Investigation of stresses in adhesive joints

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Investigation of Stresses in Adhesive Joints

Yang Yu

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of the degree
Doctor of Philosophy of Loughborough University
United Kingdom

March 2005

Supervisor: Dr. G.M. Swallowe
Physics Department
Loughborough University

Yang Yu (2005)
To

my parents

my husband and my son
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Abstract

Adhesive joints are widely used as a structural element in automotive and in aerospace applications because of their main advantage of more uniform stress distributions within lap joints relative to conventional bonding for example riveting or bolting. Adhesives can produce a stronger joint and potentially lengthen its service life. However, the stress distribution in the joint is not uniform and stresses are concentrated at the edges of the overlap. This can cause fatigue and reduce the service life of the joint. Therefore, a large number of analytical and numerical studies have been carried out to study this effect. Comparatively speaking, there is lack of experimental data to prove or cast doubt on the theoretical results.

One of the main disadvantage of adhesive joints is that they have low durability when exposed to hostile environments. Moisture is the most commonly encountered service environment among various environmental conditions, to be considered a critical factor to affect the service life of adhesive joints.

In this thesis, strain gauge, neutron diffraction, and X-ray diffraction methods have been used to directly investigate residual strains and stresses and also strains and stresses under tensile load in the adherends within adhesive joints. The residual strains and stresses have also been studied indirectly by means of a bimaterial method. In addition, the effect of moisture on the joints has been investigated by means of bimaterial and bulk adhesive samples. Neutron diffraction and bimaterial experiment results have been compared to FE predictions and good agreement achieved.

The diffraction studies show that residual stress in joints due to manufacture are small and that water diffusion into the joint is a main critical factor affecting the performance of adhesive and adhesive joints.

Yang Yu

March 2005
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Finally very special thanks to my husband and my son for everything they have done and putting up with me in the three years.
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
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<td>Area</td>
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<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>m²/s</td>
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<td>E</td>
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<tr>
<td>G</td>
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<tr>
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<tr>
<td>ΔL</td>
<td>Displacement</td>
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<tr>
<td>M</td>
<td>Mass</td>
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<tr>
<td>Q</td>
<td>Activation energy for creep</td>
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<td>R</td>
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<tr>
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<td>Relative Humidity</td>
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<td>t</td>
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<tr>
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<tr>
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<td>Poisson ratio</td>
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<tr>
<td>ρ</td>
<td>Density of material</td>
<td>g/mm³</td>
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Chapter 1 Introduction to stresses and strains in adhesive joint

1.1 Brief description of adhesive joint

The use of adhesive as fasteners in structural systems has increased greatly in the last four decades.[1] An important aspect of this enabling technology is metal to metal bonding which has been widely used in the automotive, aerospace and general engineering industries. With the growth in the use of adhesive joints, attention has been focused on studies of the formation and mechanical performance of these joints. Compared to conventional joining methods such as mechanical fastening, the adhesive joining technique has obvious advantages. First, it is the most convenient and cost effective technique; next, the adhesive joint almost eliminates the weight penalty of introducing the mechanical fastener; it also imparts an improved stress distribution and rigidity in the joint and provides very good dynamic-fatigue resistance to the bonded component. In addition, the rapid development of adhesive joining enables novel design concepts to be implemented and allows a wider choice of materials to be available to the designer; finally, adhesive joints improve the appearance of the fastened structure.[1]

In adhesive bonded joints the load is transferred from one member to the adjoining member over a continuous length of overlap thus avoiding the stress concentrations which occur at several discrete points in bolted joints. Adhesive-bonded joints are increasingly used in critical aircraft and spacecraft components because bonding achieves a more uniform load distribution than conventional joining techniques such as riveting or bolting and their strength to weight ratios are higher than those of bolted joints. Avoiding large localised stresses leads to a more reliable joint being produced. However, the stresses in adhesive joints are not uniform and stress concentrations near the edges can cause joint failure. Therefore, it is very important to know what the actual stress is, how large it is and how to reduce it in order to obtain a sound and strong joint. A further problem is the effect of environmental aging, which can have both positive and adverse effects. Water ingress has a plasticising effect on the
adhesive and thus can reduce the joint strength and also can decrease the modulus of the adhesive, which is undesirable. However, the positive effect of moisture is reducing residual stresses.

Stress analysis is one key step followed by engineers in any structural design. It should provide an engineer with reasonably accurate information on the distribution of stress or strain in the real structures subjected to specified loading and service conditions. This information will then enable the engineer to predict the strength and service life of the designed structures. Accurate determination of stress distributions in adhesive bonded joints represents one of the most challenging structural stress analysis problems. This is because bimaterial interfaces and geometric discontinuities create stress concentrations and uncertainty in material behaviour arises.\[1\]

The Lap joint (Figure 1.1) is one of the most common joints in practice, and the single lap joint has been widely used in a variety of standard tests for evaluating adhesive performances and quality control. A single-lap shear is the more usual form of joint. Two adherends of equal thickness with a single interface replace the two equal members which balance a central member of double thickness in the double-lap joint.\[1\]

![a) single lap joint](image1)

![b) double lap joints](image2)

**Figure 1.1 Most common engineering adhesive joints**

The most important stress within the adhesive in a single lap joint is the tensile stress, which appears near or at the interface. The highest stress should be precisely at the
interface and the corner [2]. Stress analysis of the single lap joint loaded in tension has received the most attention as it is a simple and convenient test geometry for evaluating adhesive joints. In this test stresses are not uniformly distributed in the adhesive layer and stress concentrations arise from the differential straining of the bonded substrates and from the eccentricity of the loading path.

Any appropriate design of a structural bonded joint must be based on reliable stress analysis and strength evaluation. It is a challenging task to adequately determine the strain and stress distribution as it is complex even for the simplest single lap joint. This is because the tensile loads in the single lap joint are not co-linear, and thus a bending moment is developed in the continuous adherend at either end of the overlap. The stresses in the adhesive or adherend are not only in shear but also in peel (the normal and tearing stress in the through-thickness direction). As adhesive is normally strong in shear and weak in peel, peel is the stress component that should always be avoided or minimized. One of the effective methods of reducing the peel stress is to taper the end of an adherend as shown in shaded area in Figure 1.1. When an adherend is tapered at its ends the local bending stiffness is then reduced.

1.2 Failure in adhesive joints

Structural adhesive joints can fail at different locations and in a variety of failure modes. Failure may occur or initiate in the adhesive or in the adherend, depending on the geometrical configuration, the materials of the adherends, the adhesive as well as the manufacturing procedure. It is hard to exactly describe and define all the possible failure modes of adhesive joints, especially for composite joints. Failure modes of adhesive joints are generally classified into five different groups:

- Adhesive failure.
- Adherend failure due to bending, tension or compression etc.
- Adherend-adhesive interfacial failure.
- Cohesive failure.
- Out of plane adherend failure due to delamination in composite adherend.
Adherend-adhesive interface failure often takes place at a macro scale when surface preparation or material quality is poor. For an adhesive bonded metal-to-metal lap joint, adhesive failure is the typical failure mode. This is because metal adherends are often stiffer and stronger than adhesives, and therefore large plastic deformation takes place in the adhesive. When the maximum principal stress or strain in the adhesive attains its limiting value, the adhesive failure starts to occur.

When joining organic composite members, particularly thin-walled composite members, an adhesive bond is often selected as the preferred way of structural joining because the adhesive itself is basically the same polymer as the resin matrix. However, due to the laminated nature of composite members and the relative weakness in the through-thickness direction, the failure mechanism of adhesive bonded composite joints becomes more complex than that of a metal-to-metal joint.

1.3 Optimal design of adhesive joint

Accurate prediction of the strength of a bonded joint and its service life is one of the most challenging tasks in structural design. It is difficult to determine the accurate geometry of the irregular adhesive spew fillet and it can significantly influence the stress concentrations at the adhesive ends. Secondly, it is hard and expensive to characterize the adhesive properties, especially when environmental effects are present. Finally, there is a lack of complete understanding and accurate modelling methodologies of failure mechanisms in various bonded joints.

Near the end of an overlap, adhesive spew fillet is formed due to adhesive overflow in the adhesive consolidation procedure. The shape and size of the adhesive spew fillet depends on many manufacturing parameters, such as pressure, curing temperature and the amount of adhesive applied between adherends. However, the size and shape of the spew fillet possesses irregularity and uncertainty and can only be measured after making the joint.

Optimal design of an adhesive joint must be based on:

- The nature of the materials to be joined.
• The method of joining
• The strength and weight analysis

When optimising a structural bonded joint, a designer should consider the following factors:

• Service conditions, such as stresses and environmental conditions, which are likely to be encountered in service
• Selection of material combinations, such as selection of suitable adhesive and adherends
• Manufacturing specifications, such as surface pre-treatment, fabrication procedures, quality assurance and protection from unacceptable hostile conditions in service.

Most work on optimisation of bonded joints [1] has tried to achieve a uniform shear stress distribution along the overlap so that maximum strength could be obtained. In practice, a uniform shear stress distribution does not exist due to fatigue and creep considerations [1]. In single lap joints, the most critical stresses are the peel stresses, which are induced by the eccentricity of the load path. Similarly, the double lap joint also suffers from peel stress concentrations, but the peak shear stresses are also important in double lap joint.

1.4 Study of strains and stresses in adhesive joints

It has been known and proved that the residual stress and strain distributions within the overlap in adhesive joints are closely related to the geometry of the joint [1-5], which includes both adherends and adhesive layer. It is relatively easier to define the geometry of the adherends even in complex shapes. The shape and size of the adhesive spew fillet depends on many manufacturing parameters, such as pressure, curing temperature and the amount of adhesive applied between adherends. However, the size and shape of the spew fillet possesses irregularity and uncertainty and can only be measured after making the joint. Research [1] shows that presence of the adhesive spew fillet can reduce the peak peel and shear stresses in the adhesive layer and thus can improve the strength of the joint. This means that more load is transferred near the overlap end. In addition, voids or defects due to entrapped air
bubbles often exist in the spew fillet or the surface of the spew fillet, which makes modelling of the spew fillet more complicated. These voids can grow when the adhesive is subject to loading and develop into a crack and further propagate to cause premature failure. Therefore, great care has to be taken in the preparation of the adhesive joint.

The methodology of shape optimisation of adhesive fillets [1] was successful in reducing critical stresses in both the single lap joint and double lap joints. The achieved reductions in peak peel stresses in the single lap joint and shear and peel stresses in double lap joint should ultimately lead to an increase in joint strength by reducing the stress concentrations causing failure initiation [1]. Adams and Peppiatt [3] investigated the effect of the spew fillet and also the effect of changing its size. The magnitude of the principal stresses obtained from such an analysis showed a large difference from results gained from analysis which assume the adhesive to have a square edge. The triangular spew fillet (45°) decreased the magnitude of the maximum principal stress by 40% compared with a square adhesive fillet. Crocombe and Adams [4] included the effect of additional parameters such as material and geometric properties in their analysis. They found that the spew fillet always reduces the stress levels from those predicted by closed form analysis (which can only accommodate a square-ended joint) and for parameters such as modulus ratio and adherend thickness. These reductions are greatest at low modulus ratios, high adhesive thickness, and low adherend thickness.

The strains and stresses in single lap adhesive joint have now been studied for several decades using both theory and different experimental methods. A large number of theoretical analysis methods (e.g. finite element) have been used to provide information about the stress distribution in single lap adhesive joints [1-12]. Volkerson presented a theoretical analysis of lap joints by considering only the stress arising from the differential straining in the lap joint in 1938 [1](P33). In other words, the rigid adherend assumption was abandoned, and the adherends are allowed to deform elastically. The differential straining within the adherends result in a non-uniform shear stress distribution in the bond line with a maximum at each end of the overlap. Volkerson’s analysis based on a shear lag model is unsatisfactory in the sense that it doesn’t include the peel stress in the bondline due to the loading eccentricity. Goland and Reissner [1] formulated a theory that includes the peel stress in 1944.
They assumed that the adhesive layer could be neglected because it is very thin compared to the adherend thickness. Their study clearly shows that the shear and peel stresses attain their maximum values at the overlap end. Their solution is suitable in two limiting cases—one in which the adherends are considered inflexible and all deformations occur within the adhesive layer, and one in which the adhesive layer is considered inflexible and all deformations occur within the adherends. Since 1944 a variety of studies have been presented. Wooley and Carver [8] and Adams and Peppiatt [3] are amongst those who first employed the finite element method to determine the stress distributions in adhesive bonded joints. Nowadays, the finite element method is widely used in analysis and design of adhesive bonded joints. A variety of important aspects, such as complex geometry, nonlinear material property and large deformation, can be taken into account in the analysis due to the rapid advance of computing power. R.D. Adams and N.A. Peppiatt studied the normal stresses along and across an adherend in an idealized lap joint by means of an approximate analytical method [8]. The adhesive shear stresses can then be obtained by differentiating these solutions. The transverse shear stress has a maximum value for metals of about one-third of the maximum longitudinal shear stress, and this occurs at the corners of the lap, thus making the corners the most highly stressed parts of the adhesive. In 1974, Stresses in a standard metal to metal adhesive-bonded lap joint were analysed by R.D. Adams and N.A. Peppiatt by using a two-dimensional finite-element method and comparisons were made with previous analysis [3]. Particular attention was paid to the stresses at the ends of the adhesive layer. Unlike previous work, which assumes the adhesive to have a square edge, the adhesive spew is treated as a triangular fillet. They found the highest stresses exist at the adherend corner within the spew. Good agreement was also obtained between some practical results and the finite-elements predictions; A.D. Crocombe and R.D. Adams studied the effect of the interaction between a realistic spew fillet and other joint parameters on the adhesive stress distribution in a single lap joint by means of a linear elastic finite element program [4]. The position of maximum adhesive stress was always found to be within the overlap region; In 1994, the three-dimensional deformation in a single lap joint specimen was investigated by M.Y. Tsai and J. Morton in a linear elastic finite element analysis in which the boundary conditions account for the geometrically non-linear effects [5]. The validity of the model was demonstrated by comparing the resulting displacement fields with those obtained from a Moiré
interferometry experiment. It was shown that three-dimensional regions exist in the specimen, where the adherend and adhesive stress distributions in the overlap near the free surface are quite different from those occurring in the interior. The results show that the longitudinal stress ($\sigma_x$) distributions on the mid-plane and free-surface have a great deal of similarity, but the values on the free surface are slightly less than those on the mid plane. The maximum stress concentration for $\sigma_x$ in the adherend is much higher than the other components. It was also observed that the maximum value of the peel stress occurs at the end of the overlap in the central two-dimensional core region, rather than at the corners where the three-dimensional effects are found.

The constant demand for improvement in the design of adhesive joints has led to the development of various experimental techniques for determining stress distributions in adhesive joint specimens. The experimental methods are employed both for checking the theoretical predictions of Finite Element Mechanics, and the evaluation of stresses in situations where mathematical approaches are unavailable or unsuited. However, since the stress cannot be measured directly, the experimental procedures, of necessity, make their approach through some types of strain measurement. The measured strains are then converted into their equivalent values in terms of stress. In order to achieve this ultimate objective, some type of strain indicating device or measuring device is required.

Strain gauges have been used to provide information on the shear strains and stresses in the surface or the interface between adhesives and adherends. In 1987, the effects of shape and size on the residual stress on the surfaces of silicon nitride/Invar alloy joints was examined by K.Suganuma and T.Okamoto by means of strain gage methods [2]. It was found that the highest residual stress perpendicular to the interface appeared near the corners in the joint, it was tensile in the silicon nitride and compressive in the Invar alloy. It was also found that the residual stress parallel to the interface in the silicon nitride was compressive while that in Invar was tensile. It was observed that a wider bond area produces larger residual stress. It was also observed that a rectangular bond face produced a larger residual stress than a circular bond face. M.E.Tuttle et. al investigated the strain within a single lap joint using embedded strain gages [12]. The results indicated that the presence of the gage is not detrimental to bond performance and excellent agreement between theory and experiment was
achieved, which is a linearly elastic response to within 90 percent of the ultimate shear strength of the bond at room temperature. The neutron diffraction technique has been used to investigate the longitudinal stresses in an adhesive single lap shear joint [13]. A comparison has also been made between the stress distributions in loaded “aged” and “unaged” joints. The experiment results have cast doubt on some of the prediction from recent finite element modelling. Stress and strain measurement in the adhesive bonded joint region by using the x-ray diffraction method has definite advantages. Compared with strain gauge techniques, it is a non-destructive and non-invasive method for determining the normal surface strain and stress distribution of the adherend. Compared with the limited availability of Neutron beam time, x-ray diffractometers are available in most research establishments, two are available in the Physics department of Loughborough University, but limitations arise due to the poor penetration of x-ray through metals.

An experiment on loaded joints to study the environmental effects of water ingress which was carried out at the ILL provided data which disagreed with the predictions of current finite element models [8]. Since large stress gradients are involved, this disagreement may be due to inaccurate predictions of curing and cooling down stresses in current FE models or due to the relatively large(1 mm³) sampling volume that is required for neutron diffraction experiments. This makes it difficult to obtain the spatial resolution required for accurate comparison with the models. Stresses on the surface can be measured by means of strain gauges or Moire techniques but strain gauges do not provide the required spatial resolution to follow rapidly changing stress levels.

There is an increasing interest in how the state of residual stress affects the mechanical properties of the adhesive joint material and its structure. The failure of a structure or a mechanical component is not only due to externally applied loading, residual stress is an important parameter in this respect. All manufacturing processes introduce a new state of residual stress. The residual stress in adhesive joints is mainly created from the curing and cooling down process and is due to different coefficients of thermal expansion between adhesive and adherend. These stresses can have a positive effect, such as increasing the fatigue limit in the case of a compressive surface stress, or they can have a negative effect e.g. decreasing the stress corrosion
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behaviour of a material in the case of tensile residual stress in the adhesive and interface. The effects of residual stress can be considerable. In modern design of adhesive components, these effects are taken into account.

Thermal residual stresses inevitably arise due to the mismatch of the coefficients of thermal expansion (CTE) between the dissimilar materials in the adhesive joints because of the high temperatures used during the curing process. In most situations, curing stress has been considered to be thermal stress. It is therefore important to investigate the thermal stress of bonded structures. Timoshenko [14] investigated the thermal stresses of bimetal thermostats under various conditions on the basis of an elementary beam theory. In his study, the internal forces and moments are assumed to be constant throughout the constituent adherends. In the analysis the interfacial peeling and shearing stresses are not considered. Although several simplified assumptions had been made in his paper, the phenomenon of stress concentration around the edge had been indicated. However, in his analysis, only the normal stresses in the thermostat strips were evaluated using an assumption that these stresses remain unchanged along the strips. Based on Timoshenko’s theory, a theory of interfacial stresses of bonded structures was developed by Suhir [15] in 1986 by introducing the longitudinal compliance. Furthermore, a revised theory was also proposed by Suhir [16] in 1989 to estimate the interfacial stresses. The magnitude and the distribution of the interfacial stresses in thermostat-like structures are determined on the basis of an elementary beam theory, with consideration of both the longitudinal and the transverse interfacial compliances of the thermostat strips.

Adhesive joints experience not only mechanical loads but also thermal loads. In the past ten years, some studies considering thermal loads in single lap adhesive joints were published: In 1992, R.D. Adams et al. studied the effect of temperature on the strength of adhesive joints [9]. It was shown that thermal effects, whether due to mismatch of the adherends or to adhesive contraction by temperature or cure, lead to significant changes in the stress state of lap joints. At the same time, the stress/strain properties of polymeric adhesives also vary considerably with temperature. The combined effect of these factors is illustrated by the variation of strength of single lap shear joints; Thermal residual stress distributions on the interface and in the vicinity of the intersections of the interface and the free surfaces of bonded dissimilar
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materials were calculated using the boundary element method by Seiji Ioka et. al. in 1996 [10]. It was found that the thermal stress singularity disappears for certain ranges of wedge angles of a pair of materials as predicted. The thermal stress analysis of an adhesively bonded single lap joint was carried out by M. Kemal Apalak and Recep Gunes considering the large displacement effects [11]. The analysis showed that the thermal and mechanical mismatches of the adhesive and adherend caused high strain concentrations through adhesive regions close to the adhesive-adherend interfaces around the adhesive free ends. The elastic analyses also showed that increasing the overlap length is not beneficial in reducing the peak stresses in the critical adhesive and adherend regions for all adherend end conditions. Thermal stress within the adhesive in double lap adhesive joint was also studied by some researchers. For example, Y. Weitsman [17] investigated the thermal stresses in a symmetric, double-lap joint which result from cooling from an elevated cure temperature down to room temperature. His analysis was based on variational principles and considers viscoelastic response for the adhesive material. The stresses within the adhesive are computed and compared with the elastic results. It is observed that a significant viscoelastic relaxation takes place within the adhesive. The viscoelastic analysis demonstrates a most significant reduction of residual thermal stress due to a temperature enhanced viscoelastic creep. The reduction, to about 40 to 50% of the elastic results, shows that the incorporation of time-dependent behavior is essential to a realistic design of adhesive joints. Adhesive bonding usually requires curing of the adhesive at temperatures higher than room temperature. When two adherends are made of dissimilar materials having different coefficients of thermal expansions, the cool-down phase of the curing process induces residual stresses in the jointed materials even in a unrestrained structure. Such situations commonly exist when one adherend is made of a metallic material and other is a laminated composite plate. In 1998, Naveen Rastogi, Som R. Soni & Arvind Nagar studied the thermal stresses in aluminium-to-composite double-lap bonded joints subjected to uniform temperature loading using a three-dimensional variational, finite element analysis technique [18]. The joint configurations consisted of an aluminium adherend in combination with four different unidirectional laminated composite adherends (Boron/epoxy, Graphite/epoxy, Glass/epoxy and Glare™). Their study found that the stress distributions are different from those when adherends are made of the same material. When the joint experiences a drop of temperature, the joint was restrained against its
free shrinkage, the stress components in the aluminium and composite adherends increased many fold. However, the magnitude of the transverse shear stress increased at the joint corner A and decreased at the joint corner B (see Figure 1.2). Further, the transverse normal stress was found to change sign from compression to tension at the joint corner B, thereby making both joint corners critical regions for initiation of debonding and subsequent failure of the joint.

![Diagram of double lap aluminium-composite sample. Four different unidirectional laminated composite adherends (Boron/epoxy, Graphite/epoxy, Glass/epoxy and Glare™).](image)

**Figure 1.2** Diagram of double lap aluminium-composite sample. Four different unidirectional laminated composite adherends (Boron/epoxy, Graphite/epoxy, Glass/epoxy and Glare™).

Although the theoretical studies provide excellent models for the changes in stress when loads are applied to a joint, they cannot readily model the residual stresses produced during the curing and cooling down processes and changes due to environmental ageing of the joint. So far, there is lack of experimental investigation of residual strains and stresses in adhesive joints. Thus, the experimental investigations of residual strains and stresses in adhesive joint are becoming more and more important, and more work is strongly required in the future. To date only a few experimental studies of residual stresses exist, in particular there was only one direct measurement of residual strains and stresses in adhesive lap joints [13]. Morton [19], Post [20] et al. and Kang et al. [21] utilized Moiré interferometry to study the state of thermal stresses in bimaterial structures. They pointed out that significant stress occurs at a very small region near to the end of interface. In 1999, longitudinal residual stresses were found to be non-uniform by means of the neutron diffraction technique[13]. These experimental result disagree with Adam's prediction [22].
For the double lap joint, due to symmetry, it is normally assumed that the outer adherend can experience longitudinal and lateral displacements, and that the middle adherend undergoes only longitudinal displacement [1].

Ideally, there should be uniform shear stresses in both the adherend and adhesive layer in the adhesive bonded-double lap joints under tensile load so as to give maximum joint efficiency. Actually and unfortunately, this ideal situation is hardly ever achieved due to differential straining in the adherends—the shear-lag effect, bending induced by the non-axial loading and end effects caused by the free surfaces at the edges of the adhesive layer. The shear-stress distributions in the adhesive layer of a double lap joint were predicted by these six analyses [3].

1. The simple Volkersen analysis [23].
2. A modification of the Volkersen analysis to take into account the fact that the shear stress must be zero at the ends. This is based on Volkersen’s more recent work [24].
3. Demarkles’s modification of Volkersen’s original analysis to take into account adherend shears [25].
4. An analysis allowing for the effects of bending of the adherends in a double lap joint derived from the equations given by Volkersen [24].
5. Finite-element results from the full-length lap model.
6. Finite element results from the half-length lap model.

The results of the above six analyses show similar trends and good agreement, which is that the maximum stress is achieved near the edge and corner and decreases towards the centre. This result is similar to that of single lap adhesive joints.

The transverse normal-stress distributions in adhesive layers were predicted from analyses 4, 5 and 6. A good agreement was obtained between the two finite element methods, but, the results are completely different compared with single lap joints. A concentration of shear stress at the ends of the overlap in double lap joints has been more recently considered in detail by Hart-Smith [26].

Since, for the double lap joint, like many adhesive joint configurations, the maximum stresses occur in the regions at the edges of the adhesive layer, it is therefore necessary and important to consider modifying the geometry of the joint in order to make joint strength enhancement possible. For instance, the existence of an adhesive
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Fillet at the edge of the adhesive layer has been indicated, using finite element techniques, to reduce the maximum stresses in the adhesive [4]. Also, it has been proved that by tapering the adherends to an almost ‘razor edge’, the peak stresses in the adhesive may be reduced [27].

Joyanto and Robert found the stresses in a different type (double butt strap) double lap adhesive joints using both theory and experimental corroboration [28]. The joint was subjected to a quasi-static load, and the viscoelastic stress analysis performed with Schapery’s Direct method of transform inversion. The variations of stresses and strains through the adhesive thickness was determined by means of modelling. The presented theory results were corroborated with the results of photoelastic and photoviscoelastic analyses of four geometries of double lap joints. They also later made a parametric study of the behaviour of double lap joints [29]. They found that the most important parameter is the ratio of the adherend modulus to the equivalent property of the viscoelastic adhesive, the stresses are highest when this ratio is one and decrease as this ratio increases. The next most important parameter is the thickness of the adhesive. With decreasing adhesive thickness, the stress distribution along the length of overlap is increasingly uniform and the gradient of the stress distribution through the adhesive thickness also decreases. The length of overlap influences only the location of the maximum shear stress, whereas a change in the relative thicknesses of the adherends has a minimum influence on the magnitudes of the stresses.

A detailed stress analysis in a CFRP/steel double-lap joints loaded in tension was made with an elastic-plastic model for a rubber-modified epoxy adhesive by R.D. Adams etc in 1986 [30]. The results of their analysis have been combined with the measured properties of the materials forming the joint in order to predict quantitatively the failure strengths of the various joint designs studied. A good agreement was achieved between the theoretically predicted and experimentally measured strengths.

1.5 Adhesive
The basic requirement of an adhesive is that it should wet the surface and make intimate molecular contact with it. To do this, the adhesive needs to be fluid. It then hardens to a cohesive solid by one of the following process.

- Loss of solvent or water, by migration or evaporation.
- Freezing of a hot melt adhesive.
- Chemical reaction.

In structural adhesives, hardening is always achieved by chemical reaction which involves polymerisation and crosslinking.

Polymers are formed by taking a small group of atoms, and using numbers of such groups to build a large molecule. The building process may join up groups into a very long chain-like molecule or into a branched or a three-dimensional crosslinked structures(Figure 1.3). As crosslinked polymers are both insoluble and infusible, it is essential that the chemical reactions that cause crosslinking occur within the assembled joint.

Figure 1.3 a) Linear  b) branched and  c) crosslinked polymers
The crosslinking process for epoxide adhesives does not need pressure, although slight pressure is always advantageous, particularly if the temperature is to be raised. It then serves to ensure maintenance of true surface contact. Some type of locating jig involving slight pressure is all that needed for this.

Epoxide adhesive has this name because one of their components, the resin, contains epoxide rings; this is a three-membered ring with two carbon atoms singly bonded to an oxygen atom. The second component is a hardener or curing agent, and hardening is by chemical reaction which produces a crosslinked polymer. Cured epoxides are hard and rigid.

Epoxide adhesives adhere to a large number of materials including metals and glasses, and can also be used as the matrix-resin in particle or fibre reinforced composites. Advantages over other reaction-curing adhesives are that no volatiles are released on cure and shrinkage is low.

Cured structural adhesives are crosslinked as this greatly reduced creep. In the early stages of cure, adhesives are thermoplastics. At first the viscosity rises steadily, but at the gel-point, when there is an average one crosslink per molecule, the viscosity rises sharply. The whole adhesive now becomes a single crosslinked network. At the gel time the adhesive has lost its ability to flow, but further crosslinking still takes place which strengthens the adhesive.

Shrinkage of the adhesive on cure may lead to stresses in joints. One advantage of epoxide adhesives is that the shrinkage on curing is low. However, volume changes on the polymerisation of monomers are much larger. Adams, Yu and Karachalios (1996) showed that [30] the shrinkage for a two-part epoxide adhesive is 3.75% at room temperature and 4.46% at 60°C; a one-part epoxide cured at 135°C gives a shrinkage of 5.13%. Shrinkage can be reduced by the addition of particulate fillers.

1.6 The effect of moisture on adhesive and adhesive joint

The corrosion of metals in adverse atmospheres has a corresponding phenomenon in polymeric materials whereby they deteriorate in the presence of oxygen and/or
moisture in the atmosphere. In some cases heat must also be present to assist these agencies. The oxidation of many polymers is catalysed by ultraviolet light but this is not usually a problem with adhesives because they are rarely exposed to light.

Adhesive systems may be exposed to various environmental conditions during their service life. Moisture is commonly encountered in the service environment. Water is the substance which gives the greatest problems in the environmental stability of adhesive joints. The performance of the adhesive systems may deteriorate to a certain extent upon exposure to harsh environments for a certain period of time. If the relative humidity is high, then the strength of joints usually falls over a period of time. Water is a problem because it is very polar and has a high value of the polar component of surface free energy. Other common liquids such as lubricants and fuels are of low or zero polarity and do not significantly weaken adhesive joints. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of adhesively bonded joints.

Water absorbed in the polymer is generally divided into free water and bound water [31, 32]. Water molecules, which are contained in the free volume of the polymer and are relatively free to travel through the microvoids and holes, are identified as free water, while water molecules that are dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water.

Research of Maggana and Yasufuku [31, 33] further suggested that bound water which exists in the polymer network can be recognized as loosely bound water, which can be released easily upon heating and strongly bound water that is “frozen” in the network and difficult to remove from the polymer. Antoon et al [34] found that water absorbed in an epoxy resin usually interacts with the polar groups by hydrogen bonding and the epoxy-water interactions are completely reversible. However, Woo and Piggot [35] suggested that water in certain epoxy systems is not bonded to any polar groups or hydrogen-bonding sites.

Moisture absorbed in a polymer matrix can lead to a wide range of effects, both reversible and irreversible, including plasticization by weakening the intermolecular interactions among the functional groups of the chains [36, 37], debonding at filler-
matrix interfaces [38-40], structural damage such as micro-cavities or crazes [32, 41], further crosslinking [42, 43], and chemical degradation of the matrix due to hydrolysis and oxidation during long-term exposure to water [44]. In response to the effects of water in polymers, the mechanical properties including tensile strength, moduli, and the failure strain [39, 45, 46], fracture toughness [46], and thermal properties such as the glass transition temperature [36] can be significantly affected. K.I. Ivanova, et al [36] investigated environmental aging effects on thermal and mechanical properties of three model electrically conductive adhesives (ECAs). Results obtained on aged samples with and without drying suggest that the conductive adhesive may have experienced both reversible and irreversible effects during environmental aging. Both plasticization that is reversible and further crosslinking and thermal degradation, which are irreversible, are indicated upon exposure of adhesives to the hot/wet environment. Studies conducted by Ivanova, et al [36] and Gonon, et al [47] showed that absorbed water cannot be totally removed by thermal annealing and the residual water in the adhesive is believed to be the one which is strongly bonded to polar sites.

Water can also weaken the strength of adhesive joints by attacking the adhesive/substrate interface. For resin-filler systems, some research has shown that absorbed water can attack the matrix/filler interface and cause debonding at the interface [38-40]. Lefebvre, et al [48] discovered in their study of an epoxy/glass model system that the critical humidity was around 70% RH, at which point an abrupt loss of adhesion, a sudden increase in water solubility and swelling in the epoxy, and a decrease in the mobility of dissolved water occurs.

Several mechanisms have been proposed to explain the degradation of the adhesive joint interface due to water absorption, though no single mechanism is applied to explain all the failure phenomena. In some circumstances, substrate corrosion may occur in adhesive joints and act as a factor that weakens the performance of the adhesive joint. Examples of gross corrosion have been reported for rubber/steel joints exposed to seawater or salt-spray [49] when an electrochemical potential is present and also in electrically conductive adhesive joints where the conductive adhesive is bonded to the non-noble metal surface [50, 51]. Davis et al., utilizing the technique of electrochemical impedance spectroscopy, observed this behavior in epoxies bonded to aluminum with surface preparations that resulted in either a weak or strong interface
They observed that the rate of crack growth was slow for strong interfaces, but for weak interfaces crack growth was detected almost immediately as moisture appeared at the interface and resulted in a fast rate of crack growth.

Diffusion into adhesive joints was studied by Zanni-Deffarges and Shanahan by comparing the calculated diffusion rates between non-bonded adhesive specimens and bonded adhesive joints [54]. They observed that the diffusion coefficient of the adhesive joint was greater than that of the bulk adhesive. They conclude that the diffusion rate at the interface was greater than in the bulk adhesive. Furthermore, they mention the effect of adhesive shrinkage at a constrained interface may result in dilation of the adhesive near the interface. Nyugen et al. [55] and Linossier et al. [56] have also compared diffusion rates between bulk specimens and adhesive joints using Fourier transform infrared spectroscopy in the multiple internal reflection mode (FTIR-MIR). They detected significant diffusion at the interface for poorly adhered adhesive systems.

Vine et al. [57] studied the moisture uptake of an epoxy bonded to aluminum adherends with various surface treatments. They observed faster diffusion in three-layer sandwich specimens than predicted, based on mass-uptake experiments performed on bulk diffusion specimens. They attributed this behavior to the presence of micro-cavities in the adhesive layer and cite work by Nyugen et al., Zanni-Deffarges and Shanahan, and Linossier et al. as evidence for diffusion at the interface as possibly faster than in the bulk.

All polymers absorb water to some extent and, although its effect on the interface is paramount, it can alter the properties of the bulk adhesive by changing the glass transition temperature, inducing cracks and crazes, or by chemical reaction (Comyn [30]). Epoxide adhesives only appears to be chemically attacked by water under extreme conditions (Antoon and Koenig [34], 1981). However, it is often found that interfacial (rather than cohesive) failure of adhesively bonded structures is the dominant failure mechanism [27, 58-60]. Therefore the attention of some studies have been focused on the degradation of the interface region [58]. One of the restrictions of studies into adhesive durability is the extensive time taken to gather information regarding the properties of the adhesive and the degradation of the joints. The
conventional way to degrade an adhesive joint is to place the complete test specimen (joint sample) in a moist environment. This allows moisture to diffuse through the perimeter of the adhesive. The process of moisture diffusion is slow due to the long diffusion path, often taking months or years to achieve a significant level of degradation. Furthermore, a non-uniform moisture distribution is established within the joint. In order to get rid of the difficulty of experiments due to the long diffusion time, Loh et al [58], Chang et al. [61] and Wylde and Spelt [62] have used an open faced concept to accelerate the moisture uptake as well as providing a uniform degradation. An open-faced specimen is a layer of adhesive cast on only one side of the substrate resulting in a large surface area of the adhesive for moisture uptake. This method gives a far shorter diffusion path than that known in conventional joints. Therefore, bimaterial samples and thin bulk adhesive specimens are used in the work described in this thesis. This significantly reduces the time taken to reach equilibrium and provides a uniform state of degradation.

A steady reduction of moisture dependent mechanical properties of AV119 as moisture content increases has been found by Loh et al [58] measured in both bulk adhesive and open-faced samples. It was also noted that these properties depended solely on the moisture content even though they were aged at different humidities and exposure times.

It is apparent that water enter joints by means of diffusion through the adhesive which can occur in all joints and is regarded by many the primary access route. Diffusion through the adherend is again inevitable with organic substrates but is generally not possible with inorganic adherends.

Joints may be weakened in a variety of ways. Water is absorbed by and plasticizes all organic adhesives. Normally, the effect of plasticisation is to weaken the joints but it has been reported that low concentrations of water may have the net effect of strengthening some joints [38]. Bowditch [38] studied the durability of adhesive joints in the presence of water. He thinks the chemical degradation of adhesive, of substrate and of chemical bonds across the interface as a result of interaction with water are all possible. It is also conceivable that joints may be weakened as a result of swelling which leads to the introduction of internal stresses. The significant weakening of
adhesive joints as a result of swelling would be associated with the absorption of large amounts of water and such materials are regarded as unsuitable for structural applications. Attack by water of the oxide substrate has been invoked as the reason for the poor durability of adhesive joints to metallic substrates, such as aluminium and titanium. The results in his study (bulk epoxy adhesive with calcium carbonate filler particles was used) shows how the failure stress of a bulk epoxy-based adhesive falls with immersion in water at 50°C. In fact, the failure may not actually be at the interface but may be through a locally weaker region of the adhesive very close to the interface. The results from aluminium-filled epoxy-based adhesive show a progressive loss of strength associated with increasing exposure of water. It was also shown that the absorption of water by adhesives leads to the plasticization of the matrix resin to reduce the strength. His study also shows that the effects of water cannot be considered without also taking into account the temperature at which tests are conducted and the time for which they run, for both factors may exert a significant influence on the observed results.

Other studies also show a loss of joint strength with time of exposure to water. The work of Minford [63], involved etched aluminium bonded with one-part epoxy-based adhesives exposed to 100% r.h. at 52°C. The results produced by Minford show joint strengths for a range of adhesives falling with progressive exposure to a wet atmosphere. Although the adhesive system degrade in the presence of water, it also retains some basic joint strength under the conditions of test. Results from work by Orman and Kerr [64] indicates that after exposure to moist atmospheres, joint strength is lost by the epoxy-bonded aluminium joints and that greater damage is experienced in the wetter environment. Generally, in most cases, much of the strength lost was recovered after drying. This is probably due to the reversible effect of plasticization. However, not all strength is recovered and it seems reasonable to suppose that the irrecoverable component is due to irreversible disruption at the interface as a result of attack by water.

Kinloch [59] et al. carried out work in which tensile butt joints were exposed to increasingly severe aqueous environments. The data shows that strength is progressively lost with exposure to water. It can also be seen that the higher the temperature of the water, the more profound the effects but in all cases the degrading
effect appears to be diminishing with time and some residual strength remains. Of particular interest are the results obtained from exposure to a humid atmosphere for it would appear that the joints are unaffected by the experience. In any event the joints survived a period of 2500h without any apparent loss of strength at 55% r.h.

1.7 The influence of temperature to the adhesive and its joint

At a low enough temperature a polymer is rigid and glassy, while on heating through the glass transition temperature it becomes relatively flexible and rubbery. At still higher temperatures polymers decompose chemically. All three temperatures exist within a moderate range of temperatures over which the properties of the common metals vary only slightly.

It is accepted [38] that elevated temperatures will accelerate degradation rates but it is also acknowledged that its use as a means of accelerating natural processes should be approached with caution. At the higher temperature, the rate of degradation or weakening of the adhesive was such that failures were exclusively cohesive and the adhesive was the weak link in the chain. At the lower temperature on the other hand, failures were found to be at or near the interface and the influence of surface preparation on the durability of the joints became apparent.

Adhesive joints will be weakened with temperature rises, this reflects both the decrease in modulus with temperature and the increase in rate of diffusion with temperature. Furthermore, when the temperature approaches Tg, the mechanical properties will be dramatically changed, the modulus rapidly decreases and the thermal expansion coefficient increases very rapidly. All these changes with temperature rises would cause the strength of joints to decrease more rapidly. This can be confirmed by means of the data of Gledhill and Kinloch [65]; Gledhill, Kinloch and Shaw [59]. In their work, butt joints in mild steel, prepared by degreasing and grit-blasting, were bonded with an epoxide adhesive DGEBA with 2,4,6-tris(dimethyl-aminomethyl)phenol-tri-2-ethylhexanoate and immersed in water. They found the diffusion coefficients of water in the adhesive increased about 25 times from room temperature to 90°C. These results reflect the rates at which joints are weakened in water. It was therefore found that the strength of the joint apparently
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decreases with increasing temperature and that this strength decrease is closely linked to water uptake.

1.8 Bulk adhesive test specimen

The design of adhesively-bonded structures often involves the use of Finite Element Analysis (FEA) to predict component performance. Accurate predictions require accurate adhesive properties data. Normally, there is no recommended mechanical properties data from the supplying industry or company. These data are often best obtained from bulk test specimens [66]. The use of bulk test specimens brings advantages in the measurement of strain (through larger gauge sections) and in the interpretation of the data (since the absence of adherends leads to simpler stress distributions). However, the bulk specimens may differ from the adhesive in the joint by incorporating voids (that act as stress concentrators to promote premature failure) or by experiencing different thermal histories (thus reaching a different state of cure). Thus, specimen preparation is an extremely important aspect of the test programme.

All the methods of bulk adhesive specimen preparation should take into account the cohesive nature of adhesives. The mould for preparing bulk specimens should be made mostly from metal to ensure good thermal conductivity. The surfaces in contact with the adhesive should be flat, dry and free from defects. They should be covered with a release coating (e.g. thin PTFE sheet) to facilitate release of the specimen. Frames or spacers are required to control the specimen thickness - 2-3 mm thickness is suitable for many tests [66]. Clamps or weights should be used to hold the mould closed whilst the specimen cures. Low viscosity adhesives may be dispensed directly into shaped moulds for the production of test specimens. However, many adhesives will not flow readily and such an operation is likely to be ineffective. These adhesives are best produced as flat plaques from which test specimens can be taken after the adhesive is cured [67]. The dispensing operation needs to be done so that additional air is not trapped in the final specimen. As supplied adhesive contains varying proportions of entrapped air, techniques such as vacuum stirring or centrifuging have
been suggested as methods for removing air from the adhesive. These techniques have varying degrees of success depending on the viscosity of the adhesive but add considerably to the cost of specimen preparation.

The bulk adhesive properties are intrinsic and not influenced by the adherends. In the case of adhesive joints adhesives are sandwiched between adherents and their properties are subjected to the influence of adherends and are thus more representative of real behaviour. Are the properties of bulk adhesive same as those of adhesives in adhesive joint? For a while, it was believed that the properties of bulk adhesive are different from the adhesive properties in adhesive bonded joints due to an improper interpretation of carefully designed tests (Adams and Coppendale) [1]. Their result show a good agreement between the shear modulus measured in the bulk adhesive form and that measured in sandwiched forms. However, it has to be noted that the quality of bulk adhesive specimens is vital, e.g. without defects (voids and porosity), because of the size and contents of defects in the thin adhesive layer in a joint, which are generally smaller than those in the bulk adhesive specimens.

Adhesives can be classified into two types: one is a brittle adhesive and the other is a ductile adhesive. For a brittle adhesive, a proportional linear relationship exists between the stress and strain, while for a ductile adhesive, a non-linear stress-strain relationship is normally observed [1] (p24). For brittle adhesives, Young's modulus and Poisson's ratio are the two adhesive properties that are required to perform a linear stress analysis for adhesive joints. However, for ductile adhesives, the entire non-linear adhesive behaviour must be adequately determined and then taken into account in the stress analysis in order to accurately predict stresses and strains in a joint, and further to predict its service life. In 1997, Tong [1] measured FM300k film adhesive using a thick adherend test and butt joint test to obtain a typical true shear and tensile stress-strain curves. Althof et al [1](P29) measured shear stress-strain curves of FM73 adhesive at room temperature using different test methods, namely Napkin ring test, and thick adherend tests. Good agreement was obtained from these three different test methods, they all show a linear relationship between shear stress and strain when the shear strain is less than about 0.05. In this thesis, all the tests are in the linear range of the adhesive, the strain is less than 0.01. Hence, the film...
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Adhesives can be treated as linear brittle adhesive when transforming strains into corresponding stresses.

References:


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Chapter 2 Basic Theory

2.1 Strain and stress

2.1.1 The Stress Tensor (or Stress Matrix)

Surface tractions, or stresses acting on an internal datum plane, are typically decomposed into three mutually orthogonal components. One component is normal to the surface and represents direct stress. The other two components are tangential to the surface and represent shear stresses.

What is the distinction between normal and tangential tractions, or equivalently, direct and shear stresses? Direct stresses tend to change the volume of the material (e.g. hydrostatic pressure) and are resisted by the body's bulk modulus (which depends on the Young's modulus and Poisson ratio). Shear stresses tend to deform the material without changing its volume, and are resisted by the body's shear modulus.

![Figure 2.1 Stress matrix. $\sigma_{ab}$ is the stress on the a plane along b direction.](image)
Defining a set of internal datum planes aligned with a Cartesian coordinate system allows the stress state at an internal point $P$ to be described relative to $x$, $y$, and $z$ coordinate directions. For example, the stress state at point $P$ can be represented by an *infinitesimal* cube with three stress components on each of its six sides (one direct and two shear components). Since each point in the body is under static equilibrium (no net force in the absence of any body forces), only nine stress components from three planes are needed to describe the stress state at a point $P$, which is shown in Figure 2.1.

These nine components can be organized into the matrix:

$$
\begin{pmatrix}
\sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz}
\end{pmatrix}
$$

where shear stresses across the diagonal are identical (i.e. $\sigma_{xy} = \sigma_{yx}$, $\sigma_{yz} = \sigma_{zy}$, and $\sigma_{zx} = \sigma_{xz}$) as a result of static equilibrium (no net moment). This grouping of the nine stress components is known as the stress tensor (or stress matrix).

### 2.1.2 Strain

"Strain" is a measure of the deformation of a solid body.

- **Global 1-D strain (engineering strain)**

Consider a rod with initial length $L$ which is stretched to a length $L'$. The strain measure $\varepsilon$, a dimensionless ratio, is defined as the ratio of elongation with respect to the original length.
If the rod is an isotropic, homogeneous body, subjected to a homogeneous load distribution at its boundary, the strain at a point will be given by Eq. (1).

\[ \varepsilon = \frac{L - L_0}{L} \]  

- True strain

The definition of strain is needed to be reconsidered when plastic deformation is appreciable. True strain \( (\varepsilon_T) \) is based on instantaneous sample length. It can be approximated by considering the total strain to result from a series of small, incremental extensions (\( \delta l \)) with the length at each increment being the instantaneous sample length. Hence,

\[ \varepsilon_T = \frac{\delta l}{\ell_0} + \frac{\delta l}{\ell_1} + \cdots = \sum \left( \frac{\delta l}{\ell_i} \right) \]  

(2)

where \( \ell_1 = \ell_0 + \delta l, \ \ell_2 = \ell_1 + \delta l, etc. \) When expressed in differential form, Eq. (2) becomes:

\[ d\varepsilon_T = \frac{dl}{\ell} \]  

(3)

On integrating Eq. (3) from \( l = l_0 \) to \( l = l_i \),

\[ \varepsilon_T = \ln \frac{\ell_i}{\ell_0} \]  

(4)

2.1.3 Material properties

2.1.3.1 Stress and strain curve

**The Tensile Stress-Strain Curve**

![Diagram](image)

Figure 2.3 Tensile stress-strain curve
A schematic tensile stress-strain curve is given in Fig. 2.3. If the material is loaded to a stress above the elastic limit, and then the load is removed, some permanent or plastic strain remains. The yield strength is a stress to cause a small but readily measurable plastic strain. It can be measured in the manner shown in Fig. 2.3. A line parallel to the initial linear line is drawn from an offset on the strain axis (typically 0.2%). The intersection of this line with the stress-strain curve defines the material’s offset yield strength. The yield strength represents the stress required to produce the offset strain. If the material were loaded to the stress and then unloaded, the resulting permanent strain would equal the offset strain. The strain reaches its maximum value at the tensile strength, this is the maximum strain for which plastic deformation is uniform along the sample length. The (engineering) stress decrease afterwards until fracture happens, this stress is called the fracture stress. This phenomenon is associated with nonuniform material deformation. Following linear elastic deformation, plastic deformation commences at a stress approximately equal to the yield strength, following yielding, the material work hardens. The maximum stress a material can tolerate in a tensile test is the tensile strength.

2.1.3.2 Isotropic and anisotropic

Isotropic------If the material property measured is identical in all directions then the body is isotropic. (Figure 2.4a)

Anisotropic------If the property is different in different directions then the body is anisotropic. (Figure 2.4b)

Most polycrystalline metallic alloys and thermoset polymers are considered isotropic, where by definition the material properties are independent of direction. Three material properties are commonly used to describe isotropic materials in the linear-elastic region, They are Young’s modulus E, Poisson’s ratio v and shear modulus G. As can be seen in the equation below only two of these properties are independent, these are normally chosen to be E and v.

\[ G = \frac{E}{2(1+v)} \]  

(5)

- 33 -
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(5)
2.1.4 Hooke’s law (Isotropic form)

Different kinds of deformation can all be related through the idea of stress and strain. Stress is the applied pressure, or a change in the applied pressure; strain is how the object changes shape in response to the stress. When the strain is directly proportional to the applied stress, the object behaves elastically, and will return to its original shape when the stress is removed. For elastic deformation, then, there is a linear relationship between the stress and strain. Outside of this linear region (beyond the elastic limit) the strain is no longer proportional to the applied stress. Hooke’s law states that strain is proportional to stress, so it applies to elastic deformation, and to the equations concerning stretching, shear, and volume deformation.

Note: Hooke’s Law is valid under linear-elastic conditions only.
• 1-D Hooke’s law

In a one-dimensional form Hooke’s law is usually written as

$$\sigma = E\varepsilon$$  \hspace{1cm} (6)

where $\sigma$ is the uniaxial stress and $\varepsilon$ is the uniaxial strain and $E$ is the Young’s modulus. Note the conditions required for linear elastic nature of the material.

• 3-D form of Hooke’s law

In the most general case, six components of strain exist “at a point”: $\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \gamma_{xy}, \gamma_{xz}, \gamma_{yz}$. The total strain $\varepsilon_{aa}$ produced by all stresses applied simultaneously is determined by “adding up” the strain caused by each individual stress component.

$$\varepsilon_{xx} = \frac{\sigma_{xx}}{E} + \frac{-\nu \sigma_{yy}}{E} + \frac{-\nu \sigma_{zz}}{E} + [0] + [0] + [0]$$

$$\varepsilon_{xx} = \frac{1}{E} [\sigma_{xx} - \nu \sigma_{yy} - \nu \sigma_{zz}]$$  \hspace{1cm} (7)

The 3-D form of Hooke’s law is therefore described as follow equations:

$$\varepsilon_{xx} = \frac{1}{E} [\sigma_{xx} - \nu \sigma_{yy} - \nu \sigma_{zz}], \quad \gamma_{yx} = \frac{2(1+\nu)\tau_{yx}}{E}$$

$$\varepsilon_{yy} = \frac{1}{E} [-\nu \sigma_{xx} + \sigma_{yy} - \nu \sigma_{zz}], \quad \gamma_{xx} = \frac{2(1+\nu)\tau_{xx}}{E}$$

$$\varepsilon_{zz} = \frac{1}{E} [-\nu \sigma_{xx} - \nu \sigma_{yy} + \sigma_{zz}], \quad \gamma_{xy} = \frac{2(1+\nu)\tau_{xy}}{E}$$  \hspace{1cm} (8)

Note: the 3-D Hooke’s law above is applied with 3 assumptions: a) Linear-elastic behaviour (yielding doesn’t happen). b) isotropic material behaviour. c) constant environmental conditions (e.g., constant temperature)
2.2 Residual stress

2.2.1 Definition

Residual stresses can be defined as those stresses that remain in a material or body after manufacture and processing in the absence of external forces or thermal gradients [1]. All residual stress systems are self-equilibrating; the resultant force and the moment which they produce must be zero.

Residual stress measurement techniques invariably measure strains rather than stresses, and the residual stresses are then deduced using the appropriate material parameters such as Young’s modulus and Poisson’s ratio.

2.2.2 Type

Three kinds of residual stresses are usually defined: the macro stresses (or stresses of first kind) over a few grains, the stresses of second kind over one particular grain and the stresses of third kind across sub-microscopic areas, say several atomic distances within a grain. The stresses of second and third kind are also called micro stresses. The different types of residual stress are shown schematically in Figure 2.5.

- **Type I**
  Macrostress (σI)—which develop in the body of a component on a scale larger than the grain size of the material.
- **Type II**
  Microstress (σII)—that vary on the scale of an individual grain. Such stresses may be expected to exist in single-phase materials because of anisotropy in the behaviour of each grain. They may also develop in multi-phase materials because of the different properties of the different phases.
- **Type III**
  Sub-microstress (σIII)—are also micro residual stresses that exist within a grain, essentially as a result of the presence of dislocations and other crystalline defects. **Type II** and **Type III** are often grouped together as microstresses.
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2.2.3 Origins

Residual stresses develop during most manufacturing processes involving material deformation, heat treatment, machining or processing operations that transform the shape or change the properties of a material. They arise from a number of sources and can be present in the unprocessed raw material, introduced during manufacturing or can arise from in-service loading [2-5]. The residual stresses may be sufficiently large to cause local yielding and plastic deformation, both on a microscopic and macroscopic level, and can severely affect component performance. For this reason it is vital that some knowledge of the internal stress state can be deduced either from measurements or modelling predictions.

Figure 2.5 Different kinds of residual stresses. note: $\alpha$ and $\beta$ may be different phases in a multiphase material, or different grains in an anisotropic single phase material.[1]
Both the magnitude and distribution of the residual stress can be critical to performance and should be considered in the design of a component. In any free standing body stress equilibrium must be maintained, which means that the presence of a tensile residual stress in the component will be balanced by a compressive stress elsewhere in the body. Tensile residual stress in the surface of a component are generally undesirable since they can contribute to, and are often the major cause of, fatigue failure, quench cracking and stress-corrosion cracking. Compressive residual stresses in the surface layers are usually beneficial since they increase both fatigue strength and resistance to stress-corrosion cracking, and increase the bending strength of brittle ceramics and glass. In general, residual stresses are beneficial when they operate in the plane of the applied load and are opposite in sense (for example, a compressive residual stress in a component subjected to an applied tensile load).

The origins of residual stresses in a component may be classified as:

- **Mechanical**

  Mechanically generated residual stresses are often a result of manufacturing processes that produce non-uniform plastic deformation. They may develop naturally during processing or treatment, or may be introduced deliberately to develop a particular stress profile in a component [6]. Examples of operations that produce undesirable surface tensile stresses or residual stress gradients are rod or wire drawing (deep deformation), welding, machining (turning, milling) and grinding (normal or harsh conditions).

- **Thermal**

  On a macroscopic level, thermally generated residual stresses are often the consequence of non-uniform heating or cooling operations. Coupled with the material constraints in the bulk of a large component this can lead to severe thermal gradients and the development of large internal stresses. An example is the quenching of steel or aluminium alloys, which leads to surface compressive stresses, balanced by tensile stresses in the bulk of the component. Microscopic thermally generated residual stresses can also develop in a material during manufacture and processing as a
consequence of the Coefficient of Thermal Expansion mismatch between different phases or constituents.

- Chemical

The chemically generated stresses can develop due to volume changes associated with chemical reactions, precipitation, or phase transformation. Chemical surface treatments and coatings can lead to the generation of substantial residual stress gradients in the surface layers of the component. Nitriding produces compressive stress in the diffusion region because of expansion of the lattice and precipitation of nitrides, and carburising causes a similar effect [7]. The magnitude of residual stresses generated in coatings can be very high – compressive stresses of the order of 6-8GPa or higher have been measured at the interface of some thermal barrier coatings.

2.3 Creep

2.3.1 Creep concept

Creep is a slow continuous deformation of a material under constant stress [8]. At temperatures greater than 0.4 to 0.5 of the melting temperature (when the temperature is expressed in degrees Kelvin) materials will slowly deform under constant loads which would not cause any plastic deformation at room temperature. This deformation is called creep.

2.3.2 creep in polymers

Creep is normally an undesirable phenomenon and is often the limiting factor in the lifetime of a part [9]. It is observed in all materials types; for metals it only becomes important for temperatures greater than about 0.4T_m (absolute melting temperature). Polymers are especially sensitive to creep deformation. Many polymeric materials are susceptible to time-dependent deformation when the stress level is maintained constant; such deformation is defined as viscoelastic creep. This type of deformation may be significant even at room temperature and under modest stress which is below the yield strength of the material. Creep tests on polymers
are carried out in by continuously applying a tensile stress, which is maintained at a constant level while strain is measured as a function of time.

2.4 Diffusion

2.4.1 Definition

Diffusion is the phenomenon of material transport by atomic motion [9]. From an atomic perspective, diffusion is just the stepwise migration of atoms from lattice site to lattice site. In fact, the atoms in solid materials are in constant motion with changing positions. For an atom to make such a move, two conditions must be met: 1) There must be an empty adjacent site, and 2) the atom must have sufficient energy to break bonds with its neighbour atoms and then cause some lattice distortion during the displacement. At a specific temperature some small fraction of the total number of atoms are capable of diffusive motion, by virtue of the magnitudes of their vibrational energies.

2.4.2 Diffusion in polymers [10]

In the glassy state, a polymer is hard and may be brittle, diffusion is intimately related to restricted polymer chain mobility. Rotation about the chain axis is limited and motion within the structure is largely vibratory within a frozen quasi-lattice. Polymers of this type are very dense structures, with very little internal void space. Hence, it is not surprising that penetrant diffusivities through such a structure are low. In contrast, polymers in the rubbery state typically are tough and flexible, with diffusion associated with freer chain motion. In this case, larger segments are thought to participate in the diffusion process due to internal micromotions of chain rotation and translation, as well as vibration. Basically, a large amount of free volume in which diffusion may take place is more readily accessible. Adhesives are generally used in the glassy state, however, as the temperature increases, transformation to a rubbery state occurs with a resultant large increase in diffusion rate.

Polymer membranes may be highly swollen by a penetrating liquid, and their properties thus altered. For liquids in polymers, sorbed volumes can be 10 to 20% or even higher. In the
presence of a swelling liquid, polymer membranes actually undergo structural rearrangements as a result of the interactions between penetrant and polymer.

2.4.3 Diffusion can be divided into steady state diffusion and nonsteady-state diffusion

- Steady state diffusion

Diffusion is a time-dependent process. That is, in a macroscopic sense, the quantity of an element that is transported within another is a function of time. Often, it is necessary to know how fast diffusion occurs, or the rate of mass transfer. This rate is frequently expressed as a diffusion flux \( F \), defined as the mass (or, equivalently, the number of atoms) \( M \) diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time. In mathematical form, this may be represented as

\[
F = \frac{M}{At}
\]  

(9)

where \( A \) denotes the area across which diffusion is occurring and \( t \) is the elapsed diffusion time. In different form, this expression becomes

\[
F = \frac{1}{A} \frac{dM}{dt}
\]  

(10)

The units for \( F \) are kilograms or atoms per meter squared per second (kgm\(^{-2}\)s\(^{-1}\) or atomsm\(^{-2}\)s\(^{-1}\)).

If the diffusion flux does not change with time, a steady-state condition exists. One common example of steady-state diffusion is the diffusion of atoms of a gas through a plate of metal for which the concentrations (or pressures) of the diffusing species on both surfaces of the plate are held constant. This is represented schematically in Figure 2.6a.
When concentration $C$ is plotted versus position (or distance) within the solid $x$, the resulting curve is termed the concentration profile; the slope at a particular point

$$\text{concentration gradient} = \frac{dC}{dx} \quad (11)$$

In the present treatment, the concentration profile is assumed to be linear, as depicted in Figure 6 b), and

$$\text{concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B} \quad (12)$$

For diffusion problems, it is usually most convenient to express concentration in terms of mass of diffusing species per unit volume of solid (kg/m$^3$ or g/cm$^3$).

The mathematics of steady-state diffusion in a single ($x$) direction are relatively simple, in that the flux is proportional to the concentration gradient through the expression

$$F = -D \frac{dC}{dx} \quad (13)$$
The constant of proportionality $D$ is called the **diffusion coefficient**, which is expressed in square meters per second. The negative sign in this expression indicates that the direction of diffusion is down the concentration gradient, from a high to a low concentration. The equation above is sometimes called **Fick's law**.

**Nonsteady-state diffusion**

Most practical diffusion situations are nonsteady-state ones. That is, the diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting. Under conditions of nonsteady state, use of equation 13 is no longer convenient; instead, the partial differential equation

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \tag{14}
\]

known as **Fick's second law**, is used. If the diffusion coefficient is independent of composition (which should be verified for each particular diffusion situation). Equation 14 can be simplified to

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{15}
\]

**2.5 Adhesive joint**

**2.5.1 Definition**

An **adhesive** is a kind of polymeric material which, when applied to surfaces, can join them together and resist separation.

A **structural adhesive** is one used when the load required to cause separation is substantial such that the adhesive provides for the major strength and stiffness of the structure.

**Adherends**: The structural members of the joint are joined together by the adhesive.

**Adhesion**: is used when referring to the attraction between the substances.
2.5.2 Adhesive

There are a variety of adhesives either organic or inorganic. Structural adhesives can be generally divided into the following groups: epoxy, polyester, acrylic, polyurethane, polyimide. Amongst these adhesives, the most widely used structural adhesives are epoxies. Epoxy adhesives typically contain several components, and the epoxide resin is the most important component. In practice, numerous epoxy adhesives can be formulated to achieve desirable properties by blending the base resins with a variety of materials, for example hardeners, flexibilisers, tougheners and fillers. Adhesives can appear in a form of a thin film, and also can be in liquid form with several parts [11].

Adhesives have been employed in nearly all technically demanding applications, such as in the transport industry, and more recent aircraft have used adhesives with great success [12].

When selecting an adhesive, an engineer should consider the following factors:[11]

Shelf life of the unmixed adhesive.

Viscosity, usable life, wetting ability and joint open time of the freshly mixed liquid adhesive.

Curing cycle and rate of strength development.

Mechanical properties, such as modulus, strength and fracture toughness, temperature and moisture resistance, creep and fatigue of hardened adhesive.

The adhesives can bond different kind of materials together, e.g. metals, plastics, honeycombs and fibre reinforced plastics.

Adhesive bonding is a process of joining two or more solid or hardened materials via application of adhesive layers. This is widely accepted and used in industry. Adhesives have been used to join timbers, plastics, metals, as well as consolidated fibre reinforced composites. Adhesive bonding can be conducted at an elevated temperature or at an ambient temperature.[11]

Adhesives need to possess desirable properties, such as high tensile fracture strain, fracture energy, and peel strength. Besides, the adhesive also needs to have a reasonably high yield stress in order to avoid excessive creep in the joint. Some glues such as rubber toughened epoxy gives a very high single lap shear strength at room temperature, reflecting its good
ductility in shear and good toughness and good resistance to crack propagation under tensile loading at this temperature, but it has a relatively low glass transition temperature (about 120°) and therefore the joint strength is poor at elevated temperatures. The combination of the good mechanical properties with a high glass transition temperature is a current aim of many adhesives technologists.

Epoxy adhesives, in use for many years, come in a wide selection of two differing types: one is cured at room temperature (polymerisation takes place at room temperature), another needs to cure at high temperature (requires the application of external heat for correct polymerisation). Both types require a clamping pressure during the curing process. Furthermore, if either type is to be used at a temperature higher than the curing temperature, then a post-cure temperature above the expected maximum test temperature should be maintained for several hours.

With epoxies, there is no solvent evaporation involved, very little shrinkage, and a good permanent bond is formed with a wide variety of materials. Epoxies also exhibit excellent moisture and chemical resistance, and can be used over a temperature range from cryogenic to 315°C [13].

An uncured adhesive, being liquid, will flow over the surfaces to be bonded and as a consequence of this intimate contact it interacts with their atomic and molecular forces. Then, as a result of the hardening process the adhesive will turn into a strong solid itself which, still being in intimate contact with the faying surfaces, will hold them both together. It is important to understand how adhesives function and it is equally important to understand why and how they fail. One of the primary reasons has been the brittleness of the traditional, high performance adhesive. In order to achieve very high shear strengths—and therefore the capacity to sustain high loads—it has been necessary to produce hard and brittle adhesives. Regrettably, such materials are particularly prone to damage when a bonded structure is shock loaded. The momentary distortion of the substrate induces powerful peel and cleavage forces which a brittle adhesive may not be able to resist.

In the case of adhesives used in engineering applications, the adhesive often is initially in the form of a 'liquid' monomer which polymerises to give the high molecular-weight polymeric adhesive. The engineer must appreciate that the load-carrying ability of the joint, and how
long it will actually last, are affected by: a) the design of the joint, b) the manner in which loads are applied to it, and c) the environment which the joint encounters during its service life.

2.5.3. Adhesive advantages

Compared with other mechanical bonding technique, the adhesive has the following advantages:[16]

- Adhesives have high ability to join dissimilar materials; such as, the joining of metals, plastics, rubbers, fibre-composites, wood, paper products, etc.
- The major advantage of adhesives is the ability to join sheet-material efficiently which includes both metallic and non-metallic materials. Compared to metallic substrates, adhesives, being based largely upon organic polymers, do not posses anywhere near the level of tensile fracture strengths exhibited by most metals but when used to join relatively thin sheets of metal their strengths are usually more than adequate.
- An improved stress distribution in the joint which imparts, for example, a very good dynamic-fatigue resistance to the bonded component.
- It is the most convenient and cost effective technique.
- Making an increase in design flexibility which enables novel design concepts to be implemented and allows a wider choice of materials to be available to the designer.
- Improving the appearance of the fastened structure.
- An improvement in corrosion resistance.

2.5.4 Adhesives disadvantages:[16]

- To achieve long service life from adhesives joints in very severe, hostile environments may often require surface pre-treatment process for the substrates being joined.
- Compared to other fastening techniques such as welding, riveting, etc. the upper service-temperatures that adhesives can withstand are limited.
- The strength and toughness of adhesives in tension or shear is relatively low compared to many metals. Hence, whilst adhesives are very effective at joining thin sheets of
metal, they are not normally used for joining thick metallic components, unless the bonded area is large or the adhesive is kept in compression.

- Non-destructive test methods for adhesive joints are relatively limited compared to other fastening methods.

2.5.5 Film adhesive

There are many forms of adhesive. For example, liquid adhesive, powder adhesive, film adhesive and hot melt adhesive. Film epoxy adhesives have been mainly used in this work. Film adhesives have many advantages over other types. These include [14]:

- High repeatability---no need for mixing or metering; Provides uniform, controlled glue line thickness.
- Ease of handling-----low equipment cost; relatively hazard-free; clean operating.
- Very little waste-----performs can be cut to required size.
- Excellent physical properties----wide variety of adhesive types available

Because of these advantages, film adhesives have been more widely used than other forms in recent years. In addition, a number of high-strength structural adhesives are currently supplied in film and tape form. However, film adhesives may be only used on flat surfaces or simple curves which is very suitable for lap adhesive joints.

2.5.6 Curing of adhesives

An adequate time allowance must be made for the adhesive to cure. Room temperature curing often require a number of hours to set, during which period the assembly must be jig-supported. Structural film adhesives generally require high bonding pressures to be sustained during hot-curing schedules [14]. Another recent approach to rapid curing at room temperature is by using ultra-violet radiation [15].

The exact conditions required for curing the adhesive joints depend on the properties of the specific adhesive used [14]. The manufacturer invariably recommends the optimum procedure. In most examples, curing is always accomplished through the application of heat or pressure, or both. Depending on the properties of the adhesive, curing pressures may range

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from contact pressure, 0.01MPa to 3.5MPa, while curing temperatures may range from room temperatures up to 350°C, although the maximum temperature usually used is 177°C.

After application of the adhesive the assembly must be mated as quickly as possible to prevent contamination of the adhesive surface [14]. The substrates are held together under pressure and heated, if necessary, until cure is achieved. The equipment required to perform these functions must provide adequate heat and pressure, maintain constant pressure during the entire cure cycle, and distribute pressure uniformly over the bond area. For adhesives curing with simple contact pressure at room temperature, extensive bonding equipment is not necessary.

2.5.7 Strength of adhesive polymers

In cases where adhesive joints fail within the adhesive, the appearance of the adhesive surface after breaking the joint can vary considerably with the temperature and rate of strain, as well as with the nature of the material. Failure can be brittle or ductile; in the first case the adhesive fails before it yields, while in the second failure is preceded by yielding.

Structural adhesives generally, and certainly those with reasonable peel resistance, like those adhesives used in this work will yield before failure.

- Creep failure

Another possible response to stress is a period of continuous deformation. Under conditions of shear, which is the only situation that has been studied in detail for adhesive joints, there is a time delay before deformation commences.

Most creep studies have been on linear polymers, none of which are used as structural adhesives. The absence of cross linking in such materials permits extensive and continuous deformation, which is one of the major reasons for rejecting them as structural adhesives. The only crosslinked material for which creep has been extensively studied is natural rubber which has properties widely different from structural adhesives.
2.5.8 Mechanical deformation of adhesives

Structural adhesives are used at temperatures below their glass transition temperatures. The mechanical properties of interest are therefore those of the material in its glassy state. Because adhesives are used in very thin films and shearing is in the plane of the film, the shear strain can be large. Shanahan (1974) measured shear strains of up to 50% while the adherends of a lap-shear joint were creeping under load. Manufacturer’s data (P196)[16], for FM73M adhesive with BR127 primer indicates that shear stress relaxation happens with increasing temperature. The same strain but with a smaller stress results because the modulus decreases with increasing temperature.

In general tensile testing of joints at room temperature and many applications of adhesive bonding only involve the adhesive in its wholly glassy state. An important aspect of viscoelasticity arises when polymers are cyclically deformed. Even at temperatures below Tg there is still some viscous component which leads to energy loss during the cycling. Advantageously, this can lead to the damping of free vibration but, disadvantageously, the energy converted into heat raises the temperature. In theory, the rise in temperature may affect the modulus and the endurance of the joint but, in practice, the relatively large mass of metal and small volume of adhesive with a large interfacial area give optimum conditions for the removal of heat. In the case of metal to metal joints the temperature rise under dynamic deformation is negligible, but this cannot be assumed for other substrates such as carbon or glass fibre composites.

The strength of a properly made adhesive joint is directly related to the mechanical properties of the adhesive of which it is made. The properties of joints also depend on the modulus of the adhesive and adherend. The modulus of adherends such as metals or carbon fibres are much higher than that of the adhesive, it can therefore be concluded that the displacement under load will be mainly due to strain in the adhesive.

Adhesives cannot be regarded as metals with a rather low modulus and strength as they principally consist of organic polymers whose properties arise from molecular rather than atomic interactions. Molecular interactions are sensitive to temperature over a range that would leave the structural metals virtually unaffected. The level of molecular motion in
organic polymers is much higher than in metals and glasses, and this makes them both more susceptible to creep and more permeable to low molecular weight substances such as atmospheric gases and water. The diffusion of water in adhesives is a key factor in the reduction of the strength of adhesive joints on exposure to humid air. In general, with a structural adhesive, the thinner the glue-line, the stronger the joint. It is not always possible to ensure a uniformly thin glue-line, particularly with substrates such as timber or concrete, and adhesives which perform well under these conditions are referred to as having good gap-filling properties [17].

2.5.9 Adherends

2.5.9.1 Surface treatment

According to the ‘weak boundary layer theory’, clean surfaces are capable of forming strong adhesive bonds, but they can be prevented from doing so by a layer of contaminant which is cohesively weak. For most clean surfaces of most materials, adhesive bonds are strong in dry conditions. In some cases of dirty surfaces, contaminants such as oils and grease can actually be removed by the adhesive dissolving them. However, it is accepted that for a good joint, the surfaces need to be clean and, whatever their chemical nature, must be coherent in the sense that they must not be powdery or friable. Material on the surface of an adherend which is cohesively weak, or which will not adhere to the substrate or adhesive with sufficient strength, may constitute a weak boundary layer. Materials which may need to be removed from a surface prior to bonding include:

- Lubricating oils and greases on metals;
- Weak oxide layers on metals;
- Dust and other particulate contamination;
- Additives and low molecular weight material on the surfaces of plastics;
- Mould-release agents such as silicones, fluorocarbons and waxes

Surface treatment of an adherend prior to adhesive bonding can bring about one or a combination of the following effects:

- remove material.
- modify the chemistry of the surface.
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- change the surface topography.

The effect of such treatments may be to increase the strength of the newly made joint, but perhaps more importantly to improve joint durability on exposure to water or water vapour.

Metals have high-energy surfaces because of the very polar oxide layer they carry. There is therefore little difficulty in getting almost any adhesive to bond to them provided they are clean and free from loose and incoherent oxide. Compared with metals, all plastics have relatively low-energy surfaces. Some of them have surfaces of very low free surface energy and are difficult to bond, such as polyethylene and polypropylene. In this work bonding was between metal and metal or metal and composite and good bonds were therefore expected in all cases.

References:

Chapter 3 Measurement of properties of adhesives

3.1 Introduction

Any design of a structural bonded joint must be based on adequate knowledge of the stresses in the joint and the strength of the joint. To determine the stresses in a structural bonded joint and further to predict its strength and service life, it is necessary to know the material properties of the adhesive and adherend [1]. The properties of structural adhesives play an important role in the residual strains and stresses as well as the strength of the adhesive joint. For example, Young's modulus $E$, thermal expansion coefficient $\alpha$, moisture expansion coefficient $\beta$, glass transition temperature $T_g$, creep data and diffusion coefficient $D$ are all properties correlated to the strength of the adhesive joint. However, the Young's modulus and diffusion coefficient $D$ vary with the temperature as well as the humidity of the environment and this directly causes changes in the strength of adhesive joints. The thermal expansion coefficient increases dramatically when the adhesive is above the glass transition temperature. Therefore, the measurement of adhesive properties is very important and necessary for analysing the strains and stresses of the adhesive joints as well as evaluating their strength. So far, there is no accurate recommended data for most properties of the adhesives used in this thesis due to the difficulty of preparing a regular size and shape and smooth sample (for measuring Young's modulus $E$ and thermal expansion coefficient). In this work, some typical properties of different adhesives were measured by means of different experimental techniques. In this thesis, 3M DP190 2-part epoxide, AV119 single part epoxy resin, FM 300-2 Film adhesive (modified epoxy resin film) and FM 73 film adhesive were tested.
3.2 Sample preparation

3.2.1 Fluid adhesive (before curing)
The 3M DP190 2-parts epoxide samples were prepared in machined aluminium grooves by making use of matched folded paper to separate the adhesive and aluminium slot, see Figure 3.1. The samples were cured at 60°C for 3 hours and then slow cooled down to room temperature at a rate of about 0.8°C/min. Both bulk and rod adhesive samples were prepared using this method.

![Figure 3.1 Mould for preparation of samples](image)

3.2.2 Film adhesive (before curing)
The FM 300-2 bulk adhesive sample was prepared by cutting the required amount of same size pieces of FM300-2 film adhesive and carefully rolling them one by one with a smoothed aluminium roller to make a firmly combined block of adhesive with a smooth surface. The sample was then cured inside a die in a press with 40MPa pressure at a temperature of 120°C for 2 hours. Teflon sheets were used to separate the sample from the die.
3.2.3 Bimaterial sample preparation
These consisted of an adhesive layer on a steel sheet. Before joining the steel and adhesive together, the steel was cleaned using p320 and p800 abrasive papers, and subsequently degreased in acetone. The sample was then prepared by carefully cutting a piece of required size of FM300-2 film adhesive and slightly pressing it onto the steel surface by binding it onto the steel using P.T.F.E tape (Tape with a low coefficient of friction, heat resistance, anti-stick and release characteristics, and chemical resistance).

The sample was immediately heated to 120°C at a rate of 3.4°C/min and was cured for 1.5 hours at 120°C in an oven with a glass door, after which, the sample was slow cooled at a rate of 1°C/min.

The bimaterial sample was prepared for the measurement of the coefficients of thermal expansion of the adhesives. (details in 3.4.3)

3.3 Young's modulus measurement

3.3.1 Introduction
The residual stress and strain in a joint created from the curing and cooling down process, is directly related to the ratio of the Young's modulus of adhesive and adherend [2]. In addition, knowledge of Young's modulus is necessary when residual strains from experiments are transformed to residual stresses. Hence, the measurement of the Young's modulus of the adhesive is essential. In this work, the Young's modulus of the adhesives were measured using Dynamic Mechanical Analyser (carried out commercially by an external company) and a rod vibration method.

3.3.2 DMA method (Dynamic Mechanical Analyser)
Dynamic mechanical analysers measure changes in mechanical behaviour, such as modulus and damping, as a function of temperature, time, frequency, stress or strain or combinations of these parameters. The forced non-resonance technique is one of the simpler dynamic mechanical methods to understand. In most commercially available instruments a periodic force is applied to a sample and the amplitude and phase of the resultant displacement are measured. All of these instruments employ a linear actuator where the force applied is calculated from a knowledge of the input
signal to the electro-magnet coils in the driver. An alternative to the above is where a force transducer is used to measure the applied load, with the sample between this transducer and the magnetic driver. During DMA, an oscillatory (sinusoidal) strain (or stress) is applied to the material and the resultant stress (or strain) generated in the material is measured.

- Measurement results
  1. 3M DP190 2-parts epoxide adhesive

![Graph showing Young's modulus E of 3M DP190 2 parts epoxide as a function of temperature.](image)

**Figure 3.2** Young's modulus measurement by DMA (single cantilevered bending) of 3M DP190. The results of Young's modulus measurement over the temperature range -50 to 110 °C by means of DMA. The blip at 0°C is an instrumental artefact and can be ignored.

2. FM 300-2 film adhesive.

The experimental results were obtained from Triton Technology Ltd.
Dynamic Properties vs Temperature - 3 point bending

![Graph showing Young's modulus E vs temperature for FM 300-2 in 3 point bending.](image)

**Figure 3.3** Young's modulus $E$ of FM 300-2 vs temperature -- 3 point bending

Dynamic Properties vs Temperature Single Cantilever Clamped Bending Sample

![Graph showing Young's modulus E vs temperature for FM 300-2 in single cantilever clamped bending.](image)

**Figure 3.4** Young's modulus $E$ of FM 300-2 vs temperature-- Single cantilever clamped bending sample
3.3.3 Rod vibration method

3.3.3.1 Basic theory
Young’s Modulus can be determined very accurately by finding the resonant frequencies of a rod of the material of interest. These are related to the propagation speed as shown below. The rod is excited by means of an electromagnetic transducer, which acts magnetically on a small ferromagnetic disc bonded to one end of the rod. By this means, the rod is excited without physical contact with the transducer. Thus the ends of the rod may be regarded as free. The vibration is received by an identical magnetic disc and transducer arrangement at the other end of the rod. Resonance occurs when both ends of the rod execute vibrations of maximum amplitude.

Longitudinal waves propagate in a rod at a speed

\[ v = \left( \frac{E}{\rho} \right)^{\frac{1}{2}} \]  

(1)

Where \( E \) is the Young’s modulus and \( \rho \) is the density of the material.

The first three resonant modes are shown in Figure 3.6.
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It can be seen that resonance occurs when:

\[ L = n\lambda / 2; (n = 1, 2, 3...) \]

since \( f = \frac{v}{\lambda} \)  \hspace{1cm} (2)

The resonant frequencies are then given by:

\[ f = \frac{n}{2L} \left( \frac{E}{\rho} \right)^{1/2}; (n = 1, 2, 3...) \]  \hspace{1cm} (3)

Therefore the Young’s Modulus is:

\[ E = \left( \frac{2nfL}{n^2} \right)^2 \rho \]  \hspace{1cm} (4)

3.3.3.2 Experiment and results

The experimental setup is shown in Figure 3.7

---

Figure 3.6 The first three resonant modes

---

Figure 3.7 Young’s Modulus measurement by making use of Vibration of rod method
The sample was prepared from a $295mm \times 9.23mm \times 10.50mm$ rod of 3M DP190 2-parts epoxide cured at $60^\circ C$ for 3 hours and then slow cooled down to room temperature.

The measurement results are shown in Table 1 and Figure 3.8

Table 1 Measurement data of Young’s Modulus using Vibration of rod.

<table>
<thead>
<tr>
<th>N</th>
<th>F(Hz)</th>
<th>E(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62</td>
<td>17.40</td>
</tr>
<tr>
<td>2</td>
<td>126</td>
<td>17.96</td>
</tr>
<tr>
<td>3</td>
<td>210</td>
<td>22.17</td>
</tr>
<tr>
<td>4</td>
<td>295</td>
<td>24.61</td>
</tr>
<tr>
<td>5</td>
<td>373</td>
<td>25.18</td>
</tr>
<tr>
<td>6</td>
<td>446</td>
<td>25.00</td>
</tr>
</tbody>
</table>

The measurement values of $E$ from the rod vibration method looks too tiny compared to the general data for Young’s modulus $E$ of adhesive 1-4GPa [5]. However, these results are similar to those obtained by DMA at $-40^\circ C$ and may therefore be correct. If this is the case modelling the ambient temperature behaviour of materials bonded with DP190 will be very difficult.

3.4 Thermal expansion measurement

3.4.1 Introduction

The residual stress and strain in an adhesive joint is produced mainly due to differential thermal expansion between adhesive and adherend when the joint experiences a drop of temperature. The magnitude of residual stress and strain strongly depends on the difference of thermal expansion coefficient of adhesive and adherend and the change in temperature [3, 4]. It is therefore necessary to measure the coefficients of thermal expansion for both adherends and adhesive in order to quantify the residual stress and strain in adhesive joints. The CTE for the adherend is normally given in published tables, particularly for adherends such as steel and aluminium which were used in this thesis. However, the adhesives used in this thesis lack...
accurate CTE data. In this work, both Microscope and bi-material experimental methods were employed to measure the CTEs of adhesives.

3.4.2 Microscope method

3.4.2.1 Basic principle:
The coefficient of thermal expansion, \( \alpha \), of a solid rod is defined as

\[
\alpha = \frac{\Delta L}{L \times \Delta T}
\]  

(5)

Where \( \Delta L \) is the change of length, \( L \) is the length of the rod, \( \Delta T \) is the change in temperature.

According to the propagation theory of uncertainty, the uncertainty (\( \delta \alpha \)) of thermal expansion coefficient is:

\[
\delta \alpha = \sqrt{\left( \frac{\partial \alpha}{\partial \Delta L} \delta (\Delta L) \right)^2 + \left( \frac{\partial \alpha}{\partial L} \delta L \right)^2 + \left( \frac{\partial \alpha}{\partial \Delta T} \delta (\Delta T) \right)^2}
\]

\[
= \sqrt{\left( \frac{1}{L \Delta T} \delta (\Delta L) \right)^2 + \left( \frac{\Delta L}{L^2} \frac{1}{\Delta T} \delta L \right)^2 + \left( \frac{\Delta L}{L \Delta T} \frac{1}{\Delta T^2} \delta (\Delta T) \right)^2}
\]  

(6)

From the equation above, we can see the error comes from three factors (\( \Delta L \), \( L \), \( \Delta T \)). Hence, suitable equipments for measuring the expansion of the sample and change in temperature should be selected based upon the requirements of uncertainties of each parameter.

3.4.2.2 Selection of measurement instruments

- Vernier microscope

In this work, a Vernier microscope was chosen for length measurement, and a thermocouple was used for measurement of temperature. Using these \( \delta L = \delta (\Delta L) = 0.02 \text{mm}; \delta T = 1^\circ \text{C} \). The uncertainty of thermal expansion coefficient \( \alpha \) can therefore be calculated using equation (6) for the sample length and temperature range used as: \( \delta \alpha = 1.15 \times 10^{-5} \). The manufacturers published thermal expansion
coefficients of 3M DP190 2-part epoxide, and FM300-2 film adhesive are between
4.5-6.5 x 10^{-5} [5]. Giving an uncertainty of $\frac{\delta \alpha}{\alpha} \approx 0.18$

This method can therefore be used to measure the thermal expansion coefficients for
both adhesives within an accuracy of 20% or better.

- **Precision Optical Measuring Machine**

From the equation (6) above, it can also be seen that the main error arises from the
measurement of $\Delta L$, while the total measurement error of $\Delta T$ and $L$ are less than 10%.
In other words, the accuracy of thermal expansion coefficient mainly depends on the
uncertainty of the length measurement instrument.

Use of the SIP (Manufacturing companies name) optical measurement instrument SIP
MU-214B which has an accuracy of $\pm 1 \mu m$, can reduce the uncertainty in $\alpha$ to be 13%
of that obtained using the vernier microscope. Using the more accurate SIP optical
machine could also reduce the required temperature range. The temperature was
controlled using a high powered heating resistance with a flat surface on which to
locate the block of adhesive. The temperature can be adjusted by varying the input
voltage and was monitored using thermocouples. Due to the difference of the
measurement methods between the vernier microscope and the SIP optical measuring
machine, a bigger physical size resistance (longer than the sample) can be used to heat
the sample to achieve better temperature equilibrium than with the vernier microscope
setup. Using different size high power resistances to heat the sample enables the
sample to have a more uniform temperature distribution.

### 3.4.2.3 Trial experiment

As illustrated in Figure 3.8, the thermal expansion coefficient of the adhesive was
obtained by measuring a 30mm x 10mm x 2mm cured epoxy sample using a vernier
microscope. The temperature of the sample was controlled by means of a high power
resistance ($R=25\Omega$). The required temperature can be acquired by adjusting the input
voltage to a value within 5V-10V and waiting until the temperature reaches an
equilibrium value.
According to the estimate of uncertainty, the larger the temperature range the more accurately the thermal coefficient value would be obtained. However, considering the glass transition temperature of adhesives and the temperature of the environment, the maximum measurement temperature should not be too high in order to keep the sample below $T_g$. A temperature range $20^\circ C$-$100^\circ C$ was initially considered reasonable for 3M DP190 2-part epoxide adhesive since the glass transition temperature of 3M DP190 2-parts epoxide is around $100^\circ C$. A trial experiment was performed in order to test the viability of this method.

The variation of the length of an adhesive sample was measured over the temperature range $20^\circ C$-$100^\circ C$. The results of the experiment are shown in Table 2.

It can be seen from the results that the data above $80^\circ C$ is showing an increased $\Delta L$ while the measurement data between $20^\circ C$-$80^\circ C$ looks to have constant increments with temperature. This can be explained by the difficulty in heating the sample uniformly at the higher temperature using this simple method due to the bigger temperature difference between room temperature and the required higher temperature of sample and possibly the closeness of the temperature to $T_g$. In addition, the thickness of the sample is also a factor. Thus, a temperature range of $20^\circ C$ to $80^\circ C$ was chosen for a formal experiment.
Table 2 Trial experimental measurement of CTE

T: temperature (°C); A1, A2: Readings (mm); L: Measured length (mm);

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>A1</th>
<th>A2</th>
<th>L</th>
<th>ΔL_n</th>
<th>ΔL</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>33.73</td>
<td>63.89</td>
<td>30.16</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>33.73</td>
<td>63.93</td>
<td>30.20</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>40</td>
<td>33.72</td>
<td>63.95</td>
<td>30.23</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>33.71</td>
<td>63.96</td>
<td>30.25</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>60</td>
<td>33.69</td>
<td>63.97</td>
<td>30.28</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>70</td>
<td>33.69</td>
<td>64.00</td>
<td>30.31</td>
<td>0.03</td>
<td>0.15</td>
</tr>
<tr>
<td>80</td>
<td>33.68</td>
<td>64.04</td>
<td>30.35</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td>90</td>
<td>33.63</td>
<td>64.08</td>
<td>30.40</td>
<td>0.09</td>
<td>0.24</td>
</tr>
<tr>
<td>100</td>
<td>33.53</td>
<td>64.18</td>
<td>30.60</td>
<td>0.29</td>
<td>0.44</td>
</tr>
</tbody>
</table>

In order to check that the sample had a uniform temperature a pre-test was carried out using thermocouples to investigate the distribution of the temperature of the sample (Figure 3.9). The data is shown in Table 3.

![Schematic of sample](image)

**Figure 3.9** Schematic of sample

From the data, it can be seen that the temperature of the sample is quite uniform and can be controlled within ± 1°C.
Table 3 Temperature distribution of the sample at $30^\circ$C and $80^\circ$C

<table>
<thead>
<tr>
<th>T($^\circ$C)</th>
<th>Top surface</th>
<th>Bottom surface</th>
<th>Left side</th>
<th>Right side</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top surface</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Bottom surface</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Left side</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Right side</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Top surface</td>
<td>30.6</td>
<td>31.0</td>
<td>30.4</td>
<td></td>
</tr>
<tr>
<td>Bottom surface</td>
<td>30.8</td>
<td>31.5</td>
<td>30.9</td>
<td></td>
</tr>
<tr>
<td>Left side</td>
<td>30.6</td>
<td>29.8</td>
<td>29.7</td>
<td>29.6</td>
</tr>
<tr>
<td>Right side</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Back surface</td>
<td>30.4</td>
<td>30.8</td>
<td>30.2</td>
<td>29.9</td>
</tr>
<tr>
<td>Front surface</td>
<td>30.1</td>
<td>30.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface of resistance</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T($^\circ$C)</th>
<th>Top surface</th>
<th>Bottom surface</th>
<th>Left side</th>
<th>Right side</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top surface</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Bottom surface</td>
<td>80.3</td>
<td>80.5</td>
<td>80.2</td>
<td></td>
</tr>
<tr>
<td>Left side</td>
<td>80.7</td>
<td>81.2</td>
<td>80.6</td>
<td>79.5</td>
</tr>
<tr>
<td>Right side</td>
<td>79.2</td>
<td>79.6</td>
<td>79.9</td>
<td></td>
</tr>
<tr>
<td>Back surface</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Front surface</td>
<td>80.0</td>
<td>80.3</td>
<td>80.2</td>
<td>80.2</td>
</tr>
<tr>
<td>Surface of resistance</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Test by means of standard sample

To validate this measurement method, a 90mm x 8mm x 0.5mm aluminium sample, which has the known highest thermal expansion coefficient among all the metals, was used as a standard test sample. The measurement data are in Table 4:

Table 4 Test of standard sample

<table>
<thead>
<tr>
<th>T($^\circ$C)</th>
<th>A1(mm)</th>
<th>A2(mm)</th>
<th>L(mm)</th>
<th>$\Delta$L(mm)</th>
<th>$\alpha \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>32.92</td>
<td>92.60</td>
<td>59.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>32.84</td>
<td>92.66</td>
<td>59.82</td>
<td>0.14</td>
<td>2.09</td>
</tr>
</tbody>
</table>
3.4.2.4 Experiment and Results

- **Vernier microscope**

The 30mm x 10mm x 1mm cured epoxy sample was measured 3 times, the data is shown in Table 5. FM300-2 film adhesive was also measured using the Vernier microscope. The results are presented in Table 6.

### Table 5 Measurement of thermal expansion coefficient of 3M DP190 2-part epoxide

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>A1(mm)</th>
<th>A2(mm)</th>
<th>L(mm)</th>
<th>ΔL(mm)</th>
<th>ΔL ( α \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>32.92</td>
<td>92.60</td>
<td>59.68</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>134</td>
<td>32.83</td>
<td>92.66</td>
<td>59.83</td>
<td>0.02</td>
<td>2.15</td>
</tr>
</tbody>
</table>

T: temperature (°C); A1, A2: Readings (mm); L: Measured length (mm);
Chapter 3

These results show that for 3MDP190 $\alpha = (9.1\pm0.55) \times 10^{-5}$

Table 6 Measurement of thermal expansion coefficient of FM 300-2 Film adhesive

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>A1(mm)</th>
<th>A2(mm)</th>
<th>L(mm)</th>
<th>$\Delta L$ (mm)</th>
<th>$\Delta L_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>38.40</td>
<td>79.45</td>
<td>41.05</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>89.5</td>
<td>38.38</td>
<td>79.56</td>
<td>41.18</td>
<td>0.13</td>
<td>5.32</td>
</tr>
<tr>
<td>29</td>
<td>38.41</td>
<td>79.44</td>
<td>41.03</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>88.5</td>
<td>38.35</td>
<td>79.54</td>
<td>41.19</td>
<td>0.16</td>
<td>6.67</td>
</tr>
<tr>
<td>28</td>
<td>38.41</td>
<td>79.45</td>
<td>41.04</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>38.36</td>
<td>79.55</td>
<td>41.19</td>
<td>0.15</td>
<td>5.80</td>
</tr>
</tbody>
</table>

According to the tables above, the thermal expansion coefficient of FM 300-2 modified epoxy resin film adhesive therefore is:

$\alpha = (5.9\pm0.4) \times 10^{-5}$
• **Precision Optical Measuring Machine**

An optical measuring machine MU-214B manufactured by SIP situated in the Wolfson Engineering school was used to measure the thermal expansion coefficient of 3M DP190 2-part adhesive.

The 30mm x 10mm x 2mm cured epoxy sample was measured 3 times by making use of a high power resistance as a heater:

The recorded temperature of the sample was the average temperature on the top surface of sample and resistance used as a heater; these were measured by using two thermocouples.

The data was achieved by waiting for 3 hours to reach the best temperature equilibrium and taking 3 readings for the same position to reduce the aiming error.

The data is shown in Table 7.

The uncertainty of CTE originates from:

1). The errors from \( L \) and \( \Delta L \) includes SIP reading error: \( \pm 0.0005 \) mm; Eye aiming error: \( \pm 0.001 \) mm. So, \( \delta L = \pm 0.0012 \) mm; \( \delta \Delta L = \pm 0.0017 \) mm.

2). Temperature error: \( (\delta T = \pm 1^\circ C ) \)

The uncertainty of CTE can therefore be obtained using equation 6: \( \delta \alpha = 1.6 \times 10^{-6} \).

The thermal expansion coefficient of 3M DP190 2-part epoxide was measured as:

\[
\alpha = (7.95 \pm 0.08) \times 10^{-5} \quad (20^\circ C - 80^\circ C)
\]

**Table 7** Thermal expansion coefficient measurement using SIP optical machine

<table>
<thead>
<tr>
<th>( T(\circ C) )</th>
<th>A1(mm)</th>
<th>A2(mm)</th>
<th>L(mm)</th>
<th>( \Delta L(mm) )</th>
<th>( \alpha \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>0.0865</td>
<td>30.1987</td>
<td>30.1122</td>
<td>0.1496</td>
<td>8.49</td>
</tr>
<tr>
<td>79</td>
<td>0.0214</td>
<td>30.2832</td>
<td>30.2618</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

- 68 -
<table>
<thead>
<tr>
<th>T(°C)</th>
<th>A1(mm)</th>
<th>A2(mm)</th>
<th>L(mm)</th>
<th>ΔL(mm)</th>
<th>α x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>0.0012</td>
<td>30.0857</td>
<td>30.0845</td>
<td>0.1426</td>
<td>7.92</td>
</tr>
<tr>
<td>78.5</td>
<td>0.0012</td>
<td>30.2283</td>
<td>30.2271</td>
<td>0.1426</td>
<td>7.52</td>
</tr>
</tbody>
</table>

3.4.3 Bimaterial method

3.4.3.1 Introduction

The bimaterial method is a mature and convenient technology which has been widely applied in different measurement fields. For instance, bimaterial micro-cantilever theory [3, 6] is normally used for temperature measurement, and classic bending beam theory [4, 7] to analyse the residual stress or strain distribution after the bimaterial sample experiences a change in temperature. In this work, the CTE of the adhesive was measured by means of classic bending beam theory. The Young’s modulus E can also be measured by means of a bimaterial sample. The basic theory of this method will be presented in chapter 4 and the resulting equation is presented here for convenience.

3.4.3.2 Theory

The thermal expansion coefficient of the adhesive can be determined from the expression:

$$\alpha_2 = \frac{1}{\Delta T} \left[ \frac{F_1}{A_1 E_1} + \frac{M_1 t_1}{2E_1 I_1} + \frac{F_2}{A_2 E_2} + \frac{M_2 t_2}{2E_2 I_2} + \alpha_1 \Delta T \right]$$  (7)

where A is the cross area of material, ΔT is the drop in temperature, M is the moment acting on the material, t is the thickness and I is the Geometrical Moment of Inertia of the material and δ is the deflection of the end of the beam from that of the straight
beam.

Figure 3.10 Bimaterial beam. 1 represents adhesive, 2 is steel

3.4.3.3. Measurement result.
The thermal expansion coefficient $\alpha$ of FM 300-2 film adhesive was measured by means of the bimaterial method as: $\alpha = 49 \times 10^{-6}$.

The measurement results of CTE from different methods are summarised in Table 8.

<table>
<thead>
<tr>
<th>Method</th>
<th>3MDP190-2 parts</th>
<th>FM300-2</th>
<th>Temperature($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscope</td>
<td>$(7.95 \pm 0.08) \times 10^{-5}$</td>
<td>$(5.9 \pm 0.4) \times 10^{-5}$</td>
<td>$20^\circ C$ - $89^\circ C$</td>
</tr>
<tr>
<td>Bimaterial</td>
<td>$(4.9 \pm 0.4) \times 10^{-5}$</td>
<td></td>
<td>$20^\circ C$</td>
</tr>
</tbody>
</table>

3.5 Glass transition temperature measurement by means of Differential Scanning Calorimetry (DSC)

3.5.1 Introduction
The glass transition temperature is a very important parameter for structural adhesives. When the temperature is above the glass transition temperature $T_g$, many important properties change dramatically compared to their values below $T_g$. For
example, the Young’s modulus $E$ decreases sharply and CTE increases greatly above $T_g$. Thus, it is certainly indispensable to measure the $T_g$ of the adhesive before measuring other properties, particularly CTE and $E$. DSC is a mature measurement method of $T_g$ in common use in industry and research. In this work, the $T_g$s of the different adhesives were obtained by making use of Mettler DSC 30 equipment.

### 3.5.2 Basic theory

When an amorphous polymer is heated to its $T_g$, something different from melting happens, melting is something that happens to a crystalline polymer, while the glass transition happens only to polymers in the amorphous state. Initially the temperature increases at a rate determined by the polymer’s heat capacity. When $T_g$ is reached, the temperature does not stop rising. There is no latent heat of glass transition. The temperature keeps going up. But, for constant heat input, the temperature doesn't increase at the same rate above the $T_g$ as below it. The polymer shows an increase in its rate of change of heat capacity when it undergoes the glass transition. Because the glass transition involves change in heat capacity, but it does not involve a latent heat, this transition is called a second order transition.

![Comparison of glass transition and melting](image)

**Figure 3.11** Comparison of glass transition and melting
3.5.3 Equipment
In power-compensated DSC, the sample and a reference material are maintained at the same temperature \((\Delta T = T_s - T_r = 0)\), \(T_s\) is the temperature of sample and \(T_r\) is the temperature of reference sample) throughout the controlled temperature programme. Any energy flow difference in the independent supplies to the sample and the reference is then recorded against the programme temperature. The apparatus is shown schematically in Figure 3.12.

![Diagram of DSC equipment](image)

**Figure 3.12** DSC equipment

Thermal events in the sample thus appear as deviations from the DSC baseline, in either an endothermic or exothermic direction, depending upon whether more or less energy has to be supplied to the sample relative to the reference material.

3.5.4 Experiment and Results

3.5.4.1 3M DP190 2-part epoxide
3M DP190 2-part epoxide disks of about 2mm diameter were obtained after curing at 60°C for 3 hours and slowly cooled down to room temperature. They were weighed by precision electric scale before and after heating, the results are shown in Table 9. The reference sample was an aluminium pan with lid.
Table 9 mass of sample (3M DP190 2-parts epoxide)

(T: heating temperature; Mₐ: mass of sample before heating; Mₐ: mass of sample after experiment; Mₐ: lost mass; P: lost mass in percentage)

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(°C)</th>
<th>Mₐ(mg)</th>
<th>Mₐ(mg)</th>
<th>Mₐ(mg)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-50—300</td>
<td>16.40</td>
<td>16.40</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>-50—500</td>
<td>11.60</td>
<td>3.72</td>
<td>7.88</td>
<td>67.9%</td>
</tr>
<tr>
<td>3</td>
<td>-50—460</td>
<td>11.61</td>
<td>4.93</td>
<td>6.68</td>
<td>57.5%</td>
</tr>
<tr>
<td>4</td>
<td>-50—460</td>
<td>16.40</td>
<td>9.27</td>
<td>7.13</td>
<td>43.5%</td>
</tr>
</tbody>
</table>

Picture 3.1 DSC curve of 3M DP190 2-parts epoxide

From the DSC curve (Picture 3.1) and Table 8 (mass changing of the sample during experiment), it can be determined:

1. the glass transition temperature Tₑ of 3M DP190 2-parts epoxide is about 23°C which is very close to the manufacturers data Tₑ = 20°C.
2. Decomposition happened over the temperature range 300°C~400°C.

3.5.4.2 AV119 single part adhesive

From the glass transition test curve results (Picture 3.2), it can be seen that the glass transition temperature of Araldite AV119 single part epoxy resin cured at 120°C is
about $T_g = 80^\circ C$ which is less than $T_g = 113^\circ C$ from the manufacturer. It can also be seen the decomposition happened above $250^\circ C$.

![DSC curve of AV119 single part epoxy resin](image)

**Picture 3.1 DSC curve of AV119 single part epoxy resin**

### 3.5.4.3 FM 300-2 film adhesive

The samples were prepared by using PTFE tape with some flat compressors and were cured at $120^\circ C$ for one and half hours and then slow cooled down to room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T(\degree C)$</th>
<th>Heating rate</th>
<th>$M_b$ (mg)</th>
<th>$M_a$ (mg)</th>
<th>$M_l$ (mg)</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0–500</td>
<td>10</td>
<td>10.20</td>
<td>2.85</td>
<td>6.35</td>
<td>69.0%</td>
</tr>
<tr>
<td>2</td>
<td>10–500</td>
<td>10</td>
<td>14.39</td>
<td>4.55</td>
<td>9.84</td>
<td>68.4%</td>
</tr>
<tr>
<td>3</td>
<td>50–500</td>
<td>2</td>
<td>13.58</td>
<td>4.99</td>
<td>8.59</td>
<td>63.3%</td>
</tr>
<tr>
<td>4</td>
<td>0–220</td>
<td>4</td>
<td>10.85</td>
<td>10.85</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>120–290</td>
<td>2</td>
<td>11.15</td>
<td>7.99</td>
<td>3.16</td>
<td>28.3%</td>
</tr>
<tr>
<td>6</td>
<td>130–190</td>
<td>1</td>
<td>11.53</td>
<td>11.53</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

From the DSC test curves shown in Picture 3.3 (using DSC 30), it is difficult to obtain the glass transition temperature of FM 300-2 Film adhesive. From both DSC curves and mass change of samples $1^e, 2^e, 3^e$ in Table10, it can be seen that decomposition
happened above 220°C, also it seems from the DSC curve of 3\# and weight loss of 5\# that a second cross linking happened over the temperature range 220°C–290°C.

**Picture 3.2** DSC curve of FM300-2 film adhesive(sample 3\#) obtained from DSC30

The measurement results of Tg of FM300-2 film adhesive by means of DSC 20 is shown in Table 11.

**Table 11** Tg (°C) measurement of FM300-2 film adhesive by using DSC 20
The result of $T_g = 143^\circ C$ is very close to the manufacturers quoted value of $144^\circ C$.

### 3.5.4.4 FM73 film adhesive

#### Table 12 Tg of FM73 film adhesive ($^\circ C$) (using DSC 30)

<table>
<thead>
<tr>
<th>sample</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg</td>
<td>95.5</td>
<td>95</td>
<td>95</td>
<td>99</td>
<td>99</td>
<td>96.7</td>
</tr>
</tbody>
</table>

![Picture 3.4 DSC curve of FM73 film adhesive](image)

The glass transition temperature ($T_g$) of FM73 adhesive can be determined from Table 12. The measurement result of $T_g = 96.7^\circ C$ is very close to the published industrial data $T_g = 95^\circ C$.

#### Table 13 A summary of Tgs

<table>
<thead>
<tr>
<th></th>
<th>3MDP190</th>
<th>AV119</th>
<th>FM300-2</th>
<th>FM73</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g (^\circ C)$</td>
<td>23</td>
<td>80</td>
<td>143</td>
<td>95</td>
</tr>
</tbody>
</table>

### 3.6 Measurement of creep of FM300-2 adhesive

#### 3.6.1 Introduction

Creep is defined as the time-dependent and permanent deformation of materials when subjected to a constant load or stress [8]. Creep is normally an undesirable phenomenon and is often the limiting factor in the lifetime of material. It is observed
in all materials types, polymers are especially sensitive to creep deformation; for metals it only becomes important for temperatures higher than about 0.4Tm (absolute melting temperature). Creep deformation often occurs easily in structural adhesives, even at room temperature. Obviously, it could have a considerable effect on the stress and strain distribution in adhesive joints within the overlap under constant load. Hence, obtaining creep data for adhesives is necessary and important before carrying the investigation of stresses and strains in adhesive joints under load. Creep tests at room temperature with different constant loads were carried out in the Mechanical Engineering School. The creep data at room temperature is the most relevant data for this work. Adhesive joints are normally in service around room temperature. All the investigations of stress distribution in adhesive joints in this work were carried out at room temperature.

3.6.2 Creep test

Creep tests are normally carried out by rapidly applying a tensile load, which is maintained at a constant level while strain is measured as a function of time. A full creep curve can be found by a method [9] which allows the changes in specimen gauge length to be monitored continually until the specimen fails. Accurate results can be obtained by directly measuring the length change of the specimen. In a conventional constant-load creep test, the creep properties are defined in terms of the initial stress on the specimen, i.e. while the applied load remains constant throughout a ‘constant load’ test, the true stress on the specimen increases as the specimen extends and the cross-sectional area decreases as creep continues. The specimen volume can be considered to remain constant so that \( l_0A_0 = lA \), where \( l_0 \), \( A_0 \) is the original length and area. During the time, \( t \), the changes in specimen dimensions will mean that the true stress on the specimen will have increased from an initial value of \( F/A_0 \) at \( t = 0 \), to a new value,

\[
\sigma = \frac{F}{A} = \frac{F}{A_0} \cdot \frac{l}{l_0} = \frac{F}{A_0} (1 + \varepsilon_E) = \sigma_E (1 + \varepsilon_E)
\]  

(8)

Where \( \sigma_E \) is the nominal stress on the specimen at the start of the test and \( \varepsilon_E \) is the nominal strain given by \( (l-l_0)/l_0 \).
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When creep tests are carried out over a wide range of test conditions, for most materials, the shapes of the creep strain/time curves recorded are usually found to differ markedly at low and high temperatures. Under low temperature conditions, the total creep strains are usually very low, typically much less than 1%, and the creep deformation rarely leads to failure.

Creep rate is the slope or gradient of the creep strain/time curve at any point.

\[ \dot{\varepsilon} = \frac{d\varepsilon}{dt} \]  

(9)

The basic information derived from a creep test is the record of the accumulation of creep strain with time at a fixed stress and temperature. The total specimen strain \( (\varepsilon_t) \) at any instant can then be written as

\[ \varepsilon_t = \varepsilon_0 + \varepsilon \]  

(10)

where \( \varepsilon_0 \) is the virtually instantaneous strain which occurs on loading, \( \varepsilon \) is the time-dependent or creep strain. Since \( \varepsilon_0 \) is the rapid strain obtained on applying a stress, \( \sigma \), in a creep test at temperature, \( T \), the value of \( \varepsilon_0 \) can also be derived from the stress/strain curve for the material at the same temperature as the strain attained at the stress, \( \sigma \). The stress/strain curve for a material varies with temperature, so the value of \( \varepsilon_0 \) depends not only on stress but also on temperature. This relationship can be written as

\[ \varepsilon_0 = f_1(\sigma, T) \]  

(11)

which means that \( \varepsilon_0 \) is a function only of stress and temperature. In contrast, the creep strain is a function not only of stress and temperature but also of time, so that

\[ \varepsilon = f_2(\sigma, T, t) \]  

(12)

the creep strain varies with time and the detailed creep strain/time plot differs at different stresses and temperatures. The exact form of mathematical expression which satisfies the equation is identified by analysis of sets of creep strain/time curves obtained at different stresses in tests carried out at different temperatures. In creep testing a constant load is applied to a specimen and the specimen’s elongation, or strain, is measured. This strain is plotted against time to form a creep curve. This curve usually contains three regimes which are shown in Figure 13, after the initial elastic strain \( (\varepsilon_0) \). The first is primary creep \((0-t_1)\) where the strain rate, \( \frac{d\varepsilon}{dt} \), is initially rapid and then decreases with time. Then the specimen enters into
secondary creep ($t_1$-$t_2$, constant rate), in which the creep rate is constant. This constant creep rate is called the steady-state creep rate, $\dot{\varepsilon}_{ss}$, or minimum creep rate, $\varepsilon_{\text{min}}^*$, since it is the slowest creep rate during the test. Finally, the specimen enters into tertiary creep ($t_2$-$t_f$, damage accumulation accelerates), in which the creep rate continually increases until the specimen breaks. This event is called creep rupture or creep failure, and is measured by the time to fracture, $t_f$.

\[
\varepsilon_{ss} = B\sigma^n
\]  

where $n$ is a material constant called the creep exponent and $B$ is a function of temperature. When plotted on log-log coordinates, the data falls along a straight line whose slope is given by $n$. It is shown in Figure 3.14.

The temperature dependence of $\dot{\varepsilon}_{ss}$ at a constant stress is usually given by an Arrhenius rate equation,

\[
\dot{\varepsilon}_{ss} = C\exp(-Q/RT)
\]  

where $C$ is a function of stress, $Q$ is the activation energy (J/mol) for creep, $R$ is the universal gas constant ($R=8.31$ J-mol$^{-1}$-K$^{-1}$) and $T$ is in degrees Kelvin. Note that as
the temperature increases, the rate increases exponentially. The value of Q is found by plotting the natural logarithm of $\varepsilon^*$ vs. $1/T$. The data should fall along a straight line of slope $(-Q/R)$.

Therefore the combined creep law is:

$$\varepsilon^* = A \sigma^n \exp(-Q/RT) \quad (15)$$

where $A$, $n$ and $Q$ are material constants that vary from material to material, and have to be found experimentally. $\varepsilon^*$ usually equal to the creep strain $\varepsilon$.

If $T$ is constant, then one may set $B = A \exp(-Q/RT)$.

In metals creep deformation occurs by the diffusion of atoms, which is faster at higher temperatures. Since diffusion occurs most rapidly at grain boundaries, creep deformation is concentrated here. This leads to separation of the grains along their boundaries, producing an intergranular fracture surface. For polymers, creep results from the fact that the long polymer chains tend to slide over each other so that there is a time-dependency to the stress-strain diagram. The major difference between polymers and metals is the time-dependent viscoelastic behavior of polymers. A load placed on a polymer material will result in an initial deformation, but with the load
remaining over time, permanent deformation will occur. Creep is the continued extension or deformation of a plastic part under continuous load. It results from the viscoelastic flow of the polymer with time. As we know, an amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures (above the glass transition temperature), and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behaviour at low temperatures may be elastic; For a rubbery polymer (above glass transition temperature) that exhibits the combined mechanical characteristics—viscoelasticity. Rubber polymers are susceptible to time-dependent deformation when the stress level is maintained constant, such deformation is termed viscoelastic creep. In this work, creep of FM300-2 film adhesive was only tested at room temperature this is much lower than its glass transition temperature.

### 3.6.3 Results

The creep of FM300-2 adhesive at room temperature can be obtained from the measurement data in Figure 3.15 leading to $\varepsilon = 7.71 \times 10^{-12} \sigma^{2.3}$

![Figure 3.15 Creep measurement data of FM300-2 film adhesive at room temperature](image-url)
The experiments were carried out by Mr Hakeen Saudi Ghamdi in the creep testing laboratory in the Mechanical Engineering School, Loughborough University

3.7 Diffusion Coefficient Measurement

3.7.1 Introduction

The use of adhesive bonding is not perfect due to its main disadvantage, which is low durability when the structure is exposed to hostile environmental conditions. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of adhesively bonded joints.

Moisture diffusion into adhesive joints seriously influences the strength of the adhesive joints due to damage of the adhesive layer and interface. The strength of a joint decreases considerably when the joint is exposed in a wet environment. This has been demonstrated in metal/epoxy joints [10-12] and composite bonded joints [13-15]. In a metallic joint, moisture diffuses into the joint through the adhesive layer and interface. It has been reported [16] that in general the moisture diffusion through the adhesive is predominant if there was no pre-existing micro-cracks and debonded areas at the interface. In this thesis, the diffusion coefficient of FM300-2 film adhesive was obtained by measurements on bulk sample at constant humidity and temperature.

3.7.2 Theory--Fick Diffusion

The diffusion coefficient is characteristic of the rate of penetrant transport for a specific penetrant-host material combination. Fickian diffusion is an ideal case that assumes the absorption process is independent of concentration and temperature. The diffusion takes place by random jumps (or random walk) of the penetrant molecule in the polymer with little interaction with the polymer matrix. In this case, the rate of relaxation of the polymer matrix is faster than the rate of penetrant diffusion. Fickian diffusion is more common in rubbery materials that have flexibility and mobility, larger free volumes, and have relatively fast relaxation times. In glassy materials the rate of relaxation of the host matrix is much slower than the absorption process. In this case, deviation from ideal Fickian diffusion, or even "non-Fickian" diffusion may occur and Fick's second law is no longer applicable.
The most common method for characterizing absorption processes and calculating the diffusion coefficient is by a mass-uptake experiment. In most mass-uptake experiments, the mass-gain of penetrant as a function of exposure time of a thin free-standing film is measured. These data can then be fit to Fick’s second law provided an equilibrium mass-uptake value is reached. For a free adhesive film of thickness $2L$ with a uniform initial concentration $(C_0)$ and the surface is kept at a uniform concentration $(C_s)$, the solution to Fick’s Law in terms of concentration is [17]:

$$
\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4L^2}\right] \cos\left(\frac{(2n+1)\pi x}{2L}\right) \tag{16}
$$

where $C(x,t)$ is the concentration of penetrant in the adhesive at any time $t$ and distance $x$. The solution to Fick’s law can be put in terms of the average mass of the moisture diffusing into the adhesive by integrating equation 18 across the thickness $2L$ of the free adhesive film. The relative mass uptake can therefore be obtained as:

$$
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4L^2}\right] \tag{17}
$$

Where $M_t$ is the mass of absorbed moisture at any time $t$ and $M_\infty$ is the equilibrium or final mass of absorbed moisture. The relative mass uptake is the scaled average water concentration; a fraction ranging from zero at $t = 0$, to one at $t = \infty$. For ideal Fickian diffusion, at short times, the initial relative mass uptake is a linear function of $\sqrt{t}$ and an equilibrium or final value $M_\infty$ is achieved with time. Therefore, equation 19 can be simplified by using the linear portion of the relative mass uptake vs. of $\sqrt{t}$:

$$
\frac{M_t}{M_\infty} = \frac{2}{L} \sqrt{\frac{tD}{\pi}} \tag{18}
$$

The diffusion coefficient can also be expressed as:

$$
D = \frac{\pi L^2}{4t} \left(\frac{M_t}{M_\infty}\right)^2 \tag{19}
$$

In addition, the diffusion coefficient can also be obtained by measuring the time $t_m$ for 99.9% maximum mass uptake [18]:

$$
D = \frac{0.67 \times 4L^2}{t_m} \tag{20}
$$
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3.7.3 Measurement results
A 120mm x 20mm x 2mm bulk FM300-2 film adhesive was investigated in a well-sealed chamber with different constant relative humidities at constant room temperature. The weights were monitored by means of a precision electric scale and the length was measured using a travelling microscope with high accuracy. The results for $D$ obtained from equation 19 are indicated in Table 14

<table>
<thead>
<tr>
<th>RH(%)</th>
<th>$D(t=22\text{hrs})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>184.94</td>
</tr>
<tr>
<td>57</td>
<td>185.35</td>
</tr>
<tr>
<td>72</td>
<td>186.09</td>
</tr>
</tbody>
</table>

3.8 Moisture expansion coefficient $\beta$

3.8.1 Introduction
When moisture goes into the adhesive joint, the adhesive expands causing swelling strains so that the residual stress in the joint varies with time and influences the strength of the joint. It is therefore important to obtain this property before investigating the residual stresses in adhesive joints.

In this work, the CME $\beta$ of FM 300-2 adhesive were obtained by measuring both bimaterial samples and bulk adhesive samples at constant temperature and different constant humidities using precision length measurements and a high resolution digital camera. Good agreement was achieved among the different humidity environments. The experimental method is described fully in Chapter 4.4.2 and the results are also presented here for completeness.
3.8.2 Results

![moisture expansion coefficients](image)

**Figure 3.16** Moisture expansion coefficient measurement of FM300-2 film adhesive

The results of moisture coefficients in Table 15 are averages and were obtained from all the data after 100 hours.

<table>
<thead>
<tr>
<th>RH</th>
<th>42%</th>
<th>57%</th>
<th>72%</th>
</tr>
</thead>
<tbody>
<tr>
<td>β (1/g)</td>
<td>0.053</td>
<td>0.062</td>
<td>0.076</td>
</tr>
</tbody>
</table>

References:

Chapter 4 Thermal and moisture induced residual stresses in adhesive joints

4.1 Introduction

The main purpose of adhesive joints is to transfer loads, but they are also subjected to environmental effects during service. The use of adhesive bonding is not perfect due to its main disadvantage, low durability when the structure is exposed to hostile environmental conditions. Adhesive systems may be exposed to various environmental conditions during the service life. The performance of the adhesive systems may deteriorate upon exposure to harsh environments for a certain period of time.

Currently residual stresses within adhesive joints are usually predicted by means of finite element analysis. Validation of the FE predictions requires the measurement of strains within a joint. The residual stresses in metal adhesive joints, particularly at the interface, are very difficult to measure using conventional experimental techniques. Neutron diffraction is the only experimental technique that can obtain 3 dimensional strain and stress distributions within the sample. However, the availability of neutron beam time is very limited, hence it is important to seek other economic and convenient experimental techniques to investigate the residual stresses and strains directly and indirectly. This chapter describes the use of strain gauges to measure the strains and stresses in the interface within the adhesive joint. In addition bimaterial samples were employed to determine the magnitude of residual stresses in the interface and at other positions in a metal strip bonded to an adhesive layer. It is recognised that this system is not the same as an adhesive joints but both bulk adhesive and bimaterial samples provide convenient methods to investigate the effect of moisture on adhesive joints.
4.2. Strain gauge

4.2.1 Aim

The aim of this experiment was to investigate the residual stress and strain distribution along the adherend in the interface of a single lap joint generated during the curing and slow cooling down process by using both foil and semiconductor strain gauges.

4.2.2 Introduction

Since stress cannot be measured directly, the experimental procedures, of necessity, make their approach through some type of strain measurement. The measured strains are then converted into their equivalent values in terms of stress. In order to achieve this ultimate objective, some type of strain indicating device or measuring device is required. Strain gauges have been used to provide the information about the shear strains and stresses in the surface of joints and the interface between adhesives and adherends. In 1987, the effects of joint shape and size on the residual stress on the surfaces of silicon nitride/Invar alloy joints was examined by K. Suganuma and T. Okamoto by means of strain gages [1]. M. E. Tuttle, et. al investigated the strain within a single lap using strain gages [2]. Kawada and Ikegami [3] studied stresses induced in epoxy resin in the curing process as well as in the cooling process using both analytical and strain gauge techniques.

When two adherends for example aluminium are bonded together by using an adhesive such as epoxide resin and then cured for 3 hours at 60°C (according to the manufacturer’s instruction) and slow cooled down to room temperature, the adhesive shrinks and creates residual stresses inside the adhesive and adherend and in the interface between adhesive and adherend. In the experiment described in this section, a small foil strain gauge was first used to investigate the residual stress during the curing process and then tiny semiconductor strain gauges were used to obtain more accurate result and achieve a record of the development of the residual stress distribution in the interface of single lap aluminium-adhesive joint sample.
4.2.3 Background:

When using a strain gauge the major requirements for accurate strain measurements are [4]:

- Small gauge size to achieve high spatial resolution.
- High gauge factor to have high strain sensitivity.
- Low transverse sensitivity to obtain distinct directional sensitivity.
- Small gauge stiffness to have negligible reaction of the gauge on the substructure.
- Stability of calibration with time and dynamic loading (reliable attachment of gauges).
- Low effect of environmental temperature, humidity and acceleration.

4.2.3.1 Wire resistance strain gauges

The strain induced in a wire will increase the resistance as the wire becomes longer ($\Delta l$) and thinner ($-\Delta d$), but it is likely that the characteristic 3-dimensional atomic pattern of a particular metal will also be affected, and thus its resistivity.

Since $R = \rho l / a$

\[
\frac{\Delta R}{R} = \frac{\Delta l}{l} - \frac{\Delta a}{a} + \frac{\Delta \rho}{\rho}
\]  \hspace{1cm} (1)

Introducing Poisson's ratio $\nu$ and using $\Delta a / a = 2 \Delta d / d$, the lateral contraction of the wire becomes:

\[
\frac{\Delta d}{d} = -\nu \frac{\Delta l}{l}
\]  \hspace{1cm} (2)

Therefore: The gauge factor $G$ (strain sensitivity) is:

\[
G = \frac{\Delta R / R}{\Delta l / l} = 1 + 2\nu + \frac{\Delta \rho / \rho}{\Delta l / l}
\]  \hspace{1cm} (3)

For most metals, $\nu \approx 0.3$, and thus the gauge factor

\[
G = 1.6 + \frac{\Delta \rho / \rho}{\Delta l / l}
\]  \hspace{1cm} (4)
Under compression the sensitivity of bonded wire resistance strain gauges is in fact lower than under tension by only 1-2%; larger deviations are more probably caused by imperfect bonding between the whole gauge and the substructure. A high resistance can be obtained from longer wires, and wire resistance strain gauges are therefore arranged in grid form, with as many as possible side-by-side. Unfortunately, if the lateral dimension of such a grid is no longer negligible in comparison with its length the gauge becomes sensitive also to transverse strain. A large length/width ratio is desirable but, since the wire spacing is limited by the manufacturing process, the requirement is difficult to reconcile with small gauge lengths.

The etched-foil gauge is a type of wire strain gauge. It is produced from thin resistance foil by a photochemical etching process. Because of its larger surface/cross-section ratio (as compared with round wire) it has a higher heat dissipation rate and better bonding properties. The transverse sensitivity is low because of the thickened loop ends.

The effects which influence the performance of wire resistance strain gauges include: hysteresis, creep and fatigue, or are brought about by the environment of the gauge, such as temperature and humidity variations.

Hysteresis and creep

Hysteresis is independent of time, i.e. strain does not vary with time at constant load. Any time-dependent strain variation at constant stress is called creep. The hysteresis and creep of strain gauge is complex as the bonded strain gauge consists of wire grid, backing and lead connections, all held together and bonded to the surface by cement. However, creep is most obviously affected by temperature. The gauge factor varies with temperature. Any large creep values occurring at room temperature are most likely due to imperfect bonding. Since creep depends on time, its effect is most severe in static measurements;
Fatigue

The junction between the wire grid and the thicker connecting leads is the most frequent location of fatigue failures. Since the gauges used in this work are subjected to very few stress cycles fatigue is not expected to be a problem.

Temperature effects

One effect of temperature, through creep, is on the bonding strength and thus on effective gauge factor of strain gauges. However, temperature variations influence the performance of wire resistance strain gauges also in other ways; in particular the variations in gauge resistance due to temperature changes can easily be of the same magnitude as those caused by strain. Therefore, in the processing of experimental data, the strain caused by the temperature should be extracted from the measured strain.

4.2.3.2 Foil Gauges

The foil gauge operates in essentially the same manner as a wire gauge. However, the sensing element consists of very thin metal foil (about 0.005mm in thick) instead of wire. In contrast to the wire gauge, in which the sensing element posses a uniform cross section throughout its entire length, the cross section of the sensing element of the foil gage may be somewhat variable from one end to the other. One of the most important advantages of the foil gauge is that the ratio of contact surface area to the volume of the resistance element is relative high, whereas in the wire gauge, due to the circular cross section, this ratio is a minimum. In general, foil gauges exhibit a slightly higher gauge factor and lower transverse response than their equivalent in wire. Since they are thinner, they conform more easily to surfaces with small radius of curvature, which means they are easier to install in fillets. As a result of their greater contact area, they can dissipate heat more readily and, in consequence, it is possible to use higher operating currents (applied voltage) with foil gauges. The relatively large contact area, especially at the ends of the grid, reduces shearing stress in the bonding agent, and consequently, foil gauges show comparatively little creep and hysteresis.
Foil gages will measure strains precisely into the range of 10 to 15 per cent depending on the carrier, the alloy, and its metallurgical condition. Its coefficient of linear expansion and resistance-temperature characteristic can be very closely matched to the coefficient of linear expansion of some arbitrarily selected material. By this means temperature compensated foil gage are produced. While the same operating principles are involved, foil gages have inherent advantages over wire gages in most cases, and for this reason the vast majority of modern metallic strain gages are the foil type.

4.2.3.3 Semiconductor strain gauges

The main attraction of the semiconductor is, of course, the high strain sensitivity of silicon, which is the favoured material for the sensing element. In other words, it has a relatively large resistance change per unit of strain. This characteristic is helpful for both high and low values of strain.

1). For high strain, the large response enables one to drive indicating devices directly without intermediate amplification. This provides a simplification which is accompanied by reduced weight and expense.

2). For low strains, which produce exceedingly small changes in resistance of metal gages, the semiconductor gages will develop unit changes about 50 times greater than foil gauges, with the result that the indications of $\Delta R/R$ can be measured conveniently and precisely.

However, semiconductor gauges have some disadvantages:

The unit change in resistance is a non-linear function of strain, although for some special conditions it can be taken as linear for small strain excursions.

The unstressed resistance value is easy to change during the process of installation due to its high strain sensitivity. Therefore, it is necessary to determine the gauge resistance following installation so that an appropriate correction can be made.

The resistance will change with temperature.

The strain sensitivity, or gauge factor will change with change in temperature.

Fragility, lack of ductility and high cost.
It is observed that high sensitivity to strain is accompanied by high sensitivity to changes in temperature. So, some compromise between strain sensitivity and temperature response may be desirable, perhaps essential, depending upon the particular application. Fortunately, by suitable doping during the manufacturing process, the strain and temperature sensitivities can be varied and adjusted to meet specified requirements. Therefore, by suitable procedures in the manufacturing process, it is possible to achieve a desired compromise, which will result in much improved temperature characteristics at the expense of a modest reduction in strain sensitivity. Practical considerations indicate that a good balance is achieved when the gauge factor is about 120.

In this work both foil gauges and semiconductor gauges were used to measure the residual stress and strain in an aluminium-adhesive single lap joint sample.

4.2.4 Basic theory

4.2.4.1 Basic measurement principle:

Strain sensitivity is defined as a basic bulk property of the strain-sensitivity alloy used in a strain gauge[5]. When this metal is formed into a grid, and provided with attachment points for lead wires, the gauge will exhibit a somewhat different relationship between resistance change and applied strain than the bare metal. The term "gauge factor" (G) is used to quantify this relationship, and is defined as:

\[ G = \frac{\Delta R / R_0}{\Delta L / L_0} = \frac{\Delta R / R_0}{\varepsilon} \]  

(5)

Where \( \Delta R \) = Resistance change in the gauge in ohms

\( R_0 \) = original or unstrained gauge resistance

\( \varepsilon \) = unit "engineering strain" in the specimen surface under the gauge grid = \( \Delta L / L_0 \)

According to Hooke's law, the stress is:

\[ \sigma = E \varepsilon \]  

(6)

where \( E \) is the elastic modulus of the adherends
4.2.4.2 Error elimination

When evaluating the residual strain in a joint the measured strain is also dependent on temperature, thus the main errors are from the temperature, in other words: one error is from the thermal expansion of adherends, another error is from the gauge factor variation with temperature.

Elimination of the error caused from thermal expansion of adherends:
The strain of one piece of adherend was measured using a strain gauge bonded to the adherend while the adherend was subjected to the same temperature path as in the curing and cooling process. The resistances obtained were subtracted from the measured resistances of the curing joint sample.
The gage factor error due to temperature is easily removed by using corrected factors calculated by using following equation for foil gauge

\[ G = G_0 \times (1 + 0.08T / 10) \]  

where \( T \) is the temperature in Celsius, \( G_0 \) is the gauge factor at room temperature, \( G \) is the gauge factor. For the semiconductor gauge we have \( G = G_0 (1 - 0.00275 \Delta T) \) to be the gauge factor compensation equation, where \( G_0 \) is the gauge factor at room temperature, \( G \) is the gauge factor and \( \Delta T \) is the variation of temperature.

4.2.5 Experiments

A QFLG-02-11 foil strain gage and AFP 350-90 semiconductor strain gages were used to investigate the residual stress due to the shrinkage of adhesive and thermal
expansion mismatch of adhesive and adherends during the curing process and slow cooling down.

4.2.5.1 Sample preparation

- Adherend:
  Two pieces of 7075 T6 aluminium alloy (60mm x 18mm x 1.5mm) were pre-treated before the bonding by rubbing the surface with an abrasive paper, degreasing with acetone and marking gauge installation position.

- Adhesive: (contains: Epoxy resin, polyamidoamine)
  The adhesive was prepared by using 3M DP 190 2-parts epoxide mix 50:50 by weight with about maximum 1% addition of 150-250 micron "Ballotini" glass spheres.

- Bonding procedures
  a. Strain gauge was carefully adhered to the marked position of one piece of Aluminium alloy with cyanoacrylate glue (super glue).
  b. A thermocouple was embedded in the measured interface to monitor the internal temperature during the curing process.
  c. The single lap joint was created by bonding two pieces of aluminium alloy together by using the pre mixed two parts epoxide with glass spheres. The spheres act as spacers to maintain a constant joint thickness.

4.2.5.2 Experiment

Repeating tests

A bare foil strain gauge was heated at 60°C for 45 minutes and then slow cooled down to room temperature, the process was repeated three times while the resistance was recorded as a function of time using a high resolution Tti 1604 digital multimeter. See Figure 4.2
Figure 4.2 Repeating test of strain gauge. Line | means cooling process started. R1, R2 and R3 are recorded resistances for 3 times repeated measurements.

From the repeating experiment results, it was found that there are almost no errors in the foil strain gauge caused by temperature cycling between room temperature and 60 °C. Thus, the resistance can be directly transferred into strain without considering the effects of repeated heating of the gauge.

Test of Thermal expansion of adherends

A strain gauge was adhered to the Aluminium surface, which was then heated and cooled down in completely the same way as was employed in the curing and cooling down process of joint samples.

Curing of bonding sample

The single lap joint sample was placed inside an oven preheated to 60° C to cure for 3 hours and then slow cooled down to room temperature
Results

1. foil gauge

![Graph of Resistance Versus Time](image1)

**Figure 4.3** Resistance was recorded as a function of time. where t (min) is time; R1(Ω) is the resistance only from thermal effects; R2(Ω) is the resistance from the combination of thermal effects and curing. Line | means cooling started.

![Graph of Strain versus Time](image2)

**Figure 4.4** Strain versus time. (The line | indicates cooling started)
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Figure 4.5 Stress versus time (The dotted line indicates cooling started)

2. Semiconductor gauge

Figure 4.6 Resistance versus time. Where t (min) is time; R1(Ω) is the resistance due to thermal effects; R2(Ω) is the resistance from the combination of thermal effects and curing. (The line | indicates cooling started)

Figure 4.7 Curing/gl strain versus time. (The line indicates cooling started)
Results and discussion:
The residual stresses and strains were calculated from measured resistances of the strain gauge. From the graphs of strain and stress obtained by the foil gauge and semiconductor gauge, it can be seen that the residual stress caused during the curing and slow cooling down process in the interface between adhesive and adherend in the single lap joint sample is a tensile stress (Figures 4.5 and 4.8). Both of them showed that the tensile residual stress was created in the first 15 minutes and considerable residual stresses developed with time in the metal surface, and at the end of the curing process they reach values of 9MPa for foil gauge and 40MPa for semiconductor gauge. It has to be noted that compressive stress produced at the very beginning of heating up and then decreased sharply until tensile stress produced. In the cooling down process, the stress suddenly decreased in the beginning and then slowly increased to be a steady value, the tensile stresses still developed to 6MPa for foil gauge and 35MPa for semiconductor strain gauge at room temperature. The result shows the cooling process gives 15~30 percent of the residual stress compared with curing process. The fact that the magnitudes of residual stresses for foil gauge and semiconductor gauge are different but have same order may be due to the fact that the positions of strain gauges fixed on the surface of the adherends are slightly different. The foil gage is closer to the corner and semiconductor is a bit closer to the centre position in the interface. The result of 35MPa from the semiconductor is believed to be more trustable for a point due to its high sensitivity relative to the foil gage and tiny contact area less than 0.5 mm². However, the measurement value of 6 MPa from the foil gage is an average stress due to its larger contact area, bigger than 4mm². It can also be seen that the residual stresses are not uniform from point stress 35MPa
and average stress 6MPa in the interface of single lap adhesive joint, which does not contradict Adams' predictions [6] and the prediction of Tsai and Morton [7]. The tensile stress observed in the interface of single lap joint, do not agree the modelling predictions of Adams et al., for curing stresses in single lap joints [6]. Adams' predictions are for shrinkage and cooling to produce tensile stresses throughout the adhesive layer which are of constant magnitude along the central region of the joint but decrease towards the joint edges. In other words, he predicts that compressive residual stresses are produced during curing and cooling processes in adherends. These experimental results therefore completely disagree with Adam's predictions.

When compared with results described in the paper "Direct measurement of longitudinal strains and stresses within single lap shear adhesive joints using Neutron diffraction" [8], the results obtained by means of strain gauges have some satisfactory agreement with the results obtained by using Neutron diffraction. The neutron results show that the stress close to the interface is not uniform along the central region, and tends to be tensile in the centre and compressive at the edges, the results of these two experiments also have same order of magnitude of stresses. According to the study of Joyanto K. Sen regarding stresses in lap joints bonded with adhesive [9], the stresses decrease as the ratio of the adherend modulus to the equivalent property of the adhesives increases. Thus, the magnitude of residual stresses in this experiment should be larger than the value in the above referenced neutron diffraction experiment as the adhesive and adherend used were different. The adhesives were 3M DP 190 2-parts epoxide and Araldite AV119 single part epoxy resin, the adherends were aluminium and mild steel. From the results achieved, the influence of modulus, as reported by Sen, can not be apparently found. This may be because of the limitation of the resolution of strain gauge method used.

Hong Bing Wang et al assessed residual stresses during cure and cooling of epoxy resins [10], they found that the residual stresses increase with cure temperature as the higher the cure temperature of sample, the faster the gelation of epoxy resin. This conclusion is supported by comparing the foil gauge experiment with the Neutron diffraction experiment because the cure temperature of the sample using strain gauges was 60°C, which is lower than the cure temperature 120°C in the neutron experiment. However, the magnitude of curing stresses and cooling stresses that were found does
not agree with their other conclusion which is that curing stress is much smaller than cooling stress.

Hiroshi Kawada and Kozo Ikegami studied the residual stresses of epoxy resin in the curing process as well as in the cooling process [3]. Compared with the current strain gauge experiments, the differences are that their cure temperature $170^\circ$C is much higher than $60^\circ$C. Indeed, the residual stresses in the work of Kawada et al. is higher than the value was obtained in the current strain gauge experiment. Thus, good agreement was achieved compared with the results of HongBing Wang et al. but the tensile stresses in the strain gauge experiment absolutely disagree with the compressive stresses found by Kawada and Ikegami.

The results of the investigation by means of foil and semiconductor gauges are 6MPa and 35MPa tensile stresses acting on the interface of the adherend. Correspondingly, about 1MPa compressive stresses acted on the interface of the adhesive. Aluminium's tensile strength is 450MPa and the yield strength is around 200MPa. These tensile stresses therefore decrease the tensile strength of the joint. For the adhesive, the tensile strength is about 70MPa and the yield stress around 50 MPa [11]. Thus, the small compressive stresses in the adhesive caused in the curing and cooling process only has a tiny influence on the tensile strength of the adhesive.

4.2.7 Suggestions for improvement:

Due to the difficulty in using multiple strain gauges to map residual stresses and strains in the interface of an adhesive joint during the curing and slow cooling down process a map was not obtained using strain gauges. In addition, the strain gauge technique is very invasive, and may therefore introduce huge errors to the results. The neutron diffraction method enables us to determine non-destructively the residual stress state of a single lap adhesive joint material. It can provide sub-surface information not obtainable by any other techniques. It is much faster and less labour intensive than conventional destructive methods, such as hole drilling and strain gauge methods. For the neutron diffraction method, complicated corrections to the data are not required because the stress state is not disturbed by the measurement. The neutron diffraction techniques can provide strains with high spatial resolution to characterise the deformation in the various zones of adhesive and adherend.
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Conventional measurement techniques are usually not able to provide the required data due to a lack of spatial resolution. Therefore, the further investigation of residual and stresses and strains within the adhesive joint were made by making use of neutron diffraction method and these are described in Chapter 5 of this thesis.

4.2.8 Conclusion:

The residual stress in the adherend at the interface in the single lap adhesive joint was studied experimentally using different types of strain gauges. The conclusions are outlined below.

In the measurement of residual stress during the curing and cooling process, a tensile stress was surprisingly found to exist in the adherend at the interface. However, the tensile residual stress decreased due to thermal mismatch of adherend and adhesive on cooling and then slowly increased by a small amount with time. This latter effect can be explained by the effect of moisture and will be discussed later in this chapter.

4.3 Bimaterial method

4.3.1 Introduction

Bimaterial samples consisting of a layer of adhesive bonded to a steel strip, as described in Chapter 3, were use to evaluate residual stresses. Residual stress generated due to curing is divided into shrinkage stress and thermal stress. Shrinkage stress is due to the chemical and physical changes during the curing and cooling processes. Thermal stress is produced when the bimaterial sample experiences a drop of temperature during the cooling process causing bending due to different thermal expansion coefficients. The residual strain includes constraint strain and stress free strain. Constraint strain is the strain which arises from the residual stress, which includes the strain due to force and bending, but does not include the stress free strain. Stress free strain is generated by free thermal expansion without restraint. This is illustrated in Figure 4.9.
Figure 4.9 Classification of residual stresses

A variety of experimental techniques have been used to study the distribution of residual stress. Each of the techniques has certain limitations. For example, indentation and X-ray diffraction techniques can only be used to estimate surface or near surface stresses [12] and strain gauge techniques are also limited to surface strain or interface strain measurements [3, 12]. Neutron diffraction can measure the strain and stresses after curing but suffers from beam time limitations and limits on spatial resolution [8]. Other methods such as photoelastic techniques are limited to transparent materials [13]. Measurements of the curvature of bimaterial samples have been used to estimate surface compression[14].

Thermal stresses are produced by the differential thermal expansion coefficients of the adhesive and adherend since the adhesives normally have a higher coefficient of thermal expansion than the adherend, Dannenberg and May give the linear free shrinkage of an ‘Araldite’ epoxy resin as 0.75% when cured at 110°C [15]. The shrinkage stress is induced from the shrink of adhesive during its cure. Most previous workers have only considered the thermal stress or the curing stress. It was thought that it is difficult and perhaps unrealistic to separate the cure shrinkage stresses from thermal expansion stresses [6]. To date, very few experiments have been reported in which curing strains are monitored during the whole of the curing and cooling down process.
E.A. Wachter et. al. [16] designed a method to determine temperature changes by measuring the bending deflection of microcantilevers due to the bimetallic effect. In their studies, the differential thermal stress was the only factor to cause the bending of the bimaterial microcantilever and this is an appropriate method to use to investigate curing stresses. The stress distribution within materials bonded together across planar interfaces (two or three layers) which have undergone differential dimensional change were analysed by H.J. Oel and V.D. Frechette[17]. The strains they predicted for two layers are constraint strains which can be directly transferred into stress, and include the strain induced from axial forces and bending moment, but it is not the residual strain. Their theory could not explain the equality of strain at the interface for adherend and adhesive. The strain defined in W. H. Loh’s thesis [18] is the residual strain, but it could not be directly transferred into stress. The best way to explain the stress and strain in bimaterials is to use two concepts, constraint strain and residual strain, which can be used to explain either stress or strain.

In this work the order of the residual stress singularity developed within an adhesive joint after curing were investigated in a series of experiments with two types of epoxy-steel bimaterial strip samples. In these samples, tangible evidence of the residual stresses is seen in the curvature of the beams. This makes them ideal for studying the magnitude of the residual stresses and for validating theoretical predictions.

The main types of residual stress can be classified as thermal stresses and shrinkage stresses. Fortunately, both types of residual stress can be analysed using the same basic equations. Thermal stresses are caused by differential thermal contractions and/or expansions in the sample and are seen when dissimilar materials are joined or when there is a non-uniform temperature distribution in the sample. Shrinkage stresses occur because of chemical and physical changes in the adhesive as it cures. This was investigated by observing changes in curvature at the curing temperature. Examination at the cure temperature after post-cure heat treatment allows post-curing effects to be determined. These results were related to DSC scans of the adhesive during cure and post-cure heat treatment. In this work, optical methods were used to investigate the residual stresses and strains in bimaterial samples. Bimaterial microcantilever theory [16, 19] and classic bending beam theory [17, 18] were used to
interpret the experimental results. The specimens used were made from FM300-2 film adhesive and steel. The methods used made it possible to separate the shrinkage stress from the residual stress. In addition, stress relaxation due to moisture ingress was also investigated.

4.3.2 Theory

4.3.2.1 Surface stress (theory 1 [19])

Bimetallic strips are widely used in many instruments to sense or control temperatures [16, 19]. This study made use of bimaterial strips consisting of a uniform layer of adhesive on steel. During curing the surface stress which cause the bimaterial sample to bend can be derived according to Roark's formulas [19]. These are based on the assumption of uniform temperature from top to bottom of in the bimaterial sample. In Figure 4.10, the bimaterial sample is bent due to differential thermal expansion effects when it experiences a drop of temperature from T1 to T0, where z is the max bending distance of the sample.

\[
\sigma_a = -\frac{z E_a t_b^2}{3(t_a + t_b)\ell^2} \left[ 3\frac{t_a}{t_b} + 2\left(\frac{t_a}{t_b}\right)^2 - \frac{E_b}{E_a} \frac{t_b}{t_a} \right] 
\]

(8)

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In the bottom surface of material b:

\[
\sigma_b = \frac{z E_b t_b^2}{3(t_a + t_b)E_a} \left[ 3 \frac{t_a}{t_b} + 2 - \frac{E_a}{E_b} \left( \frac{t_a}{t_b} \right)^3 \right]
\]  

(9)

where \( t_a \) and \( t_b \) are the thickness of material a and b, \( E_b \) and \( E_a \) are Young's Modulus of material b and a.

4.3.2.2 Interface strain and stress (theory 2)[18]

The interface strain (residual strain) between adhesive and adherend can also be obtained by means of measuring the bi-material curved beam. The analysis of this method is as follow:

![Figure 4.11 Bimaterial beam](image)

When the bi-material beam components are firmly bonded and experience a drop in temperature \( \Delta T \), where the Young's Modulus and CTE of the two materials 1 and 2 are \( E_1 < E_2 \) and \( \alpha_1 > \alpha_2 \) respectively, the beam will bend due to differential thermal expansion coefficients of material 1 and 2 as shown in Figure 11. The tensile force \( F_1 \) and compressive force \( F_2 \) are required to modify the free thermal expansion (stress free) until strain differences associated with the
mechanical forces are equal to differential thermal strain ($\Delta \varepsilon$) of materials a and b, where $\Delta \varepsilon = (\alpha_1 - \alpha_2) \Delta T$. Material 1 will have uniform tensile stress and the other material will have uniform compressive stress. The forces cause bending and there will therefore also be associated bending stresses and strains. Therefore, the longitudinal residual strain ($\varepsilon_a$) is induced from axial force, bending and contraction factors. It can be written as:

$$\varepsilon_a = \varepsilon_\sigma + \varepsilon_\delta + \alpha \Delta T$$  \hspace{1cm} (10)

[18] The strain due to axial force is:

$$\varepsilon_\sigma = \frac{F}{AE}$$  \hspace{1cm} (10)

where $A$ is the cross area of material;

The strain due to bending is:

$$\varepsilon_\delta = \frac{M \delta}{2E \ell}$$  \hspace{1cm} (11)

where $M$ is the moment acting on the material, $\ell$ is the thickness and $I$ is the inertia of material respectively.

Thus, the residual strain in materials 1 and 2 can be expressed as:

$$\varepsilon_{a1} = -\frac{F_1}{A_1E_1} - \frac{M_1 \ell_1}{2E_1I_1} + \alpha_1 \Delta T$$  \hspace{1cm} (12)

$$\varepsilon_{a2} = \frac{F_2}{A_2E_2} + \frac{M_2 \ell_2}{2E_2I_2} + \alpha_2 \Delta T$$  \hspace{1cm} (13)

$$M = \frac{EI}{R}$$  \hspace{1cm} (14)

$$R = \frac{L^2 + \delta^2}{2\delta}$$  \hspace{1cm} (15)

where, $R$ is the radius of curvature. $R_1 = R_2 = R$ with the assumption of $\ell_1, \ell_2 \ll L$ (length of beam) and $\ell_1, \ell_2 \ll R$ (radius of curvature).

Because the residual strain for materials 1 and 2 must be equal at the interface, it is clear that:
When applied to the setting FM300-2 adhesive (material 1) on steel (material 2), the following calculations can be made from the theory. With the assumption of an initially stress and strain free state at room temperature (RT) not 120° C because the curing process includes 30 minutes from RT to 120° C and 90 minutes at 120° C and then slow cooling down from 120° C to RT, the residual strain \( (\varepsilon_a) \), constraint strain \( (\varepsilon_r) \) and residual stress \( (\sigma) \) after the curing process for either adhesive (FM300-2 adhesive) or adherend (steel) at the interface can therefore be determined as follows by subtracting the thermal expansion strain of the steel from equation 17. Before crosslinking the adhesive expands along with the steel from 20 to 120 degrees without the generation of internal stress.

1). Residual strain:

\[
\varepsilon_{a1} = \frac{F_1}{A_1E_1} + \frac{M_1t_1}{2E_1I_1} + \alpha_1\Delta T - \alpha_2\Delta T
\]

\[
\varepsilon_{a2} = \frac{F_2}{A_2E_2} + \frac{M_2t_2}{2E_2I_2}
\]

2). Constraint strain

\[
\varepsilon_{r1} = \frac{F_1}{A_1E_1} + \frac{M_1t_1}{2E_1I_1}
\]

\[
\varepsilon_{r2} = \frac{F_2}{A_2E_2} + \frac{M_2t_2}{2E_2I_2}
\]

3). Residual stress at interface

\[
\sigma_1 = E_1\varepsilon_{r1}
\]

\[
\sigma_2 = E_2\varepsilon_{r2}
\]
4.3.2.3 Distribution of residual stresses along \( y \) direction (Theory 3 [20])

As illustrated in figure 10, due to the force and moment equilibrium, the classical beam theory can provide exact solutions to the problem. It leads to the following condition: (\( F \) and \( M \), force and moments, respectively, acting at the centre line of the two strips)

\[
F_1 = F_2 = F 
\]  

\[
M_1 + M_2 = \frac{F(d_1 + d_2)}{2} 
\]  

Because of the dimensions of the samples used in the experimental work, they can be assumed infinitely long. Thereafter the longitudinal stresses in different \( y \) layers can be estimated by [20]:

\[
\sigma_{1y} = -\frac{F}{A_1} \frac{M_1}{I_1} \left( y + \frac{t_1}{2} \right) 
\]  

\[
\sigma_{2y} = \frac{F}{A_2} \left( y - \frac{t_2}{2} \right) 
\]

4.3.2.4 Residual stress and strain distribution in \( y \) direction (Theory 4 [17])

The constraint strain for both adherend and adhesive can be determined according to Oel & Frechette’s study in the two-layers case [17]. The constraint strain at a point separated by a distance \( x \) from the interface in layer \( i \) is given by:

\[
\epsilon_i = \frac{n_i - x}{r_0} 
\]  

the stress at the point in layer \( i \) can therefore be expressed as:

\[
\sigma_i = E_i \epsilon_i 
\]
where \( n_i \) is the distance separating the neutral surface from the material interface.

\[
n_i = \frac{S_2 d_2^2 + 4S_1 d_1^2 + 3S_1 d_1 d_2}{-6S_1 (d_1 + d_2)} \quad (29)
\]

\[
n_2 = \frac{S_1 d_1^2 + 4S_2 d_2^2 + 3S_2 d_1 d_2}{6S_2 (d_1 + d_2)} \quad (30)
\]

where

\[
S_i = \frac{E_i d_i}{1 - \nu_i} \quad (31)
\]

d_i is the thickness, \( \nu_i \) is the poison's ratio.

Note: 1) The Young’s Modulus \( E \) of FM300-2 adhesive was given as: \( E=2.515 \) GPa [21]; and \( E=2.45 \) GPa [22]. In this work, \( E = 2.5 \) GPa is used in the calculations.

2) The thermal expansion coefficient of FM300-2 was obtained by measuring a 41mm x 8mm cured FM 300-2 modified epoxy resin film adhesive microscopically as it was heated to a range of fixed temperatures between 20 and 100 °C. The value obtained was 58 x 10^{-6}.

4.3.3 Experimental

Sample 1#, used with theory 1 consisted of a 156mm x 12mm x 0.26mm piece of FM300-2 film adhesive and a 180mm x 12mm x 0.13mm steel strip; the sample 2# for theories 2~4 was prepared by using a 180mm x 12mm piece of FM300-2 film adhesive and a 180mm x 12mm x 0.13mm thin steel strip (AISI 302 EN 58A). Bimaterial beam sample 3# for the moisture experiment (described in detail later in this section) was prepared by using a 3mm x 12mm x 0.12mm stainless steel (302) strip and a 183mm x 12mm piece of FM300-2 film adhesive.
Before joining the steel and adhesive together, the steel was cleaned using p320 and p800 abrasive papers, and subsequently degreased in acetone. The sample was prepared by carefully cutting a 12mm x 156mm FM300-2 piece of the film adhesive and slightly pressing it onto the steel surface by binding it onto the steel using P.T.F.E tape. Samples were manufactured using the recommended standard cure cycle for FM 300-2 film adhesive, which is 30 minutes to 120°C and 90 minutes at 120°C with about 0.28MPa pressure. The samples were immediately heated to 120°C at a linear rate of 3.4°C/min and cured for 1.5 hours at 120°C in an oven with a glass door, after which, the sample was slow cooled at a rate of 1°C/min. In order to observe the sample shape and hence evaluate the development of stress throughout the process, pressure was not applied to the specimen during curing. The whole curing and cooling down process was monitored using a Fuji S304 digital cameral with 3.3 mega pixel resolution.

One end of sample 1st was fixed using a clamp. Sample 2 was heated freely in the oven. All the data images were analysed using AUTOCAD software to obtain accurate values for the shape of the samples. Images were taken every 5 minutes during the heating process, every 10 minutes at 120°C and every 3 minutes in the cooling down process. An example is shown in picture 4.1.

### Table 1 Description of samples in this work

<table>
<thead>
<tr>
<th>sample</th>
<th>type</th>
<th>theory</th>
<th>special use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>bimaterial strip</td>
<td>1</td>
<td>surface stress measurement</td>
</tr>
<tr>
<td>2#</td>
<td>bent beam</td>
<td>2-4</td>
<td>shrinkage stress measurement; tested in dried desiccators for 7 days</td>
</tr>
<tr>
<td>3#</td>
<td>bent beam</td>
<td>2-4</td>
<td>for moisture measurement</td>
</tr>
</tbody>
</table>
• Shrinkage stress measurement

The first method used to measure shrinkage stress was to reheat the cured sample back to 120°C and analyse the bending remaining in the sample at 120°C in order to determine the shrinkage stress since there is only shrinkage stress left when the sample was reheated to 120°C. It is called method 1.

The second method of measuring shrinkage stress is to immediately reheat the post-cured sample from room temperature at a very slow rate to a temperature above 120°C in order to find the stress-free temperature where the sample is again straight. The shrinkage stress is obtained by equating it to the thermal stress generated from the temperature difference between 120°C and stress-free temperature. It is called method 2. An advantage of method 2 is that the residual stress can be calculated from thermal expansion coefficients avoiding having to consider the shrinkage stress while calculating the residual stress. The residual stress can be treated as the thermal stress produced from a drop of temperature, that is stress-free temperature to room temperature, which is equal to the sum of thermal stress generated from 120°C to room temperature and the shrinkage stress during the curing and cooling down process.
• The aged samples were prepared by storing the cured bent samples at room temperature for about 40 days exposed to the normal room environment. The samples were then heated for 4 hours at 100°C, followed by continued slow heating to 120°C at a rate of 0.5°C/min and then slow cooling to room temperature. The purpose was to investigate the difference in bending between the aged sample at room temperature before and after reheating.

• All the samples were used for stress relaxation experiments and shrinkage stress measurements. The procedure used in these experiments was as follows: sample 2\# was cured in an oven according to the recommended standard curing process. It was then slow cooled down to room temperature. The temperature was measured by means of a thermocouple positioned near the sample. The shape and size of sample during the complete process were recorded using the digital camera.

After cooling to room temperature the sample was immediately reheated back to 120°C to measure the shrinkage stress. The sample 2\# was then slow cooled to 100°C and held at this temperature for 2 hours to obtain an absolutely dried sample. It was then slowly heated to the stress free temperature in order to estimate the shrinkage stress. The process was repeated so that a further shrinkage stress value could be found.

The reheated aged sample 2\# was placed in a dessicator and kept dry for 7 days and its shape change monitored.

Sample 3\# was prepared for use in experiments in which the stress relaxation in different humidities could be measured. Sample 3\# was kept in a constant temperature room whose humidity varied with the prevailing weather conditions for about 40 days and the sample shape was measured two times each day. The sample 3\# reheated at 100°C for 4 hours and was then placed in a sealed container which contained air at about 75% humidity at 20°C and its shape was measured at hourly intervals. It is noted that the errors from the variation of temperature were removed by means of transferring the change of temperature into corresponding bending distance on the basis of the bending distance after cure.
As well as the amount of bending the weights of samples were measured at all stages in order to assess weight changes due to uptake or loss of moisture.

4.3.4 Results

4.3.4.1 Residual stresses and strains

Surface stress
The surface stresses of the bimaterial strip (sample 1) were obtained by means of equation 8 and 9. A comparison of the results with those obtained using equations 28-32 and equation 26 and 27 is set out in Table 2. It can be seen that the stress values are quite close even though they are results from different samples.

<table>
<thead>
<tr>
<th>Methods</th>
<th>top surface of FM300</th>
<th>bottom surface of steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>equation 8 and 9</td>
<td>2.58</td>
<td>60.4</td>
</tr>
<tr>
<td>Equation 28-32</td>
<td>2.87</td>
<td>83.5</td>
</tr>
<tr>
<td>equation 26 and 27</td>
<td>3.57</td>
<td>83.8</td>
</tr>
</tbody>
</table>

Interface strain and stress
The bent beam (sample 2#) was analysed to obtain the constraint strain, residual strain and residual stress at interface according to the methods associated with equations 18-23 and 28-32. The results of the analysis are shown in Table 3.
### Table 3 Interface strain and stress comparison using different methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Sample</th>
<th>Constraint strain</th>
<th>Residual strain</th>
<th>Residual stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>equation 18-23</td>
<td>FM300-2</td>
<td>3.20E-03</td>
<td>-5.06E-04</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
<td>-5.06E-04</td>
<td>-5.06E-04</td>
<td>-106.3</td>
</tr>
<tr>
<td>Equation 28-32</td>
<td>FM300-2</td>
<td>3.00E-03</td>
<td>-5.10E-04</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
<td>-5.10E-04</td>
<td>-5.10E-04</td>
<td>-107.0</td>
</tr>
<tr>
<td>Equation 26 and 27</td>
<td>FM300-2</td>
<td></td>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
<td></td>
<td></td>
<td>-106.7</td>
</tr>
</tbody>
</table>

In addition, the thermal expansion coefficient of FM 300-2 film adhesive was obtained on the basis of equation 2.14, and the result of \( \alpha = 5.1 \times 10^{-5} \) was very similar to the value measured by means of the microscope as described in Chapter 3, \( \alpha = 5.8 \times 10^{-5} \).

- **Residual strains and stresses**

The residual stresses and strains in different layers were obtained from the analysis of the bent bimaterial beam according to theory 3 and 4. Both Table 1 and Table 2 show that both the surface stress and the interface stress achieved excellent agreement when the results were analysed by means of three different analysis methods and using two different sets of experimental results. Figure 4.12b, shows that, as must be the case, the residual strains are equal at the steel/adhesive interface, and it can also be seen from Figure 4.12a that the constraint strains for adhesive and steel are different at the interface due to differential mismatch and equilibrium theory, reflecting the same trend as the stress in Figure 4.12c. For steel, the maximum compressive stress of \(-107\) MPa was generated at the interface and then gradually decreased to zero at the neutral surface, at further distances from the interface the stress becomes tensile reaching a maximum value of \(+84\) MPa at the surface. In the adhesive, the stress is tensile.
throughout the layer, and the maximum stress 7.6 MPa is also found at the interface, and then slowly declines to 2.8 MPa at the top surface of the adhesive.

Figure 4.12 Results of residual strain and stresses distribution
4.3.4.2 Shrinkage stress

The reduction in volume of the adhesive due to shrinkage during cure is a possible mechanism of introducing stress into the joint. The fluidity of the adhesive during the initial part of the curing process will enable stress relaxation to occur and shrinkage is therefore only likely to introduce stress when the rigid polymer network is firmly established. Experiments were carried out in order to assess the contribution of this effect to the total stress.

Weight loss of adhesive was used to indicate the volume reduction experienced during cure. The sample was reheated to the cure temperature for a second and third time after the initial, manufacturer recommended, cure time in order to see if the reaction was actually fully completed during the first cure. The weight loss of FM 300-2 film adhesive samples during the curing process were measured using a Mettler DSC 30 system and precision electric scale. The amount of water evaporation was also checked by means of measuring the gradients of DSC curves in each stage. The results were given in Tables 4 and 5:

**Table 4 Weight loss of FM300-2 adhesive (mg).**

<table>
<thead>
<tr>
<th>sample</th>
<th>weight (mg)</th>
<th>weight after curing</th>
<th>1 heat</th>
<th>weight after curing</th>
<th>2 heat</th>
<th>weight after curing</th>
<th>weight after curing in percentage</th>
<th>weight after 3 times heating</th>
<th>weight after 3 times heating in percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.63</td>
<td>15.50</td>
<td>15.44</td>
<td>15.44</td>
<td>0.13</td>
<td>0.83%</td>
<td>0.19</td>
<td>1.22%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18.31</td>
<td>18.22</td>
<td>18.14</td>
<td>18.14</td>
<td>0.09</td>
<td>0.49%</td>
<td>0.17</td>
<td>0.93%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17.89</td>
<td>17.79</td>
<td>17.78</td>
<td>17.77</td>
<td>0.1</td>
<td>0.56%</td>
<td>0.12</td>
<td>0.67%</td>
<td></td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>17.76</td>
<td>17.76</td>
<td>0.1</td>
<td>0.56%</td>
<td>0.12</td>
<td>0.67%</td>
<td></td>
</tr>
</tbody>
</table>

- 117 -
Table 4 indicates that the adhesive is not fully cured after the initial ‘cure’. Samples of the adhesive were therefore also studied in a Mettler DSC-30 and the completion, or otherwise, of the reaction estimated from the DSC curves.

Table 5 The gradients of DSC curves in different stages

<table>
<thead>
<tr>
<th>sample</th>
<th>Curing</th>
<th>1heat</th>
<th>2heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.031</td>
<td>0.028</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.026</td>
<td>0.025</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.029</td>
<td>0.022</td>
<td>0</td>
</tr>
<tr>
<td>average</td>
<td>0.029</td>
<td>0.025</td>
<td>0</td>
</tr>
</tbody>
</table>

It can be seen from the gradients in table 5 that the reaction rate of the adhesive in the curing process is about 1.2 times as that in the first reheating. However, there is no further reaction in the second reheating as is indicated in Table 4. The error between the results from measuring gradients and the results of weight loss by using scale is due to the measurement of gradient in ‘curing’ stage didn’t include the cross linking process where some water evaporation already happened before the adhesive and adherend are firmly bonded together.

It can be seen from the gradients in Table 5 that after the post cure the reaction rate of the adhesive has dropped to zero indicating that no further reactions are taking place. This confirms the results of Table 4 which indicate that curing is complete after the first post cure.

Shrinkage stress measurement:

In the experiment to measure the shrinkage stress, the stress free temperature was more accurately found to be 122.7°C rather than the 120°C used for curing. The shrinkage stresses for steel at the interface were obtained by means of equation 22. Results from the two methods are given in table 6:
Table 6 Shrinkage stress for steel at interface (meth1inp and meth2inp: the shrinkage stress in percentage which compared with residual stress for steel at interface)

<table>
<thead>
<tr>
<th></th>
<th>method1(+-0.5MPa)</th>
<th>method2(+-0.2MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before cool down</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>after curing</td>
<td>0.43</td>
<td>0.2</td>
</tr>
<tr>
<td>after further curing</td>
<td>2.8</td>
<td>2.99</td>
</tr>
</tbody>
</table>

The results in Table 6 indicate that the shrinkage stress after initial curing is small, but that the further shrinkage which happens after further curing gives rise to a non-negligible stress. Hence, the shrinkage stress is only a small fraction of the residual stress.

4.3.4.3 Stress relaxation

This section describes the results of the experiments carried out to determine the effect of moisture content on the residual stress in bimaterial strips. Sample 2# used in the cure stress experiments was stored in a desiccator (after the final cure) for 7 days. The bending size δ and weight of the sample 2# are shown in Table 7.

Table 7 Bending δ(±0.03mm) and weight of sample 2# after multiple cure. (All the data were obtained at 23°C)

<table>
<thead>
<tr>
<th>Stage</th>
<th>bending size (mm)</th>
<th>weight(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before curing</td>
<td>0</td>
<td>3.87779</td>
</tr>
<tr>
<td>after curing</td>
<td>29.93</td>
<td>3.87056</td>
</tr>
<tr>
<td>after further cure</td>
<td>31.57</td>
<td>3.87008</td>
</tr>
<tr>
<td>after 7 days in dry desiccator</td>
<td>31.28</td>
<td>3.87016</td>
</tr>
</tbody>
</table>

From table 7, it can be seen that the bending size hardly changed after the sample was placed in a dry desiccator. In another word, the residual stress remained constant if no water was absorbed by the sample.

Sample 3# was placed in the oven at room temperature in order to keep the temperature constant after further curing. The results are shown in Figure 4.13. All the data was obtained at 21°C.
Figure 4.13 Experiment data of sample 3\(^\text{rd}\) at room temperature in an oven. Figure a shows the change in weight with time. Figure b and c indicates how the bending distance change with weight and weight change. Note: Bending size is the bending distance $\delta$ in Figure 4.11.
Chapter 4

Figure 4.13 a) shows that the weight of the sample, which was kept exposed to normal room conditions, varied considerably with time. The variation followed variations in the prevailing weather conditions decreasing on dry days and increasing in wet weather. Figure 4.13b) shows that the bending size z varies with the weight of the sample. In other words, δ decrease when the weight of sample increase and increases when the weight of sample decreases. Plot c) also show that change in δ is proportional to the weight change. It can therefore be seen that the magnitude of stress relaxation is proportional to the amount of the water absorbed into the sample and that the process is reversible.

Sample 3* was placed in a humid environment (desiccator containing some water in the base – not in contact with the sample) for about 5 hours. The sample was removed, weighed and δ determined at the time intervals indicated in Figure 4.15. These measurements took 255 minutes. All the data was obtained at 21°C (sample 3*).
Figure 4.14 Sample 3\textsuperscript{a} at room temperature in humid desiccators. Figure a shows how the weight varies with time, figure b and c illustrated the bending size which reflects how the stress changes.

It can be seen from Figure 4.14 that $\delta$ decreases and the weight increases very quickly when the cured sample was put in a humid environment. Compared with the results obtained in the normal room environment, the rate of change of $\delta$ is much larger in the humid environment. It was also found that the sample is easily damaged in the humid environment with debonding of the adhesive from the adherend occurring after about 5 hours. For the adhesive lap joint, such damage will be less rapid than in bimaterial samples as the adhesive is between the adherends and diffusion will proceed much more slowly. The graph indicates that the bending size change is almost proportional with the weight change. This supports the proposition that the stress relaxation is only due to the water absorption by the sample and not to creep of the epoxy.

The residual stress after reheating the aged sample still includes the thermal stress and shrinkage stress. The thermal stresses do not change after repeated heating, assuming constant coefficient of thermal expansion, during the cooling down process, but the
shrinkage stresses are different. The shrinkage stress is directly related to the quantity of water inside the sample. The shrinkage stress is produced only from part of the water content. In other words, the residual stress after reheating the aged sample is larger than the residual stress from the curing process due to the different shrinkage stresses in the two processes. This can be seen from the weight loss results of FM300-2 film adhesive. However it is difficult to estimate the ratio between these two shrinkage stresses since some water has evaporated out from the sample before the bond is formed, but the residual stress only starts to be generated after the bonding between steel and adhesive. Table 8 shows the bending size $z$ or $\delta$ for different samples at different stages of the multiple curing process.

<table>
<thead>
<tr>
<th>sample</th>
<th>after curing</th>
<th>after further cure</th>
<th>before reheating</th>
<th>reheating aged samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#(z)</td>
<td>61</td>
<td></td>
<td>53</td>
<td>64</td>
</tr>
<tr>
<td>2#(z)</td>
<td>29.93</td>
<td>31.57</td>
<td>22.69</td>
<td>31.46</td>
</tr>
<tr>
<td>3#(z)</td>
<td>40.2</td>
<td>42.31</td>
<td>24.06</td>
<td>42.07</td>
</tr>
</tbody>
</table>

4.3.5 Discussion

4.3.5.1 Residual stresses and strains

Kawada and Ikegami [3] found the residual stress reached values of $-200\text{MPa}$ for steel at a steel/epoxy interface. However, the adhesive used in their work was not FM300 and had a higher curing temperature of $170^\circ\text{C}$. This will produce greater residual stress after curing. The results of this work therefore confirm that the stresses achieved in the work of Kawada and Ikegami are possibly realistic.

Swallowe et al. [8] quoted values in the range $-35\text{MPa}$ to $45\text{MPa}$ for measurements made using neutron diffraction with a steel/epoxy joint where the epoxy was not FM-300 but had the same cure temperature of $120^\circ\text{C}$. The range of stress for steel in this thesis $-107 \sim +83\text{MPa}$ is larger than $-35\text{MPa} \sim +45\text{MPa}$. Because the neutron technique averages over a 1mm length scale $-35\text{MPa}$ to $+45\text{MPa}$ will not represent the
full range of stress in the sample. Thus, it can also be said that quite good agreement is obtained between these two sets of measurements.

Adams et. al predicted the magnitude of maximum shrinkage stress in a double lap adhesive joint with the same adhesive curing temperature and Young's modulus but a different adherend (aluminium) [6]. The maximum longitudinal curing stress for the adhesive was given as +31 MPa. This assumed no stress relaxation and that the shrinkage stress and shear stresses are zero. This value is high compared with the maximum stress 8 MPa in Table 2, but some unrealistic assumptions were used in their prediction.

The surface stress of steel summarised in Table 1 can be compared with Hong-bing Wang's measurement results of sample #2 which has same curing temperature but different Tg and other properties [10]. The surface stress value +83 MPa in Table 1 resulted as tensile stress which agree with their study but disagrees with the magnitude of their result +7.3 MPa.

However, the results described in this work were for a bimaterial strip while the results quoted from the work of other authors is mainly for single lap shear joints. These will not be directly comparable but should be of the same magnitude. Since the bimaterial strip is a very convenient method of measuring residual stress, the relationship between bimaterial strip and joint results is worthy of further investigation.

4.3.5.2 Shrinkage stress

Comparing the results of Table 4 and table 5, it can be seen that good agreement is obtained between two methods. Both tables show that some of water still remained inside the sample after the standard curing process. In addition, these results could explain why the bending distance (z in Figure 9 and δ in Figure 10) of the further cured sample is larger than the standard cured sample. In other words, the extra strain and stress were induced from the remaining water inside the sample after cure. The results in Table 6 further confirm that considerable shrinkage stress was generated from a further curing process.

The shrinkage of FM300-2 adhesive was considered to be same as the weight reduction of FM300-2 adhesive in percentage terms, assuming the volume and weight
are proportional. It therefore can be said that the measured weight loss of FM300-2 adhesive produces a volume change which is very close to the Dannenberg and May value of the linear free shrinkage of an ‘Araldite’ epoxy resin of 0.75% when cured at 110°C [15].

4.3.5.3 Stress relaxation

The results described above strongly support the view that stress relaxation in bonded joints is primarily due to moisture content. Creep of the polymer is therefore unlikely to be anything other than a minor contributor to stress relaxation. Brewis et al. investigated the weight change of film adhesive with time by immersion of the adhesive in water [11]. The result for an epoxide adhesive immersed in water at 45°C is that the weight increases dramatically initially and then increases slowly up to a constant value. Brewis’s study generally agrees with this experiment work in which the weight of a dry sample increased much faster initially and slowly varied over a small range which depends on the weather.

The effect of absorbed water on the mechanical properties of films of some structural adhesives has been reported by Brewis, Comyn and Shalash (1982, 1983) [11]. The data (p218) shows that water lowers tensile strength and modulus but increases elongation at break, but these very largely recover on drying. These results agree with the experiment results of this work (Table 10). The data 3.20134 after complete cure and 3.20150 after reheated the aged sample show that the weight of sample slightly increased even after ‘complete’ drying in the oven. This means that a small amount of water remains inside the sample, which agrees with J.Comyn’s result [21] that when films of cured epoxide resins are left in water for some time, a small residue remains after evaporation of the water.

4.3.6 Conclusion

It is found that almost all the curing stress in a metal/epoxy joint is thermally generated from the cooling down process. A number of different theoretical
approaches have been adopted in the analysis of the data and good agreement for the residual stress after curing in an FM300-2 adhesive and steel bimaterial beam are obtained from different theoretical and experimental methods. The initial shrinkage stress was found to be negligible. However, considerable shrinkage stress is produced after a further 2 hours curing. The stress relaxation of samples after curing is mainly due to moisture absorption.

4.4 Effect of moisture

4.4.1 Introduction

Tangible evidence of the effect of water to adhesive joints is seen in the bimaterial experiment above. Further work is required to prove the moisture influence on the strength of adhesive joints. Previous work has indicated that the effect of moisture seriously influences the strength of the adhesive joints due to damage to the adhesive layer and interface. The strength of the joint decreases when the joint is exposed in a wet environment. This has been proved in metal/epoxy joints [23-25] and composite bonded joints [26-28].

In the adhesive joint study of Wahab et al [23], the adhesive used was Ciba Geigy’s Aradite 2007. The specimens were immersed in water at 60°C until saturation. Their results show that the E-modulus, yield stress and ultimate stress decrease when the adhesive becomes wet, while the strain to failure increases. In other words, moisture increases the flexibility and ductility of the adhesive. It was also found that the maximum swelling strain at saturation reaches 3%. In a metallic joint, moisture diffuses into the joint through the adhesive layer and along the interface. It has been reported [29] that, in general, the moisture diffusion through the adhesive is predominant if there were no pre-existing micro-cracks and/or debonded areas at the interface. Recently, many researchers have concentrated on studying the durability performance of bonded joints. Wylde and Spelt [25] used open-faced specimens in order to accelerate ageing in an aluminium/epoxy double cantilever beam. Bistac et al. [30] studied the durability of steel/polymer immersed in an aqueous environment (liquids such as water, salt, acid and basic solutions). Knox
and Cowling [31] investigated the durability performance of thick adherend steel lap shear joints and bulk adhesive using accelerated ageing techniques.

The effect of change in elastic modulus and swelling on joint strength was discussed in [17]. Moisture absorbed in a polymer matrix can lead to a wide range of effects. Some effects on the polymeric material are reversible and can be erased on removal of water. Others are irreversible and result in permanent changes in the performance of polymers. Water absorption into polymer materials can cause plasticization and swelling, which are both reversible processes. Water acting as a plasticizer can reduce the strength and modulus of the adhesive. Ivanova [32] demonstrated that the introduction of water in the polymeric materials causes swelling, which may have introduced swelling stresses into the adhesive system. For resin-filler systems, some research has shown that absorbed water can attack the matrix/filler interface and cause debonding at the interface [33-35]. Studies conducted by Ivanova, et al [32] and Gonon, et al [36] showed that absorbed water cannot be totally removed by thermal annealing and the residual water in the adhesive is believed to be the one which is strongly bonded to polar sites.

It can be seen from previous research work described above that water acting as a plasticizer can reduce the strength and modulus of the adhesive. A plausible explanation for these effects is that the reduction in modulus of the adhesive due to moisture can reduce the stress concentration at the edges, which leads to a beneficial effect on the joint strength. However, the tensile residual strain in the adhesive layer which is near to the interface may be decreased due to the swelling of the adhesive so that the compressive strain in the adherend close to the interface would be decreased, which could lead to loss of the joint strength. However, change of residual stress depends on both swelling strain and Young’s modulus. If the effect of change of modulus is greater than that of swelling, it would benefit the joint strength. Otherwise, it would cause a reduction of joint strength.

It has been known for a long time that the use of saturated salt solution is an accepted and reliable method for generating a known relative humidity in the air. The operating principle is based on the properties of salt and water solutions, which can generate a
stable humid air environment in a sealed chamber. Saturated salt solutions provide a reliable measurement environment for a lot of research work as the humidity levels generated by these solutions and their behaviour at different temperatures are well documented and have been verified by many researchers.

The use of bulk adhesive test specimens brings advantages in the measurement of swelling strain of adhesive (through larger gauge sections) and in the interpretation of the data (since the absence of adherends leads to simpler stress distributions). However, the bulk specimens may differ from the adhesive in the joint by incorporating voids. Bulk adhesive specimens should be cured under conditions that approximate those that occur in the adhesive when the bonded component is cured. Tests on bulk test specimens are the most accurate method for obtaining some mechanical property data for adhesives. However, to obtain data that is truly representative of the materials in joints requires careful specimen preparation. Standard methods for preparing such specimens have been developed. There are a number of key points that should be considered when producing test specimens. For example, specimens should be prepared using methods that minimise the inclusion of air in the test specimens; cure condition needs to be exactly same as the recommended cure process for the adhesive joint.

In this study, the effect of water to FM300-2 film adhesive was investigated by means of measuring a bimaterial sample and a bulk sample in a well sealed chamber with different constant relative humidities at room temperature. The chamber was located on a special vibration-prevention table in order to improve the accuracy of the optical measurements of size and shape changes. The volume of the bulk adhesive and the weight were monitored in different humidity environments. Weight changes were used to represent the quantity of water absorbed in order to obtain a function of volume (or swelling strain) against the moisture content to quantify the swelling strains due to moisture. Weight can also be used to find if there is residual water after total annealing of the aged sample.
4.4.2 Theory

4.4.2.1 Swelling strain of FM300-2 adhesive

Assume the swelling of the adhesive due to water invasion is uniform. The longitudinal strain can therefore be expressed as follows:

\[ \varepsilon = \frac{\Delta L}{L} \]  \hspace{1cm} (32)

where \( L \) is the length of bulk adhesive, \( \Delta L \) is the change of length of bulk adhesive.

Note: the thickness has to be very thin in order to achieve uniform deformation of the sample in a short time.

4.4.2.2 Measurement of Young’s modulus \( E \) of FM 300-2 adhesive

Assume strain in \( y \) and \( z \) direction can be ignored for a thin and long bulk adhesive sample, according to Hooke’s law:

\[ \sigma = E \varepsilon \]  \hspace{1cm} (33)

where \( \sigma \) is the elastic stress in the material in the \( x \) direction, \( \varepsilon \) is the elastic strain along the \( x \) direction and \( E \) is the elastic constant.

The Young’s modulus can therefore be derived:

\[ E = \frac{\sigma}{\varepsilon} \]  \hspace{1cm} (34)

Here \( \varepsilon \) can be treated as the swelling strain of the bulk adhesive sample due to moisture, \( \sigma_H \) can be regarded as the hygroscopic stress of the adhesive which leads to the adhesive swell.

Hygroscopic stress was obtained from measuring the bimaterial sample at the same time as measuring the bulk sample in same environment. The hygroscopic stress of the adhesive at any time can be obtained by means of the difference between residual stress \( \sigma \) after cure and the residual stress \( \sigma_m \) at this moment which decreased due to moisture content. It is:

\[ \sigma_H = \sigma - \sigma_m \]  \hspace{1cm} (35)
The hygroscopic stress achieved by the bimaterial sample at any time at constant temperature is mainly caused by the swelling of the adhesive itself because of moisture. Using the equation above to work out Young’s modulus as a function of moisture content is therefore feasible and reasonable. The residual stress of the bimaterial sample can be obtained by means of the bimaterial method (4.3.2.4) described earlier.

Swelling strain can be measured using the bulk sample or the bimaterial sample using strain gauge or optical methods. Optical methods can provide a more convenient means for measurement of the swelling strain of the adhesive, particularly for FM300-2 adhesive with its higher cure temperature. In addition, the strain measured in the bulk sample is the swelling strain of the adhesive, but the strain measured in the bimaterial sample is the total strain of adhesive which includes mechanical and swelling strain. Thus, the swelling strain was investigated by means of bulk sample using an optical method in this work.

If the swelling strain of the adhesive is kept constant, but the modulus changes, the mechanical strain would change (bimaterial sample) due to different force and bending moments. It has been known for a long time that the modulus decreases with moisture adsorption and also with increasing temperature. For the bimaterial sample, the hygroscopic stresses obtained from bimaterial methods vary with both the modulus of the adhesive and the swelling strain. In addition, the stress in the interface is expected to change as it is the source of bending of the bimaterial sample. If, in the bent bimaterial sample after water absorption, the modulus of the adhesive decreases even without swelling, then the mechanical strain would decrease due to a decrease of residual stress. Whatever the modulus or swelling strain change, the combined effect would be sensed by means of the hygroscopic stress, in other words the hygroscopic stress can be observed by means of the change of bending distance $\delta$.

4.4.2.3 Transfer effect of moisture into thermal effect.

In order to clearly show (or quantify) the effect of moisture on the adhesive joints, in other words, see how much influence the swelling strain of adhesive has on the
adhesive joints, it is convenient to use a bimaterial sample instead of attempting to measure swelling strain directly in the bulk adhesive. The hygroscopic stress can be clearly observed in the curvature of the bimaterial strip and knowing the modulus the swelling strain can be calculated using the following equations.

For a bimaterial sample, the total strain of the adhesive includes two parts—mechanical strain and thermal strain as follows:

\[ \varepsilon_a = \varepsilon_f + \varepsilon_b + \alpha \Delta T \]  

(36)

The total residual strain in the interface is:

\[ \varepsilon_{nt} = -\frac{F_1}{A_t E_1} - \frac{M_1 t_1}{2E_1 I_1} + \alpha_1 \Delta T - \alpha_2 \Delta T \]  

(37)

The swelling strain of the adhesive due to water can be treated as a thermal strain \( \alpha_1 \Delta T_0 \), equivalent to a thermal expansion due to an increase of temperature \( \Delta T_0 \).

\[ \varepsilon_s = \alpha_1 \Delta T_0 \]  

(38)

\[ \Delta T_0 = \frac{\varepsilon_s}{\alpha_1} \]  

(39)

It has to be noted that only the adhesive experience the 'thermal expansion' (moisture expansion), but the adherend has no expansion due to a very low moisture absorption coefficient. Thus, the expansion of the adhesive can then be transferred into the expansion of the whole bimaterial sample due to an increase of temperature \( \Delta T_w \), where \( \Delta T_w \) is equivalent temperature change in both materials that would produce the observed curvature change in a bimaterial strip, as follow:

\[ \alpha_1 \Delta T_0 = \alpha_1 \Delta T_w - \alpha_2 \Delta T_w \]  

(40)

combining equation 39 and 40, therefore:

\[ \Delta T_w = \frac{\alpha_1 \Delta T_0}{\alpha_1 - \alpha_2} = \frac{\varepsilon_s}{\alpha_1 - \alpha_2} \]  

(41)
4.4.2.4 Diffusion coefficient

The detailed theory was described in 3.7.2

4.4.2.5 Moisture coefficient $\beta$(CME).

Coefficient of Moisture Expansion - CME is defined as the fractional increase in length per unit mass variation due to the moisture desorption or absorption.

The CME is determined by measuring the moisture content change and the strain change between two moisture equilibrium states. It is shown as follow:

$$\varepsilon = \beta \Delta M$$  \hspace{1cm} (42)

where $\varepsilon$ is the strain, $\beta$ is the Coefficient of Moisture Expansion—CME, $\Delta M$ is the mass variation due to the moisture desorption or absorption. In this work, the moisture change is measured using a balance with a resolution of $10^{-5}$ g. The strain change was monitored by means of a precision travelling microscope with a resolution of 0.001mm.

4.4.3 Measurement methods for the bulk specimen:

4.4.3.1 Telescope method:

The method is illustrated in Figure 4.15. The measurement accuracy of the telescope is $\pm 0.01$mm. After the test, it was found that the main error comes from the human error induced from the measurement of the length due to the erroneous judgement of the overlapping position between scale of telescope and the object. This reduces the precision to $\pm 0.1$mm.
4.4.3.2 Digital camera

Tests by means of a tripod mounted digital camera (3.2 Mega pixels) at 50% RH humidity with the sample inside a well sealed glass chamber at room temperature were carried out and the results are shown in Figure 4.16.
Figure 4.16 Measurement data by using digital camera

Estimation of accuracy:

The optical resolution of the digital camera is 3.2 Mega pixels, the object size is about 120mm x 80mm. Hence, it can be estimated that the accuracy of this method is 0.055mm assuming that the object roughly fills the field of view.

\[
\delta = \sqrt{\frac{120 \times 80}{3.2 \times 10^6}} = 0.055 \text{mm}
\]
From the data and resolution of the digital camera, it can be seen the accuracy of this method still not good enough to directly measure the tiny swelling strain of bulk adhesive.

However, the effect is different for a bimaterial sample. The tiny swelling strain of a bulk adhesive sample corresponds to a many times magnified bending distance. In this work, the camera was used to sense the bending distance of a bimaterial sample in order to measure hygroscopic stress. The accuracy of the digital camera to measure the bending distance of the bimaterial sample can be transferred into a corresponding accuracy of swelling length of the bulk adhesive sample. FM300 film adhesive (thickness is 0.26mm) and steel (0.13mm thick) were used in the experiment, the length of bimaterial specimen is 180mm and the length of bulk adhesive specimen is 100mm. The bending distance is about 43mm for 100°C drop in temperature, the transferred accuracy therefore is 0.0006mm

\[
\delta_i = \frac{\delta \alpha \times 100\text{mm} \times 100^\circ\text{C}}{43} = 0.0006\text{mm}
\]

Where \( \alpha \) is the thermal expansion coefficient of FM300-2 film adhesive.)

Using this method an equivalent swelling length change of 0.6µm in a 100mm long bulk adhesive specimen can be measured.

4.4.3.3 Camera and scanner

An alternative direct photographic method to the use of the digital camera is to use a 35mm camera and high resolution film. Measurements are made by scanning the fine pictures obtained from high-resolution camera (high resolution lens and film) by means of high-resolution scanner.

Calculation of System Resolution:

Method 1:
The overall resolution of the system of the lens, film, camera and scanner is not simply the average of the resolution of the lens, the film and scanner, nor is it just the worst of the three either. Instead, the overall system resolution is:

\[
\text{system resolution} = \frac{1}{\left(\frac{1}{\text{lens Ipmm}} + \frac{1}{\text{film Ipmm}} + \frac{1}{\text{scanner Ipmm}}\right)}
\]

Where \(\text{Ipmm}\) is line per mm. \(R\) (lpmm) is the resolution of whole system; \(l\) (lpmm) is the resolution of lens; \(f\) (lpmm) is the resolution of film; \(s\) (lpmm) is the resolution of scanner.

If an enlarger lens is added into the above equation, it will further reduce the overall system resolution typically by 15-25%. A superior lens that delivers 600 lpmm aerial resolution combined with film resolution of 100 lpmm and a high-resolution scanner, gives a resulting whole system resolution of about 70 lpmm according to equation 44.

In another words 0.014mm. Normally, it only can reach 0.017mm (60 lpmm).

Method 2

Assume high-resolution film (24 x 36mm,) and scanner with high optical resolution 2400dpi x 5000dpi (or 125 lpmm) is used. The size of object is about 250mm x 100mm for two samples; 120mm x 100mm per sample.

The sample will be located about 1m from the lens (135mm) of camera.

Therefore the accuracy \(\delta_1\) of this method in length direction for the sample is about 0.035mm. \((\delta_1 = \frac{25.4\text{mm}}{5000} \times \frac{250\text{mm}}{36\text{mm}} = 0.035\text{mm})\)

The longitudinal measurement accuracy for one bulk adhesive sample is therefore about 0.016mm. \((\delta_2 = \frac{25.4\times120}{5000 \times 36} = 0.016\text{mm})\)

It can be seen that the accuracy is still not high enough to sense the tiny swelling strain of the adhesive. In addition, this method is costly and time consuming.
4.4.3.4 Micro-travel-microscope:

This is a precision length instrument with fine track. The resolution of this instrument is: $\delta_a = \pm 0.001\text{mm}$. The length of the sample:

$$L = L_1 - L_2$$

According to the theory of propagation of uncertainty, the uncertainty $\delta_L$ of length of bulk adhesive sample is:

$$\delta_L = \pm 0.0014\text{mm (715 lpm)}$$

Since the accuracy of this instrument is much higher than that which can be achieved using other methods and the swelling strain was estimated to be very tiny after a short time exposed in the air, it was therefore decided that the bulk specimen would be measured using micro-travel-microscope. As a result, digital camera and micro-travel-microscope were selected to be the measurement equipment.

4.4.4 Experiments:

The FM 300-2 film adhesive and steel strip were used to prepare a 120mm x 20mm x 2mm bulk adhesive sample and a 180mm x 12mm bimaterial sample.

Two large containers (glass chambers) were used to create stable environments. One of the glass chambers was used to measure the swelling strain and Young’s modulus $E$, another one was regarded as a reference chamber for monitoring the weight of the sample. Two small glass containers within the large containers were separately used to hold the saturated salt solutions used to regulate the humidity. The temperature inside the chambers is held constant at $21\pm0.3^\circ\text{C}$. A precision hygrometer monitors both the temperature and RH of the chamber.

Two post-cured samples (bulk adhesive and bimaterial sample) were immediately exposed inside one well-sealed chamber. The constant humidity environments were achieved within 6 hours. Samples were studied at 42%, 57% and 72% RH values.
created by means of potassium acetate, sodium bromide and sodium chloride salt solutions. Before changing the RH value, the samples were reheated at around 120°C to remove the water existing inside sample so that the changed properties of the adhesive are recovered.

The bimaterial sample was measured by means of digital camera (3.2 Mega pixels) with a standard steel ruler was fixed in the same surface as the specimen to calibrate the value of the length. The digital camera was kept in a fixed position on a tripod throughout to achieve reliable results. The pictures were then analysed by means of AutoCAD software to obtain quantitative results. As well as taking pictures of the bimaterial specimen, the bulk adhesive sample, marked with two straight ruled lines, was measured by using a travel microscope with accuracy ±0.001mm. Before the experiment started, the microscope was first adjusted by means of a fine level and was fixed with a clamp on the measurement table. The experimental set up is shown in Picture 4.2. The weights of the two samples were measured before and after the experiment. In order to keep the samples in a constant humidity and motionless all the time so that more accurate measurement results can be obtained, another reference bulk sample with exactly same size and properties as that bulk sample for swelling strain measurement, was prepared in order to study the variation of moisture content. This was stored in another well sealed glass chamber with the same constant humidity and temperature as the first chamber. The weight of the reference bulk sample was measured at the same time as the length measurement by means of a precision electric scale with resolution ±0.01mg. The weight of the reference sample was measured as quickly as possible and then it was immediately put back into the glass chamber.
4.4.5 Results:

The glass containers were maintained at temperature of 21° C±0.2° C at a relative humidity of 57% and 42%. The temperature was held at 20° C±0.5° C at RH of 72%.
Table 9 Weight of sample after complete cure and re-drying after water invasion

<table>
<thead>
<tr>
<th>weight(g)</th>
<th>Complete cure</th>
<th>1st reheat</th>
<th>2nd reheat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.84175</td>
<td>2.8429</td>
<td>2.84405</td>
</tr>
</tbody>
</table>

moisture variation with time

Figure 4.17 Moisture content variation with time

swelling strain variation with time

Figure 4.18 Swelling strain variation with time
swelling strain variation with moisture

![Swelling strain variation with moisture](image)

**Figure 4.19** Swelling strain variation with diffused moisture content

Hygroscopic stresses

![Hygroscopic stresses](image)

**Figure 4.20** Hygroscopic stress
Figure 4.21 Young's modulus $E$ of FM300-2 variation with time

Figure 4.22 Young's modulus $E$ variation with moisture content

Figure 4.23 Moisture expansion coefficients of FM300-2 adhesive
The data of Table 9, indicates that small amounts of residual water still exists inside the sample after drying by means of heating in the oven. This result agrees with the results of 4.3 and also with the studies of Ivanova [32] and Gonon [36], their work showed that absorbed water cannot be totally removed by thermal annealing and the residual water in the adhesive is believed to be the one which is strongly bonded to polar sites. Table 9 also shows that almost 98% of the water can be removed by drying. This observation could explain why much of the strength lost in adhesive joints due to moisture was recovered in most cases after drying [37, 38].

The results of the swelling strain experiments clearly shows that the swelling strain of FM300-2 adhesive increases at different rates in different humidity environments. However, there is a common regular pattern in how swelling strain varies in different RH circumstances. Firstly, the swelling strain initially increases rapidly, then the rate of increase in strain tends to zero. Secondly, the swelling strain is almost proportional to the amount of moisture absorbed independent of the RH of the environment. This agrees with the work of Loh [39] et al., who reported that the swelling of AV119 is a function of the amount of moisture and does not indicate any significant dependence on the RH in which it was exposed. It is, however, noticeable that the increasing rate of swelling strain against moisture content differs in different RH environments, the higher the RH the larger swelling strain rate as a function of moisture content. In addition, Figure 4.18 and 4.19 shows that the maximum swelling strain reached by FM300-2 adhesive was 0.32% within the limited time of the experiment. Wahab [23] found that the maximum swelling strain of Ciba Geigy 2007 adhesive was about 3%. It has to be noted that his specimen was immersed in water at 60°C until saturation.

The graph of Young’s modulus against time (Figure 4.21) indicates that the Young’s modulus decrease sharply with time initially, then gradually decreases to a constant value. With a higher rate of decrease in higher RH. According to the graph of E variation with diffused moisture (Figure 4.22), it is seen that E is dependent mainly on

### Table 10 Moisture coefficients β/(g)

<table>
<thead>
<tr>
<th>RH</th>
<th>42%</th>
<th>57%</th>
<th>72%</th>
</tr>
</thead>
<tbody>
<tr>
<td>β (1/g)</td>
<td>0.053</td>
<td>0.062</td>
<td>0.076</td>
</tr>
</tbody>
</table>
Chapter 4

the moisture content. These results agree with most of the research of previous workers. For instance, the study of Wahab [23] and Loh [39]. Wahab studied adhesive joints formed using Ciba Geigy 2007. His results show that the modulus decreases when the adhesive becomes wet. The bulk sample (AV119) was studied by Loh et.al, their sample was exposed to different higher RH environments---81%, 96% and 100% at 50°C. The maximum decrease of E is around 1000MPa which is quite close to the result of this work 1500 MPa.

Further results

The relationship between the curvature of bimaterial sample and moisture content.

![Comparison of estimated and measured swelling strain](image)

**Figure 4.24** Comparison of the directly measured swelling strains of the bulk sample and the swelling strain of the bulk sample estimated from the bent bimaterial sample.
Figure 4.25 Corresponding equivalent rise of temperature with moisture expansion

The estimated swelling strain in Figure 4.24 above was derived from measured bimaterial sample with assumption that Young’s modulus remains constant at the published value of 2500 MPa. From the graph, the difference between the actual value and estimation gradually increases due to the actual Young’s modulus decreasing with time due to absorption of moisture. Figure 4.25 shows that the moisture creates a large effect on the adhesive and its joint which is equivalent to the effect of a very high increase in temperature.

In addition, it was found from the bimaterial specimen that moisture could easily invade the interface of low quality joints in higher RH so that a debonding phenomenon was often observed at the interface. This has also been proved by means of work which has shown that absorbed water can attack the matrix/filler interface and cause debonding at the interface [33-35]. This kind of phenomenon may explain why it was often found that interfacial (rather than cohesive) failure of adhesively bonded structures is the dominant failure mechanism [40-43]. Indirect agreement is
achieved between this work and Davis study [44]. His work shows that the rate of crack growth was slow for good quality adhesive joints, but crack growth was detected almost immediately for low quality interfaces as moisture intruded into the interface and resulted in a fast rate of crack growth.

4.4.6 Discussion:

The accuracy of the results of this work was influence by errors in both theory and experiments. The detailed error analysis is presented below:

4.4.6.1 Theory error:

In equation 35, hygroscopic stress/swelling strain = E, assuming that strain in the other two directions can be ignored. Hygroscopic stress is obtained from the bimaterial sample; swelling strain from the bulk sample. Young's modulus of the adhesive varies with water absorption. However, constant E was used in working out the hygroscopic stress of the bimaterial sample. Also, due to different type of sample, the quantity of water needed to reach to equilibrium for bimaterial and bulk samples are different. The amount of water required for the bulk sample is bigger than that for the bimaterial sample because the thickness of the bimaterial sample is much smaller than the bulk sample. This could explain why the expansion rate of the bulk sample is slower than the corresponding rate of decrease of bending distance of the bimaterial sample. It should be noted that the quantity of water per unit mass of adhesive after equilibrium is reached is the same for both bi-material strip and bulk samples. However, the water enters the sample only from one direction for the bimaterial sample, but from two sides for the bulk sample. In other words it is possible that the diffusion rates are different. If the diffusion rate of the bulk sample is larger than the bimaterial sample, it would reduce the error induced from different thicknesses between bulk and bimaterial samples.
4.4.6.2 Experiment error

- Instrumental errors which include uncertainties of microscope and camera methods.

- Imperfect samples might cause debonding phenomenon to occur when the sample is exposed in higher humidity environments; slight thickness difference of bulk sample could lead to non uniform expansion.

- Moisture already diffused into the sample during the period between the samples were weighted after cool down and before set up inside the sealed chamber. This would cause an error in the initial (set at zero) value of swelling strain. The RH needs some time to reach the required constant value, which normally takes a few hours. The magnitude of the influence of both these factors gets smaller when the required RH is close to the natural RH.

- The main errors in the weight measurement of the reference sample stems from two factors. A few minutes are required to weight the sample in room humidity and the humidity varies because of the opening of the lid of the chamber.

- Infinity mass was used to work out diffusion coefficient $D$ in equation 19 in Chapter 3 is estimated value from measurement data due to the limited time.
Although this work contains quite a lot of potential errors, the exact amount of error is difficult to work out, it is thought that the care taken in preparing perfect samples, decreasing the time of setting up and weighting to minimum value and also taken more microscope readings to reduce these potential errors means that these methods are reasonable and feasible on the basis of error theory. This experiment could be improved by exposing samples in the RH environments for a longer time.

4.4.7 Conclusions

In conclusion, this work clearly shows that moisture is a main critical factor affecting the performance of adhesives and adhesive joints even though only bimaterial and bulk adhesive samples were investigated. Good agreements among three different constant RH environments were obtained, in the variation of the properties of adhesive, for example, swelling strain, Young's modulus, diffusion rate and moisture expansion coefficient, which are shown to almost solely depend on the diffused moisture contents. It is also indicated from both the results of bimaterial sample and the bulk sample that the residual stresses for both bimaterial sample and bulk sample are reduced by moisture. In addition, this experiment possibly shows moisture easily damages low quality adhesive joints, particularly when RH is higher than about 70%. As a result of swelling, the significant weakening of adhesive joints may be closely related to the absorption of moisture.

References:


Chapter 5 X-ray and Neutron diffraction methods

5.1 Basic theory of strain measurement

5.1.1 Basic principle

The measurement of strain by means of X-ray or neutron diffraction techniques is widely used for non-destructive testing and evaluation, and is a mature approach for obtaining relevant data in many industrial circumstances. Both X-ray and Neutron diffraction are based on the same theory. When a crystalline material is irradiated by a monochromatic X-ray/neutron beam with wavelength $\lambda$ of the same order of magnitude of the lattice spacing, an increase of the scattered intensity can be observed in the neighbourhood of a few $2\theta$ angle values. This increased intensity, called diffraction peaks, comes from a constructive interference of the X-ray photons scattered by the atoms of the crystal. The stress analysis techniques utilises the distance between atomic planes of a crystalline sample as an internal strain gage. For any reflection hkl, the lattice plane spacing $d_{hkl}$ can be determined from the angular position $\theta$ of the appropriate diffraction peak through Bragg’s law: (see Figure 5.1)

$$\lambda = 2d\sin\theta$$

where $\lambda$ is the wavelength of the incident beam, $\theta$ is the diffraction angle and $d$ is the lattice spacing.

The lattice spacing of crystallographic planes {hkl} on which the measurement is performed is related to the position $\theta$ of the diffraction peak through Bragg’s Law. A homogeneous elastic deformation of the crystal will result in a change of the spacing $d_{hkl}$, because the planes tend to get closer when in a compressive stress state and to separate when in a tensile state. The measured strain can be expressed in relation to a reference state of the material called the stress-free state. In this state, the lattice spacing of planes {hkl} equals to $d_0$ which is a function of the lattice parameters of the stress-free crystal. Because of an elastic deformation, the lattice spacing will be equal to $d$. The measured strain can then be calculated from $d$ and thus from $\theta$: 
\[ \varepsilon = \frac{(d - d_0)}{d_0} = -\cot\theta \Delta\theta \]  

where \( \varepsilon \) is the strain; \( d_0 \) is the unstressed lattice spacing of the hkl planes; \( d \) is the stressed lattice spacing of the hkl planes. \( \Delta\theta \) is the difference in Bragg angle between the strained and unstrained states.

Figure 5.1 Basic principle of strain measurement by means of X-ray or neutron diffraction

5.1.2 Diffraction peak and grain size

Consider the case when a polycrystalline specimen is irradiated by a X-ray or neutron beam. Since there are a number of grains (single crystals) in the specimen, with different orientations to the incident beam, planes of different spacing may be available for diffraction from each grain. Thus a monochromatic beam will diffract at different angles from different grains, causing a number of spots on the detector. A diffraction peak is an interference function which results from the coherent scattering of the X-ray beam or neutron beam on the periodic structure of the crystal. This means that only periodic domains of the material can be analysed by this experimental technique. Hence, in a polycrystalline aggregate, each elementary diffracting volume is limited by the discontinuities of the material (vacancies, dislocations, grain boundaries, holes, cracks) which delimit small crystallites without any defect, called coherently diffracting domains. The coherently diffracting domain can be much
smaller than the grain. Generally, for a given direction, all coherently diffracting domains of a grain do not diffract simultaneously. Therefore, the diffraction peak results from the simultaneous contribution of a great number of coherently diffracting regions, scattered in the grains of the irradiated volume (Figure 5.2)

![Diagram of diffraction peak formation](image)

**Figure 5.2 Formation of a diffraction peak**

Assuming the specimen to be analysed contains large crystallites whose size can exceed 100 µm, the volume irradiated by X-rays or neutrons may then contain only a small number of grains. In this case, the number of crystallites in the diffracting volume will not be sufficient to lead to a diffracting peak with regular shape. There are very few crystallites diffracting together to form the diffraction peak and thus it becomes "jagged" and its shape varies dramatically with sample position. The localization of peaks in different directions might then become very difficult and the strains will be measured with poor accuracy. To solve this problem, the number of crystallites in the diffracting volume should be increased until the peak becomes smooth and regular. When the grain size gets smaller, the number of the crystallites in the irradiated volume increases, and a larger number of crystallites may diffract at a given 2θ angle. These crystallites may be at various orientations with respect to the incident beam. A beam, for example neutron, with a high penetration depth will make the situation better but with X-rays there are often not enough grains. For the purpose
of the work described in this thesis, the ideal adherend should have small grain size in order to obtain more accurate strain measurement values. However, it should be borne in mind that very small (submicron) grains lead to considerable size broadening of the peaks which can make accurate peak position measurement difficult. Therefore, it is very important to measure the grain size of the sample materials.

5.2 X-ray

5.2.1 Aim

The purpose of the X-ray work carried out as part of this investigation was to make direct measurements of the residual stresses in two directions (longitudinal and perpendicular to the joint plane) in the metal adherends at an array of points on the edge surface over the whole of the bonded area of a single-lap shear adhesive joint for both aged and unaged samples in order to achieve stress maps in two directions (longitudinal and perpendicular stresses). This was achieved by making use of the X-1 diffractometer in Berlin Neutron Scattering Centre (BENSC). The experimental results were then compared with the predictions of Finite Element Mechanics to verify the theoretical analysis.

5.2.2 Introduction

5.2.2.1 X-ray

Among all the stress and strain measurement techniques, X-ray diffraction has a particular place because it enables a non-destructive evaluation of surface or near surface stresses. Compared with conventional techniques, the X-ray diffraction method is non-destructive and enables local measurements and real-time analysis of stress evolution. Compared with the Neutron diffraction method which has recently been developed and requires a specialised source, an X-ray beam, can be supplied to the experiments in any institute and industrial environment.
5.2.2.2 Optical theory

The basic optic principal of X-ray diffraction equipment is shown in Figure 5.3.

![Diagram of X-ray diffraction equipment]

**Figure 5.3 Basic optical principal of X-ray diffraction equipment**

On the X-ray source side, a line source of X-rays passes through a series of slits called Soller slits that define and collimate the incident beam. After the beam has been diffracted by the sample, it passes through another set of slits, the antiscatter slit reduces the background radiation, improving the peak to background ratio, by making sure that the detector only can receive X-rays from the specimen area. The beam converges on passing the receiving slit, which defines the width of the beam admitted to the detector. An increase in slit width increases the maximum intensity of the reflections in the diffraction pattern but generally results in some loss of resolution. A change in slit width does not change the ratio of integrated intensities of two peaks, \( I_1/I_2 \) (I is integrated intensity), but it most likely changes the ratio of the maximum intensities \( M_1/M_2 \) (M is maximum intensity). That is why the integrated intensity is always be used. Furthermore, because it is difficult to measure absolute intensities, the relative integrated intensities of the reflections is always taken.
5.2.3 Adherend material selection

5.2.3.1 Introduction

Aluminium’s specific gravity is only 2.7g/cm\(^3\) as compared with 7.8 g/cm\(^3\) for steel and 8.8 for copper. For this reason the metal is used extensively in the form of alloys, for aerospace and automobile parts for structures of all types. In the last case the extreme lightness of the alloys enables a much greater volume to be used for a given weight, with a resultant increase in rigidity. In addition, aluminium is non-magnetic and has a low neutron absorption.

Aluminium and the alloys are fairly strong: high strength alloys can be treated to achieve 400MPa, pure grades 150MPa and alloyed grades typically 200 – 300MPa. The alloy used in this work was 7075 T6 which is a very high strength (reaches 550MPa) material used for highly stressed structural parts. Unlike steel, aluminium alloys become stronger at low temperatures and do not suffer the ductile/brittle transition of steel. At these strengths aluminium becomes less easy to work but softer conditions allow fabrication prior to final heat treatment and strengthening.

In this work, two types of aluminium alloy (2024 T3 and 7075 T6) were supplied. The ideal adherend is small grain size aluminium alloy. In order to find suitable material for the experiment, different aluminium alloys were tested to obtain their grain size before the diffraction experiments.

5.2.3.2. Grain Size Measurement (carried out in Wolfson school of Mechanical and Manufacturing Engineering)

The following procedure was used

- Fine polish (both 2mm thick bared and clad samples):
- Make a mold and mount the sample.
- Heat and apply pressure with using Buehler “Transoptic” powder and Thermoplastic resin
- Polish using silicon carbide with 120, 240, 320, 400 and 600 grades, wet and dry paper.
- Polish using 6 micron then 1 micron diamond paste on rotary polishers.
• Etch using Kellers (2 ml HF; 3 ml HCl; 5 ml HNO3 and 190 ml water) reagent for 20 seconds and then wash with water; rinse with methanol. Finally, heat and dry the sample.

• Measurement of grain size: Obtain the metallographs (Picture 1) of samples by means of microscope. The average grain sizes were obtained by means of the photos of the samples.

![Picture 1 metafullgraphs of samples](image)

**Picture 5.1 metallographs of samples**

Results of test

**2024 T3 aluminium alloy**

1). Edge surface: The grain size is about 70±20μm.

2). The grain size for flat surface is around 80±15 μm.

**7075 T6 Aluminium alloy.**

The diameter of grain is about 50±10 μm.

The grain size of 7075 T6 Aluminium alloy is too large to obtain good results for X-ray diffraction. Considering the difficulty of gaining of beam time, mild steel samples were also prepared for this work since previous experience of many workers shows that the grain size is such as to give reliable X-ray results.

**5.2.4 Theory [1]**

The approach used is based on the Sin²φ method which is described below.
For each inclination of the sample, defined by two angles $\phi$ and $\psi$, the strain $\varepsilon_n$ in the direction normal to the diffracting planes, is related to the corresponding lattice spacing $d_n$. The distance $d_n$ is also linked directly to the diffraction angle $\theta_n$ by Bragg's law.

$$\varepsilon_n = \frac{\sin \theta_n - \sin \theta_s}{\sin \theta_n}$$  (3)

A relation between the strain $\varepsilon_n$ and the stress tensor components is then derived, called the $\sin^2 \phi$ law

$$\varepsilon_n = \frac{1}{2} S_{2(hkl)} \sigma_{\phi} \sin^2 \psi + \varepsilon_\perp$$  (4)

In Figure 5 the plot of $\varepsilon_n$ vs. $\sin^2 \phi$ gives a straight line, whose slope allows the stress component $\sigma_\phi$ in the direction $\phi$ of the surface to be calculated, as the elastic constant $1/2S_{2(hkl)} ((1+v)/E)$ is well known.
5.2.5 Experimental:

5.2.5.1 Sample

The samples were prepared by using 7075 T6 aluminium alloy and mild steel adherends, and film FM 300-2 adhesive and were of size 100mm x 25mm x 3mm. The joint overlap area was 40mm x 25mm.

The procedures for adherend pre-treatment were as follows:

1. Were grit blasted and subsequently degreased in acetone to remove all traces of oil and grease.
2. Were demagnetised.
3. Were vacuum annealed for 4 hours at 600 °C (7075 T6 at 100°C) and then slow cooled in order to reduce the level of residual stress in the adherends before bonding.
4. BR 127 Primer was used to cover the surface in order to offer superior durability and resistance to hostile environments within the bond line and protect outside the bonded areas.

The specimens were immediately cured under 0.28MPa pressure for 2 hours, which includes 30 minutes to 120°C and 90 minutes at 120 °C.

The aged samples were prepared by immersion in aerated tap water at 60°C for approximately 14 days.

5.2.5.2 Experiment
In this experiment, the steel adhesive joint was measured after preliminary diffraction tests of aluminium sample using an X-ray diffractometer in BENSC.

In this work, Chromium radiation CrKα was used whose wavelengths are Kα1=2.28962 Å and Kα2=2.29351 Å.

The strains were measured at 7 different angles (φ) (0; ±30; ±40; ±50) at each position. The measured strain can be converted to stresses by using theoretical value of 219GPa from Young's Modulus of the 211 reflection.

The analysis peak used was the Fe 211 peak, which is the most suitable sensitive peak, giving a 2θ = 155.5°.

- Stress free position determination (unstressed lattice plane d₀ determination)

The unstressed lattice plane d₀ was obtained by measuring one piece of unbonded adherend using a 3mm diameter collimator with the measured strain normal to the surface.

- curing stress measurement:

![Figure 5.6 The array of measured points. Origin and directions of coordinate system. • were only measured in longitudinal direction in dry sample.](image-url)
The longitudinal (x direction) and transverse (y direction) strains and stresses over the joint area were separately measured by making use of 1mm diameter collimator and 0.4mm wide slit. For the dry sample, 17 points were measured on one edge surface in the longitudinal direction and 15 points were measured in the transverse direction. For the aged sample, due to the limited X-ray beam time, only 10 points were measured over the joint area in the longitudinal direction. Figure 5.6 illustrates the array of measured points.

5.3 Pulsed neutron source

5.3.1 Introduction

The neutron diffraction technique has many advantages over conventional stress measurement techniques. Firstly, neutron diffraction is a non-destructive non-contacting method with high penetration depth which applied to nearly all crystalline materials. It can provide sub-surface information not obtainable by any other technique. Secondly, neutron diffraction is much faster and less labour intensive than conventional destructive methods, such as hole drilling or X-ray diffraction followed by surface removal. Finally, because the stress state is not disturbed by the measurement, complicated corrections to the data are not required. In addition, it can be used to validate finite element predictions used for design calculation and thus lead to more reliable performance or lifetime predictions.

Pulsed neutron sources, such as ISIS, provide data which is analogous to energy dispersive X-rays. If we consider Bragg's equation, at a nuclear reactor or monochromatic X-ray source, we use a single wavelength. Changes in d-spacing are monitored as changes in the diffraction angle. Correspondingly, the scattering angle can be fixed, and instead monitor changes in d-spacing as changes in wavelength. The major advantage of the pulsed neutron technique over reactor sources, is that an entire diffraction spectra is produced for a fixed detector angle. This means multiple phases can be easily monitored, and experimental apparatus to make measurements at a fixed sample orientation is much simpler.
At a pulsed source the integrated neutron flux over any wavelength range is much lower than on a reactor [2]. However it is inherent in the operation of a pulsed source that all of the neutrons in each pulse can contribute to the measured spectrum making efficient use of the available neutrons. Each pulse represents a wavelength scan which is analogous to scanning in $2\theta$ from 0 to $180^\circ$ [2]. At a pulsed neutron source, neutrons are produced by spallation, which occurs when energetic particles interact with target nuclei. Heavy element targets offer the best efficiency for emitted neutrons per unit energy of the incident pulse. Proton bunches are accelerated and then are directed at a tungsten target. The target nuclei are excited and “boil off” neutrons and fragments of the target nuclei in an evaporation process. Each incident proton bunch produces a pulse of highly energetic neutrons. For diffraction experiments the fast neutrons from the initial pulse must be thermalised using a moderator.

The main advantage of the pulsed white beam of neutrons is that strains may be measured from many lattice planes. The diffracted maximum intensity for each lattice spacing occurs at a discrete wavelength. All the lattice reflections are recorded with the same resolution in each spectrum, so that simultaneous strain measurements in different directions are possible, a spectrum can be recorded at any angle (subject to geometry) of the component and multiphase materials can easily be examined. The strain is determined from the change in time of flight between the measured and unstrained value. Thus, the simplest method to improve the resolution of a spectrometer on a pulsed source is to increase the path length or the time of flight between the target and detector. However, the improved resolution is often compromised by beam losses along the flight path and ultimately “frame overlap” occurs when the slow neutrons from one pulse are overtaken by fast neutrons of its successor. Since the measurement of stresses is usually limited by the intensity of the neutron beam, the highest resolutions are normally not reached.

On a reactor (constant) source [2], only a small number of grains are examined because there is only one lattice reflection. Thus, the measurement result may not represent the bulk material or just represent a special case. Due to the diffraction spectrum from pulsed neutron sources including many different lattice reflections, a
more detailed survey of the lattice reflection or the residual stresses can be made at a pulsed source.

Efficiency of measurement of stress is crucial for examining components which involve small sampling volumes and large path lengths. The smaller gauge volume and the longer path lengths, the better resolution can be achieved, but the lower the efficiency of measurement. Hence, in order for efficient use of the beam time, a compromise must be made between resolution and number of points measured.

Diffraction measurements of residual lattice strains examine the elastic strain present in the grains contributing to the diffraction peaks. However this may result both from the macroscopic strain effects or from grain interaction effects which may be loosely associated with macrostress and microstress residual stress. The engineer is usually only concerned with the macrostress.

5.3.2 Basic theory

When a stress measurement is made using neutrons, an incoming neutron beam is diffracted from the sample. From Bragg’s law the lattice parameter can be determined, as a function of direction within the sample. The incoming and outgoing beams are collimated [3] so that only a certain region within the sample contributes to the diffraction spectra. By moving the sample around within the beam, the position of the sampling volume within the sample can be scanned, providing a map of atomic lattice plane distances. Alternatively the sample may be held within a loading rig, capable of applying stress or pressure, a furnace or a cryostat. The sample can then be monitored during in situ variation of the thermo-mechanical environment. Accurate measurement of lattice parameter (accuracy of $-3 \times 10^{-4}$ is typical) is required to allow a correct evaluation of strain changes.

The ENGIN-X facility at the ISIS neutron source is a new instrument developed to measure elastic strain variations under conditions such as at elevated temperature or applied load, up to 50mm beneath the surface of engineering metals and ceramics. The Neutron Strain Scanning technique, uses the crystal lattice as an atomic strain gauge to measure distributions with a sub-millimetre spatial resolution to an accuracy
ENGIN-X is the first instrument in the world designed and optimised exclusively for making measurements on engineering components that can be up to about a metre in size.

Once the principal strains are known, the associated three-dimensional stress state can be calculated using the appropriate compliance tensor. Point by point resolution better than 1.5mm is achieved using a very fine beam (typically 1mm x 1mm) and a detector focused on a 1.5mm x 1mm cross-section. A map of elastic strain distribution is built up by scanning the component through the beam in three dimensions. When the proton pulse interacts with the target, a neutron is created at a known time and position, its wavelength on detection can be determined from the distance and time it took to travel to the detector. Thus the collimation of beam between the detector and specimen is not needed as the wavelength is inferred from the geometry of the scattering process and the time of flight (TOF). Each pulse contains a continuous spectrum of energies thus the Bragg equation for all the lattice planes will always be satisfied by all directions. The lattice spacings, d, are determined by a fixed diffraction angle and scanning wavelength. The wavelength is inversely proportional to the velocity thus the time of flight t is proportional to the wavelength \( \lambda \). By measuring the flight times t of detected (diffracted) neutrons, their wavelengths are calculated and diffraction spectra recorded. According to Bragg’s law, the lattice strain \( \varepsilon \) can then be calculated from changes in these values:

\[
\varepsilon = \frac{\Delta d}{d} = \frac{\Delta \lambda}{\lambda} = \frac{\Delta t}{t}
\]  

(5)

where \( t = \frac{L}{v} = \frac{(\lambda m h) L}{h} \) is the time taken for a neutron with mass m and velocity \( v \) to travel a path length, and \( h \) is Planck’s constant.

5.4 Reactor source

The neutron beam from the reactor is first monochromized to a chosen wavelength \( \lambda \) by Bragg reflection from a large single crystal monochromator. This monochromized beam is defined by a Soller slit collimator, or by apertures, to pass over the ‘sample axis’ about which the detector rotates. The detector counts neutrons scattered through an angle 2\( \theta \) (see Figure 7), with the scattered beam again defined in direction by a Soller slit assembly. Both the incident beam and the beam towards the detector are
defined in area by vertical and horizontal slits in a neutron absorbing mask, for example cadmium. The gauge volume is defined by the intersection of the incident and scattered beam is shown in Figure 7. A sample will be moved through the gauge volume so as to obtain a map of strain. The strain can be obtained from Bragg's law: 
\[ \lambda = 2d \sin \theta \]  
where \( d \) is the lattice spacing of planes.

**Figure 5.7** The principles of strain measurement by means of neutron reactor source

The detector is scanned through 2\( \theta \) to determine the peak-count angle, which, in the case of a large sample, corresponds to the average \( d \) of the grains in the gauge volume sampled. The average lattice macrostrain in the volume sample is then determined by:

\[ \varepsilon = \frac{(d - d_0)\theta}{d_0} = -\cot \theta \Delta \theta \]  
(6)
where \( d_0 \) is the lattice spacing of a ‘stress free’ sample of the same material composition, and \( 2\theta \) is the corresponding diffraction angle. Thus neutron diffraction at a reactor source operates on exactly the same principles as X-ray techniques.

The direction of the measured strain is along \( Q \) axis (in Figure 5.7). As the lattice spacing can only change elastically it is an elastic strain which is always measured, but this may be a result of intergranular strains arising from a plastic deformation or thermal treatment of the sample. If an accurate value of \( d_0 \) (or \( 2\theta_0 \)), can be measured, the obtained strain should be very accurate. However, obtaining a true \( d_0 \) is very difficult, in fact even may be impossible. A small annealed sample with measurements made in several orientations and averaged, or an extreme part of a component, could be taken to be in zero strain.

In order to determine the strain in different directions in the sample the sample must be rotated accurately about the centre of the gauge volume so that each direction lies along \( Q \). This is usually difficult to do in practice. For this reason, careful alignment and centring of the sample is required. Large samples might hit the spectrometer hardware, or path lengths of the beam in the sample may become excessive, preventing some orientations from being used. It has to be noted that the gauge volume within the sample depends on the horizontal width of the slit in the scattered beam. In order to increase intensity, the width can be as large as possible considering the size of the required strain. \( 2\theta = 90^0 \) is the optimum scattering angle for definition of the gauge volume. Although the resolution in strain increases with \( 2\theta \), \( 90^0 \) scattering at both monochromator and sample is often a good compromise. However, an angle of \( 2\theta \) bigger or smaller than \( 90^0 \) may have the advantage that it can provide more ready access to the point in the sample at which the strain is to be measured. The gauge volume shape and size must be chosen with consideration of the direction and magnitude of the strain gradient, the intensity of scattering, the corresponding measurement time and the grain size of the sample.

At the Studsvik reactor source, the double-lap steel adhesive sample was scanned with fixed wavelength and a single diffraction peak was observed, this may include a small
number of grains because there is only one lattice reflection. Hence, the measurement may not be as representative of the bulk material as with a pulsed source.

5.5 Results of residual stresses in single lap steel adhesive joint by means of X-ray diffraction in BENSC.

5.5.1 Results

The stresses were calculated from strains measured at 7 different angles relative to the surface. Strains were calculated relative to the measured stress free \( d_0 \) \( \sin \theta_0 = 0.977; \) \( d_0 = 0.1172 \) nm. The elastic constant used is the theoretical value 219 GPa. 3 lines parallel to the joint line were measured, \( y = 0.6 \) line is 0.6 mm above the glue line, \( y = 1.5 \) line is in the middle line of the edge surface of adherend, \( y = 2.5 \) line is the top line near the flat free surface of adherend (see Figure 5.6). All the diffraction peaks obtained from the experiments were fitted by using double Gaussian functions. Good fit results were achieved to all the diffraction peaks, the uncertainty of the fit usually is ±0.01° in 2θ.

![Figure 5.8 Sketch of sample. Single lap adhesive joint.](image)

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5.5.1.1 Longitudinal stresses of the dry sample

The measured residual stresses of the dry sample in the longitudinal direction over the joint area are shown in Table 1 and Figure 5.11.

Table 1 stresses (±30MPa) of unaged sample in longitudinal direction

<table>
<thead>
<tr>
<th>X</th>
<th>y=0.6</th>
<th>y=1.5</th>
<th>Y=2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-120.42</td>
<td>-153.87</td>
<td>-189.55</td>
</tr>
<tr>
<td>2</td>
<td>-133.8</td>
<td>-167.25</td>
<td>-173.94</td>
</tr>
<tr>
<td>5</td>
<td>-169.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-162.79</td>
<td>-173.94</td>
<td>-207.39</td>
</tr>
<tr>
<td>35</td>
<td>-256.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>-147.18</td>
<td>-189.55</td>
<td>-200.7</td>
</tr>
<tr>
<td>39</td>
<td>-205.16</td>
<td>-223</td>
<td>-216.31</td>
</tr>
</tbody>
</table>
Figure 5.11 Distribution of longitudinal stresses of unaged sample

From the table and graph shown above, it can be seen that the longitudinal stresses in three lines are not uniform and vary in nearly the same regular pattern. The results show unexpectedly large compressive stresses created in all the joint area. The stress values at the right corner are obviously larger than in other areas, especially for the glue line and middle line.

5.5.1.2 Aged sample

Since one of the purposes of the experiment is to compare the stresses distribution over the joint area between aged and unaged sample, the longitudinal stresses of the aged sample and stresses comparison with unaged sample are shown in Table 2 and Figure 5.12.

Table 2 stresses(±30MPa) comparison between aged and unaged sample

<table>
<thead>
<tr>
<th>x</th>
<th>y=0.6(aged)</th>
<th>y=0.6(unaged)</th>
<th>y=1.5(aged)</th>
<th>y=1.5(unaged)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-120.4</td>
<td>-310</td>
<td>-153.9</td>
<td>-156.1</td>
</tr>
<tr>
<td>2</td>
<td>-133.8</td>
<td>-207.4</td>
<td>-167.3</td>
<td>-263.1</td>
</tr>
<tr>
<td>38</td>
<td>-147.2</td>
<td>-207.4</td>
<td>-189.6</td>
<td>-182.9</td>
</tr>
<tr>
<td>39</td>
<td>-205.2</td>
<td>-225.2</td>
<td>-223</td>
<td>-153.9</td>
</tr>
</tbody>
</table>
The stresses in the aged joints are clearly different from the unaged joints, most of them have increased. This does not seem reasonable because the water seeping into the glue should cause a compressive stress to be added to the adhesive in a longitudinal direction as the glue stretches towards the free side and therefore the compressive stresses produced in the adherend should be decreased. In other words, the water should relax the compressive stresses in the adherend. This phenomenon was only found in some places, for example at the right corner (Figure 5.12 b). This might cast doubt about the reliability of these measurements.

5.5.2 Discussion

The residual stress results of the unaged sample in the longitudinal direction summarised in Table 1 can be compared with the finite element predictions of Adams et al about curing stresses in a single lap joint [4]. Adam's predictions are for tensile stresses to be created throughout all the adhesive layer which are of constant magnitude along the central region of the joint but decrease towards the joint edges. Correspondingly, compressive stresses will be produced in the adherend and will possess the same distribution pattern as the stress in the adhesive. The experimental results agree with Adam's prediction of ununiform compressive stresses produced in adherend, but for the 3 measurement lines, the stresses were greater on the right side which is close to the free glue edge and slowly decreased towards the corner close to the free adherend edge from the central region, this does not completely agree with Adam's predicted pattern.

Considering the results of the stresses measurement within a single lap joint using Neutron diffraction by Swallowe et al [5]. The stress close to the interface in Swallowe's work is not uniform and tends to be tensile in the centre and compressive at the edges, the results of this experiment differ from them in that large compressive stresses are found in the adherend over all the joint.
However, both the adherend (mild steel) and adhesive (FM-3 film adhesive) used in this experiment are different from those in Adam’s prediction and the Neutron diffraction experiments. In addition, the measurement uncertainty (±30MPa) and the error from the determination of $d_0$ should also be considered. Therefore, a direct comparison of the magnitude of the residual stresses is not absolutely valid but the results still should testify the direction of stresses and the stress pattern.
5.6 Results of residual stresses in double lap steel adhesive joints using neutron diffraction (NFL Studsvik)

5.6.1 Sample

The DLS (double lap shear adhesive joints) sample consists of adherend and adhesive. The joint overlap area was 25mm × 20mm. The thickness of the adhesive is 0.05mm and the thickness of adherend is 5mm. It is shown in Figure 5.13.

![Figure 5.13 Mild steel double lap adhesive joints sample](image)

The samples were prepared using as adherends unclad 7075 T6 aluminium alloy and mild steel with Young's modulus $E \approx 220\text{GPa}$, and FM 73 film adhesive and were of size 150mm x 20mm x 3mm. The procedures for adherend pre-treatment followed the procedure set out in 5.2.5.1. Trication Zinc Phosphate treatment for the steel adherends were done by Chemetall plc.

The bonded specimen were cured immediately after preparation with 0.28MPa pressure for 1.5 hours, which includes 30 minutes to 120°C and 60 minutes at 120°C. It has to be noted that a suitable size of aluminium slot mold was designed for preparing good joints, Teflon was also used in the bonding procedure to separate the sample from the mold.

The aged sample was prepared by immersing the cured sample into distilled water at 50°C for 17 days.
5.6.2 Experiment

Due to limited neutron beam time, a careful selection of measurement points within the whole of bonded area in the adherends has to be made during the experiments so that these representative points can be suitable to provide strain and stress information for comparison with FE models.

Two directions of strains and stresses were measured, one of them is the longitudinal direction which is parallel to the load direction, the other is the transverse direction which is perpendicular to the longitudinal direction but parallel to the joint plane. It has been long known that the stresses in these two directions are the most important residual stresses in double-lap adhesive joints.

The experiment was carried out with using a 1mm width slit in the incident beam and a 1mm width output slit of height 5mm giving a gauge volume of 5mm$^3$ in the longitudinal residual stresses measurement. A 2mm input slit and output slit with 1mm height creating a 4mm$^3$ gauge volume was used for the transverse residual stresses measurement. A stress map on either side of the interface in the adherends was obtained with 0.1mm spatial resolution in the transverse and longitudinal directions. 1mm spatial separation of points in the longitudinal direction was used near the edges of the adhesive joints where the stress gradient is greatest. Due to the limited time only the middle points in each layer along the longitudinal direction were scanned in the middle area where the stresses are expected to be more uniform. In addition, because the joints are symmetrical, only a quarter of the joint was investigated in this whole experiment. Finally, in order to ensure the complete gauge volume for all the measurement points was within the adherend, a surface scan was first done to determine the exact position of edge of the adherend before each experiment. The positions of the measurement points chosen are shown in Figure 5.14.
Figure 5.14 Residual stresses measurement in dried double-lap steel adhesive joints

The maximum spatial resolution in stress measurements by using neutron diffraction can be obtained by having a $90^\circ$ angle between incident beam and diffracted beam. In other words, $2\theta$ should be as close as possible to $90^\circ$. Therefore, the best peak to use in residual stress measurement in this work is 211 because the neutron wavelength used in this equipment is 1.7 Å, which gives a $2\theta$ of $93.6^\circ$.

The determination of the zero stress position in the sample is very important particularly for residual stress measurement as the residual stress is supposed to be
small according to theoretical predictions. Because the accuracy of zero stress \( d_0 \) plays a major role in determining the magnitude of residual stresses within the lap joint, the \( d_0 \) position was chosen far away from the joint in the middle plate since the effect of curing and humidity can be ignored in this position. \( d_0 \) was also measured in three different positions in middle line in middle plate of the sample.

![Figure 5.15 \( d_0 \) position](image)

\textbf{5.6.3 Results and discussion}

All the residual strains were obtained from strains measured relative to the zero strain, which was taken as the average value of \( d_0 \) in different zero stress positions chosen far away from the joint in middle plate. The residual stresses were evaluated by using elastic constant 220GPa. All Bragg peaks were fitted by using both Gaussian and Voigt function in a linear slope background. Good fits and excellent agreement between Gaussian and Voigt function for all peaks were achieved, which generally give an accuracy of fitting \( \pm 0.002^\circ \) in \( 2\theta \). The centre positions of Gaussian or Voigt fitting peaks was regarded as a measure of the position of \( 2\theta \). The uncertainty of the longitudinal residual stresses is within \( \pm 4\)MPa; for the transverse residual stresses, the accuracy is within \( \pm 5\)MPa.
a) Longitudinal residual stresses in dried sample

b) Longitudinal residual stresses in wet sample
Figure 5.16 Distribution of residual stresses

Figure 5.16a) shows that a considerable longitudinal residual stresses within the joint is produced during the curing process, which varied within a small but significant range of $-26\text{MPa} - +14\text{MPa}$. It also indicates that the residual stresses are not uniform within lap joints. It can be clearly seen that most of the longitudinal residual stresses
in the middle plate are compressive, these are much higher than those in the outer plate, especially in the position near the joint edge. This distribution is reasonable because the compressive residual stresses in the middle steel plate were induced from double adhesive layers. But, the compressive longitudinal residual stresses in the outer plate were only from one adhesive layer. However, some of longitudinal residual stresses are tensile. The results agree somewhat with Adam's prediction about residual stresses in single lap adhesive joint [6]. For example, Adam's prediction suggests that the residual stresses produced in the adhesive layer are non-uniform and longitudinal tensile stresses are created throughout all the adhesive layer. Correspondingly, compressive stresses are produced in the adherend, particularly close to the interface. The longitudinal residual stresses predicted by Adams in the adhesive within Al-Al double lap adhesive joints is about 30Mpa. His prediction was based on the assumptions that the shrinkage stresses in the adhesive do not affect the strain in the adherends, and that the strain in the adhesive is equal to the strain in the adherends, hence the longitudinal residual stresses value obtained from this neutron work is not unreasonable when considering all the factors mentioned above.

It is also seen from graph Fig 13 a) that the magnitudes of stresses are not large, they are within \(-26\text{MPa} \pm 14\text{MPa}\), which totally disagree with Hiroshi Kawada's study of residual stresses in a resin block which contains a steel block by means of strain gauges on the interface[7]. Their work indicates that about \(-200\text{MPa}\) compressive stress were induced in steel after cooling down, about \(-100\text{MPa}\) compressive stress arose in the steel according to their FEM (Finite element method) calculations. Their results, particularly the experimental result of \(-200\text{MPa}\), is much larger than maximum stress of \(-30\text{MPa}\) found in this work. If one only looks at the thermal expansion coefficients, the residual stress should be similar between this neutron work and Kawada's work as the CET of adhesive and adherend are almost same in these two different studies. This work therefore casts doubt on the results of Kawada's work. However, the large difference of residual stress could be explained by further comparison of the two experiments. Firstly, the samples are different even if the materials used are similar. Kawada's sample is an epoxy-resin block containing a steel block with 10mm thickness of resin and 2mm thickness of steel. As the ratio of thickness of steel and epoxy is 1:5, which is much smaller than the ratio of 100:1 in this work, the residual stress in their sample apparently should be larger than this.
double lap joint [8]. Secondly, the curing conditions are different; they are 5 hours at 170° C for their sample, but this lap joint was cured at 120° C for 2 hours. Due to the larger drop of temperature 150° in their work, which is 50° higher than 100° in this work, the residual stress induced would be larger than this work. In addition, the bonding type are different. Thus, the large difference of residual stress between these two different studies may somehow be explained. However, the strain gauge method is not a precise measurement method because it is very invasive and has other disadvantages. For example, the non-linear relationship between strain and temperature, which could bring considerable errors to the results. Compared to strain gauge measurements, neutron diffraction measurements are more reliable and precise due to its main advantage of non-contact and high penetration ability with good resolution. Thus, the comparison makes the results of this neutron diffraction work the more believable.

The results of this work agree quite well with the work of Hongbing Wang et al, who studied residual stresses of epoxy resin during cure and cooling processes [8] by means of bending bimaterial samples and using a new specially designed stress-tracking device. Their samples consisted of aluminium and different types of epoxy resins. One of the epoxy resins used in their work has similar properties to the FM73 film adhesive used in this work. About 7.3 MPa tensile residual stress for this adhesive was found in their study. On the contrary, bigger compressive residual stresses should exist in the adherend.

Compared to the results of 100MPa residual stresses in the bimaterial work (Chapter 4), the magnitude of residual stresses in this work is obviously smaller, this is most likely due to different thickness of steel and different type of joints.

These results agree with the previous results of neutron diffraction (ILL) [5]. Firstly, even though the adhesive used and joint type are different, the magnitude of residual stresses for both neutron diffraction measurements are still of the same order. Secondly, the measurement results of the single lap joint at the ILL shows that the stresses close to the interface are not uniform which completely agrees with the results in this work. In addition, both sets of data show that most of residual stresses are compressive and some of them are tensile stresses.
The uncertainty of ±4MPa for this work is obviously better than ±10MPa in the previous ILL experiments. This suggests that the results from neutron diffraction in NFL are more reliable and believable.

Comparing graph Figure 5.16a) and b), it can be seen that there are indications that the compressive residual stresses in the measurement line close to interface were slightly released in wet steel adhesive joints due to the water's effect, particularly in the position near the edge. This completely agrees with results of bimaterial experiment (Chapter 4), which was that the curing stresses decreased with moisture content.

Graph Figure 5.16c) and d) show considerable transverse residual stresses created from curing stresses but the distributions are quite difficult to explain. It revealed that the transverse residual stresses close to the interface, especially in the area near the edge, decreased a lot due to water invasion as can be seen by comparison of graph Figure 5.16c) and d). This graph also displayed that the magnitude of transverse stresses are not smaller than the Longitudinal stresses. It might be reasonable because the adhesive undergoes contraction during cooling down and absorb moisture after cure approximately equally in both directions.

Both longitudinal and transverse stresses were decreased due to the effect of moisture. This agrees with Joyanto and Robert's work [9], they found that the most important parameter is the ratio of the adherend modulus to the equivalent property of the viscoelastic adhesive, the stresses are highest when this ratio is one and decrease as this ratio increases. The ratio would be increased due to water invasion because Young's modulus $E$ of adhesive decreases because of the influence of humidity. The residual stress reduction due to moisture in this work therefore agree with their conclusion.

5.7 Conclusion of residual stresses in adhesive joints: Chapters 4 and 5

Tensile residual stress was surprisingly found in the interface along the adherend in single lap adhesive joint by using the strain gauge technique. The expected
compressive residual longitudinal stresses were not obtained from strain gauge experiments, which is probably because either only one point in the interface was measured by using a strain gauge or error from the invasive strain gauge technique itself.

The curing stresses in steel using the bimaterial technique was proved to vary from $-100\text{MPa}$ to $+83\text{MPa}$ by means of experimental measurements and FEA. The magnitude of residual stresses achieved from the bimaterial technique obviously cannot be concluded to be the same as the residual stresses in adhesive joints.

It was also found that the curing stress apparently decreases due to moisture. Hence, it can be said that the residual stresses in adhesive joints should include the effect of moisture. However, adhesive lap joint and bimaterial samples are different types of joint. The diffusion rate in lap joints will be different from bimaterial samples. In other words, the rate of reduction of residual stresses in adhesive lap joints will be smaller than in bimaterial samples. In any case it can be concluded that the residual stresses in the adherend in adhesive joints should be smaller than the curing stress.

The results of residual stresses experiments in single lap adhesive joint obtained from BENSC seem disproportionately large. They cast doubt to the reliability of this experiment because of the unreasonably large compressive stresses in dry sample and the observation of the compressive stress increasing after water invasion which is apparently not right. The huge error in this experiment may be due to the error in $d_0$ measurement. The larger uncertainty of the peak fitting was thought to arise from the small gauge volume. The error of the $d_0$ measurement is considered to be mainly sourced from the surface treatment of the adherend. Some residual stresses might already exist in the sample before bonding. Hence, the result of residual stresses in single lap adhesive joint from BENSC is concluded to be unreasonable.

For the measurement of residual stresses in double lap adhesive joints in NFL, $d_0$ is not changed by surface treatments therefore the uncertainty of $d_0$ was reduced to a minimum. Also, the accuracy of the measurement by means of the neutron diffractometer in NFL obtained from the experiment is about $\pm 4\text{MPa}$, which is much
smaller than ±30MPa in BENSC. Therefore, the results of residual stresses from NFL are considered to be accurate.

It has been shown by direct measurement of residual stresses using the neutron diffraction technique, and by comparing the results of this work and other earlier experimental research, that, considerable but not large longitudinal residual stresses are created during the curing and cooling down process in steel adhesive joints, which vary in the range of -28MPa --+14MPa. This work also points out that significant transverse curing stresses are produced within adhesive joints. In addition, it indicates that both longitudinal and transverse residual stresses in the adherend are released due to moisture effects.

This experiment could be further improved by some alteration in the measurements. For instance, reduced gauge volume and increased counting time to raise the spatial accuracy of the stress distribution. In addition, \( d_0 \) could be obtained from powder or more points could be scanned far from the joint overlap area.

References


Chapter 6 Experimental measurement of stress distribution under load

6.1 Introduction

Small residual strains and stresses have been predicted by analytical and FEA methods and found by means of different experimental techniques (chapters 4 and 5). In order to predict the mechanical performance and failure of adhesively bonded joints, the main task is to analyse the effect of mechanical loads on the stresses and strains in the joint. Hence, it is very important and necessary to investigate the distribution of strains and stresses in adhesive joints under tensile load, which is the loading configuration usually encountered in industry.

The double lap joint is one of the most common joint designs employed in industry. It is known that there is no net bending moment on a symmetrical double-lap joint, unlike in a single lap joint, because the load is applied through the adhesive to the adherend plates away from their neutral axes. The double lap joint experiences internal bending, as shown in Figure 6.1. In a symmetrical double-lap joint, the centre adherend experiences no net bending moment, but the outer adherends bend, giving rise to tensile stresses across the adhesive layer at the end of the overlap where they are not loaded, and compressive stresses at the end where they are loaded, see Figure 6.1. Such a stress distribution was also demonstrated by the research result of Adams et al on CFRP/steel double lap joints loaded in tension [1].
Figure 6.1 Bending moment induced in the outer adherends of a double lap joint

The double lap samples used in this work are illustrated in Figure 6.2. This improves the stress distribution by including a small spacer between the two equal members at the end of the sample which almost eliminates the bending of the two outer adherends. The outer adherend size of the samples used in this work (same thickness for all adherends) is different from Figure 6.1 in which thickness of the middle plate is double that of the outer plates.

Figure 6.2 Sample in this work

Over the last sixty years, many researchers have studied the stresses and strains in both single lap joints and double lap joints by means of different theoretical and experimental methods [2]. It has been shown that the stresses under load in the adhesive and adherend are not uniform along the overlap length and that the stress is concentrated at the ends of the joint overlap and reach maximum value at the corners of the lap. This prediction was also confirmed by various researchers and experimental techniques either for single lap joint or double lap joint [1, 3-12]. Adams and Peppiatt [13] carried out stress analysis of metal to metal adhesive bonded lap
joints and think that differential straining in the adherends gives rise to a non uniform shear stress distribution in the adhesive. The maximum shear stress occurring at the ends of overlap. High tensile and compressive stresses are predicted in the corners of the adhesive layer. Joyanto and Robert studied the stresses in double lap adhesive joints through theory and experimental corroboration [14]. Good agreements were obtained between finite element results and the results of photoelastic measurements. They subsequently made a parametric study of the behaviour of double lap joints [15]. L.Tong et.al. investigated the effect of adherend alignment on the behaviour of adhesively bonded double lap joints [16]. Their study shows that the end mismatch introduces local bending and also increases the shear stresses especially peel stress in the adhesive.

Adams and Peppiatt also studied the effect of Poisson’s ratio strains in adherends on stresses of an idealized lap joint [17], it has been shown theoretically that transverse shear stresses exist in the adhesive layer even when bending is prevented. The transverse stresses are a direct result of the Poisson’s ratio effect of the adherends and have maximum value at the corner of the lap.

Fatigue analysis and testing of adhesive joints was studied by S.Krenk et.al. using both FE and experimental methods[18]. Their study did not show any significant influence of adhesive thickness in the fatigue tests.

The investigation of internal stress using neutron diffraction is a fast growing field. Neutron diffraction is currently one of two techniques (neutron diffraction and synchrotrons) available for the non-destructive measurement of residual stress in the interior of polycrystalline components due to the high penetration depths of neutrons. As far as this author is aware the study described in this chapter is the first time a double lap joint has been investigated using the neutron diffraction technique.
6.2 Direct measurements of longitudinal and transverse shear stresses in double lap adhesive joints under tensile load (at ISIS)

6.2.1 Experimental

6.2.1.1 Samples

In this work steel-adhesive DLS joints and Al-adhesive DLS joints were separately investigated. Their dimensions are shown in Figure 6.3.

Figure 6.3 samples
The adherends were prepared from unclad 7075 T6 Aluminium alloy and mild steel. The adhesive used was FM 73 film adhesive.

The properties of the materials are indicated in Table 1.

<table>
<thead>
<tr>
<th>Item</th>
<th>adhesive (FM73)</th>
<th>mild steel</th>
<th>adherend (7075T6)</th>
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<tr>
<td>Young’s modulus $E$</td>
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<tr>
<td>Poisson’s ratio</td>
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<td>Glass transition $T_g$</td>
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6.2.1.2 Experiment

Because the measurements were carried out under 430kg–1000kg tensile loads, the influence from residual stresses could be ignored. The value of $d_0$ was obtained by means of the average lattice spacing measured at points remote from the overlap area and without load.

The experiments were carried out using the ENGIN-X instrument in ISIS with two large detectors fitted with radial collimators centred at 90° in $\theta$. The gauge volume was 1.5mm x 1.5mm x 1mm for the Al-Al sample and 2mm x 1mm x 1mm for the steel adhesive joints, and the wavelength range was used was between 1.6Å - 3.5Å. The length of the neutron flight path is 50m.

The longitudinal and transverse strains and stresses within the overlap area in the double lap joints were measured with different applied loads by making use of a special designed stress rig. It is shown in Picture 6.1. The vibration of the stress rig was tested before the experiments using a laser vibrometer. This showed that the vibration level of the ENGIN-X Instron was too high for Moiré work. A stress rig was therefore built in Loughborough University for both Neutron and Moiré work.
The lattice constants were obtained by fitting all peaks using the Rietveld method in order to achieve the most accurate results.

In the experiments, due to very limited neutron beam time and the symmetry of the DLS, only a small part (1/8) of the overlap was investigated. The symmetry of the joint and loading is such that investigation of this section should provide a complete picture of the stress in the joint. It is indicated in Figure 4 which shows the region measured as well as the coordinates used in the whole study.

In the experiment on aluminium adhesive joints, two Al samples were measured. For sample 1, the x direction strains were measured in different-y-layers through the adhesive-line in the middle z position under both 430kg(57MPa) load and 783kg(100MPa) load. The z direction strains were also measured in same y layers near the transverse end line of the outer plate under 430kg load.
a) aluminium to aluminium double lap adhesive joints. Measurement region and coordinate system. The origin is the point in the middle position in bottom outer plate. Point A is the start measurement position which is in the middle position in middle plate. The region wrapped by the wider dotted line is the measurement region.

b) steel to steel double lap adhesive joints. Detailed measurement positions and coordinate system. The origin is the point in the middle position on the surface in the middle plate.

Figure 6.4 Illustration of measurement positions and coordinate system
For sample 2, the x direction strains were measured in y-layers through the adhesive-line in the middle z position under both 410kg(54MPa) load and 810kg(106MPa) load. Another set of x direction strains were measured through the glue line in the z position near the longitudinal free surface under 410kg load. The z direction strains were also measured in same y-layers near the transverse end line of the outer plate under 410kg load and 810kg load.

Each sample was first measured in different positions within the overlap area without load in order to check the residual stress distribution as well as obtain the $d_0$ value. In this experiment, a 1.5mm x 1.5mm x 1mm gauge volume was chosen to achieve the best compromise between spatial resolution and measurement accuracy.

In the experiment on steel adhesive joints, due to limited beamtime only one sample was investigated under a 940kg(94MPa) tensile load. The detailed measurement positions were shown in Figure 4b.

### 6.2.1.3 Checking of grain size

The grain size of unclad 7075 T6 aluminium alloy used in the test was checked after the experiment by measuring a polished sample using a microscope to obtain metallographs of the samples. The average measured grain size is about $50\pm10$ µm. (60±10µm in flat surface and 20±10µm in transverse surface). Therefore, the selected gauge volume 1.5mm*1.5mm* 1mm was sufficiently large to include enough grains to obtain accurate results.
6.2.2 Results and discussion

6.2.2.1 Aluminium to aluminium double lap adhesive joints

A summary of the longitudinal strains are shown in table 3, table 4 and figures 6.5-6.12.

The average lattice constants were obtained from the measured longitudinal and transverse neutron diffraction spectra without load and were separately accepted to be free of longitudinal stress and transverse stress (shown in Table 2). All the strains were calculated relative to these free lattice spacings.

<table>
<thead>
<tr>
<th>Table 2 Stress Free average lattice constants</th>
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<tr>
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<tr>
<td>sample 1</td>
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<td>sample 3</td>
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In the tables of results y = -4.85 is in the centre plane of the middle plate, the y = -5.675 plane is adjacent to the central plane of the middle plate but close to the interface, the y = -7.3 plane is in outer plate near to the interface, the y = -8.125 plane is the highest plane which is in the centre plane of the outer plate. The numbers are mm relative to the zero position.

The lattice constants d were evaluated by fitting all the peaks in range 0.4Å- 4 Å using a computer programme available at ISIS based on the Rietveld method. The results generally give an error of ±0.05-0.12 x 10^{-3} for longitudinal strain. Since the magnitude of the transverse strain is small and the scattering of measurements large, the strain distribution in this direction is not considered to be reliable. As a result, only graphs of longitudinal strains are shown and analysed below.

Some of the data is compared to FEA results calculated by S. Erpolat of the Loughborough department of Mechanical Engineering, they are shown in Figures 13 & 14.

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In addition, Moire interferometry (MI) was performed by Dr Ruiz in the Wolfson school on same samples with same load as a test of the FEA accuracy. The comparison of FEA and Moiré Interferometry are shown in Figures 15&16.

Table 3 longitudinal strain (strain x 10^3) distribution of sample 1 under load 430kg and 783kg. All position dimensions are in mm. The accuracy of strain in the middle plate is about ±0.06, the strain accuracy in the outer plate is about ±0.01. note: positive strains value represent tensile strain, negative value is compressive strain.

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<th>Y=4.85</th>
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Table 4 transverse strains(strain x 10^3) distribution of sample 1 under load 430kg and 783kg. Accuracy of strain ( x 10^3) measurement is about ±0.01–±0.05

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Table 5 longitudinal strains (strain x 10^3) distribution of sample 2 under load 410kg and 810kg. All position dimensions are in mm. Accuracy of strain measurement is about ±0.13 in middle plate, ±0.04 in outer plate. Note: positive strains value represent tensile, negative value is compressive strain.

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Table 6 transverse strains x 10^3 of sample 2 under load 410kg and 810kg. Error: ±0.01–0.06.

<table>
<thead>
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<th>X</th>
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Figure 6.5 longitudinal strain along x direction in middle plane with 430kg load (sample 1)

Figure 6.6 longitudinal strain along x direction in middle plane x1 with 783kg load for sample 1

Figure 6.7 longitudinal strain along z direction with 430kg load for sample 1
Figure 6.8 longitudinal strain along x direction in middle plane x1 with 410kg load for sample 3

Figure 6.9 longitudinal strain along x direction in middle plane x1 with 810kg load for sample 3

Figure 6.10 longitudinal strain along x direction in plane x2 near edge with 410kg load for sample 3
Figure 6.11 longitudinal strain along z direction with 410kg load for sample 3

Figure 6.12 longitudinal strain along z direction with 810kg load for sample 3
Figure 6.13 Aluminium-aluminium double lap adhesive joints. Comparison of FEA and Neutron Diffraction ($Z = 0; L = 810$kg). Typical error in Neutron strain is $\pm 0.04 - 0.13$.

Figure 6.14 Comparison of FEA and Neutron Diffraction ($Z = 0; L = 410$kg). The sample is Aluminium-aluminium double lap adhesive joints. Typical error in Neutron strain is $\pm 0.04 - 0.13$. 
Figure 6.15 Comparison of FEA and Moiré Interferometry ($Z = 12.5; L = 840$ kg)

Figure 6.16 Shifting Moiré curves using boundary conditions ($x = 0 \rightarrow \epsilon_x = 0$ for the outer adherends and $x = 25$ mm $\rightarrow \epsilon_x = 0$ for the middle adherend)
6.2.2.2 Steel to steel adhesive joint

For this sample only longitudinal strains were measured with sufficiently reliability to have confidence in the results. The results are illustrated in Figure 6.18. This sample was also measured using MI performed by Dr Ruiz with same load as a test of ND in ISIS. The comparison of FEA and Moiré Interferometry are shown in Figure 6.19.

Figure 6.17 shows a schematic view of the two component Moiré Interferometer that has been designed to measure surface strain distributions while at the same time internal strains are measured with ND at ENGIN-X facilities. The environmental vibration content at the ND laboratory, together with the space availability around the neutron collimators and detectors imposed the main design constraints on the interferometer. In order to reduce the sensitivity of the system to vibration, a single optical fibre is used to deliver the light that is diffracted by a pair of crossed gratings G, in order to produce two pairs of beams in the xz and yz planes. Four mirrors (M_x and M_y) steer the beams coming from the grating towards the sample S, which has a reflection diffraction grating replicated onto its surface. By translating the gratings and imaging the sample with a high-speed camera C, phase shifted interferograms are obtained from which strain distributions are evaluated.

![Figure 6.17 Schematic of Moiré Interferometer](image-url)
strains in steel adhesive joints with 940 kg load (near grating surface)

![Graph a)

strains in adhesive joints with 940 kg load (middle lane)

![Graph b)

strains in adhesive joints with 940 kg load

![Graph c)

Figure 6.18 Longitudinal strains in steel to steel double lap adhesive joints

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Chapter 6

Comparison between ND and MI

\[ y=0(MI) \]
\[ y=2(MI) \]
\[ y=3(MI) \]
\[ y=5(MI) \]
\[ y=0(ND) \]
\[ y=2(ND) \]
\[ y=3(ND) \]

Figure 6.19 Comparison between strains on grating surface of MI and strains near grating surface of ND

For both the Al and steel samples, the distribution of transverse strains has not been reliably measured due to the large scatter in the data. The absolute magnitude of the transverse strains is, as expected, considerably less than the longitudinal strains and the distribution therefore is more influenced by the accuracy of measurement. However, most of data clearly indicates that considerable compressive transverse shear strains and stresses are induced due to the Poisson’s ratio which agrees Adams and Peppiatt’s prediction [17] that significant transverse shear stresses arise in both the adhesive layer and adherends because of Poisson’s ratio strains associated with the tensile loading of the adherends.

It can be seen from the results of both aluminium and steel joints, that the longitudinal strains in the middle area of the overlap in the adherends are quite uniform with a smaller (or bigger) magnitude than the value near the edge particularly at the corner. The results agree well with those in R.D.Adams and N.A.Peppiatt’s study [13] Their study clearly states that differential straining in the adherends give rise to a non uniform shear stress distribution in the adhesive. The maximum shear stress occurring
at the ends of overlap. The highest stresses exist at the adherend corner within the spew.

Both results (Figure 6.5 - 6.19) also show that the strains within the overlap in the middle adherend plate are much bigger than those in the outer plates due to different stresses in the outer and middle plates. Figure 6.8 and 6.9 show that most of strains close to interface in the middle plate near the end of the overlap are about 2-4 times greater than in the outer plates (The estimated load from the strains in Fig 6.8 is about 850kg in end of middle plate and about 2000 kg from Fig 6.9; End of outer plate is about 170kg in Fig 6.8 and 350kg in Fig 6.9. The applied load is 410kg for Fig 6.8 and 810kg for Fig 6.9). This is greater than the 2 times increase that would be expected from simple consideration of the force distribution in the loaded sample. It is possibly due to compressive stresses across the adherend (outer plate) at the end of the overlap where they are not loaded, balancing tensile stresses induced across the adhesive layer at the end of the overlap where they are not loaded as described by R.D. Adams and N.A. Peppiatt's [13]. This effect causes the stresses to decrease at the end of the overlap where they are not loaded in the outer plate. However, the centre adherend experiences almost no bending moment. Hence, the larger strains difference between middle plate and outer plate at the end of the overlap could be explained by the bending effect. It thus indicates that the bending effect still possibly exists even when there is a spacer between two outer plates. However, the bending effect was obviously reduced. The sample with spew fillets is not a standard double lap joint sample because there is a spacer between the two outer plates. The spacer largely reduces the normal stresses given rise to in the adherend from the effect of adherend bending. The estimated loads from measurement strains in the middle positions is about 320Kg in Fig 6.8 and 840kg in Fig 6.9, which are similar with the applied load 410kg and 810kg. It can therefore be seen that the bending is not a serious problem.

The experiment didn't show that the distance from the interface has a significant influence to the order of stresses. However, it does indicate that the higher stress exist near the free surface (end of the lap).
It also can be seen from Figure 6.19 that the agreement between Moiré and Neutron diffraction is quite poor. This might be due to the scattering of ND and the measurement error of $d_0$.

Figure 6.13 and 6.14 clearly shows that satisfactory agreement was obtained between FEA and ND for strain distribution under load although the scatter of the neutron data about the FE prediction is rather larger than had been anticipated. As a result, the neutron diffraction directly validated acceptance of FEA, which is different from Swallowe’s work [19], their results cast doubt on prediction of FE. Figure 16 shows that comparison of surface strains between FEA and MI method. Perfect shape agreement was achieved between FEA and MI even though a considerable offset exits.

6.2.3 Conclusion

The investigation of internal strains using neutron diffraction is a fast growing field. Neutron diffraction is currently the only technique available for the non-destructive measurement of internal stress due to the high penetration depths of neutrons. The main disadvantage of neutron diffraction technique is the scarcity of strain scanning facilities and limited beam time.

So far, the strain information gathered from within double lap joints under tensile load using the neutron diffraction method employed in this study, has demonstrated that the PND method is useful and feasible, and can be expected to provide more accurate results from further measurement in the future. In addition, good agreements among three different technique (ND, FEA and MI) for the aluminium double lap joints provided strong and useful evidence regarding the strain distribution within double lap adhesive joints under tensile load.
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References:

Chapter 7 Comparisons of Experimental results and FEA

7.1 Introduction

Since 1944 a variety of Finite element analyses have been presented of the stress distribution in adhesive joints. Wooley and Carver (1971) [1] and Adams and Peppiatt [2, 3] are amongst those who first employed the finite element method to determine the stress distributions in adhesive bonded joints. Nowadays, the finite element method is widely used in the analysis and design of adhesive bonded joints. A variety of important aspects, such as complex geometry, nonlinear material property and large deformation, can be taken into account in the analysis due to the rapid advance of computing power. This makes it easier for the predictions of FEA to approach the real stress distribution. Although many FEA predictions [1-7] have been made, there is still a lack of experimental data to validate these predictions. In this thesis, experimental results regarding the stresses within adhesive joint were obtained by means of different experimental techniques. Since there may be doubts about the results from just one experimental technique, the results from a variety of experiments can be used to confirm the values obtained and validate FE predictions. In this chapter, experimental results obtained in this work are compared to FEA results. Because of the different assumptions made and different materials and size of samples used by previous workers, direct comparison of strains and stresses cannot be made between them and the experimental results from neutron diffraction but the general trends should be similar. However, some FEA predictions relating to the samples used in this work were provided by Dr. I. Ashcroft of the Wolfson school of Loughborough University. Hence, direct comparisons between neutron diffraction experiments and FEA of I. Ashcroft are possible.
7.2 Residual stresses

In this thesis, residual strains and stresses in the adherend were investigated by means of bimaterial methods, strain gauge, x ray diffraction and neutron diffraction. The residual stresses in the adhesive were also obtained from the bimaterial method. In conclusion, small magnitude and non-uniform residual stresses were shown to exist in the adherends. The maximum magnitude of residual stress for the steel adhesive joint was concluded to be around 30MPa. In other words, the maximum magnitude of residual stress in the adhesive was less than 1MPa by inference.

These experimental results for residual stresses do not agree with the FEA result of Adams and Coppendale [8]. In their work, an aluminium to aluminium lap joint was analysed when joined with an epoxy adhesive. The aluminium adherends were assumed to have a coefficient of linear expansion of $23 \times 10^{-6} \, ^{\circ}\text{C}^{-1}$, the adhesive was assumed to have a Young's modulus of 2.5GPa, a Poisson's ratio of 0.37 and a coefficient of linear expansion of $100 \times 10^{-6} \, ^{\circ}\text{C}^{-1}$, and the temperature reduction was $100^{\circ}\text{C}$ corresponding to a free linear shrinkage in the adhesive of 1%. The double lap joint was modelled as having an overlap length of 12.7mm and an adhesive thickness of 0.13mm. A triangular spew fillet was included and the adherend corner was represented as having a 0.025mm by 45\(^{\circ}\) chamfer. The FE analysis showed that in the overlap region, the predominant stress in the adhesive is tensile in the x-direction (along the length of the adhesive layer). It is uniform in the central region but decreases towards each end. The magnitude of the stress in the adhesive is about 31MPa. The difference in parameters between their FEA and the neutron diffraction experiment carried out as part of this work in NFL Studsvik is mainly presented in the coefficient of linear expansion, the material of the adherend, and length of overlap. Firstly, the adherend used for residual stresses measurement is mild steel, which possesses about 3 times higher Young's modulus than Aluminium and about half the thermal expansion coefficient of aluminium. If only the effect of the adherend material is considered, there might be about 80MPa higher stress in the steel sample than in the aluminium bimaterial sample according to E.A.Wachter's theory [9]. This obviously could not be directly used in the double lap adhesive joints. However, it at least can be said the stresses in an aluminium lap joint is less than in steel lap
adhesive joint using the same adhesives. Considering the combined effect of Young’s modulus and coefficients of thermal expansion, the residual stress in the adhesive (at the interface) in an aluminium sample should be about 2 times higher than in a steel sample. Even though a higher residual stress is predicted in the adhesive for an aluminium sample relative to the steel sample, 31MPa still seems ridiculously large for the residual stress in the adhesive. Secondly, the coefficient of thermal expansion of the adhesive $100 \times 10^{-6}$ in Adam’s work is doubled compared to the measured coefficient of $50 \times 10^{-6}$ for the adhesive used in this work. This difference might slightly increase the residual stress. It appears from previous work that the length of overlap does not have any significant influence on the magnitude of residual stress.

The distribution of residual strains and stresses in adhesive joints were obtained from direct measurement by means of the neutron diffraction technique in NFL (see Figure 1). The experimental results of stress distribution mostly doesn’t agree with Adam’s prediction [8]. According to Adams’s prediction, the longitudinal residual stress in the adherend should be uniform in the centre of the overlap and decrease towards each end. However, Figure 1a) shows that the longitudinal residual stresses are not uniform and do not all decrease as predicted by Adams.

N. Rastogi et al. studied thermal stresses in aluminium to composite double lap bonded (double butt strap) joints by using a three-dimensional variational, finite element analysis technique [5]. Their sample configuration considers aluminium adherends in combination with 4 different composites subjected to uniform cooling with $\Delta T$ of $-111 \, ^{\circ}\mathrm{C}$ during the curing and cooling down process. Even though the type and material and curing temperature of their samples are different from the steel adhesive double lap joints measured using neutron diffraction, some agreement was still obtained. For instance, Rastogi found that the joint corners are critical regions for debonding initiation, and the neutron results found that maximum stresses in the adherend exist in the corner.
a) longitudinal residual stresses in dried sample

b) transverse residual stresses in dried sample

**Figure 1** Residual stresses in steel double lap adhesive joints
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Figure 2 strains in double lap aluminium adhesive joints under tensile load

(a) Comparison of I.Ashcraft's FEA results and Neutron Diffraction \((Z = 0; L = 810\, \text{kg})\).

(b) Comparison of FEA of I.Ashcraft and Neutron Diffraction \((Z = 0; L = 410\, \text{kg})\). Poor agreement in outer plate might be due to the scatter of neutron diffraction measurement from insufficient data acquisition time.

Figure 2 strains in double lap aluminium adhesive joints under tensile load
7.3 Stresses under load

R.D. Adams and N.A. Peppiatt studied the shear stresses obtained by means of differentiating the normal stresses within the adherend in an idealized lap joint using an approximate analytical method and a finite difference technique [3]. Their work considers the experience of shear stresses in the adhesive layer and direct stresses in the adherends acting at right-angles to the direction of the applied load, these stresses being caused by Poisson’s ratio strains in the adherends. The effect of bending was ignored and the adhesive was treated as an infinite number of shear springs, i.e. tearing and peeling stresses and longitudinal normal stresses in the adhesive were also ignored. Their results show that the transverse shear stress has a maximum value for metals of about one-third of the maximum longitudinal shear stress, and this occurs at the corners of the lap, thus making the corners the most highly stressed parts of the adhesive. In this thesis the maximum stresses occur at the corners of the lap in both the aluminium and steel adhesive joints, in agreement with the predictions. However, the one third relationship between the maximum value of transverse and longitudinal shear stresses can not be seen due to scatter of the neutron diffraction results. In addition, direct comparison cannot be made in the magnitude of strains and stresses between neutron diffraction and Adam’s study results because of the different material and size of sample and different tensile load. For instance, Adam’s sample was a single lap aluminium-steel adhesive joint with 0.25mm thickness adhesive, 1.62mm thin aluminium and 12.7mm thick steel, and 25.4mm x 25.4mm lap. The applied load was about 5-6KN. The joint overlap area for the samples in this work was 25mm x 25mm. The thickness of the adhesive was 0.13mm for al-al double lap joints and 0.05mm for steel-steel double lap adhesive joints. The thickness of aluminium is 3.15mm and the steel is 5mm. The applied tensile loads were 4.3KN and 8.1KN.

In 1974, stresses in a standard metal to metal adhesive-bonded lap joint were analysed by R.D. Adams and N.A. Peppiatt by using a two-dimensional finite-element method and comparisons were made with previous analysis [2]. Particular attention was paid to the stresses at the ends of the adhesive layer. Unlike previous work, which assumed the adhesive to have a square edge, the adhesive spew was treated as a triangular fillet.
which is close to the geometry in the neutron experimental work. Their study found the highest stresses exist at the adherend corner within the spew. It also can be said by inference that the highest stresses in the adherend exist at the adherend corner. This can be verified by the neutron results (see Figure 2a and b) by looking at the stresses near the glue line, in particular the aluminium sample with 810kg load (y=5.68). However, although Adams and Peppiatt [3] showed that the lap joint problem is three-dimensional, they also showed that longitudinal stresses in the adherends are not significantly influenced by the transverse stresses due to Poisson’s ratio effects. Both single lap and double lap adhesive joints were studied in their work. The double lap joints have been considered in two different ways. The first model used symmetry about the centre-line of the double lap and lateral restraints are applied along the centre line (p187, Figure 3a [3]). The second model used the fact that if the adherends are equally thick (as is the case for the samples in this thesis), the loads in the adherends are equal at the centre of the overlap and the double lap can be represented by a “half-length” model, with consequent economy of computing effort. The load was applied uniformly across the adherends at the mid-section of the joint. There was reasonable agreement between the two finite element solutions----half-length lap and full-length lap. Their prediction shows that the highest tensile stress in the adhesive exists at the corner of the adhesive adjacent to the loaded adherend. It also agrees with the neutron results (Figure 2). It has to be noted that only stresses near the glue line in the adherends in the samples investigated by neutron diffraction could be compared to Adam’s results.

Comparing the neutron results with Tsai and Morton’s prediction of 1994 [4], some good agreements were also achieved. The single sample used in their study was similar to the aluminium double lap sample in this thesis. Their sample consisted of 2.3 mm thick aluminium alloy and 0.13 mm thick epoxy adhesive. The overlap size of their sample was 25.4mm x 25.4mm. The load applied in their study was about 2.6 KN. Their results show that 3 dimensional stress regions exist in the specimen, this is kind of seen from the considerable transverse strains (Table 3 and 5 in Chapter 6) existing in both steel and aluminium experimental samples. Their study also shows that the adhesive and adherend stress distributions in the overlap near the free surface are quite different from those occurring in the interior. This cannot be seen from the neutron diffraction experimental results (Figure 3). However, it also could not be said
that neutron's results disagree with their prediction. They also observed that the stresses on the free surface are slightly less than those on the midplane. But the experiment results in Figure 3 completely disagree with this prediction because the strains near free surface (Figure 3a) looks larger than the mid-plane (Figure 3b). In addition, Tsai found that the maximum stress concentration for longitudinal stress in the adherend is much higher than the other components. This can be confirmed from the results of the aluminium sample (Table 2-5 in chapter 6).

In our experiment (ISIS), due to the spacer the bending effect has been slightly decreased, the resultant stresses distribution therefore has less difference between stress of the loaded adherend and unloaded adherend. (Figure 14 and Figure 17 in Chapter 6).

Joyanto and Robert [6] made a parametric study of the behaviour of double lap joints with a viscoelastic adhesive by means of finite element analysis. They found that the most important parameter is the ratio of the adherend modulus to the equivalent property of the adhesive. The stresses are highest when this ratio is one and decrease as this ratio increases. For the two experimental samples in this work, the ratio for the aluminium joint is about 36 and it is about 88 for the steel adhesive joints. According to Joyanto's prediction, the stresses in the adherend for aluminium joints should be higher than steel adhesive joints. This is actually validated by maximum stress of 90MPa (8.1KN) for the aluminium sample and about 30MPa (9.4KN) for the steel adhesive joints. They also found that the thickness of the adhesive is another important parameter to influence the stress. That is, with decreasing adhesive thickness, the stress distribution along the length of overlap is increasingly uniform and the gradient of the stress distribution through the adhesive thickness also decreases. This also agrees with experimental results by means of comparing the longitudinal strains distribution of the steel sample with 0.05mm adhesive thickness and the aluminium adhesive joints with 0.13mm thickness adhesive. It can be seen from Figure 2 and Figure 17 in Chapter 6 that the longitudinal strain distribution for steel adhesive joints is more uniform than for the aluminium adhesive joints.
Figure 3 Comparison of strains near the free surface and in the midplane. Accuracy of strain measurement is about ±0.13 in middle plate, ±0.04 in outer plate. Positive strain values represent tensile, negative values compressive strain.
References

Chapter 8 Discussion

The aim of this work is to use different experimental methods to investigate the residual stresses and strains in adhesive joints and study the stresses and strains under load by making use of neutron diffraction methods. Among all the experimental methods, neutron diffraction is undoubtedly the only powerful technique capable of investigating 3 dimensional stresses and strains within adhesive joints. With the development of the neutron strain scanning technique and continual improvement of neutron equipment in the last 2 decades, more and more research work in different areas including studies of stresses and strains have achieved valuable results. However, due to limited neutron beam time, other experimental techniques are still very useful and helpful, particularly for the study of residual strains and stresses. X-ray diffraction, strain gauges and moiré interferometry can be used to investigate the surface strains and stresses directly. The strains and stresses can also be measured by means of embedded strain gauges. X-ray diffraction is a non-contact measurement technique, which can measure the surface strains and stresses within adhesive joints. However, the resolution depends on both equipment and the material of the adherend. The grain size of the adherend plays an important role in the measurement. Because a large number of grains must be included in the gauge volume, in this work good results could be obtained on the surface of steel using X-rays, but not for aluminium since the grain size of aluminium was too big. Due to the limitations of each direct measurement experimental method, it is profitable to find other methods to study the strains and stresses so that the limited Neutron and X-ray experimental results for strains and stresses in adhesive joints and the FE predictions can be validated. In this thesis, the bimaterial method was used to study residual stresses and strains in steel-adhesive joints indirectly. In addition, the effect of moisture on the adhesive joints has been studied by means of measurement of bulk adhesive and epoxy-steel bimaterial samples.
Chapter 2 discusses the measurement of the properties of different adhesives. All the predictions of residual strains and stresses in adhesive joints and some of experimental investigation in residual stresses of the lap joints must be based on knowledge of the mechanical and thermal properties of adhesive and adherends. The properties of metallic adherends are normally readily available. However, most of the properties of adhesives are not available. For example, Young’s modulus $E$, thermal expansion coefficient $\alpha$, moisture expansion coefficient $\beta$, glass transition temperature $T_g$, creep data and diffusion coefficient $D$. All the properties are correlated to the strength of the adhesive joint. The Young’s modulus and diffusion coefficient $D$ vary with the temperature as well as the humidity of the environment which directly causes the stress in the adhesive to change bringing beneficial or detrimental influences to the strength of the adhesive joint. The thermal expansion coefficient increases greatly when the adhesive is above the glass transition temperature. It is therefore necessary and important to measure these properties of adhesives so as to analyse the strains and stresses in adhesive shear joints properly.

Due to limited experimental time, only some of the properties of the adhesives used in this work were measured. These include 3M DP190 2-parts epoxide and AV119 single part epoxy resin, FM 300-2 Film adhesive (modified epoxy resin film) and FM 73 film adhesive.

In the sample preparation work, it is difficult to prepare high quality bulk adhesive samples of 3M DP190 2-parts epoxide and AV119 single part epoxy resin because of their liquid state at room temperature. The bulk adhesive specimens prepared to measure thermal expansion were different from the adhesive used in adhesive joints because there was no pressure applied to the sample during curing process. In addition, some small bubbles and voids were found within the bulk adhesive specimen. Both of these factors could introduce errors to the measurements. This might be improved by using some thick Teflon paper to cover the top of the sample before the adhesive solidified and to apply the required pressure to it during the curing process. For the film adhesive specimen preparation, voids and defects within the sample have been reduced to a minimum, comparable with commercial joints. However, the value of the small pressure required could not be controlled accurately due to the wide range of the available pressure machine (0-10 tons). This is much
bigger than the required pressure 40MPa. Since the magnitude of pressure influences the thickness, shape of spew fillet and properties of adhesive this is also an important factor and can create errors in the measurement of properties.

In the diffusion coefficient and moisture expansion measurement of FM300-2 film adhesive, the accuracy of the results is mainly associated with the quality of the sample (applied pressure during curing and defects within the sample); the exposure time outside the chamber between finishing curing and before putting into the chamber; and the accuracy of the instrument. Different applied pressures could produce different adhesive properties from the adhesive in the adhesive joints so that some error is generated in the results of diffusion coefficient and moisture expansion coefficient. Microvoids and bubbles inside the bulk sample also could produce a difference in the results, which might make the results in moisture expansion coefficient smaller. The longer exposure time could bring considerable error to the diffusion coefficient, in particular to the lower and higher R.H environment. An improved method is to prepare good quality bulk adhesive samples in a small range pressure machine, set the oven, electric scale and chamber in a same room to reduce the exposure time, and use a good quality travelling microscope with high accuracy. It is not simple to estimate the differences between the experimental results in this work and their value in adhesive joints. However, they are not expected to have a major influence on the measured properties of the adhesives.

In Chapter 4 the curing stresses in adhesive joints during curing and the cooling down process were experimentally investigated using open faced bimaterial samples. Good agreement was achieved between experiments and theoretical predictions. It is found that almost all the curing stress in a metal/epoxy joint are thermally generated from the cooling down process. A number of different theoretical approaches have been adopted in the analysis of the data and good agreement for the curing stress in an FM300-2 adhesive and steel bimaterial beam are obtained from different theoretical and experimental methods. The initial shrinkage stress (due to water evaporation) was found to be negligible. However, considerable shrinkage stress is produced after a further 2 hours curing. It was also found that the stress relaxation of samples after curing is mainly due to moisture absorption.
The research results of Adams et. al. [1] indicate that the shrinkage of the adhesive on cure may lead to stresses in joints. They think one advantage of epoxide adhesives is that the shrinkage on curing is low. It was presented in their research that the shrinkage for a two-part epoxide adhesive is 3.75% at room temperature and 4.46% at 60°C; a one-part epoxide cured at 135°C gives a shrinkage of 5.13%. It was found in this work (chapter 4.2), that the water loss after curing for both FM300-2 adhesive and FM73 film adhesive is almost zero. However, considerable water's loss (1%) after further curing was found in FM300-2 film adhesive in this work. It is therefore suggested that a longer time curing or curing at higher temperature for FM300-2 film adhesive may be needed. It has to be note that the shrinkage in the Adams study is from both differential thermal strain and water loss during curing. Apparently, the shrinkage is mainly from differential thermal strain. However, the shrinkage in this work is only due to water loss. Hence, it can't be said that agreement was not obtained between this work and Adam's study.

In this study, the effect of moisture on FM300-2 film adhesive was investigated by means of measuring bimaterial and bulk samples in a well sealed chamber with different constant relative humidities at room temperature. The results of this work show how the swelling strain and modulus vary with the exposure time within 3 different RH environments, they also show the relationship between swelling strain and moisture content. The moisture expansion coefficients and diffusion coefficients of FM300-2 adhesive in 3 different constant RH circumstances were also obtained from this work.

In conclusion, the work described in Chapter 4 on bimaterial and bulk adhesive samples showed that moisture is the main critical factor affecting the performance of adhesive and adhesive joints. The variation of the swelling strain, Young's modulus, diffusion rate and moisture expansion coefficient, were found to almost solely depends on the diffused moisture content. It was also found from both results of the bimaterial sample and bulk sample that the residual stresses for both bimaterial and bulk samples are released due to moisture absorption. In addition, this experiment possibly shows, from the bimaterial sample results, that moisture easily damages low quality adhesive joints, particularly when RH is higher than about 70%. As a result of
swelling, the significant weakening of adhesive joints may be closely related to the absorption of moisture.

Further investigation exposing the samples to controlled moisture environments for longer time to reduce the experimental error would be advantageous. Different type of adhesives should be investigated in future work to further validate the effect of moisture on the adhesive and adhesive joints.

Diffusion into adhesive joints was studied by Zanni-Deffarges and Shanahan by comparing the calculated diffusion rates between non-bonded adhesive specimens and bonded adhesive joints. [2] They observed that the diffusion coefficient of the adhesive joint was greater than that of the bulk adhesive. Nyugen et al. [3] and Linossier et al. [4] have also compared diffusion rates between bulk specimens and adhesive joints using Fourier transform infrared spectroscopy in the multiple internal reflection mode (FTIR-MIR). They detected significant diffusion at the interface for poorly adhered adhesive systems. This phenomenon has been found during experiments in this work. Further more accurate investigation of water’s effect could be obtained by means of measuring thinner bulk adhesive sample and bimaterial and adhesive joints over longer time periods. A comparison of the diffusion rate among the adhesive lap joints, bimaterial sample and bulk adhesive sample could be carried out in order to determine the diffusion rate in the 3 types of joint.

Use of a strain gauge is an invasive experimental method to investigate the interface strains and stresses in adhesive joints. In this work, curing strains and stresses in a single lap Aluminium-adhesive joint during the whole curing and cooling down process were investigated using foil gauges and semiconductor strain gauges.

Due to the difficulty of operation with multiple strain gauges within a joint and in particular the fragility of semiconductor gauges of strain gauge, a map of residual stresses and strains in the interface surface between adherend and adhesive during the curing shrinkage and slow cooling down process was not obtained. A single point measurement of strain during the curing process was however recorded. The foil strain gauge technique is very invasive, this could introduce large errors to the results. This might be why tensile stresses were found in the adherend interface. This doesn’t
agree with the results of M.E. Tuttle’s study, who investigated the strain within a single lap joint using embedded strain gages. His results indicate that the presence of the gage is not detrimental to bond performance [5].

Hence, the strain gauge technique might be unsuitable to investigate the residual stress distribution within the adhesive joints, and the experimental results in this work could be doubted.

The neutron diffraction strain scanning method enables us to determine non-destructively the residual stress state of a single lap adhesive joint material. It can provide sub-surface information not obtainable by any other technique. It is much faster and less labour intensive than conventional destructive methods, such as hole drilling and strain gauge methods. For the neutron diffraction method, complicated corrections to the data are not required because the stress state is not disturbed by the measurement.

The neutron diffraction techniques provides lattice displacements/strains with good spatial resolution to characterise the elastic deformation in the various zones of adhesive and adherend and the interface. Conventional measurement techniques are usually not able to provide the required data due to a lack of spatial resolution. A map of residual stresses in the interface and other surfaces can be obtained, but a map of residual stresses and strains during curing and cooling processes couldn’t be achieved by means of the neutron diffraction technique because of the limitations of the neutron diffraction instrumentation.

Y. Weitsman’s [6] study found that a significant reduction of residual thermal stress is due to a temperature enhanced viscoelastic creep. However, in the investigation of shrinkage stresses of the bimaterial sample, it seems there was no apparent stress relaxation at high temperature. The experimental result doesn’t agree with Y. Weitsman’s analysis result, this could be due to short time at which the sample was held at high temperature.

Research in [7, 8] (ch1) suggested that bound water which exists in the polymer network can be recognized as loosely bound water, which can be released easily upon
heating and strongly bound water that is "frozen" in the network and difficult to be removed from the polymer. This suggestion agrees with the experiment results in chapter 4.2 and 4.3, which describe the recovery of the curvature of bimaterial samples by reheating the aged sample, which has a significant increase in curvature due to swelling of the adhesive both from 'free water' and 'loosely bond water' which can be easily released by reheating. After repeatedly reheating the aged sample, it was found that there were still small amounts of water remaining in the adhesive which can be seen from the weight of sample. This phenomenon can be explained by the presence of difficult to be removed 'strongly bond water'.

Chapter 5 presented the work of direct measurements of residual strains and stresses in single lap and double lap adhesive joints by means of X-ray diffraction in BENSC and neutron diffraction in NFL.

Previous research work [9] found that the most important residual stress within the adhesive in a single lap joint is the tensile residual stress, which appears near or at the interface. The highest stress should be precisely at the interface and the joint corner. Correspondingly, the most important compressive residual stress within the adherend appear close to the interface or at the interface. In this thesis, residual stress distributions in a single lap steel-adhesive joint were investigated using the X-1 diffractometer in BENSC. Significant compressive residual stresses were found in the adherend. However, the magnitude of stresses seem ridiculously large compared to FE results and other analysis. This may be due to an error in zero-stress measurement and the quality of sample. Non-uniform compressive stresses in the adherend might exist before the bonding process so that large compressive stress appears after curing, although the metal had been annealed before bonding in order to reduce these. The joint would be improved by annealing the adherend for a longer time than that used and choosing a position far from the lap joint to be d₀ position. Another potential problem with the BENSC data is that it is an X-ray technique and any unrelaxed surface stresses due to sample preparation could lead to erroneous results.

Small magnitude residual strains and stresses were found in double lap steel adhesive joints in the neutron measurement at NFL. These are in good agreement with predictions [9, 10, 11]. The stress distribution also agree with Adam's study [10]
which is that maximum stress is achieved near the edge and corner and decreases towards the centre. In addition, NFL's results validate the stress relaxation due to the effect of water absorption by means of the measurement of the wet sample. In view of the results of residual stresses in the adherend from both BENSC and NFL experiments, it can be seen that the stresses are not uniformly distributed within the overlap joint in the adherend, this agrees with the results of previous work.

From the standard test methods frequently used in the past (for single lap joints), it can be seen that the stresses are not uniformly distributed in the adhesive layer and the stress concentrations arise from the differential straining of the bonded substrates and from the eccentricity of the loading path. In this thesis, the strains and stresses under load were only investigated in double lap joints. Non-uniform strains were also found in double lap adhesive joints which match well with previous standard test results. The previous results [12] show that the longitudinal stress($\sigma_x$) distributions on the mid-plane and free-surface have a great deal of similarity, but the values on the free surface are slightly less than those on the mid-plane. This agrees well with the experimental results in the aluminium adhesive double lap joints obtained at ISIS [12]. The maximum stress concentration for $\sigma_x$ in the adherend is much higher than the other components. This type of stress distribution has already been proved by all the results in this thesis.

All the strain and stress investigation by means of neutron diffraction technique in this thesis only achieved reasonable and reliable longitudinal strains, the transverse strains looks unreasonable and not reliable so that accurate stresses can't be obtained. This may be due to relatively large gauge volume($2\text{mm}^3$-$5\text{mm}^3$) and shorter counting time used in the transverse measurements, which make it is difficult to obtain good spatial resolution in order to achieve more accurate strain results. An improvement would be to decrease the gauge volume and increase the counting time so that more reliable and accurate strains would be obtained. The stresses on the surface can be measured by means of strain gage or Moire techniques but strain gauges do not provide the required spatial resolution to follow rapidly changing stress levels and neither technique can map internal strains. Hence, more accurate work by means of neutron diffraction is required in the future to investigate different material adhesive joints to validate the stress distribution in this thesis and FE predictions in general.
Joyanto and Robert [13] found that the most important parameter is the ratio of the adherend modulus to the equivalent property of the viscoelastic adhesive, the stresses are highest when this ratio is one and decrease as this ratio increases. The next most important parameter is the thickness of the adhesive. With decreasing adhesive thickness, the stress distribution along the length of overlap is increasingly uniform and the gradient of the stress distribution through the adhesive thickness also decreases. The length of overlap influences only the location of the maximum shear stress, whereas a change in the relative thicknesses of the adherends has a minimum influence on the magnitudes of the stresses. Due to limited time, investigations regarding the influence of the parameters mentioned above on the stresses, were not further investigated in this thesis. It is suggested that the influence of the ratio of the modulus and the relative thickness of the adherends, could be investigated by means of bimaterial samples because of their low cost and convenience. The influence of the length of overlap has to be validated by means of neutron diffraction.

Adhesive systems may be exposed to various environmental conditions during their service life. Moisture is commonly encountered in the service environment. Water is the substance which gives the greatest problems in the environmental stability of adhesive joints. The performance of the adhesive systems may deteriorate to a certain extent upon exposure to harsh environments for a certain period of time. If the relative humidity is high, then the strength of joints usually falls over a period of time. Water is a problem because it is very polar and has a high value of the polar component of surface free energy. Other common liquids such as lubricants and fuels are of low or zero polarity and do not significantly weaken adhesive joints. Moisture/water is the most commonly encountered service environment, and must be considered a critical factor in determining the long-term durability of adhesively bonded joints.

In conclusion, some good agreements between FEA and experimental results indicated that FEA analysis can provide an accurate picture of the stresses within adhesive joints under load. However, it is difficult to predict accurate residual stresses within joints by means of FEA due to the complication, including adhesive cure, producing residual stress within joints.
Future work

- An improvement would be to decrease the gauge volume and increase the counting time so that more reliable and accurate strains would be obtained. This could perhaps be achieved at a synchrotron source.
- Further diffraction work is required in the future to investigate different material adhesive joints to validate the stress distribution in this thesis and FE predictions in general.
- Further investigation exposing the samples to controlled moisture environments for longer time to reduce the experimental error would be advantageous. Different type of adhesives should be investigated in future work to further validate the effect of moisture on the adhesive and adhesive joints.
- It is suggested that the influence of the ratio of the modulus and the relative thickness of the adherends, could be investigated by means of bimaterial samples because of their low cost and convenience. The influence of the length of overlap has to be validated by means of neutron diffraction.

References:


