

2-D MODELING OF MOISTURE AND HEAT DIFFUSION IN ADHESIVELY
BONDED JOINTS

by

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Marco Gerini Romagnoli

ABSTRACT

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Adviser: Sayed Nassar, Ph.D.

In this dissertation research, a novel two-dimensional model is proposed for adhesively-bonded Single Lap Joints (SLJ) under combined mechanical loads and moisture/heat diffusion. Governing partial differential equations of the constitutive stress-diffusion model are formulated and solved numerically. Various scenarios for individual and combined diffusion of moisture and heat through the joint substrates and directly into the adhesive layer are analyzed. The resulting location-dependent material model is fed into the governing partial differential equations. Shear and peel stresses in the adhesive layer are investigated. Results are presented, with a focus on the improvements brought by the capability of the proposed model to predict the effects of diffusive patterns that are perpendicular to the axial tensile-shear load. Moisture diffusion across the joint width is found to have a significant effect on the shear stress distribution for structural epoxy adhesives with high elastic modulus. Numerical comparison with a linear Finite Elements Analysis is provided. Material properties are derived from experimental testing of commercially available two-component epoxy and polyurethane adhesives. This document is organized as follows:

Chapter One "Introduction and Literature Review" includes a description of the analytical, numerical, and experimental work that serves as foundation for this

dissertation. A previous one-dimensional analytical model is revised, and the motivations driving this research effort are illustrated.

Chapter Two "Modeling of Heat and Moisture Diffusion" lays the groundwork for the analysis of diffusive patterns in the joint substrates and in the adhesive layer. Multiple scenarios of moisture and heat diffusion are explored, and their effect on the elastic properties of the adhesive is investigated. Governing partial differential equations are derived, and solution strategies are discussed.

Chapter Three "Elastic Model" includes the formulation of coupled stress-diffusion partial differential equations for the shear and peel stresses in the adhesive layer, resulting from the application of an external tensile-shear load on the two adherends. Equilibrium considerations, stress-strain, and strain-displacement relationships are used to generate the constitutive equations, with adequate assumptions and simplifications.

Chapter Four "Elastic Modulus of Structural Adhesives: Relationship to Bulk Material Temperature" contains the experimental procedure and results for the bulk adhesive tests. The elastic moduli of two-component epoxy and polyurethane adhesives are measured using a DMA Q800[®], and a linear law relating temperature to material properties is inferred.

Chapters Five, Six, and Seven present the results of the shear and peel stress models for adhesive joints subjected to two-dimensional moisture-only, heat-only, and combined moisture/heat diffusion, respectively. A convergence study is performed on the two-dimensional solution to the heat equation governing moisture and heat diffusion in the adhesive layer. Stress gradients along the length and width of the bondline are analyzed, and the results are compared to the previous one-dimensional coupled stress-diffusion model.

The results of the two-dimensional model are compared with a Finite Elements Analysis in Chapter Eight "FEA Comparison". Chapter Nine "Conclusions and Future

Work" summarizes the major findings of this dissertation research, and outlines the potential for future work.

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LIST OF ABBREVIATIONS

CZM	Cohesive Zone Modeling
DCB	Double-Cantilever Beam
DLJ	Double Lap Joint
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
ENF	End-Notched Flexure
FEA	Finite Elements Analysis
SD	Standard Deviation
SLJ	Single Lap Joint

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Adhesive joints are increasingly common in critical, lightweight structures in the aerospace, automotive, and infrastructure fields. They present several advantages over more traditional joining methods, such as riveting, bolting, and welding. The use of structural adhesives allows for improved design flexibility, reduced weight, increased manufacturing and assembly efficiency, and it minimizes stress concentration [1]. However, the major shortcoming of structural adhesive joints is the difficulty to determine the full stress field in the bond layer under mechanical and environmental loads.

1.2 Literature Review

Several analytical studies in the literature have laid the foundation for the stress analysis of adhesive joints. A variety of assumptions allowed to simplify the problem, and most of the literature focused on the effect of external forces on the stress distribution in the adhesive layer of SLJs. Iterative and numerical solutions were derived when closed-form explicit formulations were impractical or could not be found.

Some authors used plane strain and full 3-D FEA models to validate the results obtained by the classical analytical studies. The use of FEA allowed to investigate the interaction of the joints with complex environmental variables such as heat, moisture, and other forms of induced material degradation. With the introduction of damage modeling and cohesive elements, FEA methods became able to predict the failure loads for adhesive joints, but large experimental work was required to characterize the adhesive material.

Experimental studies in the literature traditionally focused on the determination of quasi-static strength of adhesive joints under a diverse spectrum of loading and

environmental conditions. Although most standardized testing was performed using SLJs or Double Lap Joints (DLJs), experimental studies were not bound by the geometric limits of analytical models. However, measuring adhesive stresses across the bondline is challenging, and only a handful of authors used techniques such as Moiré interferometry or rubber models to validate the results from analytical and numerical methods.

1.2.1 Classical Analytical Models

Volkersen [2] introduced the idea of differential strain, where the external load is elastically transferred from one adherend to the other through shear strain of the adhesive layer. The free end of the substrates experiences zero normal strain, which causes the shear strain in the adhesive layer to vary along the bondline, as shown in Figure 1.1. The quantity P represents the applied external load per unit width b . Volkersen's model did not consider the normal strain in the adhesive layer caused by bending of the SLJ.

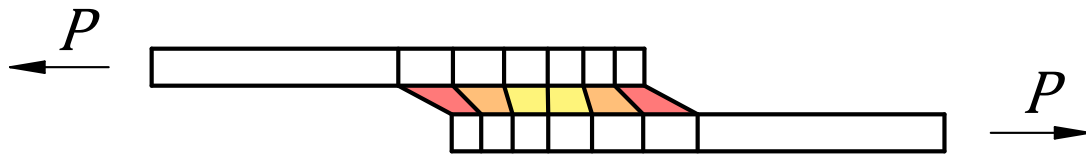


Figure 1.1: Differential strain: shear deformations in a SLJ [2]

Later, Goland and Reissner's elastic model [3] expanded Volkersen's work by taking into account the bending moment and transverse shear that induce normal (peel) and shear stress, respectively, in the adhesive layer. They calculated the deflection and rotation of the adherends at the edges of the overlap using classical beam theory and used them to define the boundary conditions for the system. The bending moment M_0 and the

transverse shear V_0 at the edges of the bondline can be calculated as

$$M_0 = \frac{\cosh(\sqrt{\frac{P}{D_1}}c)}{\cosh(\sqrt{\frac{P}{D_2}}c) + 2\sqrt{2}\sinh(\sqrt{\frac{P}{D_2}}c)} \frac{Pt_s}{2} \quad (1.1)$$

$$V_0 = \frac{\cosh(\sqrt{\frac{P}{D_1}}c)}{\cosh(\sqrt{\frac{P}{D_2}}c) + 2\sqrt{2}\sinh(\sqrt{\frac{P}{D_2}}c)} P \sqrt{3(1-\nu_s^2)} \frac{P}{E_s t_s} \quad (1.2)$$

where P is the external load F per unit width $2b$, D_1 and D_2 are the flexural rigidities of the adherends and of the joint, respectively, t_s is the thickness of the substrates, $2c$ is the overlap length of the SLJ, E_s and ν_s are the elastic modulus and the Poisson ratio of the adherends. A simplified, symmetric model was used, with the two adherends equal in size and material. Figure 1.2 shows Goland and Reissner's model under load.

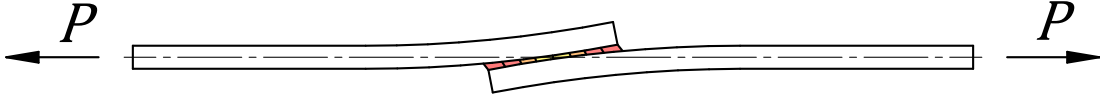


Figure 1.2: SLJ deformation in Goland and Reissner's model [3]

A comparison between the shear stress τ_a distribution obtained from Volkersen's and Goland and Reissner's models, for a representative 25.4 mm wide SLJ with 1.6 mm thick steel adherends and epoxy adhesive, is shown in Figure 1.3a. Volkersen's model underestimates the peak shear stress. The integral of both curves along the overlap length is equal to the applied external load. Figure 1.3b shows the peel stress σ_a distribution along the bondline, as calculated using the model by Goland and Reissner. The peak peel stress occurs at the edge of the bond area, and integration along the joint overlap gives

zero, because no load is applied in the direction perpendicular to the longitudinal axis of the SLJ.

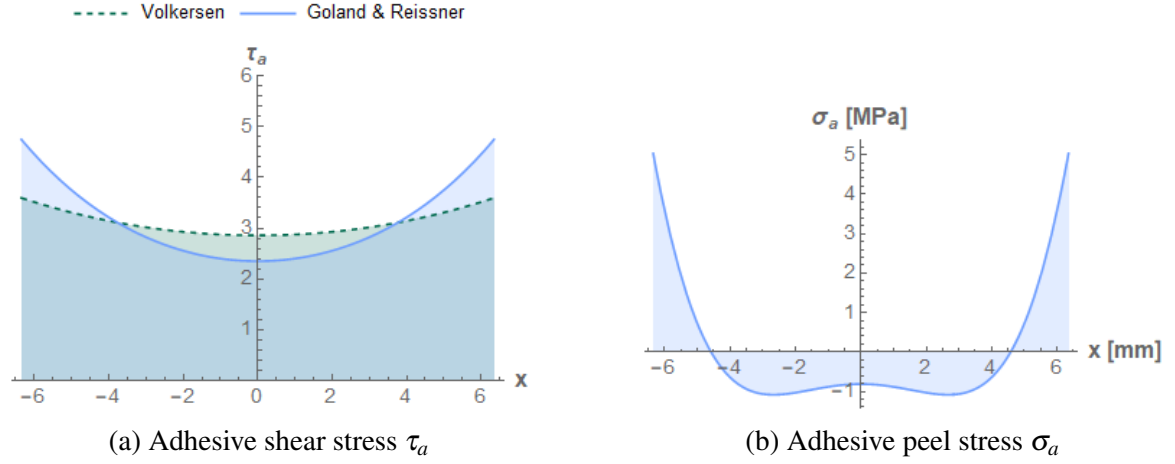


Figure 1.3: Adhesive stresses: Volkersen [2] vs Goland and Reissner [3]

Hart-Smith [4] expanded the previous model by Goland and Reissner by improving the formulation of vertical deflection at the edges of the bondline. Goland and Reissner's definition of bending moment M_0 approached a nonzero asymptote for indefinitely large values of overlap length, and therefore it was restricted to light loads and short overlaps. Hart-Smith overcame this limitation by calculating the bending moment M_0 as

$$M_0 = P \frac{t_s + t_a}{2} \frac{1}{1 + \sqrt{\frac{P}{D_1}} c + \frac{Pc^2}{6D_1}} \quad (1.3)$$

where t_a is the thickness of the adhesive layer. For very large values of overlap length $2c$, the new formulation of M_0 returns 0, and the shear stress distribution converges to the average stress τ_{avg} . Furthermore, Hart-Smith took the elasto-plastic behavior of the adhesive into account, in the shear direction. The adhesive layer is split in three: in the

outer plastic regions, the shear stress is equal to the plastic stress τ_p , while in the inner region the adhesive's behavior remains elastic (Figure 1.4).

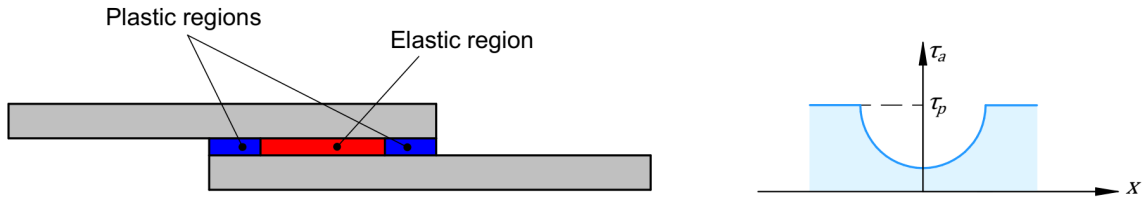


Figure 1.4: Hart-Smith: elasto-plastic model for SLJ [4]

The above-mentioned models [2–4] calculate the average value of peel and shear stress across the thickness of the adhesive layer at a given location in the joint overlap. In 1978, Ojalvo and Eidinoff [5] expanded Goland and Reissner's [3] model, to allow for shear stress variations through the adhesive thickness; they concluded that for joints with very short overlap, thick adherends, and stiff adhesives, the stresses in the adhesive layer can be higher than the mid-thickness average calculated by Goland and Reissner at points near one of the two adhesive interfaces. Through-thickness or transverse stresses can cause large deformations in the adherends near the interface when the substrates are made of laminated composites with low transverse shear moduli. Less significant through-thickness variations were observed for more conventional joints with a ratio of adhesive thickness to overlap length smaller than 0.02.

Statics considerations show that the shear stress in the adhesive layer should be zero at the free edges of the overlap [6]: no external shearing action is present on the outermost infinitesimal element of adhesive. However, the classical models [2–5] do not respect this condition. Allman [6] developed a theory that allowed to correlate the location

of the peak adhesive shear stress to the relative stiffness of the adherends. His stress model was based on calculating the strain energy density of a SLJ. The analysis included the effects of bending of the adherends. Goland and Reissner's analysis was found to overestimate the peak shear stress in the adhesive layer, because static equilibrium was obtained with stress values rising rapidly near the ends of the bondline. Chen and Cheng [7] expanded on Allman's work and found that when the adhesive layer is relatively flexible with respect to the adherends, the distance between the limit of the bond area and the peak shear stress is equal to approximately 20% of the adherend thickness. Therefore, for SLJs with thin and stiff adherends, the classical models [2–4] offer a reasonable approximation of the adhesive stress distribution, and their simpler analysis allows for easy manipulations of the parameters.

Tong [8] improved the Hart-Smith formulation by allowing non-linear deformation of the adhesive in both shear and peel directions. Through-thickness stress variations were neglected. Arbitrary undefined strain-stress relationships were used to calculate the stress field in the adhesive layer. Therefore, any functions that describe the measured stress-strain curve obtained from experimental testing can be used within Tong's analysis. Numerical methods were required to solve the constitutive equations, but simple explicit formulas that allowed to calculate the ultimate load were formulated. With the improved model, Tong investigated the effect of different failure criteria for adhesive joints: pure peel and pure shear failures, in which the joint strength could be determined from the maximum tensile and shear energy densities, respectively, and a mixed-mode strain energy density criterion for failures characterized by a determined shear-to-peel phase angle. Finally, Tong noted that the product of the strain energy density and the adhesive thickness was equal to the energy release rate of mode I (peel) or mode II (shear).

Oplinger [9] used the shear and normal deformations in the adherends to formulate adhesive stress constitutive equations. In his study, the deflections of the adhesive layer

were allowed to decouple the different sections of the adherends in the bending analysis, which allowed to reproduce the results obtained by the existing models [2, 3], and to significantly improve them for joints with a relatively thick adhesive layer.

Tsai et al. [10] analyzed DLJs as well as SLJs, and revised the classical models by Volkersen [2] and Goland and Reissner [3], to allow for linear shear deformations in the adherends. They used Moiré interferometry to measure the horizontal strain of joints with graphite-epoxy quasi-isotropic and unidirectional adherends. They observed that the classical models [2, 3] overestimate the nonuniformity of the stress distribution when the adherends have low transverse stiffness. Therefore, the improved analytical model correlated better than the previous formulations [2, 3] with the experimental data for joints with laminated composite adherends.

Bigwood and Crocombe [11] developed a more general formulation to determine the adhesive shear and peel stresses regardless of the joint configuration. The stress field of the adhesive layer is a function of bending moment, transverse shear, and tensile load at the edges of the bond area. Moreover, they developed a simplified formula that allows to calculate the value of peak shear and peel stresses in a SLJ given the joint's geometry, for similar and – with some limitations – dissimilar adherends. Later [12] Bigwood and Crocombe expanded their previous analysis, including transverse loading scenarios for SLJs and considering the plastic properties of the adhesive. The adhesive's nonlinear response is modeled using the Von Mises deformation energy criterion, and the equations are solved numerically.

A study published by Sawa et al. [13] analyzed the stresses at the adhesive/substrate interface, for a SLJ with identical, isotropic adherends. The joint is subjected to a conventional tensile shear load, and the equations are solved numerically. The results show that decreasing the flexural rigidity of the adherends (i.e. reducing thickness and elastic modulus of the substrate) increases the peak interfacial stresses near

the ends of the bond area. Later, Sawa et al. [14] extended their analysis to take into account dissimilar adherends. They concluded that the maximum stresses occurred near the edge of the bondline at the interface between the adhesive and the adherend with the lowest flexural modulus. An optimum value of adherends thickness ratio was formulated that would minimize interfacial stresses. The results were validated using FEA. More details on analytical models for adhesively bonded SLJs can be found in the book and comparative studies authored by Da Silva et al. [15, 16].

Frostig et al. [17] used a closed-form high-order theory to model the adhesive stresses in a SLJ. The spew fillets were analytically modeled as tension bars, and the formulation fulfilled point and general equilibrium. Square end and triangular fillets were considered, and the resulting stress distribution was validated using Goland and Reissner's model, as well as FEA. Spew fillets were observed to increase joint performance. More significant effects were obtained when the size of the fillet was larger than twice the adhesive thickness.

An analytical model for the stress distribution in the adhesive layer of a SLJ with anisotropic adherends was developed by Wah [18]. The transverse shear stresses deriving from the assumption of cylindrical bending and plane strain were not neglected, and the anisotropy of the adherends was considered in the equilibrium equations. The correction stresses resulting from the appearance of out-of-plane shear stresses (in the case of dissimilar adherends) were observed to be several orders of magnitude smaller than those obtained by the classic analyses [2, 3]. The author concluded that although there are some cases in which the transverse stresses would introduce a significant correction, in most instances they can be neglected, simplifying the calculations. Moreover, in practical applications, small deviation of the applied constraints from the theoretical boundary conditions are sufficient to render the implementation of the correction stresses irrelevant.

1.2.2 Existing Finite Elements Models

Analytical models can be used to determine the stresses in the adhesive layer of a SLJ to a satisfying degree. However, FEA models are becoming increasingly popular, thanks to the computational power offered by modern computers, and allow to overcome the basic limitations that constrain the application of analytical analyses. 3-D FEA models constitute a bridge between experimental and analytical studies, complementing the results obtained from mechanical testing in a laboratory with information on the stress state at any point in the joint structure, provided that the spatial discretization is adequately fine. 2-D FEA plane strain, or more rarely plane stress, models can be used to reduce the computational time in case of large parametric studies of joints with simple geometric characteristics (e.g. SLJs and DLJs). However, when it is not possible to ensure that specimen geometry, material properties, and other phenomena are invariant in the direction perpendicular to the load axis, the use of a 3-D FEA model is required.

Simulation of damage growth within the adhesive using Cohesive Zone Modeling (CZM) has been implemented in FEA analyses in the last decades, allowing to predict the failure load of bonded joints [19]. Triangular and trapezoidal cohesive laws are commonly used for typical structural materials. The traction-separation laws require knowledge of the adhesive's mode I and II strain release rate G_I and G_{II} , as well as of its mode I and II fracture toughness G_{IC} and G_{IIC} , respectively. A combination of Double-Cantilever Beam (DCB), End-Notched Flexure (ENF), and SLJ specimens are used to measure the CZM parameters.

Da Silva et al. incorporated CZM progressive damage modeling into interface finite elements to predict the lap shear strength of SLJs with adhesives of various thicknesses. The Drucker-Prager model was used to describe the adhesive's plastic behavior and failure criterion, with the deviatoric stress components being less dominant

when the hydrostatic stress was positive (tension). A triangular mixed-mode traction separation law was implemented to drive damage in the adhesive layer, and the CZM elements were used as interface between the steel substrates and the adhesive. This increased the fracture energy capacity of the system, which lead to overestimation of the failure load. They concluded that the lap shear strength increased as the adhesive thickness decreased, which confirmed Crocombe's original global yielding criterion [20].

In a similar study, Carlberger and Stigh investigated the effect of the thickness of the adhesive layer on the CZM parameters and on the optimal shape of the traction-separation law [21]. They observed that the fracture toughness in the peel direction (G_{IC}) increased monotonically with the adhesive thickness, until the layer's thickness reached a critical value of approximately 1 mm, after which a slight decrease was noted. The correlation between adhesive thickness and the fracture toughness in the shear direction (G_{IIC}) was not equally as strong, but a similar trend was observed. Moreover, a slight decrease in bulk adhesive strength with increasing thickness was measured in both loading modes. A triangular traction-separation law was found to be a better fit for joints with thin adhesive layers, while bigger values of adhesive thickness required a trapezoidal shape.

FEA can also be useful to model the effect of environmental factors on the distribution of adhesive stresses: combining mechanical loads with environmental exposure can lead to premature joint failure. Heat, humidity, and other aging factors can diffuse in the adhesive layer, altering the distribution of stresses under load, and deteriorating the bond integrity at the interface.

Abdel Wahab et al. [22] studied the diffusion of moisture in composite joints. They used a combination of analytical methods, experimental tests, and Finite Elements models to determine the moisture content in the adhesive layer and in the adherends. The effect of the adhesive fillet shape (convex round, triangular, or square) was investigated.

Furthermore, moisture-conditioned lap-strap joints were tested for their fatigue threshold, in the attempt to identify an empirical relationship between performance degradation and water absorption. The results from the analytical and FEA models showed that round and triangular fillets altered the ingress of moisture in the adhesive layer significantly, while the results for square fillets closely matched a simple 1-D analysis: tapered fillets (round and triangular) increased moisture uptake significantly in the early stages of diffusion. Moisture transport from the adherends to the adhesive was studied, with two distinct analyses: in the first one, the adherends were effectively impermeable, while in the second one water uptake in the substrates was allowed. Saturated permeable composite adherends were observed to deliver large amounts of moisture to the bondline, which is caused by the thin form factor of the adhesive layer.

In a subsequent study, Abdel Wahab et al. [23] implemented the results of moisture uptake experiments into a Finite Elements analysis, and observed the deterioration of the material properties and its effect on the peak stresses in the adhesive layer. A Fickian diffusion model was used to analytically describe moisture transport within the adhesive, and diffusion coefficient and moisture concentration were converted to values of thermal conductivity and temperature, respectively, in the Ansys-based FEA model. In transient conditions, with the adhesive not yet saturated, localized swelling resulting from moisture uptake at the edges of the bond area caused compressive stresses that reduced the peak peel stress. Abdel Wahab et al. observed that the joint's strength experienced a slight initial increase, because of the stress redistribution. However, they noted that the effect quickly subsided due to the degradation of the material properties, and at saturation the swelling strains were uniform across the bondline. The effect of moisture diffusion on the strength of adhesively-bonded butt joints was also investigated. The authors found that in transient conditions the stresses in the dry center of the adhesive

layer experienced a significant increase, which was caused by the decrease in the portion of the load carried by the softened outer annulus, and resulted in lower joint strength.

1.2.3 Experimental Studies

Experimental studies can be devised to validate and confirm the results obtained from analytical and FEA models, as well as to investigate the effect of variables that cannot be easily included in theoretical and numerical analyses. Moreover, experimental testing is often required to obtain material properties to use in analytical and FEA models: quantities such as mode I and II energy release rates are related to parameters that regulate the traction separation law and the damage evolution for CZM elements.

When the bond is formed in an adhesive joint, a complex interphase region at the interface between the adhesive layer and the substrate is formed [24]. This region is formed because of the migration of reactive complexes from the substrate to the uncured polymeric structure of the adhesive, and it is characterized by heterogeneous morphology and chemical structure, and by a steep gradient in mechanical properties in the thickness direction, which leads to the formation of most of the observed post-cure residual stresses [25]. When adhesive joints are exposed to high humidity environments, the interphase region is responsible for the diffusion of moisture at the interface, which may cause corrosion and bond degradation.

Moisture can be transported across the bondline in a SLJ via diffusion in the polymeric structure of the adhesive, diffusion in the interphase and interfacial regions, and capillarity in the adhesive cavities [24,26]. Corrosive reactions can occur at the interface when significant moisture transport happens in the interphase region of the adhesive layer. Kinloch et al. [27] observed that when adhesive joints were subjected to combined mechanical and environmental (high humidity) loads, the crack tip was an extremely favorable location to an accelerated corrosion mechanism. The alkaline environment due

to the formation of hydroxyl ions at the crack tip caused cathodic delamination, and segregation of charge-carrying species in the corroded region, thereby worsening the degradation of the bond. Surface deterioration was observed to increase and accelerate for dissimilar-substrate joints, due to phenomena of galvanic corrosion.

Cognard [28] observed that some adhesive joints bonded with an epoxy-amine adhesive showed blistering after being exposed to water vapour at high temperature and pressure. Smaller voids present in the interphase region diffuse under the osmotic pressure caused by moisture condensation, and merge, forming larger blisters. These blisters were thought to be partially responsible for the bond degradation in high-humidity environments.

The loss in mechanical performance experienced by adhesive joints subjected to environmental loads is not only caused by the deterioration of the chemical bonds between the adhesive and the substrates. Plasticization of the adhesive plays a major role, altering its viscoelastic properties [29]. At low concentrations, water molecules connect to polar sites in the polymeric chain of the adhesive via hydrogen bonds. At concentrations near saturation, clusters of water appear in the material, filling the voids between chains, causing adhesive swelling. The resulting depression of the glass transition temperature T_g of the adhesive reduces the elastic modulus of the interlayer, and advances nonlinearities in the stress-strain curve [30].

Nassar and Sakai [31,32] studied the effect of environmental cycling on the lap shear strength and the durability of multi-material lightweight SLJs with different joining methods. They observed that in some cases, and for some adhesives, exposure to high temperature and high humidity can have a positive effect on the static strength of bonded joints, if the cure was incomplete. However, the durability performance was greatly reduced. SLJs made with permeable, fiber-reinforced adherends were more susceptible to through-substrate moisture diffusion, which caused the bond degradation to accelerate.

Galvez et al. [33] investigated the effect of heat and humidity on the static lap shear strength of SLJs bonded with a one-component and a two-component polyurethane adhesive. In the first stages of humidity cycling, the two adhesives showed opposite behaviors: moisture diffusion and high temperature promoted further cure of the two-component polyurethane adhesive, confirming the findings of previous studies [31,32], while the strength of SLJs bonded with the one-component adhesive decreased immediately. High temperature and humidity content in the air are instrumental to the cure of two-component polyurethanes, catalyzing and initiating the crosslinking reaction [34]. When the SLJs were cycled at high temperature and low relative humidity, Galvez et al. observed that post-curing processes took place with both one- and two-component adhesives. For longer exposure times and higher temperatures, however, polymeric softening was followed by irreversible thermal degradation. Moisture penetrated and diffused exclusively near the interface between adhesive and substrate for the joints bonded with the two-component polyurethane adhesive, triggering interfacial failure for the aged SLJs. Conversely, water was transported by the interlayer as well as at the interface in joints bonded with the one-component polyurethane adhesive, showing mixed failure mode. Infrared spectroscopy was used to identify changes in the adhesive composition during the degradation process, but the spectra remained fundamentally unaltered. Differential Scanning Calorimetry (DSC) analysis, however, showed a gradual decrease in the glass transition temperature, confirming the plasticizing effect induced by moisture and temperature diffusion.

Mubashar et al. [35] developed a methodology to predict adhesive stresses under cyclic moisture conditioning. They observed that significant residual stresses were introduced via the curing process, but polymeric swelling as a result of moisture absorption caused some level of stress relief. Moreover, the strength loss due to moisture diffusion was observed to be partially reversible by slowly drying the SLJs after

conditioning, with some permanent damage to the adhesive layer. Moisture history-dependent material properties were used in a FEA model, which revealed that the peel stresses in the adhesive layer were largely unaffected by moisture diffusion, suggesting that the joint strength loss was primarily due to adhesive softening and not to bond degradation. Similarly, Sugiman et al. [36] investigated the effect of moisture on the static strength of aluminum SLJs bonded with epoxy film adhesive. Bulk adhesive testing showed a linear correlation between moisture content, swelling strains, and properties degradation (elastic modulus and tensile strength). Failure mode and damage evolution were monitored using backface strain technique (the joints were instrumented with strain gauges mounted on the adherends in correspondence to the edges of the bondline) and video microscopy. The backface strain curves were able to discriminate the damage in the adhesive layer more readily than the conventional load-displacement plots. The damage was observed to initiate at the end of the overlap, and the crack length at peak load was recorded, for dry and conditioned SLJs. The damaged portion of the adhesive layer was significantly larger in dry joints than for cycled specimens, which confirmed that moisture deteriorated the load carrying capacity of the adhesive.

Pereira et al. [37] studied the effect of saline environment on the static and fatigue behavior of high strength steel SLJs bonded with an epoxy-based adhesive. The joints were tested at baseline, and after conditioning in deionised water, neutral saline solution, and exposure to high temperature and humidity, for multiple exposure times. The coupons that were submerged in deionised water and saline solution showed a decrease in static strength that was proportional to the exposure time. The failure mode switched to adhesive (interfacial) because of the steel surface degradation caused by the corrosive action of the saline solution. The surface degradation also promoted multipoint failure initiation, for samples that were conditioned in the saline solution. The authors observed that the ingress and transport of moisture through the bondline occurred because of three

separate mechanisms: (a) diffusion in the adhesive layer, (b) transport along the interface, and (c) capillary action through cracks in the epoxy. Exposure to deionised water had a detrimental effect on the fatigue strength, but the joints that were conditioned in saline solution showed the largest reduction in fatigue life. Corrosion and degradation at the interface caused faster crack propagation.

In an experimental study, Hua et al. [38] subjected aluminum SLJs to salt spray cycles, and then measured their residual static strength. They observed an initial increase in strength for short exposure times, after which the mechanical properties of the joints decreased significantly with aging. The authors used Energy Dispersive Spectroscopy (EDS), infrared spectrum analysis, and optical microscopy to investigate the causes of the initial spike in static strength. Visual and optical analysis of the fracture surfaces suggested that adhesive hygroscopic swelling initially relieved the residual stresses that were created during the curing process: the fractured adhesive showed a smoother surface, without voids and microcracks, for aging times corresponding to the observed strength increase. EDS results confirmed that the failure mode had switched to the interface for samples with long exposure times. The analysis of the transmittance plots obtained by infrared spectroscopy highlighted a decrease in concentration of hydrogen bonds in the adhesive layer, which proved that moisture diffusion caused plasticization of the epoxy. The authors then concluded that two competing phenomena occur as a result of the exposure to salt spray cycles: (a) hygroscopic expansion allows the adhesive to relieve the residual stresses created by the curing process, increasing the strength of the SLJs, and (b) moisture causes plasticization of the adhesive layer, affecting the mechanical properties of the adhesive. After longer environmental exposure, the softening of the adhesive becomes the dominant factor affecting joint strength.

The effect of moisture diffusion in the adhesive layer of bonded SLJs before the completion of the cure process was investigated by Lu et al. [39]. Open-faced steel/epoxy

joints were aged in a hot-humid environment and subsequently assembled and cured. Water uptake tests were performed to estimate the extent of moisture diffusion in the adhesive layer. The results showed a steep decrease in static strength in the first 24 hours of environmental exposure, with longer time yielding less rapid deterioration. Fractography and EDS analyses highlighted discolored areas containing Zinc on the adhesive surface after failure. The authors concluded that when moisture diffusion occurs before the completion of the cure process, hydrolysis and plasticization of the epoxy are the primary causes of the decrease in quasi-static joint strength.

Zhang et al. [40] studied the effect of hygrothermal (humidity and heat) exposure on adhesively-bonded SLJs. Multi-material and aluminum joints were subjected to history-dependent humidity and temperature cyclic profiles, before quasi-static mechanical testing. For aluminum-only joints, the failure mode shifted to the interface, regardless of the type of environmental exposure. The extent of strength deterioration for multi-material samples was determined by the weaker interface, which depended on the dominant environmental agent: joints that were predominantly subjected to high temperature cycles showed extensive damage to the steel surface, while the aluminum/adhesive interface was responsible for the strength decrease for samples cycled at low temperature. Moreover, no correlation was observed between conditioning and aging history and strength loss. Hence, the authors concluded that the loss in static performance of bonded SLJs was driven by the cumulated environmental damage on the adhesive and the bond interface, and that accelerated conditioning at high temperature and humidity was representative of multiple exposure cycles.

1.2.4 Survey of Coupled Stress-Diffusion Analytical Models

The literature shows the need for analytical studies that include the effect of diffusive phenomena on the stress distribution in adhesive joints. Weitsman [41] analyzed

the bonding stresses at the adherend-adhesive interface when the exposed edges of the adhesive were subjected to moisture ingress and when the temperature of the entire joint was elevated. In this study, the author used variational calculus to calculate the plane-strain stresses in the adhesive layer, including effects from adhesive swelling (as a result of moisture and heat diffusion). The deformation of the adherends was neglected. First, the author analyzed the case of a totally constrained joint (in which the adhesive stresses derived from adhesive swelling alone), then the variational equations were solved for a completely unconstrained system. The stress distribution was obtained by superposition of the two particular solutions. The numerical calculations were performed for a commercially available epoxy adhesive, and moisture was assumed to diffuse in the interlayer according to Fick's law. A first order approximation for the swelling strains in the adhesive was obtained for the first 4 hours using the error function $\text{erf}(x)$, and the normal and shear stresses were calculated at 5 points in time, and for multiple values of adhesive thickness. Moisture and heat affected the stress distribution in the bondline, decreasing the peak stress in correspondance to the edges of the overlap, and increasing the stresses in the center of the joint. For the fully saturated case, the adhesive thickness did not have any effect on the peak stress at the edges of the adhesive, but the stress distribution was altered, with major changes at $x = 0$ (the center of the overlap).

Nassar and Mazhari [42] assumed that Fickian diffusion would control the one-dimensional moisture transport in the adhesive layer. The edges of the overlap were considered saturated, and the moisture concentration C at a location x in the bondline, at time t could then be described as

$$C(x,t) = 1 + \frac{2}{\pi} \sum_{m=1}^{\infty} \frac{(-1)^m - 1}{m} \sin \left[\frac{m\pi}{2c} \left(x + \frac{2c}{2} \right) \right] e^{\frac{-Dm^2\pi^2t}{(2c)^2}} \quad (1.4)$$

where D is the moisture diffusivity of the adhesive layer. The authors estimated that the minimum amount of terms required for the convergence of Equation (1.4) was dependent

on diffusion time: for a representative steel-to-steel SLJ bonded with an epoxy adhesive, while 1 month of moisture diffusion required 15 terms, only 1 term was needed for diffusion times longer than 2 years (i.e. steady state was reached). Linear and exponential scenarios formulating the relationship between moisture concentration and the elastic moduli of the adhesive were investigated; the linear scenario was found to be less computationally intensive and more representative of experimental data. Therefore, the shear modulus G_a of the adhesive that would alter Volkersen's original shear stress distribution could be written as

$$G_a(x, t) = G_0 + (G_\infty - G_0)C(x, t) \quad (1.5)$$

where G_0 and G_∞ are the dry and saturated values of the shear modulus G_a , respectively. The graph in Figure 1.5 compares the distribution of the shear stress τ_a in the bondline for dry and moisture-conditioned adhesive. In transient conditions, the softened edges of the adhesive layer contributed to a positive stress redistribution, with less severe deviations from the average shear stress model.

Mazhari and Nassar [43] extended their original approach [42] in a subsequent study. The authors derived the distribution of the peel stress σ_a in the adhesive layer, with the integration of the diffusion-dependent material model in the Goland-Reissner [3] and Hart-Smith [4] formulations. Adhesive softening was initially considered in the derivation of the bending moment and transverse shear M_0 and V_0 at the edges of the overlap. However, their values showed no appreciable change with diffusion time, and simplified material-independent formulas were used. Similarly to the previous, shear-only study, plasticization caused by moisture diffusion reduced the peak stresses at the limits of the bondline. Figure 1.6 shows the distribution of the peel stress σ_a in the adhesive layer in dry conditions, and after 200 days of diffusion, using the Hart-Smith [4] model.

Mazhari et al. [44] later implemented an elasto-plastic material model in the modified Hart-Smith formulation, and validated the results using FEA. The visco-elastic material properties allowed the authors to calculate the lap shear strength of the bonded joints, assuming that the failure mode remained fully cohesive (i.e. the bond at the interface was not affected). Several scenarios were analyzed, with different values of the ratio between the saturated and dry elastic moduli E_{∞}/E_0 of the adhesive. The results showed good correlation between FEA and the analytical model, with the lap shear strength dropping significantly after the first few months of moisture diffusion, then stabilizing once the adhesive layer asymptotically reached near-saturation.

The main shortcoming of these one-dimensional coupled stress-diffusion models is that they could not predict the negative effects of diffusion phenomena occurring transversally to the load axis, such as those described by Abdel Wahab et al [23]. One-dimensional diffusion helps redistribute the stress in the adhesive layer, reducing the peak stress values, as shown in Figures 1.5 and 1.6. Moisture diffusion from the lateral sides of a SLJ, however, would reduce the load carried by the plasticized portions of the adhesive, increasing the peak stress values in the dry center of the bondline.

Moisture is not the only environmental agent that causes adhesive softening: the elastic modulus of most structural adhesives decreases at high temperature. Furthermore, the interaction of heat and moisture diffusion in polymeric materials, especially in the form of rapidly increased moisture diffusivity at higher temperature, has been exhaustively studied in the literature [45], but it has not been applied to models able to calculate the stress distribution in SLJs.

1.3 Proposed Revision of Existing One-Dimensional Stress-Diffusion Models

In this section, a revision of the reviewed one-dimensional coupled stress-diffusion models [42,43] is proposed. The authors implemented location-dependent adhesive elastic

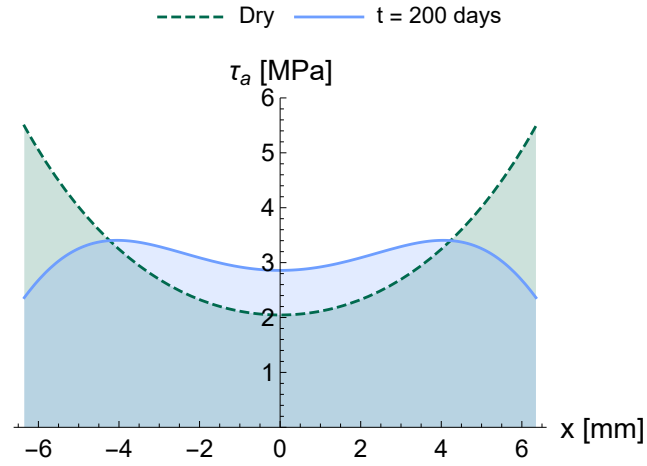


Figure 1.5: Shear stress τ_a before and after 200 days of moisture diffusion [42]

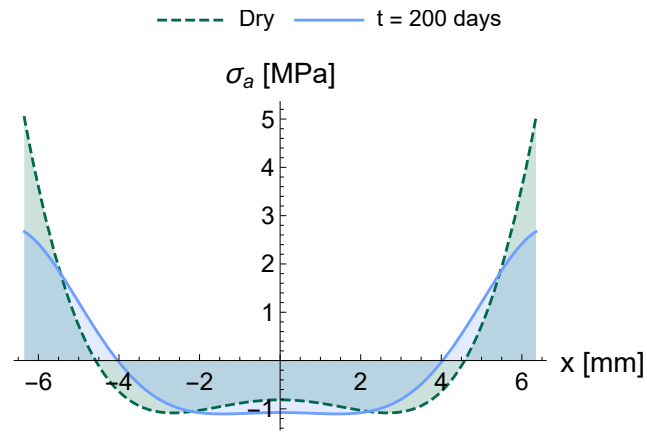


Figure 1.6: Peel stress σ_a before and after 200 days of moisture diffusion [43]

moduli in the classical models by Volkersen [2], Goland and Reissner [3], and Hart-Smith [4], obtaining complex constitutive equations that are substantially different from the original ones. Using Volkersen's model as an example, the original constitutive equation for the shear stress τ_a is

$$\frac{d^2\tau_a}{dx^2} - \frac{2G_a}{E_s t_s t_a} \tau_a = 0 \quad (1.6)$$

where t_s and t_a are the thickness of the substrates and of the adhesive, and E_s is the elastic modulus of the adherends. The shear stress distribution is found by imposing the appropriate boundary conditions at the edges of the overlap, given by

$$\frac{d\tau_a(\pm c)}{dx} = \mp \frac{PG_a}{E_s t_s t_a} \quad (1.7)$$

Once a location-dependent adhesive elastic modulus is considered, the constitutive equation becomes

$$\begin{aligned} \frac{d^2\tau_a}{dx^2} - \frac{2}{G_a(x)} \frac{dG_a}{dx} \left(\frac{d\tau_a}{dx} - \frac{1}{G_a(x)} \frac{dG_a}{dx} \tau_a(x) \right) \\ - \frac{1}{G_a(x)} \frac{d^2G_a}{dx^2} \tau_a(x) - \frac{2G_a(x)}{E_s t_s t_a} \tau_a(x) = 0 \end{aligned} \quad (1.8)$$

with boundary conditions given by

$$\frac{d\tau_a(\pm c)}{dx} = \frac{1}{G_a(\pm c)} \frac{dG_a(\pm c)}{dx} \tau_a(\pm c) \mp \frac{PG_a(\pm c)}{E_s t_s t_a} \quad (1.9)$$

Comparing Equations (1.6), (1.8), (1.7), and (1.9), the difference between the two constitutive formulations is significant. However, variable substitutions for the shear stress τ_a and the peel stress σ_a are introduced as

$$\zeta(x) = \frac{\tau_a}{G_a} \quad (1.10a)$$

$$\xi(x) = \frac{\sigma_a}{E_a} \quad (1.10b)$$

Using the variable $\zeta(x)$ in Equation (1.10a), the coupled stress-diffusion formulation in Equation (1.8) becomes identical to Volkersen's original model in Equation (1.6), and it can be simplified as

$$\frac{d^2\zeta}{dx^2} - \frac{2G_a}{E_s t_s t_a} \zeta = 0 \quad (1.11)$$

The boundary conditions are unified and simplified as well, and are given by

$$\frac{d\zeta(\pm c)}{dx} = \mp \frac{P}{E_s t_s t_a} \quad (1.12)$$

A solution can be numerically calculated for $\zeta(x)$, and the shear stress distribution can be obtained inverting Equation (1.10a). Similarly, it is possible to re-write the constitutive equations for the subsequent coupled stress-diffusion models [43], maintaining them identical to the classical formulations [3, 4]. The equation for the shear stress τ_a obtained using Goland and Reissner's model is

$$\frac{d^3\zeta}{dx^3} - \frac{8G_a}{E_s t_s t_a} \frac{d\zeta}{dx} = 0 \quad (1.13)$$

and it can be solved using the appropriate boundary conditions, given by

$$\int_{-c}^c \zeta(x) G_a(x) dx + P = 0 \quad (1.14a)$$

$$\frac{d\zeta(\pm c)}{dx} = \mp \frac{1}{E_s t_s t_a} \left(P + 6 \frac{M_0}{t_s} \right) \quad (1.14b)$$

The equations for the peel stress σ_a can be simplified to

$$\frac{d^4\xi}{dx^4} + \frac{2E_a}{D_1 t_a} \xi = 0 \quad (1.15)$$

and its boundary conditions are

$$\frac{d^2\xi(\pm c)}{dx^2} = \frac{M_0}{2b t_a D_1} \quad (1.16a)$$

$$\frac{d^3\xi(\pm c)}{dx^3} = \pm \frac{V_0}{2b t_a D_1} \quad (1.16b)$$

The constitutive equations for the stress-diffusion model that uses Hart-Smith's formulation are identical to Equations (1.13) through (1.16b), except for the last term of Equation (1.13), which contains the Poisson ratio of the adherends

$$\frac{[2 + 6(1 - \nu_s^2)]G_a}{E_s t_s t_a} \frac{d\zeta}{dx} \quad (1.17)$$

Without using the variable substitution in Equation (1.10a), Equation (1.13) becomes [43]:

$$\begin{aligned} \frac{d^3 \tau_a}{dx^3} - \frac{d^3 G_a}{dx^3} \frac{\tau_a(x)}{G_a(x)} - 3 \frac{d^2 G_a}{dx^2} \left(\frac{1}{G_a(x)} \frac{d\tau_a}{dx} - \frac{dG_a}{dx} \frac{\tau_a(x)}{G_a(x)^2} \right) \\ - \frac{8G_a(x)}{E_s t_s t_a} \frac{d\tau_a}{dx} - 3 \frac{dG_a}{dx} \left(\frac{d^2 \tau_a}{dx^2} \frac{1}{G_a(x)} - \frac{d^2 G_a}{dx^2} \frac{\tau_a(x)}{G_a(x)^2} - \right. \\ \left. \frac{2}{G_a(x)^2} \frac{dG_a}{dx} \frac{d\tau_a}{dx} + \left(\frac{dG_a}{dx} \right)^2 \frac{2}{G_a(x)^3} \tau_a(x) \right) = 0 \end{aligned} \quad (1.18)$$

with comparatively complex boundary conditions. A similar amount of terms can be found in Equation (1.15), if the variable substitution in Equation (1.10b) is not performed [43].

The dry and saturated values of the elastic moduli of the adhesive can significantly affect the calculated shear stress distribution. In the previous analytical studies [42–44], high values of Young's modulus were used ($E_0 = 6000$ MPa, $E_\infty = 2000$ MPa), typical only of very stiff, unmodified Epoxies [46, 47]. In dry conditions, these extreme material properties accentuated the difference between the shear stress at the center of the bondline and the peak stress located at the edges of the adhesive layer (Figure 1.5). In transient conditions, the plasticization of the adhesive portions at the ends of the overlap reduced significantly the peak shear stress.

However, the elastic modulus of a typical toughened epoxy adhesive is lower [35]. Using the properties of the toughened epoxy adhesive tested by Mubashar et al. [35] in Equation (1.11), the shear stress distribution shown in Figure 1.7a is obtained. The graph in Figure 1.7b presents the shear stress distribution for a SLJ bonded with a typical polyurethane adhesive, whose dry elastic modulus E_0 is equal to 1100 MPa [48]. The

peak stress values before and after 200 days of moisture diffusion are significantly closer together for joints bonded with toughened epoxy adhesive. A trend inversion is observed for the polyurethane adhesive: after moisture diffusion, the peak shear stress is located in the center of the bondline, and it is higher than the peak stress in the dry adhesive.

Nevertheless, the edges of the overlap still experience the maximum peel stress. The shear stress distribution after 200 days of moisture diffusion in Figure 1.7b follows closely the curve describing the location-dependent elastic modulus of the adhesive. This is due to the relatively low stiffness of the adhesive, which causes the shear stress distribution in dry conditions to only slightly deviate from the average shear stress. Therefore, a good approximation of the shear stress distribution when the SLJs are bonded with a relatively soft adhesive, can be obtained with a simpler formula (derived from the assumption of constant shear strain along x) as

$$\tau_a(x, t) = \frac{G_a(x, t)}{\int_{-c}^{+c} G_a(x, t) dx} P \quad (1.19)$$

The result of Equation (1.19) is compared in Figure 1.8 to the shear stress distribution calculated with Equation (1.11) and its boundary conditions, for the same polyurethane-based adhesive of Figure 1.7b and 200 days of moisture diffusion. For the considered adhesive material, with dry and saturated elastic moduli E_0 and E_∞ equal to 1100 MPa and 400 MPa, respectively, the simplified formula in Equation (1.19) approximates the shear stress distribution in the bondline with a maximum relative error of less than 5%.

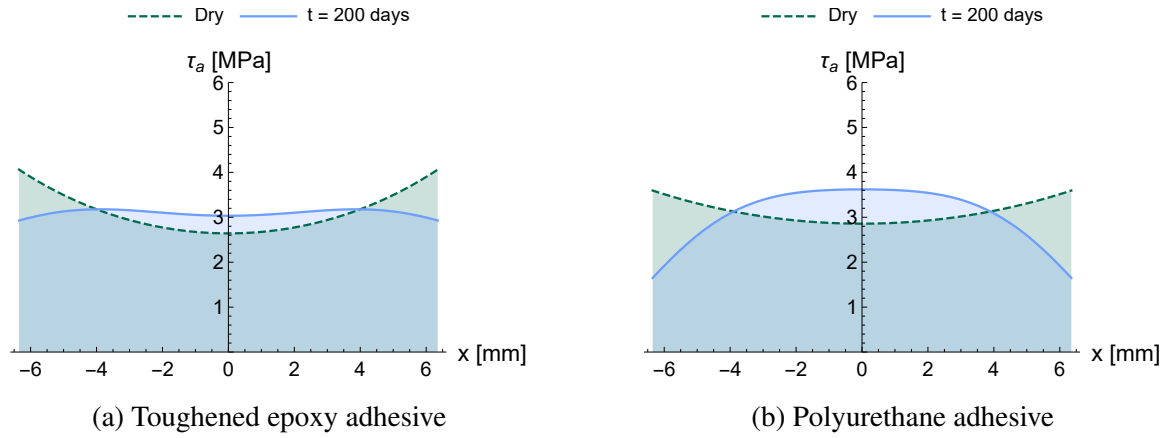


Figure 1.7: Shear stress τ_a for typical toughened epoxy (a) and polyurethane adhesives (b)

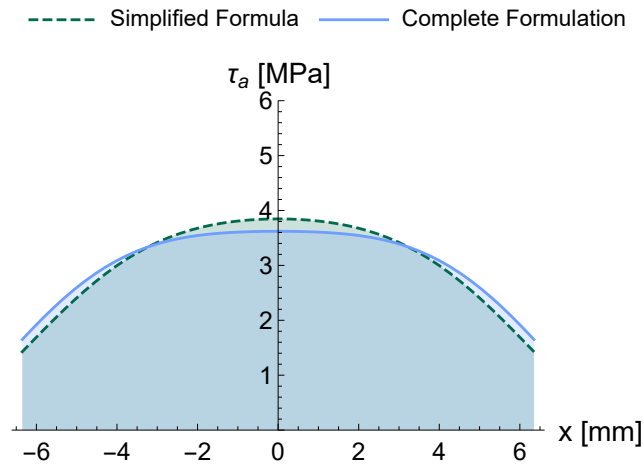


Figure 1.8: Simplified vs Complete formulation of shear stress τ_a for typical polyurethane adhesives

CHAPTER TWO

MODELING OF HEAT AND MOISTURE DIFFUSION

2.1 Introduction

The need for two-dimensional analytical studies that include the effect of diffusive phenomena on the stress distribution in adhesive SLJs is identified in the literature review in Chapter One. Existing one-dimensional models are capable of predicting the stresses in the adhesive layer when polymeric softening occurs along the longitudinal axis of the joint. The results from such studies tend to underestimate the negative effects of diffusive phenomena, as initially recognized by Abdel Wahab et al [23].

In this Chapter, the effect of two- and three-dimensional heat and moisture diffusion on the elastic properties of the adhesive is discussed, and a material model for the bondline layer is developed. The effects of the diffusion of heat and moisture are first investigated as separate phenomena, then as they interact in the adhesive layer. Heat transfer preferably takes place through the thickness of the SLJ, and a scenario with heat-insulated adherends is considered. Moisture ingress and Fickian diffusion into the adhesive layer are modeled from the sides of the SLJ, and the moisture concentration in the bondline can be described solving the two-dimensional heat equation. The elastic properties of the adhesive are then calculated using the location- and time-dependent values of temperature and moisture concentration.

A mid-thickness slice of the bond area is shown in Figure 2.1. The origin is located at the mid-thickness of the adhesive layer. The bond area is defined by $-c \leq x \leq c$ and $-b \leq y \leq b$. The bond thickness is defined by $-t_a/2 \leq z \leq t_a/2$. $2c$ and $2b$ are the length and the width of the bondline, respectively.

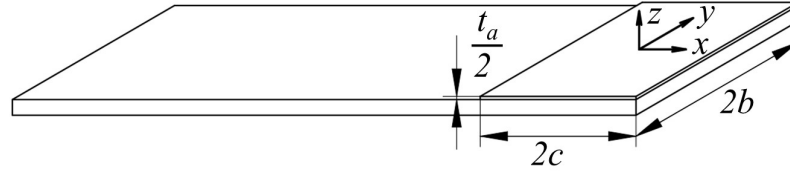


Figure 2.1: Bond area geometry

2.2 Heat Diffusion

Heat transfer can occur along the three main axes of a SLJ. However, geometry and materials of typical joints are usually markedly favorable to diffusion taking place through the thickness of the SLJs, which becomes the dominant heat flow direction. The full thickness of the joint sandwich, which includes the two adherends and the adhesive layer, is typically between 2 and 8 mm, while values of width and length of the overlap in standard SLJs are between 12.5 and 25.4 mm. Moreover, when metallic adherends are employed (steel, aluminum, and magnesium being the most common examples [15]), their extremely high conductivity relative to the adhesive layer greatly reduces the thermal resistance of the joint in the through-thickness direction.

2.2.1 Insulated Adherends

A schematics of the heat flow into the adhesive layer of SLJs with insulated adherends is shown in Figure 2.2. Heat diffusion takes place from the sides towards the center of the bondline, via conduction in the adhesive, and it is driven by the heat flux from the environment to the edges of the overlap.

The 2-D heat equation is used to describe the temperature distribution in the adhesive layer when the adherends are insulated. When the values of adhesive conductivity k_a , mass density ρ_a , and specific heat c_a are known, the 2-D heat equation

can be written as

$$\frac{\partial T}{\partial t} = \frac{k_a}{\rho_a c_a} \Delta T(x, y, t) \quad (2.1)$$

where $T(x, y, t)$ is the temperature in a generic (x, y) location in the adhesive layer, at the instant t , and Δ is the Laplace operator. Convective boundary conditions can be applied at the edges of the bond area, causing a temperature gradient to form across the adhesive layer, and are given by

$$(\nabla T \cdot \vec{n})|_{\partial\Omega} = h[T_h - T(\partial\Omega, t)] \quad (2.2)$$

where h is the convective heat transfer coefficient, $\vec{n}$ is the vector normal to the boundary $\partial\Omega$ of the adhesive layer, and T_h is the air temperature. The heat equation is solved numerically for the temperature distribution $T(x, y, t)$.

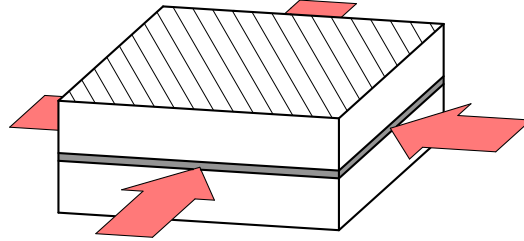


Figure 2.2: Heat Flow into SLJ with Insulated Adherends

2.2.2 Through-thickness Heat Diffusion

A schematics for the heat flow into a SLJ with non-insulated adherends is shown in Figure 2.3. Heat flows from the environment to the boundary of the joint, and transfers through the thickness of the overlap, in addition to diffusion from its sides, as in the case with insulated adherends.

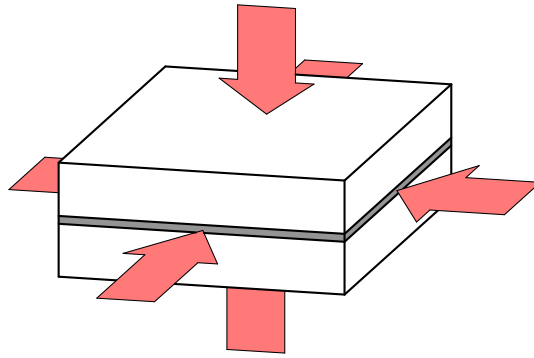


Figure 2.3: Heat Flow into SLJ with Non-Insulated Adherends

Because of the thin aspect ratio of conventional SLJs, when heat transfer occurs along the joint thickness direction, volume conductivity greatly outperforms surface convection. The Biot number (Bi) is a dimensionless quantity that is used to determine whether temperature gradients can be neglected, and is defined as

$$Bi = \frac{h}{k}L \quad (2.3)$$

For a SLJ with through-thickness heat diffusion, k and L are the thermal conductivity and the thickness of the joint sandwich, respectively. The Biot number for conventional bonded joints is $0.002 < Bi < 0.005$; values of $Bi < 0.1$ usually indicate negligible

temperature gradients along the characteristic length L [49]. Therefore, a lumped-mass model can be used to describe the thermal state of the joint. For joints with non-insulated adherends, the temperature in the adhesive layer is a function of time t only and it can be defined as

$$T(t) = T_h + (T_i + T_h) \cdot e^{-\frac{2h}{\rho_a c_a t_a + \rho_{su} c_{su} t_{su} + \rho_{sl} c_{sl} t_{sl}}} \quad (2.4)$$

where T_i is the initial temperature of the SLJ. The quantities t , c , and ρ are the thickness, the specific heat capacity, and the mass density of upper adherend, lower adherend, and adhesive, with respective subscripts su , sl , and a .

Guided by previous studies by Anasiewicz and Burchardt [47,48], the Young and Shear moduli E_a and G_a of the adhesive are varied linearly with temperature, according to

$$E_a(x, y, t) = E_{a\text{RT}} \{1 + \alpha_E [T(x, y, t) - T_0]\} \quad (2.5a)$$

$$G_a(x, y, t) = G_{a\text{RT}} \{1 + \alpha_G [T(x, y, t) - T_0]\} \quad (2.5b)$$

where α_E and α_G are empirical quantities that relate temperature and material properties, and the suffix RT refers to the room temperature T_0 (20 °C).

2.3 Moisture Diffusion

Moisture ingress from the sides of the overlap ($x = \pm c$, $y = \pm b$) and transport through the adhesive layer are modeled using the 2-D heat equation, given by

$$\frac{\partial C}{\partial t} = D^2 \Delta C(x, y, t) \quad (2.6)$$

where $C(x, y, t)$ is the moisture concentration relative to its saturated value at a generic location (x, y) at the time instant t , and D is the moisture diffusivity coefficient. When the joint is submerged in water, the edges of the bond area are saturated. The applied set of boundary conditions is

$$C(\pm c, y, t) = 1, \quad C(x, \pm b, t) = 1 \quad (2.7)$$

An analytical solution is available for Equation (2.6) with the boundary conditions in Equation (2.7). The moisture content in the adhesive layer at time t is given by

$$C(x,y,t) = 1 - \frac{16}{\pi^2} \sum_m \sum_n \frac{1}{(2m+1)(2n+1)} \sin\left(\frac{(2n+1)\pi(x+c)}{2c}\right) \sin\left(\frac{(2m+1)\pi(y+b)}{2b}\right) e^{-D^2\pi^2\left(\frac{(2n+1)^2}{4c^2} + \frac{(2m+1)^2}{4b^2}\right)t} \quad (2.8)$$

where the quantities $2b$ and $2c$ are the width and the length of the bond area, respectively, and the origin for the x and y coordinates is in the center of the joint, as shown in Figure 2.1. Guided by the previous studies by Nassar and Mazhari [42–44], the elastic properties of the adhesive vary linearly with moisture concentration, between dry and saturated values, as

$$E_a(x,y,t) = E_{a0} + (E_{a\infty} - E_{a0}) C(x,y,t) \quad (2.9a)$$

$$G_a(x,y,t) = G_{a0} + (G_{a\infty} - G_{a0}) C(x,y,t) \quad (2.9b)$$

The subscripts 0 and ∞ refer to the dry and saturated quantities, respectively.

2.4 Effect of Elevated Temperature on Moisture Diffusion

The temperature of the bulk material affects the diffusion of moisture into most polymers used for structural adhesive applications [45, 50]. Moisture diffusion accelerates significantly with temperature, following an Arrhenius law, and the diffusivity coefficient can be written as

$$D(T) = D_0 \exp\left(-\frac{E_D}{kT}\right) \quad (2.10)$$

E_D is a material-specific energy barrier to diffusion, $k = 8.83 \times 10^{-5}$ eV/K is the Boltzmann constant, and D_0 is the asymptotic value of the diffusivity coefficient. Both material constants E_D and D_0 can be determined experimentally, and typical values for epoxy-based and polyurethane-based adhesives can be found in the literature [50].

Jansen et al. [51] analyzed the water absorption of epoxy specimens at different temperatures, confirming the validity of the law in Equation (2.10) in both the absorption and desorption phases. The mechanism that drives the relationship in Equation (2.10) is still largely unknown, but several theories have been proposed. Studies by Yang et al. [52] and Jansen et al. [51] have hypothesized that the increase in moisture diffusivity at high temperatures is partly due to the increased molecular activity in the dispersion-type bonds that are typical of crosslinked, heat-cured long polymer chains. However, this effect alone does not explain the significant acceleration of diffusive phenomena when the temperature increase is moderate (10 - 20 °C) [45]. According to a second theory advanced by the same authors [51,52], thermal expansion could be the primary cause of the decreased resistance to moisture diffusion. When the material swells, water molecules are transported more easily through the polymeric chains. According to Jansen et al. [51], thermal expansion could also explain an observed rise in absolute moisture concentration at saturation, with higher water uptake in increased free volumes and micro cavities. The absolute saturation concentration C_{∞}^{abs} correlates linearly to temperature [51], and is

$$C_{\infty}^{\text{abs}} = a_1 + a_2 T \quad (2.11)$$

where a_1 and a_2 are material constants [45,51]. Accordingly, the saturated elastic moduli $E_{a\infty}$ and $G_{a\infty}$ of the adhesive vary with temperature, and are given by

$$E_{a\infty}(T) = E_{a\infty}(T_0) \cdot \frac{a_1 + a_2 T_0}{a_1 + a_2 T} \quad (2.12a)$$

$$G_{a\infty}(T) = G_{a\infty}(T_0) \cdot \frac{a_1 + a_2 T_0}{a_1 + a_2 T} \quad (2.12b)$$

In general, diffusion of heat through the adhesive layer occurs at a much faster rate than moisture diffusion, regardless of whether it happens through the thickness of the overlap, or only from the joint sides. The lowest positive net heat flux into the adhesive

layer is obtained with convective boundary conditions, and insulated adherends. Meanwhile, moisture diffusion is fastest at high temperature, and extremely slow in ambient conditions. Assuming temperatures close to the boiling point of water at atmospheric pressure ($T = 100\text{ }^{\circ}\text{C}$), the square of the moisture diffusivity D_0^2 for structural adhesives is several orders of magnitude smaller than the thermal diffusivity $k_a/(\rho_a c_a)$. Therefore, the two sets of differential equations governing heat and moisture diffusion in the adhesive layer (Equations (2.1) and (2.6)) can be decoupled in the time domain. When the bond area is simultaneously exposed to both heat and moisture, the temperature of the adhesive can be considered equal to the ambient temperature, uniformly along the bondline, without introducing significant errors.

CHAPTER THREE

ELASTIC MODEL

3.1 Introduction

In this chapter, the derivation of the 2-D elastic formulations for the shear and peel stress distribution in the adhesive layer is discussed. The structure of the stress-diffusion model is shown in the flow chart in Figure 3.1. The heat and moisture diffusion equations are solved separately, and the results are included in the elastic model via the location- and time- dependent elastic moduli $E_a(x,y,t)$ and $G_a(x,y,t)$ of the adhesive.

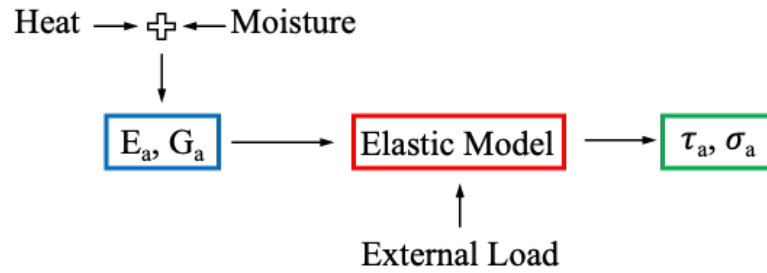


Figure 3.1: Flow chart of coupled stress-diffusion model

3.2 Constitutive Modeling of 2-D Shear Stress-Diffusion

Volkersen's approach [2] is expanded to formulate the two-dimensional shear stress-diffusion governing differential equations. The effects of the bending moment that results from the implicit imbalance of SLJs is still neglected. Diffusion only affects the elastic moduli E_a and G_a of the adhesive. Figure 3.2 shows the free body diagram of an infinitesimal section of lower and upper adherends; the subscripts u and l refer to upper

and lower substrates, respectively, that may be different in thickness and elastic moduli. It is assumed that both substrate materials would approximately have the same Poisson's ratio ν_s , however.

Following Volkersen's approach [2], the stress distribution $\tau_a(x, y)$ in the adhesive layer at the time instant t may be expressed as

$$\tau_a(x, y, t) = G_a(x, y, t) \frac{u_u - u_l}{t_a} \quad (3.1)$$

where u_u and u_l are the longitudinal displacements of the upper and lower adherends, respectively, and t_a is the adhesive thickness. Using the variable substitution for the shear stress $\zeta(x, y, t)$ defined in Equation (1.10a), the stress-displacement relationship of Equation (3.1) becomes

$$\zeta(x, y, t) = \frac{u_u - u_l}{t_a} \quad (3.2)$$

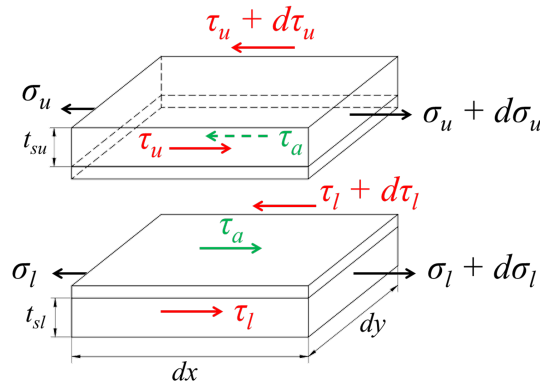


Figure 3.2: Free body diagram of infinitesimal sections of upper and lower adherends

If the thicknesses of the upper and lower adherends are written as t_{su} and t_{sl} , respectively, and the reference system defined in Figure 2.1 is used, the equilibrium

equations in the x (horizontal) direction are given by

$$\frac{\partial \sigma_u}{\partial x} = \frac{\partial \tau_u}{\partial y} + \frac{\zeta(x, y, t) G_a(x, y, t)}{t_{su}} \quad (3.3a)$$

$$\frac{\partial \sigma_l}{\partial x} = \frac{\partial \tau_l}{\partial y} - \frac{\zeta(x, y, t) G_a(x, y, t)}{t_{sl}} \quad (3.3b)$$

Recalling Hooke's law, the normal strain in the upper and lower adherends can be written as

$$\frac{du_u}{dx} = \frac{\sigma_u}{E_{su}} \quad (3.4a)$$

$$\frac{du_l}{dx} = \frac{\sigma_l}{E_{sl}} \quad (3.4b)$$

where E_{su} and E_{sl} are the elastic moduli of the upper and lower adherends, respectively.

Differentiating Equation (3.2) and substituting Equations (3.4a) and (3.4b), gives

$$\frac{\partial \zeta}{\partial x} = \frac{1}{t_a} \left(\frac{\sigma_u}{E_{su}} - \frac{\sigma_l}{E_{sl}} \right) \quad (3.5)$$

Differentiating Equation (3.5) along x gives

$$\frac{\partial^2 \zeta}{\partial x^2} = \frac{1}{t_a} \left(\frac{1}{E_{su}} \frac{\partial \sigma_u}{\partial x} - \frac{1}{E_{sl}} \frac{\partial \sigma_l}{\partial x} \right) \quad (3.6)$$

Substituting Equations (3.3a) and (3.3b) in Equation (3.6) returns

$$\frac{\partial^2 \zeta}{\partial x^2} = \left(\frac{1}{E_{su} t_{su}} + \frac{1}{E_{sl} t_{sl}} \right) \frac{G_a(x, y, t)}{t_a} \zeta(x, y, t) + \frac{1}{t_a} \left(\frac{1}{E_{su}} \frac{\partial \tau_u}{\partial y} - \frac{1}{E_{sl}} \frac{\partial \tau_l}{\partial y} \right) \quad (3.7)$$

Neglecting out-of-plane strain variations in the x direction ($\partial w_{su}/\partial x$ and $\partial w_{sl}/\partial x$, where w_{su} and w_{sl} are the transverse displacements of the upper and lower adherends, respectively), it is possible to re-write the terms defining the shear stress in the upper and lower substrates as

$$\tau_u = -G_{su} \frac{\partial u_u}{\partial y} \quad (3.8a)$$

$$\tau_l = -G_{sl} \frac{\partial u_l}{\partial y} \quad (3.8b)$$

Equation (3.2) can be differentiated along y , obtaining

$$\frac{\partial \zeta}{\partial y} = \frac{1}{t_a} \left[\frac{\partial u_u}{\partial y} - \frac{\partial u_l}{\partial y} \right] \quad (3.9)$$

Substituting Equations (3.8a) and (3.8b) into Equation (3.9), and differentiating once more along y gives

$$\frac{\partial^2 \zeta}{\partial y^2} = \frac{1}{t_a} \left[\frac{1}{G_{sl}} \frac{\partial \tau_l}{\partial y} - \frac{1}{G_{su}} \frac{\partial \tau_u}{\partial y} \right] \quad (3.10)$$

Recalling the assumption of equal Poisson ratios for the upper and lower adherend materials, Equation (3.10) can also be written as

$$\frac{1}{2(v_s + 1)} \frac{\partial^2 \zeta}{\partial y^2} = \frac{1}{t_a} \left[\frac{1}{E_{sl}} \frac{\partial \tau_l}{\partial y} - \frac{1}{E_{su}} \frac{\partial \tau_u}{\partial y} \right] \quad (3.11)$$

Finally, the constitutive equation given by the substitution of Equation (3.11) in Equation (3.7) may be expressed as

$$\frac{\partial^2 \zeta(x, y, t)}{\partial x^2} + \frac{1}{2(v_s + 1)} \frac{\partial^2 \zeta(x, y, t)}{\partial y^2} - \left(\frac{1}{E_{sutsu}} + \frac{1}{E_{sltsl}} \right) \frac{G_a}{t_a} \zeta(x, y, t) = 0 \quad (3.12)$$

The first and third terms of Equation (3.12) correspond to Volkersen's [2] model (Equation (1.11)). Boundary conditions are imposed on the 4 edges of the bond area. The two Neumann-type boundary conditions at $x = \pm c$ that match Volkersen's formulation are

$$\left. \frac{\partial \zeta}{\partial x} \right|_{x=c} = -\frac{F}{2E_{sutsu}t_a b} \quad (3.13a)$$

$$\left. \frac{\partial \zeta}{\partial x} \right|_{x=-c} = \frac{F}{2E_{sltsl}t_a b} \quad (3.13b)$$

where F is the applied tensile shear load. The two Robin-type boundary conditions at $y = \pm b$ are given by

$$\frac{\partial \zeta}{\partial y} G_a + \frac{\partial G_a}{\partial y} \zeta = 0, \quad y = \pm b \quad (3.14)$$

The solution to the governing differential equation in Equation (3.12) gives a distribution in the variable $\zeta(x, y, t)$. The shear stress distribution $\tau_a(x, y, t)$ may be

expressed as

$$\tau_a(x, y, t) = \zeta(x, y, t) G_a(x, y, t) \quad (3.15)$$

where the variable transformation $\zeta(x, y, t)$ is defined by Equation (1.10a).

3.3 Constitutive Modeling of 2-D Peel Stress-Diffusion

A 2-D peel stress-diffusion model is derived using Goland and Reissner's approach [3]. Normal stresses develop in the bondline as a result of bending moment and transverse shear in the joint overlap, caused by the unbalanced nature of SLJs. The diffusion of heat and moisture affects the elastic moduli of the adhesive, giving rise to a two-dimensional stress distribution. The free body diagram in Figure 3.3 shows the loads and stresses acting on a section of the overlap. In the upper adherend, the bending moment M_u , transverse shear V_u , and normal tensile/compressive load N_u are balanced by the shear and peel stresses τ_a and σ_a in the adhesive, and by the shear stresses τ_{uyz} and τ_{uyx} in the substrate. Similar loads and stresses are applied to the section of lower adherend, with subscript l . The two adherends are assumed to be equal in thickness and material.

Manipulations of the vertical equilibrium equations for the upper and lower adherend sections, with width dy , length dx , and thickness t_s give

$$\frac{\partial V_u}{\partial x} = t_s d\tau_{uyz} + dy \sigma_a(x, y, t) \quad (3.16a)$$

$$\frac{\partial V_l}{\partial x} = t_s d\tau_{lyz} - dy \sigma_a(x, y, t) \quad (3.16b)$$

Applying the variable transformation in Equation (1.10b), Equations (3.16a) and (3.16b) become

$$\frac{\partial V_u}{\partial x} = t_s d\tau_{uyz} + dy E_a(x, y, t) \xi_a(x, y, t) \quad (3.17a)$$

$$\frac{\partial V_l}{\partial x} = t_s d\tau_{lyz} - dy E_a(x, y, t) \xi_a(x, y, t) \quad (3.17b)$$

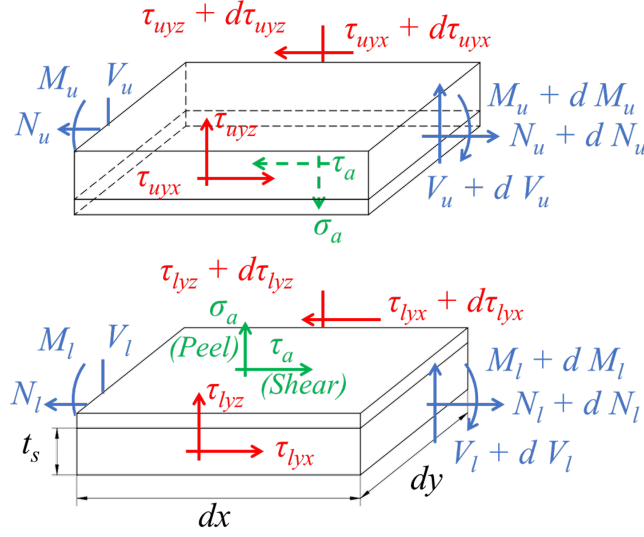


Figure 3.3: Free body diagram of infinitesimal sections of adherends with out-of plane stresses

Similarly, the equations for moment equilibrium in the adherends sections can be re-written as

$$\frac{\partial M_u}{\partial x} = V_u - \tau_a(x, y, t) dy \frac{t_s}{2} \quad (3.18a)$$

$$\frac{\partial M_l}{\partial x} = V_l - \tau_a(x, y, t) dy \frac{t_s}{2} \quad (3.18b)$$

Adapted equations from thin plate theory give the relationship between bending moment and adherend rotation, as

$$\frac{\partial^2 v_u}{\partial x^2} = -\frac{M_u}{D_1 dy} \quad (3.19a)$$

$$\frac{\partial^2 v_l}{\partial x^2} = -\frac{M_l}{D_1 dy} \quad (3.19b)$$

where D_1 is the flexural rigidity of the adherends, and v_u and v_l are the vertical displacements of upper and lower adherends, respectively. The stress-strain relationship in

the adhesive layer can be written as

$$\sigma_a(x, y, t) = E_a(x, y, t) \frac{v_u - v_l}{t_a} \quad (3.20)$$

Re-writing it with the variable substitution from Equation (1.10b) gives

$$\xi(x, y, t) = \frac{v_u - v_l}{t_a} \quad (3.21)$$

Differentiating Equation (3.21) twice along x , and substituting Equations (3.19a) and (3.19b), gives

$$\frac{\partial^2 \xi}{\partial x^2} = \frac{M_l - M_u}{D_1 t_a dy} \quad (3.22)$$

Equation (3.22) is differentiated once more along x , and is expressed as

$$\frac{\partial^3 \xi}{\partial x^3} = \frac{1}{D_1 t_a dy} \left(\frac{\partial M_l}{\partial x} - \frac{\partial M_u}{\partial x} \right) \quad (3.23)$$

Equations (3.18a) and (3.18b) are substituted in Equation (3.23), giving

$$\frac{\partial^3 \xi}{\partial x^3} = \frac{V_l - V_u}{D_1 t_a dy} \quad (3.24)$$

Equation (3.24) is differentiated one more time along x , and becomes

$$\frac{\partial^4 \xi}{\partial x^4} = \frac{1}{D_1 t_a dy} \left(\frac{\partial V_l}{\partial x} - \frac{\partial V_u}{\partial x} \right) \quad (3.25)$$

Equations (3.17a) and (3.17b) can be substituted in Equation (3.25), which gives

$$\frac{\partial^4 \xi}{\partial x^4} = \frac{t_s}{D_1 t_a} \left(\frac{\partial \tau_{lyz}}{\partial y} - \frac{\partial \tau_{uyz}}{\partial y} \right) - \frac{2E_a(x, y, t)}{D_1 t_a} \xi(x, y, t) \quad (3.26)$$

Neglecting out-of-plane strain variations in the z direction ($\partial w_{su}/\partial z$ and $\partial w_{sl}/\partial z$, where w_{su} and w_{sl} are the transverse displacements of the upper and lower adherends, respectively), it is possible to re-write and combine the terms defining the shear stress in the upper and lower substrates, as

$$\tau_{lyz} - \tau_{uyz} = G_s \left(\frac{\partial v_l}{\partial y} - \frac{\partial v_u}{\partial y} \right) \quad (3.27)$$

Differentiating Equation (3.27) along y , and substituting it in Equation (3.26) gives

$$\frac{\partial^4 \xi}{\partial x^4} = \frac{G_s t_s}{D_1 t_a} \left(\frac{\partial^2 v_l}{\partial y^2} - \frac{\partial^2 v_u}{\partial y^2} \right) - \frac{2E_a(x, y, t)}{D_1 t_a} \xi(x, y, t) \quad (3.28)$$

The second y -derivatives of the vertical displacements of the substrates can be obtained by differentiating the stress-strain relationship in Equation (3.21) twice along y , as

$$\frac{\partial^2 v_l}{\partial y^2} - \frac{\partial^2 v_u}{\partial y^2} = t_a \frac{\partial^2 \xi}{\partial y^2} \quad (3.29)$$

The fourth-order coupled stress-diffusion constitutive equation for the peel stress in the adhesive layer is obtained by substitution of Equation (3.29) in Equation (3.28), and it may be expressed as

$$\frac{\partial^4 \xi}{\partial x^4} + \frac{2E_a(x, y, t)}{D_1 t_a} \xi(x, y, t) - \frac{G_s t_s}{D_1} \frac{\partial^2 \xi}{\partial y^2} \quad (3.30)$$

The first boundary condition on the (c, y) edge of the overlap can be found by taking Equation (3.22) and imposing the bending moments M_l and M_u acting on the lower and upper adherends to be $M_l = M_0$ and $M_u = 0$. The constant M_0 is defined in Equation (1.1). Similarly, the first boundary condition on the edge located at $x = -c$ is found by substituting $M_l = 0$ and $M_u = -M_0$ in Equation (3.22), and is written as

$$\left. \frac{\partial^2 \xi}{\partial x^2} \right|_{x=\pm c} = \frac{M_0}{2b t_a D_1} \quad (3.31)$$

The second set of boundary conditions on the edges located at $x = \pm c$ is found by substituting $V_l = 0$ and $V_u = V_0$ at $x = -c$, and $V_l = V_0$ and $V_u = 0$ at $x = c$, giving

$$\left. \frac{\partial^3 \xi}{\partial x^3} \right|_{x=\pm c} = \pm \frac{V_0}{2b t_a D_1} \quad (3.32)$$

The constant V_0 is the value of transverse shear that is applied at the edges of the overlap, and it is given by the expression in Equation (1.2). The Robin-type boundary conditions

on the edges at $y = \pm b$ are given by

$$\left. \frac{\partial \xi}{\partial y} \right|_{y=\pm b} = 0 \quad (3.33)$$

The solution of Equation (3.30) with the application of the boundary conditions in Equations (3.31), (3.32), and (3.33) gives the value of $\xi(x, y, t)$ at all points in the adhesive layer. The peel stress distribution $\sigma_a(x, y, t)$ is obtained by multiplication of the variable $\xi(x, y, t)$ with the elastic modulus of the adhesive $E_a(x, y, t)$, which gives

$$\sigma_a(x, y, t) = \xi(x, y, t) \cdot E_a(x, y, t) \quad (3.34)$$

CHAPTER FOUR

EXPERIMENTAL CORRELATION BETWEEN BULK MATERIAL TEMPERATURE AND ELASTIC MODULI

4.1 Introduction

The relationship between adhesive temperature and bulk material properties is experimentally investigated in this chapter. When the temperature of thermoset, highly crosslinked polymers is raised above their glass transition temperature, the elastic modulus suffers a drastic drop, which is due to the loss in chain rigidity and to the increased intermolecular mobility [53]. Adhesives used in structural applications are polymers composed of several base chains (usually copolymers, although in rare cases epoxy adhesives can be cured by catalytic homopolymerization), and different additives are included in the formulation, to achieve the desired mechanical performance [53,54]. Due to these impurities that are incorporated in the polymer matrix, the drop in elastic modulus at temperatures approaching the glass transition temperature of structural adhesives is more gradual than in pure polymers. When the temperature is sufficiently far from the thermal degradation point, the effect of temperature on the polymeric softening and on the mechanical properties of the adhesive can be approximated using a linear law [54,55].

4.2 Experimental Setup

The elastic moduli of two 2-component structural adhesives - a polyurethane-based and a toughened epoxy-based adhesive - are tested in a DMA Q800. A centrifugal mixer is used to ensure proper mixing of resin and hardener, and the uncured adhesive is pressed between two plates to form a single 0.2 mm-thick sheet. The sheet is then cured in an oven according to the manufacturer specifications, with controlled temperature ramps of ± 1 °C/min to minimize residual stresses. Samples are obtained by cutting thin

rectangular fibers out of the adhesive sheet. An epoxy adhesive specimen is shown in Figure 4.1a, next to a portion of the cured adhesive sheet. The relatively small dimensions of the bulk adhesive samples (Figure 4.1b) allow to minimize the heat capacity of the specimen.

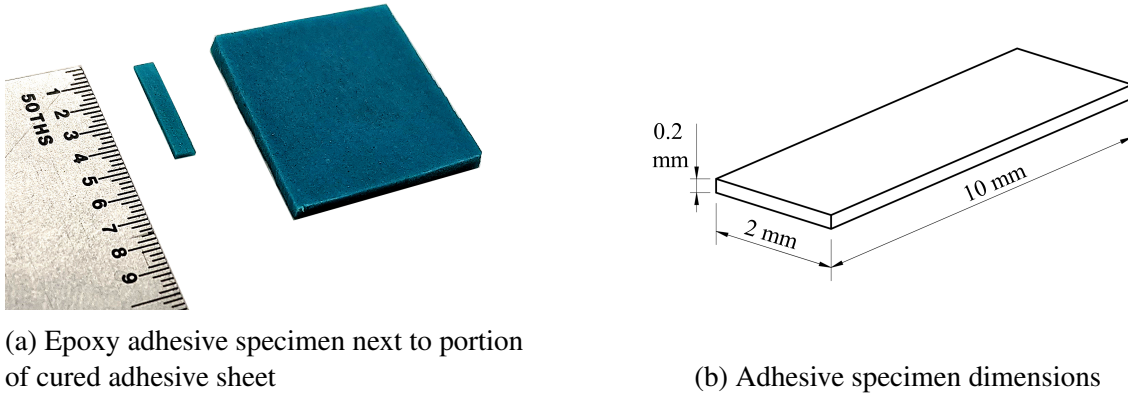


Figure 4.1: Geometry and photograph of an epoxy adhesive tensile test specimen

The specimens are mounted in the DMA Q800 using the thin film/fiber fixture, as shown in Figure 4.2, and a torque of 0.45 Nmm is applied to tighten the two holding screws. The gauge length is measured automatically, and the low stiffness of the adhesive sample allows to neglect the deformation of the frame. The temperature of the furnace is raised at a rate of 1 °C/min while the specimen is unloaded, and a dwell period of 60 minutes after the target temperature is reached ensures that the adhesive is in thermal equilibrium with the surrounding air. Temperature readings are taken using the two thermocouples located in the furnace. Tensile tests are performed, at a strain rate of 0.5 s⁻¹, until a force reading of 5 N, or yielding of the specimen are detected.



Figure 4.2: Epoxy adhesive specimen mounted on thin film/fiber fixture

Engineering stress-strain curves are drawn for the tested specimens. The bulk adhesive elastic modulus is obtained by measuring the slope of the curve in the linear portion. At lower temperatures, negligible plasticity is observed. However, when nonlinearities become significant, the elastic modulus is obtained by calculating the slope of the linear intercept at the point of 0.2% permanent set. The polyurethane and epoxy samples were tested at 10 °C temperature increments, from Room Temperature (20 °C) to 90 °C. Three samples are tested at each temperature, and the results are averaged.

4.3 Test Data

Table 4.1 the results for the epoxy and polyurethane bulk adhesive specimens. Values of Standard Deviation (SD) are included. For test temperature ranging from 20°C to 70°C, the polyurethane samples exhibited a significantly lower elastic modulus than the

epoxy adhesive. Moreover, at temperatures above 70°C, the stiffness of the polyurethane specimens was too low to obtain reliable readings, and the results are omitted from Table 4.1. The test data is plotted in the graph in Figure 4.3. Linear curve fitting was performed with MATLAB[®] software, using the appropriate toolbox. Vertical error bars represent the SD of the data at each temperature point. The calculated values of the empirical quantity α_E used in Equation (2.5a) are shown in Table 4.2, for the epoxy and the polyurethane adhesives.

Table 4.1: Adhesive Elastic Moduli Vs. Bulk Material Temperature

Temperature (°C)	Epoxy		Polyurethane	
	Elastic Modulus (MPa)	SD (MPa)	Elastic Modulus (MPa)	SD (MPa)
20	1,585	61	980	42
30	1,490	47	874	98
40	1,401	106	745	75
50	1,232	32	674	66
60	1,121	117	467	91
70	920	163	298	58
80	700	79	-	-
90	500	24	-	-

Table 4.2: Values of α_E for epoxy and polyurethane adhesive

	Epoxy	Polyurethane
α_E (°C ⁻¹)	-9×10^{-3}	-1.2×10^{-2}

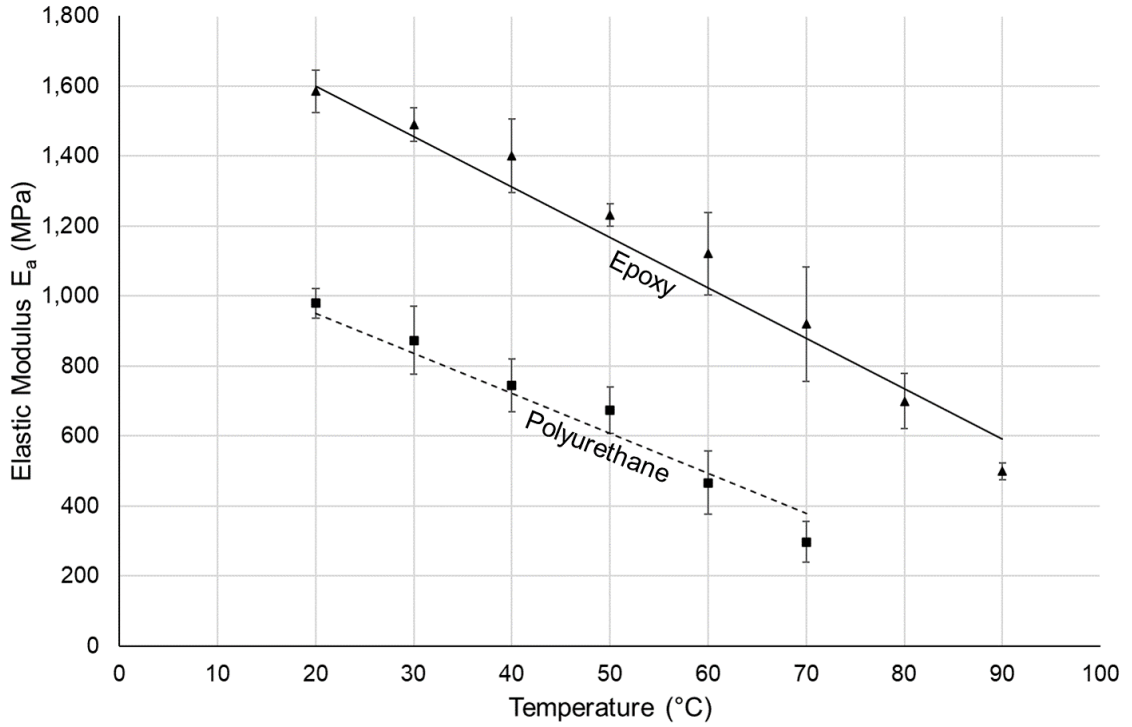


Figure 4.3: Elastic modulus of epoxy and polyurethane adhesive, with 1σ error bars

In this dissertation, the material properties of the epoxy adhesive in Table 4.2 are used in the elastic model. The low elastic modulus of the polyurethane adhesive, and the lower drop at higher temperatures, result in shallower stress distribution in the adhesive layer, and in less observable differences between the effects of loading and environmental conditions. Moreover, the larger temperature range in which it was possible to collect data for the epoxy bulk adhesive allows for wider scenarios of interaction between heat and moisture diffusion.

CHAPTER FIVE

EFFECT OF HEAT DIFFUSION ON THE STRESS DISTRIBUTION IN ADHESIVE JOINTS

5.1 Introduction

In this chapter, a 2-D model is proposed for the effect of heat diffusion on the distribution of shear and peel stresses in the adhesive. Stresses are formulated for various scenarios of heat diffusion in the bond area defined by $-c \leq x \leq c$ and $-b \leq y \leq b$ (Figure 2.1). The evolution of the stresses in time is visualized with the help of section cuts at different y locations, until thermal equilibrium with the surrounding environment is reached. Observations and conclusions are provided.

5.2 Heat diffusion in the adhesive layer: non-insulated adherends

Heat diffusion in a SLJ with non-insulated adherends is dominated by the heat flow in the through-thickness direction. The Biot number (Equation (2.3)) for typical adhesive SLJs is at least 1 order of magnitude within the threshold under which the temperature of the joint can be described with a lumped-mass model as in Equation (2.4) [49]. In this section, the heat equation is solved for a SLJ subjected to through-thickness heat diffusion, and the results are compared with the output of Equation (2.4).

5.2.1 Piecewise heat equation

When heat flows through the exposed faces of the adherends, with convective boundary conditions, the temperature at any point of the SLJ can be described with the

sets of partial differential equations given by

$$\begin{cases} \frac{\partial T}{\partial t} - \frac{k_{su}}{\rho_{su}c_{su}} \frac{\partial^2 T}{\partial z^2} = 0 & t_a/2 \leq z \leq t_{su} + t_a/2 \\ \frac{\partial T}{\partial t} - \frac{k_a}{\rho_a c_a} \frac{\partial^2 T}{\partial z^2} = 0 & -t_a/2 \leq z \leq t_a/2 \\ \frac{\partial T}{\partial t} - \frac{k_{sl}}{\rho_{sl}c_{sl}} \frac{\partial^2 T}{\partial z^2} = 0 & -t_{sl} - t_a/2 \leq z \leq -t_a/2 \end{cases} \quad (5.1a)$$

$$\begin{cases} \frac{\partial T}{\partial z} \Big|_{z=(t_{su}+\frac{t_a}{2})} = -h [T_h - T(t_{su} + \frac{t_a}{2}, t)] \\ \frac{\partial T}{\partial z} \Big|_{z=-(t_{sl}+\frac{t_a}{2})} = h [T_h - T(-t_{sl} - \frac{t_a}{2}, t)] \\ T(z, 0) = T_i \\ T\left(z \rightarrow \frac{t_a}{2}^+, t\right) = T\left(z \rightarrow \frac{t_a}{2}^-, t\right) \\ T\left(z \rightarrow -\frac{t_a}{2}^+, t\right) = T\left(z \rightarrow -\frac{t_a}{2}^-, t\right) \\ k_{su} \frac{\partial T}{\partial z} \Big|_{z \rightarrow \frac{t_a}{2}^+} = k_a \frac{\partial T}{\partial z} \Big|_{z \rightarrow \frac{t_a}{2}^-} \\ k_a \frac{\partial T}{\partial z} \Big|_{z \rightarrow -\frac{t_a}{2}^+} = k_{sl} \frac{\partial T}{\partial z} \Big|_{z \rightarrow -\frac{t_a}{2}^-} \end{cases} \quad (5.1b)$$

where T_i denotes the initial temperature of the SLJ.

Continuity of temperature T and heat flux $k \cdot \partial T / \partial z$ at the adhesive/substrate interfaces is imposed in the last 4 terms in Equation (5.1b). A numerical solution for the set of piecewise-defined heat equations is calculated using Wolfram Mathematica[©] software. Most numerical solvers do not allow the definition of boundary conditions in the integrating domain, but the solution of a system of n-th order partial differential equations is an n-1 continuous function. Therefore, a substitution for the spatial variable is needed in order to guarantee continuity at the interfaces, and it may be expressed as

$$d\eta = dz \cdot k \quad (5.2)$$

where k is a piecewise-defined function in z that is equal to the respective thermal conductivity of the substrates and the adhesive. An equality can be written as

$$\frac{\partial T}{\partial \eta} = k \frac{\partial T}{\partial z} \quad (5.3)$$

A first-order continuous solution to Equation (5.1a) is found for $T(\eta)$. Recalling the equality in Equation (5.3), the solution guarantees continuity of temperature and heat flux at $z = \pm t_a/2$.

5.2.2 Temperature distribution in the adhesive layer

The temperature profile in Figure 5.1 is obtained for a SLJ with similar adherends, and with geometric and thermal properties listed in Table 5.1, after 100 seconds of forced convection on the exposed faces of the substrates. The mid-thickness section of the adhesive layer experiences the lowest temperature.

Table 5.1: Parameters for through-thickness heat diffusion

Variable	Value and Unit	
$t_{su} = t_{sl}$	1.6	mm
t_a	0.2	mm
$k_{su} = k_{sl}$	50.2	W m ⁻¹ K ⁻¹
k_a	0.2	W m ⁻¹ K ⁻¹
$c_{su} = c_{sl}$	420	J kg ⁻¹ K ⁻¹
c_a	1000	J kg ⁻¹ K ⁻¹
$\rho_{su} = \rho_{sl}$	8005	kg m ⁻³
ρ_a	1250	kg m ⁻³
h ($v = 1\text{m/s}$)	22.5	W m ⁻² K ⁻¹
T_h	80	°C
T_i	20	°C

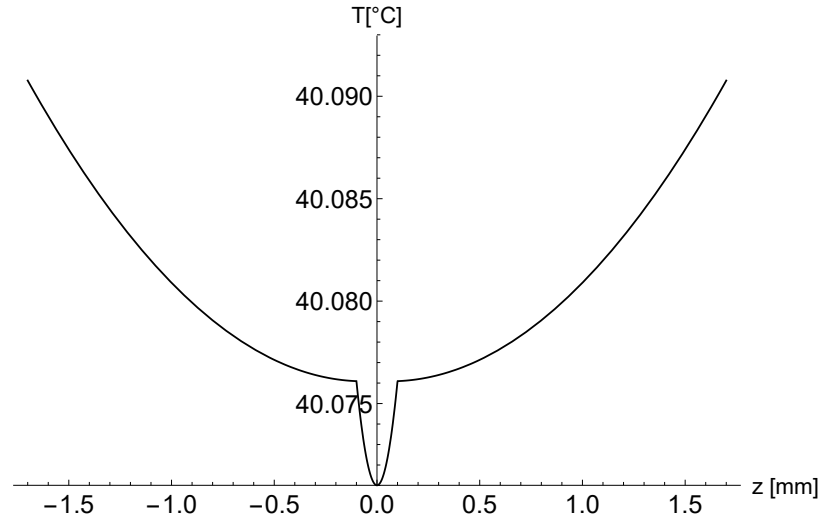


Figure 5.1: Temperature distribution across the thickness of SLJ with non-insulated, steel adherends after 100 s (convection)

The temperature gradient in Figure 5.1 across the thickness of the SLJ is negligible, as originally suggested by the low value of the Biot number obtained with Equation (2.3). The graph in Figure 5.2a contains a comparison between the mid-thickness adhesive temperature obtained from the solution of Equation (5.1a) and the results from the lumped-mass model in Equation (2.4). The two lines are fully superimposed, and the magnitude of the relative error shown in Figure 5.2b is well below 0.1%. After 1000 seconds, the temperature of the adhesive layer is within 1 °C of thermal equilibrium.

When the adherends are made of fiber-reinforced composite materials with an epoxy matrix, the specific heat capacity, mass density, and heat conductivity can be assumed to be invariant across the joint thickness. The resulting temperature distribution across the thickness of the joint is shown in Figure 5.3, for an exposure time of 100 seconds. The boundary conditions and the SLJ geometric properties listed in Table 5.1 are applied. The temperature gradient in the joint is more significant than for SLJs with metallic adherends, because of the lower thermal conductivity of the substrates. The Biot

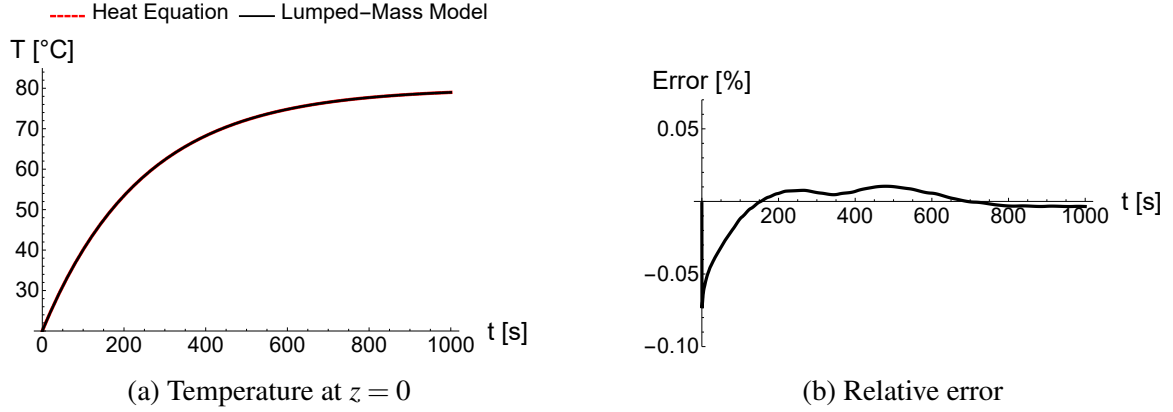


Figure 5.2: Temperature and relative error at $z = 0$ mm calculated with Eqs. (2.4) and (5.1a) (steel adherends)

number is equal to 0.38 when the entire joint thickness is considered, and it drops below 0.1 when only the portion of heat conduction that occurs across the adhesive layer is taken into account.

The comparison with the lumped-mass model is shown in the graph in Figure 5.4a, and the relative difference between the two models is plotted in Figure 5.4b. The magnitude of the error introduced by the lumped-mass model exceeds 10% in the first instants, reducing to 5% after 30 seconds, and stabilizing to values below 1% after 1 minute. In particular, the higher relative difference observed in the first 15 seconds is caused by the lower initial temperature: the absolute error does not exceed 3 °C, and remains lower than 1 °C after 1 minute of exposure. Counter-intuitively, significantly less time is required to reach a state of near-thermal equilibrium for a SLJ with composite adherends when compared to a steel joint. The higher specific heat capacity of the epoxy resin is more than offset by the higher mass density of steel.

The unrealistic scenario of fixed-temperature heat conduction at the exposed faces of the adherends is worth exploring, for its peculiar results. Assuming perfect contact between the steel adherends and an external body of temperature T_h , thermal equilibrium

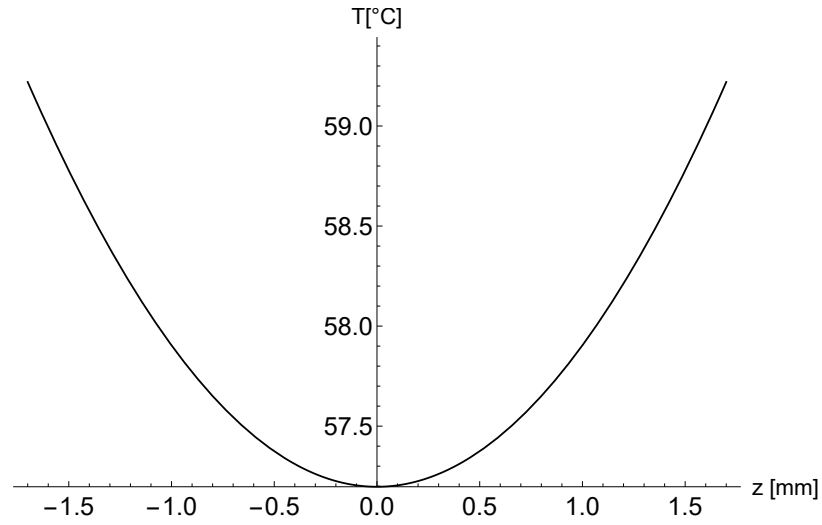


Figure 5.3: Temperature distribution across the thickness of a SLJ with non-insulated, composite adherends after 100 s (convection)

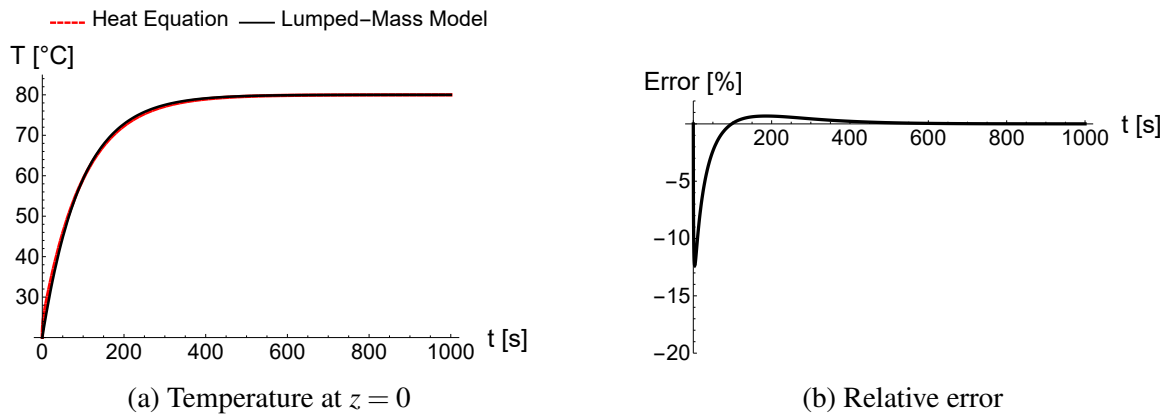


Figure 5.4: Temperature and relative error at $z = 0$ mm calculated with Eqs. (2.4) and (5.1a) (composite adherends)

is reached in the first few seconds. The temperature distribution across the thickness of the SLJ is shown in the graphs in Figures 5.5a and 5.5b, after 0.15 and 1.5 seconds of heat conduction, respectively.

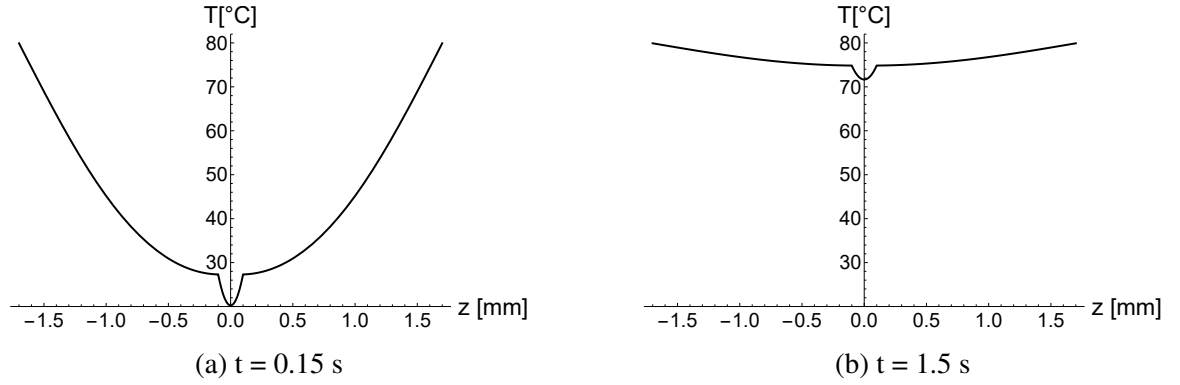


Figure 5.5: Temperature distribution across the thickness of a SLJ with non-insulated adherends (conduction)

When a lumped-mass model is used to describe the bondline temperature, the elastic modulus of the adhesive is not dependent on the coordinates (x, y) , and it can be derived from Equation (2.5a). The graphs in Figures 5.6a and 5.6b show the time evolution of the elastic modulus for steel and composite joints, respectively, subjected to forced convection at 80 °C. The material properties of the epoxy adhesive (E_{aRT} and α_E) are listed in Tables 4.1 and 4.2.

5.3 Heat diffusion in the adhesive layer: insulated adherends

Heat diffuses into a SLJ with insulated adherends from the exposed edges of the adhesive layer. The surface available for convective boundary conditions is relatively small with respect to the width $2b$ and the length $2c$ of the overlap. The resulting Biot

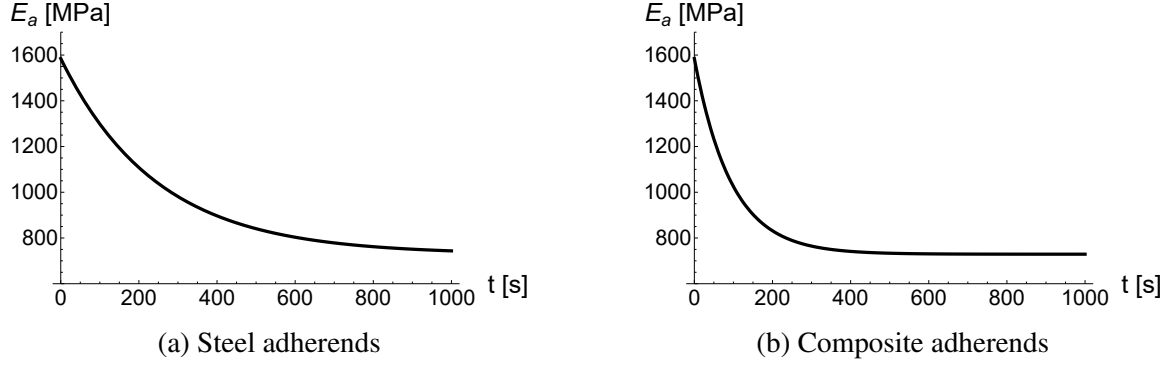


Figure 5.6: Elastic modulus of the adhesive E_a vs heat diffusion time, for steel and composite adherends

number is in excess of 2.8 when considering heat diffusion occurring perpendicularly to the longitudinal axis of the SLJ. Therefore, Equations (2.1) and (2.2) are used to derive the temperature distribution in the adhesive layer, and the results are shown in Figure 5.7a for one quarter of the bond area, after 100, 200, and 300 seconds of heat diffusion. The graph in Figure 5.7b tracks the temperature of the coldest point in the overlap, located at (0, 0). After 1500 seconds, the temperature of the adhesive layer is within 1 °C of thermal equilibrium.

The curves of tensile and shear elastic moduli E_a and G_a at various y locations in the adhesive layer are displayed in Figures 5.8a and 5.8b, respectively, for 100 seconds of heat diffusion. Adhesive softening is highest near the edges of the bond area, where the temperature is elevated, and gradually decreases towards the center. Within less than 5% of the width and length of the overlap, the adhesive experiences the largest decrease in elastic moduli. The results are symmetric about the $y = 0$ and $x = 0$ axes.

5.4 Stress distribution in the adhesive layer

In this section, the distributions of shear and peel stresses in the adhesive layer are presented for SLJs subjected to heat diffusion. The parameters used in the elastic models

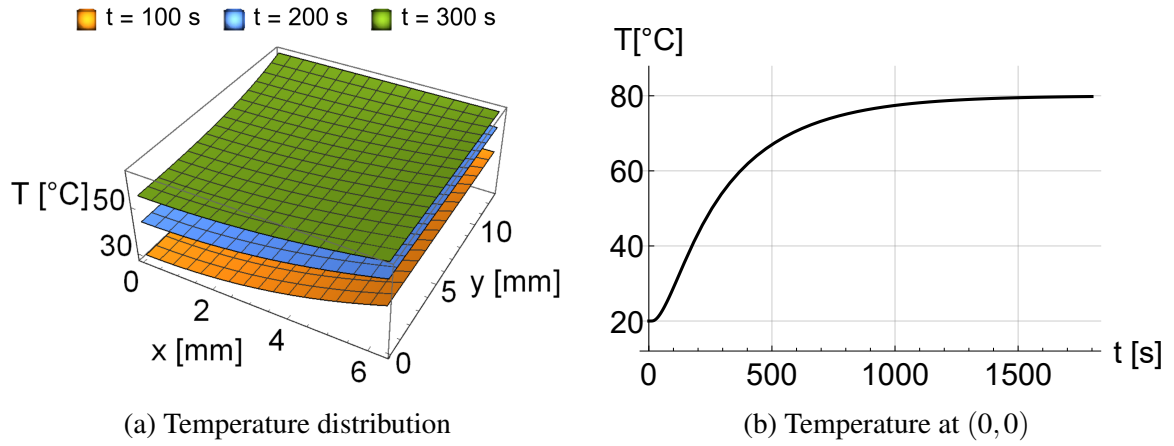


Figure 5.7: Temperature in the adhesive layer at various times of heat diffusion

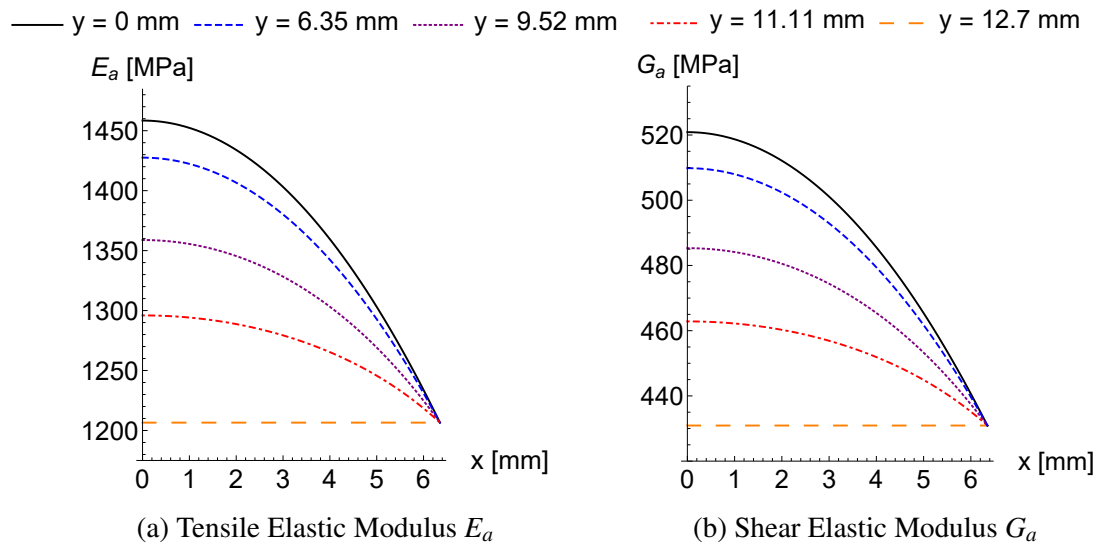


Figure 5.8: Elastic moduli of the adhesive at various y locations, after 100 s of heat diffusion

are listed in Table 5.2, where l is the length of the adherends. The substrates are assumed to have identical dimensions and material properties. The thickness of the adhesive is 0.2 mm, and a tensile shear load of 1000 N is applied to the SLJ.

Table 5.2: Elastic model parameters and joint dimensions

Variable	Value	Variable	Value
b	12.7 mm	$E_{su} = E_{sl}$	200 GPa
c	6.35 mm	$E_{a_{RT}}$	1585 MPa
l	101.6 mm	ν_a	0.4
$t_{su} = t_{sl}$	1.6 mm	ν_s	0.3
t_a	0.2 mm	P	39.4 N/mm

5.4.1 Stress distribution for joints with non-insulated adherends

With reference to Figure 3.1, the stress distribution is dependent on the spatial variable y only if the elastic modulus of the adhesive varies across the width b of the joint. When a lumped-mass model for the bondline temperature is used, as in the case of SLJs with non-insulated substrates, the material properties can be considered constant in x and y , and the resulting shear or peel stress distribution does not vary across the width of the joint.

The one-dimensional shear stress distribution for a steel SLJ subjected to heat convection on all its exposed sides is shown in Figure 5.9. The parameters regulating heat diffusion in the adhesive and substrates are listed in Table 5.1. The curves are mirrored about the plane at $x = 0$, because of the symmetry of the joint. The shear stress distribution after 60, 120, 300, and 600 seconds of heat diffusion is compared to the results obtained with the joint at thermal equilibrium and at the initial temperature T_i . Generalized

softening of the adhesive causes a gradual decrease of the peak shear stress located at the edges of the bondline, and an increase in the values of stress at $x = 0$. In this scenario, a favorable, more uniform stress distribution is achieved not only at steady-state, but also in transient conditions. After about 20 minutes of convective heat transfer, with the joint nearing thermal equilibrium, the value of peak shear stress is reduced by 0.4 MPa.

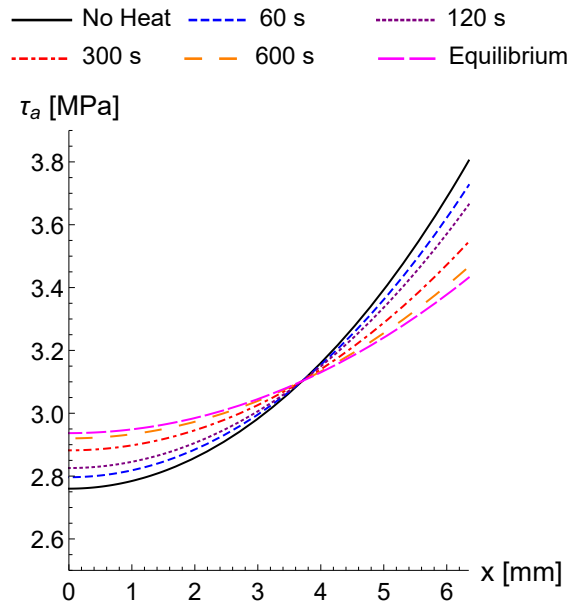


Figure 5.9: Shear stress distribution for a SLJ with non-insulated adherends

The peel stress distribution in the adhesive layer of a steel SLJ with non-insulated adherends is shown in Figure 5.10. The stress distribution is one-dimensional, with no variations across the width of the bondline, and curves are displayed for 0, 60, 120, 300, and 600 seconds of heat diffusion, as well as for the joint at thermal equilibrium. Given the symmetry of the SLJ, due to the adherends being similar in thickness, length, and material, the stress distribution is mirrored about the vertical plane at $x = 0$. The thermal

softening of the adhesive causes a significant decrease in the value of peel stress at the edge of the overlap, with less prominent changes elsewhere. For the considered joint materials and geometry, the value of the peak peel stress decreases by 2 MPa when steady-state conditions are reached.

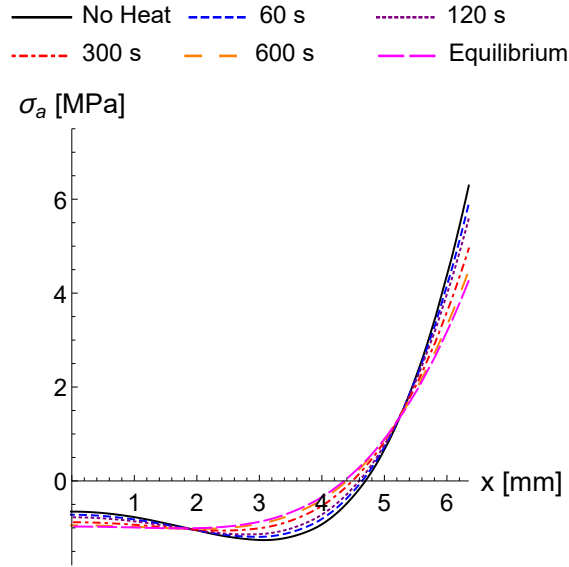


Figure 5.10: Peel stress distribution for a SLJ with non-insulated adherends

5.4.2 Stress distribution for joints with insulated adherends

Heat diffusion in the adhesive layer of a SLJ with insulated adherends gives rise to a two-dimensional temperature profile in the bondline. In transient conditions, the elastic moduli of the adhesive E_a and G_a show slight variations across the width of the joint, which affects the distributions of shear and peel stress.

Figures 5.11a, 5.11b, and 5.11c show the shear stress distribution at key y locations in the bondline, corresponding to the edge ($y = \pm b$), to the plane at $y = \pm 2b/3$,

and to the middle ($y = 0$), respectively. The shear stress observed at the edge of the joint, in Figure 5.11a, shows slight differences when compared to the other two locations (Figures 5.11b and 5.11c), when a temperature gradient across the bondline is present. In transient conditions, the softened adhesive at $y = \pm b$ causes an increase in the load that is carried by the less plasticized internal portion of the bondline. This effect, however, is minimal: the fast internal heat conduction, combined with the slow convective heat flux at the exposed edges of the adhesive layer, does not generate a sufficiently steep gradient in the the shear elastic modulus G_a .

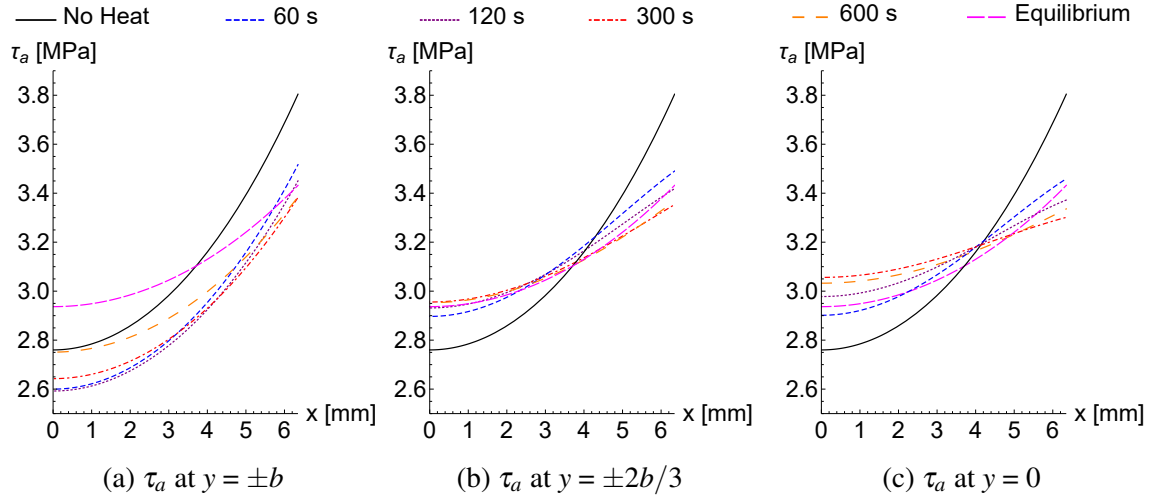


Figure 5.11: Time evolution of shear stress distribution at separate y locations (heat diffusion)

The full two-dimensional shear stress distribution is shown in Figure 5.12a, for 120 seconds of heat diffusion. The three individual y locations that are considered in the analysis are marked with red, green, and blue lines. In Figures 5.12b - 5.13b, the output of the 2-D model at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$ is compared to the results obtained using

the 1-D model detailed by Nassar and Mazhari [42] for 120 seconds of heat diffusion. Although the observed differences are minimal for this scenario, the 1-D model cannot predict the further plasticization of the adhesive on the side edges of the bondline, resulting in a slight underestimation of the values of peak shear stress. As shown in Figure 5.13b, a generalized increase in shear stress across the entire overlap length is observed at $y = 0$, where the amount of adhesive softening is lowest.

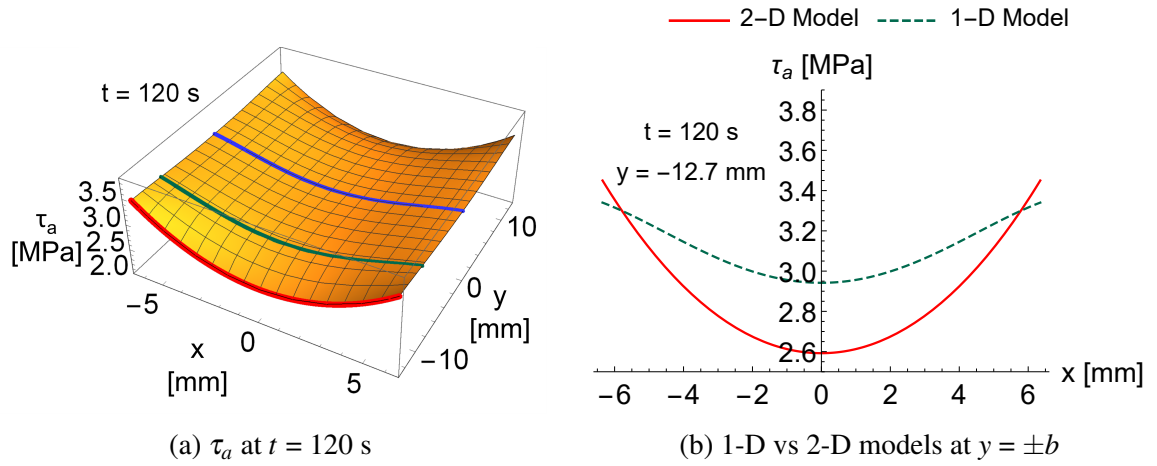


Figure 5.12: Shear stress distribution in the adhesive layer and at $y = \pm b$ after 120 seconds of heat diffusion

The distribution of peel stress in the bondline is shown in Figures 5.14a - 5.14c, for heat diffusion times of 0, 60, 120, 300, and 600 seconds, and for a SLJ in thermal equilibrium with the surrounding environment. Variations across the joint width are limited. Peel stress in the adhesive arises from the action of an internal balancing moment, rather than from an external load on the joint, and its integration over the overlap returns zero. Consequently, the impact of the outer portions of the bondline (near or at $y = \pm b$) experiencing higher thermal softening than the inner sections is lessened.

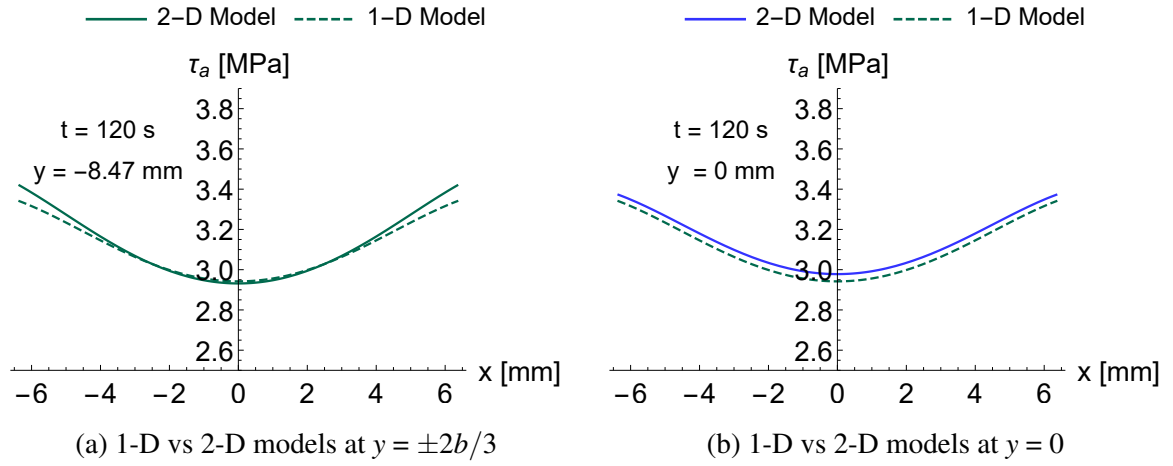


Figure 5.13: Shear stress distribution at two y locations after 120 seconds of heat diffusion

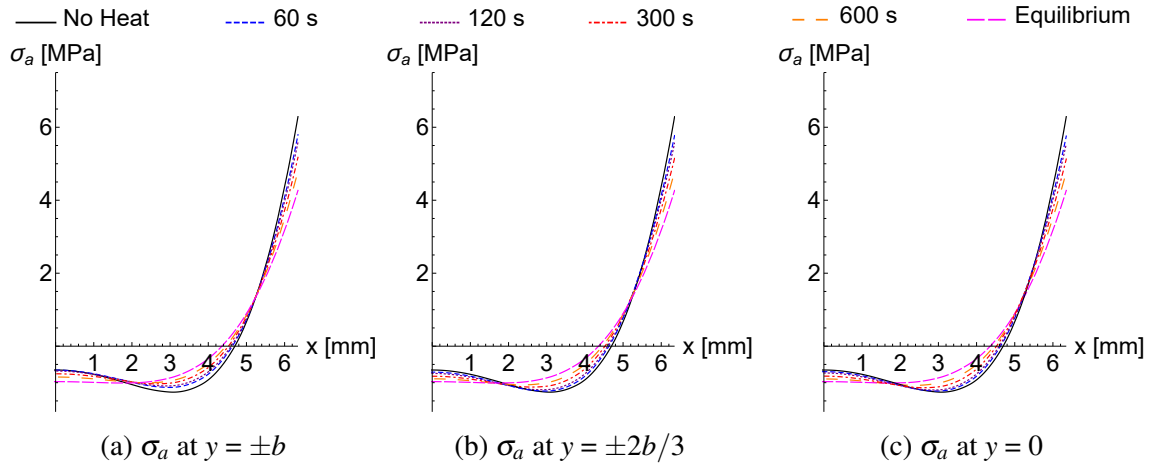


Figure 5.14: Time evolution of peel stress distribution at separate y locations

The complete distribution of the peel stresses in the adhesive layer is shown in Figure 5.15a, for 120 seconds of heat diffusion. Section cuts are taken at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$, and are highlighted on the distribution the Figure. The results from the 2-D model are compared to the 1-D formulation by Mazhari and Nassar [43] in Figures 5.15b - 5.16b. For the calculation of peel stresses in a SLJ subjected to heat diffusion with convective boundary conditions, the error introduced by the use of a one-dimensional model can be neglected.

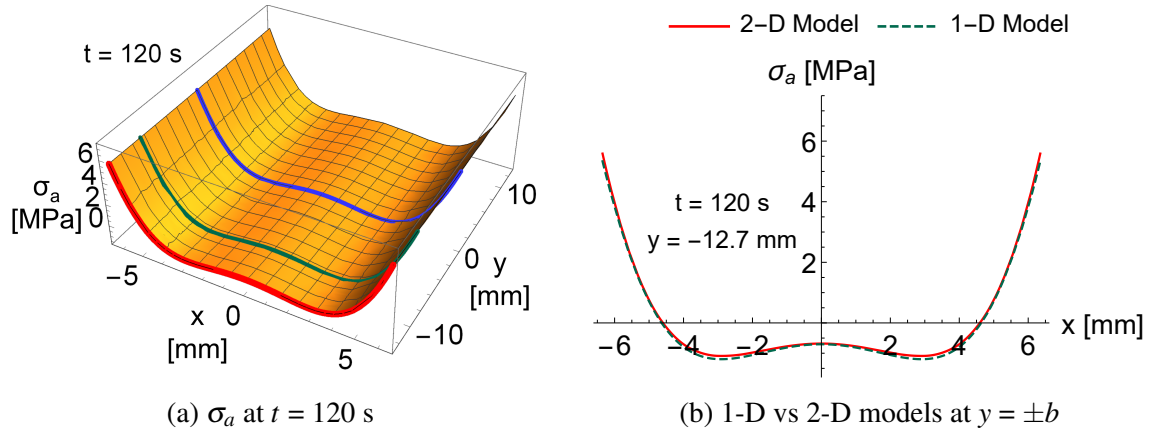


Figure 5.15: Peel stress distribution in the adhesive layer and at $y = \pm b$ after 120 seconds of heat diffusion

5.4.3 Stress distribution for joints with insulated adherends and slow internal conduction

In ordinary SLJs, the high internal conductivity does not favor the formation of significant temperature gradients across the width and length of the bondline. In this section, results are presented for a joint with an artificially low value of adhesive thermal conductivity $k_a = 0.02 \text{ W m}^{-1} \text{ K}^{-1}$, and insulated adherends. The curves in Figure 5.17 are obtained after 120 seconds of heat conduction, and show a comparison between the results

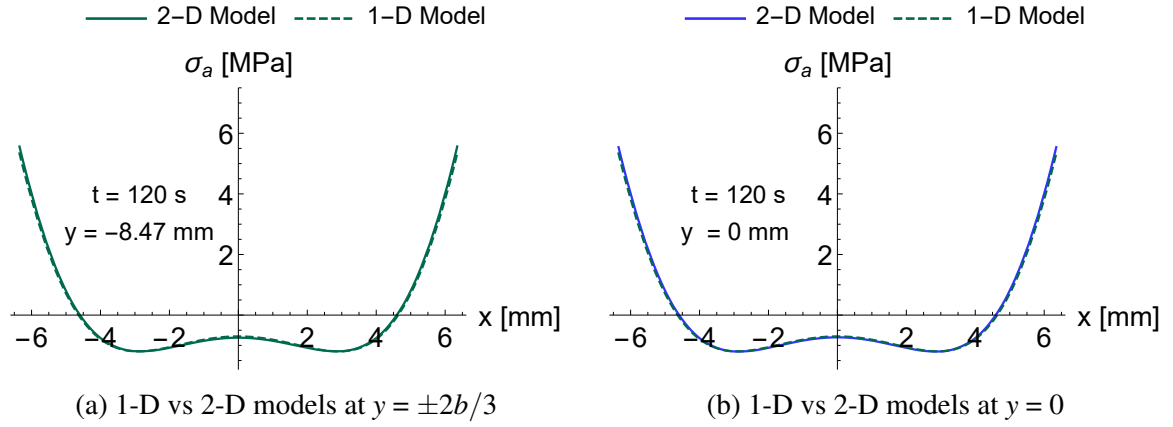


Figure 5.16: Peel stress distribution at two y locations after 120 seconds of heat diffusion

of Nassar and Mazhari's 1-D model [42] and the proposed 2-D formulation. More significant differences are observed between the two models, with the shear stresses at $y = \pm 2b/3$ being slightly underestimated by the one-dimensional approach. This is due to the larger temperature gradient that is formed across the width of the joint.

Figure 5.18 shows the peel stress distribution in the adhesive layer of a joint subjected to 120 seconds of heat diffusion and slowed internal conduction. The results of the proposed 2-D model are compared to the previous 1-D formulation [43]. Although some marked differences are observed in correspondence to the lateral edges of the bondline (Figure 5.18a), it is worth noting that the value of peak peel stress is not significantly underestimated when the one-dimensional approach is used. No appreciable differences are observed at $y = \pm 2b/3$ (Figure 5.18b) and $y = 0$ (Figure 5.18c). Therefore, a 1-D model is sufficient to predict the peel stress in joints subjected to heat diffusion with artificially slowed internal conduction.

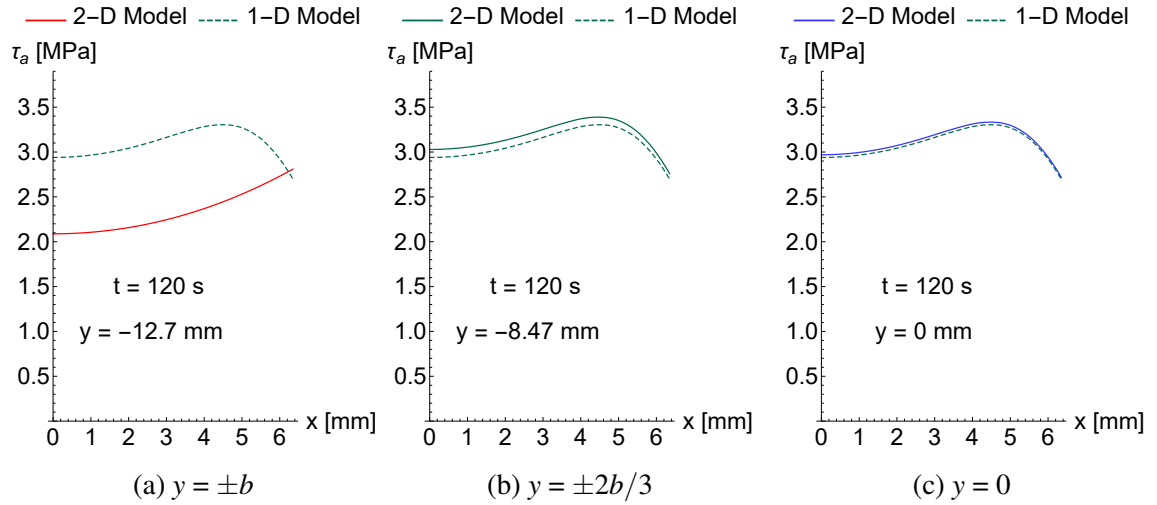


Figure 5.17: Comparison between 1-D and 2-D shear stress model results in a joint with slow internal conduction

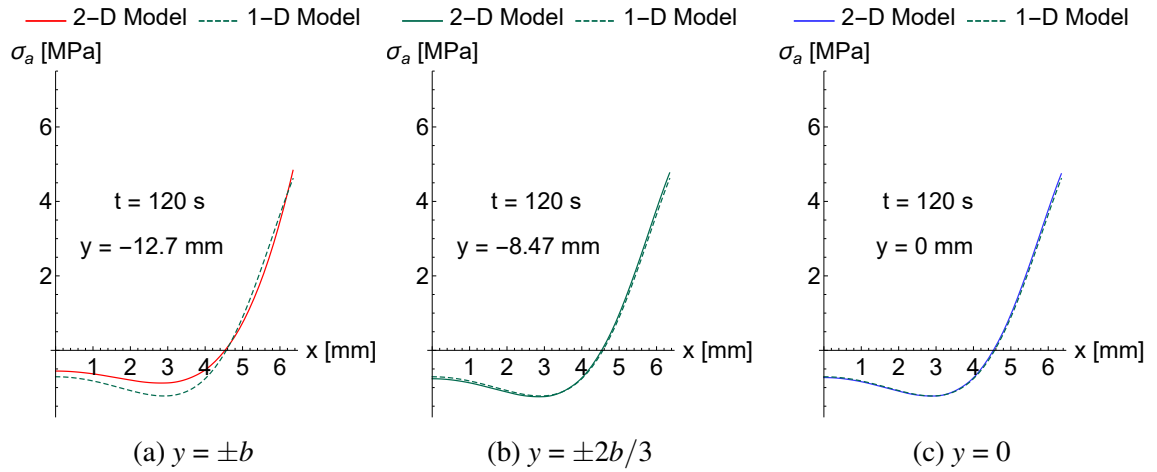


Figure 5.18: Comparison between 1-D and 2-D peel stress model results in a joint with slow internal conduction

CHAPTER SIX

EFFECT OF MOISTURE DIFFUSION ON THE STRESS DISTRIBUTION IN ADHESIVE JOINTS

6.1 Introduction

In this chapter, a 2-D model is proposed for the effect of moisture diffusion on the distribution of shear and peel stresses in the adhesive. A convergence study is performed on the Fourier solution to the 2-D heat equation that describes the concentration of moisture in the overlap. Then, moisture diffusion and its effect on the elastic moduli of the adhesive is analyzed. Finally, the shear and peel stress distributions are presented for several diffusion times, at different locations in the bondline, and are compared to the dry and saturated stresses. Observations and conclusions are provided.

6.2 Moisture diffusion in the adhesive layer

Two-dimensional moisture Fickian diffusion in the bondline is governed by Equations (2.6) and (2.7). The analytical solution, in Equation (2.8), is a double Fourier Sine series in the indexes n and m , in the x and y directions, respectively.

6.2.1 Convergence Study

It is necessary to identify the minimum number of Sine terms that is required to reach convergence of the solution, as a function of moisture diffusivity and diffusion time. To this purpose, a MATLAB[®] algorithm is devised. The two indexes n and m are varied independently. Convergence is defined as a stable improvement in the prediction of moisture concentration at the center of the bondline of less than 1%, resulting from a step increase in any of the summation terms.

In order to ensure that transient improvements, cyclic in nature and common for short diffusion times, are not considered by the algorithm as stable, a population matrix is generated, with the number of terms of each summation as its row and column indexes; a 1 is assigned to step improvements lower than 1%, and a 0 is input otherwise. When a convergence point needs to be tested for its stability, the subsequent element vectors in the population matrix are multiplied in every direction. If all of the products Π returns 1, the convergence point is assumed to be stable. An example of this calculation is given in Figure 6.1, in which the solid boundaries delimit regions of step improvements under the 1% threshold, for a very short diffusion time ($t = 1$ day). In the Figure, a convergence point is tested for its stability, with element-wise multiplication being performed on subsequent vectors in two directions. It is possible to see that regardless of the choice of direction, all the products would eventually return 0, confirming the instability of the tested point. Stable points are shaded in green, and the minimum number of summation terms needed for convergence of the solution (for 1 day of moisture diffusion) is 170 n terms in the x direction, and 89 m terms in the y direction, for a total 15,130 terms in Equation (2.8).

The population matrix in Figure 6.1 also highlights the importance of varying independently the two summation indices, in a two-dimensional convergence study. If the number of n and m were assumed to be equal, the convergence problem would become one-dimensional, and it would be greatly simplified. However, applying the same constraints as for the two-dimensional problem where the indices are varied independently, the minimum number of terms of each individual summation would become 170, which would give a total of 28,900 terms in Equation (2.8), corresponding to a 91% increase in calculation time.

The minimum amount of terms to achieve convergence of the moisture concentration solution is plotted in Figure 6.2 against a parameter that includes diffusion

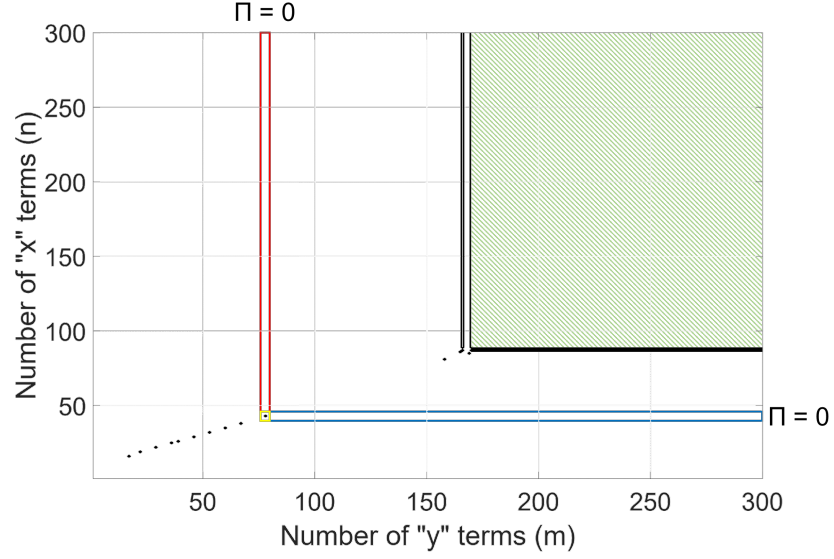


Figure 6.1: Population matrix for the convergence of moisture concentration

time t and diffusivity coefficient D^2 . The required upper bound of the summations that ensures stable convergence decreases exponentially with diffusion time (and diffusivity coefficient). The total number of terms in Equation (2.8) is given by the product of the upper bounds for n and m .

6.2.2 Moisture concentration

Moisture diffuses in the adhesive layer from the saturated edges of the bondline (where the concentration C is equal to 1) towards the dry center. The diffusivity coefficient D^2 in Table 6.1 governs internal moisture transport in a typical epoxy-based adhesive [45]. The elastic moduli of the interlayer are assumed to vary linearly between the dry and saturated values listed in Table 6.1, according to Equations (2.9a) and (2.9b).

Equation (2.8) is used to calculate the moisture concentration in the adhesive layer, with the minimum number of terms showed in Figure 6.2. The results are shown in Figure 6.3a for a SLJ with geometric properties as listed in Table 5.2, and the diffusivity

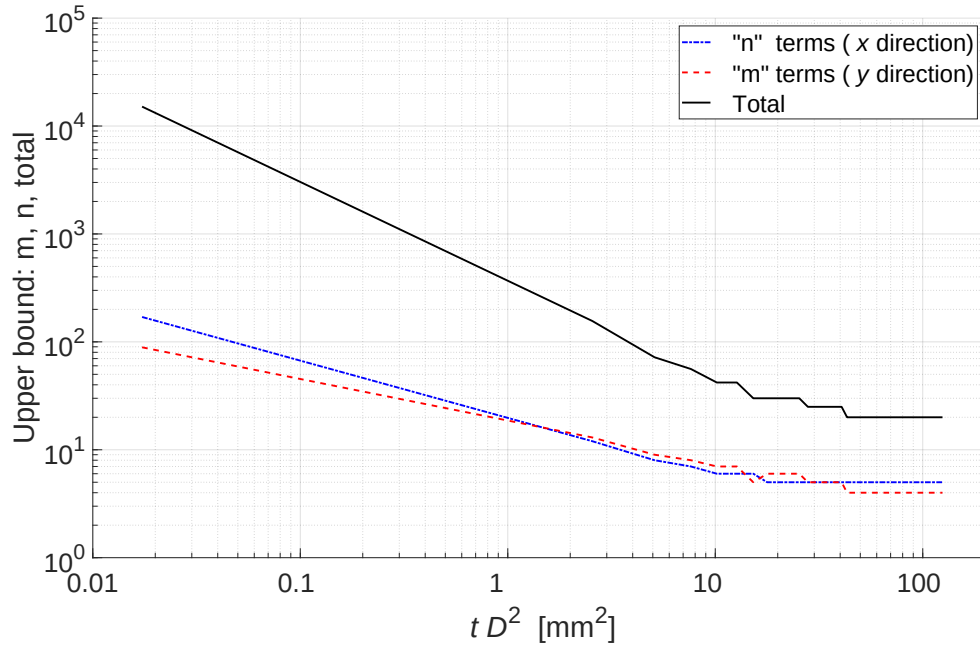


Figure 6.2: Convergence of moisture concentration vs. the combined time-diffusivity parameter tD^2

coefficient in Table 6.1. The two-dimensional moisture concentration in Figure 6.3a is displayed for 60 days, 1.5, and 4 years of diffusion, for one quarter of the overlap. In the first two months, moisture affects only the outer 2 mm of the adhesive layer, with the rest of the bondline remaining substantially dry. Water finally reaches every portion of the overlap by the 8-month mark, with significant levels of moisture concentration observed after 1.5 and 4 years.

Figure 6.3b shows the moisture concentration at the center of the adhesive layer, as well as the total water uptake of the entire overlap. After the initial period, moisture concentration at (0,0) increases rapidly, reaching 90% of the saturated value after 70 months of diffusion. When considering the entire adhesive layer, however, near-saturation

Table 6.1: Moisture Diffusivity, Dry, and Saturated Elastic Moduli

Variable	Value and Unit
D^2	$2 \cdot 10^{-7} \text{ mm}^2 \text{ s}^{-1}$
E_{a0}	1585 MPa
$E_{a\infty}$	1000 MPa
G_{a0}	566 MPa
$G_{a\infty}$	357 MPa

values are achieved more quickly: the bondline absorbs 90% of its total water uptake capacity after only 50 months of diffusion.

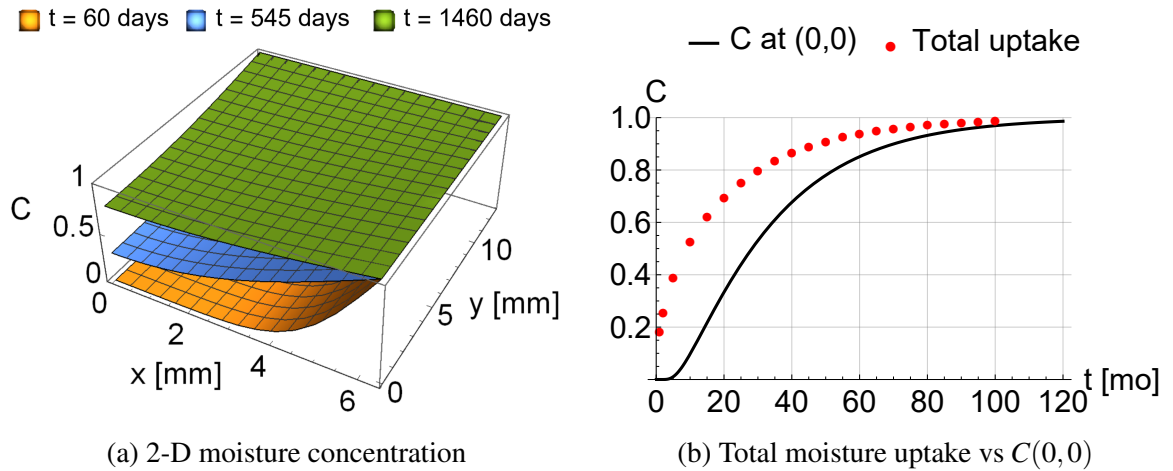


Figure 6.3: Moisture concentration in the adhesive layer at various diffusion times

Curves of tensile and shear elastic moduli E_a and G_a resulting from 365 days of moisture diffusion in the adhesive layer are shown in Figures 6.4a and 6.4b, respectively, for multiple y locations in the bondline. Large gradients in the material properties are

formed, with significantly plasticized adhesive near the four edges of the overlap. The results are symmetric about the vertical planes at $x = 0$ and $y = 0$.

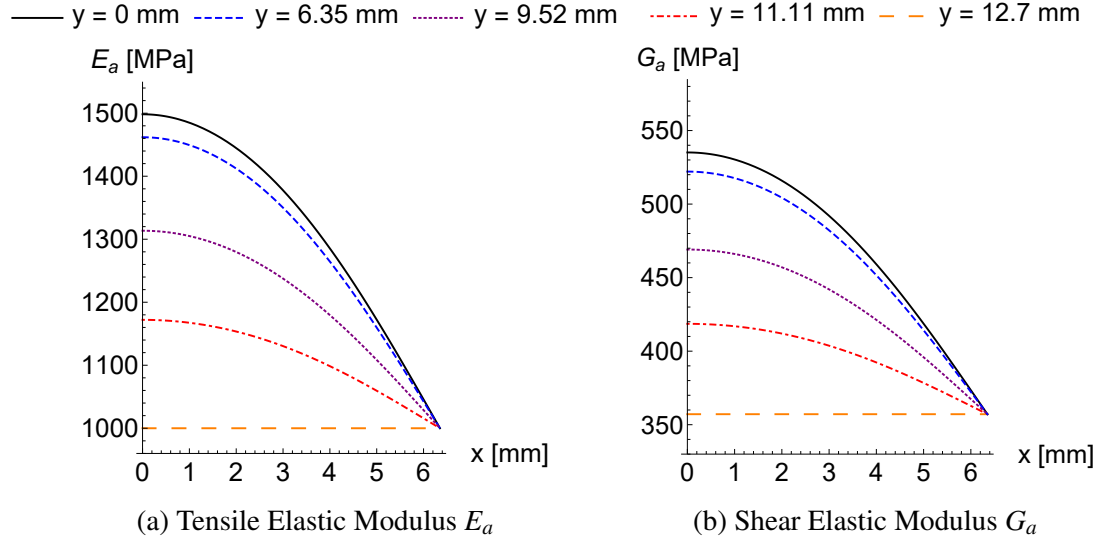


Figure 6.4: Elastic moduli of the adhesive at various y locations, after 365 days of moisture diffusion

6.3 Stress distribution in the adhesive layer

In this section, the shear and peel stress distributions are presented for SLJs subjected to moisture diffusion. The joint parameters listed in Table 6.2 are used in the analysis. Substrates similar in material, thickness, and length are assumed. The adhesive layer is 0.2 mm thick, and the total applied external load on the 25.4 mm-wide SLJ is equal to 1000 N.

Table 6.2: Elastic model parameters

Variable	Value	Variable	Value
b	12.7 mm	$E_{su} = E_{sl}$	200 GPa
c	6.35 mm	$E_{a\infty}$	1000 MPa
l	101.6 mm	ν_a	0.4
$t_{su} = t_{sl}$	1.6 mm	ν_s	0.3
t_a	0.2 mm	P	39.4 N/mm

6.3.1 Shear stress distribution

The evolution of the shear stress distribution in the adhesive layer with moisture diffusion time is shown in Figure 6.5. Curves of shear stress at the lateral edge of the overlap ($y = \pm b$) are shown in Figure 6.5a. In transient conditions, the adhesive near the edge of the joint experiences considerably higher levels of plasticization when compared to the internal regions of the bondline. This results in lower amounts of the external load being carried by the outer regions of the adhesive layer, as shown by the curves obtained after 30 and 120 days of environmental exposure. With the progression of moisture diffusion towards the middle of the bondline, the gradient of the material properties between outer and inner regions of the overlap decreases in magnitude. A gradual stress redistribution occurs, as evidenced by the curves calculated after 180 and 365 days of moisture diffusion, with stress values rising with diffusion time. Small differences are observed between the shear stress in dry and saturated conditions.

In transient conditions, when the shear elastic modulus gradient is maximum, the lower elastic modulus of the adhesive near the edges of the overlap causes the shear stress to increase significantly in the inner regions of the adhesive, as shown in Figures 6.5b and 6.5c. Specifically, values of peak shear stress at $y = 0$ are as high as in a dry joint (before moisture diffusion), and are 40 % higher than the peak shear stress at $y = \pm b$ after 180

days of moisture diffusion. The integral of the shear stress distribution across the width and length of the bondline must be equal to the externally applied shear tensile load. When the outer portions of the adhesive layer experience a drastic stress decrease, the inner part of the bondline is responsible for satisfying the static equilibrium conditions.

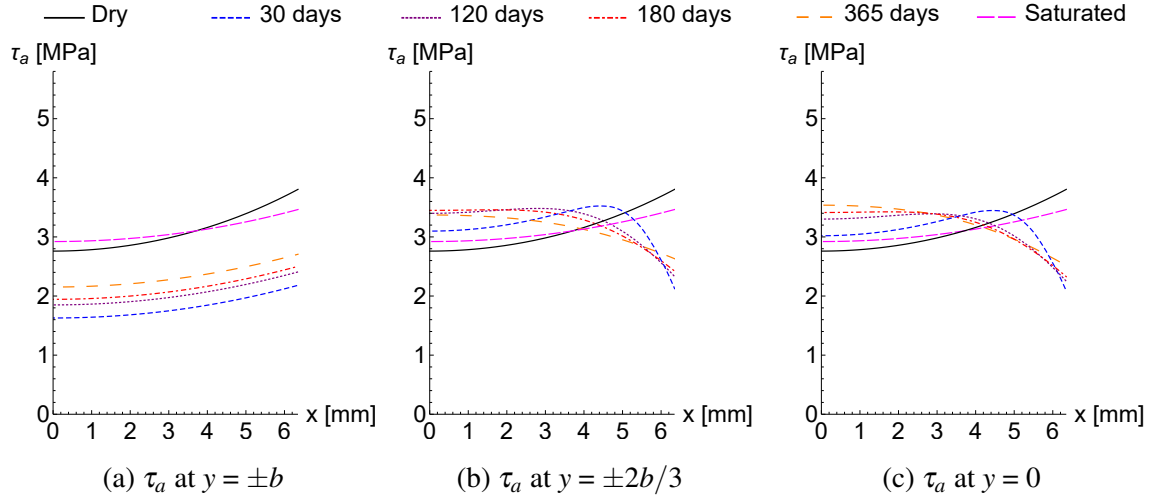


Figure 6.5: Time evolution of shear stress distribution at separate y locations (moisture diffusion)

The two-dimensional shear stress distribution in the adhesive layer after 120 days of moisture diffusion is shown in Figure 6.6a. Red, green, and blue lines on the stress surface identify the section cuts at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$, respectively. The plot in Figure 6.6a highlights the positive shear stress gradient that appears in transient conditions along the y axis, towards the center of the bondline.

The results obtained with the proposed two-dimensional model are compared to the previous 1-D approach [42], depicted by the dashed line, in Figures 6.6b, 6.7a, and 6.7b. At $y = \pm b$ (Figure 6.6b), the overestimation of the shear stress resulting from the use

of a 1-D model is of relatively low importance. At $y = 0$, the two approaches yield similar results, with more pronounced variations along the length of the bondline being overlooked by the 1-D approach. However, when considering the shear stress distribution at or near $y = \pm 2b/3$ (Figure 6.7a, a significant underestimation of peak stress values may occur when using a 1-D model with SLJs subjected to two-dimensional moisture diffusion patterns. In this case, the actual peak shear stress at $y = 0$ is 7% higher than the value calculated using a one-dimensional approach.

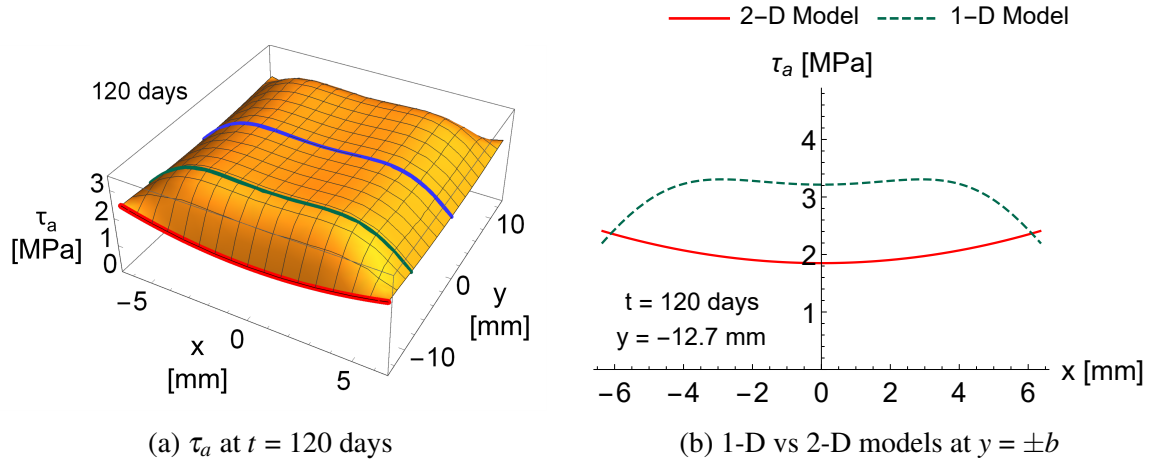


Figure 6.6: Shear stress distribution in the adhesive layer and at $y = \pm b$ after 120 days of moisture diffusion

6.3.2 Peel stress distribution

The evolution of the peel stress distribution in the bondline when the adhesive layer is subjected to 2-D moisture diffusion is shown in Figure 6.8. No significant differences are observed in the values of peak peel stress across the width of the joint. The peel stress distribution in transient conditions is very similar to the results obtained with a

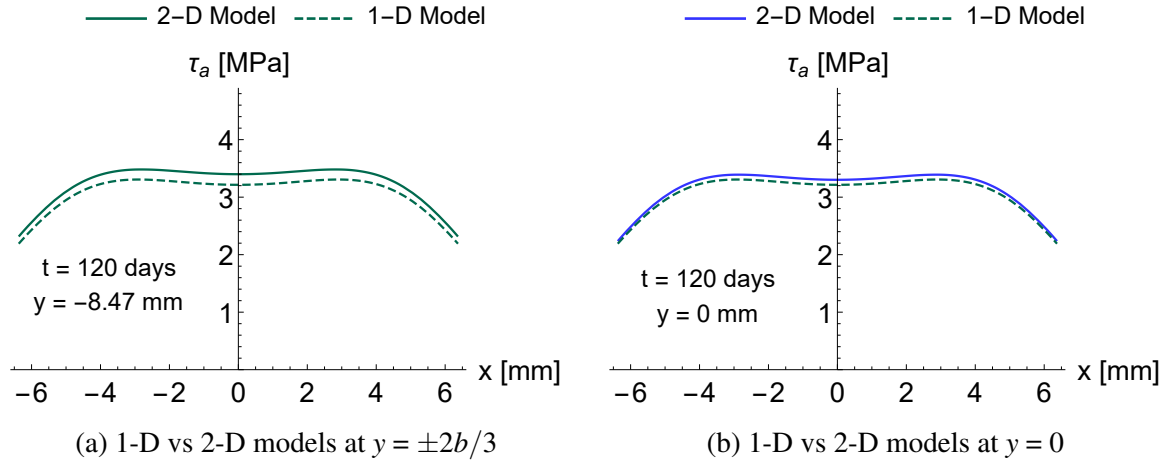


Figure 6.7: Shear stress distribution at two y locations after 120 days of moisture diffusion

fully saturated adhesive layer, even for a relatively short time of moisture diffusion: in Figures 6.8a - 6.8c, the curves obtained after 30 and 120 days of moisture diffusion are within 5% of the saturated values for $x > 2c/3$. Some significant deviation can be observed only near the lateral edges of the bondline (Figure 6.8a), towards the center of the overlap.

The full two-dimensional peel stress distribution is shown in Figure 6.9a, with the three section cuts at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$ being highlighted on the stress surface. At these locations, the results obtained from the proposed 2-D peel stress model are compared to the previous 1-D approach [43] in Figures 6.9b - 6.10b. The results suggest that the use of a one-dimensional model to predict the peel stresses in the adhesive layer of a SLJ subjected to two-dimensional moisture diffusion is adequate, and does not introduce significant errors. However, the difference between the two approaches near $y = \pm b$ (Figure 6.9b) is worth analyzing. The 1-D model underestimates slightly the magnitude of the peel stress in the central portion of the overlap, which causes a very small underestimation of the peak peel stress value, observed at $x = \pm c$.

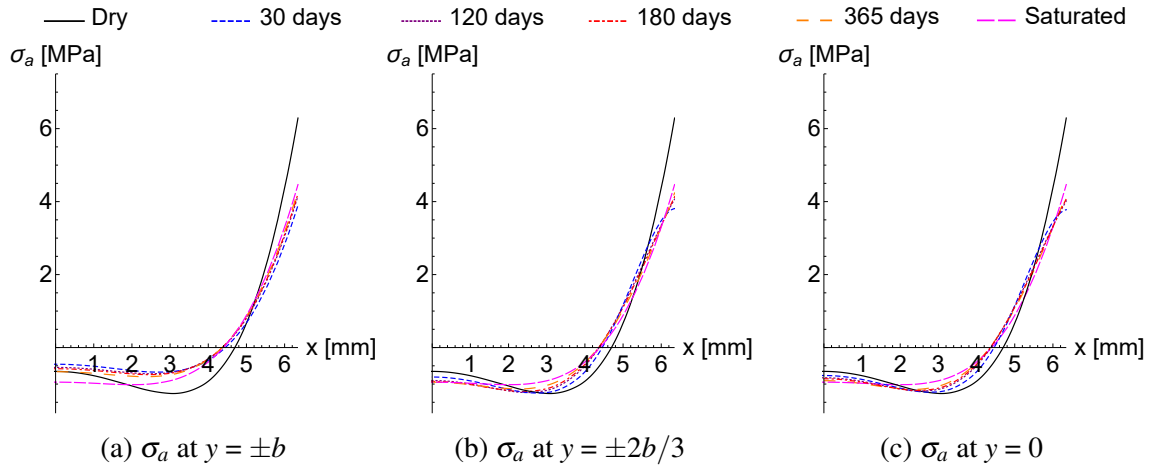


Figure 6.8: Time evolution of peel stress distribution at separate y locations (moisture diffusion)

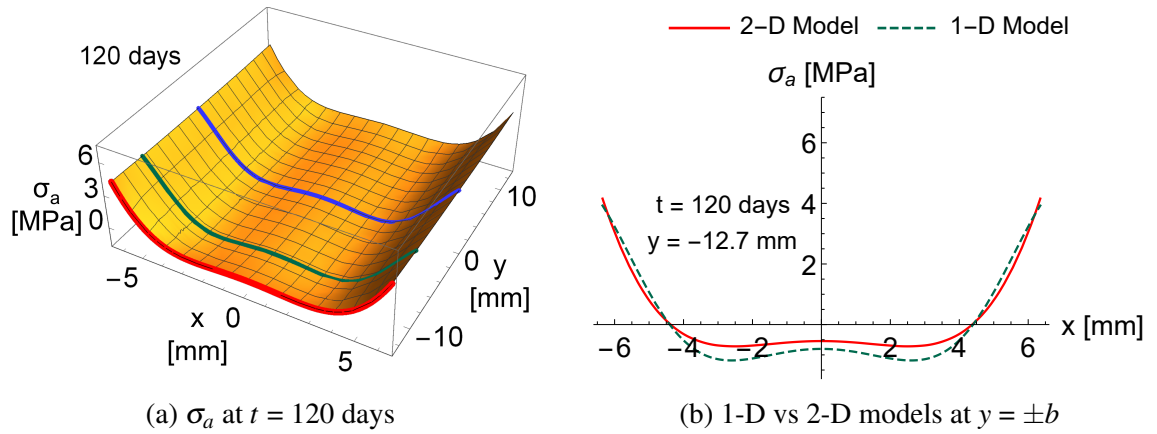


Figure 6.9: Peel stress distribution in the adhesive layer and at $y = \pm b$ after 120 days of moisture diffusion

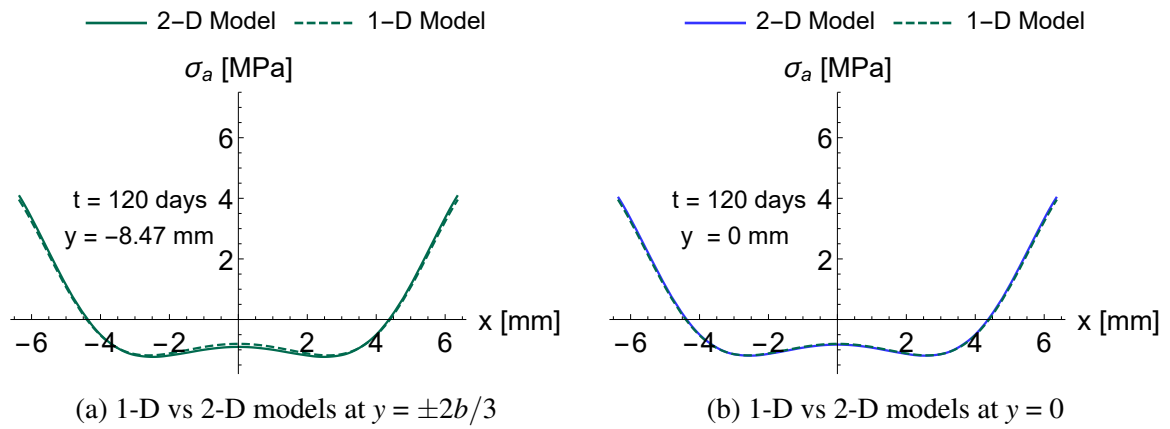


Figure 6.10: Peel stress distribution at two y locations after 120 days of moisture diffusion

CHAPTER SEVEN

EFFECT OF COMBINED MOISTURE AND HEAT DIFFUSION ON THE STRESS DISTRIBUTION IN ADHESIVE JOINTS

7.1 Introduction

In this chapter, a 2-D model is proposed for the effect of combined heat and moisture diffusion on the distribution of shear and peel stresses in the adhesive. Moisture transport at high temperature is compared to the results obtained at room temperature, and the location-dependent adhesive material properties are calculated. Shear and peel stress distributions are derived and discussed for joints undergoing moisture diffusion at high temperature, but that are consequently cooled down before mechanical loading, and for SLJs that are loaded at 80°C. Results are presented at different locations in the bondline, and for several diffusion times. Observations and conclusions are provided.

7.2 Moisture diffusion at high temperature

Heat diffusion in the adhesive layer occurs at a much faster rate than moisture diffusion. Therefore, as discussed in section 2.4, the SLJ is assumed to have reached near-thermal-equilibrium with the surrounding environment when moisture diffusion starts. The diffusivity coefficient of the adhesive at the temperature T_h is calculated using the Arrhenius law in Equation (2.10). The values of the asymptotic coefficient D_0 and of the energy barrier E_D are listed in Table 7.1.

Figure 7.1a shows the moisture concentration in the adhesive layer $C(x,y)$ after 10, 60, and 180 days of diffusion through the four edges at 80°C. Symmetry about the vertical planes at $x = 0$ and $y = 0$ is observed. The outer third of the adhesive layer experiences significant levels of moisture concentration after as little as 10 days, and the entire overlap reaches quasi-saturation in 6 months of moisture diffusion. The total water uptake in the

Table 7.1: Values of adhesive properties at low and elevated temperatures

Variable	Value and Unit	
E_D	5.97×10^{-20}	J
k	1.38×10^{-23}	J K ⁻¹
D_0	5.2×10^{-7}	mm ² s ⁻¹
T_h	80	°C
a_1	1.6	
a_2	0.035	
α_E	-9×10^{-3}	°C ⁻¹

bondline is shown in Figure 7.1b, together with the moisture concentration at the center of the adhesive layer. While it takes longer for the moisture concentration at (0, 0) to reach saturation, the adhesive layer absorbs 99% of its total capacity after as little as 8 months, when it is heated to 80°C.

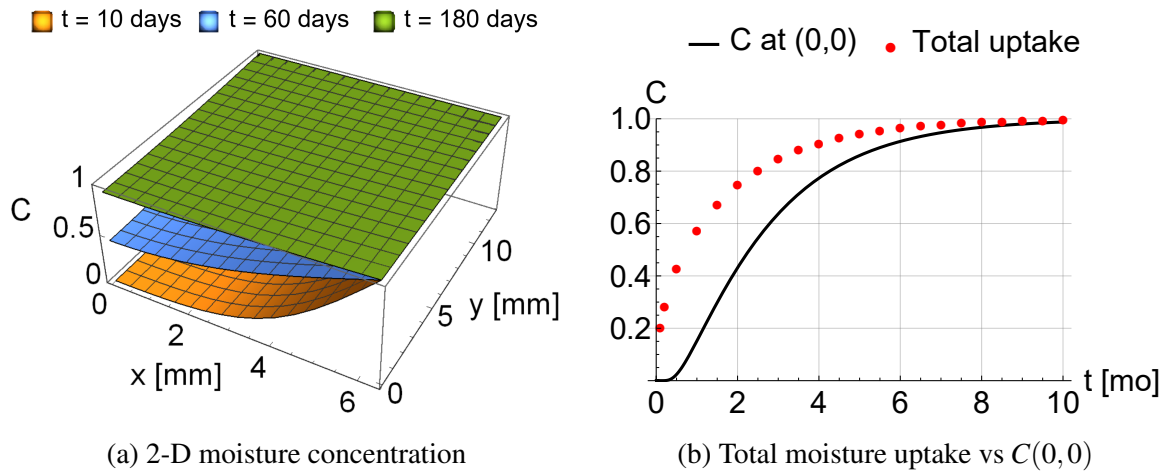


Figure 7.1: Moisture concentration in the adhesive layer at various diffusion times ($T = 80^\circ\text{C}$)

Figure 7.2 shows a comparison between moisture diffusion occurring at room temperature and at T_h ($T = 80^\circ\text{C}$). The moisture concentration at the center of the bondline and the total water uptake in the adhesive layer are presented in Figures 7.2a and 7.2b, respectively. The moisture diffusion rate is dramatically increased at high temperature, with joints at room temperature taking nearly 10 times longer to reach near-saturated conditions.

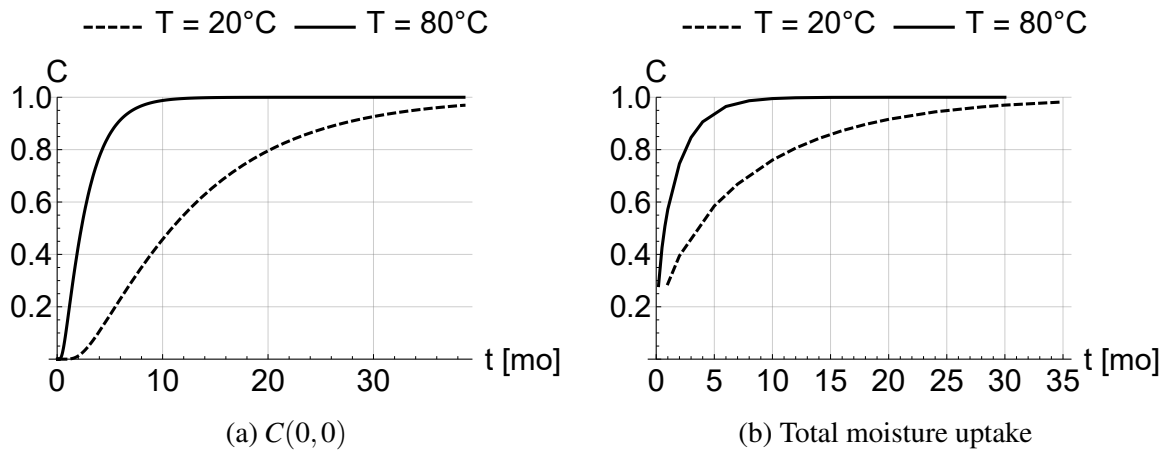


Figure 7.2: Comparison of moisture concentration between SLJs at 20°C and at 80°C

7.3 Effect of combined heat and moisture diffusion on adhesive elastic moduli

In this section, the values of the elastic moduli E_a and G_a of the adhesive layer are presented, for two different scenarios. In the first case, a SLJ experiences moisture diffusion at high temperature, but it is cooled down before the load is applied. Therefore, no thermal softening is observed in the bondline. In the second case, the SLJ is loaded while at $T = 80^\circ\text{C}$, and the adhesive softens under the combined action of heat and moisture.

7.3.1 Elastic moduli after adhesive cooldown

The elastic moduli E_a and G_a after 30 days of moisture diffusion at 80°C and subsequent cooldown of the adhesive layer are presented in Figures 7.3a and 7.3b, respectively. A steep gradient is formed along both axes of the overlap, analogous to the case of moisture diffusion at low temperature. However, as discussed in the previous section, this gradient appears in only few days of exposure. The results are mirrored about the vertical planes at $x = 0$ and $y = 0$.

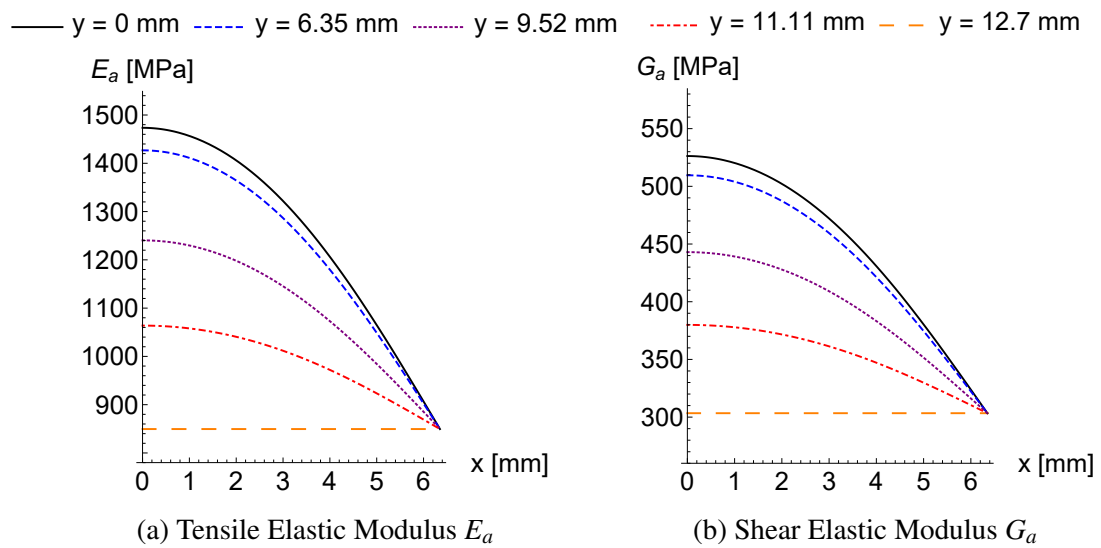


Figure 7.3: Elastic moduli of the adhesive at various y locations, after 30 days of moisture diffusion at 80 °C and subsequent cooldown

7.3.2 Elastic moduli at high temperature

When a SLJ is not cooled down before the application of a tensile-shear load, the adhesive is plasticized by the combined effect of moisture and heat diffusion. The resulting elastic moduli E_a and G_a are presented in Figures 7.4a and 7.4b, respectively, at

various y locations in the bondline. A gradient of similar entity as in the previous scenario forms in the material properties of the adhesive along the two axes of the overlap. However, the elastic moduli vary between dry and saturated values that are significantly lowered by the high bondline temperature, as given by Equations (2.5a) and (2.5b).

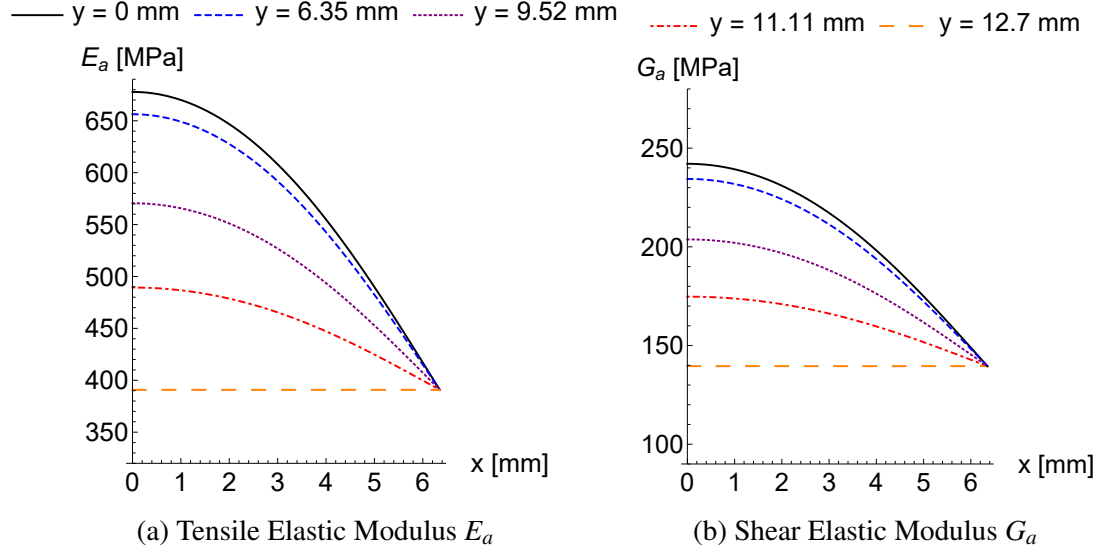


Figure 7.4: Elastic moduli of the adhesive at various y locations, after 30 days of moisture diffusion at 80 °C

7.4 Stress distribution in the adhesive layer

In this section, the shear and peel stress distributions are presented and discussed for the two scenarios introduced in section 7.3. The parameters used in the elastic analysis are listed in Table 7.2. The adherends are identical in material and dimensions. The bondline layer is 0.2 mm thick, and the saturated elastic modulus of the adhesive at room temperature $E_{a\infty}|_{RT}$ is 1000 MPa, similarly to the case explored in the previous chapter (moisture-only diffusion).

Table 7.2: Elastic model parameters: combined heat/moisture diffusion

Variable	Value	Variable	Value
b	12.7 mm	$E_{su} = E_{sl}$	200 GPa
c	6.35 mm	$E_{a\infty} _{RT}$	1000 MPa
l	101.6 mm	ν_a	0.4
$t_{su} = t_{sl}$	1.6 mm	ν_s	0.3
t_a	0.2 mm	P	39.4 N/mm

7.4.1 Shear stress distribution after joint cooldown

The evolution of the shear stress distribution in the adhesive layer of a SLJ subjected to 5, 15, 60, and 120 days of moisture diffusion at 80°C and subsequent cooldown is shown in Figure 7.5, at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$. Curves showing the results for dry and saturated joints are displayed and compared to the shear stress calculated in transient conditions. After short diffusion times, a significant gradient along the two axes of the overlap is observed. Values of peak shear stress are measured in the area next to the point at $(\pm 2c/3, \pm 2b/3)$. When moisture diffusion starts, the shear stress in correspondence to the lateral edge of the bondline ($y = \pm b$) experiences a significant drop, because of the sudden decrease in the elastic modulus of the adhesive.

Figure 7.6a shows the two-dimensional shear stress distribution for a SLJ subjected to 15 days of moisture diffusion at 80°C, after it is cooled down to 20°C. The three section cuts at different y locations shown in Figures 7.6b, 7.7a, and 7.7b are highlighted on the stress surface by red, green, and blue lines, respectively. The results obtained with the 2-D model are compared to the previous 1-D approach [42]. At $y = \pm b$, the predictions of the two models differ significantly, while the one-dimensional approach underestimates the shear stress in the inner portion of the adhesive layer, calculating a value of peak stress 7% lower than the proposed model.

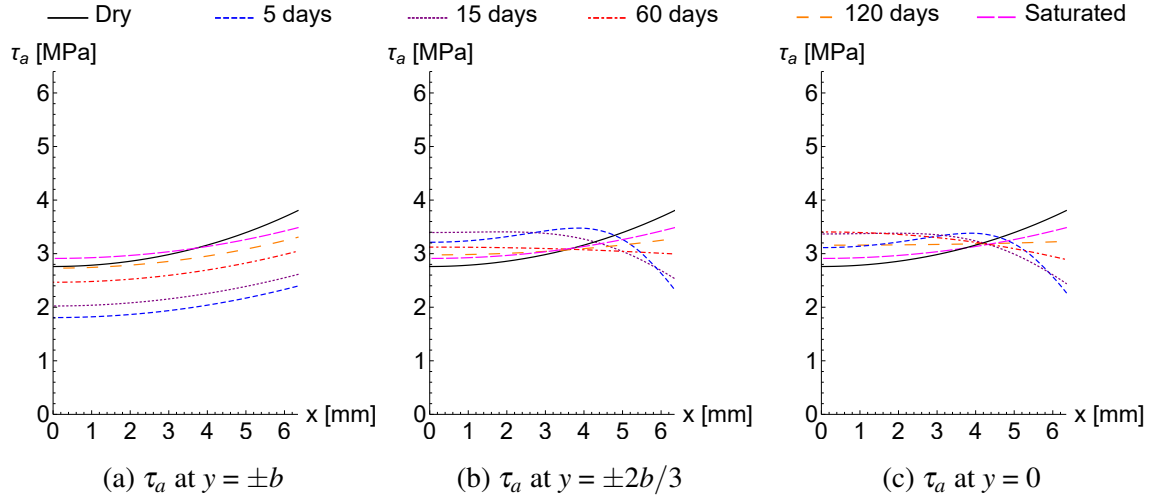


Figure 7.5: Time evolution of shear stress distribution at separate y locations (after cooldown)

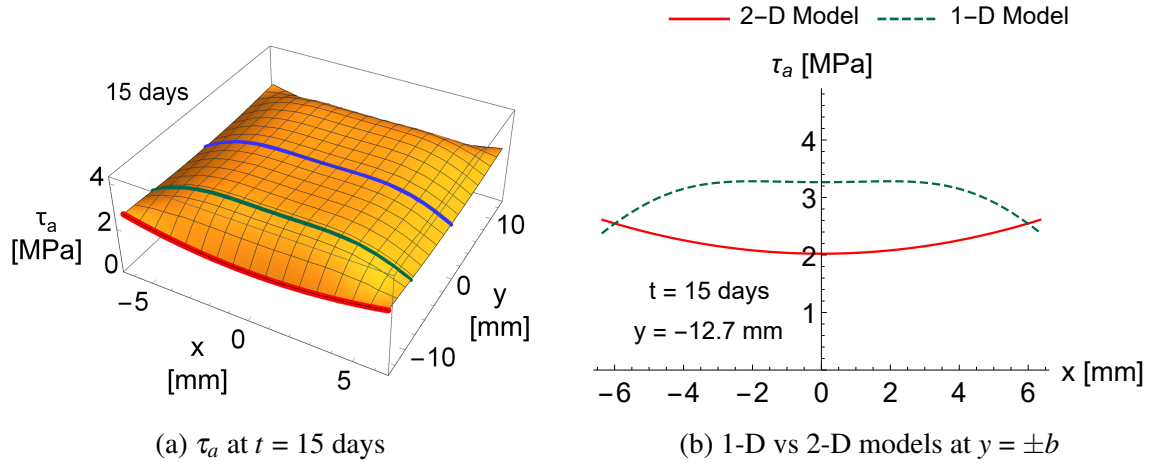


Figure 7.6: Shear stress distribution in the adhesive layer and at $y = \pm b$ after 15 days of moisture diffusion at 80°C and subsequent cooldown

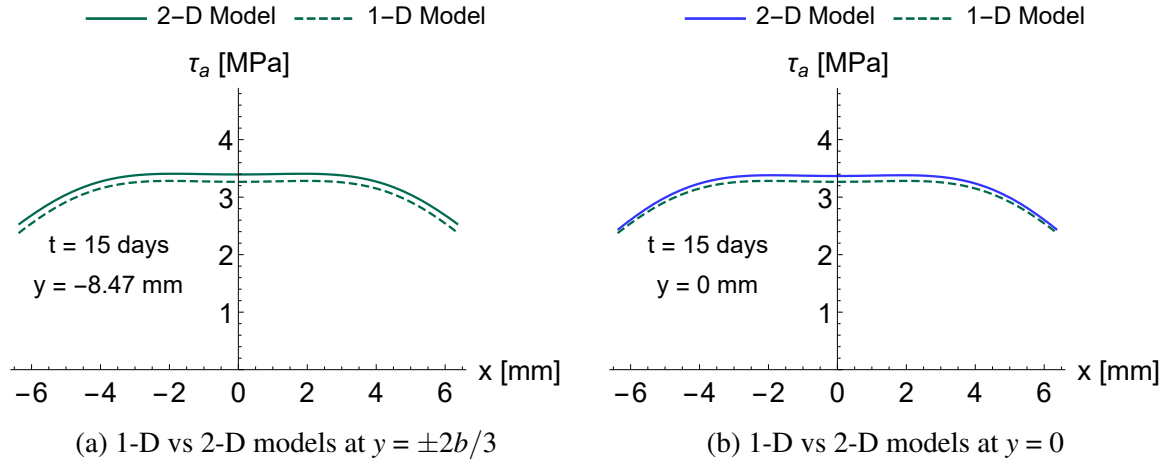


Figure 7.7: Shear stress distribution at two y locations after 15 days of moisture diffusion at 80°C and subsequent cooldown

7.4.2 Shear stress distribution at 80°C

The evolution of the shear stress in the adhesive layer of a SLJ subjected to 5, 15, 60, and 120 days of moisture diffusion at 80°C is shown in Figure 7.8, with reference dry and saturated distributions. Curves of shear stress at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$ are plotted in Figures 7.8a, 7.8b, and 7.8c, respectively. Very limited variations with diffusion time are observed in the inner regions of the bondline. However, in correspondence to the saturated $y = 0$ edge of the overlap, a sharp increase is visible in the shear stress during the first 5 days of moisture diffusion.

The surface plot in Figure 7.9a shows the two-dimensional shear stress distribution for a SLJ subjected to 5 days of moisture diffusion at 80°C . The results obtained at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$ are compared to the output of the previous 1-D model [42] in Figures 7.9b, 7.10a, and 7.10b. Although the results for the inner portions of the overlap suggest that a one-dimensional approach would not introduce significant errors in the shear stress derivation, there is a significant discrepancy between the two models in the area at and

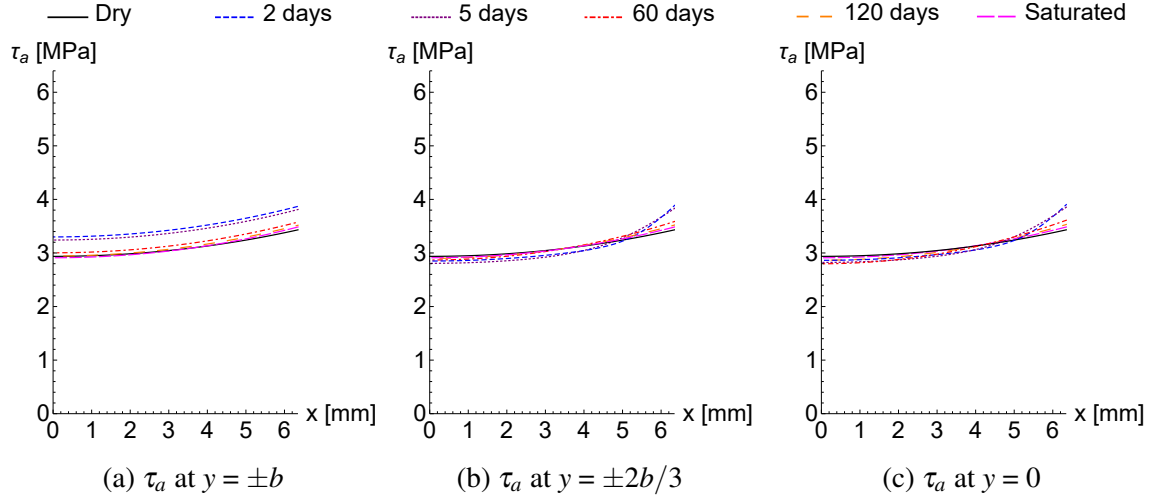


Figure 7.8: Time evolution of shear stress distribution at separate y locations (at 80°C)

near the lateral edges of the bondline ($y = \pm b$), as shown in Figure 7.9b. There, the value of shear stress is underestimated by over 10%, when a one-dimensional approach is used.

7.4.3 Peel stress distribution after joint cooldown

The evolution of the peel stress distribution in a SLJ subjected to moisture diffusion at 80°C and subsequently cooled down before the application of the tensile-shear load is displayed in Figure 7.11. Very limited stress gradients are observed across the width of the joint, with the peel stress distribution approaching rapidly the saturated curve even after only 5 days of moisture diffusion. Some significant differences can be identified near the lateral edge of the overlap, but the value of peak peel stress (located at $x = \pm c$) does not vary with diffusion time.

The two-dimensional peel stress distribution is shown in Figure 7.12a, for a SLJ subjected to 15 days of moisture diffusion at 80°C and consequently cooled down to 20°C , before the application of the external load. The results in Figures 7.12b, 7.13a, and 7.13b confirm that the use of a one-dimensional approach to determine the peel stresses in

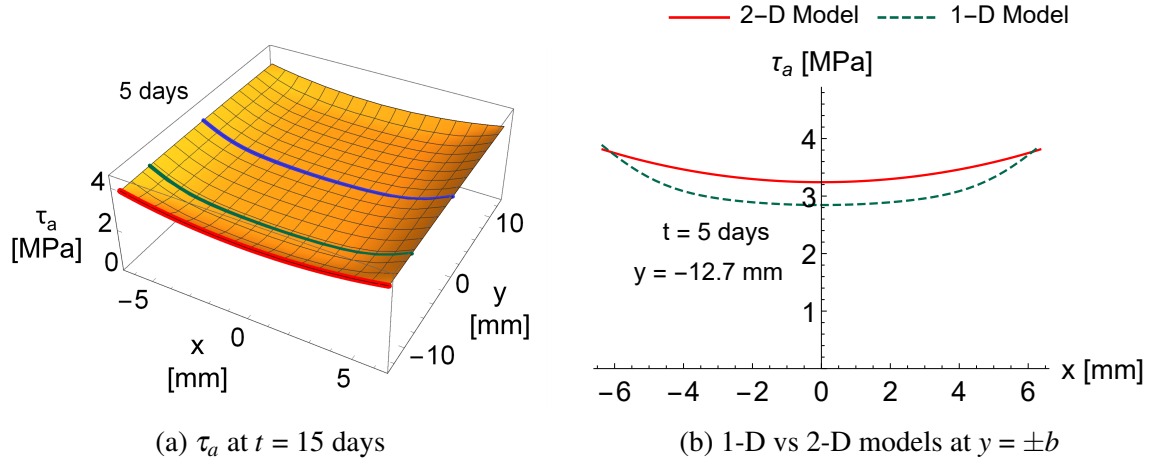


Figure 7.9: Shear stress distribution in the adhesive layer and at $y = \pm b$ after 15 days of moisture diffusion at 80°C

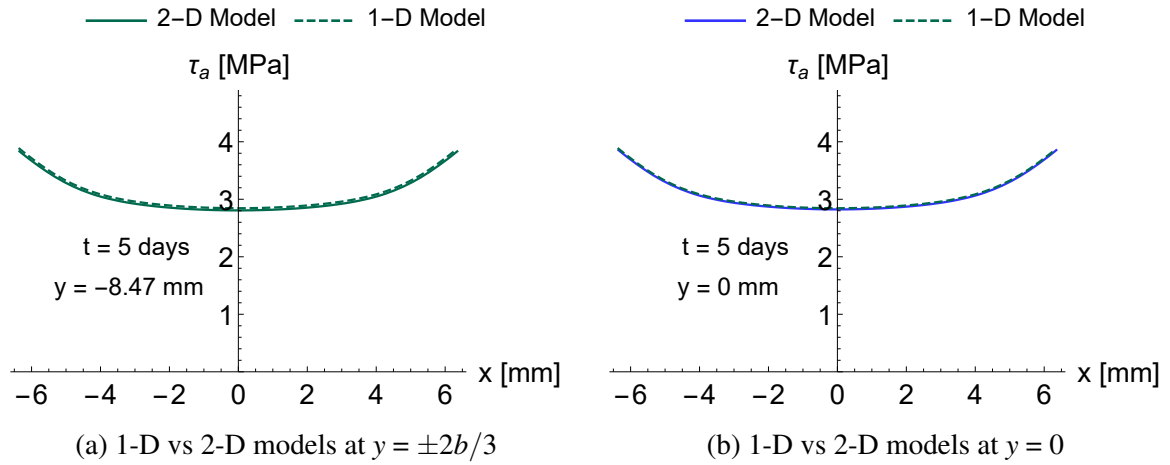


Figure 7.10: Shear stress distribution at two y locations after 15 days of moisture diffusion at 80°C

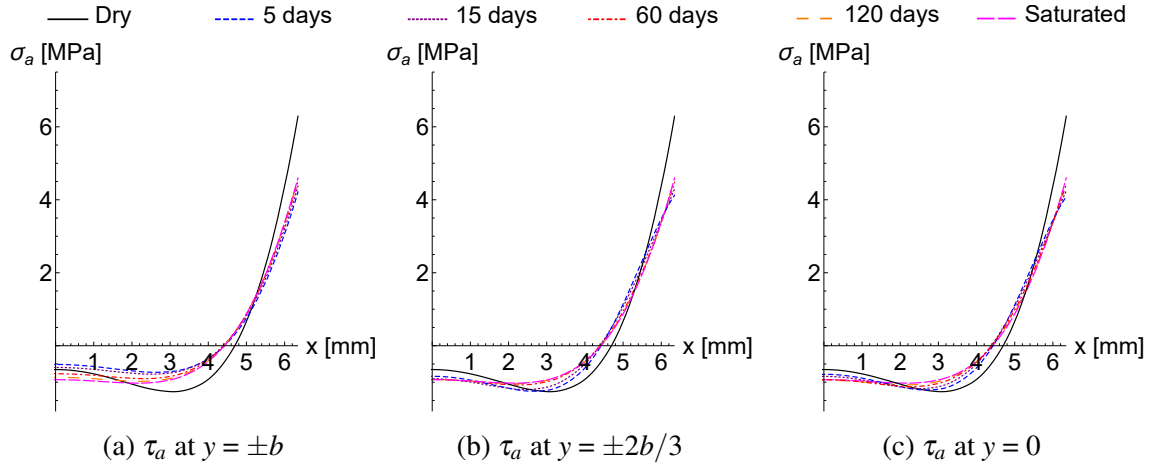


Figure 7.11: Time evolution of peel stress distribution at separate y locations (after cooldown)

an adhesive joint with similar material properties and geometry is adequate and does not introduce significant errors. Some notable discrepancies between the 1-D and the 2-D models can be observed in Figure 7.12b, with the one-dimensional model slightly underestimating the peak stresses at the edges of the overlap.

7.4.4 Peel stress distribution at 80 °C

The time evolution of the peel stress distribution for a SLJ subjected to mechanical loading at 80°C, after 2, 4, 60, and 120 days of high-temperature moisture diffusion is shown in Figure 7.14. The large amount of thermal softening that is combined to the plasticizing action of moisture diffusion causes a general "flattening" of the peel stress distribution, with no variations in time, and across the width of the joint. When the adhesive is subjected to the simultaneous effect of moisture and heat diffusion, the use of a fixed-value softened elastic modulus in the traditional model derived by Goland and Reissner [3] is sufficient to accurately predict the peel stress in the bondline.

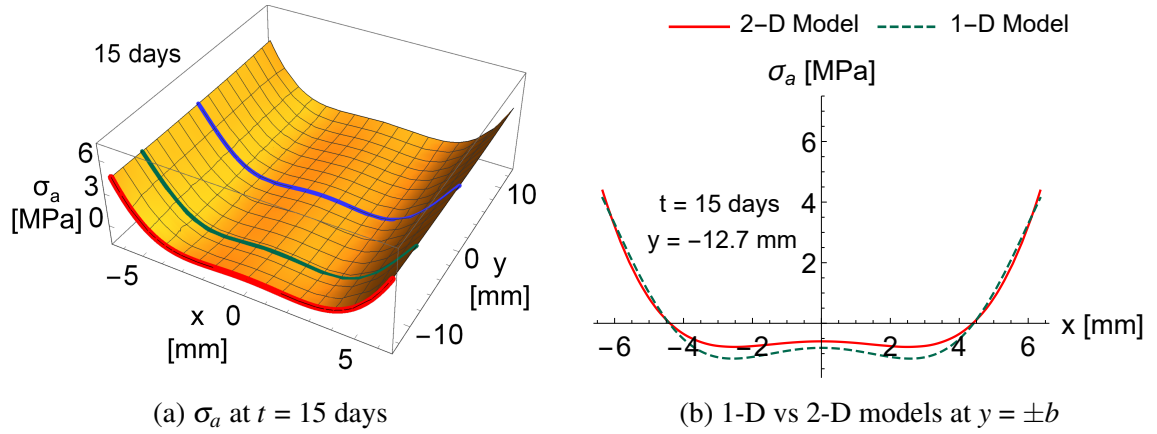


Figure 7.12: Peel stress distribution in the adhesive layer and at $y = \pm b$ after 15 days of moisture diffusion at 80 °C and subsequent cooldown

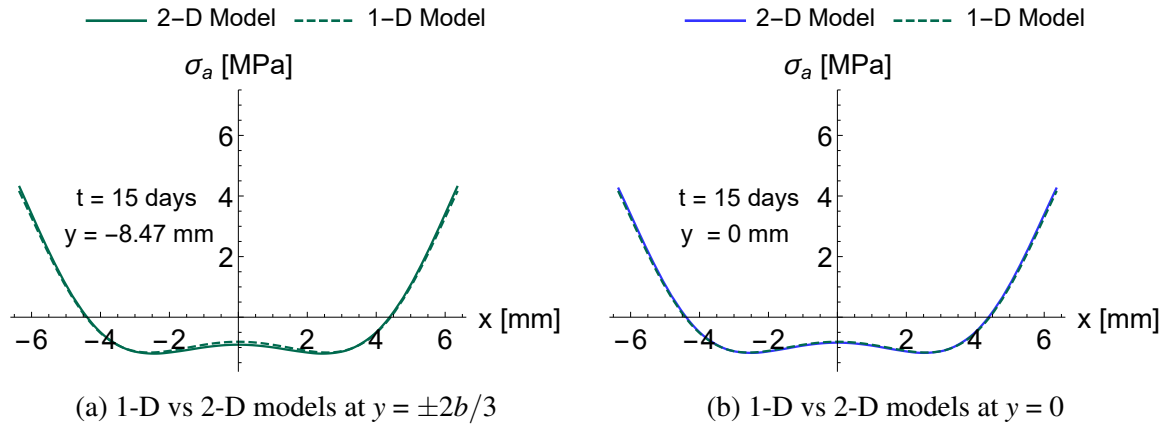


Figure 7.13: Peel stress distribution at two y locations after 15 days of moisture diffusion at 80 °C and subsequent cooldown

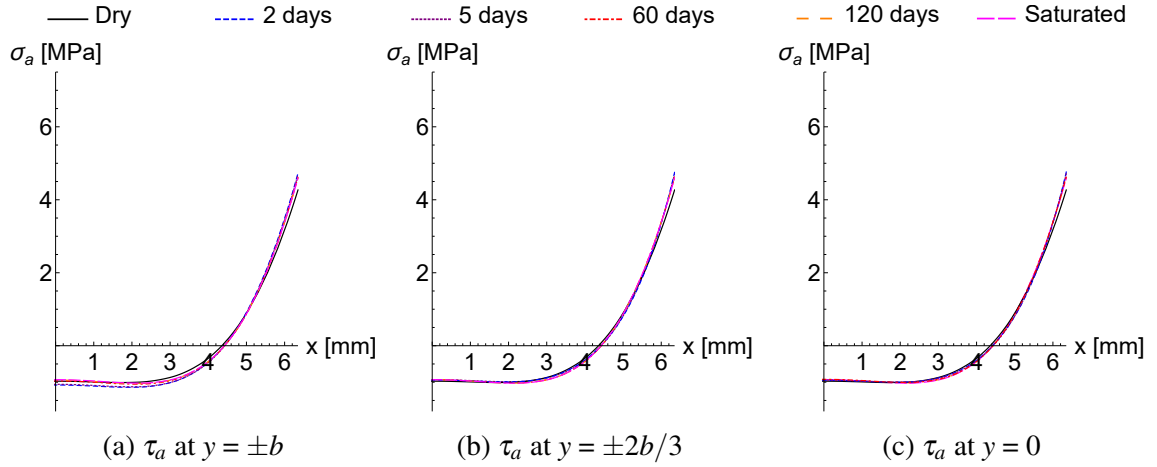


Figure 7.14: Time evolution of peel stress distribution at separate y locations (at 80 °C)

The lack of a gradient in the direction transverse to the axis of shear-tensile load application can be observed in the stress surface in Figure 7.15a. The curves in Figures 7.15b, 7.16a, and 7.16b confirm that the use of a two-dimensional model does not introduce sizeable improvements, for the prediction of peel stresses in the bondline of a SLJ with a heavily plasticized adhesive.

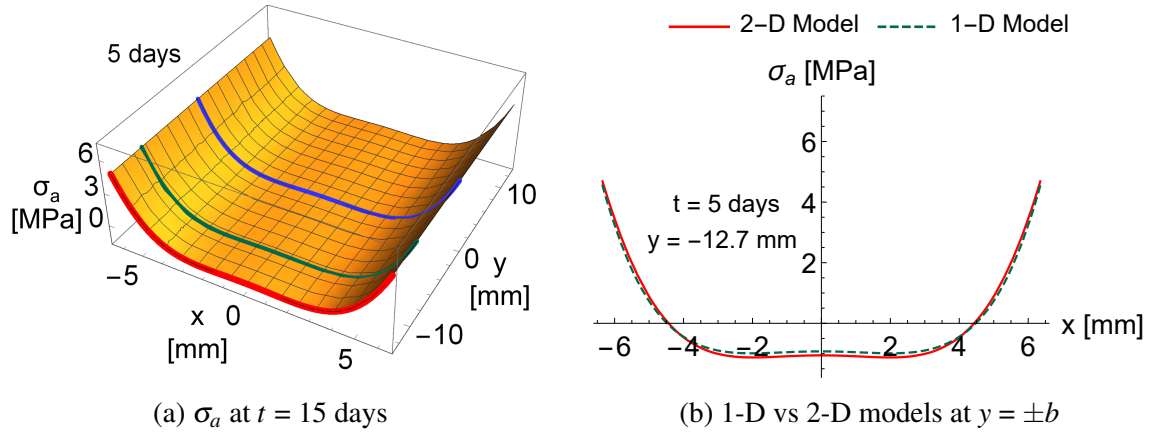


Figure 7.15: Peel stress distribution in the adhesive layer and at $y = \pm b$ after 15 days of moisture diffusion at 80 °C

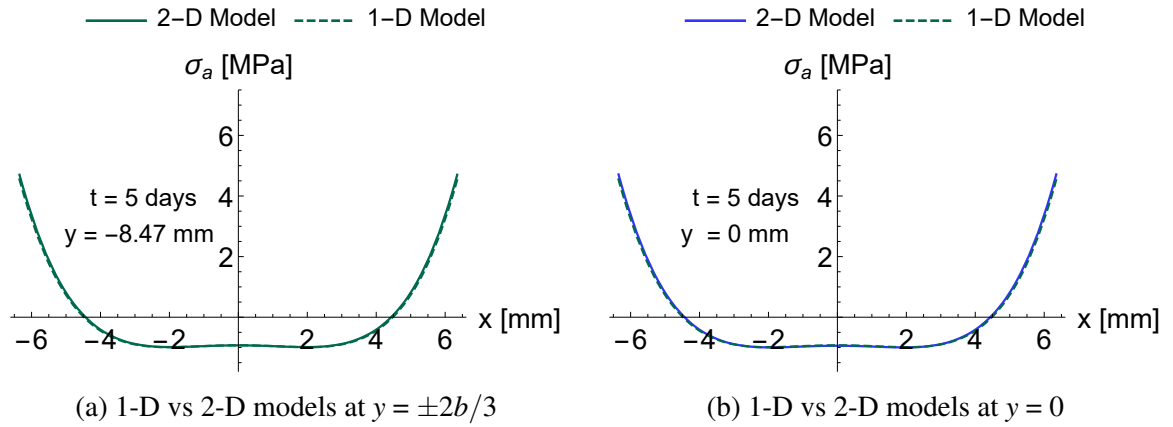


Figure 7.16: Peel stress distribution at two y locations after 15 days of moisture diffusion at 80 °C

CHAPTER EIGHT

COMPARISON OF PROPOSED MODEL PREDICTION WITH FEA RESULTS

8.1 Introduction

In this chapter, the results of the proposed coupled two-dimensional coupled stress-diffusion model are compared to the output of a three-dimensional Finite Elements Analysis, for the moisture-only diffusion scenario outlined in Chapter Six. Boundary conditions and assumptions from the analytical model are replicated in the numerical analysis. Values of adhesive shear and peel stresses are evaluated at multiple locations in the overlap. The differences between the two models are compared to previous studies in the literature.

8.2 FEA Model Parameters

The geometry and material properties of the SLJ used in the FEA model are listed in Table 6.2. ABAQUS[®] 6.14 software is used for the analysis. The adhesive layer is modeled using three-dimensional, 8-node C3D8RT coupled displacement-temperature "brick" elements, with reduced integration and hourglass control. 3200 elements are used across the entire overlap, in one layer (the adhesive thickness is equal to the height of a single element). Three-dimensional, 8-node C3D8R elements with reduced integration and hourglass control are used in the substrates. In correspondence to the joint overlap, the size of the elements in the adherends is equal to exactly 4 times that of the elements in the adhesive layer.

The joint assembly is created by coupling nodal displacements at the adhesive/substrate interfaces. The configuration of loads and constraints on the model reflects the assumptions of the models derived in Chapter Three, as shown in Figure 8.1. In order to compare the FEA model to the results of the shear stress constitutive equation

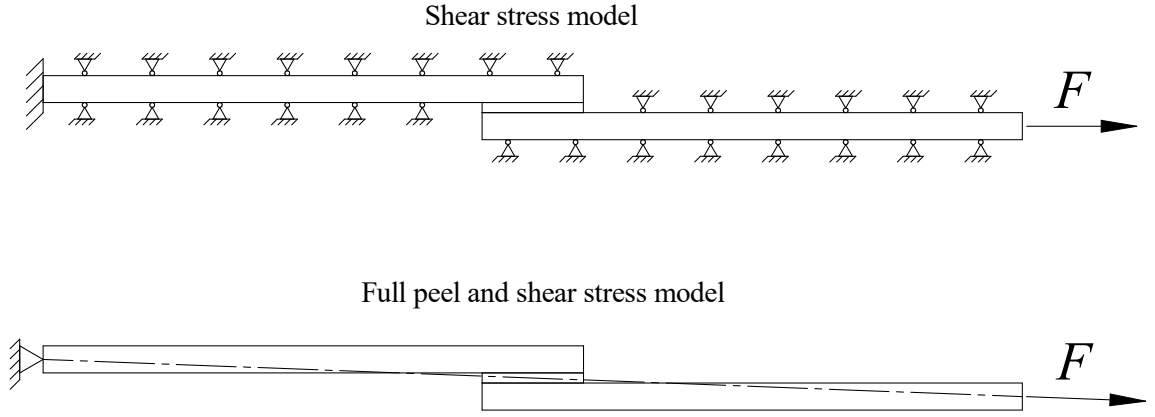


Figure 8.1: Loads and constraints in the FEA model

(Equation (3.12)), bending is restricted by constraining the nodal displacements in the z direction for the entire joint, and the external load is aligned with the x axis. One of the free ends of the SLJ is fixed.

The boundary conditions of the peel stress model are replicated by constraining the mid-thickness translations in every direction at one of the free ends, and by applying the external load as shown in Figure 8.1. Bending of the SLJ is allowed. Finite rotations and shear locking of the elements in the joint are minimized by imposing the line of action of the external load to pass through the hinge support at the constrained end.

Moisture diffusion in the adhesive layer is simulated by setting the values of adhesive heat conductivity, specific heat capacity, and density, such that

$$\frac{k_a}{\rho_a c_a} = D^2 \quad (8.1)$$

The edges of the adhesive layer are maintained at a fixed temperature T_b , and the initial condition of the bondline is $T = T_i$, with $T_i < T_b$. The material properties of the adhesive are varied linearly between dry and saturated values, according to

$$E_a(x, y, t) = E_{a0} + (E_{a\infty} - E_{a0}) \frac{T(x, y, t) - T_i}{T_b - T_i} \quad (8.2)$$

8.3 Shear Stress Comparison

Curves of shear stress obtained with the analytical formulation are compared to the results of the FEA model in Figure 8.2, at $y = \pm b$, $y = \pm 2b/3$, and $y = 0$, for 100 days of moisture diffusion. The results of the proposed analytical model are in reasonable agreement with the numerical simulation. Some differences are observed near the lateral edge of the bondline, in Figure 8.2a, due to the finite width of the brick FEA elements. Moreover, the results of the FEA model satisfy the static requirement of zero shear stress at the free edge of the overlap, which is not respected by the analytical formulation. This is a well-documented shortcoming affecting all the classical analytical models developed for bonded SLJs [2–6, 42–44].

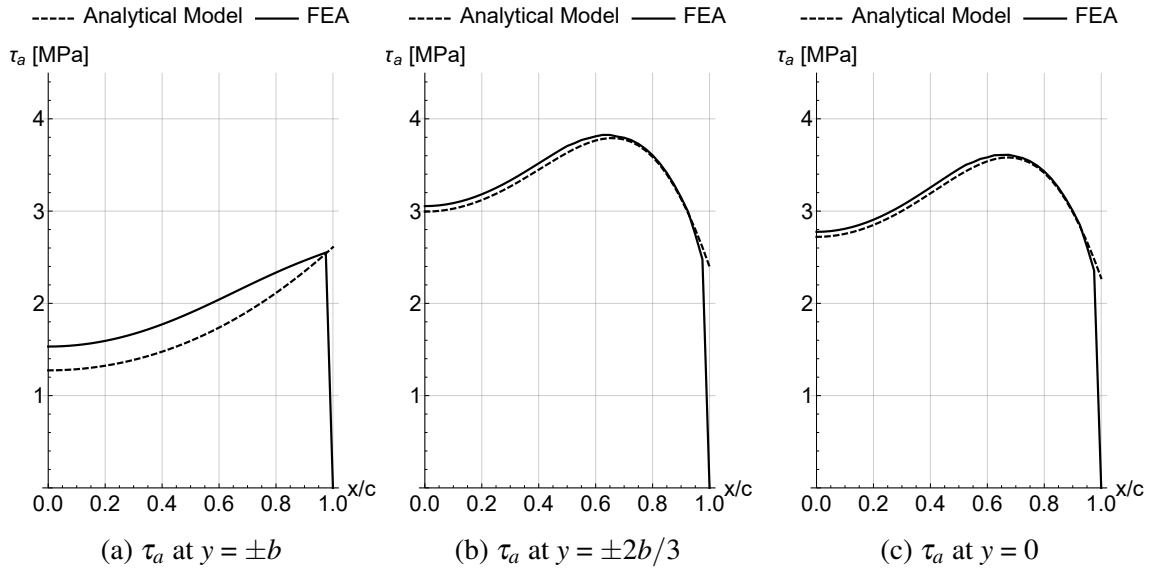


Figure 8.2: Comparison of shear stress distribution between analytical and FEA models at separate y locations

8.4 Peel Stress Comparison

The peel stress distribution in the adhesive layer as calculated by the analytical model is compared to the results of the Finite Elements Analysis in Figure 8.3. Peel stress curves are presented for the y locations of $y = \pm b$, $y = \pm 2b/3$, and $y = 0$, after 100 days of moisture diffusion. The results from the two models are in good agreement, with differences at the edge of the overlap similar to those measured by Mazhari and Nassar in their one-dimensional peel stress-diffusion model [43]. The largest disagreement between the two approaches is observed in correspondence to the edges of the overlap, where the FEA results show a sudden drop in peel stress within the last element of the adhesive layer. The relative difference between the values of peak stress is as high as 30%, for the section of adhesive near $y = \pm 2b/3$.

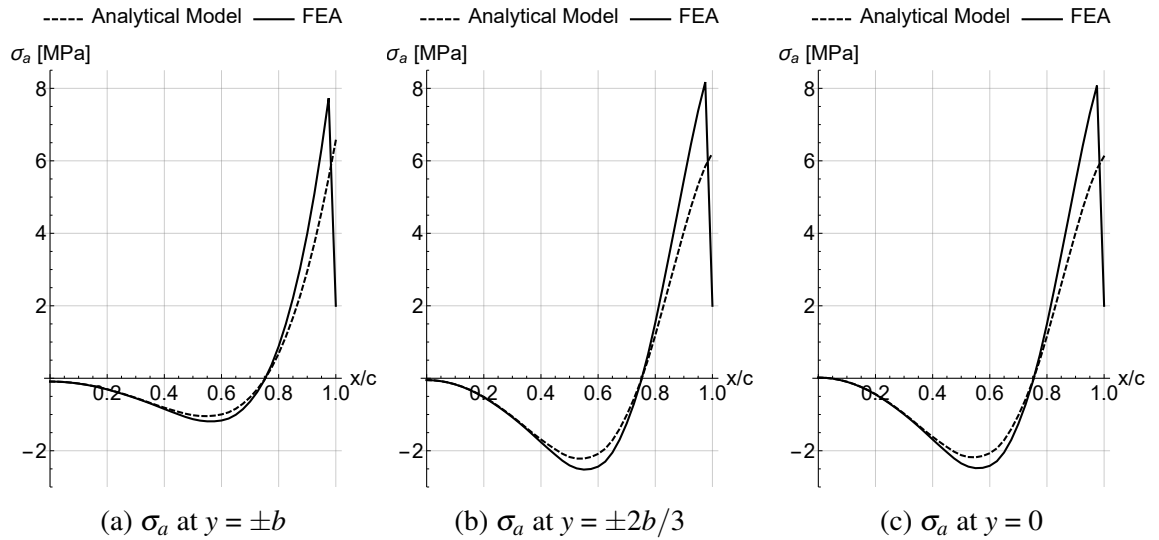


Figure 8.3: Comparison of peel stress distribution between analytical and FEA models at separate y locations

CHAPTER NINE

CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

In this dissertation research, a model for the shear and peel stresses in the adhesive layer of Single Lap Joints subjected to two-dimensional moisture and heat diffusion is proposed. The results are compared to previous one-dimensional approaches and to a three-dimensional Finite Elements Analysis. Experimental data on the thermal softening of two commercially available structural adhesives is collected.

The results from the 2-D analytical model of coupled stress-diffusion in bonded SLJs show a more accurate prediction of the distribution of shear and peel stresses in the adhesive layer, as compared to the previous 1-D formulations. Diffusion of heat or moisture that occurs perpendicularly to the longitudinal axis of the joint leads to significantly increased shear stresses in the non-plasticized area away from the lateral edges of the bondline. Diffusive patterns in the direction of the applied tensile-shear load re-distribute the shear stress in the adhesive layer, decreasing the values of peak stress.

The largest differences between the proposed 2-D model and the previous 1-D approach are observed in conditions with large gradients across the width of the joint: in the first 100 days of moisture diffusion at 20°C, in the first 60 seconds of heat diffusion with thermally-insulated adherends, and in the first 10 days of moisture diffusion at 80°C. The peel stress gradients across the width of the joint are less pronounced than the shear stress gradients, for all investigated scenarios. Significant differences between the previous 1-D model and the proposed 2-D formulations are observed for the prediction of peak peel stress values, located at the edges of the overlap ($x = \pm c$).

Stress gradients across the width of a joint with insulated adherends, and subjected to heat diffusion from the exposed sides of the bondline, are more marginal than in joints subjected to moisture diffusion. Fast thermal conduction within the adhesive reduces temperature differences across the bond area. The case of a joint with artificially slowed internal conduction is investigated, yielding more significant stress gradients in the y direction, for both shear and peel stress distributions. The temperature in joints with non-insulated adherends is considered uniform across the adhesive layer, and a lumped-mass model is used.

Simultaneous diffusion of heat and moisture in the adhesive layer can be decoupled in the time domain. Thermal equilibrium with the surrounding environment is reached before the moisture uptake in the adhesive layer reaches 0.1% of the saturated value. Moisture diffusion is significantly accelerated at high temperature: conditions of near-saturation are reached in 8 months at 80°C, and in 60 months at 20°C. The saturated concentration in the adhesive layer is only slightly affected by heat diffusion. The extreme plasticization of the adhesive layer under the combined action of moisture and heat reduces the transverse gradients in the stress field.

The results of the proposed analytical model are in reasonable agreement with a three-dimensional Finite Elements Analysis. The nonzero width of the brick elements in the FEA model cause some differences in the calculated shear stress near the lateral edges of the bondline. Test data shows that for test temperatures ranging from 20°C to 90°C the elastic moduli of the adhesive can be linearly correlated with bulk material temperature.

A revision of the previous 1-D coupled stress-diffusion model is proposed. The shear stress distribution is successfully approximated with a constant-strain formulation for low-modulus adhesives subjected to 1-D moisture diffusion. Variable substitutions are introduced, yielding simplified constitutive equations and boundary conditions.

9.2 Future Work

Future work to extend this research may include the application and validation of a 2-D adhesive elasto-plastic material model, and further experimental investigation of the interaction between moisture and heat diffusion in structural adhesives.

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