

THE ROLE OF THE EPOXY RESIN: CURING AGENT RATIO ON COMPOSITE INTERFACIAL STRENGTH AND THERMAL PERFORMANCE

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Abstract

This paper focuses on analyzing the interfacial and thermal properties of an epoxy resin glass fibre reinforced composite. The interface was studied using the microbond test to investigate interfacial shear strength values while thermo-mechanical analysis and differential scanning calorimetry were used to find variations in the glass transition temperature and coefficient of thermal expansion. For both, the role of the epoxy resin: curing agent ratio was studied to see if it influenced fibre-matrix adhesion and whether it had similar effects on thermal properties. It was found that the epoxy resin: curing agent ratio did indeed influence both interfacial and thermal properties, with maximum performance occurring around the stoichiometric point.

1. Introduction

With the world's continual growing interest in renewable energy, the designers of wind turbine blades are now under more pressure than ever to produce larger, more powerful wind turbine blades. As such the demand to produce glass fibre reinforced composites that possess superior mechanical properties has never been higher, with a great level of investment having been placed into research with the goal of broadening our understanding of how to optimize mechanical performance.

If this performance is to be maximized then it is critical to optimize the stress transfer capability of the interfacial region which exists between the glass fibre and the polymer matrix. If this region is weak, with poor adhesion between the fibre and the matrix, then the composite will fail to reach its true potential in terms of mechanical properties. One accepted mechanically measureable value which can be used to define the strength of the interface is the interfacial shear strength (IFSS) which can be influenced by several factors including the surface chemistry [1], the chemistry of the epoxy system used [2] and the testing temperature [3].

Recent work [3] has concluded there does seem to be a relationship that exists between stoichiometry, testing temperature and the resulting performance of the interface. However, more work on this subject was warranted in order to fully understand what was occurring at the interface level.

This paper focuses on the role of the epoxy resin: curing agent ratio in terms of interface strength (IFSS) and thermal performance. Stoichiometry is of interest due to the nature of fibre sizing, with the level of coating typically not being consistently equal along the whole length of the fibre. As such, there is potential for the epoxy resin system mixture to vary in terms of composition along the entire length of each fibre which could threaten overall performance. Thus this topic on the interface was studied through the use of the microbond test while the thermal properties such as glass transition temperature (T_g) and coefficient of thermal expansion (CTE) were analysed using different scanning calorimetry (DSC) and thermo-mechanical analysis (TMA).

2. Experimental

2.1. Materials

The experiments were carried out using boron free E-glass fibres, sized with γ -aminopropyltriethoxysilane (APS), taken from larger roving's manufactured by Owens Corning-Vetrotex. The epoxy resin used was Araldite 506® (DGEBA) and the curing agent used was Triethylenetetramine (TETA) with a technical grade of 60%. Both were produced by Sigma Aldrich.

2.2. Sample Preparation

2.2.1 Microbond Samples

The procedure for preparing the microbond samples followed a simple checklist procedure, with each batch of samples undergoing the same process, to as much the same timescale as possible. Each individual batch consisted of 60 samples in order to reach the statistical parity required to allow for results to be compared.

The process began with the application of the glass fibres to sections of 20 mm gauge length card through a combination of double sided tape and Loctite® super glue. Care was taken to ensure that the exposed sections of fibre to be used for the test were protected from as much contamination as possible, whether through surface or human contact. With the fibres in place, the next task was to apply the droplets of the epoxy resin system.

The mixture of the epoxy system was varied for each batch, with the weight of curing agent applied to the mixture being varied while the weight of epoxy resin was maintained at 5 g. This in turn allowed for predefined percentages of TETA to be applied relative to the system as a whole, for example the stoichiometric ratio (12.3%) where the ratio of the amine: epoxy group is equal to one. The weights were monitored to the nearest 0.01 mg using a XSE 205 Dual Range analytical balance, manufactured by Mettler Toledo with percentages ranging from as low as 4% up to 30%. Once combined and mixed, the epoxy system would be degassed for 15 minutes using a composite vacuum pump to ensure a level of homogeneity. The mixture was then applied to the fibres with as little time delay as possible to maintain consistency.

The application process involved applying several smaller droplets to each fibre, due to the difficulty in producing only a single droplet which would not be too large to test successfully. A bonus feature of having multiple droplets was that it allowed for the most suitable one in terms of size, shape and condition to be chosen for testing. The application of the droplets was completed using a modified scalpel [4], which possessed a piece of 50 μ m steel wire attached to the end of the blade, creating a precise tool. This allowed for the end of the wire to be dipped into the epoxy system, transferring

several droplets onto its surface before then being applied to the glass fibre by gently touching the wire against the fibre. The position/orientation of the fibre during this procedure varies from lab to lab but in this case the fibres were suspended horizontally during the procedure. A 5mm gap between the droplet and the frame edge of the card was maintained for each sample.

Once the application process was complete, the samples were placed in an oven to cure at a consistent program which was used throughout the study with the first step of the heating program taking the temperature within the furnace up to 60 °C at a rate of 2 °C/minute and being held isothermally for one hour. The temperature was then ramped up again at a rate of 2 °C/minute before it reached 120 °C whereupon this was maintained for two hours, resulting in a total time of three hours, 50 minutes spent in the furnace (not including cool down time).

Once cured the final step before testing was to have a number of dimensions measured using an optical microscope. The optical microscope allowed for samples to be viewed under 200x magnification and photographed, allowing for the measurement of the fibre diameter (D_f), droplet diameter (D_d) and embedded length (L_e) to be calculated. These measurements were required if the IFSS was to be correctly calculated since the embedded area of the droplet needs to be known [5, 6] as shown in Equation 1 where F_{max} is the maximum load applied to the droplet before it de-bonds.

$$\tau = \frac{F_{max}}{\pi \cdot D_f \cdot L_e} \quad (1)$$

2.2.2 Thermal Analysis Samples

The samples for the DSC and TMA were prepared together, undergoing the same curing conditions used for the microbond samples. Like the microbond samples, the epoxy resin and TETA were weighed, mixed together and degassed with seven different ratios tested.

The major difference in sample preparation methods was that the epoxy system mixtures were poured into silicon moulds for the curing process, producing 5 mm³ cubes used for the TMA test. These TMA samples were each thoroughly sanded to ensure as smooth a surface as possible in order to produce accurate results.

The DSC samples were crafted from unused TMA samples, with them being shaped into small flat discs weighing between 15-20 mg. This allowed them to fit comfortably into TA classic aluminium pans, product number 900760.901, which used TA standard aluminium lids, product number 900779.901.

2.3. Microbond Test

The effect of altering the epoxy resin: curing agent on the adhesion properties of the composite was investigated using the microbond test method. The microbond test is generally accepted as a universal test for measuring the important adhesion properties at work between the fibre and the polymer matrix [7]. An example of such a property is the interfacial shear strength (IFSS) which details the ability of the interface of the composite to deal with any shear stress placed upon it [8].

The microbond test apparatus can vary greatly from institute to institute, with multiple methods for clamping the specimen being used. Each has benefits and drawbacks but the main goal of each is to ensure that the glass fibre can pass freely through but the micro-droplet cannot, leading to the de-bonding process.

The particular setup used for this study was for an Instron 3342 tensile test machine that used a specially designed rig [4, 6]. This rig was composed from two sharp blades which were extended out until they practically grasped the micro-droplet, with said droplet positioned underneath the blades.

Particular care had to be taken to ensure that the blades were not over tightened to prevent the fibre being partially damaged or entirely severed in some cases. This also prevented the blades from coming into contact with each other which would have severely damaged them.

Once the sample was in place, and the details inputted into the Instron computer program, the tensile machine would gradually pull the fibre upward at a rate defined by the user. In this case the rate for these experiments was maintained at a constant value of 0.1 mm/s. Thus the micro-droplet would gradually be pulled upwards into the two blades until reaching a critical point where the droplet lost adhesion with the fibre and de-bonded, breaking its connection with the fibre and slipping down the fibre or in some cases completely off the fibre. Typically the de-bonded droplet left tell-tale signs of where it had had once been in the form of a meniscus. The graph of a successful de-bonding is provided in Figure 1 with the sharp drop off representing the point of de-bonding, and the latter load representing friction as the droplet passed along the fibre.

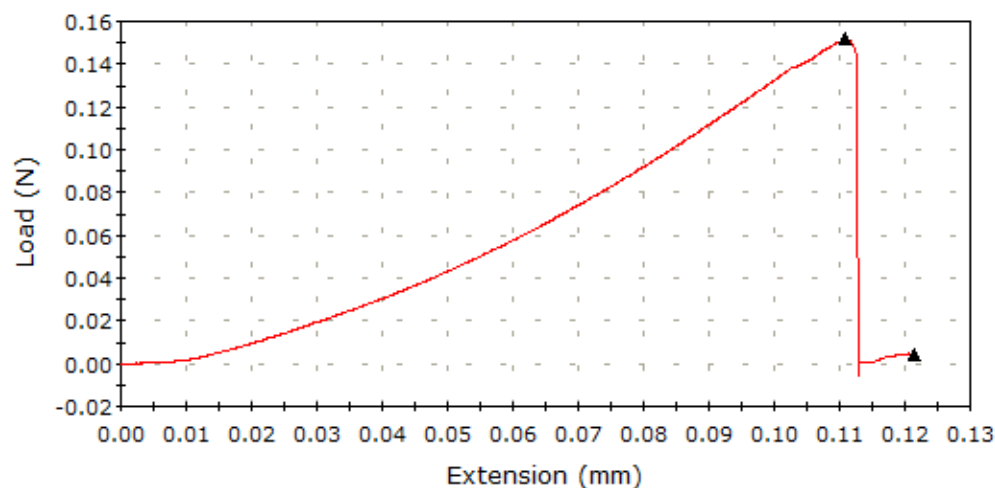


Figure 1. Load-Extension Graph of a successful de-bond

2.4. Thermal Analysis

The use of thermal analysis to evaluate a composites performance is nothing new, with multiple techniques having been developed to study several different properties which are known to influence mechanical performance. This study focused on the use of two primary techniques: differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). Both were capable of evaluating the glass transition temperature (T_g) of the epoxy resin system.

DSC is an established process which may provide a relatively quick technique for evaluating the changing specific heat capacity of a material over a predefined temperature range. For this study, a Q20 differential scanning calorimeter was used to measure the heat flow to the material as the temperature was increased at a set rate, allowing for the glass transition temperature to be found for the clear step changes visible on the resultant thermal curve of heat flow plotted against temperature. This is in accordance with the ASTM standard E1356-08 [9].

As such the chosen temperature range for the study was from -10 to 150 °C with the following procedure used for each test: the sample would be equilibrated at -10 °C then held isothermally for 10 minutes before the temperature is ramped at a rate of 10 °C per minute up to 150 °C and again held isothermally for 10 minutes. The temperature would then be ramped at a rate of 20 °C per minute down to -10 °C and held isothermally for 10 minutes before increasing the temperature again at a rate of 10 °C per minute up to 150 °C. The two heat ramps to 150 °C were necessary since during the first ramp there would exist a considerable degree of noise, damaging the accuracy of the results. Each test

was conducted within an environment of nitrogen gas, supplied at 50 ml per minute.

Thermo-mechanical analysis is another established technique for studying several different thermal properties of a composite material, in this case the glass transition temperature (T_g) and coefficient of thermal expansion (CTE). The tests were carried out according to ASTM standards E831-12 and E1545-11 respectively [10, 11], with the process constantly measuring the change in dimension of the specimen as a function of temperature whilst the temperature is increased under a defined atmosphere. For this study a Q400 was used for all TMA tests.

The same temperature range as the DSC tests was used for the TMA study, with the sample being equilibrated at -10 °C and held isothermally 5 minutes. The temperature was then ramped at 2 °C per minute up to 150 °C, with the process then being repeated a second time. The ramp was smaller than that proposed in the standard due to the inherent thickness of the test samples. Again the atmosphere chosen was nitrogen, which was supplied at a rate of 50 ml per minute.

For both techniques, the glass transition temperature was calculated using the plots produced by the systems. For DSC, the Heat Flow/ Temperature plots were used while for TMA the Dimension Change/ Temperature plots were used. The coefficient of thermal expansion was calculated using Equation 2.

$$CTE = \frac{\Delta L}{\Delta T \cdot L} = \frac{\text{gradient of curve}}{L} \quad (2)$$

3. Results

The results for the microbond test focused around 8 different epoxy resin: curing agent ratios while the thermal analysis results were based around 7 different ratios respectively. For the microbond test, the primary plots of interest were Max Load/ Embedded Area plots which were used to calculate the IFSS values, with a typical plot shown in Figure 2.

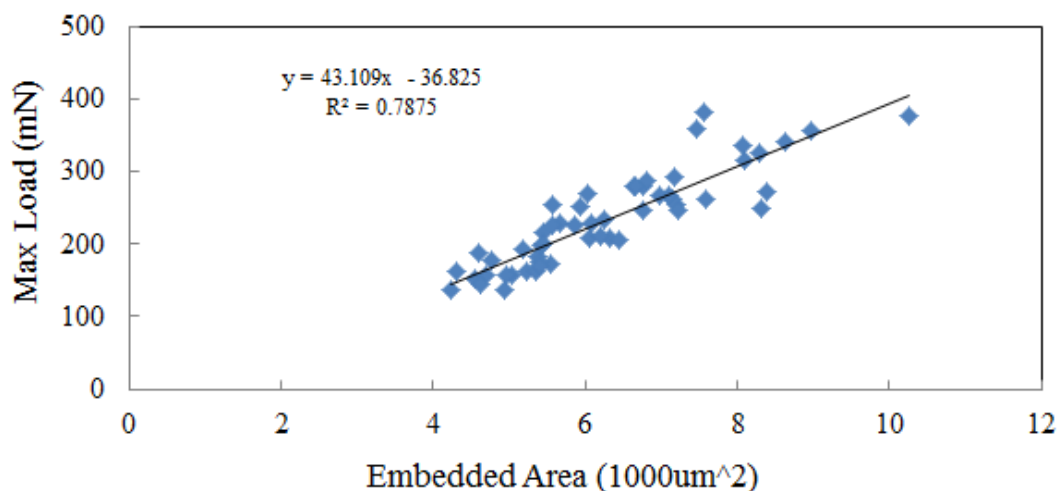


Figure 2. Typical Load vs Embedded Area Plot

When each of the average values of IFSS were calculated and plotted they produced Figure 3. It can be seen clearly that interface performance did indeed vary with the ratio of the epoxy system with peak performance occurring around the stoichiometric value (Amine: Epoxy Group ratio of 1). For the thermal analysis, a similar relationship was shown for the glass transition temperature by both the TMA and DSC data shown in Figure 4. Again, max performance seemed to occur around the stoichiometric value, with performance dropping off sharply at the extreme values of excess hardener

or epoxy.

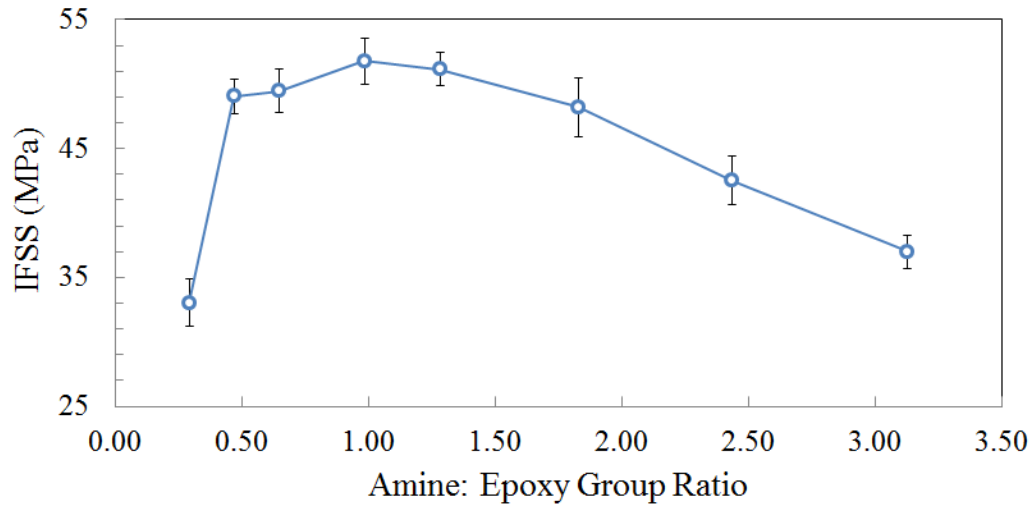


Figure 3. Microbond – IFSS vs Ratio of Amine: Epoxy Group

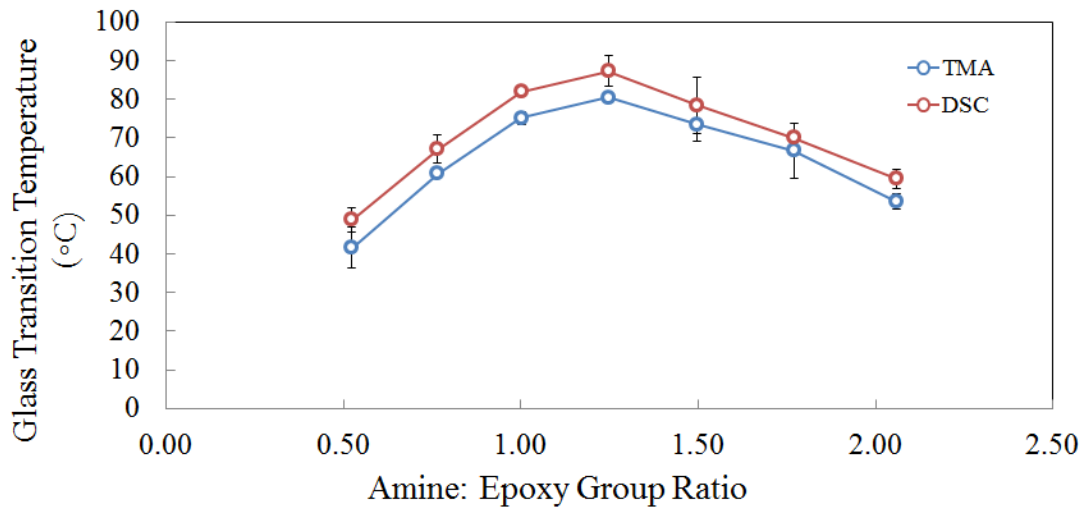
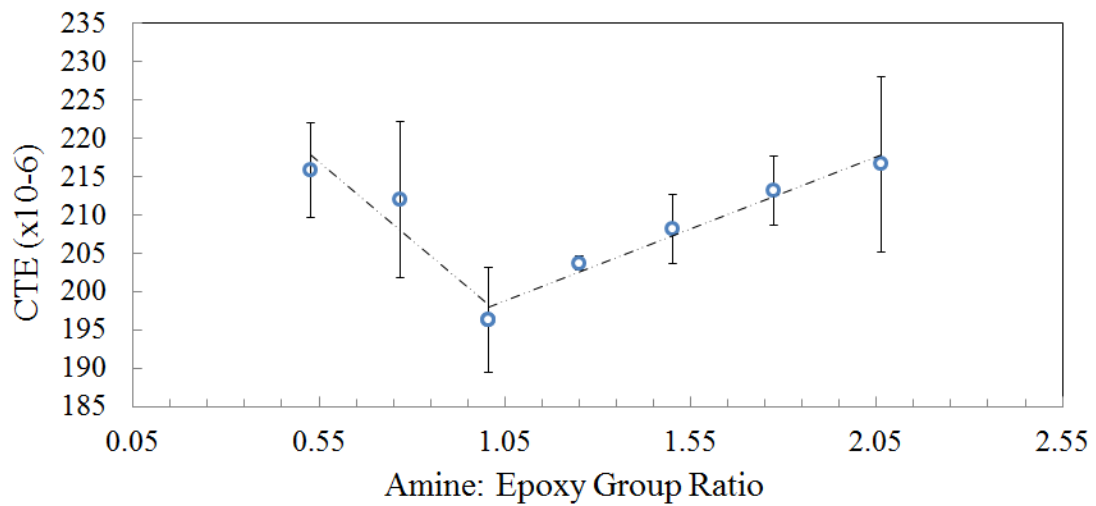


Figure 4. Glass Transition Temperature vs Ratio of Amine: Epoxy Group



Excerpt from ISBN 978-3-00-053387-7

Figure 5. Coefficient of thermal expansion, between 90-130°C (above T_g)

The coefficient of thermal expansion also appeared to be influenced by the ratio of curing agent within the epoxy resin system, both for temperatures below and above the glass transition temperature. However the primary changes occurred above the glass transition temperature as shown in Figure 5.

4. Discussion

Past studies [2] of the role of the mixing ratio of the epoxy system suggested that the relationship shown in Figure 3 could have been due to several different explanations. For instance the reaction between the epoxy system and the APS size applied to the fibres, which with the extra amine groups provided by excess TETA may have influenced the adhesion in the system.

However the data provided shows an interesting correlation between how both the IFSS results and the variance in T_g were influenced similarly by the ratio of the epoxy system. It has been discussed in past literature how thermal and residual stresses due to cure shrinkage can be responsible for a large degree of interface performance. In turn these stresses can be tied to the cross linking density of the material structure which is known to be influenced by the mixing ratio of the system [3].

As such it seems fair to postulate that the changes in T_g and IFSS are both occurring to changes to these residual stresses located at the interface due to the cross linking density varying with the mixing ratio. This fits with the theory that the ideal structure would occur around the stoichiometric value, thus producing the best results as suggested by Figures 3 and 4. It is notable however that for the interface and thermal analysis, the optimum point is not located exactly at the stoichiometric point like is typically quoted but is shifted slightly to the right. This could be due to several possible reasons such as the materials used, the curing schedule used and the true accuracy of the tests conducted.

The results of Figure 5 does show that there appears to be two linear relationships which exist between the mixing ratio and the CTE, above and below the stoichiometric range with the pivot appearing to be at the stoichiometric point. This picture fits with that shown by Palmese et al [12] and suggests that the CTE might possess an inverse relationship with the cross linking density within the polymer. This would make sense since this gradually increases until reaching a maximum at the stoichiometric point, before then decreasing again, inversely matching Figure 5.

5. Conclusion

From the data gathered in this investigation, the mixing ratio of the epoxy system does clearly influence the level of adhesion between the reinforcing fibre and the polymer matrix. Past work has deduced that the chemistry of the system directly influenced the bonding potential within the material, creating stronger links between the fibre and polymer. Although chemistry does definitely appear to play a key role, it may not be specifically in terms of bonding but actually its role in defining the cross linking density of the epoxy system which in turn influences the thermal and residual stresses located at the interface.

The data provided for both interface and thermal properties highlights similar patterns, which match the variation in cross linking density, with optimum performance occurring around the stoichiometric point – the point at which the cross linking density is at its maximum. Thus as the cross linking density decreases, the level of thermal and residual stress due to cure shrinkage will change, in turn altering the interface that forms between the fibre and polymer and influencing the overall performance of the final composite.

As such the need for further research regarding interfacial and thermal analysis of such systems would be beneficial to understanding whether this is what is occurring, or whether it is a combination of this theory and the more established bonding theory.

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