

Micromechanical and spectroscopic characterisation of the curing performance of epoxy resins in the microbond test

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Abstract. In the present work, the microscale curing performance of two epoxy resin systems was investigated. It was shown that the degree to which these resins formed cured axisymmetric droplets suitable for microbond testing was influenced by the inclusion of a room-temperature pre-cure stage. Immediate curing at elevated temperature of these systems resulted in the formation of under-cured, soft droplets that deformed under loading. The introduction of a protracted room temperature standing time increased the apparent interfacial shear strength substantially. Fourier-transform infrared spectra generated by a novel technique allowed for the glass transition temperature of microdroplet samples to be determined and detected deviations from stoichiometry. Good correlation was shown between the two methods, in that an increase in IFSS was commensurate with spectra indicating droplets were closer to the ideal stoichiometric ratio, and had both higher degrees of cure and glass transition temperatures.

1. Introduction

The fibre-matrix interface region is critical to the mechanical performance of a composite, thus optimisation of the stress transfer capability of this region is extremely important. Accordingly, it is essential to be able to characterise the interface and associated level of adhesion through a robust methodology in order to fully understand the composite performance. While the use of the microbond test developed by Miller *et al.* [1] to characterise the adhesion between various fibre and polymer systems has been widely reported in the literature, only a very small number 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. If the microbond test is to be presented as an efficient and robust methodology for effectively characterising the fibre/matrix interface it is essential for this phenomenon to be understood in greater detail.

Analysis of the relevant literature indicates that, while the issue of microdroplet curing is recognised by a relatively small number of authors, there is little general agreement on what the cause behind this observed loss in performance is, with studies in fact providing conclusions entirely contrary to one another. Investigations by Haaksma *et al.* [2], Rao *et al.* [3,4], and Ozzello *et al.* [5] examined an epoxy/metaphenylene diamine (m-PDA) system and attributed the loss in microdroplet glass transition temperature (T_g) to a stoichiometric imbalance due to evaporation of curing agent. Laurikainen [6,7] and Dirand [8] similarly agree that diffusion of curing agent was the cause of the problem in vinyl ester systems (due to the large surface-to-volume ratio) though the former states that this could not have been the case for the same effect observed in their epoxy system due to insignificant vapour pressures. Instead



it was proposed that a phase separation occurred during sample preparation, or possible interaction with atmospheric moisture. Pyrolysis gas chromatography analysis conducted on under-cured microbond samples showed huge emissions in the thermal desorption step compared to fully cured resin samples, a result indicative of the degree of cure in the microdroplet being significantly lower than that of a bulk matrix sample subjected to the same curing schedule. Charlier *et al.* [9] report that processing and curing conditions had a significant effect on the apparent interfacial shear strength (IFSS) in an acrylic system. Without the addition of paraffin wax, radical polymerisation was not possible at elevated temperatures due to the rapid evaporation of methyl methacrylate (MMA) out of the droplets. Zinck *et al.* [10] refute that evaporation was the cause of the issue in amine-cured epoxy samples and proposed instead that imine formation reducing available amine functions available to react with the oxirane ring was to blame. For an anhydride-cured epoxy they suggested fibre surface moisture or hydrolysis of the anhydride during the pre-cure as the root cause; and, that surface oxidation may also be a contributing factor.

In a glass fibre/cyanate ester system, Bartolomeo *et al.* [11] reported good correlation between the degree of conversion (α) of bulk resin and microdroplet samples after 30 minutes ($\alpha_{\text{resin}} = 0.4$, $\alpha_{\text{microdroplet}} = 0.35$) and 1 hour ($\alpha_{\text{resin}} = 0.52$, $\alpha_{\text{microdroplet}} = 0.51$) of isothermal curing at 180°C. At low degrees of conversion measured IFSS remained relatively constant (in the region of 8 MPa) before increasing significantly once the gel point of the system ($\alpha_{\text{gel point}} = 0.6$) had been reached. Curing at higher temperature produced no significant effect on the adhesion, leading to the assertion that IFSS was dependent only on the degree of monomer conversion. Furthermore, as the values of IFSS at low conversion were the same regardless of fibre used, it was proposed that the IFSS is entirely matrix dependent at low degrees of conversion, while at high degrees of conversion both fibre and matrix interactions become apparent. Failure mode was dependent on microbond sample processing and resultant degree of monomer conversion present in the sample. Low conversions resulted in a fragile fracture of the matrix while in high-conversion specimens exhibited the expected linear interfacial behaviour and showed "stick-slip" phenomenon characteristic of two-dimensional interfacial behaviour.

Montgomery [12] has reported that both the Tg and degree of cure increased with cure temperature. Furthermore, the measured IFSS increased linearly in relation to Tg. Samples cured at room temperature had a degree of cure of 79% and 91-99% for samples that underwent a post-curing procedure. The author indicates that the change in measured IFSS values was likely a result of changes in residual stress. Peters and Springer [13] conclude that while the curing temperature and degree of cure affected the mechanical properties of resin systems, an increase in the degree of cure did not necessarily correspond to an increase in mechanical properties, and may in fact decrease as degree of cure increases. The tenacity of the fibre/resin bond strength, however, was affected by curing temperature and the maximum interfacial strength occurred at a curing cycle different to that resulting in the maximum bulk matrix strength.

A number of authors have reported on the effect of different curing schedules on matrix microstructure. Patel *et al.* [14] demonstrated that while the inclusion of a standing time (and gelation) had little effect on the decomposition temperature, static flexural tests, or storage modulus, a profound effect was noted in the composite fatigue performance. Mak *et al.* [15] showed that in order for the microdroplets to share a similar microstructure to the bulk sample, a much lower curing temperature must be used while conversely, Charlier *et al.* [16] propose that a higher temperature was needed to fully cure both acrylic and epoxy droplets compared to schedule used for macroscale composite parts. They propose that as a result of the change in scale, phenomena such as auto-acceleration/Trommsdorff's effect do not occur as it would in a bulk sample of several grams and accordingly, does not reach comparable local temperatures resulting in a lessened extent of reaction.

Methods employed in order to overcome this issue are also discussed. Both Rao *et al.* [3] and Ozzello *et al.* [5] saw great improvement by introducing a pre-cure/standing time, allowing the comonomers to react at low temperature and, in theory, preventing vaporisation of curing agent. Zinck *et al.* [10] reported contradictory results in that no change was seen after a 48-hour pre-cure in an amine-cured system and in fact, that it had a hugely detrimental effect on anhydride-cured samples. Rao *et al.* [3] saw a measure of improvement, though still not ideal, by curing the samples in an amine-rich environment

though Biro *et al.* [17] employed a similar procedure and saw no discernible difference between the samples cured in the presence of curing agent vapours. Laurikainen [7] reports that curing under a styrene-rich environment alleviated curing problems in vinylester droplets. Zinck *et al.* [10] proposed that amine-cured systems should be cured under inert atmosphere (and at 120°C or below) to prevent loss of Tg from imine formation though Biro *et al.* reported no difference between samples cured in air and nitrogen using an epoxy and an aromatic amine. Laurikainen [6,7] was able to produce cured epoxy microdroplets by allowing the resin viscosity to increase before application, amounting to much the same process as a protracted room temperature pre-cure. Phase separation was thought to be prevented due to the existence of covalent bonds between the resin and amine oligomers.

The above, and the present work, casts reasonable doubt on the abundance of literature published on the utilisation of the microbond test in works where no apparent problem was detected or discussed. Though the testing method has been employed in conjunction with a number of different fibre and matrix materials, whether these works make successful use of the microbond must be carefully considered. This study was undertaken in order to show that, for a number of amine-cured epoxy systems, microdroplet samples exhibit properties that are different from those of the bulk material, and to characterise the effect of these differences as relates to the use of the microbond test. Unanswered questions appear to remain in regards to how much cure shrinkage is effectively locked in place prior to the gel point. It is important that a greater understanding of the relationship between gel point, Tg, residual stress and interfacial shear strength in the microbond test be developed.

2. Experimental

2.1. Materials

Two multiple-component commercial resin systems designed for use in wind turbine blades were selected for investigation. The first was Epotec YD-535 LV cured with Epotec TH7257 hardener at a stoichiometric ratio of 100: 35 pbw. Olin Airstone™ 780E was cured with Olin Airstone™ 785H hardener at a stoichiometric ratio of 100: 31 pbw. In order to minimise the complexity of the interface, experiments were conducted using bare (water-sized) E-glass fibres taken from larger rovings supplied by Owens Corning. For Fourier-transform infrared spectroscopy (FTIR) measurements, the glass fibres were replaced by annealed AISI 302 steel wire of diameter 50 µm purchased from Goodfellow to improve signal clarity.

2.2. Methodology

The basic procedure for the microbond test involves a single filament being pulled from a small droplet of cured matrix while measuring the force required to detach the filament. The procedure for preparation and testing of microbond samples and the development of the specific apparatus has been described in detail in previous literature [18].

Differential scanning calorimetry was performed to characterise the degree of cure according to ASTM Standard E2160-04 *Standard Test Method for Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry* using a TA Instruments Q20 DSC. Scans from -50 to 300°C were made at a rate of 10°C following a number of room temperature standing times in order to characterise the degree of conversion during the room-temperature pre-cure. Tg of off-stoichiometric compositions were also determined by DSC.

FTIR analysis was performed using a 4100 ExoScan FTIR fitted with a spherical diamond attenuated total reflectance (ATR) interface, adjustable probe and benchtop docking station. Glass fibres were substituted for lengths of 50 µm diameter steel wire in order to create larger droplets of consistent dimensions and to exclude the influence of chemical interactions with fibre sizing. The use of steel wire allowed for accurate application of a single droplet per sample by preventing a capillary effect creating multiple droplets from the initial application as is observed with deposition onto glass or carbon fibres. Signal strength in collecting spectra is improved both by the use of a larger droplet and a reflectance effect of the steel wire, allowing for conventional FTIR apparatus to be used in the analysis of microscale

samples. Microbond tests ensured that curing issues were prevalent across both glass fibre ($L_c \approx 120 \mu\text{m}$) and steel wire ($L_c \approx 380 \mu\text{m}$) samples to verify that size effects alone were not responsible for the discrepancies in curing behaviour. Microbond samples were prepared at the stoichiometric ratio, applied to the steel wire, and then either cured ($65^\circ 3.5 \text{ hr} + 75^\circ 7 \text{ hr}$) immediately, or with a room temperature pre-cure ranging between 0.5 and 24 hours followed by post-curing at 65 and 75°C . Samples with altered stoichiometric ratio were created by mixing resin with reduced amounts of curing agent in 10% decrements before syringing a small bead ($\approx 10\text{--}20 \text{ mg}$) on release film and curing according to the same schedule. Individual droplets were then placed on the ATR interface of the apparatus and the probe fully lowered to ensure maximum contact with the sample. Results were plotted as a normalised average of 30 independent samples. Degree of cure/monomer conversion (α) was quantified using the reduction of the area of the oxirane/epoxy group at 915 cm^{-1} against the invariant peak at 1507 cm^{-1} ($\text{C}=\text{C}$ stretching) as an internal standard [19].

The experimental configuration is illustrated in Figure 1 and shows a typical optical micrograph of a steel wire-mounted epoxy droplet at 100x magnification.

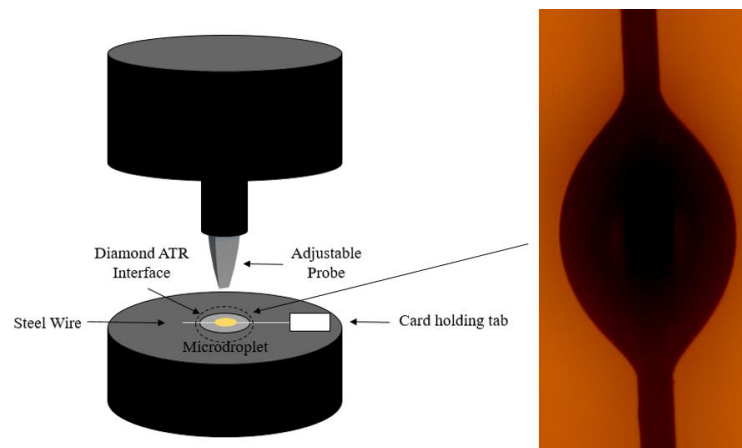


Figure 1: Schematic view of microbond ATR FTIR experimental set-up.

3. Results and Discussion

As illustrated in Figure 2, microbond testing results showed that the room-temperature pre-cure had a profound effect on the apparent IFSS of both the Epotec and Olin resins. It was not possible to accurately measure the IFSS of samples cured immediately due to the plastic deformation of the samples. It was found that a 3-hour room-temperature standing time was sufficient to ensure good curing and interfacial adhesion, and that further standing times of up to 48 hours showed no significant improvement. A standing time of only 1 hour was insufficient to ensure good curing and such samples showed only some tackiness while still deforming under load. Plotted alongside the interfacial adhesion data is the degree of cure to which samples had cured prior to undergoing elevated temperature curing as measured by DSC. Samples did not reach particularly high degrees of cure prior to heating.

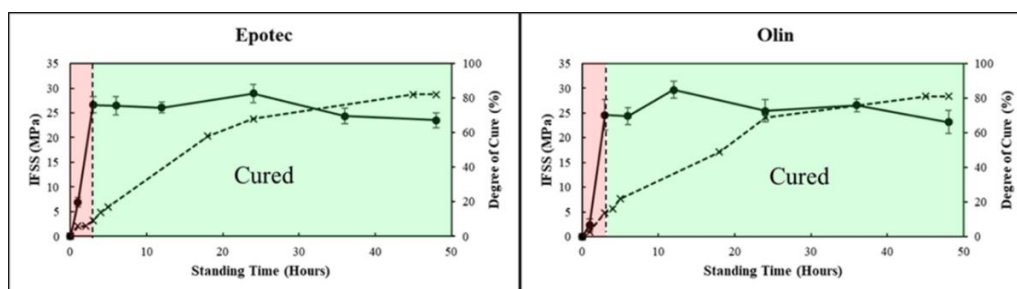


Figure 2: IFSS vs room-temperature pre-cure time.

The deformation of microbond samples under loading and the increases in IFSS after allowing a pre-cure can be plausibly attributed to whether the samples were allowed to gelate prior to exposure to elevated temperature. The observed deformation of the 0-hour and 1-hour samples would further indicate that the Tg of these samples was sub-ambient. The FTIR microbond method was developed in order to directly measure the Tg of microdroplet samples and to detect deviations from stoichiometry, if any, not present in bulk matrix samples. Previous studies have characterised the properties of microdroplet samples using FTIR microscopy [2], a novel TMA technique using similarly sized droplet clusters [3], modelling thin film thickness as an equivalent to embedded length [10], and pyrolysis gas chromatography [6]. Conventional thermal analysis using DSC was initially applied to microdroplet samples but it was found that sample size was insufficient to generate a signal from which Tg measurements could be made. Using clusters of similarly sized droplets in a similar manner to [3] indicated that, while signal strength was improved, Tg appeared to increase with the number of droplets. In any case, the Tg values measured were about 50°C lower than that of the bulk sample. Furthermore, the FTIR method allowed for the use of samples directly comparable to those used in the microbond test, as thin films did not consider sample geometry or surface-to-volume ratio.

In order to generate a range of spectra for off-stoichiometric composites, samples with curing agent reductions in 10% decrements were assessed. DSC was utilised in order to determine the relationship between amount of curing agent and Tg. Spectra of microdroplets cured after varying lengths of pre-cure were then collected, degree of conversion calculated, and collated with the data below to determine the droplet Tg and how much curing agent had been lost. Table 1 details the DSC Tg and FTIR data for both resin systems. A DSC stoichiometry study was similarly linked to TMA droplet Tg measurements in [3] though Tg was equated between the two methods rather than degree of cure.

Table 1: DSC and FTIR stoichiometry study

Curing Agent Reduction	DSC Tg (°C)		FTIR α	
	Epotec	Olin	Epotec	Olin
0%	92.3	93.5	0.93	0.89
10%	79.5	75.8	0.90	0.82
20%	60.5	53.2	0.87	0.77
30%	47.7	44.1	0.80	0.75
40%	23.5	21.2	0.72	0.77
50%	16.8	11.1	0.69	0.71
60%	-2.7	-0.8	0.55	0.66
70%	-14.8	-16.5	0.36	0.4
80%	-19.6	-22.0	0.30	0.31

Figure 3 shows the FTIR spectra for the stoichiometry study of the Epotec resin system. Spectra of the Olin resin system samples follow an identical trend. The C-O deformation of the oxirane ring, also known as the epoxy group, is located at 915 cm⁻¹ and the C-H stretch of the ring is found at 3050 cm⁻¹. The broad band observed at around 3500 cm⁻¹ is assigned to the O-H stretching of hydroxyl group. Bands corresponding to ether linkage are found between 1000-1100 cm⁻¹. Development of the hydroxyl band is a qualitative indicator of extent of reaction, though their use in quantitative analysis is limited as a result of the shape and overlapping bands.

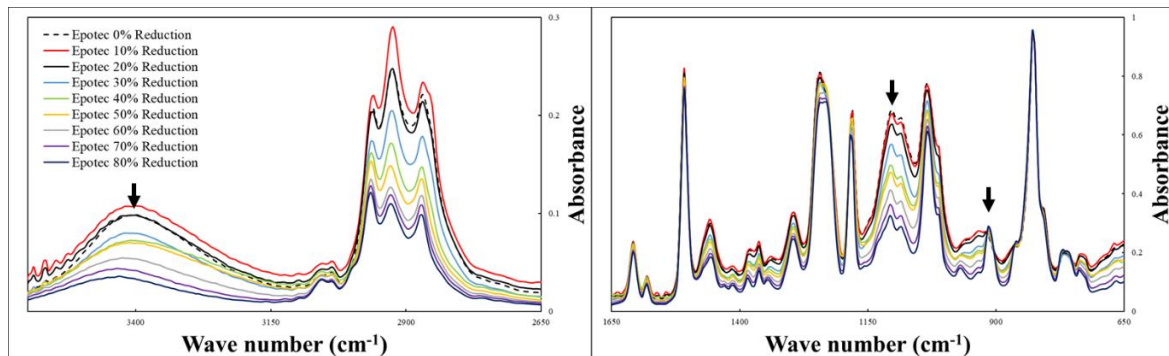


Figure 3: FTIR spectra of stoichiometry study

Changes in the concentration of species related to the curing process in the mIR range is primarily concerned with the broad band between 3000-3400, the sharp peak at 1100 cm^{-1} and the peak at 915 cm^{-1} . As the epoxy curing reaction progresses the oxirane ring opens and the band reduces, then disappears [20]. The reduction and disappearance in the bands located at 3056 and 915 cm^{-1} is an indication of the opening of the oxirane/epoxy ring. Due to the larger peak, and relative separation from neighboring peaks, the reduction in the band at 915 cm^{-1} is most commonly used for quantitative analysis. Furthermore, direct analysis of amine content is generally only possible using nIR methods.

The most apparent changes in microbond FTIR spectra can be observed in the comparison of 0-hour and 24-hour pre-cured samples as is shown in Figure 4. The micromechanical data presented previously would indicate that in the former case, these samples have IFSS values that were too small for accurate measurement and deformed plastically in the former case, and in the latter showed good interfacial adhesion and had an IFSS value in the range of 25-30 MPa.

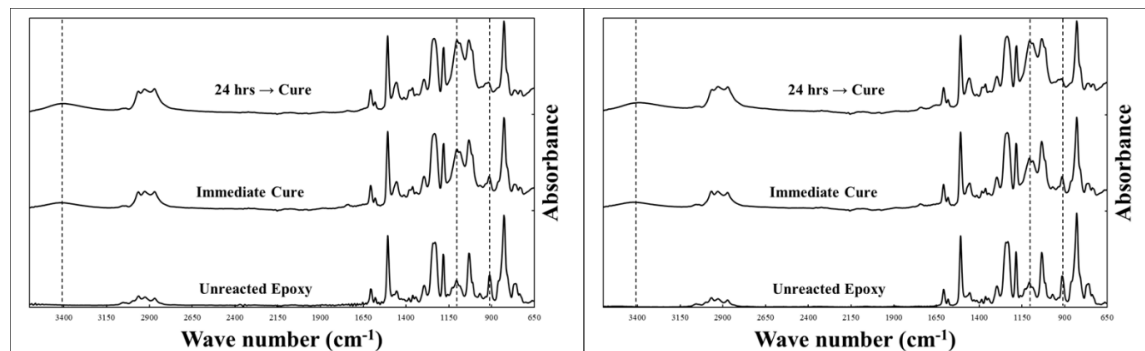


Figure 4: FTIR microbond spectra for Epotec (left) and Olin (right) resins

Samples cured immediately clearly show unreacted epoxy groups, reduced hydroxyl group accumulation and a weaker etherification peak, commensurate with spectra indicating an off-stoichiometric formulation. It is possible that curing agent evaporation following exposure to immediate high-temperature curing is the cause of the issue. Quantitative analysis of the epoxy peak indicated that microbond samples cured immediately had degrees of cure in the region of 0.55, loss of up to 60% of the curing agent, and T_g below zero. Conversely, samples that were allowed to pre-cure at room temperature and reach the gel point prior to heating at elevated temperatures produced spectra much closer to a stoichiometric mixture, high degrees of cure, and T_g of 80°C or greater, comparable to that of bulk matrix samples. The values for the amount of curing agent lost are somewhat higher than those reported by Rao and Drzal [3], though this is possibly due to the use of different curing agents between the studies. The full results of the pre-cure standing time investigation are detailed in Table 2.

Table 2: Summary of FTIR, DSC, and micromechanical data

Pre-Cure Time (Hrs)	α		$\approx T_g(^{\circ}\text{C})$		IFSS (MPa)	
	Epotec	Olin	Epotec	Olin	Epotec	Olin
0	0.55	0.55	-2.7	-1	0	0
0.5	0.71	0.69	23	11	-	-
1	0.68	0.62	16	4	6.9	2.33
2	0.87	0.9	60	75	-	-
3	0.87	0.81	60	46	26.6	24.6
6	0.89	0.84	73	49	26.5	24.4
24	0.91	0.93	80	92	28.9	25.5

4. Conclusions

Micromechanical interface testing using the microbond test has shown that in two amine-cured epoxy systems, the apparent IFSS was dependent on the inclusion of a room-temperature pre-cure prior to exposure to elevated curing temperature. A stand time of 3 hours was sufficient to ensure well-cured droplets and increasing the pre-cure to upwards of 48 hours had little significant effect on the IFSS. The exclusion of a pre-cure resulted in the formation of low-IFSS droplets with sub-ambient T_g .

The development and use of a novel FTIR technique appeared to show good correlation with the micromechanical testing results. Spectra generated from individual microbond samples was consistent with a non-stoichiometric epoxy-amine network, a sub-ambient T_g and significant loss of curing agent. Samples that were allowed to stand before curing showed a linear increase in degree of cure and T_g , two parameters which directly contribute to the value of IFSS. A plateau in the IFSS data after 3 hours of pre-cure was consistent with the FTIR measurements in the Epotec system, though this behaviour was slightly less pronounced in the Olin system. High degrees of conversion corresponded to increased T_g and IFSS.

The results presented can be interpreted as possible further evidence for the evaporation of curing agent out of microbond samples in these two systems. Exposure to elevated temperature curing prior to allowing microbond sample gelation resulted in low-IFSS samples that deformed plastically. It is possible that evaporation of the curing agent out of the samples during this early stage accounts for the loss in material properties. It is also possible that alterations to the curing schedule affect the contributions of residual stress present to varying degrees. What does appear to be clear, is that such effects take place early in the curing reaction.

Interfacial testing methods are often employed to measure the influence of factors such as fibre surface treatment, application and screening of sizings, and degradation thereof. Changes in IFSS as the result of such alterations are, however, typically significantly smaller than 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 must be carefully considered. We have ourselves observed that the curing issues are not prevalent in triethylenetetramine-cured epoxy samples [21] and further research involves extending the study to a range of amine chemistries, curing atmosphere, and oversaturation of curing agent.

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