)	No cure	Cured
Olin	4	31.0	<1.33 (@20 °C)	No cure	Cured
IPD	4	25.0	1.57 (@20 °C)	No cure	Cured (inconsistent)
PPD	4	33.8	100 Pa (@100 °C)	No cure	Cured
DAP	4	10.9	<1100 (@20 °C)	No cure	No cure
DETA	5	12.1	Not available	–	No cure
TETA	6	14.3	<1 (@20 °C)	Cured	Cured
TEPA	7	15.9	Not available	Cured	Cured

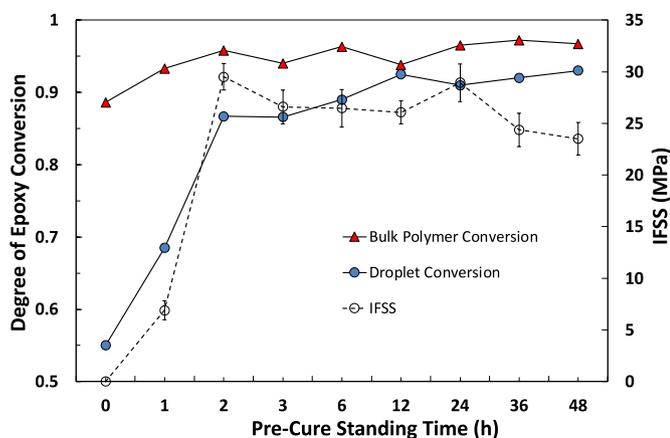


Fig. 15. Comparison of apparent IFSS for the Epotec epoxy system and the degree of epoxy conversion in a microdroplet versus a bulk polymer sample with different pre-cure standing times [38].

be susceptible to a range of microscale curing phenomena depending on the curing agent selected. Their epoxy microdroplets have significantly different chemical and physical properties compared to bulk scale polymerized polymer and all the epoxy systems which they investigated suffered from these issues to differing levels. They further stated that curing behaviour of microbond droplet specimens should always be considered when analysing and interpreting results of the microbond test and this may be of particular concern in glass fibre/epoxy systems due to the wide range of curing agent chemistries available and the small droplet sizes typically involved in the test.

4.3. Issues with vinyl ester thermoset samples

A significant volume of data regarding the microbond testing of various fibres with epoxy resins and with many different thermoplastic polymers can be found in the literature. Reports on microbond testing using polyesters, and in particular, vinyl esters are less prevalent although some can be found [39–42]. Work by Ash et al. attributed incomplete polyester microbond sample curing and subsequent data scatter to evaporation of 50–60% of the initial styrene content out of the droplets [39]. Dirand [40] and Laurikainen [41] reported a similar hypothesis relating to evaporation of styrene out of vinyl ester microbond samples. Significant problems were noted during their microdroplet sample preparation using the picolitre scale volumes, which resulted in

poor curing of the resins. Based on the observations made on the behaviour of their VE resin, and on previous work presented on microdroplet testing of a similar VE resin, it was proposed that the cause of the problem was vaporisation of the styrene from the resin droplets [40]. Laurikainen claimed that this effect could be counteracted by placing the curing droplets in a high styrene content atmosphere such as a closed container [41]. More recently Bénéthuilère et al. also stated that they used this method successfully when preparing microdroplets with VE resin [42].

VE resins can have complex formulations which use small amounts of initiator and catalysts. Although the exact make-up of these low concentration additives is not always available for commercial VE resin systems it is well known that these families of compounds can be sensitive to the presence of oxygen in the environment [43,44]. For large scale bulk polymerisation this may not be a problem for some VE systems. Nevertheless, it has been shown that the presence of oxygen can significantly inhibit the polymerisation reaction of VE resins [43,44] and the strength of VE resin samples cured in an open mould exposed to the air have been shown to be reduced by up to 65% [44]. It was noted that this effect could become increasingly pronounced as specimen thickness is reduced and could even become “catastrophic” for very thin samples. Given the previous discussion of the scale of the microbond droplet and in particular the surface to volume ratio and the short diffusion lengths, it might be expected that curing of VE microdroplets could also exhibit some issues.

Thomason et al. have recently presented some results indicating that curing of VE microdroplets can indeed be problematic [45]. The issue of undercured “soft” microdroplets when using a low viscosity bisphenol epoxy based vinyl ester resin, with a 50% styrene content, mixed with an organic peroxide type C initiator was reported and discussed. Values obtained for the microbond IFSS of this resin with a commercially available glass fibre GF (SE3030) are given in Fig. 16. Very low values of apparent IFSS were obtained when initial curing for 24 h was carried out under an air atmosphere (Air). In reality the droplets did not cure and solidify sufficiently to bear load, so there was no measurable interfacial strength by this method. Allowing the droplets to cure in a styrene rich atmosphere, to minimise styrene evaporation from the droplet, did produce a small improvement in the apparent IFSS (Styrene). However, the droplets did still exhibit appreciable deformation during load application indicating that their T_g was still below room temperature. Performing the initial 24 h cure under inert nitrogen (N₂) allowed sufficient curing of droplets such that they could bear load during the microbond test, yielding a value of 13.2 MPa. An additional post-cure at 60 °C (N₂ PC) raised the IFSS further to 18.8 MPa. Similar trends, with somewhat lower final values of IFSS, were observed when an unsized fibre (OCb) was used. The conclusion was that the most critical step in the preparation of VE specimens for microbond testing is initial curing

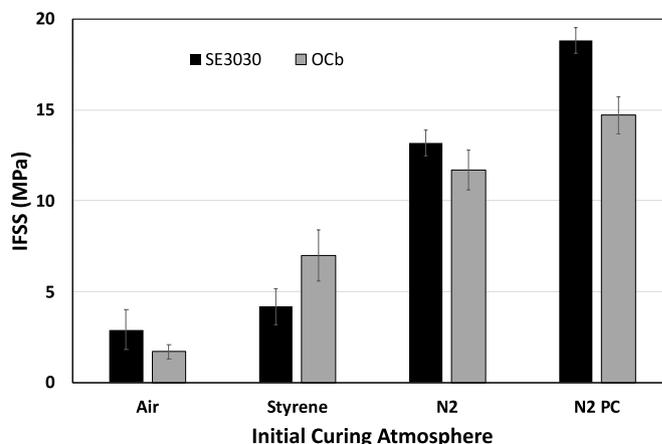


Fig. 16. Influence of curing atmosphere on IFSS of GF-VE system [45].

under an inert atmosphere such as nitrogen. Doing so significantly reduces the oxygen inhibition effect which acts against the network forming polymerisation reaction.

Despite the lack of any standards for the preparation and testing of samples in the microbond test it is certainly the case that there are many similarities in some of the aspects of microbond specimen preparation employed by the many different researchers using the test. One such aspect is that single fibres are frequently mounted to some kind of support, often a card window of the type used in single fibre tensile testing. The fibres are fixed to the support with glue which is frequently of the fast setting cyanoacrylate type (see Fig. 3). The role of this fibre adhesive in microbond testing is only to restrain the individual filaments on the support so that droplets of the resin under study can be applied in a controlled manner. It is not considered that it should have any influence on the test, because it is applied and allowed to fully dry before the resin droplet is introduced. The fibre adhesive is always used in sufficient volume that the fibre will not slip during testing; the embedded length of fibre within this adhesive is many times larger than the embedded length within the resin droplet being tested.

Thomason et al. recently came across an unexpected, and as yet not fully understood, negative interaction of cyanoacrylate (CA) superglue with a microbond fibre-matrix system [45]. Following on from the results on VE curing atmosphere presented above a large number of fibre sizings (Variants on the SE3030 sizing) were screened for IFSS in a range of VE resins, where the samples were all mounted on card windows and secured using CA superglue. These systems all exhibited a microbond IFSS in the 15–22 MPa range. However, most unexpectedly, when the same samples were prepared using an epoxy based glue to secure the test fibres microbond IFSS values in the 40–56 MPa range were obtained. No such large differences in IFSS values for epoxy or PP droplets had been observed between the two sample mounting methods (see Fig. 17).

Further results of the investigation of this phenomenon are also shown in Fig. 17. It can be seen that there was no significant effect of the glue on the IFSS results for unsized bare glass fibres in the VE resin. There was also no glue effect detected when an epoxy compatible fibre (SE2020) was embedded in an epoxy resin droplet. However, a similar large effect of glue on the IFSS was found when using SE3030 in the same epoxy resin droplets. The issue with the superglue lowering microbond IFSS results with the GF-VE system was also checked with a number of other VE resins and VE compatible glass fibres and found to be present in all cases [45]. It was concluded that these results point to some very specific negative interaction between cyanoacrylate glue and the sizing on VE compatible glass fibres which very significantly reduces the level of IFSS measured in the microbond test.

Given the widespread use of cyanoacrylate glue in the mounting of single fibres for microbond testing (and fibre tensile testing) it was

considered expedient to consider the possible nature of the observed negative interaction. It was shown that the effect could not be caused by wicking of the glue along the test fibre to interact with the microdroplet. However, it is known that CA adhesive produces vapour which can react with a variety of chemical compounds on any nearby surface. This phenomenon is the basis of the CA fuming method used by criminal investigators for developing latent fingerprints [46]. A further range of experiments was carried out which confirmed that cyanoacrylate vapours deposit on the fibre test surface during mounting and prior to application of the polymer droplet. It was proposed that the phenomenon appears to be related to the deposition of CA vapours onto the surface of the fibres during the setting of the CA glue before the application of the resin microdroplet. This CA deposit appears to negatively interact with either some component common to VE compatible fibre sizings or may possibly interfere locally with the curing reactions of the applied VE resin droplet resulting in significant lowering of the value of IFSS obtained in microbond testing. Unfortunately the chemical formulation of glass fibre sizings is confidential and so possibilities for further investigation of the specific chemical interaction are limited. Nevertheless, it was concluded that all fibre samples affixed with CA superglue in microbond sample preparation have the potential to have CA vapours deposited on the sample surface. How, or whether, this will affect the results of further microbond testing will be a function of the chemical formulation of the fibre sizing and of the droplet polymer matrix.

5. Conclusions and concluding remarks

The results of the microbond test have been clearly shown to be highly dependent on the properties of the microdroplet (modulus and T_g) and that changes in the droplet properties can have much larger effects on the test outcome than changes in the fibre-polymer interface. The mass of the polymer droplets employed in the microbond test can be as little as 20 ng. It has been concluded that on this scale, in many cases, the structure and properties of the polymer in such microdroplets is not representative of the same polymer, with the same thermal and environmental exposure history, prepared on the macroscale. A large number of examples, in a range of typical composite matrix polymers, have been presented and reviewed as to how this could be the case.

The dilemma facing researchers interested in the composite fibre-matrix interface and its influence on composite macroscale performance is that micromechanical, single fibre, testing is one of the only available routes to directly probe the mechanical performance of the interface region. Nevertheless, the scaling issue challenge in the preparation of microbond droplets that properly reflect the properties of macroscale composites is one that should not be underestimated. This paper has highlighted many of the potential reasons why the microstructure and properties of microbond droplets are not the same as a polymer sample produced on the macroscale under the identical conditions. It seems likely that the list of scaling issues highlighted in this paper is by no means exhaustive. Given the high number of, the many unanticipated, issues highlighted here it seems reasonable to suggest that there are probably many more, as yet undocumented, scaling issues which should be taken into account by researchers using the microbond test. Consequently, it also seems reasonable to suggest that researchers should approach the microbond test assuming that their droplets actually do not reflect the properties of a macroscale sample and consider what that means for the proper interpretation of the test results.

These results may also have significant implications for the reliability of the existing body of literature where the microbond test has been used. There is no obvious single uniform solution to these challenges and each different fibre-matrix combination may be subject to unexpected and previously unpublished artefacts of sample preparation and conditioning that can affect the obtained IFSS values much more significantly than any material-related effects that may be under investigation. It is concluded that great care must be taken in ensuring

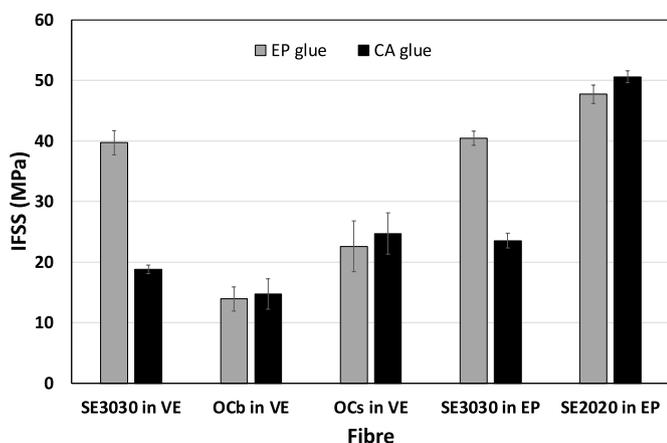


Fig. 17. Influence of fibre mounting glue on the IFSS of various GF-polymer combinations [45].

that any effects observed using the microbond test are evidence of real characteristics of interface behaviour and not artefacts of scaling issues in sample preparation and testing.

Credit author statement

James Thomason: Funding acquisition, Conceptualization, Methodology, Investigation, Writing- Original draft preparation. Writing- Reviewing and Editing.

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Declaration of competing interest

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References

- [1] J. Kim, Y. Mai, *Engineered Interfaces in Fiber Reinforced Composites*, Elsevier Science Ltd, Oxford, 1998.
- [2] F.R. Jones, in: D.M. Brewis, D. Biggs (Eds.), *Handbook of Polymer-Fibre Composites*. Polymer Science and Technology, Longman Scientific and Technical, Essex and New York, 1994.
- [3] P.J. Herrera-Franco, L.T. Drzal, Comparison of methods for the measurement of fibre/matrix adhesion in composites, *Composites* 23 (1992) 2–26.
- [4] S. Zhandarov, E. Mäder, Characterization of fiber/matrix interface strength: applicability of different tests, approaches and parameters, *Compos. Sci. Technol.* 65 (2005) 149–160.
- [5] R.J. Gray, Experimental techniques for measuring fibre/matrix interfacial bond shear strength, *Int. J. Adhesion Adhes.* 3 (1983) 197–202.
- [6] L. Yang, J.L. Thomason, Development and application of micromechanical techniques for characterising interface strength in fibre-thermoplastic composites, *Polym. Test.* 31 (2012) 895–903.
- [7] M.J. Pitkethly, The use of interfacial test methods in composite materials development, in: *Fiber, Matrix, and Interface Properties*, ASTM STP 1290, 1996, pp. 34–46.
- [8] B. Miller, P. Muri, L. Rebenfeld, A microbond method for determination of the shear strength of a fiber/resin interface, *Compos. Sci. Technol.* 28 (1987) 17–32.
- [9] U. Gaur, B. Miller, Microbond method for determination of the shear strength of a fiber/resin interface: evaluation of experimental parameters, *Compos. Sci. Technol.* 34 (1989) 35–51.
- [10] J. Black, R.A. Latour Jr., B. Miller, Failure of desiccator storage to maintain interfacial bond in some thermoplastic/fiber systems, *J. Adhes. Sci. Technol.* 3 (1989) 65–67.
- [11] B. Miller, U. Gaur, D.E. Hirt, Measurement and mechanical aspects of the microbond pull-out technique for obtaining fiber/resin interfacial shear strength, *Compos. Sci. Technol.* 42 (1999) 207–219.
- [12] C.T. Chou, U. Gaur, B. Miller, The effect of microvisc gap width on microbond pull-out test results, *Compos. Sci. Technol.* 51 (1994) 111–116.
- [13] Z. Liu, X. Yuan, A.J. Beck, F.R. Jones, Analysis of a modified microbond test for the measurement of interfacial shear strength of an aqueous-based adhesive and a polyamide fibre, *Compos. Sci. Technol.* 71 (2011) 1529–1534.
- [14] N.S. Choi, J.E. Park, Fiber/matrix interfacial shear strength measured by a quasi-disk microbond specimen, *Compos. Sci. Technol.* 69 (2009) 1615–1622.
- [15] J.L. Thomason, L. Yang, Temperature dependence of the interfacial shear strength in glass-fibre polypropylene composites, *Compos. Sci. Technol.* 71 (2011) 1600–1605.
- [16] B. Morlin, T. Czigan, Cylinder test: development of a new microbond method, *Polym. Test.* 31 (2012) 164–170.
- [17] J.T. Ash, W.M. Cross, J.J. Kellar, Estimation of the true interfacial shear strength for composite materials with the microbond test, in: *Proceedings of the ASME 2013 International Mechanical Engineering Congress and Exposition*, 2013.
- [18] K.A. Downes, J.L. Thomason, A method to measure the influence of humidity and temperature on the interfacial adhesion in polyamide composites, *Compos. Interfac.* 22 (2015) 757–766.
- [19] J.L. Thomason, L. Yang, D. Bryce, R.F. Minty, An exploration of the relationship of chemical and physical parameters in the micromechanical characterisation of the apparent interfacial strength in glass fibre epoxy, *IOP Conf. Ser. Mater. Sci. Eng.* 139 (2016), 012048.
- [20] R.A. Haaksma, M.J. Cehelnik, A critical evaluation of the use of the microbond method for determination of composite interfacial properties, *MRS Proceedings* 170 (1989) 71–76.
- [21] R.J. Day, J.V. Cauch Rodrigez, Investigation of the micromechanics of the microbond test, *Compos. Sci. Technol.* 58 (1998) 907–914.
- [22] H. Heilhecker, W. Cross, R. Pentland, C. Griswold, J.J. Kellar, The vice angle in the microbond test, *J. Mater. Sci. Lett.* 19 (2000) 2145–2147.
- [23] M. Nishikawa, T. Okabe, K. Hemmi, N. Takeda, Micromechanical modeling of the microbond test to quantify the interfacial properties of fiber-reinforced composites, *Int. J. Solid Struct.* 45 (2008) 4098–4113.
- [24] G. Pandey, C.H. Kareliya, R.P. Singh, A study of the effect of experimental test parameters on data scatter in microbond testing, *J. Compos. Mater.* 46 (2012) 275–284.
- [25] J.L. Thomason, L. Yang, Temperature dependence of the interfacial shear strength in glass-fibre epoxy composites, *Compos. Sci. Technol.* 96 (2014) 7–12.
- [26] J.L. Thomason, L. Yang, D. Bryce, R.F. Minty, An exploration of the relationship of chemical and physical parameters in the micromechanical characterisation of the apparent interfacial strength in glass fibre epoxy, *IOP Conf. Ser. Mater. Sci. Eng.* 139 (2016), 012048.
- [27] L. Yang, J.L. Thomason, W. Zhu, The influence of thermo-oxidative degradation on the measured interface strength of glass fibre-polypropylene, *Compos. Appl. Sci. Manuf. Part A Appl. Sci. Manuf.* 42 (2011) 1293–1300.
- [28] A. Pawlak, E. Piorkowska, Crystallization of isotactic polypropylene in a temperature gradient, *Colloid Polym. Sci.* 279 (2001) 939–946.
- [29] J. Krajenta, M. Safandowska, A. Pawlak, The re-entangling of macromolecules in polypropylene, *Polymer* 175 (2019) 215–226.
- [30] J.L. Thomason, G. Porteus, An investigation of glass-fibre reinforced polyamide 66 during conditioning in various automotive fluids, *Polym. Compos.* 32 (2011) 1369–1379.
- [31] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975, pp. 44–103.
- [32] V. Rao, L.T. Drzal, Loss of curing agent during thin film (droplet) curing of thermoset material, *J. Adhes.* 22 (1991) 245–249.
- [33] P. Zinck, H.D. Wagner, L. Salmon, J.F. Gerard, Are microcomposites realistic models of the fibre/matrix interface? I. Micromechanical modelling, *Polymer* 42 (2001) 5401–5413.
- [34] P. Zinck, H.D. Wagner, L. Salmon, J.F. Gerard, Are microcomposites realistic models of the fibre/matrix interface? II. Physico-chemical approach, *Polymer* 42 (2001) 6641–6650.
- [35] P. Zinck, J.F. Gérard, Thermo-hydrolytic resistance of polyepoxide-glass fibres interfaces by the microbond test, *Compos. Sci. Technol.* 68 (2008) 2028–2033.
- [36] D. Bryce, J.L. Thomason, L. Yang, Micromechanical and spectroscopic characterisation of the curing performance of epoxy resins in the microbond test, *IOP Conf. Ser. Mater. Sci. Eng.* 942 (2020), 012019.
- [37] D. Bryce, Investigation of a Micromechanical Methodology for Assessing the Influence of Processing Variables and Fibre Sizing on Composite Interphase, PhD Thesis, University of Strathclyde, UK, 2021.
- [38] D. Bryce, J.L. Thomason, L. Yang, Thermoset Droplet Curing Performance in the Microbond Test, *Composite Interfaces Submitted*, 2022.
- [39] J.T. Ash, W.M. Cross, J.J. Kellar, Estimation of the true interfacial shear strength for composite materials with the microbond test, in: *Proceedings of the ASME 2013 International Mechanical Engineering Congress and Exposition*, vol. 1, 2013, pp. 1–10.
- [40] X. Dirand, B. Hilaire, J.P. Soulier, M. Nardin, Interfacial shear strength in glass-fiber/vinylester-resin composites, *Compos. Sci. Technol.* 56 (1996) 533–539.
- [41] P. Laurikainen, Characterization of the Aging of Glass-Fibre Reinforced Polymers, MSc Thesis, Tampere University of Technology, 2017.
- [42] T. Bénéthuilère, J. Duchet-Rumeau, E. Dubost, C. Peyre, J.F. Gérard, Vinylester/glass fiber interface: still a key component for designing new styrene-free SMC composite materials, *Compos. Sci. Technol.* 190 (2020), 108037.
- [43] T.F. Scott, W.D. Cook, J.S. Forsythe, Kinetics and network structure of thermally cured vinyl ester resins, *Eur. Polym. J.* 38 (2002) 705–716.
- [44] S. Nouranian, J. Lee, G.W. Torres, T.E. Lacy, H. Toghiani, C.U. Pittman, Effects of moulding condition and curing atmosphere on the flexural properties of vinyl ester, *Polym. Polym. Compos.* 21 (2013) 61–64.
- [45] J.L. Thomason, P.G. Jenkins, G. Xypolias, Microbond testing of the interface in glass fibre vinylester composites, *Compos. Interfac.* (2021), <https://doi.org/10.1080/09276440.2021.2011593>.
- [46] S.P. Wargacki, L.A. Lewis, M.D. Dadmun, Understanding the chemistry of the development of latent fingerprints by superglue fuming, *J. Forensic Sci.* 52 (2007) 1057–1062.