An exploration of the relationship of chemical and physical parameters in the micromechanical characterisation of the apparent interfacial strength in glass fibre epoxy systems

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Abstract. This paper focuses on the cure shrinkage and the thermomechanical properties of an amine cured epoxy resin system and its adhesion to glass fibre. The fibre-matrix interfacial shear strength (IFSS) was characterized using the microbond test over a range of test temperatures and a range of amine:epoxy ratios. The apparent IFSS in this glass-epoxy system was shown to be strongly dependent on the testing temperature and the matrix stoichiometry. High levels of cure shrinkage were measured in the IFSS microdroplets which resulted in internal stresses causing significant levels of droplet deformation. The results presented here can be interpreted as providing further support for the hypothesis that a significant fraction of the interfacial stress transfer capability in epoxy composites can be attributed to a combination of residual radial compressive stress and static friction at the fibre-matrix interface.

1. Introduction

The performance of fibre-reinforced polymer composites is defined by a combination of the fibre and matrix properties and the ability to transfer stresses across the fibre–matrix interface. It is well recognised that optimization of the stress transfer capability of the fibre-matrix interface region is critical to achieving the required composite performance level. The ability to transfer stress across this interface is often reduced to a discussion of ‘adhesion’ that is a simple term to describe a combination of complex phenomena on which there is still significant debate as to their relative significance and their characterisation. Certainly, one of the generally accepted manifestations of ‘adhesion’ is the mechanically measured value of interfacial shear strength (IFSS).

Despite the high level of attention commonly focused on chemical influences on glass fibre-epoxy adhesion, a number of authors have also commented on the role of shrinkage stresses contributing to the stress transfer capability at the fibre-matrix interface [1-7]. Recent work has shown that the level of apparent adhesion in glass fibre reinforced composites may be strongly influenced by the glass transition temperature (Tg), thermal expansion coefficient, and modulus-temperature relationship of the composite matrix (or interphase) [3-7]. In epoxy polymers these factors are known to be dependent on the ratio of curing agent to epoxy resin and the thermal history of the system. In addition to the thermal stresses at the interface caused by the heating-cooling cycle during composite production thermosetting matrices also undergo a volume change during their chemical reaction due to the phenomenon of cure-shrinkage. Since the epoxy matrix is shrinking while its Tg is simultaneously increasing due to the polymerisation it is possible for a proportion of

this cure shrinkage to be frozen into the system causing additional stress at the fibre-matrix interface.

It is also well known that the performance of the fibre-matrix interface is critically related to the nature of the surface coating (or size) which has been applied to the fibres during their manufacture. The sizings used on glass fibres used to reinforce epoxy resin polymers will nearly always contain epoxy molecules [8,9] although the exact nature of such glass fibre sizes is often kept an industrial secret. Consequently, there is a strong possibility of the stoichiometry of a composite matrix or, more likely a local interphase region around the fibres being different from that of the initial resin system preparation [10]. Clearly all of the above factors can be tied together with the local stoichiometry and the thermal history of the epoxy system. In this work a study was undertaken to characterise the effects of variation of the epoxy-curing agent ratio on the thermal and mechanical performance of an epoxy polymer. Furthermore, the effect of these chemical changes on the level of cure shrinkage and the apparent level of adhesion in glass fibre-epoxy microbond specimens was evaluated.

2. Materials and methods

Boron free E-glass fibres (OC-APS) with average diameter of 17.5µm and coated with γ-aminopropyltriethoxysilane were supplied by Owens Corning. Araldite 506 epoxy resin and Triethylenetetramine (TETA) curing agent were purchased from Sigma-Aldrich. The stoichiometric ratio (amine:epoxy ratio r=1) for this system was calculated at 12.0% by weight of TETA. The epoxy and TETA were thoroughly mixed in appropriate proportions and degassed under vacuum for 12 minutes. Droplets were then deposited on a single glass fibre using a thin wire. Approximately 40 droplets were placed on individual fibres before these samples were transferred into a convection oven, where they were heated first to 60 °C and held isothermally for 1 hour followed by another 2 hours heating at 120°C. After heating, the samples were left in the oven to cool down. The configuration and development of the microbond test (MBT) and TMA-Microbond test (TMA-MBT) rigs has been reported previously [7,11]. Differential scanning calorimetry (DSC) was carried out in a TA Instruments Q2000 DSC under a nitrogen gas flow of 50 ml/minute. The pre-cured epoxy material was cut down to specimen sizes with a mass in the range of 15-20 mg. These samples were subjected to a DSC heat-cool-heat cycle from -10 °C to +150 °C at 10 °C/minute. The Tg values reported are mid-point values from the second heating ramp.

The change in dimensions of the typical epoxy microdroplets during curing was observed in a Mettler Toledo FP90 hot-stage placed under a Olympus BX51 microscope. The hot-stage heating schedule was similar to the microbond samples oven curing, heat from 20 °C to 60 °C at 2 °C per minute, isothermal at 60 °C for 60 minutes, then further heating to 120 °C. Images of the samples were recorded at one minute intervals. These droplet images were approximated as ellipses and the major and minor dimensions of each was measured to obtain an estimate of the droplet volume. Ten droplets were measured at each of five amine:epoxy group ratios investigated.

3. Results and discussion

3.1. IFSS dependence on measurement temperature

The results for IFSS obtained for an r=1 epoxy matrix, measured at test temperatures in the range 20 °C to 150 °C, are summarized in Figure 1 that shows the average values with 95% confidence limits (between 10-20 samples per temperature). It can be clearly seen that there exists a significant temperature dependence of measured IFSS in this thermosetting system. The IFSS falls from 54 MPa measured at 20 °C to just 2 MPa when measured at 150°C. It is noticeable that the highest rate of change of IFSS with temperature is also in the region of the Tg of this epoxy system which occurs in the range 70-90 °C [7]. The magnitude of the IFSS with this fibre and an epoxy matrix (GF-EP) is much greater than for the same fibre in polypropylene (GF-PP) at any particular temperature [5]. This supports the general expectation that the stress transfer capability of the GF-EP interface is much greater than that of GF-PP. However, there is also a striking similarity in the form of the IFSS versus temperature dependence for these two very different composite systems. Both systems exhibit a significant step-change in the IFSS around the associated matrix Tg [5,7].

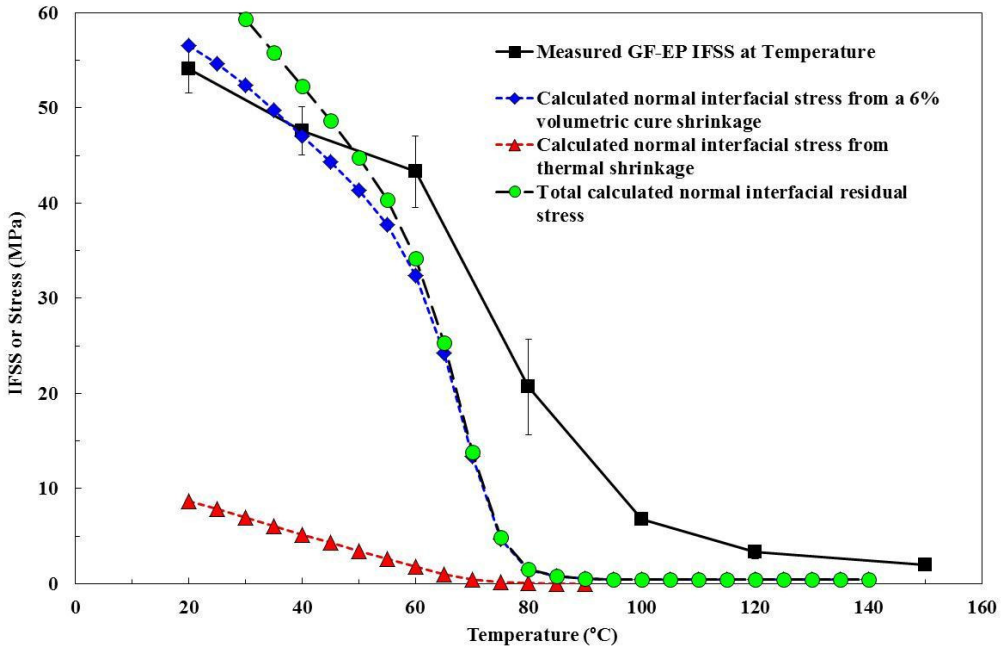

Figure 1. Glass Fibre-Epoxy (r=1) IFSS versus temperature compared to residual radial compressive stress at the interface [7]

Figure 1 also shows the maximum potential contribution to the interfacial radial compressive stress from thermal and cure shrinkage where a 6% volumetric cure shrinkage had been employed [7]. These are maximum values since it has been assumed that no relaxation of the stresses occurs below the matrix Tg. Furthermore the buildup of the stress values have been calculated using a temperature step of 5 °C reducing from a Tg value of 80 °C and using temperature dependent measured input values of the epoxy matrix modulus (by DMA) and expansion coefficient (by TMA) [7]. It can be seen that the residual radial interfacial stress obtained from such a level of cure

shrinkage is significantly greater than the residual thermal stress. This result appears to be well aligned with the results of other researchers [12]. It is clear from the data in Figure 1 that the sum of thermal and cure shrinkage related residual radial interfacial stress is of an appropriate magnitude in order for acceptable values (<1) of the coefficient of static friction to deliver an interfacial stress transfer contribution of similar magnitude to the measured IFSS. Previous work has indicated that a large fraction of the IFSS in thermoplastic composites can be attributed to residual radial compressive stresses at the interface [5,6]. It appears from the current results that it is also possible to make a case for residual stress combined with static friction being a major contributor to the apparent IFSS in a thermoset system.

However, a major challenge to this hypothesis is the weight of opinion that the chemistry and chemical reactions in the system must in some way play a role in the stress transfer capability of the interface. In order to maintain the primary hypothesis of residual compressive stress being a major contribution to the apparent IFSS it becomes necessary to investigate how the chemistry of the polymerising matrix system could affect the major drivers of this residual stress. Hence it is pertinent to investigate parameters such as IFSS, matrix Tg, expansion coefficient, modulus, and cure shrinkage as a function of temperature and the stoichiometry of the epoxy matrix.

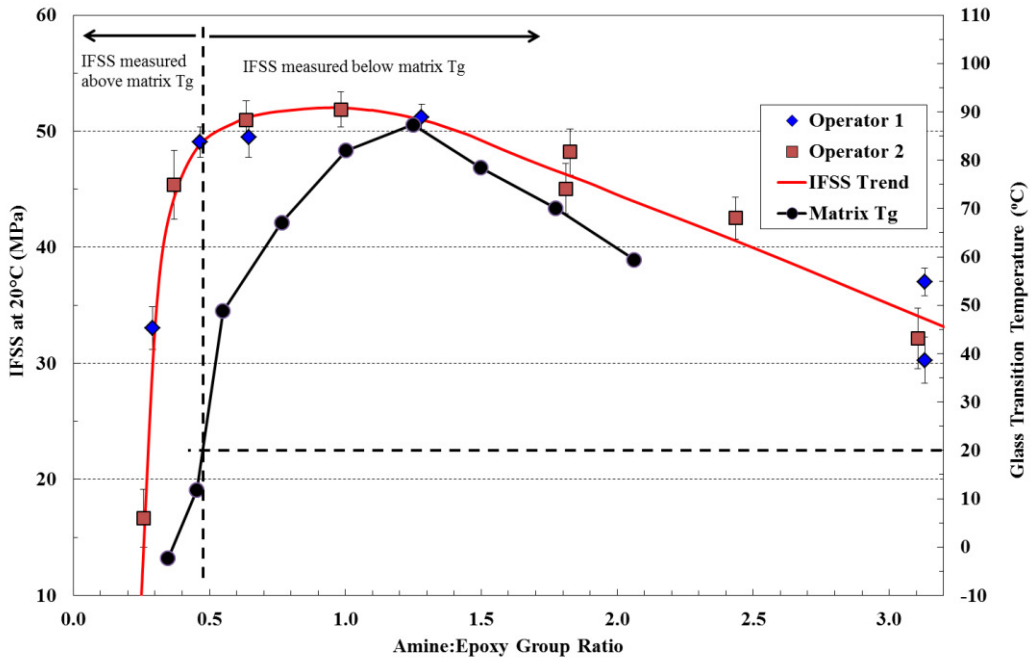

Figure 2. IFSS and matrix Tg versus amine:epoxy group ratio in matrix

3.2. IFSS room temperature dependence on matrix stoichiometry

Figure 2 presents the IFSS results (from two different operators) obtained for the OC-APS fibres as a function of the matrix r value (amine/epoxy group ratio). Each data-point represents an average of approximately 40 individual successful microbond measurements. The line in this Figure is added purely as a guide to the apparent trend. The primary observation in this Figure is that the IFSS exhibits a broad peak about the stoichiometric value (r=1) for this epoxy matrix system.

Consequently, a reasonable conclusion could be that small local variations in the matrix composition around the fibre (in the interphase if one exists) due to epoxy or amine groups present in the fibre sizing may not lead to significant variations of the IFSS. It appears that local variations in the value of r of greater than ±0.5 from the stoichiometric ratio would be necessary to significantly change the level of IFSS. Nevertheless, a second important observation from Figure 2 is the extremely steep drop in IFSS observed when the r ratio drops below approximately 0.5. It can be seen that if for any physical reason $r<0.5$ it would have serious consequences for the apparent adhesion in this system and presumably also for the further mechanical performance of a composite. It will be interesting to see if these trends are maintained when the IFSS is measured at higher temperatures.

In terms of the modelling of the residual compressive stresses (from both thermal and cure shrinkage) at the fibre-matrix interface, the temperature at which such stresses are "frozen-in" and cannot easily relax away is an important parameter. In epoxy based systems it is accepted that the characteristic temperature at which this occurs is the matrix Tg. The results for the DSC determined cured polymer Tg are also shown in Figure 2 as a function of the system stoichiometry. The maximum Tg for this epoxy system appears to be in the range $1<r<1.2$ close to the calculated stoichiometric ratio. Samples with either an excess of epoxy or an excess of hardener gave a much lower Tg value. This Tg dependence of stoichiometry has been observed in epoxy resins by other researchers [13–15].

Theoretically, for r=1, all amine hydrogens react with all epoxide groups, giving a network of interconnected rings [15]. These rings consist of two or three epoxidic chains, which have reacted with the corresponding amine group. In the epoxy-rich systems ($r<1$) a fraction of the available epoxy groups remain unreacted. This results in a network with some less restrained, bulky groups situated at the end of the chains. This increase of the number of chain ends increases the free volume of the polymer, decreasing the Tg. In the systems with an excess of amine ($r>1$), the epoxy groups react initially with the primary amine groups, but there are unreacted secondary amine groups remaining. Under these conditions, the epoxy tends to give branched structures [16], and occasionally may give rings consisting of the partially reacted tri-amine molecules and the epoxide chain. These structures contribute to an increase of the free volume of the system and consequently exhibit a lower Tg [15]. It is observed that the presence of unreacted epoxy groups ($r<1$) has a more noted effect on the polymer Tg than the same amount of unreacted amine groups ($r>1$).

Comparison of the general trends observed in Figure 2 for IFSS and matrix Tg as a function of the matrix stoichiometry reveal some similarity with a maximum value occurring around r=1 and both IFSS and Tg reducing as r moves away from unity (in either direction). A particularly interesting correlation is the position of the large step down in IFSS when $r<0.5$. It is also at this approximate value of r that the matrix Tg drops below room temperature. Consequently, the very low values of IFSS observed for $r<0.5$ in Figure 2 were measured at a temperature above the matrix Tg when presumably there is little build-up of residual radial interfacial stress to contribute to the apparent measured IFSS. This appears to be the same phenomenon observed in Figure 1 where the experiment design involved a fixed matrix Tg (≈80 °C for r=1) and measurement of IFSS at temperatures above and below this value. In Figure 2 the experiment is designed with a constant IFSS measurement temperature but a changing epoxy matrix Tg. In both cases a similar effect can be observed of reduced IFSS when the measurement temperature is above the Tg of the matrix

polymer. Further work to characterise the system IFSS as a function of both r value and temperature is planned.

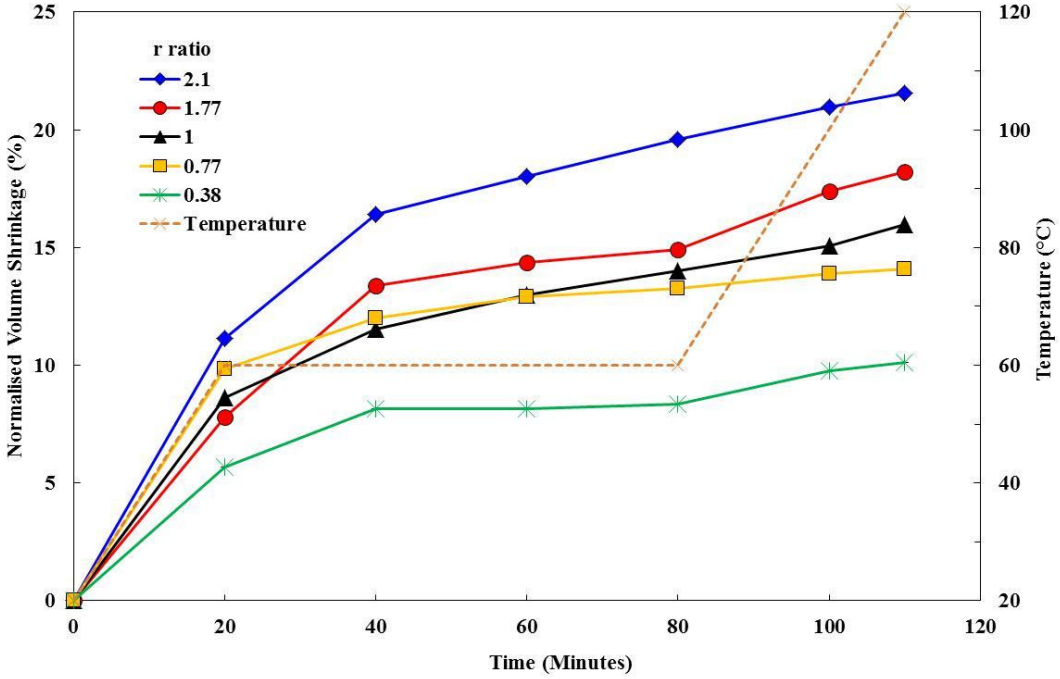

Figure 3. Normalised volumetric shrinkage of microbond droplets during curing

3.3. Droplet shrinkage during curing

The results for the volumetric shrinkage normalised to the original droplet volume for different r ratio droplets are shown in Figure 3. Each data point is the average of the dimension change of ten different droplets. It is interesting to note that the over-riding change in volume is shrinkage, even during the first heating period (0-20 min) the cure shrinkage is greater than the increase in droplet volume due to thermal expansion with a volumetric shrinkage of 6-11% in this period depending on the droplet stoichiometry. The droplets continue to shrink during the isothermal period (20-80 min) at 60 °C and shrink even further during the final heating step (80-110 min) to 120 °C (again overcoming any thermal expansion during heating). The overall volumetric cure shrinkage during the droplet curing is in the range of 11-21% with a clear trend towards increasing cure shrinkage with increasing r ratio. These values are well in excess of the 6% volumetric cure shrinkage which was used in the modeling of the residual radial compressive stress at the fibre-matrix interface shown in Figure 1. There is a great deal more work required to fully quantify the effect of this cure shrinkage; however these results clearly indicate that there is potentially sufficient volume change in the preparation of microdroplets for IFSS measurement to explain the values of apparent adhesion using residual stresses alone.

3.4. Residual stress and microdroplet deformation

An interesting result of the continual monitoring of the microdroplets during the epoxy curing was the observation of sudden deformations appearing in the droplet shape, frequently during the final heating step to 120 °C. Figure 4 shows an example of this phenomenon. Figure 4a shows a well

formed droplet (typical of what is often seen in other microbond publications) before curing. A large deformation of the droplet after cure can be observed in Figure 4b.

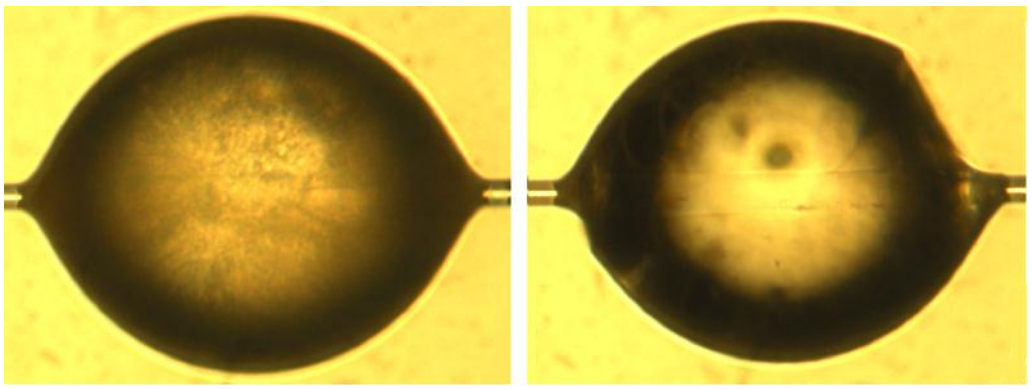

Figure 4. Optical micrographs of epoxy droplet on glass fibre. (a) before cure. (b) after cure

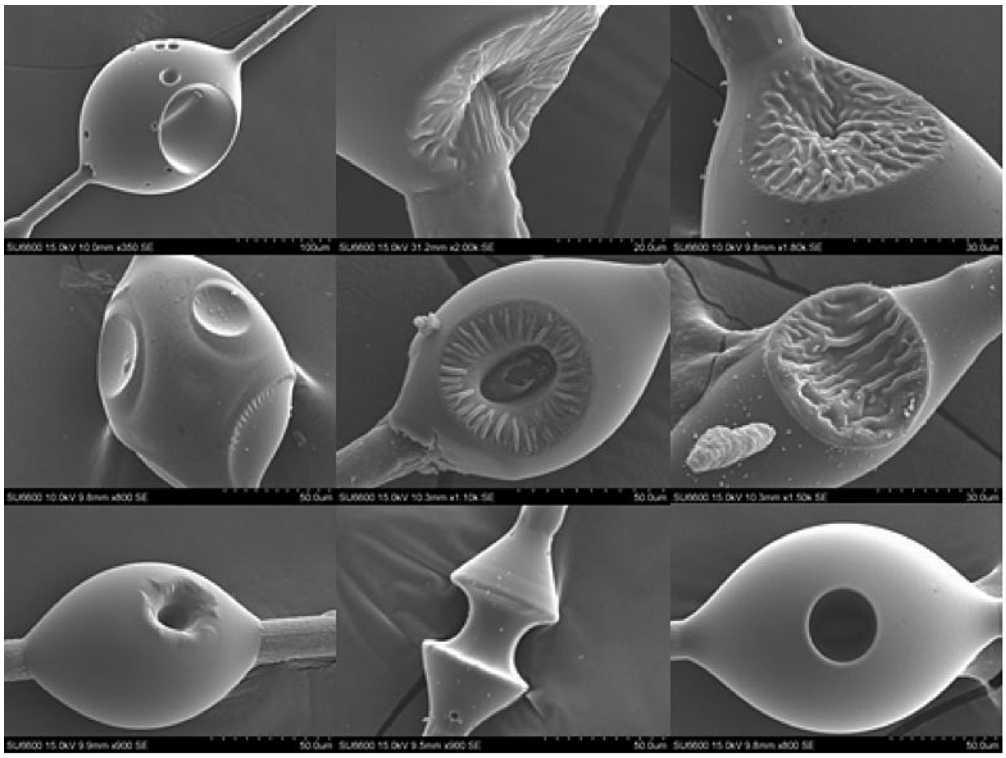

Figure 5. SEM micrographs showing various deformations of cured microbond samples

The phenomenon was also captured on video in certain cases and it appears to be the result of a buildup, during the isothermal cure at 60 °C, of residual cure-shrinkage stress in the droplet. This residual stress becomes frozen in as the Tg of the reacting droplet rises above the isothermal cure temperature. However, on further heating, the droplet is again placed in the rubbery state and the local relaxation of some of the built up residual stress can apparently cause these deformations. These droplet deformations are not well resolved in optical microscopy however a broad survey of cured microdroplets in the scanning electron microscope (SEM) revealed the wide range of

deformation types and sizes. A few examples are shown in Figure 5. A further attempt was made to semi-quantify this deformation effect. Every droplet produced for the microbond testing in this work had been photographed to estimate its dimensions. It appears that many of these droplet deformations are not clearly visible in optical microscopy – unless you are specifically searching for them. It is certainly the case that there does not appear to be any reference to these deformations in the existing literature on microbond testing in epoxy systems.

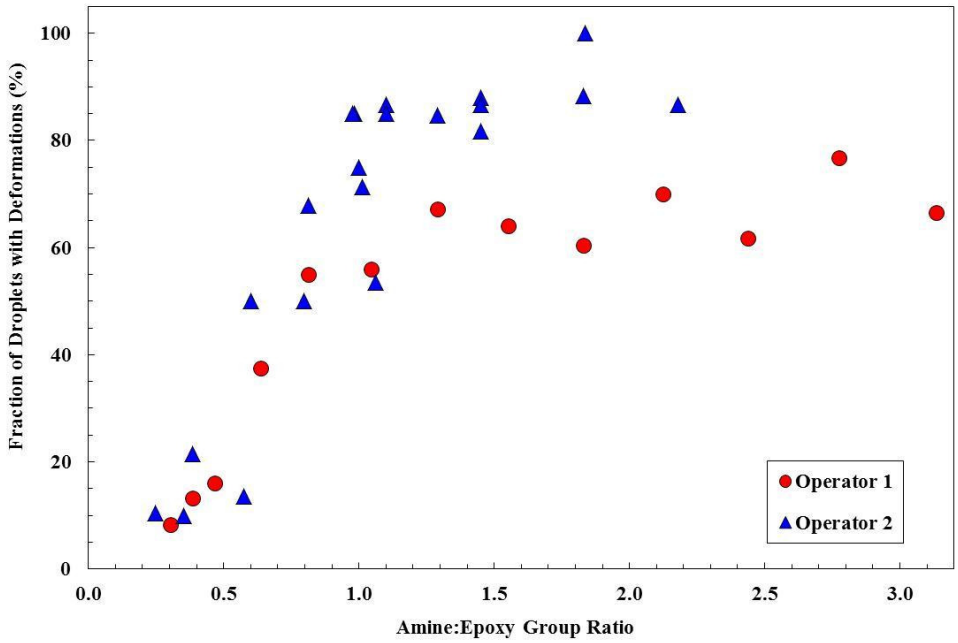

Figure 6. Observation of droplet deformations versus amine:epoxy group ratio in matrix

Figure 6 shows the results of a review of all these droplet micrographs in terms of the fraction of droplets which exhibited deformations. As stated above, the data can only be considered semi-quantitative at this time as there is clear evidence of an operator bias. However both datasets clearly indicate the same trend. At very low r ratios there is little evidence of deformations in the microdroplets. However, the fraction of deformed droplets rises rapidly as the r value is raised above 0.5. As discussed above it is at this r value that the Tg of the droplet rises above room temperature and residual stress can start to build in the droplet. Once again this phenomenon clearly requires further investigation, not least as a source for the variability often obtained in microdroplet evaluation of IFSS in epoxy systems. However, the apparent correlation between the lack of residual stress in the droplets with $r<0.5$ (as evidenced by the low fraction exhibiting deformations) with a very low value of IFSS is very interesting in terms of the hypothesis that apparent adhesion may by explained by residual radial compressive stresses at the fibre-matrix interface alone – even in reactive thermosetting systems.

4. Concluding remarks

The results presented here can be interpreted as providing further support for the hypothesis that a significant fraction of apparent interfacial shear strength (IFSS) in fibre-reinforced epoxy composites can be attributed to a combination of residual radial compressive stress and static friction at the fibre-matrix interface. The temperature dependence of apparent IFSS of a glass fibre-epoxy system in the range 20°C up to 150°C showed a highly significant inverse dependence on testing temperature, with a major step change in the glass transition region of the epoxy matrix. This temperature dependence of the glass fibre-epoxy IFSS was compared to the change in residual radial compressive stresses at the interface as the test temperature is changed. The analysis indicated that the magnitude of the thermal residual stress due to mismatch in the thermal expansion coefficients of fibre and matrix was insufficient to explain the magnitude the of system IFSS. However, when the additional potential residual stress generated by a 6% cure shrinkage of the epoxy matrix was considered, then the magnitude of the residual stress at the interface could be found to be of the same order of magnitude as the measured IFSS. Results on the room temperature dependence of the IFSS in the same system as a function of the amine:epoxy group ratio (r ratio) in the matrix revealed a strong dependence of the IFSS and the matrix thermal and mechanical properties on the r ratio. At $r<0.5$ a correlation was observed between large reduction of IFSS with the lowering of the matrix Tg below room temperature. Direct optical measurement of the cure shrinkage of IFSS microdroplets revealed volumetric shrinkage in the range 11-21% during curing depending on the matrix r ratio. It was also observed that the resultant residual stress in the microdroplets was sufficient to cause severe deformations of the droplets during curing and the occurrence of these deformations was also shown to be dependent on the matrix r value and most likely on the matrix Tg. These observations are important to all researchers actively using the microbond technique to characterise fibre-matrix IFSS.

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