THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Adhesively Bonded Functionally Graded Joints

by

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ABSTRACT

The use of adhesive bonding gives a stress distribution more uniform than with the other traditional methods of fastening such as bolts or rivets and offers the potential for reduced weight and cost. That is the main reason why adhesively bonded joints are increasingly being used in aerospace and automotive industries.

The single lap joint with metallic or composite flat plates is the most common mainly due to its simplicity and efficiency. However, one of the problems associated to this joint is the fact that the stress distribution (shear and peel) is concentrated at the ends of the overlap. This leads to joint premature failures at the ends of the overlap, especially if the adhesive is brittle, if composites with low transverse strength are used or low strength substrates. The objective of this work was to develop ways of reducing these concentrations for more efficient adhesive joint strength. We obtained an adhesive functionally modified with properties that vary gradually along the overlap allowing a true uniform stress distribution along the overlap. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap.

The process that was tested in the present thesis was a differentiated adhesive cure. If the adhesive can have several degrees of cure, then a gradient in the rigidity of the adhesive along the overlap can be obtained. This differentiated cure was carried out with induction heating. Induction heating is a fast heating method because it focuses heat at or near the adhesive bondline. A suitable design of the heating coil was made to ensure a gradual degree of cure along the overlap length. The induction coil surrounds the joints at the ends of the overlap in order to concentrate the temperature at the ends of the overlap. In order to ensure that the temperature gradient along the overlap (being concentrated at the ends of the overlap and less in the middle of the overlap) is obtained, a cooling system was developed for cooling the middle of the bondline.

An analytical model was developed in order to predict the failure load, obtaining a fast analysis of the functionally graded joints using a simple closed-form analysis. This analytical analysis is based on Volkersen's analysis, and was solved with power series expansion for a reduced number of expansion terms (21 terms). The criterion used to predict the failure load for this simple analytical model was that the failure occurs when the maximum shear stress exceeds the shear strength of the adhesive. Numerical modelling by finite element analysis (FEA) was also performed to validate the analytical model.

The specimens were manufactured and tested statically with and without post-cure. The simple analytical model developed to predict the failure load was shown to be a valid tool to predict the maximum failure load of the functionally graded joints. The graded cure apparatus was shown to be a viable technique to obtain a joint with adhesive functionally modified along the overlap. The functionally graded joints, when compared with joints cured isothermally, was shown to have the best performance (highest failure load) and similar displacement than the joints cured isothermally with a ductile behaviour. For joints cured gradually, the strength increases with an increase of the adhesive thickness. The functionally graded joints subjected to post-cure at low temperatures (below the glass transition temperature of the fully cured network, $T_{g\infty}$) show a slight decrease of the strength and the joints cured isothermally show a slight increase of the strength. With increase of the post-cure temperature (above $T_{g\infty}$) the joints cured gradually and isothermally exhibit similar strength, but the functionally graded joints have a slightly higher strength.

The functionally graded cure technique was also performed in wood beams specimens, repaired with carbon fibre reinforced polymer (CFRP) patches. These were compared with specimens cured isothermally. A numerical analysis by FEA using cohesive zone model (CZM) was carried out in order to validate the experimental results obtained, predict the failure mechanism as the failure load. The specimens cured gradually show an increase of the strength when compared with specimens cured isothermally.

Keywords: Epoxy adhesives, induction heating, functionally graded joints, cure-temperature, post-cure, carbon fibre reinforced polymer, repair, stress distribution, analytical analysis, numerical analysis.

RESUMO

A utilização de adesivos estruturais permite uma distribuição de tensões mais uniforme do que outros métodos tradicionais de fixação, tais como parafusos ou rebites e oferece a possibilidade de reduzir o peso e custo de estruturas, sem prejudicar o seu desempenho. Essa é a principal razão para que as juntas adesivas sejam cada vez mais empregues na indústria aeroespacial e automóvel.

De todas as configurações de juntas utilizadas na induústria, as juntas de sobreposição simples, com substratos metálicos ou compósitos, são as mais comuns, principalmente devido à sua simplicidade e eficiência. No entanto, um dos problemas associados a este tipo de junta é o facto da distribuição de tensão (corte e arrancamento) apresentar picos de tensão nas extremidades do comprimento de sobreposição. Isto causa roturas prematuras das juntas nas extremidades da sobreposição, especialmente se o adesivo for frágil e se forem usados substratos de compósito com baixa resistência transversal (através da espessura). O objetivo deste trabalho foi então desenvolver formas de reduzir estas concentrações, de modo a obter uma junta adesiva mais eficiente. Obteve-se um adesivo funcionalmente modificado, com propriedades que variam gradualmente ao longo da sobreposição, permitindo uma uniforme distribuição da tensão ao longo da sobreposição. A rigidez do adesivo varia ao longo da sobreposição, sendo máxima no centro e mínima nas extremidades da sobreposição.

O processo que foi testado nesta tese consistiu na cura diferenciada de um adesivo. Se o adesivo permitir vários graus de cura, então um gradiente na rigidez do adesivo ao longo da sobreposição pode ser obtido. Esta cura diferenciada foi obtida com aquecimento por indução. O aquecimento por indução é um método de aquecimento rápido porque concentra o calor apenas na área de adesão do adesivo. A geometria da serpentina de aquecimento foi ajustada de modo a assegurar um grau de cura gradual ao longo do comprimento de sobreposição. Esta serpentina de indução rodeia as juntas nas extremidades de sobreposição a fim de concentrar a temperatura nas extremidades da sobreposição. Para assegurar que o gradiente de temperatura ao longo da sobreposição é obtido (concentrado nas extremidades da sobreposição e menos no centro da

sobreposição), um sistema de arrefecimento foi desenvolvido para o arrefecimento da junta adesiva no centro.

Um modelo analítico foi desenvolvido para prever a força de rotura, obtendo-se uma análise rápida das juntas funcionalmente graduadas usando uma análise simples do tipo ‘closed-form’. Este modelo é baseado na análise de Volkersen, e foi desenvolvido com expansões de séries de potência para um número reduzido de termos de expansão (21 termos). O critério utilizado para prever a força de rotura para este modelo analítico simples assume que a rotura ocorre quando a tensão máxima de corte excede a resistência ao corte do adesivo. Foi também realizado um estudo numérico alternativo, recorrendo à análise de elementos finitos (FEA) para validação do modelo analítico.

Os provetes foram fabricados e testados estaticamente com e sem pós-cura. O modelo de análise simples desenvolvido para prever a força de rotura demonstrou ser uma ferramenta válida para prever a força máxima de rotura das juntas funcionalmente graduadas. O uso do equipamento de cura graduada mostrou ser uma técnica viável para a obtenção de juntas com adesivo funcionalmente modificado ao longo da sobreposição. As juntas funcionalmente graduadas, quando comparadas com juntas curadas isotermicamente, demonstraram ter um melhor desempenho (força de rotura mais alta) e deslocamento semelhantes ao das juntas curadas isotermicamente com um comportamento dúctil. Para juntas curadas gradualmente, a força aumenta com um aumento da espessura de adesivo. As juntas graduadas funcionalmente, quando submetidas a uma pós-cura a baixas temperaturas (abaixo da temperatura de transição vítrea da rede totalmente curada, $T_{g\infty}$), exibem uma ligeira diminuição da força e as juntas curadas isotermicamente mostram um ligeiro aumento da resistência. Com o aumento da temperatura de pós-cura (acima da $T_{g\infty}$) as juntas curadas gradualmente e isotermicamente apresentam forças de rotura semelhantes, mas as juntas funcionalmente graduadas têm uma resistência ligeiramente superior.

A técnica de cura funcionalmente graduada também foi realizada em provetes de madeira reparados com polímero reforçado com fibra de carbono (CFRP) e foram comparados com provetes curados isotermicamente. Uma análise numérica por FEA com modelos zona coesivos (CZM) foi realizada a fim de validar os resultados

experimentais obtidos, prever o mecanismo de falha e a força de rutura. Os provetes curados gradualmente mostram um aumento da resistência, quando comparado com provetes curadas isotermicamente.

Palavras-chave: adesivos epóxidos, aquecimento por indução, juntas funcionalmente graduadas, temperatura de cura, pós-cura, polímero reforçado com fibre de carbono, distribuição de tensões, análise analítica, análise numérica.

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This thesis is dedicated to the memory of my grandfather.

CONTENTS

LIST OF PUBLICATIONS

1. R.J.C. Carbas, E.A.S. Marques, L.F.M. da Silva, A.M. Lopes, Effect of cure temperature on the glass transition temperature and mechanical properties of epoxy adhesives, The Journal of Adhesion, 2013, DOI: 10.1080/00218464.2013.779559.

2. R.J.C. Carbas, L.F.M. da Silva, E.A.S. Marques, A.M. Lopes, Effect of post-cure on the physical and mechanical properties of epoxy adhesives, Journal of Adhesion Science and Technology, 2013, DOI: 10.1080/01694243.2013.790294.

3. R.J.C. Carbas, L.F.M. da Silva, M.L. Madureira, G.W. Critchlow, Modelling of functionally graded adhesive joints, The Journal of Adhesion, 2013, submitted.

4. R.J.C. Carbas, L.F.M. da Silva, and G. Critchlow, Functionally graded joints by induction heating, 2013, submitted patent.

5. R.J.C. Carbas, L.F.M. da Silva, G.W. Critchlow, Adhesively bonded functionally graded joints by induction heating, International Journal of Adhesion and Adhesives, 2013, submitted.

6. R.J.C. Carbas, L.F.M. da Silva, G.W. Critchlow, Effect of post-cure on adhesively bonded functionally graded joints by induction heating, Journal of Materials: Design and Applications, 2013, submitted.

7. R.J.C. Carbas, G.M.S.O. Viana, L.F.M. da Silva, G.W. Critchlow, Functionally Graded Adhesive Patch Repairs in Civil Applications, Composites Part A, 2013, submitted.

SUMMARY OF THESIS

1. Introduction

1.1. Background and motivation

Structural adhesives show many advantages over classical mechanical fasting methods such as bolts or rivets. One of the main advantages of adhesive joints is that the stress distribution is more uniform. Such advantages include a continuous bond, reduction in structural weight, good fatigue resistance and vibration damping properties. The major concerns include the poor chemical resistance and vulnerability to hostile environments, the necessity for good surface preparation, the process controls and the in service repairs.

Adhesive bonding permits to work with smaller load bearing areas leading to weight savings. That is the main reason why adhesives were initially used in the aeronautical industry where the weight is a crucial matter. Nowadays, structural adhesively bonded joints are increasingly being utilised in many industries, particularly in aerospace, but the automotive industry is the most growing applications. That is obviously because the car industry is looking at ways to reduce fuel consumption by a weight reduction.

The adhesive joint most studied in the literature and most common that can be found in practice is the single lap joint (SLJ), due to its simplicity and efficiency. The main problem associated with this type of joint is the absence of a uniform stress distribution (peel and shear) in the adhesive layer, the stress being concentrated at the ends of the overlap [1]. One of the main areas of investigation in the field of adhesive bonding is to develop ways of reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings. In the literature, several methods to improve the joint strength have been proposed, but none give a uniform stress distribution in the adhesive [2].

The strength of SLJs can be improved through modification of the adherend geometry by inclusion of a taper in the adherend [3-5], by rounding the adherend corners [6-9], or by modifications of the joint and geometry with a spew fillet [10-15]. In joints geometrically modified by inclusion of a taper in the adherend the concentrated load transfer can be more uniformly distributed if the local stiffness of the joint is reduced, the strength of the joint increases substantially and the stress concentration at the ends of the overlap decreases [3-5]. Joints with rounded adherends at the ends of the overlap reduce significantly the shear and peel [6-9]. Modifications of the joint end geometry with a spew fillet provide a smoother load transfer over a larger area, with a great reduction in the adhesive stresses (shear and peel) concentration, and also alter the stress intensity factors [10-15]. However, as the complexity of the geometry increases, so does the difficulty of manufacturing the joint. Therefore, such purely geometrical solutions are not always possible to realize in practice.

Another technique is the use of more than one adhesive (so-called mixed adhesive joints) which consists in using a stiff and strong adhesive in the middle of the overlap and a flexible and ductile adhesive at the ends of the overlap to relieve the high stress concentrations at the ends of the overlap [16-26]. This allows having a more uniform stress distribution which leads to joint strength increases in relation to a stiff adhesive alone [17-22]. da Silva and Adams [14] investigated theoretical and experimental dual adhesive metal/composite joints. The study has shown that that there is a real improvement in joint strength, especially if the difference of coefficients of thermal expansion is high. Fitton and Broughton [20] determined theoretically and experimentally that the variable modulus adhesive is an effective way of reducing stress concentration (especially in peel loadings) and showed that variable modulus bondlines can reduce stress concentrations, increasing joint strength and changing the mode of failure. Marques and da Silva [5], Marques *et al.* [23] and da Silva and Lopes [26] have shown that the mixed adhesive technique gives joint strength improvements in relation to a brittle adhesive alone in all cases. The mixed adhesive joint (with ductile and brittle adhesives) gives a joint strength higher than the joint strength of the adhesives used individually. The mixed adhesive joint technique can be considered a rough version of a functionally graded material.

More recently, there have been several studies in the improvement of the joint strength by making use of functionally graded materials [27-29], and functionally graded bondlines [30-31]. Ganesh and Choo [27], Boss *et al*. [28] and Apalak and Gunes [29] have used functionally graded adherends. Ganesh and Choo [27] and Boss *et al*. [28] evaluated the performance of adherend modulus grading in single-lap bonded joint with uses of a braided preform with continuously varying braid angle and obtained an increase of 20% joint strength, which was obtained mainly due to a more uniform stress distribution. Apalak and Gunes [29] have studied the flexural behaviour of single lap joints with adherends composed of a functionally gradient layer between a pure ceramic (Al_2O_3) layer and a pure metal (Ni) layer. But these studies are not supported with experimental results and the adhesive stress distribution was not hugely affected. There have been some attempts to modify the adhesive along the overlap. Sancaktar and Kumar [30] used rubber particles to modify locally the adhesive at the ends of the overlap and Stapleton *et al*. [31] used glass beads strategically placed within the adhesive layer in order to obtain different densities and change the stiffness along the overlap. But, these techniques (the physical modification of the adhesive with adhesive doped by rubbery particles or glass beads) can be considered a rough version of an adhesive functionally graduated along the bondline. However, the dispersion of particles (rubber particles or glass beads) throughout the adhesive layer is a complex bonding technique which is inconvenient to perform in practice.

Properties of structural adhesives can vary greatly as a function of the cure temperature and it is essential to understand the mechanical and physical behaviour as a function of the cure temperature. In **Paper 1** the mechanical and physical behaviour of different structural adhesives were studied as a function of the cure temperature. Also, and not less important, the effect of post-cure conditions on mechanical and physical behaviour of adhesives were evaluated (**Paper 2**). It is very important to have a good knowledge of the T_g and mechanical properties of the adhesive after being exposed to temperature for a certain time (post-cure conditions). This thorough knowledge of the adhesive's behaviour is required as adhesives are commonly subjected to a wide range of temperatures during and after manufacture in industrial applications. Therefore, with this two studies (**Paper 1** and **2**) the influence of the cure temperature and the post-cure conditions on adhesives properties are completely understood. This is crucial so that a graded joint with the desired mechanical properties along the overlap can be obtained.

In the literature, several analytical and numerical models to analyse the stress distribution in the adhesive layer can be found [1]. For simple structures, the stress distribution can be obtained quickly and easily by a closed-form analysis. The first attempt to analyse the SLJ was carried out by Volkersen [32]. For complex geometries and elaborate material models, obtaining the stress distribution by a finite element analysis (FEA) is preferable [33-34]. But, due to the increasing interest and research in functionally graded joints, it was essential to develop a simple analytical model for a rapid analysis of the stress distribution along the overlap length and to predict the joint strength (**Paper 3**).

In order to test experimentally the functionally graded joints it was necessary to develop a technique to obtain a graded cure along the bondline. The developed technique ensures a true continuously functionally modified adhesive along the overlap length of the joint and was achieved by induction heating. With this technique the adhesive stiffness varies gradually along the overlap, being maximum in the middle and minimum at the ends of the overlap. This is achieved by the use of a differential cure process along the overlap length, by induction heating (**Paper 4**). An induction coil was designed made in order to obtain the desired temperature distribution along the length of the overlap to achieve a gradual degree of cure. The joints obtained by this apparatus show a more uniform stress distribution along the overlap length and the stress concentrations at the ends of the overlap of the joints are reduced, allowing for stronger and more efficient adhesive joints.

The joint strength performance of the functionally graded joints was compared with joints with homogenous adhesive properties (isothermal cure) along the overlap (**Paper 5**). The influence of the post-cure on the functionally graded cure was performed, to evaluate and understand the performance of functionally graded joints when subjected to different temperatures after manufacture in industrial applications (**Paper 6**). For example, in the assembly lines of the automotive industry, structural adhesives used to bond the different parts of the automobile are subjected to post-cure conditions; the post-cure occurs during the painting process where the entire body is subjected to high temperature to cure the paint. The simple analytical model proposed (**Paper 3**) was used to predict the failure load of the functionally graded joints tested experimentally (**Paper 5** and **6**).

Wood beams are used in different civil applications, so it is important to study the repairs of these beams. In **Paper 7** a study was made on the two most common types of damage of wood beams under bending loads. The types of damage are: compression failure (with the patch on the upper side) and cross grain tension failure (with the patch on the bottom side). The differential cure technique by induction heating was also performed in specimens of wood beams repaired with adhesively bonded carbon fibre reinforced polymer patch. These specimens were compared with the specimens cured isothermally, in order to evaluate the gain performance between the cure techniques (**Paper 7**).

1.2. Problem definition

SLJ is the most studied bonded joint configuration and also the most easily found in industry. The main problem associated with these joints is that the stress distribution (peel and shear) along the overlap is not uniform, being concentrated at the ends of the overlap, leading to premature failure of the adhesive. That is why one of the main areas of investigation in the field of adhesive bonding is to develop ways of reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings. In the literature, several methods to reduce these stress concentrations can be found, allowing for a more efficient adhesive joint strength and additional weight savings. However, none gives a uniform stress distribution along the adhesive layer.

1.3. Objectives

Nowadays, there is a strong trend towards the use of functionally graded joints, with particular importance for the joints with functionally modification of the adhesive along the overlap length. The main goal of this work was to study a joint with functionally modified adhesive in order to have mechanical properties that vary gradually along the bondline, allowing a uniform stress distribution and a higher joint strength.

The objectives were:

- To determine what is the effect of the cure temperature on several types of adhesives;
- To relate the mechanical properties of adhesives with the cure temperature;
- To study the influence of a post-cure below and above the T_g of the adhesive on the mechanical properties of the adhesive;
- To design an apparatus that applies a graded heating along the overlap;
- To manufacture graded joints in a controlled and repetitive way;
- To test statically graded joints and compare their strength with joints that have uniform properties;
- To study the effect of a post-cure on the strength of graded joints;
- To develop an analytical model to predict the strength of graded joints in a practical way;
- To study the applicability of the graded cure concept (performance of CRFP patch repair of wood structures with a functionally graded bondline).

1.4. Research methodology

The methodology followed in this doctoral research is as follows:

- Paper 1 – Different adhesives were studied in order to evaluate the influence of the curing temperature on the mechanical properties;
- Paper 2 – The adhesives that show a high variation of the mechanical properties as a function of cure temperature were subjected to different post-cure temperatures in order to evaluate the influence of the post-cure temperature on the mechanical properties;
- Paper 3 – A simple analytical analysis based on Volkersen's analysis [32] was developed in order to obtain a quick analysis (shear stress distribution along the bondline and failure load prediction). Also, a numerical analysis with the finite element method was done in order to validate the analytical analysis developed.
- Paper 4 – The induction heating technology was studied and a set of coils designed, drawn into a patent, and a complete working apparatus was assembled in order to obtain a functionally graded adhesive along the overlap;
- Paper 5 – The specimens were manufactured and tested statically. The functionally graded joints were compared with joints cured isothermally in order to prove the gain performance of the graded joints;
- Paper 6 – The functionally graded joints and the joints cured isothermally were subjected to different post-cure conditions (below and above the glass transition temperature, T_g, of the adhesive) in order to understand the influence of post-cure on the joint strength;
- Paper 7 – The specimens of wood beams repaired with adhesively bonded CFRP were cured gradually along the bondline by induction heating and compared with the specimens cured isothermally. In order to predict the failure mechanism and maximum load a numerical analysis by FEA using CZM was carried out.

1.5. Outline of the thesis

This thesis consists of five appended papers, a patent (**Paper 4**) and a summary.

Paper 1 R.J.C. Carbas, E.A.S. Marques, L.F.M. da Silva, A.M. Lopes, Effect of cure temperature on the glass transition temperature and mechanical properties of epoxy adhesives, The Journal of Adhesion, 2013, DOI: 10.1080/00218464.2013.779559.

Abstract of Paper 1: *Effect of cure temperature on the glass transition temperature and mechanical properties of epoxy adhesives*. This paper describes the influence of the curing temperature on the physical and mechanical properties of three structural adhesives. This work was undertaken to improve the understanding of the effect of curing temperature in the glass transition temperature, T_g, and stiffness of epoxy adhesives. The mechanical properties (Young's modulus and yield strength) of the adhesives were measured in bulk specimens. T_g was measured by a dynamic mechanical analysis using an in-house developed apparatus. The curing process was the same for all tests, consisting of a curing stage followed by a post cure stage. The initial stage was performed at different temperatures. T_g and the mechanical properties was found to vary as a function of the cure temperature of the adhesive. When cured below the cure temperature, T_{cure}, at which the T_g of the fully cured network, $T_{g\infty}$, is achieved, the strength and stiffness of the adhesive increase as the cure temperature increases and the T_g is higher than the cure temperature. When cured above the T_{cure} at which the $T_{g\infty}$ is achieved, the strength and stiffness decrease as the cure temperature increases and the T_g is higher than the cure temperature.

Paper 2 R.J.C. Carbas, L.F.M. da Silva, E.A.S.Marques, A.M.Lopes, Effect of post-cure on the physical and mechanical properties of epoxy adhesives, Journal of Adhesion Science and Technology, 2013, DOI: 10.1080/01694243.2013.790294.

Abstract of Paper 2: *Effect of post-cure on the physical and mechanical properties of epoxy adhesives*. The effects of post-curing and cure temperature on the glass transition temperature, T_g, and mechanical properties of epoxy adhesives were studied. T_g was measured by a dynamic mechanical analysis (DMA) apparatus developed in-house and the mechanical properties of the adhesives (yield strength, Young´s modulus and failure strain) were measured by a tensile machine. The relationships between T_g and mechanical performance under various post-cure conditions, were investigated. The curing process was the same for all tests, consisting of an initial stage performed at different temperatures followed of a cooling at room temperature. Three sets of specimens were considered, sharing the same initial cure process, but with a different post-curing procedure. In the first set, the specimens were only subjected to a curing process; in the second set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature below the T_g of the fully cured network, $T_{g\infty}$; and in the third set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature above the $T_{g\infty}$. When post-cured at a temperature above $T_{g\infty}$, the mechanical and physical properties tend to have a constant value for any cure temperature.

Paper 3 R.J.C. Carbas, L.F.M. da Silva, M.L. Madureira, G.W. Critchlow, Modelling of functionally graded adhesive joints, The Journal of Adhesion, 2013, submitted.

Abstract of Paper 3: *Modelling of functionally graded adhesive joints*. Nowadays, there is a strong trend towards the use of functionally graded materials, with particular importance for the functionally graded joints. The main objective of this work was to study a functionally modified adhesive in order to have mechanical properties that vary gradually along the overlap of a joint, allowing a uniform stress distribution along the overlap. This allows for a stronger and more efficient adhesive joint and would permit to work with much smaller areas, reducing considerably the weight of the structure which is a key factor in the transport industry. In the proposed joint, the adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap. The functionally graded joint was found to have a higher joint

strength compared to the cases where the adhesive has homogenous properties along the overlap.

A simple analytical model to study the performance of the functionally graded joints was developed. The differential equation of this model was solved by a power series. Numerical modelling by finite element analysis was performed to validate the analytical model developed.

Paper 4 R.J.C. Carbas, L.F.M. da Silva, and G. Critchlow, Functionally graded joints by induction heating, 2013, submitted patent.

Abstract of Paper 4: *Functionally graded joints by induction heating*. The main objective of this invention was to develop a technique to obtain an adhesive functionally modified in order to have mechanical properties that vary gradually along the overlap, allowing a uniform stress distribution along the overlap and to reduce the stress concentrations at the ends of the overlap of lap joints. This allows for a stronger and more efficient adhesive joint. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap.

An induction coil was designed to achieve a graded cure so that an adhesive with graded properties is obtained along the overlap of a lap joint. A suitable design of the heating coil was made in order to obtain the desired temperature distribution along the length of the overlap to achieve a gradual degree of cure.

Paper 5 R.J.C. Carbas, L.F.M. da Silva, G.W. Critchlow, Adhesively bonded functionally graded joints by induction heating, International Journal of Adhesion and Adhesives, 2013, submitted.

Abstract of Paper 5: *Adhesively bonded functionally graded joints by induction heating*. The main objective of this work was to develop an adhesive functionally modified in order to have mechanical properties that vary gradually along the overlap, allowing a more uniform stress distribution along the overlap and to reduce the stress concentrations at the ends of the overlap. This allows for a stronger and more efficient adhesive joint. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap.

In this study, grading was achieved by induction heating, giving a graded cure of the adhesive along the joint. The functionally graded joint was found to have a higher joint strength compared to the cases where the adhesive is cured uniformly at low temperature or at high temperature. Analytical analysis was performed to predict the failure load of the joints with graded cure and isothermal cure.

Paper 6 R.J.C. Carbas, L.F.M. da Silva, G.W. Critchlow, Effect of post-cure on adhesively bonded functionally graded joints by induction heating, Journal of Materials: Design and Applications, 2013, submitted.

Abstract of Paper 6: *Effect of post-cure on adhesively bonded functionally graded joints by induction heating*. Functionally graded joints with an adhesive functionally modified by induction heating confer a more uniform stress distribution along the overlap and reduce the stress concentrations located at the ends of the overlap. The adhesive stiffness varies gradually along the overlap, being maximum in the middle and minimum at the ends of the overlap.

The effect of post-curing on functionally graded joints obtained by induction heating was studied in order to understand the performance of functionally graded joints when submitted to different post-cure temperatures. Three different post-curing conditions were considered, with temperatures above and below the glass transition temperature of the fully cured network, $T_{g\infty}$. The functionally graded joints (with and without post-cure) were compared with joints cured isothermally (with and without post-cure). The cure temperature values applied to the ends and to the middle of the graded joint are the same temperatures used to cure the isothermally cured joints. Analytical modelling to assist with the prediction and assessment of the possible effectiveness of a graded joint concept. The functionally graded joints subjected to post-cure at low temperatures (below $T_{g\infty}$) show a slight decrease of the strength and the joints cured isothermally show a slight increase of the strength. With increase of the post-cure temperature (above $T_{g\infty}$) the functionally graded joints exhibit strength similar to that of the joints cured isothermally. However, even for the highest post-cure temperatures, the functionally graded joints have a slightly higher strength.

Paper 7 R.J.C. Carbas, G.M.S.O. Viana, L.F.M. da Silva, G.W. Critchlow, Functionally Graded Adhesive Patch Repairs in Civil Applications, Composites Part A, 2013, submitted.

Abstract of Paper 6: *Functionally Graded Adhesive Patch Repairs in Civil Applications*. Several investigations have been made concerning the fracture behaviour of scaled specimens of wood beams repaired with adhesively bonded carbon fibre reinforced plastic. However, one of the problems associated to these joints is the fact that the stress distribution (shear and peel) is concentrated at the ends of the overlap, leading to premature failure of the joint. Some solutions to this problem have been developed, such as hybrid joints, adherend shaping, adherend rounding and fillets at the ends of the overlap. Some of these methods tend to increase the weight of the structure and others are very expensive due to its complex manufacturing process.

The stress concentration can be reduced with use of a functionally graded adhesive, in which the mechanical properties vary along the bondlength. This can be achieved with a graded cure, in which the temperature varies along the bondlength. In order to perform a graded cure, induction heating was used. This technique has already been successfully tested in single lap joints to obtain a more uniform stress distribution along the bondlength, increasing the strength of the joint. In this project, the repair of wood structures with Carbon-Fibre Reinforced Plastic (CFRP) was made using a homogeneous cure and a graded cure.

Two common types of defects on beams under bending solicitations were analysed. Scaled specimens of damaged wood beams were repaired and tested under four point

bending. The results show that the beams repaired with a graded bondline were able to withstand higher loads.

2. Adhesives tested

Two bi-component paste epoxy adhesives Araldite® 2011 (Huntsman, Basel, Switzerland) and Loctite Hysol® 3422 (Henkel, Dublin, Ireland) were studied. The chemical formulation of adhesive Araldite® 2011 is bisphenol A for the epoxy resin and polyaminoamide for the hardener. The chemical formulation of adhesive Loctite Hysol® 3422 is bisphenol A diluted with bisphenol F for the epoxy resin, and 3-Aminopropylmorpholine and polyoxypropylene diamine for the hardener.

Firstly (in **Paper 1),** the mechanical and physical properties behaviour of different structural adhesives (Araldite® 2011, Araldite® AV 138M (Huntsman, Cambridge, England) and Sikadur®-30 LP (Sika, Zurich, Switzerland)) as a function of the cure temperature was characterized so that the relation mechanical properties vs. cure temperature is known. This study was performed in order to evaluate which adhesive shows the highest variation of the mechanical properties as a function of the cure temperature.

In **Paper 2**, Araldite® 2011 and Loctite Hysol® 3422, which were the adhesives that showed the largest variation of the mechanical properties as a function of the cure temperature were further studied. Both adhesives mechanical and physical behaviour was studied when submitted to different post-cure conditions, in order to understand the effect of post-cure conditions on the mechanical and physical properties.

In order to completely understand the adhesive properties along the overlap length two types of tests were performed (failure strength and non-destructive tests).

For the failure strength properties, tensile tests were performed to obtain the tensile properties of the adhesives (stress-strain curves) as a function of the cure temperature and/or post-cure conditions. Typical stress-strain curves of the adhesive Araldite® 2011 as a function of the cure temperature are shown in Figure 1.

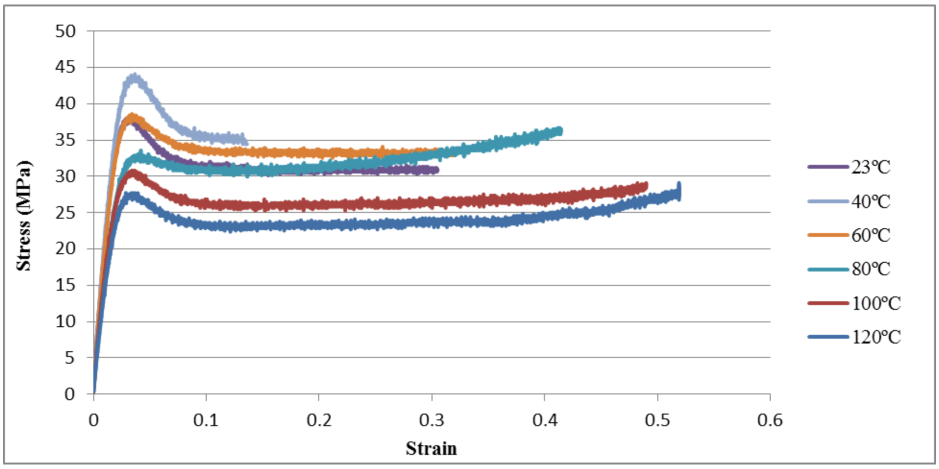

Figure 1 – Tensile stress-strain curves of Araldite® 2011 adhesive as a function of the cure temperature.

The variation of the Young´s modulus and yield strength of adhesive Araldite® 2011 as a function of the cure temperature is shown in Figure 2. The data obtained shows an increase of the adhesive strength and stiffness with increasing cure temperature below $T_{g\infty}$. Above $T_{g\infty}$, as the cure temperature increases, the adhesive strength and stiffness decrease (Figure 2). For specimens cured near $T_{g\infty}$, the adhesive shows the best performance (highest strength and stiffness).

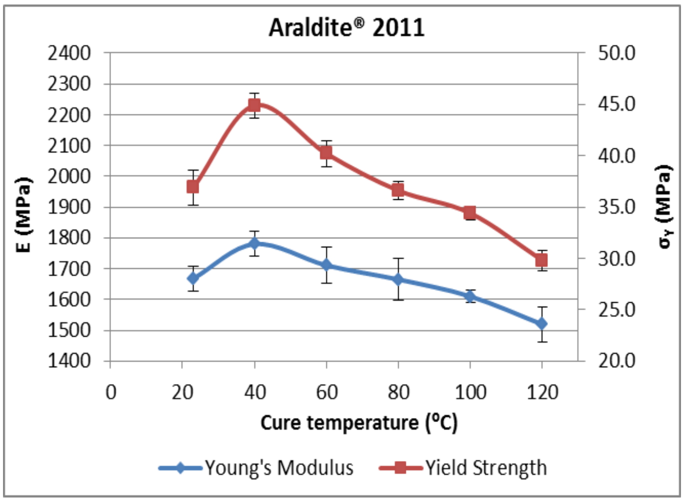

Figure 2 – Young's modulus and yield strength as a function of cure temperature

The non-destructive tests performed were dynamic mechanical analysis (DMA), in order to get the T_g of the adhesive as a function of the cure temperature and/or post-cure conditions. The determination of T_g is important to understand how the mechanical properties vary, to know when the adhesive is fully cured and what is the effect of a post-cure on T_g. The DMA apparatus used to measure T_g was developed in-house. Figure 3 illustrates the behaviour of the measured T_g of adhesive Araldite® 2011as function of the cure temperature.

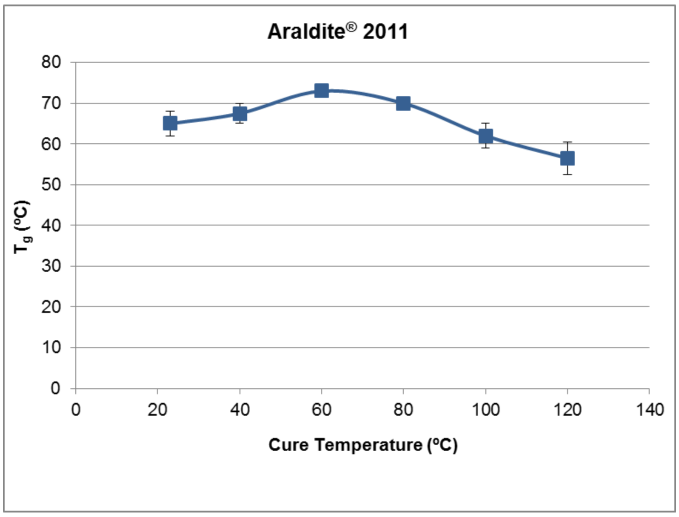

Figure 3 – T_g as a function of the cure temperature.

In the design of adhesively bonded functionally graded joints, the availability of reliable damage models to predict their fracture behaviour when cured at different temperatures is fundamental. Therefore, in order to apply a fracture mechanics or damage mechanics approach, it is essential to have the fracture toughness of the material.

In **Paper 7** the fracture toughness of the adhesive Loctite Hysol® 3422 was studied in pure mode I and II for different cure temperatures (23, 60 and 100 ºC). For this, the double cantilever beam (DCB) specimen is used for pure peel (mode I) deformation and the end notched flexure (ENF) specimen, for pure shear (mode II) deformation was performed. The mode I and II toughness values of the adhesive as a function of the cure temperature are shown in Figure 4.

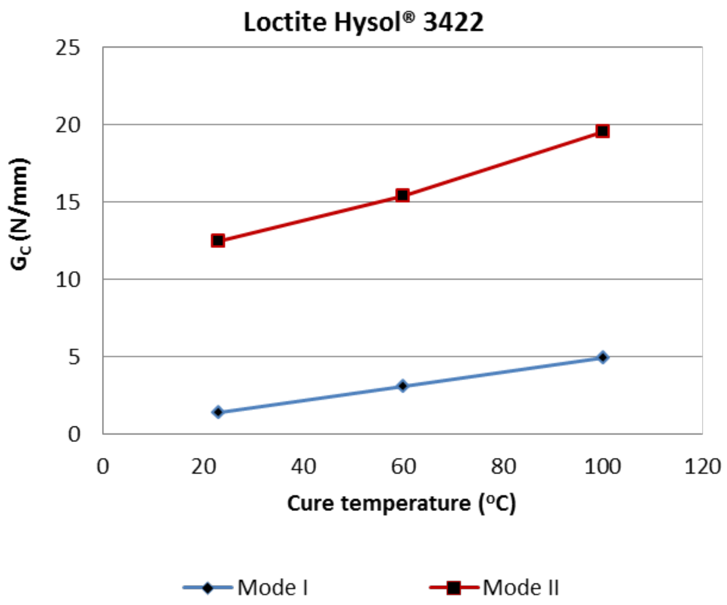

Figure 4 – Toughness in modes I and II as a function of the temperature of cure.

The mode I and II toughness of the adhesive show an increase with increase of the cure temperature. As expected, with increase of the cure temperature the adhesive becomes more ductile.

3. Analytical modelling

Due to the increasing interest and research in functionally graded joints, it was essential to develop a simple analytical model for a rapid analysis of the stress distribution along the overlap length and to predict the joint strength (**Paper 3**). This simple analytical model was developed by making use of power series expansions and was based on Volkersen equation [32]. The shear stress distribution obtained by this novel analytical model was validated by FEA. Figure 5 shows that the adhesive shear stress distribution of functionally graded joints obtained by both methods (analytical and numerical analysis) with an overlap length of 50mm compare quite well. For this simple analytical model, the criterion of failure load prediction used is when the maximum shear stress exceeds the shear strength of the adhesive.

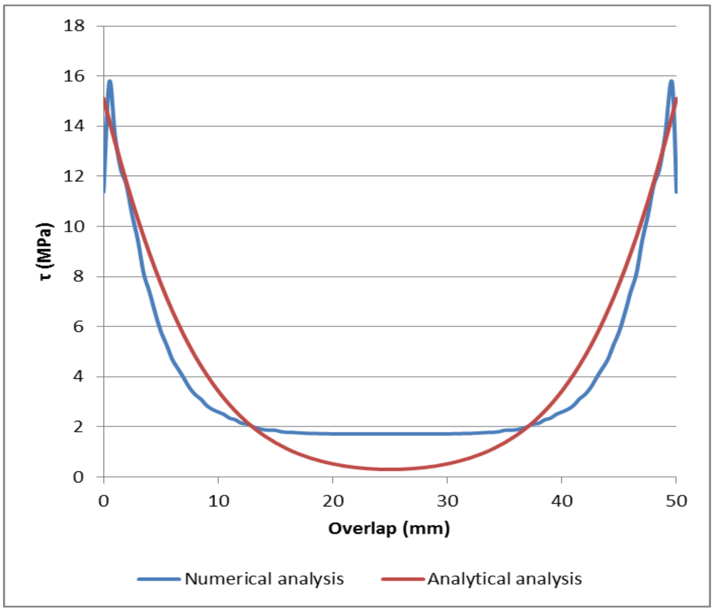

Figure 5 – Comparison of analytical and numerical analyses for a SLJ with an overlap length of 50mm.

In order to take into account the plastic behaviour of the adhesive, an elastic-plastic analysis was used. The simple elastic-plastic adhesive behaviour proposed Adams and Mallick [35] that introduced the linear 'effective modulus' solution. This analysis consists in considering the energy under the stress-strain curve obtained through tensile tests and this energy is used to construct a theoretical line (called the linear 'effective modulus' solution), which has the same shear strain energy and strain to failure of the full elastic-plastic curve (see Figure 6).

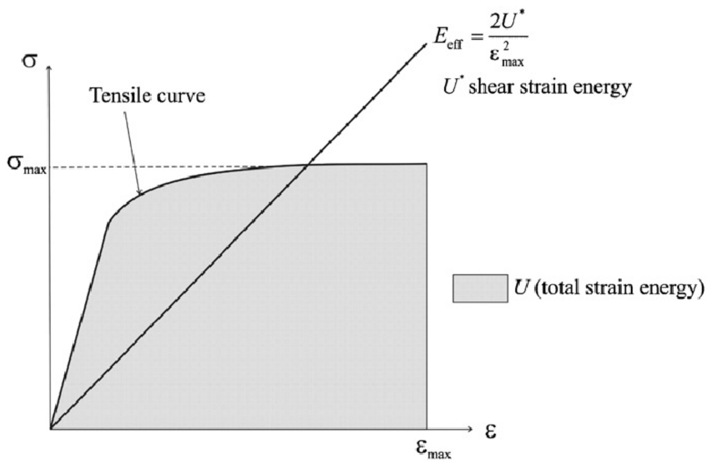

Figure 6 – 'Effective modulus' solution proposed by Adams and Mallick [35].

This simple analytical analysis also was used to predict the failure load of the experimental tests of the functionally graded joints (**Paper 5** and **6**). For each functionally graded joint studied, this analytical model gave good failure load predictions.

4. Numerical modelling

Numerical modelling provides a good prevision of the mechanical behaviour of adhesive joint. In **Paper 7** the FEM analyses were performed in ABAQUS 6.10 program using CZM, to predict the failure load, the stress distribution and the formation and propagation of cracks of the repaired beams. The typical mesh used is showed in Figure 7. In order to simulate the variation of the mechanical properties of the adhesive along the bondline, 50 partitions were made in the adhesive layer so that the transition between mechanical properties became the smoothest possible.

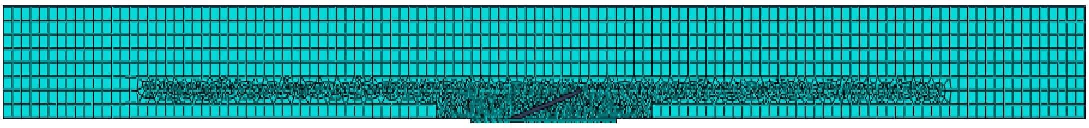

Figure 7 – Mesh of the cross grain tension repair.

Figure 8 shows the stress distribution along the overlap of the cross grain tension repairs specimens for a 40 mm repair.

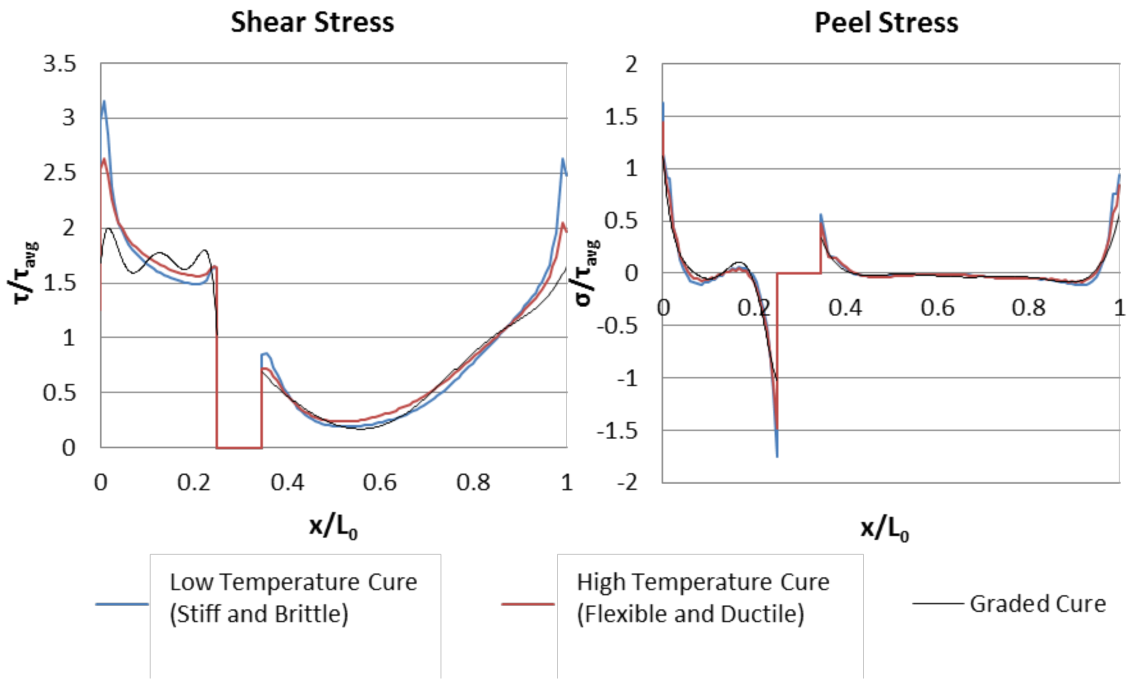

Figure 8 – Shear and peel stress distribution in the 40 mm repair cross grain tension specimen.

The maximum stress (both peel and shear) occurs at the ends of the overlap. However, the stress concentration is attenuated for repaired beams gradually cured. The specimens that show the higher stress concentration at the ends of the overlap is the specimens cured at low temperature. The graded cure was able to create the most uniform stress distribution.

5. *Graded heating apparatus design*

An apparatus (**Paper 4**) was developed in order to obtain a functionally graded joint, where the ends of the overlap are cured to obtain flexible and ductile properties while the middle was cured to obtain a stiff and strong adhesive. This differentiated cure was obtained by induction heating. The patent (**Paper 4**) explains the developed apparatus that ensures a graded heating and hence graded adhesive properties along the overlap length of the joint by induction heating. In order to obtain the desired temperature distribution along the overlap length to achieve a gradual degree of cure, suitable induction and cooling coils were designed. Steel adherend specimens were used in this work bonded with two distinct epoxy adhesives.

6. *Joint strength*

The tests were performed at a constant displacement rate of 1 mm/min. For each case five specimens were tested in laboratory ambient conditions (room temperature of 23ºC, relative humidity of 55%).

After the characterization of adhesive properties, the behaviour of joints with functionally modified adhesives was analysed. The geometry and dimensions of the SLJ used are detailed in Figure 9. The dimensions selected for this work were an adherend thickness of 2 mm, an adhesive thickness of 1 mm and an overlap length of 50 mm.

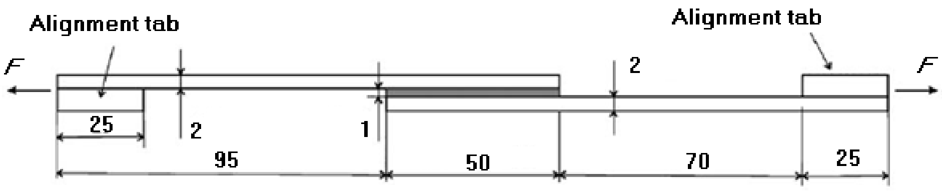

Figure 9 – Geometry of the SLJ test specimens (dimensions in mm).

The adherend selected was a high strength steel (DIN C65 heat treated) with (tensile strength of the adherend of 1260 MPa to avoid plastic deformation of the adherend [36 - 38].

SLJs with functionally modified adhesive were compared with SLJs with homogenous adhesive properties along the overlap (**Paper 5**). Typical load-displacement curves obtained by tensile tests of the SLJ specimens are represented in Figure 10, showing clearly the higher strength of graded joints.

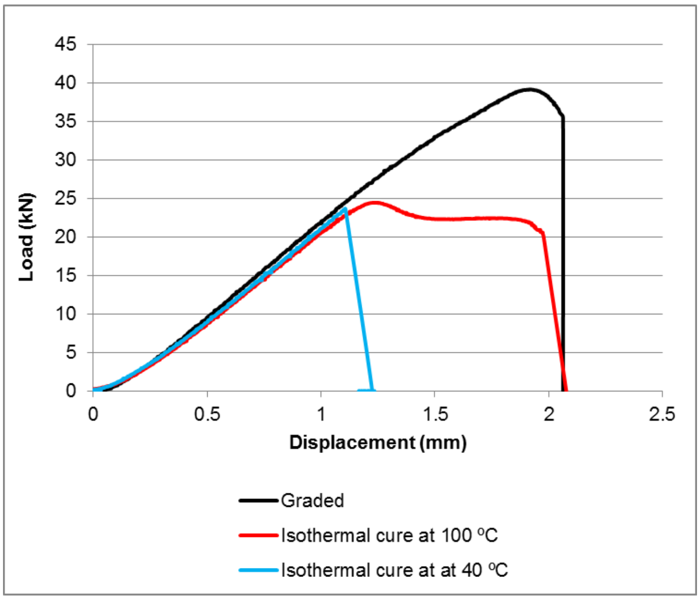

Figure 10 – Typical load-displacement curves of joints with isothermal cure and graded cure for adhesive Araldite® 2011.

Also, functionally graded joints were compared with homogeneous adhesive joints when submitted to different post-cure conditions (**Paper 6**). For all cases, with or without post-cure, the functionally graded joints showed the highest strength, when compared with joints with homogeneous adhesive joints.

Specimens of Portuguese *Pinus Pinaster* beams were repaired with bonded carbon fibre reinforced polymer (CFRP) and tested under four point bending (Figure 11). Bending tests on damaged and undamaged beams were compared with the results of repaired beams. The repaired beams were manufactured with two different methods, by differential cure along the bondline and by isothermal cure along the bondline (**Paper 7**).

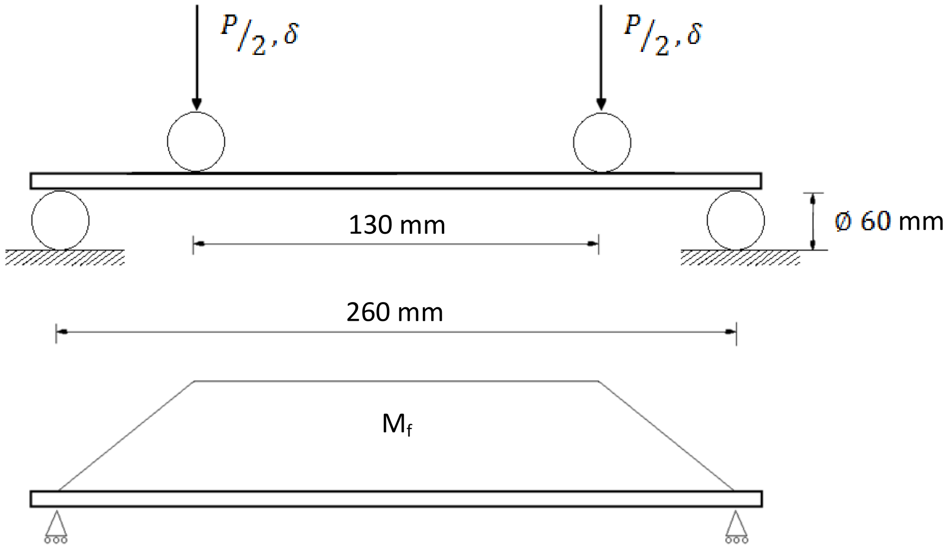

Figure 11 – Bending moment (M_f) of a beam under four point bending.

Figure 12 shows the geometry of a cross grain tension specimen with a bondlength of 40 mm.

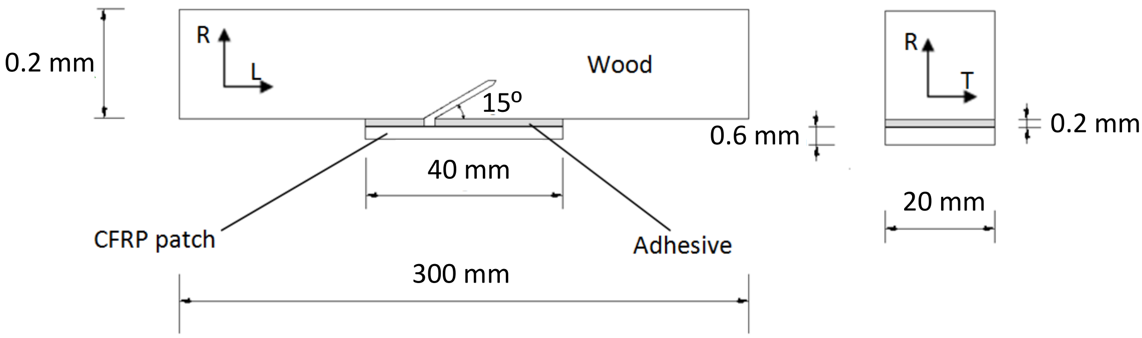

Figure 12 – Schematic representation of the cross grain tension specimen.

Figure 13 shows the typical experimental *P*-*δ* curves of the undamaged beam, unrepaired and repaired cross grain tension specimens.

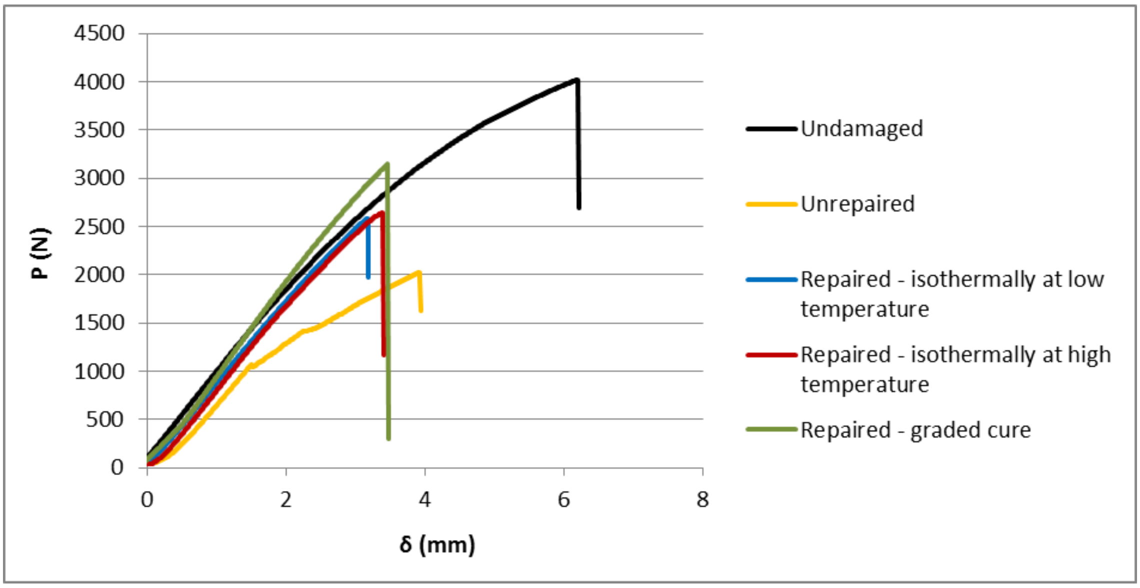

Figure 13 – Typical experimental *P-δ* curves of wood beams.

The repaired specimens show a strength increase when compared with unrepaired specimens. The specimens repaired with isothermal cure at high temperature (adhesive with ductile behaviour) were stronger than the beams repaired with isothermal cure at low temperature (adhesive with brittle behaviour). The strongest repaired specimens were those repaired with gradual cure (adhesive with gradually modified properties along the overlap). However, the strength of the repaired specimens cured gradually is below that of the undamaged beams.

7. Conclusions

The objective of this research was to develop a technique to obtain a joint with the adhesive properties functionally graduated along the bondline. Various structural adhesives were studied to understand the influence of the cure temperature and post-cure temperature on the adhesive mechanical properties and in order to find an adhesive that shows a large variation in properties as a function of the cure temperature. A simple analytical model was developed in order to analyse functionally graded joints easily and quickly.

The joints gradually modified along the overlap were obtained by induction heating. It was proved experimentally that these joints show a high strength when compared with joints cured isothermally. For both adhesives, the functionally graded joints (when compared with joints cured isothermally) were shown to have the highest strength (performance gain of more than 60% for all cases that are not submitted to any post-cure conditions) and similar displacement than the joints cured isothermally at high temperature (ductile behaviour). When submitted to a post-cure condition below $T_{g\infty}$, the functionally graded joints show a slight decrease of the failure load and the joints cured isothermally show an increase of the failure load value. For post-cure conditions above $T_{g\infty}$, the joints cured gradually and isothermally tend to show similar failure load and displacement, but the functionally graded joints have a slightly higher strength. The repaired beams cured gradually show a considerable increase of the strength when compared with repaired beams subjected to isothermal cure.

This technique to obtain a functionally graded joint could be a good way to reduce weight of the bonded structures and to obtain a more efficient bonded area.

8. *Future work*

In this thesis an apparatus was developed to allow the manufacture of a functionally graded joint. The following step should be to use the apparatus with different materials for the adherends, such as composites and aluminium, and also other adhesives with larger mechanical property variation as a function of the cure temperature.

In order to convert the apparatus to be more versatile, the logical step forward should be the optimization of the apparatus. There is a need to develop a more efficient cooling system where it is possible to change the level of cooling. The actual cooling system uses cool water and forced air to cool the bondline in the middle. Also, the heating system should also be optimized in order to more easily change the heating coil and allow different joints to be heated (change of position and/or configuration).

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APPENDED PAPERS

Paper 1

Effect of cure temperature on epoxy adhesives

Effect of cure temperature on the glass transition temperature and mechanical properties of epoxy adhesives

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Abstract

This paper describes the influence of the curing temperature on the physical and mechanical properties of three structural adhesives. This work was undertaken to improve the understanding of the effect of curing temperature in the glass transition temperature, T_g, and stiffness of epoxy adhesives. The mechanical properties (Young's modulus and yield strength) of the adhesives were measured in bulk specimens. T_g was measured by a dynamic mechanical analysis using an in-house developed apparatus. The curing process was the same for all tests, consisting of a curing stage followed by a post cure stage. The initial stage was performed at different temperatures. T_g and the mechanical properties was found to vary as a function of the cure temperature of the adhesive. When cured below the cure temperature, T_{cure}, at which the T_g of the fully cured network, $T_{g\infty}$, is achieved, the strength and stiffness of the adhesive increase as the cure temperature increases and the T_g is higher than the cure temperature. When cured above the T_{cure} at which the $T_{g\infty}$ is achieved, the strength and stiffness decrease as the cure temperature increases and the T_g is higher than the cure temperature.

Keywords: Epoxy adhesives, Glass transition temperature, Cure temperature, Mechanical properties

1. Introduction

In this study, we examined the influence of the curing temperature on the glass transition temperature (T_g) of three epoxy adhesive. The physical and mechanical properties of cured epoxy resins strongly depend on the cure conditions, such as time and temperature of cure. The T_g is the temperature at which the transition between the glassy and rubbery state of amorphous solids occurs. It is considered the most important thermal property of a cured adhesive [1].

The T_g is a direct measurement of molecular mobility and depends on its degree of cure. Below T_g, whole molecules cannot move away from each other. This is because the molecule is confined at the site with a very limited group or branch movement freedom, and its free volume is relatively small. Above T_g, whole molecules can shift or slide away from each other. This is because the molecules have much more freedom of movement, and their free volume increase faster with the temperature [2]. The change in molecular mobility of amorphous materials through the duration of the glass transition interval brings unavoidable changes in their mechanical properties, therefore, the cure temperature upon the T_g values of the mechanical properties are substantially reduced [3]. The T_g of an adhesive depend on its degree of cure. The T_g is a temperature range over which the mobility of the polymer chains increases significantly and the bulk material changes from a glassy state to more of a rubber state. The temperature range over which this transition takes place is very dependent on the kind of adhesive. T_g is influenced by several factors such as composition of the resin molecule, cross-link density, polar nature and molecular weight of the resin molecule, curing agent or catalyst, curing time and curing temperature. These factors influence the magnitude of the temperature region where the T_g occurs [4, 5]. The polar groups in polymers increase intermolecular forces and thus reduce the free volume and increase T_g. There is a relation between molecular weight of a polymer and its T_g; with an increase in molecular weight there is a decrease in T_g.

The thermosetting polymers with stiff backbones always have high T_g and are brittle. T_g of a thermoset is low if the barriers for segmental motion of the backbone are low, and these barriers depend strongly on the chemical structure of backbone and side groups [6]. Thermosetting polymers with flexible backbones exhibit higher flexibility and have a lower T_g. This is because the activation energy for conformational changes is lower and the conformational changes can take place at lower temperatures [7, 8]. Longer molecular chains, polar or polarizable groups and highly crosslinked networks require very large amounts of thermal energy to enable the system to transition to a rubbery state, resulting in a higher T_g [9]. On the other hand, the thermosetting polymers with symmetric (non-polarized) molecular structures or with plasticizer tend to have a lower T_g [2]. Basically, an increase in chain length limits the packing ability of rigid thermosetting more than it does in flexible one and in that way exerts a stronger influence on their brittleness. This approach emphasizes the importance of flexibility/stiffness of both backbone and side groups [6, 10].

An isothermal time-temperature-transformation (TTT) cure diagram is illustrated in Figure 1. The main features of this diagram can be obtained by measuring the times of events that occur during isothermal cure at different temperatures, T_{cure}.

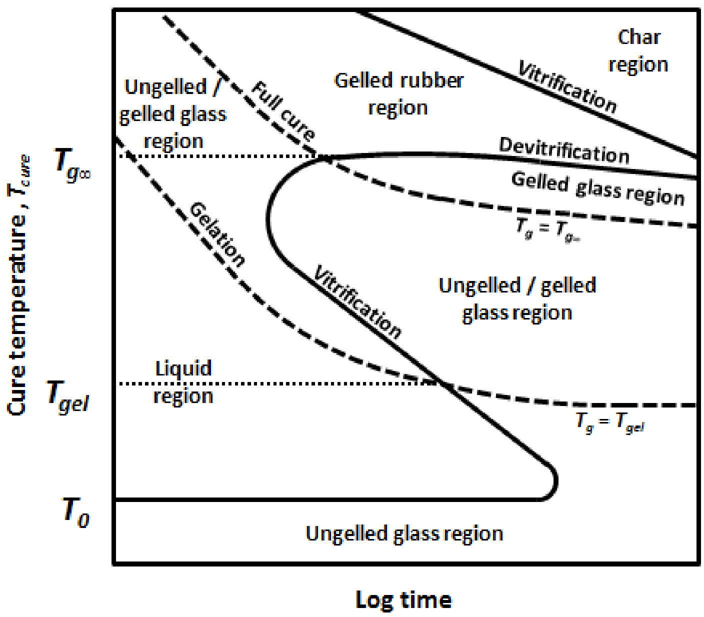

Figure 1 – Time-temperature-transformation (TTT) isothermal cure diagram for a thermosetting system (adapted from Gillham, 1986; Menczel and Prime, 2009).

These events are the phase separation, gelation, vitrification, full cure, and devitrification. Phase separation may occur by precipitation of rubber from solution in rubber-modified formulations, or by the formation of gel particles, by crystallization in crystallisable systems, and by the formation of monomer-insoluble oligomeric species. Gelation defines the upper limit of the work life, the time the adhesive can be processed and bonded after mixing. Vitrification is glass formation caused by T_g increasing from below to above cure temperature as a result of the cure reaction, and the T_g coincides with the cure temperature (T_g = T_{cure}). The reaction of a thermosetting system, proceeds generally at a rate dictated by chemical kinetics if T_{cure} is greater than T_g; however, if T_{cure} is less than T_g the reaction rate may decrease by orders of magnitude due to a relative lack of mobility of the reactive groups. Devitrification occurs when the T_g decreases through the isothermal temperature, as due to thermal degradation, and marks the lifetime for the material to support a substantial load. Three critical temperatures are marked on the temperature axis of the TTT cure diagram: T_o, the transition of the completely unreacted thermoset; T_{gel}, the temperature at which gelation and vitrification coincide; and $T_{g\infty}$, the glass transition temperature of the fully cured network. Full cure is attained most readily by reaction above $T_{g\infty}$, and more slowly by curing below $T_{g\infty}$ to the full-cure line (T_g = $T_{g\infty}$). At temperatures below T_o, reaction is therefore slow to occur and takes place in the glassy state. At temperatures between T_{gel} and $T_{g\infty}$, the gelation precedes vitrification, then to a cross-linked rubbery network form and finally to a glass. As the cure temperature increase, the T_g of the network increase continuously, that is, the crosslinked density increases, to $T_{g\infty}$. At temperatures below $T_{g\infty}$, the T_g matches the T_{cure} if the reactions were quenched by the process of vitrification. In practice, measured T_g is higher than T_{cure} because**,** during the heating scan employed for measurement a small post-cure is induced. Above $T_{g\infty}$, the network remains in the rubbery state after gelation, and a thermal degradation or oxidative cross-linking can occur with a change of the properties [11-15].

Many studies show that increasing the cure temperature until $T_{g\infty}$ (or below the T_{cure} at which the $T_{g\infty}$ is achieved), results in an increase of T_g values until T_{cure} = T_g, and the mechanical properties of the adhesive increase [9, 16, 17]. This is attributed to an increase in density (or decrease in free volume) and a predominance in short-range structural motions. A cure above $T_{g\infty}$ (or above the T_{cure} at which the $T_{g\infty}$ is achieved) can result in lowering of the T_g and also degrades the mechanical properties [18].

In this work, the influence of the curing temperature on the T_g and mechanical properties of three structural adhesives was performed, to evaluate and understand the T_g, strength and stiffness behavior of epoxy adhesives. The curing temperature was made at various temperatures, starting at the glassy region, through the glass transition region and until the rubbery region, for each epoxy adhesive. This study thereby covers a wide range of curing temperatures and shows the influence of the T_g and mechanical properties as a function of curing temperature.

With this study the variation of properties depending on the curing temperature can be seen. This variation is a key aspect in obtaining a functionally graded joint. The functionally graded joint is obtained by a gradual cure of the adhesive and this can only be effectively done when the relationship between curing temperatures and mechanical properties of the adhesive is fully understood. In this work that relationship between curing temperatures and mechanical properties was studied.

2. Principles of a novel method of T_g measurements

Measurement of the T_g provides important data in the choice of material for an engineering project. The thermal analysis techniques than have been widely used to determine the T_g of polymers are differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). DSC is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a sample and an inert reference material, where both specimens are subjected to similar temperature regimes in an environment heated or cooled at a controlled rate [19]. TMA measures a physical response i.e. the coefficient of thermal expansion, as a function of time at a given temperature or at a linear heating rate. DMA measures the viscoelastic response of materials under an oscillating load and as a function of time at a given temperature or at a linear heating rate and frequency [20].

Each of these techniques measures a different result of the change from glass to rubber and consequently different T_g. Also, different values of T_g can be obtained with the same technique by varying the test parameters, this difference may be only few degrees or reach up to 20ºC [21-23] and also few minutes or reach up to 120 minutes of test [24]. T_g is a kinetic parameter that depends on the heating rate and on the measurement conditions. For slower cooling rates, the lower the T_g, however, the long-time temperature heating may change the curing state of the specimen [20].

The objective of the apparatus used in the present study is to measure the T_g easier and faster, without post-cure of the polymer, compared with the previous methods. This method of rapid measurement of the glass transition temperature was initially developed by Prof. R.D. Adams at the University of Bristol to be easier and faster than other commercials techniques [25]. It involves excitation of the test specimen during the heating and the cooling. T_g is measured by registering the damping of the specimen as a function of temperature. T_g is obtained by determining the temperature at which the peak value of damping is observed. The heating rate should be such as to ensure a homogeneous temperature distribution in the specimen. However, it cannot be too great not to cause a post-cure in the specimen. Figure 2 shows a schematic diagram of the rapid method of measuring the T_g.

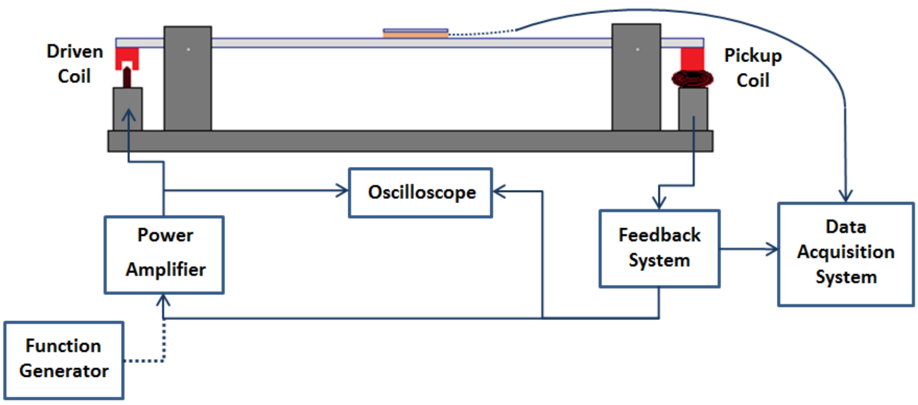

Figure 2 – Schematic diagram of the apparatus used in the testing of the T_g.

The vibration of the specimen is due to a sinusoidal alternating current of known frequency, previously amplified using a power amplifier and sent to the driving coil. This coil (fixed to the support base) causes a lateral excitation at the end of the specimen due to the magnet interaction with the magnetic field. Another coil ('pickup') and magnet is also used at the other end of the specimen to measure the amplitude of vibration. The magnet is bolted on the ends of specimen. In order to ensure the vibration of the specimen the coils are misaligned 90º to avoid interference in the magnetic fields. The support rig must be adjusted to maintain the perfect distance between the coil and the magnet, needed for them to develop a strong magnetic field. The flexural vibration (amplitude of vibration) of the magnet over the 'pick-up' coil produces a voltage proportional to its size.

The feedback circuit allows maintaining the system at resonant oscillation regardless of variations in the resonant frequency. The variation of temperature (heating and cooling) of the specimen causes changes in properties such as damping, modulus and even geometrical dimensions. As a result, to keep the system vibrating at resonance the frequency of the input signal needs to be constantly adjusted. The feedback unit maintains the oscillation of the specimen at resonance adjusting continuously, ensuring a very quick response to any sudden change in the resonant frequency caused by factors such as temperature.

The feedback unit receives the 'pick-up' coil signal and adjusts it in order to provide a signal to the driven coil at resonant frequency, but also provides a signal to a 'DC level' that is used to monitor the amplitude of vibration and outputs it to a data-acquisition system where the signal is monitored and recorded. The signal from the specimen at resonance is sent to the data acquisition system in order to record the change of amplitude with time.

The temperature is not measured directly on the specimen at resonance because by putting the thermocouple wire on it, an extraneous constraint and damping source could lead to a distortion of the results. The technique of reference junction (dummy specimen) is used in monitoring and measuring the temperature. The signal from the dummy specimen is also sent to the data acquisition system in order to record the change of temperature with time (see Figure 3). Both graphs (graphs of amplitude and temperature as a function of time) can be merged in order to obtain a graph of amplitude as a function of temperature.

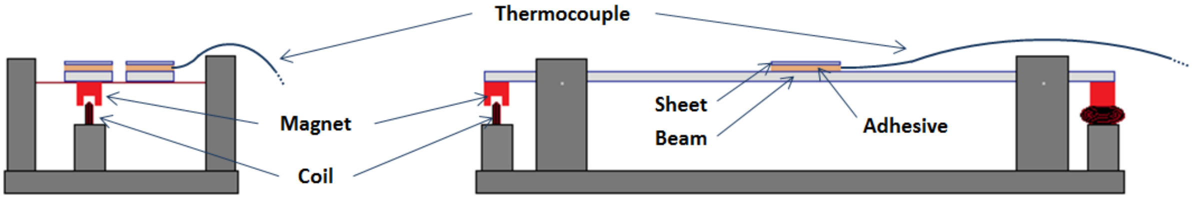

Figure 3 – Dummy specimen in testing.

3. Experimental details

3.1. Materials

Three two part paste epoxy adhesives with different values of T_g and mechanical properties, were characterized. Adhesive Araldite® 2011 (Huntsman, Basel, Switzerland). T_g measured by DMA for a cure of 20 min at 100ºC is approximately 63ºC. The chemical formulation of this adhesive is bisphenol A for the epoxy resin and polyaminoamide for the hardener.

Adhesive Araldite® AV 138M (Huntsman, Cambridge, England). T_g measured by DSC for a cure of 4 hr at 60ºC is approximately 85ºC. The chemical formulation of this adhesive is bisphenol A/B for the epoxy resin and polyaminoamide for the hardener.

Sikadur®-30 LP (Sika, Zurich, Switzerland) is an epoxy resin. T_g measured by DMTA for a cure of 2 hr at 80ºC is 72ºC.

3.2. Curing process

In order to study how the curing process affects the T_g of the adhesives, the specimens should be cured at various temperatures. The curing process consisted of a curing stage followed by a post cure stage (Figure 4). The initial stage for adhesives Araldite® 2011 and Araldite® AV138M/HV 998 was done at various temperatures (23, 40, 60, 80, 100 and 120ºC) for each individual specimen along 30 min and for adhesive Sikadur®-30 LP it was done at various temperatures (23, 40, 60, 80, 100, 120 and 140ºC) for each individual specimen along 2 hours. The post curing stage was always performed at room temperature and ensured a complete cure of the adhesive or near that. The adhesives were left for 2 weeks at room temperature and at relative humidity of 55%, before being tested.

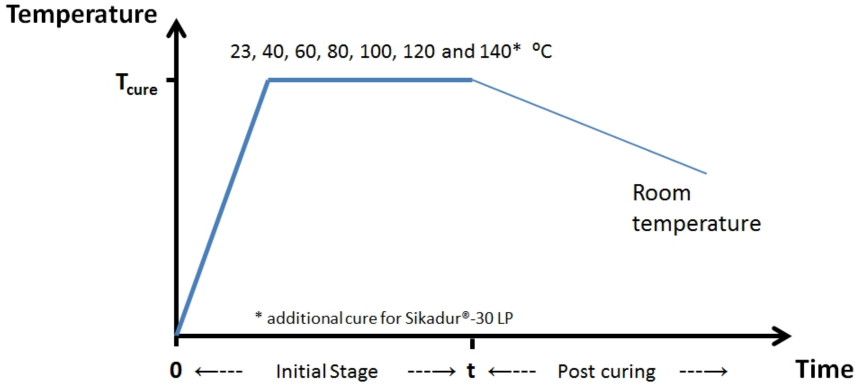

Figure 4 – Diagram of the cure process used.

3.3. Specimens manufacture

The specimen preparation is extremely important. The adhesive is stored in separate containers (resin and hardener) and before application, the two part adhesives need proper mixing. A centrifuging technique was used to mix the adhesive in order to remove the air bubbles and to ensure a homogeneous mixture.

3.3.1. Resonance specimen

The specimens are formed by layers of the beam, adhesive and the sheet and are adhered together using the adhesive to be tested. The beams and sheets were made of aluminium 2024 with dimensions 250 x 12.5 x 3 mm^3 and 30 x 12.5 x 1 mm^3, respectively (see Figure 5). This material was chosen for its low specific heat capacity, thereby ensuring a homogeneous temperature distribution in the specimen. The adhesives have similar dimension to the sheet but with twice the thickness (2 mm).

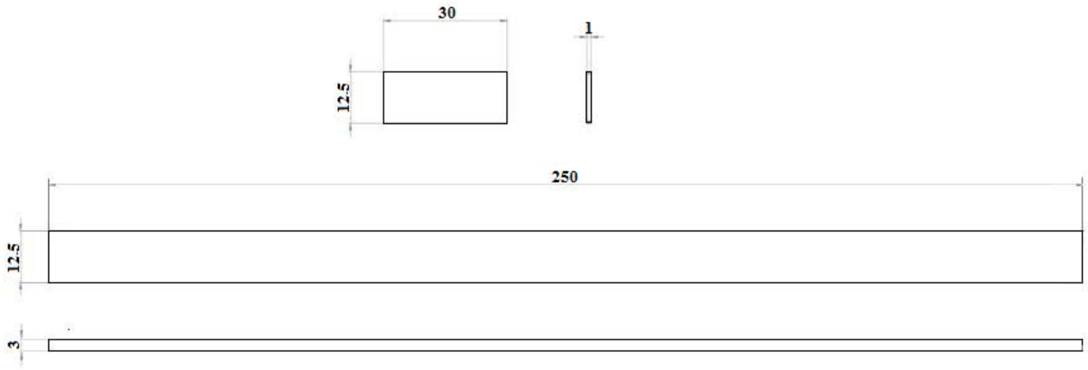

Figure 5 – Dimensions of the beam and the sheet (in mm).

The specimens were produced using a mould (Figure 6). The specimens that will be at resonance are located in the central positions of the mould and the dummy specimens connected with thermocouple on adhesive (than is used to monitor the temperature during the test) are located at the far ends of the mould.

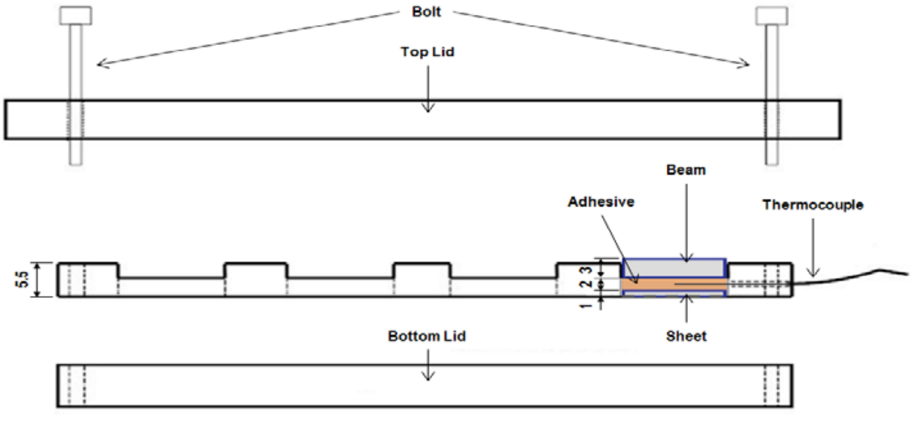

Figure 6 – Schematic representation of the specimen's production (dimensions in mm).

3.3.2. Tensile specimen

Thin adhesive sheets were produced according to the French standard NF T 76-142 [26]. The bulk adhesive sheets were produced between steel plates of a mould with a silicone spacer frame. The hot plate press was then heated up to the intended curing temperature. When the plates achieved the curing temperature, the closed mould was placed inside the hot press (2 MPa), as shown schematically in Figure 7 a) and then opened after the adhesive was fully cured (Figure 7 b)).

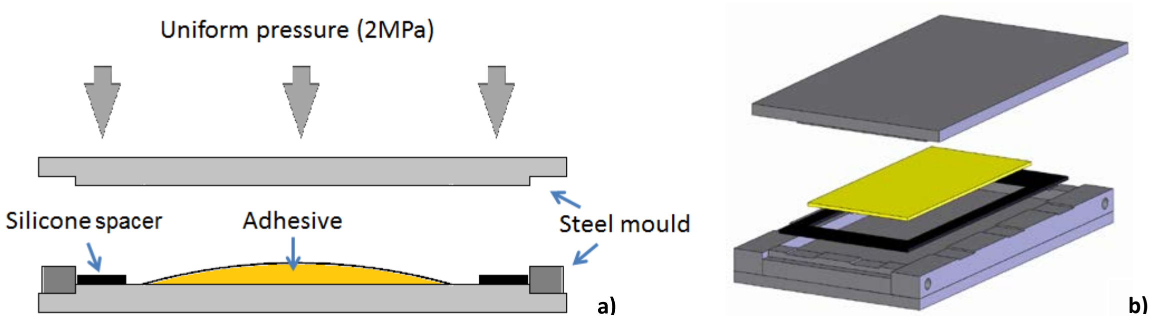

Figure 7 – Representation of the technique used to manufacture bulk specimens: a) schematic and b) design

In order to study how the curing process affects the mechanical properties of the adhesive, the bulk adhesive sample were cured at various temperatures.

The adhesive plate specimen was machined into dogbone specimens (Figure 8), in accordance to BS 2782 standard [26].

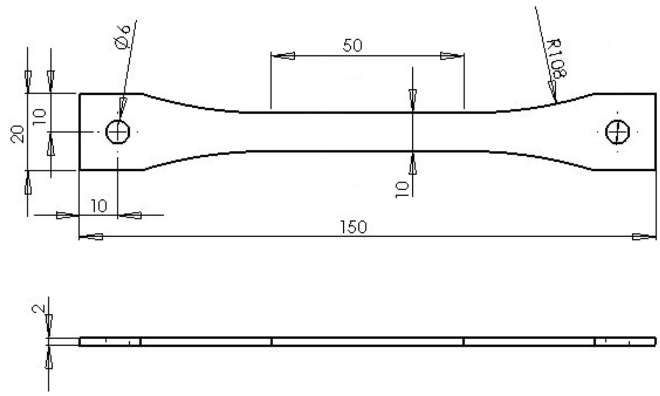

Figure 8 – Tensile test specimen geometry bulk specimen (dimensions in mm).

4. Experimental results

The T_g and the mechanical properties were measured for each adhesive cured at different temperatures (23, 40, 60, 80, 100, and 120ºC) using a dynamic mechanical analysis device developed in-house and a tensile machine, respectively. 3 specimens were used for each case.

4.1. Dynamic mechanical test

The T_g was measured for two pairs of specimens for each adhesive using a dynamic mechanical analysis device developed in-house. The T_g was measured during the heating and cooling stages. The T_g values measured during a heating and cooling stage were obtained from a curve of 1/displacement amplitude, where is a value proportional to the damping of the adhesive, versus temperature for the heating and cooling cycles for each cure temperature and adhesive. Figure 9 gives the curves type of damping as a function of temperature for the heating and cooling stages.

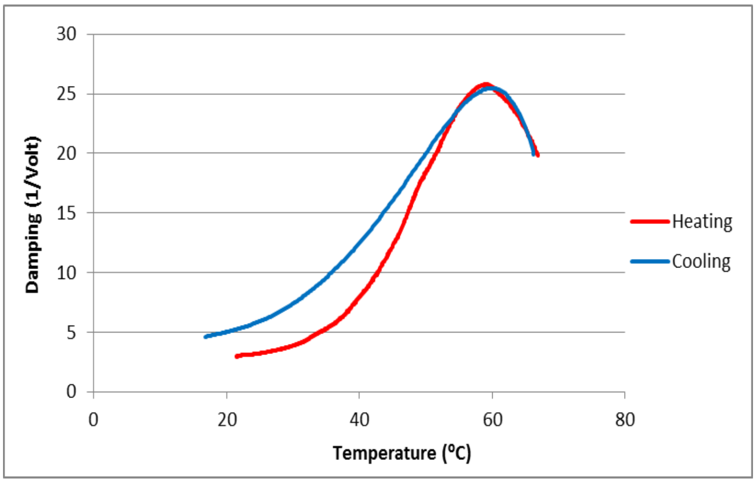

Figure 9 – Dynamic mechanical test results for the epoxy adhesive Araldite® 2011 with a cure of 100ºC for 30 min.

The main problems associated with this novel method of T_g measurements, relate to thermodynamics. The thermal diffusivity of polymers, typical of these kinds of adhesives, is 100 times lower that of aluminium (beam and plate). This means that heat diffuses slowly into the polymer, resulting in a temperature gradient therein. Consequently, this method cannot ascribe an exact temperature to a given time as there will always be a variation. The speed of the test is therefore a compromise. Too slow can to cause a significant additional cure and result in a post-cure effect or moisture loss. Too fast can to have a less certain temperature to quote. The difference of the rate of heating and cooling, which can lead to heterogeneities of temperature during heating in the specimens and thus leading to values of T_g slightly changed. The T_g measured in the cooling is higher than that in the heating. In the latter, there will be a range of temperatures in the specimen, the maximum being at the outer surface (beam and plate) and the minimum at the mid-layer (adhesive). The damping peak will be shifted to a higher temperature than for the true peak. However, during cooling, the opposite will be the case (the minimum being at the outer surface and the maximum located at the mid-layer). This will happen provided that the specimen damping properties have not changed during the test. Therefore, by measuring the damping peak at increasing and decreasing temperatures (heating and cooling), a value near to that of the true peak will be obtained. The curve for heating will be displaced to lower temperature as this will be the coolest part of the specimen. The reverse is true for cooling and, a value near to the true T_g can be obtained by averaging the values on heating and cooling. If the temperature variation through the thickness is small or if the T_{cure} of the specimen is done at temperature at which the $T_{g\infty}$ is achieved, the two peaks will be almost coincidental [25].

Figure 10 illustrates the behaviour of the measured T_g as function of the cure temperature. The plotted values are an average between the T_g values obtained during the heating and cooling stage.

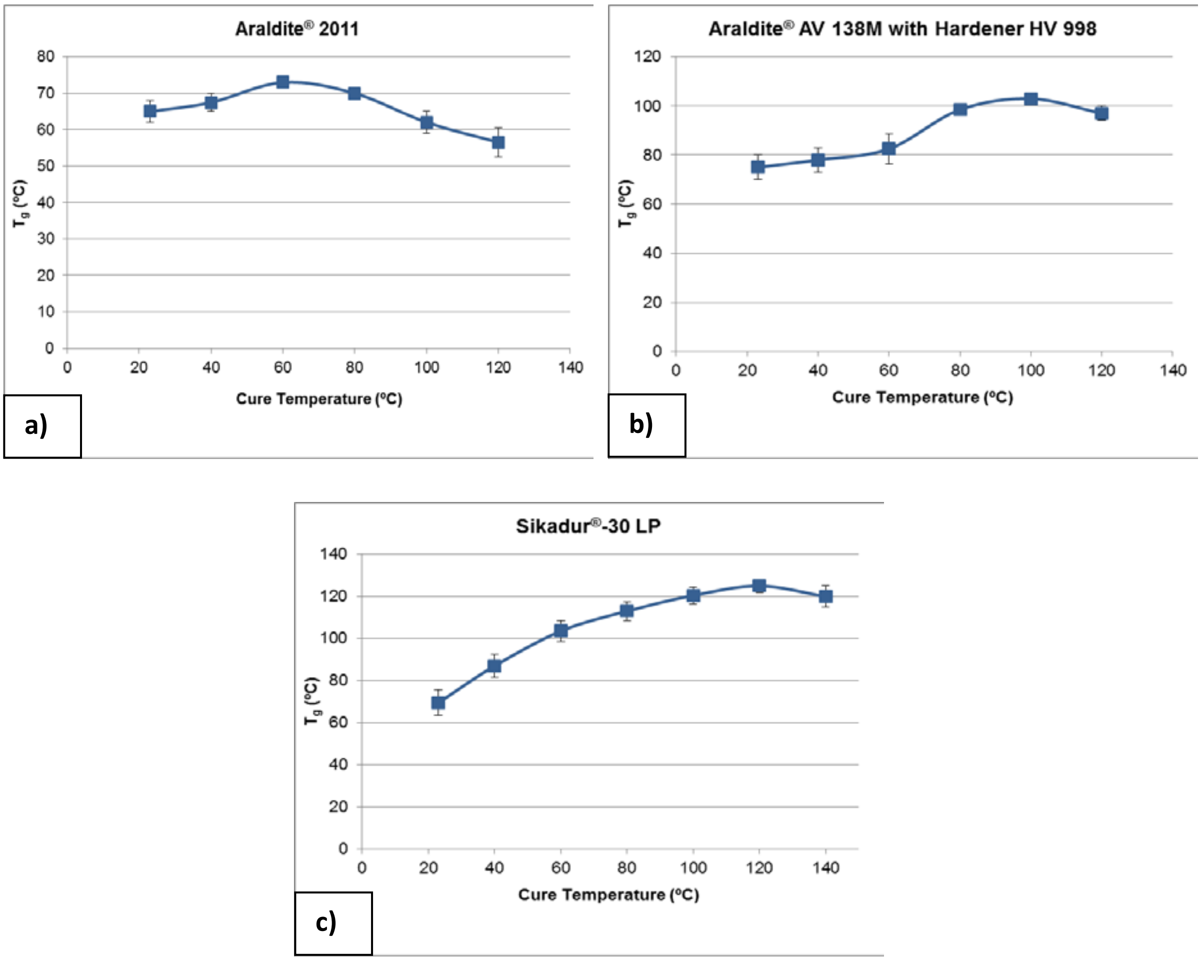

Figure 10 – T_g as a function of the cure temperature.

As expected, up to the temperature at which the $T_{g\infty}$ is achieved, there is a progressive increase of T_g. When the cure temperature exceeds the $T_{g\infty}$ there is a progressive decrease in the T_g. According to Wu [27], for lower post-cure temperatures (below $T_{g\infty}$), T_g increases almost linearly with the post-cure temperature. However, for higher post-cure temperatures (above $T_{g\infty}$) T_g tends to stabilize at constant value independently of the cure temperature or T_g decrease [17, 28].The thermal degradation or oxidative cross-linking (for T_{cure} above the $T_{g\infty}$ of the adhesive) is held responsible for the decrease of T_g with increasing T_{cure}. For Araldite® 2011, this phenomenon happen for T_{cure} > 60ºC, for Araldite® AV 138M/HV 998 for T_{cure} > 100ºC and for Sikadur®-30 LP for T_{cure} > 120ºC. The highest T_g value ($T_{g\infty}$) observed in these three adhesives is obtained at 60 ºC, 100ºC and 120ºC, respectively.

4.2. Tensile test

The mechanical properties were measured using a MTS servo-hydraulic machine with a load cell of 10 kN under a crosshead rate of 1 mm/min. The displacement was measured with a MTS extensometer (25 mm gauge length). Three specimens were tested to failure for each individual temperature in laboratory ambient conditions (room temperature of 23ºC, relative humidity of 55%).Typical stress-strain curves of the adhesive as a function of the cure temperature are shown in Figure 11.

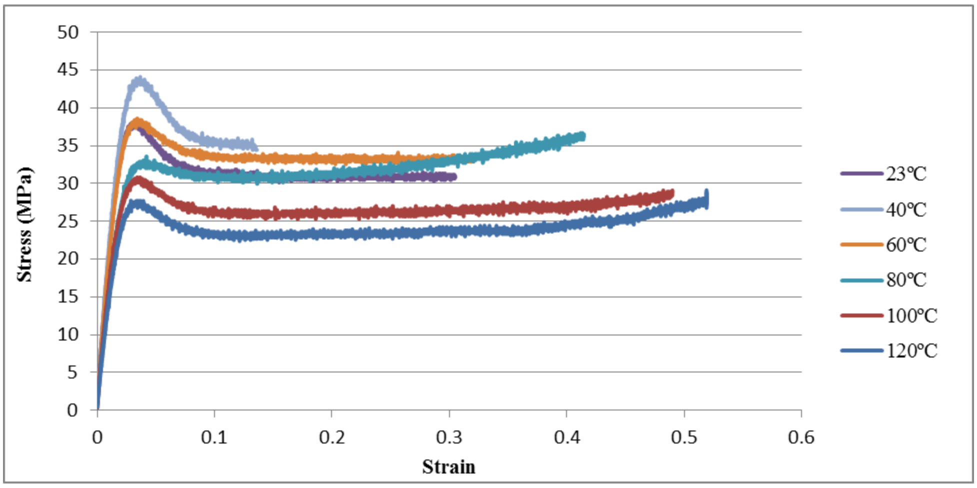

Figure 11 – Tensile stress-strain curves of Araldite® 2011 adhesive as a function of the cure temperature.

The values for Young´s modulus were calculated from the tangent at the origin to the tensile stress-strain curve by making use of a polynomial approximation of the curve. The MTS extensometer could not record the strain at fracture of the Araldite® 2011 specimens cured at 100ºC because of the extensometer length limitation.

The variation of the Young´s modulus and yield strength as a function of the cure temperature is shown in Figure 12. The data obtained shows an increase of the adhesive strength and stiffness with increasing cure temperature below $T_{g\infty}$. Above $T_{g\infty}$, as the cure temperature increases, the adhesive strength and stiffness decrease (Figure 12 a) and b) and c)). Mravljak and Šernek [3] used epoxy resins and also found that above $T_{g\infty}$ the mechanical properties decrease as the cure temperature increases. Also, for specimens cured near $T_{g\infty}$, the adhesive shows the best performance (highest strength and stiffness).

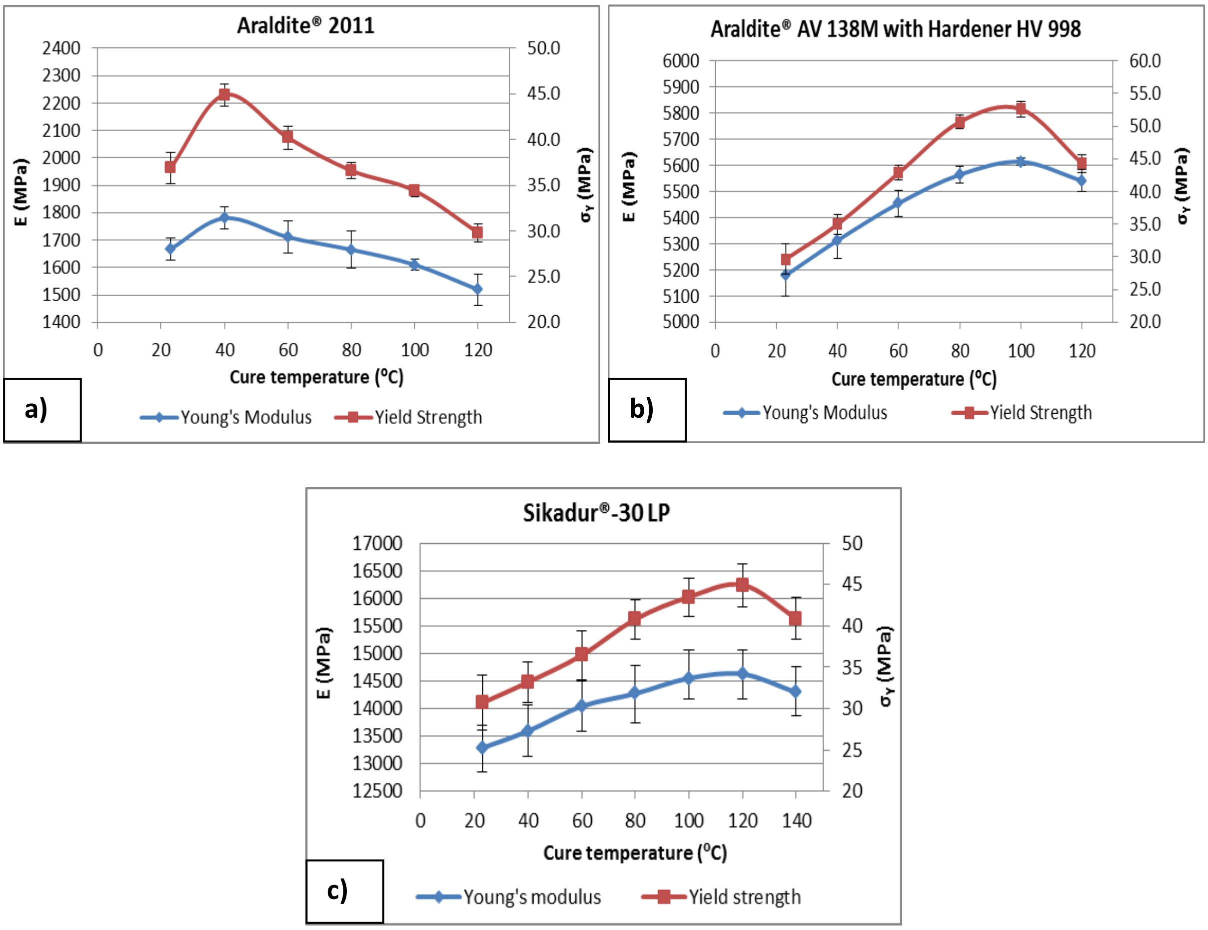

Figure 12 – Young's modulus and yield strength as a function of cure temperature

The thermal degradation or oxidative cross-linking (for T_{cure} above the $T_{g\infty}$ of the adhesive) is held responsible for the decrease of strength and stiffness with increasing T_{cure}. For Araldite® 2011 this phenomenon happens for T_{cure} > 40ºC, for Araldite® AV 138M/HV 998 for T_{cure} > 100ºC and for Sikadur®-30 LP for T_{cure} > 120ºC. The best performance (highest strength and stiffness) observed in these three adhesives is obtained at 40ºC, 100ºC and 120ºC, respectively.

5. Discussion

The effect of curing temperature on the mechanical properties of the three epoxy adhesives studied here revealed an increase of the performance of the adhesive (e.g. strength and stiffness) with increasing cure temperature below the T_{cure} at which the $T_{g\infty}$ is obtained. This is probably because of increase of the crosslinking with increasing of the T_{cure}, and decrease the free volume. For T_{cure} at which the $T_{g\infty}$ is obtained, we conclude that the crosslinking is complete and the adhesive is fully cured, because the adhesive reaches its maximum strength and stiffness. Above $T_{g\infty}$, as the temperature increases the adhesive performance decreases. This decrease of the adhesive performance is probably due to the thermal degradation or oxidative cross-linking. Above $T_{g\infty}$, the network degradation can occur and with it comes a change of the properties.

The highest strength and stiffness of Araldite® 2011 is obtained for T_{cure} of 40°C and $T_{g\infty}$ is obtained for a curing temperature of 60°C, then it can be concluded that the T_{cure} to obtain the highest strength, stiffness, and $T_{g\infty}$ is achieved for a cure temperature of between 40 and 60°C. The highest strength, stiffness, and $T_{g\infty}$ of Araldite® AV 138M / HV 998 is achieved for a T_{cure} of 100°C. For Sikadur®-30 LP the highest strength, stiffness, and $T_{g\infty}$ is achieved for a T_{cure} of 120°C, since the increase in mechanical properties for T_{cure} between 100 and 120°C is only residual.

As expected, the mechanical properties (i.e. stiffness and strength) and the T_g properties have similar behaviour. There is a progressive increase of T_g, stiffness and strength up to a cure temperature equal to the T_{cure} at which the $T_{g\infty}$ is achieved. When the cure temperature exceeds the T_{cure} at which the $T_{g\infty}$ is achieved, there is a progressive decrease in the T_g, stiffness and strength. This decrease is due to thermal degradation at which the adhesive is subjected when cured at temperatures above $T_{g\infty}$.

6. Conclusions

In this paper, the T_g and mechanical properties were measured for three epoxy adhesives (Araldite® 2011, Araldite® AV 138M / HV 998 and Sikadur®-30 LP) as a function of the curing temperature. The following conclusions can be drawn:

1. The T_g was measured using a dynamic mechanical analysis device developed in-house. Which is faster and less expensive than the commercial devices available;

2. When below the T_{cure} at which the $T_{g\infty}$ is achieved, the strength and stiffness of the adhesive increase as the cure temperature increases. When above the T_{cure} at which the $T_{g\infty}$ is achieved, there is an opposite behaviour, i.e. the strength and stiffness decrease as the cure temperature increases;

3. For the adhesive Araldite® 2011 the greater strength and stiffness is obtained for the curing temperature of 40°C and $T_{g\infty}$ is obtained for a curing temperature of 60°C. Then it can be concluded that the curing temperature to obtain the best performance (highest strength and stiffness, and $T_{g\infty}$) is achieved for a cure temperature of between 40 and 60°C;

4. For the adhesive Araldite® with AV 138M / HV 998, the highest strength and stiffness, and $T_{g\infty}$ is achieved for a cure temperature of 100°C;

5. For the adhesive Sikadur®-30 LP, the highest strength and stiffness, and $T_{g\infty}$ is achieved for a cure temperature of 120°C;

6. T_g and the mechanical properties, as expected, have a similar behaviour. It was found that the T_g, strength and stiffness vary as a function of the cure temperature of the epoxy adhesive. When cured below the T_{cure} at which the $T_{g\infty}$ is achieved, the T_g, strength and stiffness increase as the cure temperature increases. When cured above the T_{cure} at which the $T_{g\infty}$ is achieved, the T_g, strength and stiffness decrease as the cure temperature increases.

Acknowledgments

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Paper 2

Effect of post-cure on epoxy adhesives

Effect of Post-Cure on the Glass Transition Temperature and Mechanical Properties of Epoxy Adhesives

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Abstract

The effects of post-curing and cure temperature on the glass transition temperature, T_g, and mechanical properties of epoxy adhesives were studied. T_g was measured by a dynamic mechanical analysis (DMA) apparatus developed in-house and the mechanical properties of the adhesives (yield strength, Young´s modulus and failure strain) were measured by a tensile machine. The relationships between T_g and mechanical performance under various post-cure conditions, were investigated. The curing process was the same for all tests, consisting of an initial stage performed at different temperatures followed of a cooling at room temperature. Three sets of specimens were considered, sharing the same initial cure process, but with a different post-curing procedure. In the first set, the specimens were only subjected to a curing process; in the second set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature below the T_g of the fully cured network, $T_{g\infty}$; and in the third set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature above the $T_{g\infty}$. When post-cured at a temperature above $T_{g\infty}$, the mechanical and physical properties tend to have a constant value for any cure temperature.

Keywords: Epoxy adhesives, Glass transition temperature, Cure temperature, Post-cure, Mechanical properties

1. Introduction

Epoxy adhesives are the most commonly used materials for bonding and repair structures and attract the interest of the industry and investigation community, because they allow great versatility in application, performance and formulation since there are many resins and many different hardeners. Epoxies show an excellent balance between various properties such as mechanical and physical properties, high degree of adhesion properties to almost any adherends, humidity resistance, and heat resistance. The epoxy adhesives can be cured at room temperature or high temperatures and so the correct selection of cure conditions and post-cure conditions is an important factor to be considered in the project. It is clear that the cure process and post-cure conditions affect the mechanical and physical properties, and therefore, it is fundamental to understand the dependence of the adhesive properties as a function of the cure conditions.

The physical and mechanical properties of cured epoxy resins strongly depend of the temperature and conversion (or extent of reaction) during the cure. When cured above cure temperature, T_{cure}, at which the glass transition temperature of the fully cured network, $T_{g\infty}$, is achieved, the conversion, x, attains its maximum value ($T_{cure} \approx T_{g\infty} \rightarrow x = 1$). When cured below $T_{g\infty}$, vitrification will occur ($T_{cure} \leq T_{g\infty} \rightarrow x < 1$). Glass transition, or vitrification, is characterized by the conversion at which the polymer begins to exhibit the typical properties of a glass (transformation from a liquid or rubbery state to a vitreous state). The cause of the vitrification is through the formation of covalent bonds, reducing the system's mobility. Vitrification is up to that the cooperative movements of large portions of the polymer, which are characteristic of liquid and rubbery states, are no longer possible [1]. Below $T_{g\infty}$, the strength and stiffness of the adhesive increase as the cure temperature increases and the T_g is higher than the cure temperature. With more thermal energy supplied to the system more curing reactions can take place more frequently and a higher degree of cross-linking within the network can occur. This rigid, more tightly knit molecular network requires more energy to permit chain motion and as such an increased glass transition temperature is manifested. The increase of the cross-linking density permits the development of more and more cooperative processes. In densely cross-linked materials, the relaxation of the cross-linked network leads to important mechanical losses. Above $T_{g\infty}$, the strength and stiffness decrease as the cure temperature increases and the T_g is lower than the cure temperature. As the cure temperature increases the network becomes more freely mobile and this is potential evidence of thermal degradation that may occur at temperatures above the $T_{g\infty}$. The T_g is the temperature at which the transition between the solid of rubbery state of amorphous solids occurs. It is considered the most important thermal property of a cured adhesive [2-7]. The epoxy networks exhibit a β-relaxation in the glassy state which have a strong effect on the mechanical properties (dynamic and static mechanical properties) [8-10]. But this effect is present in epoxy networks at low temperatures (significantly below T_g).

The influence of conversion on mechanical and physical properties is not linear, and for many epoxy systems there is a great difference when conversion is less than one or close to one. [11]. The T_g and stiffness of an epoxy resin increases as the conversion increases [12]. Recently, Carbas *et al.* [13] studied the effect of cure temperature on the mechanical properties and the T_g of epoxy adhesives. It was shown that adhesive achieve its best performance (high stiffness and $T_{g\infty}$) is achieved for T_{cure} near the $T_{g\infty}$, and consequently conversion close to one.

The post-cure at low temperatures, in a very short period, promotes completion of the cross-linking process. This completion of the cross-linking process ensures the mechanical stability of the polymer, while introducing a relaxation to the cross-link network. The increase of cross-link density improves mechanical stability of the polymer, and the relaxation of the molecular network has the potential to increase its ductility and, thus, the energy absorption during fracture. The relaxation of the molecular network, results in a more uniform structure of the polymer network, this relaxation facilitates the deformation of the polymer chains, thus enhancing toughness [14-17]. Tucker *et al.* [17] studied the effect of post-cure on the mode I interlaminar fracture toughness of pure vinylester resin and glass-fibre reinforced vinylester, and concluded that the post-cure enhances the toughness of the glass-fibre/vinylester composite, mainly due to the increase of resin toughness.

In thermosets exposed to temperatures below the T_g for long periods of time (annealing) there is an increase in mass density (volumetric relaxation) and this phenomenon is known as physical ageing. The characteristic mechanisms of physical ageing for glassy materials (e.g. epoxy) are focused on physical changes to the molecular structure (e.g. reduction in free volume) during annealing [18]. The physical ageing has an influence on mechanical properties of epoxies. There is an increase of the elastic modulus of epoxy with increasing levels of physical ageing [19-21]. Ophir *et al.* [22] demonstrated that for epoxies the failure strain decrease with increasing physical ageing times. Physical ageing in glassy thermosets systems has been associated with increases in density, T_g, modulus and yield stress, and also decreased free volume [18, 23-25]. Resins fully cured by an initial high cure temperature or a high post-cure temperature remove any artifacts of physical ageing regardless of the initial cure state. The physical ageing is inhibited with advancing the cure state of a resin, as the density, modulus and yield stress decreases [26]. For this reason, the effect of post-cures at various temperatures has been studied here to understand the effect of temperature exposure on the adhesive mechanical properties.

Exothermic curing reactions occur as the polymer chains start to cross-link and chain mobility reduces, which is activated more aggressively at higher cure temperatures. The process is more dependent on the temperature of the post-cure than it is upon the duration. At higher post cure temperatures, the thermoset cure more quickly and more fully. [27] Stewart *et al*. [27] studied the mechanical properties of an epoxy adhesive as a function of cure level and they clearly showed that as the temperature of the post-cure increases, the T_g value increase is more reduced, and this decrease of the value of the T_g is more accentuated for long periods of cure. Wu [28] studied the influence of post-curing and temperature effects on mechanical properties and T_g and has shown that with the increase of the post-cure temperature up to $T_{g\infty}$, the T_g linearly increases. Above the $T_{g\infty}$, with the increase of the post-cure temperature, the T_g slightly decreases and which tend to a constant value. The high value of T_g (or $T_{g\infty}$) is attributed to the increase in cross-link density. Ziaee and Palmese [29] showed that the tensile strength, Young's modulus and T_g increased with increasing post-cure temperature, up to $T_{g\infty}$, while the ultimate elongation, inversely decreased. The low ultimate elongation is due to the more densely cross-linked and so the segmental motion is much restricted. The increase of tensile strength and Young's modulus with increasing post-cure temperature were expected because the higher post-cure temperature (near the $T_{g\infty}$) is intuitively expected to result in an increase in cross-link density and, as a consequence, increases strength and stiffness.

In this work, the influence of the curing temperature followed by a post-cure, on the T_g and mechanical properties of two structural adhesives was performed, to evaluate and understand the T_g, strength and stiffness behaviour of the epoxy adhesives. The curing process was the same for the all tests, consisting of an initial stage that was performed at various temperatures followed by cooling at room temperature until the adhesive was completely cured or close to that. Three different post-curing procedures were considered, but sharing the same initial cure process. In the first set, the specimens were only subjected to a curing process; in the second set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature below the $T_{g\infty}$, and in the third set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature above the $T_{g\infty}$. The yield strength, Young's modulus, ultimate elongation and T_g for different cure temperatures were investigated to understand the adhesive performance as a function of the post-cure conditions.

This study was carried in the context of functionally graded joints obtained by a gradual cure of the adhesive. The authors are currently working on a bonded functionally graded joint where the adhesive properties vary gradually along the overlap by a gradual cure of the adhesive. However, this can only be effectively done when the relationship between curing temperatures and mechanical properties of the adhesive is fully understood. Moreover, this solution can only be used widely in industry when there is a good knowledge of the T_g and mechanical properties of the adhesive after being exposed to temperature for a certain time [30].

2. Principle of the T_g method measurements

Measurement of the T_g provides important data in the choice of material for an engineering project. The thermal analysis techniques than have been widely used to determine the T_g of polymers are differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). DSC is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a sample and an inert reference material, where both specimens are subjected to similar temperature regimes in an environment heated or cooled at a controlled rate. [31] TMA measures a physical response, i.e. the coefficient of thermal expansion, as a function of time at a given temperature or at a linear heating rate. DMA measures the viscoelastic response of materials under an oscillating load and as a function of time at a given temperature or at a linear heating rate and frequency. [32, 33]

Each of these techniques measures a different result of the change from glass to rubber and consequently a different T_g. Also, different values of T_g can be obtained with the same technique by varying the test parameters, this difference may be only few degrees or reach up to 20ºC [34-36] and also few minutes or reach up to 120 minutes of test [37]. T_g is a kinetic parameter that depends on the heating rate and on the measurement conditions. For slower cooling rates, the lower the T_g, however, the long-time temperature heating may change the curing state of the specimen. [33]

The objective of the apparatus used in the present study is to measure the T_g easier and faster, without post-cure of the polymer, compared with the previous methods. This method of rapid measurement of the glass transition temperature was initially developed by Prof. R.D. Adams at the University of Bristol to be easier and faster than other commercials techniques, see [38]. It involves excitation of the test specimen during the heating and the cooling. T_g is measured by registering the damping of the specimen as a function of temperature. T_g is obtained by determining the temperature at which the peak value of damping is observed. The heating rate should be such as to ensure a homogeneous temperature distribution in the specimen. However, it cannot be too great not to cause a post-cure in the specimen. Figure 1 shows a schematic diagram of the rapid method of measuring the T_g.

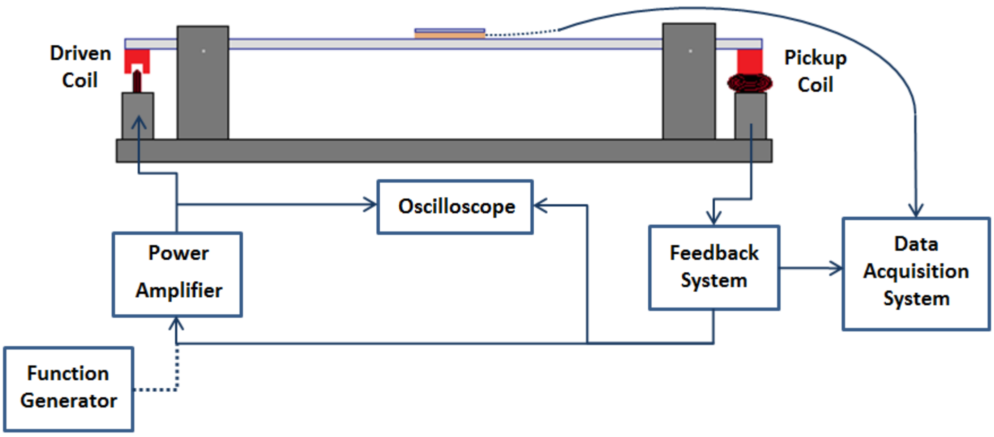

Figure 1 – Schematic diagram of the apparatus used in the measurement of T_g.

The vibration of the specimen is due to a sinusoidal alternating current of known frequency, previously amplified using a power amplifier and sent to the driving coil. This coil (fixed to the support base) causes a lateral excitation at the end of the specimen due to the magnet interaction with the magnetic field. Another coil ('pickup') and magnet is also used at the other end of the specimen to measure the amplitude of vibration. The magnet is bolted on the ends of the specimen. In order to ensure the vibration of the specimen the coils are misaligned 90º to avoid interference in the magnetic fields. The support rig must be adjusted to maintain the perfect distance between the coil and the magnet, needed for them to develop a strong magnetic field. The flexural vibration (amplitude of vibration) of the magnet over the 'pick-up' coil produces a voltage proportional to its size.

The feedback circuit allows maintaining the system at resonant oscillation regardless of variations in the resonant frequency. The variation of temperature (heating and cooling) of the specimen causes changes in properties such as damping, modulus and even geometrical dimensions. As a result, to keep the system vibrating at resonance the frequency of the input signal needs to be constantly adjusted. The feedback unit maintains the oscillation of the specimen at resonance frequency adjusting continuously in order to ensure that the specimen is at its resonant frequency. This gives a very quick response to any sudden change in the resonant frequency caused by external factors such as temperature.

The feedback unit receives the 'pick-up' coil signal and adjusts it in order to provide a signal to the driven coil at resonant frequency, but also provides a signal to a 'DC level' that is used to monitor the amplitude of vibration and outputs it to a data-acquisition system where the signal is monitored and recorded. The signal from the specimen at resonance is sent to the data acquisition system in order to record the change of amplitude with time.

The temperature is not measured directly on the specimen at resonance because by putting the thermocouple wire on it, an extraneous constraint and damping source could lead to a distortion of the results. The technique of reference junction (dummy specimen) is used in monitoring and measuring the temperature. The signal from the dummy specimen is also sent to the data acquisition system in order to record the change of temperature with time (see Figure 2). Both graphs (graphs of amplitude and temperature as a function of time) can be merged in order to obtain a graph of amplitude as a function of temperature.

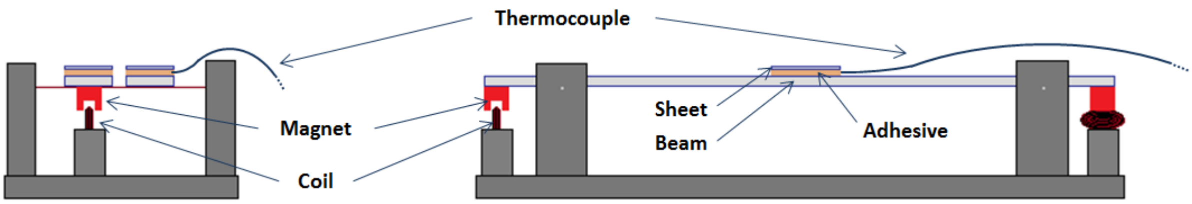

Figure 2 – Dummy specimen in testing.

3. Experimental details

3.1. Materials

Two bi-component epoxy adhesives were characterized: Araldite® 2011 (Huntsman, Basel, Switzerland) and Loctite Hysol® 3422 (Henkel, Dublin, Ireland). The T_g of Araldite® 2011 measured by DMA for a cure of 20 min at 100ºC is approximately 63ºC. The chemical formulation of this adhesive is bisphenol A for the epoxy resin and polyaminoamide for the hardener. The T_g of Loctite Hysol® 3422 measured by DMA for a cure of 7 days at 23ºC is 63.8ºC. The chemical formulation of this adhesive is bisphenol A diluted with bisphenol F for the epoxy resin, and 3-Aminopropylmorpholine and polyoxypropylene diamine for the hardener.

3.2. Cure temperature

The effect of different post-cure conditions on T_g and mechanical (yield strength, Young's modulus and ultimate elongation) properties of epoxy adhesives were studied. In order to study how the post-cure conditions affect the T_g, yield strength, Young's modulus and ductility of the adhesives, the specimens were cured at various temperatures and post-cure conditions. The curing process was the same for all tests, consisting of an initial stage performed at different temperatures (23, 40, 60, 80 and 100ºC) for each individual specimen for 30 min (Araldite® 2011) or 1 hour (Loctite Hysol® 3422), followed by cooling at room temperature (Figure 3).

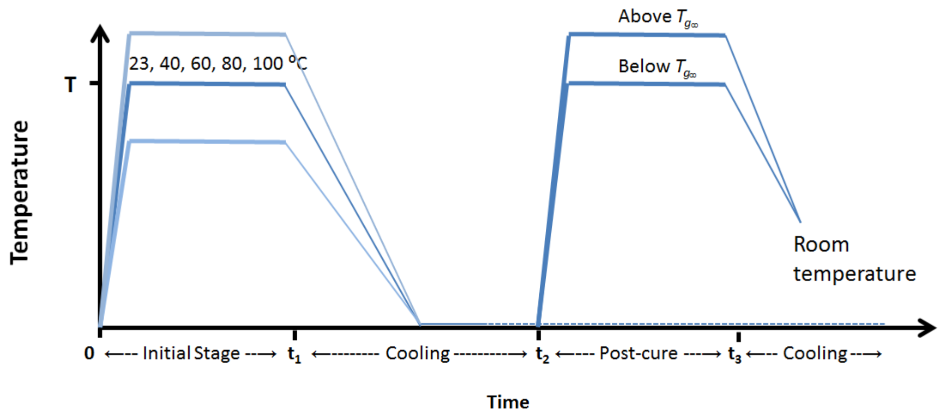

Figure 3 – Diagram of the cure process used.

Three sets of specimens were considered, sharing the same initial cure process, but with a different post-curing procedure (Figure 3). In the first set, the specimens were only subjected to a curing process; in the second set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature below the $T_{g\infty}$; and in the third set, the specimens were subjected to a curing process followed by a post-cure performed at a temperature above the $T_{g\infty}$.

The post-cure for lower temperatures (below $T_{g\infty}$) used for each adhesive were done at the temperature of the T_{cure} at which the adhesive achieved its $T_{g\infty}$. The post-cure for higher temperatures (above $T_{g\infty}$) used for both adhesives was 100 ºC. The time of post-cure at which the adhesives were exposed was 2 hours.

The reason for this post-cure, below and above the $T_{g\infty}$, is to understand the effect of the post-cure at temperatures of the glassy and rubbery region, respectively, on the mechanical and physical properties of the adhesive. Reference samples were used, subject to similar cure conditions but without a post-cure.

3.3. Specimens manufacture

The specimen preparation is extremely important. The adhesive is stored in separate containers (resin and hardener) and before application, the two part adhesives need proper mixing. A centrifuging technique was used to mix the adhesive in order to remove the air bubbles and to ensure a homogeneous mixture.

3.3.1. Resonance specimen

The specimens are formed by layers of a beam, the adhesive and a constraining sheet and are adhered together using the adhesive to be tested. The beams and sheets were made of aluminium 2024 with dimensions 250 x 12.5 x 3 mm^3 and 30 x 12.5 x 1 mm^3, respectively (see Figure 4). This material was chosen for its low specific heat capacity, thereby ensuring a homogeneous temperature distribution in the specimen. The adhesives have a similar dimension to the sheet but with twice the thickness (2 mm).

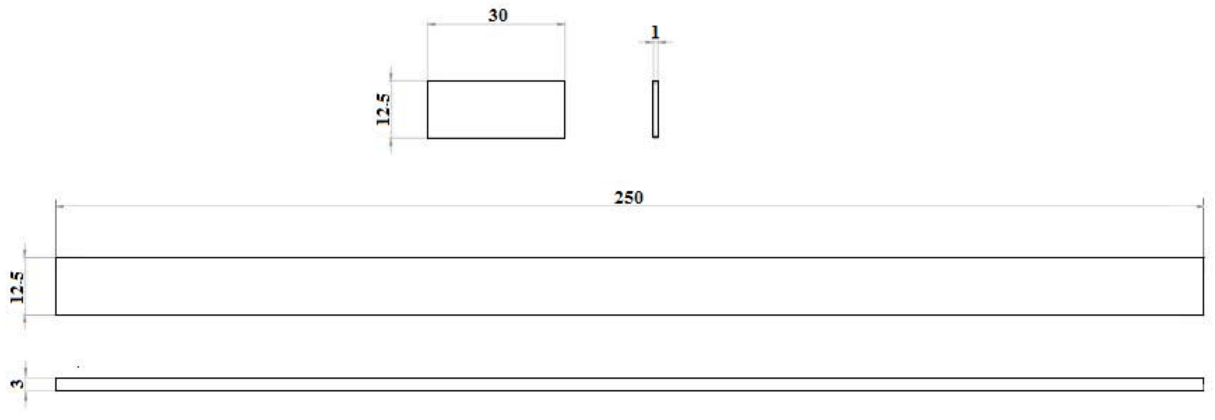

Figure 4 – Dimensions of the beam and the sheet (in mm).

The specimens were produced using a mould (Figure 5). The specimens that are at resonance are located in the central positions of the mould and the dummy specimens connected with a thermocouple in the adhesive (that is used to monitor the temperature during the test) are located at the far ends of the mould.

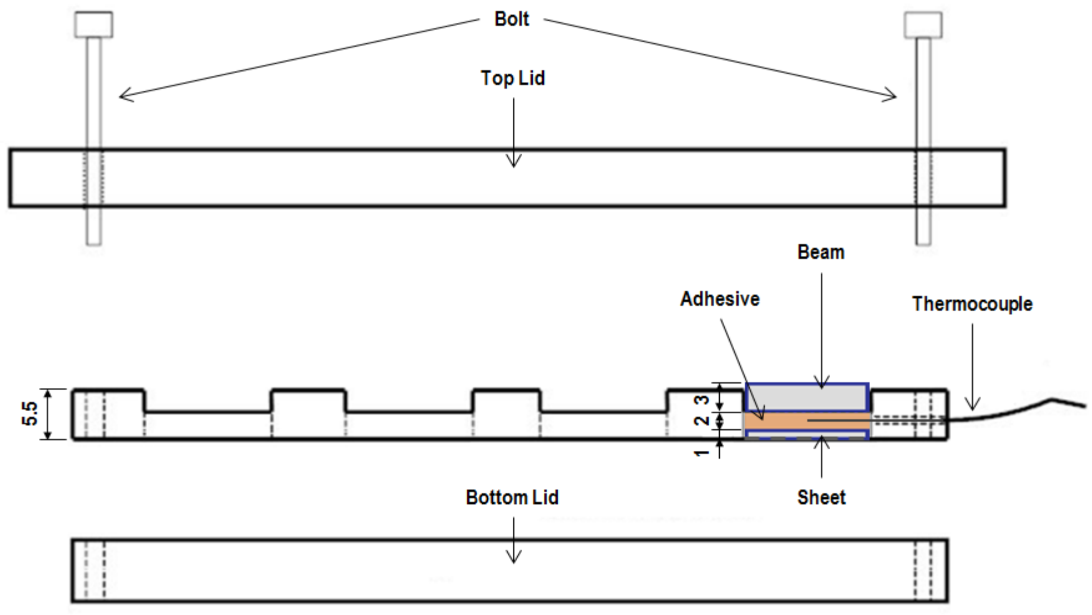

Figure 5 – Schematic representation of the specimen's production (dimension in mm).

3.3.2. Tensile specimen

Thin adhesive sheets were produced according to the French standard NF T 76-142. [39] The bulk adhesive sheets were produced between steel plates of a mould with a silicone spacer frame. The closed mould was placed in hot press (2 MPa), as shown schematically in Figure 6 a) and then opened after the adhesive was fully cured (Figure 6 b)).

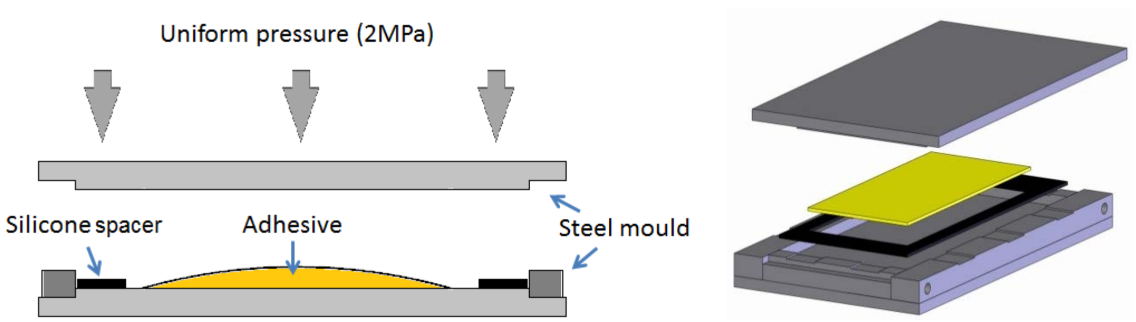

Figure 6 – Representation of the technique used to manufacture bulk specimens: a) schematic and b) exploded view of the mould.

In order to study how the curing process affects the mechanical properties of the adhesive, the bulk adhesive samples were cured at various temperatures.

The adhesive plate specimen was machined into dogbone specimens (Figure 7), in accordance to BS 2782 standard.

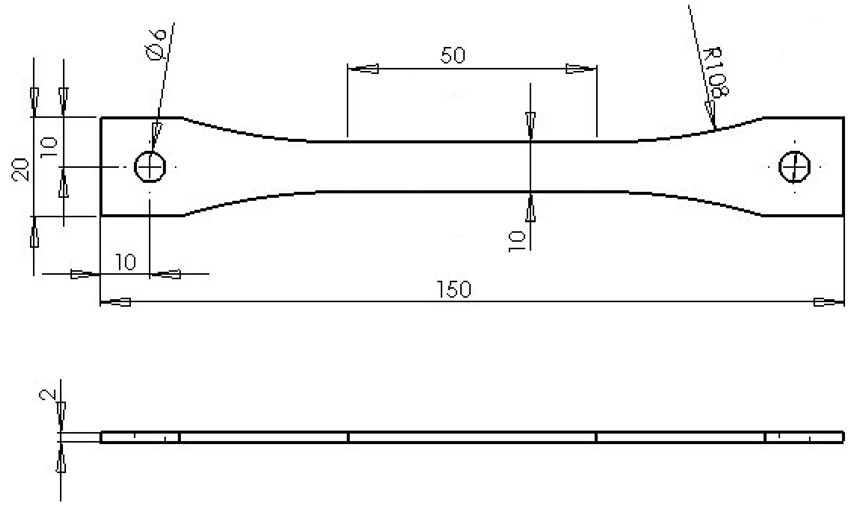

Figure 7 – Tensile test specimen geometry bulk specimen (dimensions in mm).

4. Experimental results

The T_g and mechanical properties (yield strength, Young´s modulus and failure strain) were measured for each adhesive cured at different temperatures (23, 40, 60, 80 and 100 ºC) followed by post-cure conditions.

4.1. Dynamic mechanical test

The T_g was measured during the heating and cooling stages. The T_g values measured during the heating and cooling stage were obtained from a curve of 1/displacement amplitude, which is a value proportional to the damping of the adhesive, versus temperature for the heating and cooling cycles for each cure temperature and adhesive.

Figure 8 gives the curves type of damping as a function of temperature for the heating and cooling stages.

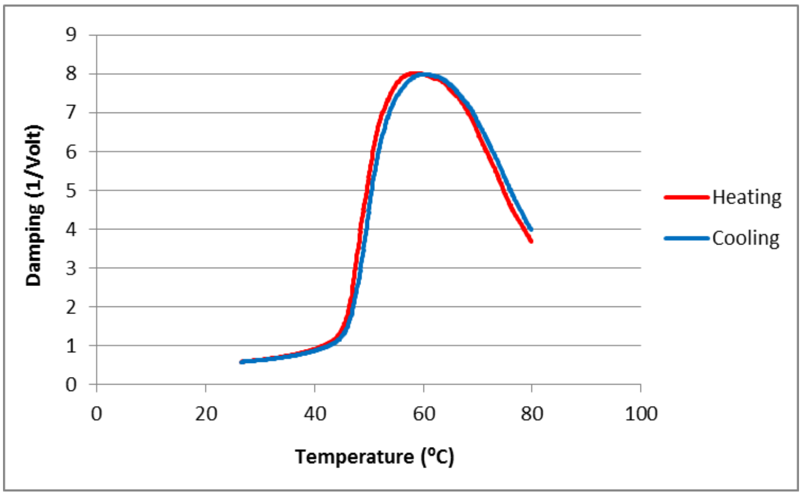

Figure 8 – Dynamic mechanical test results for the epoxy adhesive Loctite Hysol® 3422 with a cure of 40°C for 1 hour without post-cure.

The main problems associated with this novel method of T_g measurements, relate to thermodynamics. The thermal diffusivity of polymers, typical of these kinds of adhesives, is 100 times lower that of aluminium (beam and plate). This means that heat diffuses slowly into the polymer, resulting in a temperature gradient therein. Consequently, this method cannot ascribe an exact temperature to a given time as there will always be a variation. The speed of the test is therefore a compromise. Too slow can to cause a significant additional cure and result in a post-cure effect or moisture loss. Too fast can to have a less certain temperature to quote. The difference of the rate of heating and cooling, which can lead to heterogeneities of temperature during heating in the specimens and thus leading to values of T_g slightly changed. The T_g measured in the cooling is higher than that in the heating. During heating, there will be a range of temperatures in the specimen, the maximum being at the outer surface (beam and plate) and the minimum at the mid-layer (adhesive). On heating, the damping peak will be shifted to a higher temperature than for the true peak. During cooling, the opposite will be the case (the minimum being at the outer surface and the maximum at the mid-layer). On cooling, the opposite will be the case, provided the specimen damping properties have not changed during the test. Therefore, by measuring the damping peak at increasing and decreasing temperatures (heating and cooling), a value near to that of the true peak will be obtained. The curve for heating will be displaced to lower temperature as this will be the coolest part of the specimen. The reverse is true for cooling and, a value near to the true T_g can be obtained by averaging the values on heating and cooling. If the temperature variation through the thickness is small or if the T_{cure} of the specimen is done at temperature at which the $T_{g\infty}$ is achieved, the two peaks will be almost coincidental. [38]

Figure 9 illustrates the behaviour of the measured T_g for the three different post-cure conditions as a function of the cure temperature. The plotted values are an average between the T_g values obtained during the heating and cooling stage.

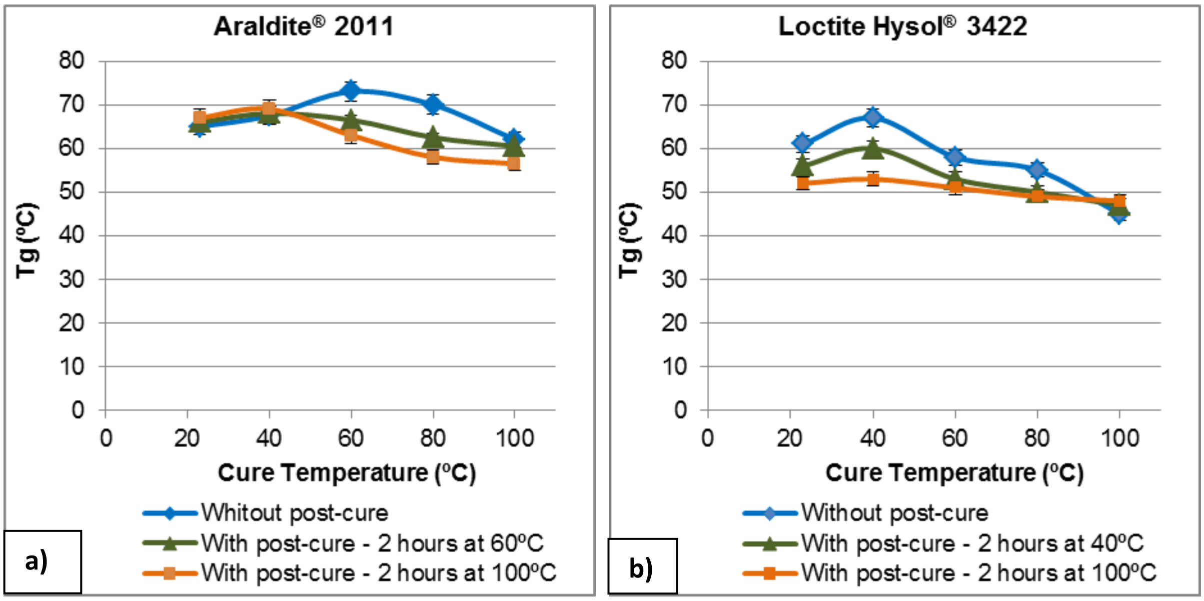

Figure 9 – T_g for different post-cure conditions as a function of cure temperature.

According to Wu [28], for lower post-cure temperatures (for T_{cure} below the $T_{g\infty}$ of the adhesive), T_g increases almost linearly with the post-cure temperature. This phenomenon occurs up to T_{cure} at which the adhesive has not achieved its full cross-linking (e.g. Araldite® 2011). When the adhesive achieves its full crosslinking, the post-cure will decrease the value of T_g and this decrease is larger with an increase of the post-cure temperature (e.g. Loctite Hysol® 3422). However, for higher post-cure temperatures (for T_{cure} above the $T_{g\infty}$ of the adhesive) T_g tends to stabilize at constant value independently of the cure temperature or T_g decrease. [29, 40] The thermal degradation or oxidative cross-linking (for T_{cure} above the $T_{g\infty}$ of the adhesive) is held responsible for the decrease of T_g with increasing T_{cure}. For adhesive Loctite Hysol® 3422, the stabilization of T_g at constant value independently of the cure temperature is noted, with increase of the post-cure. For adhesive Araldite® 2011, the T_g decreases and this decrease is more evident for high temperatures of post-cure.

It can be seen that adhesive Araldite® 2011 is more sensitive to post-cure, measuring that the thermal degradation or oxidative cross-linking can occur more easily. However, adhesive Loctite Hysol® 3422 shows a tendency of uniformity of the value of T_g when it is subjected to a post cure and this uniformity is more noticeable for higher temperatures of post-cure.

As expected, the $T_{g\infty}$ for Araldite® 2011 without post-cure is obtained for a T_{cure} at 60ºC and with post-cure it is obtained for a T_{cure} at 40ºC. According Carbas *et al.* [13], the $T_{g\infty}$ for this adhesive is achieved for a cure temperature of between 40 and 60ºC. $T_{g\infty}$ for Loctite Hysol® 3422 is obtained for a T_{cure} at 40ºC.

4.2. Tensile test

The mechanical properties were measured using a universal testing machine Instron (High Wycombe, England) model 3367 with a load cell of 10 kN under a crosshead rate of 1 mm/min. The displacement was measured with an Instron extensometer (25 mm gauge length). Three specimens were tested to failure for each individual temperature in laboratory ambient conditions (room temperature of 23ºC, relative humidity of 55%).Typical stress-strain curves of the adhesive as a function of the cure temperature are shown in Figure 10.

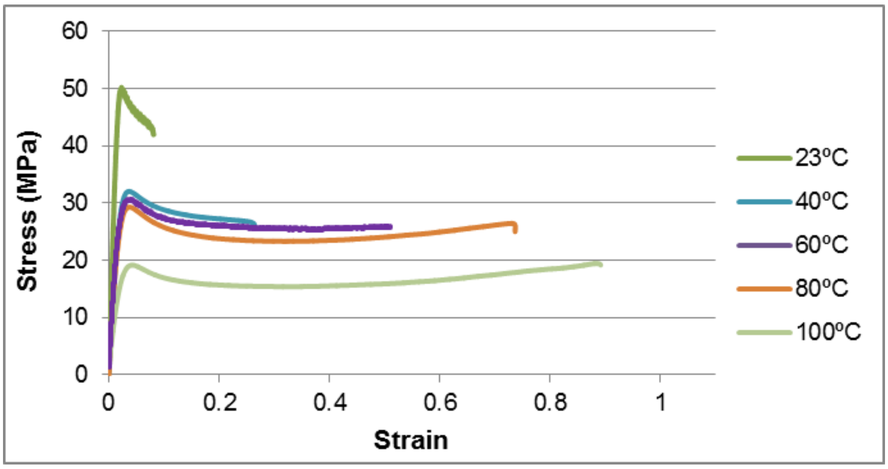

Figure 10 – Tensile stress-strain curves of Loctite Hysol® 3422 adhesive without post-cure as a function of the cure temperature.

The values for Young´s modulus were calculated from the tangent at the origin to the tensile stress-strain curve by making use of a polynomial approximation of the curve. The variation of the Young´s modulus of the adhesives submitted at different post-cure as a function of the cure temperature is shown in Figure 11.

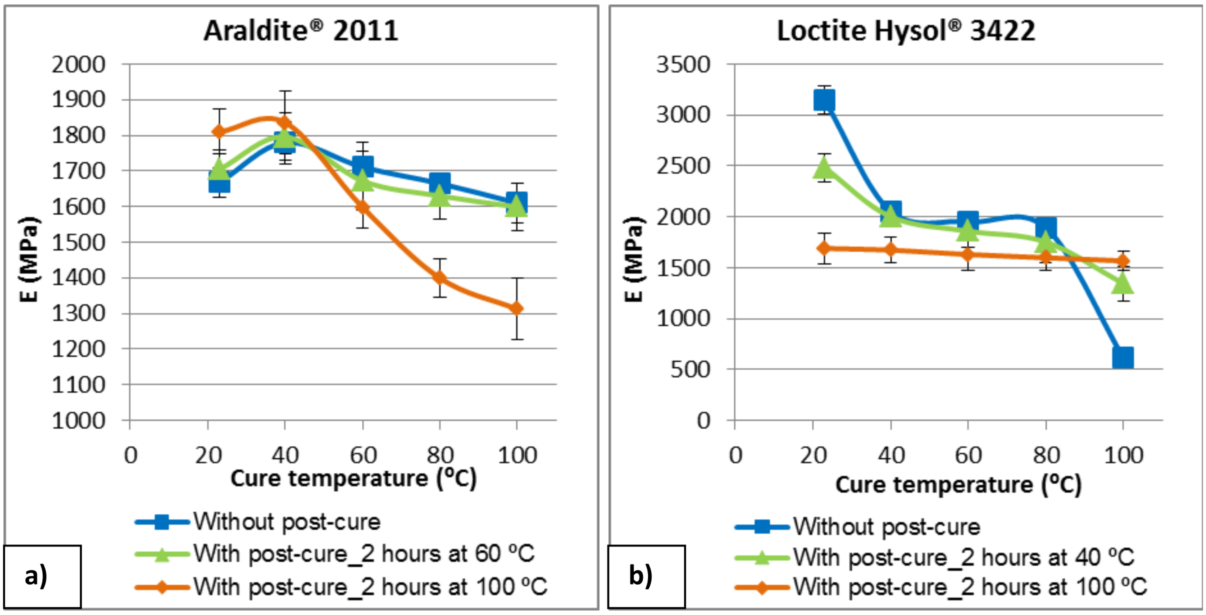

Figure 11 – Young's modulus of the two epoxy adhesives submitted to different post-cure conditions as a function of the cure temperature.

The variation of the yield strength of the adhesives submitted at different post-cure as a function of the cure temperature is shown in Figure 12.

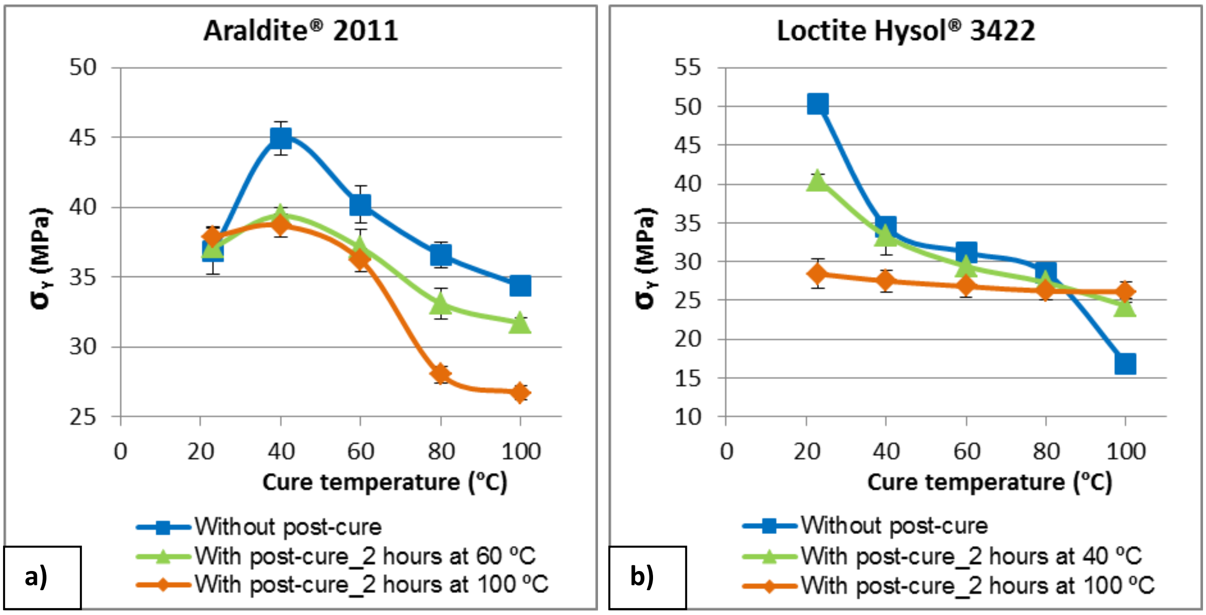

Figure 12 – Yield strength of the two epoxy adhesives submitted to different post-cure conditions as a function of the cure temperature.

The data obtained shows that for Araldite® 2011 there is an increase of the stiffness and strength with increasing post-cure temperature, but for T_{cure} below the T_{cure} at which the $T_{g\infty}$ is achieved. For T_{cure} above $T_{g\infty}$, the stiffness and strength decrease with increasing post-cure temperature (Figure 10 a) and 11 a)). The initial increase of stiffness and strength may be due to the physical ageing. The decrease of stiffness and strength for a post-cure above $T_{g\infty}$ may be due to the fact that the thermal degradation or oxidative crosslinking can occur, but this phenomenon is more notorious to high temperatures of post-cure. For Loctite Hysol® 3422 the stiffness and strength decrease with post-cure conditions, and with increasing temperature of the post-cure the stiffness and strength tend to a constant value for any cure temperature (Figure 10 b) and 11 b)).

The variation of the failure strain of the adhesives subjected to different post-cure temperatures as a function of the cure temperature is shown in Figure 13.

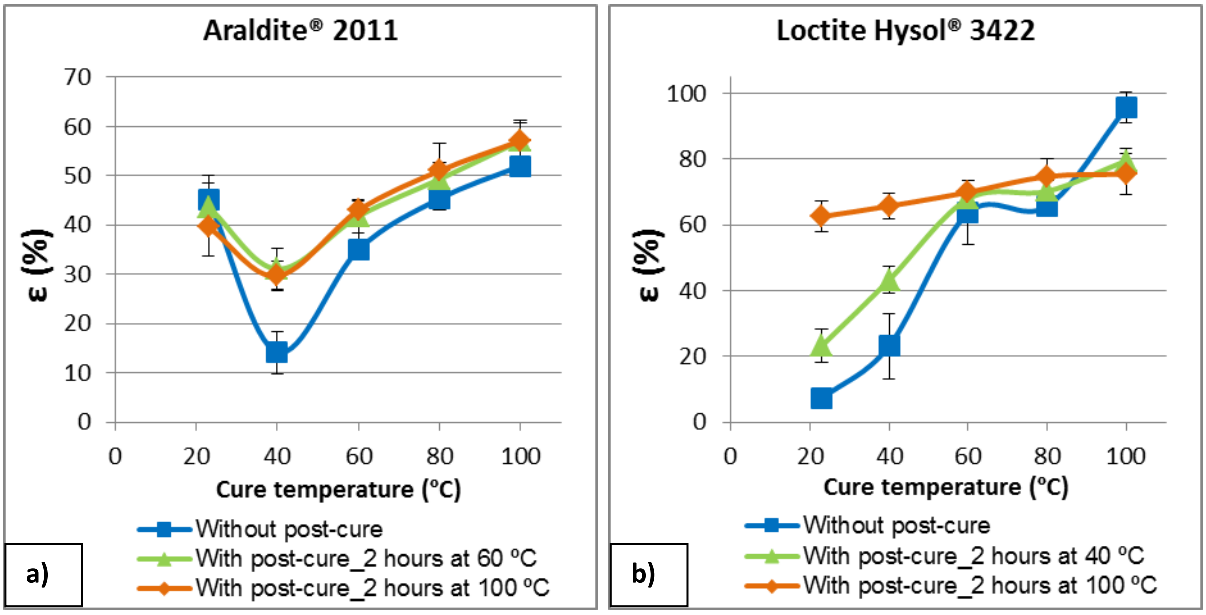

Figure 13 – Failure strain of the two epoxy adhesives submitted to different post-cure conditions as a function of the cure temperature.

The data obtained shows that for Araldite® 2011, for T_{cure} below the T_{cure} at which the $T_{g\infty}$ is achieved, there is a decrease of the failure strain with increasing post-cure temperature. For T_{cure} above, the failure strain increases with increasing post-cure temperature (Figure 13 a)). The failure strain behaviour is similar to that of the stiffness and strength, but with an opposite tendency. For T_{cure} at which the adhesive shows the highest stiffness and strength (40ºC), the failure strain shows its lowest value. For Loctite Hysol® 3422 the failure strain tends to a constant value for any T_{cure}, when submitted at post-cure conditions. This phenomenon is more evident to high temperatures of post-cure.

As expected, the highest strength, stiffness and lowest strain, for Araldite® 2011 without and with post-cure is obtained for a T_{cure} at 40ºC. The highest strength, stiffness and lowest strain, for Loctite Hysol® 3422 without and with post-cure is obtained for a T_{cure} at 23ºC.

It can be concluded that T_g and mechanical properties of the adhesive Loctite Hysol® 3422 exhibit greater variation as a function of T_{cure}. In opposition, Araldite® 2011 shows only a slight variation of the mechanical properties as a function of the T_{cure}. Also, Araldite® 2011 exhibits greater variation for the post-cure conditions, undergoing thermal degradation or oxidative cross-linking more easily and with increase of the post-cure temperature the mechanical properties become lower (degraded). For Loctite Hysol® 3422 with increased post-cure temperature, the mechanical properties tend to a constant value. We can conclude that this adhesive is more sensitive to T_{cure} and resistant to post-cure (mechanical properties do not decrease but tend to a constant value).

5. Discussion

T_g and mechanical properties of the two epoxy adhesives studied here were submitted to different post-cure conditions and it was shown that the post-cure has a strong influence on the T_g and mechanical properties. Without post-cure, there is a progressive increase of T_g and mechanical properties up to a T_{cure} equal to the T_{cure} at which the $T_{g\infty}$ is achieved, and when the cure temperature exceeds the T_{cure} at which the $T_{g\infty}$ is achieved, there is a progressive decrease in T_g and mechanical properties. For adhesives without post-cure, Loctite Hysol® 3422 shows larger variation of mechanical properties as a function T_{cure}, when compared with the adhesive Araldite® 2011. Araldite® 2011 shows a slight variation of the mechanical properties as a function of the T_{cure}, but shows a larger variation with different post-cure conditions. After the process of cure and post-cure that this two epoxy adhesives were submitted to, the phenomenon of thermal degradation or oxidative crosslinking is more evident for adhesive Araldite® 2011 (the mechanical properties become degraded). On the other hand, for adhesive Loctite Hysol® 3422 the mechanical properties tend to a constant value with increase of the post-cure temperature, independently of T_{cure}.

As expected, T_g and mechanical properties (i.e. stiffness, strength and failure strain) have a similar behaviour. This study has three different behaviours of the adhesive. – Without post-cure, there is a progressive increase of T_g, mechanical properties up to a T_{cure} equal to the T_{cure} at which the $T_{g\infty}$ is achieved, and when the cure temperature exceeds the T_{cure} at which the $T_{g\infty}$ is achieved, there is a progressive decrease in T_g and mechanical properties. – With post-cure at lower temperature (below $T_{g\infty}$), the adhesive can be two different behaviour. If the crosslinking is incomplete, so with post-cure there is an increase in T_g and mechanical properties. In the other hand, if the crosslinking is complete, with post-cure there is a decrease in T_g and mechanical properties. – With post-cure at higher temperature (above $T_{g\infty}$), there is a progressive decrease in the T_g and mechanical properties. This decrease is due to thermal degradation or oxidative crosslinking and is more marked for higher temperatures of post-cure. But this decrease is more noted for adhesive Araldite® 2011 and less for adhesive Loctite Hysol® 3422.

The two adhesives used in this study could be used to obtain functionally graded joints. However, they present two distinct behaviours. The adhesive Araldite® 2011 would confer to the joint a small variation on the mechanical properties along the length of overlap. When subjected to post-curing temperatures, this joint maintains graded characteristics and its strength would decrease with an increase in post-cure temperature. The adhesive Loctite Hysol® 3422 would confer to the joint a higher variation of mechanical properties along the length of the overlap, but when subjected to a post-cure temperature the joint tends to present characteristics of an isothermally cured joint. When subjected to post-curing temperatures, the graded joint bonded with Loctite Hysol® 3422 loses the graded characteristics of the bondline and the adhesive strength tends to a constant value, a value equal to that of an adhesive cured isothermally and subjected to a similar post-cure.

6. Conclusions

In this paper, the T_g and mechanical properties were measured for two epoxy adhesives (Araldite® 2011, Loctite Hysol® 3422) as a function of the curing temperature and for different post-cure conditions. The following conclusions can be drawn:

1. With post-cure the behaviour is similar to that of the adhesive without post-cure: there is a progressive increase of T_g, mechanical properties up to a T_{cure} equal to the T_{cure} at which the $T_{g\infty}$ is achieved, and when the cure temperature exceeds the T_{cure} at which the $T_{g\infty}$ is achieved, there is a progressive decrease in T_g and mechanical properties;

2. For adhesive with incomplete crosslinking (Araldite® 2011), when cured below the T_{cure} at which the $T_{g\infty}$ is achieved, with increase post-cure conditions the T_g and mechanical properties increase. On the other hand, when cured below the T_{cure} at which the $T_{g\infty}$ is achieved, with increasing post-cure temperatures the T_g and mechanical properties decrease;

3. For adhesives with complete crosslinking (Loctite Hysol® 3422), cured below or above the T_{cure} at which the $T_{g\infty}$ is achieved, with increasing post-cure temperatures the T_g and mechanical properties decrease;

4. Araldite® 2011 shows a slight variation of the mechanical properties as a function of the T_{cure}, but is more sensitive to post-cure conditions. With post-cure conditions at high temperature (above $T_{g\infty}$, at 100 ºC), there is a progressive decrease in the T_g and mechanical properties. For this adhesive, at high temperatures of post-cure the thermal degradation or oxidative crosslinking is more marked.

5. Loctite Hysol® 3422 shows a great variation of the mechanical properties as a function of the T_{cure}. With an increase of post-cure temperature, the T_g and mechanical properties tends to a constant value, and this trend is most notable for high temperature of post-cure, independent of the T_{cure}. For this adhesive, with post-cure conditions at high temperatures (above $T_{g\infty}$, at 100 ºC), the thermal degradation or oxidative crosslinking is negligible.

6. For adhesive Araldite® 2011 the greater strength and stiffness, without and with post-cure, is obtained for the T_{cure} of 40 °C. Without post-cure, the $T_{g\infty}$ is obtained for a T_{cure} of 60 °C and with post-cure it is obtained for a T_{cure} of 40 ºC. As expected, it can be concluded that the T_{cure} to obtain the best performance (highest T_g and mechanical properties) is achieved for a T_{cure} of between 40 and 60 °C;

7. For adhesive Loctite Hysol® 3422 the $T_{g\infty}$, without and with post-cure, the highest performance is obtained for the T_{cure} of 40 °C. With or without post-cure, the greater mechanical properties are obtained for the T_{cure} of 23 °C. Therefore it can be

concluded that the T_{cure} to obtain the best performance (highest T_g and mechanical properties) is achieved for a T_{cure} of between 23 and 40 °C;

8. Adhesive Loctite Hysol® 3422 could provide a functionally graded joint with a high variation in mechanical properties along the length of the overlap. However, with an increase of the post-cure temperature the adhesive strength tends to stabilize at a constant value.

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Paper 3

Analytical modelling of functionally graded joints

Modelling of functionally graded adhesive joints

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Abstract

Nowadays, there is a strong trend towards the use of functionally graded materials, with particular importance for the functionally graded joints. The main objective of this work was to study a functionally modified adhesive in order to have mechanical properties that vary gradually along the overlap of a joint, allowing a uniform stress distribution along the overlap. This allows for a stronger and more efficient adhesive joint and permits to work with much smaller areas, reducing considerably the weight of the structure which is a key factor in the transport industry. In the proposed joint, the adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap. The functionally graded joint was found to have a higher joint strength compared to the cases where the adhesive has homogenous properties along the overlap.

A simple analytical model to study the performance of the functionally graded joints was developed. The differential equation of this model was solved by a power series. Numerical modelling by finite element analysis was performed to validate the analytical model developed.

Keywords: Finite element analysis, Power series, Single-lap-joint, Shear stress distribution, Mechanical properties, Functionally graded joints.

1. Introduction

Over the past 70 years, adhesive joints have been intensively investigated and have been increasingly used due to their improved mechanical performance when compared with classical mechanical fixing methods. To predict the joint strength, one must have the stress distribution and a suitable failure criterion. In order to analyse the stress distribution in the adhesive layer several analytical and numerical models are found in the literature. The adhesive joints analyse range from simple mathematical considerations up to complex special purpose finite element models. For simple structures, the stress distribution can be obtained quickly and easily by a closed-form analysis. Most of the analytical solutions assume plane strain conditions since the analyses are based on beam theory principles. For complex geometries and elaborate material models, obtaining the stress distribution by a finite element analysis (FEA) is preferable [1].

The adhesive joint most studied in the literature and most common in practice is the single lap joint (SLJ), due to its simplicity and efficiency. The first attempt to analyse this joint was carried out by Volkersen [2], who introduced the concept of *differential shear*. However, this analysis ignored the adherend bending effects, caused by the eccentric load path of SLJ, and thus ignoring the transverse straining of the adhesive layer (the so-called shear lag analysis). Volkersen's analysis was later refined by adopting a two-parameter elastic foundation approach, considering the peel stresses and the bending moment factor. The first model to consider these effects was that of Goland and Reissner [3]. This model takes into account the effect of large deflections of the adherends, but assumes that the adherends are integral. Goland and Reissner [3] approach is accurate enough for short and long overlaps, but with an infinitely thin adhesive layer. Hart-Smith [4] examined the elastic-plastic adhesive behaviour in shear. This model represents a considerable improvement over the elastic solution of Goland and Reissner [3]. The main limitations of the classical analyses developed by Volkersen [2] and Goland and Reissner [3], were the fact that they do not account for variations of the adhesive stresses through the thickness direction and the fact that the peak shear stress occurs at the ends of the overlap, which violates the stress-free condition and, finally, the fact that the adherends were considered as thin beams, ignoring the through-thickness shear and normal deformations. Several authors have tried to overcome these limitations and proposed new models for analysing adhesive bonded joints [5-7]. It can be considered that Volkersen [2] and Goland and Reissner [3] formed the basis for many investigations of the structural response of adhesive joints.

The main problem associated to SLJ is that the stress distribution (peel and shear) in the adhesive along the overlap is not uniform, being concentrated at the ends of the overlap. In the literature, we can find several methods for reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings, but none gives a uniform stress distribution in the adhesive [1].

The joint strength improvement can be obtained through modification of the adherend geometry by inclusion of a taper in the adherend [8-10], and by sharp adherend corners [11-14], or by modifications of the joint end geometry with a spew fillet [15-20]. Another technique to improve the joint strength is the use of more than one adhesive (so-called mixed adhesive joints) and consists on using a stiff and strong adhesive in the middle of the overlap and a flexible and ductile adhesive at the ends of the overlap [21-30]. More recently, there have been several investigations to improve the joint strength by making use of functionally graded materials [31-33], and functionally graded bondlines [34-35].

An efficient technique for joint strength improvement is to obtain a more uniform stress distribution in SLJs through the use of gradually modified adhesives. The use of mixed adhesive joints can be considered as a rough version of a functionally graded adhesive. The first author to introduce the idea of using mixed adhesive joints to increase joint strength and minimizing the maximum adhesive stresses was Raphael [36]. The analysis of Raphael [36] is based on the shear lag concept of Volkersen [2]. In order to analyse the functionally graded joints with gradually modified adhesive, it is proposed in this work to develop a simple shear analysis based on the Volkersen's model.

Due to the increasing interest and research in functionally graded joints, it is essential to develop a simple analytical model for a rapid analysis of the stress distribution along the overlap length. This simple analytical model was developed by making use of power series expansions. Different mechanical properties variations along the overlap length were studied in order to obtain the more uniform shear stress distribution. The shear stress distribution obtained by this novel analytical model was validated by finite element analysis, and for each overlap length similar distributions were obtained (analytical and numerical analysis). In order to prove the joint strength performance of the joints gradually modified when compared with homogeneous joints, an analysis was performed for an adhesive that shows a high variation of mechanical properties.

2. Functionally graded joint analytical model

The Volkersen's shear lag analysis assumes that the adherends are membranes that can deform in tension (they are considered elastic) and that the adhesive layer deforms only in shear. The shear stress is concentrated at the ends of the overlap and is much lower at the middle. The simple differential equation which describes the adhesive shear strain in terms of the differential stretching of the adherends is obtained by considering a force equilibrium of the elemental diagram shown in Figure 1.

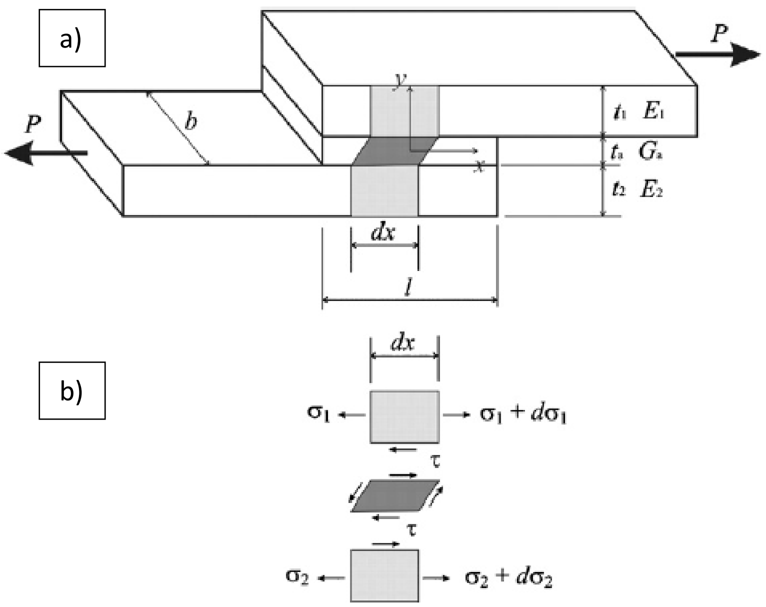

Figure 1 – Single-lap joint analysed by Volkersen [2]: a) geometry and b) elemental diagram.

The differential equation obtained by Volkersen's shear lag analysis, is

$$\frac{d^2\sigma_2(x)}{dx^2} - \lambda^2 \cdot \sigma_2(x) + C_0 = 0 \qquad (1)$$

With

$$\lambda^2 = \frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right) \qquad (2)$$

$$C_0 = \frac{P}{t_a \cdot b \cdot E_2 \cdot t_2 \cdot t_1} \cdot G_a \qquad (3)$$

where $\sigma(x)$ is the stress on the adherends, t_a is the thickness of the adhesive, t is the thickness of the adherends, E is the adherends Young´s modulus, P is the load applied, b is the weight of the adherends and G_a is the adhesive shear modulus.

Substituting Equation (2) and (3) in Equation (1), results in:

$$\frac{d^2\sigma_2(x)}{dx^2} - \frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right) \cdot \sigma_2(x) + \frac{P}{t_a \cdot b \cdot E_2 \cdot t_2 \cdot t_1} \cdot G_a = 0 \qquad (4)$$

Volkersen [2] proposed Equation (5) to analyse the shear stress ($\tau(x)$) of the adhesive along the overlap for SLJs with homogenous mechanical properties of the materials. This equation works well for thin adhesive layers and for short overlap lengths.

$$\tau(x) = \frac{b \cdot l}{P} \cdot \frac{\sqrt{\frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right)} \cdot l}{\left(\frac{E_1 \cdot t_1}{E_2 \cdot t_2} + 1\right) \cdot \sinh\left(\sqrt{\frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right)} \cdot l\right)} \cdot \left[\left(\frac{E_1 \cdot t_1}{E_2 \cdot t_2}\right) \cdot \cosh\left(\sqrt{\frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right)} \cdot (l - x)\right) + \cosh\left(\sqrt{\frac{G_a}{t_a} \cdot \left(\frac{1}{E_1 \cdot t_1} + \frac{1}{E_2 \cdot t_2}\right)} \cdot x\right)\right] \qquad (5)$$

2.1. Mathematical formulation

For functionally graded joints the mechanical properties of the adhesive vary along the overlap length. Therefore the adhesive shear modulus (G_a) is a function ($G(x)$) that represents the functional variation of adhesive mechanical properties along the overlap. Equation (3) was rewritten for functionally graded joints, and a new function ($G(x)$) was included to represent the mechanical properties variation of the adhesive. This new differential equation for functionally graded joints (Equation (6)) is a non-linear differential equation of second order.

$$\frac{d^2\sigma_2(x)}{dx^2} - \frac{G(x)}{t_a}\cdot\left(\frac{1}{E_1\cdot t_1}+\frac{1}{E_2\cdot t_2}\right)\cdot\sigma_2(x) + \frac{P}{t_a\cdot b\cdot E_2\cdot t_2\cdot t_1}\cdot G(x) = 0 \tag{6}$$

Non-linear second order differential equations hardly have a solution with an analytical expression, i.e. closed-form. Power series is a possible technique used to solve non-linear second order differential equations. This technique has the capacity to represent any function with an algebraic series. To solve the non-linear differential Equation (6) a power series solution in $x - \frac{l}{2}$ was considered. This solution represents the function $\sigma(x)$ in its convergence interval.

$$\sigma(x) = \sum_{k=0}^{\infty} a_n\cdot(x-\tfrac{l}{2})^n \quad , \quad \left|x-\tfrac{l}{2}\right| < R \tag{7.1}$$

$$\frac{d^2\sigma(x)}{dx^2} = \sum_{n=0}^{\infty}(n+2)\cdot(n+1)\cdot a_{n+2}\cdot(x-\tfrac{l}{2})^n \tag{7.2}$$

where a_n represents the coefficient of the nth terms and R represent the radius of convergence [37].

Substituting this series expansions into Volkersen's equation (Equation (6)) results in

$$\sum_{n=0}^{\infty}\left[(n+2)\cdot(n+1)\cdot a_{n+2}\cdot(x-\tfrac{l}{2})^n\right] - \sum_{n=0}^{\infty}\left[\left(\frac{G(x)}{t_a}\right)\cdot\left(\frac{1}{E_1\cdot t_1}+\frac{1}{E_2\cdot t_2}\right)\cdot a_n\cdot(x-\tfrac{l}{2})^n\right] + \frac{P}{t_a\cdot b\cdot E_2\cdot t_2\cdot t_1}\cdot G(x) = 0 \tag{8}$$

2.1.1. Adhesive shear modulus model

The mechanical properties of the adhesive vary gradually along the length of the overlap. The shear modulus is a function ($G(x)$) and in order to use the Volkersen's equation it was also expressed as a power series. For the mathematical formulation, a generic equation was considered for the mechanical properties variation of the adhesive along the bondline.

2.1.2. Boundary conditions

In order to simplify the analysis, only half of the overlap length was considered. To solve the second order differential equation (Equation (8)), it is necessary to use two boundary conditions. The boundary conditions used were:

$$\begin{cases} x = \frac{l}{2} \rightarrow \sigma_2(x) = 0 \\ \frac{P}{2 \cdot b} = \int_0^{\frac{l}{2}} \tau(x) \cdot ds \end{cases} \quad (9)$$

Volkersen [2] proposed a simple conversion of the stress distribution of the adherend ($\sigma(x)$) to the shear stress ($\tau(x)$) distribution along the bondline, as shown in Equation (10).

$$\frac{d\sigma_2(x)}{dx} = \frac{\tau(x)}{t_{s_2}} \quad (10)$$

2.2. Resolution of the governing equation

For this study, similar adherends in terms of material ($E_1 = E_2$) and thicknesses ($t_1 = t_2$) were considered. The non-linear second order differential equation (Equation (8)) was simplified in order to show clearly the resolution steps used to solve this equation. The constants below were used.

$$A = \frac{2}{t_s \cdot t_a \cdot E} \quad (11)$$

$$B = \frac{P}{t_s \cdot b \cdot E \cdot t_a^{\ 2}} \quad (12)$$

Constants A and B take into account the geometry and mechanical properties of the adherends, and the load applied to the joint. A linear adhesive shear modulus variation along the bondline was considered

$$G(x) = m \cdot x + K \tag{13}$$

The non-linear second order differential equation can be rewritten as

$$\frac{d^2\sigma(x)}{dx^2} - A \cdot (m \cdot x + K) \cdot \sigma(x) + B \cdot (m \cdot x + K) = 0 \tag{14}$$

Substituting the power series expansions into the non-linear second order differential equation

$$\sum_{n=0}^{\infty}[(n+2)\cdot(n+1)\cdot a_{n+2} - A \cdot K \cdot a_n]\cdot\left(x-\frac{l}{2}\right)^n - A \cdot m \cdot \sum_{n=0}^{\infty} a_n \cdot \left(x-\frac{l}{2}\right)^{n+1} + B \cdot K + B \cdot m \cdot x = 0 \tag{15}$$

The system of n equations for n unknowns is:

(constant terms)	:	$2 \cdot a_2 - A \cdot K \cdot a_0 + B \cdot D = 0$	(16.1)
(coefficient of x)	:	$6 \cdot a_3 - A \cdot K \cdot a_1 - A \cdot m \cdot a_0 + m \cdot B = 0$	(16.2)
(coefficient of x^2)	:	$12 \cdot a_4 - A \cdot K \cdot a_2 - A \cdot m \cdot a_1 = 0$	(16.3)
…		…	
(coefficient of x^n)	:	$(n+1)\cdot(n+2)\cdot a_{n+2} - A \cdot K \cdot a_n - A \cdot m \cdot a_{n-3} = 0$	(16.n)

Which can be written as:

$$a_2 = \frac{A \cdot K \cdot a_0 - B \cdot D}{2} \tag{17.1}$$

$$a_3 = \frac{A \cdot K \cdot a_1 + A \cdot m \cdot a_0 - m \cdot B}{6} \tag{17.2}$$

$$a_4 = \frac{A \cdot K \cdot a_2 + A \cdot m \cdot a_1}{12} \tag{17.3}$$

and recursively

$$a_{n+2} = \frac{A \cdot K \cdot a_n + A \cdot m \cdot a_{n-3}}{(n+1)\cdot(n+2)} \tag{17.n}$$

The boundary conditions used to solve the equation (6) were:

Boundary conditions

1. : $a_0 = 0$ (18.1)

2. : $2 \cdot b \cdot t_a \cdot \left[\left(a_0 + a_1 \cdot \left(\frac{l}{2}\right) + a_2 \cdot \left(\frac{l}{2}\right)^2 + \cdots + a_n \cdot \left(\frac{l}{2}\right)^n \right] = P$ (18.2)

The solution of this equation system was obtained in the Maple program (Waterloo Maple Inc., Canada). After determining the unknowns a_1, a_2, a_3,…,a_n recursively, these were substituted in the power series expansion (Equation (5)), to obtain the stress distribution of the lower adherend ($\sigma(x)$) for functionally graded joints.

Equation (19) represents the adhesive shear stress ($\tau(x)$) distribution along the bondline for only 2 terms of the power series expansion and for a linear adhesive shear modulus variation along the bondline. For higher order terms the equation becomes more complex but there is also a repetition of terms with an increase of order.

$$\tau(x) = \frac{32 \cdot P \cdot (6 \cdot l \cdot x \cdot A \cdot K - 8 \cdot x^3 \cdot A \cdot m + x^2 \cdot A^2 \cdot K^2 \cdot l - 24 - 12 \cdot x^2 \cdot A \cdot K + 3 \cdot x^2 \cdot A \cdot m \cdot l)}{b \cdot t_a \cdot l \cdot (-768 + 16 \cdot l^2 \cdot A \cdot K + l^4 \cdot A^2 \cdot K^2)} \quad (19)$$

2.3. Study of model convergence

In order to understand the optimum number of terms necessary to use in the power series expansion to obtain a correct $\tau(x)$ distribution, a convergence study was done. This convergence study was done for a different number of terms of the power series expansion. Figure 2 represents the $\tau(x)$ distribution along the overlap with different number of terms of the power series expansion. For a high number of terms, the complexity of the analytical model increases but the $\tau(x)$ distribution along the overlap is smoother. As it can be seen in Figure 2, more than 21 terms for the power series expansion, will not improve significantly the accuracy of the solution.

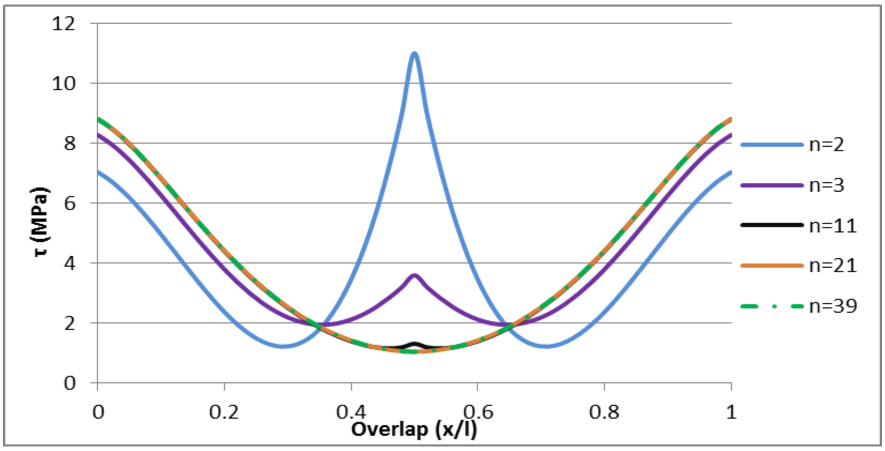

Figure 2 – Convergence of the analytical model for functionally graded joints.

3. Analytical analysis of functionally graded joints

3.1. Material

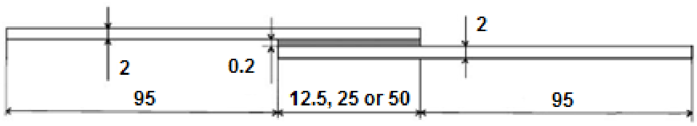

Figure 3 – Geometry of the single lap joint specimen (dimensions in mm).

Single lap joints with three overlap lengths (12.5, 25 and 50 mm), 0.2 mm of adhesive layer and 2 mm of adherend thickness were considered (see Figure 3). Both adherends were of steel with 210 GPa of Young's modulus, and the adhesive Young's modulus varied from 2000 MPa at the ends of the overlap up to 6500 MPa in the middle. These Young's modulus values were considered in order to ensure a gradual variation of the adhesive stiffness.

3.2. Functionally variation of adhesive mechanical properties

Different adhesive Young´s modulus distributions along the overlap length were considered in order to achieve the best performance of the joint. Square, linear and exponential mechanical property distributions along the overlap were considered, as can be seen in Figure 4. In this analysis it was considered that the mechanical properties behaviour in the bondline were symmetric.

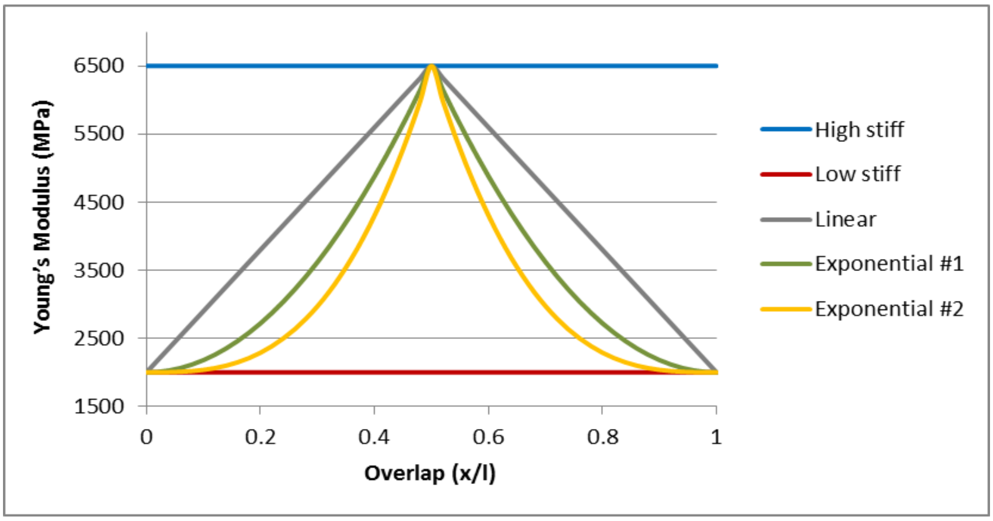

Figure 4 – Different mechanical properties variation along the overlap length.

For the analytical formula developed for functionally graded joint, the mechanical properties (E) distribution of the adhesive along the overlap length was converted in shear modulus (G) with Equation (19).

$$G = \frac{E}{2\cdot(1+\nu)} \qquad (19)$$

where ν is the Poisson ratio of the adhesive (a value of 0.33 was used).

3.3. Shear stress behaviour

The model developed for functionally graded joints (with linear adhesive modulus properties variation along the overlap) was compared with the Volkersen's model for homogeneous joints. For this analysis two homogenous joints were considered; one with a stiff adhesive and another one with a flexible adhesive. These adhesives correspond to the adhesive properties in the functionally graded joint, in the middle and at the ends of the joint respectively. Figure 5 shows the shear stress distribution along an overlap length of 12.5 mm, for different distributions of adhesive modulus properties (homogeneous and linear) and under a load of 5 kN.

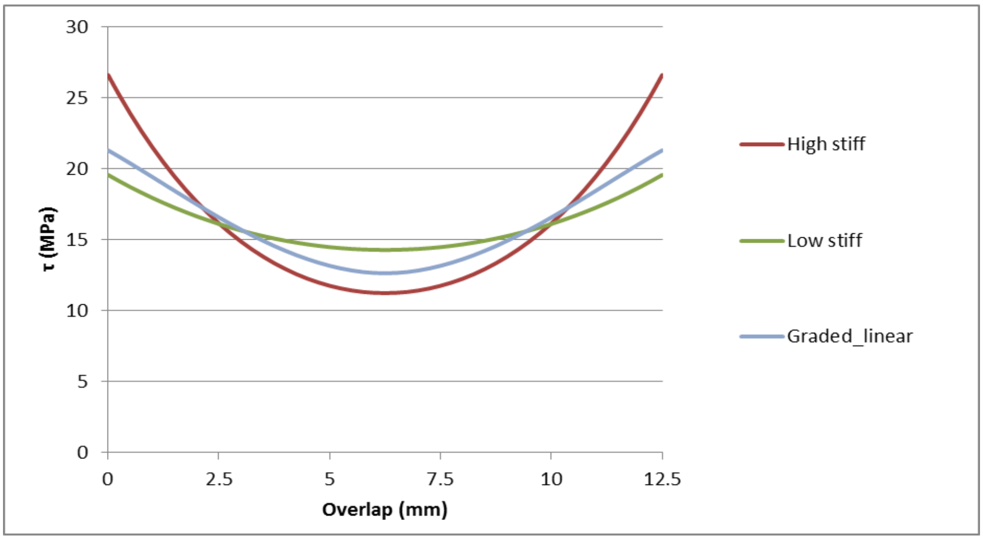

Figure 5 – Comparison between joints with homogeneous and graded mechanical properties for an overlap of 12.5 mm.

Figure 6 shows the shear stress distribution along an overlap length of 25 mm, for different distributions of adhesive modulus properties (homogeneous and linear) and under a load of 5 kN.

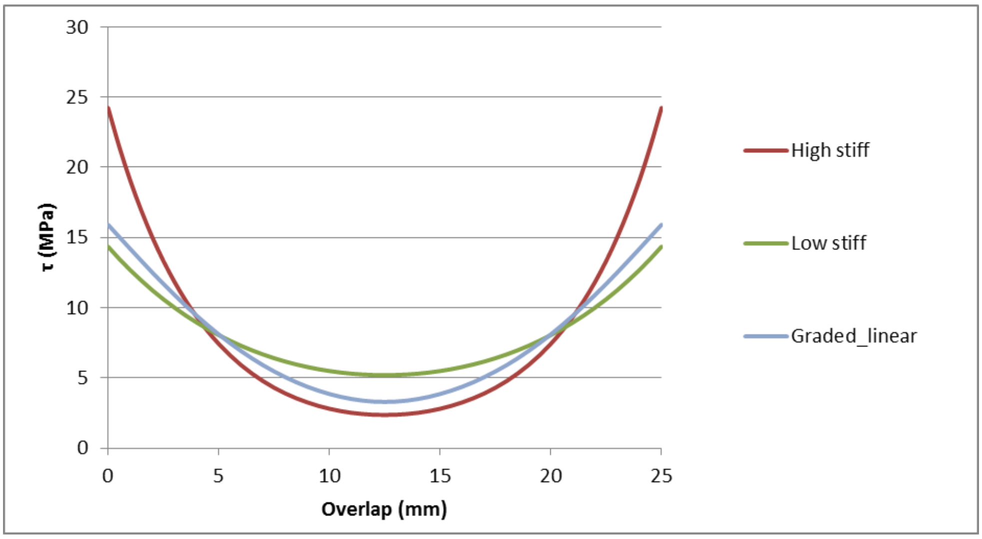

Figure 6 – Comparison between joints with homogeneous and graded mechanical properties for an overlap of 25 mm.

Figure 7 shows the shear stress distribution along an overlap length of 50 mm, for different distributions of adhesive modulus properties (homogeneous and linear) and under a load of 5 kN.

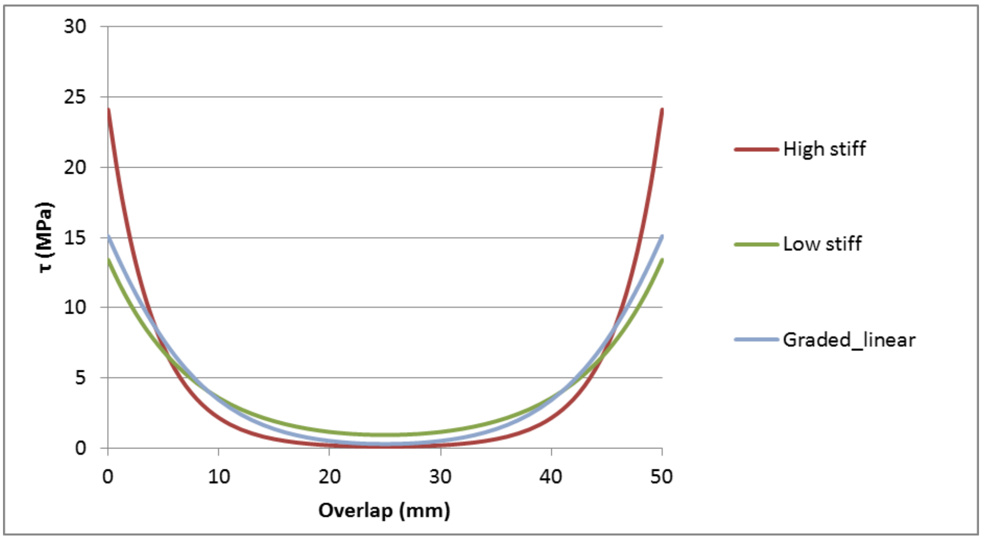

Figure 7 – Comparison between joints with homogeneous and graded mechanical properties for an overlap of 50 mm.

It can be seen in Figures 5-7, the area under the $\tau(x)$ curve for the homogenous joints and for the same for functionally graded joint is the same. To obtain a more uniform $\tau(x)$ along the bondline of a SLJ, it is necessary to concentrate the stiffness adhesive in the middle and the flexible adhesive at the ends of the overlap.

4. Numerical analysis of functionally graded joints

Since the 1970s [38], finite element methods have been increasingly used to analyse the behaviour of adhesive joints. Accurate analysis of a SLJ can be performed by a finite element analysis (FEA) and this is a tool that can provide physical insight and accurate results [1].

4.1. Finite element model

The numerical modelling of the graded joint was carried out in ABAQUS 6.10 program (Dassault Systèmes Simulia Corp. Providence, RI, USA). A two-dimensional finite element analysis was used to study the behaviour of the SLJ with an overlap gradually modified (functionally graded joint) under tensile loading. The adherends and the adhesive of the functionally graded joint were assumed to behave as linear elastic and as an isotropic material. For the adhesive with mechanical properties grading, the overlap length was divided into different equal regions. The number of divisions was chosen so that the transition between divisions (mechanical properties) became the smoothest possible. The boundary conditions and loadings are shown in Figure 8. In order to simulate the load applied on the joint, a uniformly distributed unit stress was applied to the right of the joint, and the left side was constrained in all degrees of freedom. This model was used to obtain the adhesive shear stress distribution.

Figure 8 – Model used in FE analysis.

The element used was CPE8R, which consists on 8-node bi-quadratic plane strain quadrilateral elements, with reduced integration to enable faster calculation. As indicated in the literature [1] a finer mesh at the ends of the overlap is necessary due to the existence of large stress gradients. To capture accurate stress values the region adhesively bonded is more refined and a coarse mesh in the substrates is used (Figure 9). The stress was taken in the middle of the bondline to avoid the singularities.

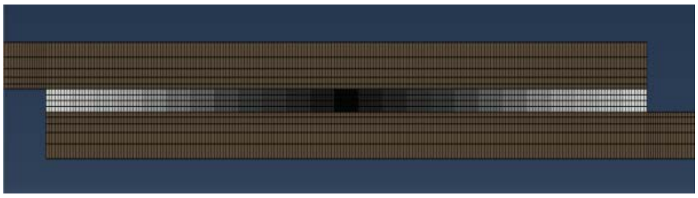

Figure 9 – Meshing of the model in detail.

It was considered that the adhesive Young's modulus has a multi-step variation of modulus along the overlap as shown in Figure 10 for a linear distribution.

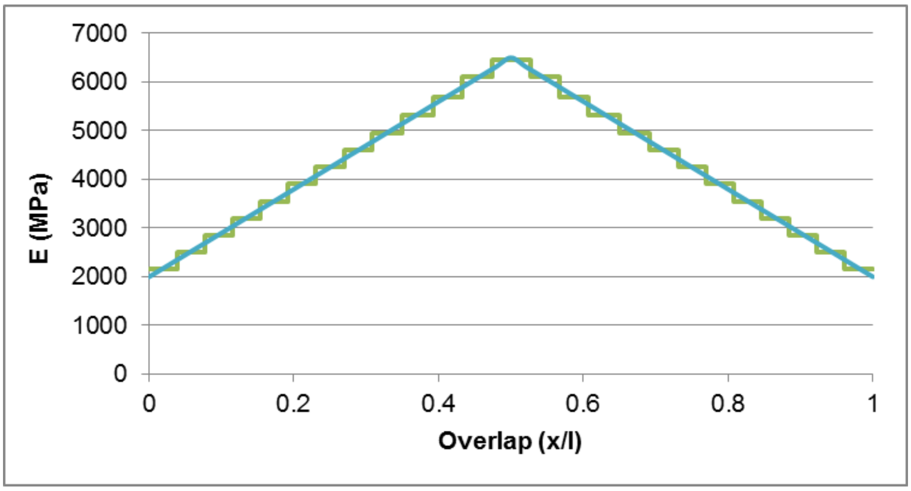

Figure 10 – Representation of the adhesive multi-step variation of Young's modulus along the overlap in finite element analysis.

4.2. Comparison between analyses

In order to validate the analytical equation developed, the power series expansion for functionally graded joints was compared with the numerical analysis. The adhesive shear stress distributions obtained by both analyses, for a linear adhesive modulus distribution, were compared for same load of 5 kN. Figure 11 shows the adhesive shear stress distribution of functionally graded joints obtained by both methods (analytical and numerical analysis) for a linear adhesive modulus distribution with an overlap length of 12.5 mm.

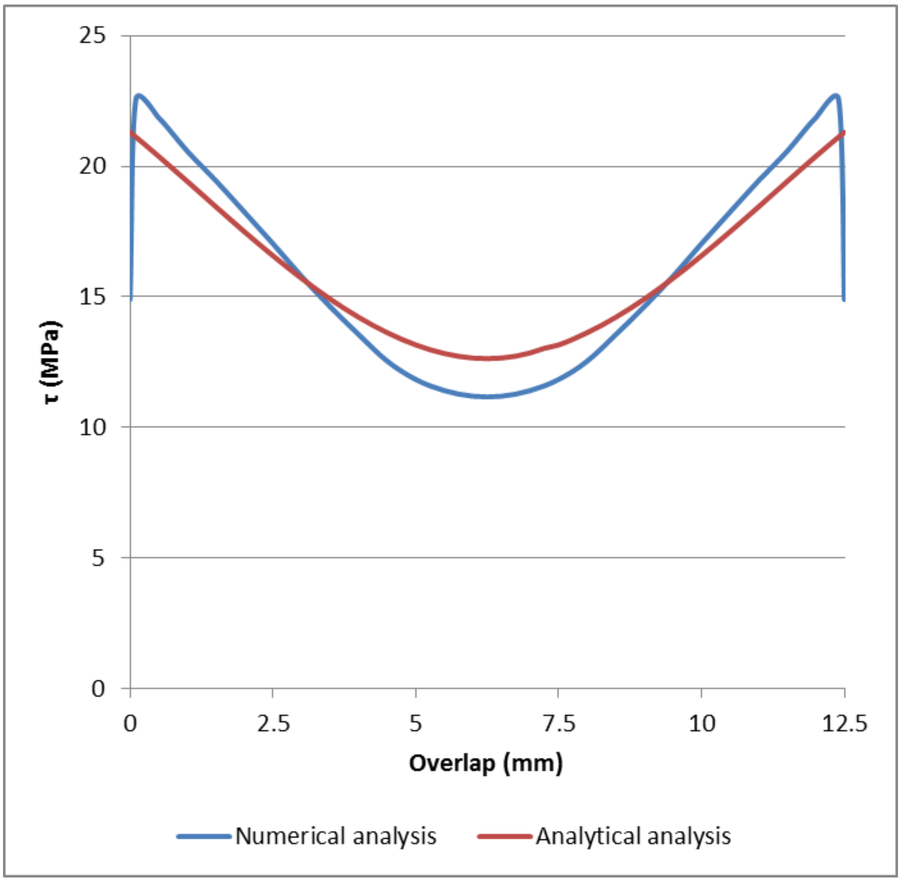

Figure 11 – Comparison between analytical and numerical analyses with an overlap length of 12.5 mm.

Figure 12 shows the adhesive shear stress distribution of functionally graded joints obtained by both methods (analytical and numerical analysis) for a linear adhesive modulus distribution with an overlap length of 25 mm.

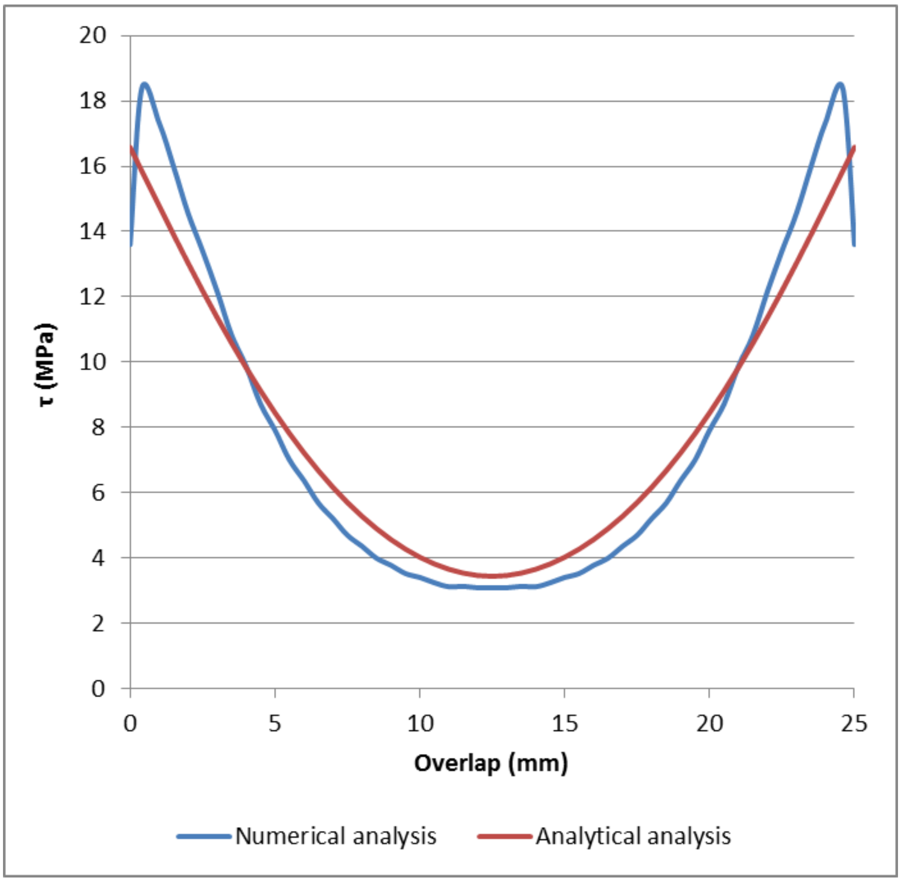

Figure 12 – Comparison between analytical and numerical analyses with an overlap length of 25 mm.

Figure 13 shows the adhesive shear stress distribution of functionally graded joints obtained by both methods (analytical and numerical analysis) for a linear adhesive modulus distribution with an overlap length of 50 mm.

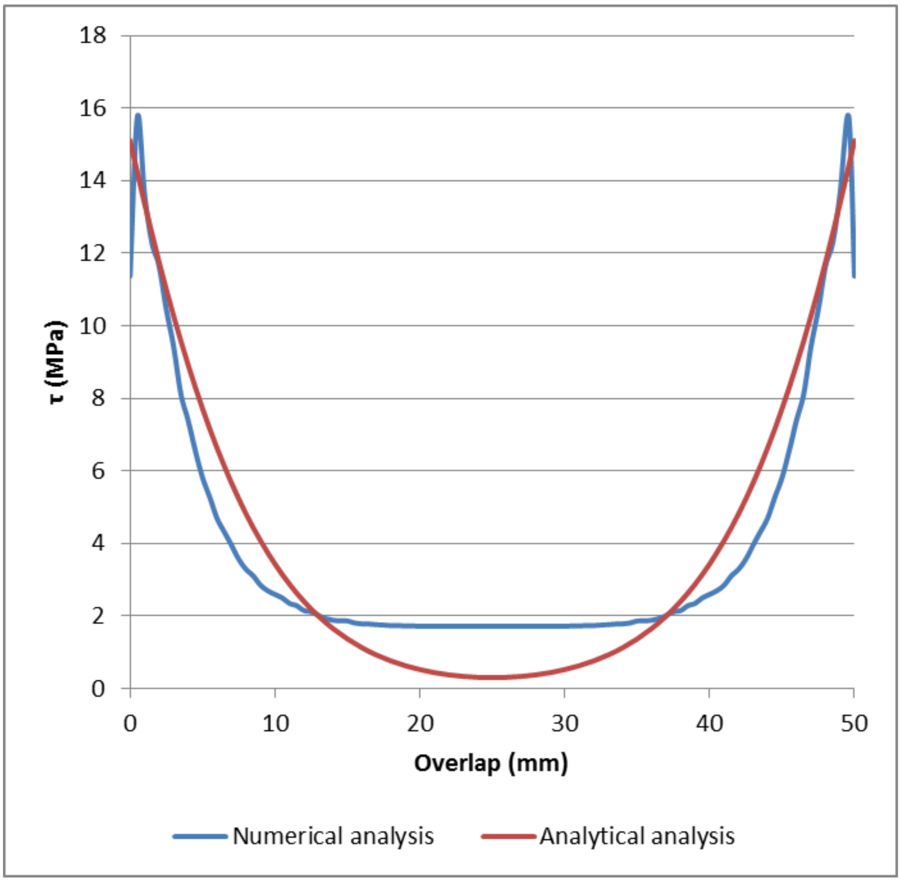

Figure 13 – Comparison between analytical and numerical analyses with an overlap length of 50mm.

The adhesive behaviour shows similar behaviour, and the curves do not match only at the ends of the joint. This limitation arises from the base equation of the analytical analysis (Volkersen's analysis [2]) which neglects the fine stress condition at the ends of the overlap. In order to validate this novel analytical analysis, these curves can be analysed in terms of energy and the area under both curves was the same. One can conclude that, notwithstanding the behaviour at the ends of the overlap, the novel analytical analysis gives a good prediction of the adhesive shear stress behaviour for functionally graded joints for a linear-elastic analysis.

5. Failure load prediction

5.1. Joints with homogenous mechanical properties

For joints with homogenous brittle mechanical properties along the overlap, the failure load was predicted with Volkersen's analysis [2] for brittle behaviour (Equation (5)) and with the global yielding criterion [39] for ductile behaviour. According to Volkersen's analysis [2] the failure occurs when the maximum shear stress at the ends of the overlap exceeds the shear strength of the adhesive. For joints with homogenous ductile mechanical properties along the overlap, the failure load predicted by global yielding criterion [34], corresponding to the total plastic deformation of the adhesive and is given by

$$F_a = \tau_y \, w \, l \qquad (20)$$

where F_a is the failure load of the adhesive, τ_y the shear yield strength of the adhesive, w the joint width and l the overlap length. This type of behaviour is expected for the adhesive located at the ends of the overlap in the graded joint.

5.2. Functionally graded joints

For joints with functional modification of the adhesive along the overlap the Equation (19) was used.

In order to understand the failure mechanism and have into account the plastic behaviour of the adhesive, an elastic-plastic analysis was carried out. The simple elastic-plastic adhesive behaviour proposed by Adams and Mallick [40] was used. Adams and Mallick [40] introduced the linear 'effective modulus' solution. This analysis consists on considering the energy under the stress-strain curve obtained through tensile tests and this energy is used to construct a theoretical line (called the linear 'effective modulus' solution), which has the same shear strain energy and strain to failure of the full elastic-plastic curve. (see Figure 14).

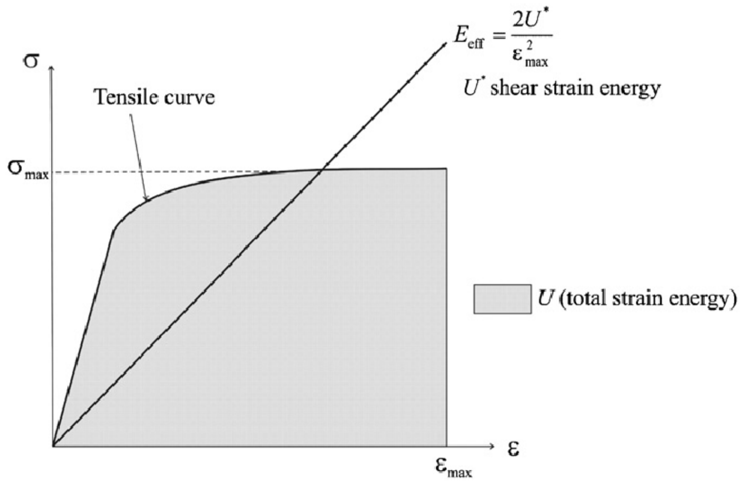

Figure 14 – 'Effective modulus' solution proposed by Adams and Mallick [40].

The shear stress of the adhesive was chosen for failure strength prediction as the shear stress distribution allows a quick and relevant assessment of the stress state in the functionally graded joint. For this analysis it was considered that the failure occurs when the maximum shear stress that acts along the overlap exceeds the shear strength of the adhesive along the overlap.

Figure 15 shows the stress-strain curves of an adhesive as a function of cure temperature and the respective effective modulus for each curve that was considered in the analysis. These theoretical curves are typical of structural adhesives.

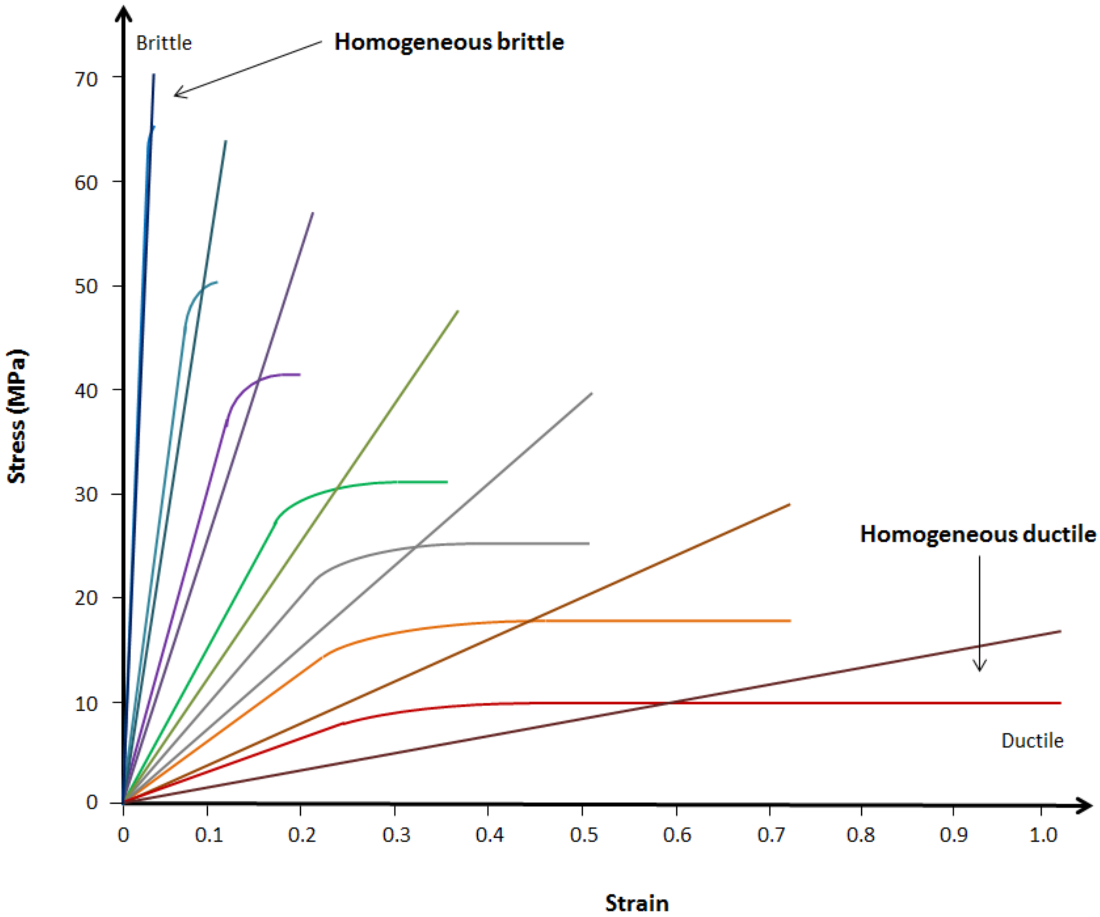

Figure 15 – Typical tensile stress-strain curves as a function of cure temperature.

The effective modulus ($E_{eff.}$) was determined by making use of the the linear effective modulus solution proposed by Adams and Mallick [40]. Figure 16 shows how the effective modulus ($E_{eff.}$) varies along the overlap as well as the maximum effective shear stress ($\tau_{eff.}$).

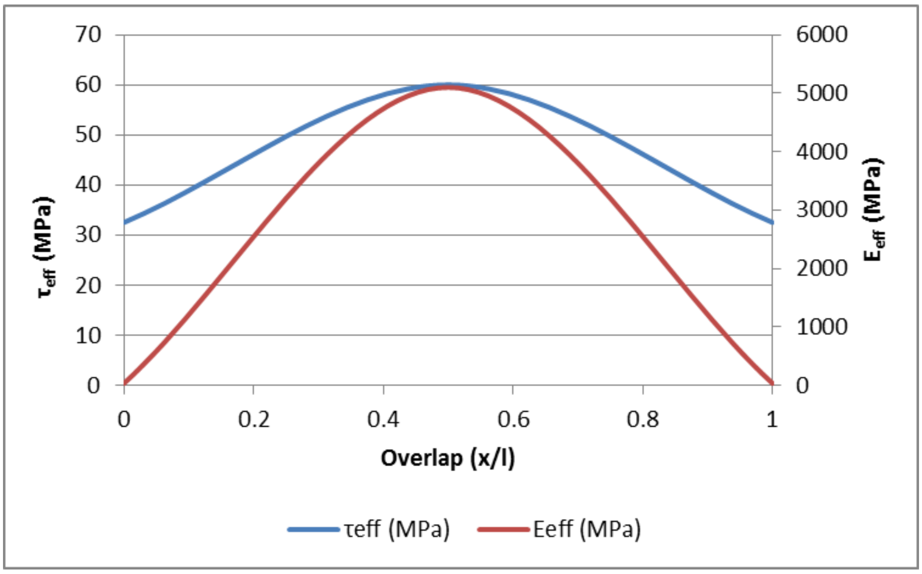

Figure 16 – Variation of the effective modulus ($E_{eff.}$) and effective shear stress ($\tau_{eff.}$) along the overlap of a graded joint.

5.3. Results

Table 1 shows the predicted failure load obtained by the analytical analysis for joints with homogeneous (brittle and ductile behaviour) and functionally modified adhesive properties along the overlap (12.5, 25 and 50 mm).

Table 1 – Failure load prediction for joints with homogeneous and functionally modified adhesive properties along the 12.5, 25 and 50 mm.

Joints	**Predicted failure load [kN]**		
	12.5 mm	**25 mm**	**50 mm**
with functionally modification properties of the adhesive	8.9	13.8	18.0
with homogenous properties of the adhesive for high stiff	8.5	9.3	9.4
with homogenous properties of the adhesive for low stiff	4.3	7.4	10.1

It is clear that functionally graded joints show the highest performance (strength), when compared to the joints with homogeneous adhesive properties along the overlap. The high performance of the functionally graded joints increases with the increase of the overlap length.

6. Conclusion

In this paper a novel analytical analysis of functionally graded joints was proposed. The shear stress distribution along the overlap length of functionally graded joints was obtained by an analytical method and was validated with a numerical analysis. The following conclusions can be drawn:

1. Power series expansion provides a good accuracy of the solution for a non-linear second order differential equation for a reduced number of expansion terms (21 terms);
2. The analytical analysis of functionally graded joints, based on Volkersen's analysis, was shown to be a valid tool to predict the shear stress distribution along the overlap length for linear-elastic behaviour;
3. For the different mechanical properties distribution along the overlap length, the distribution that confers a more uniform shear stress distribution was the logarithmic distribution;
4. Comparing the analytical analysis by Power series expansion with the numerical analysis by a FE analysis, both shear stress distribution of the bondline were found to have a similar behaviour;
5. The joints with the adhesive properties functionally modified along the overlap show a high strength when compared with the joints with homogeneous adhesive properties along the overlap and this behaviour becomes more accentuated with an increase of the overlap length.

Acknowledgments

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Paper 4

Invention to obtain functionally graded joints

Functionally graded joints by induction heating

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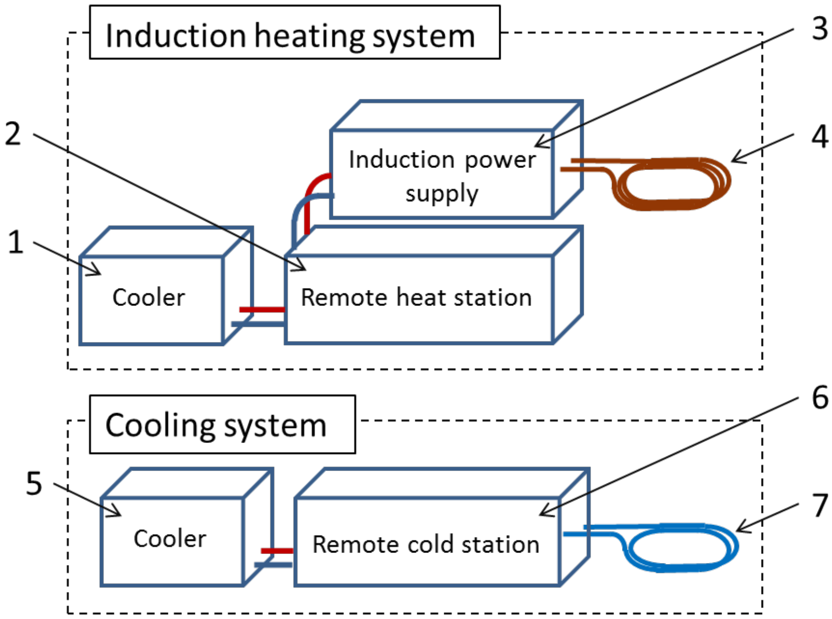
Abstract

The main objective of this invention was to develop a technique to obtain an adhesive functionally modified in order to have mechanical properties that vary gradually along the overlap, allowing a uniform stress distribution along the overlap and to reduce the stress concentrations at the ends of the overlap of lap joints. This allows for a stronger and more efficient adhesive joint. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap.

An induction coil was designed to achieve a graded cure so that an adhesive with graded properties is obtained along the overlap of a lap joint. A suitable design of the heating coil was made in order to obtain the desired temperature distribution along the length of the overlap to achieve a gradual degree of cure.


Induction heating system
3
2
Induction power supply
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1
Cooler
Remote heat station
Cooling system
6
5
Cooler
Remote cold station
7

FIG. 1

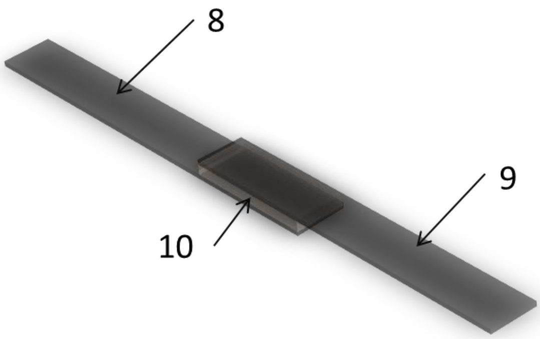
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FIG. 2

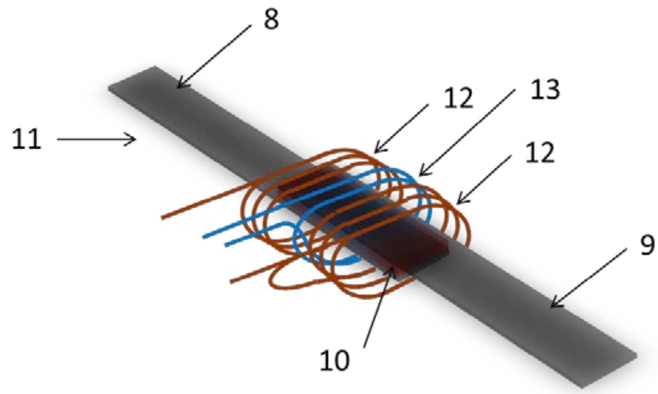
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FIG. 3

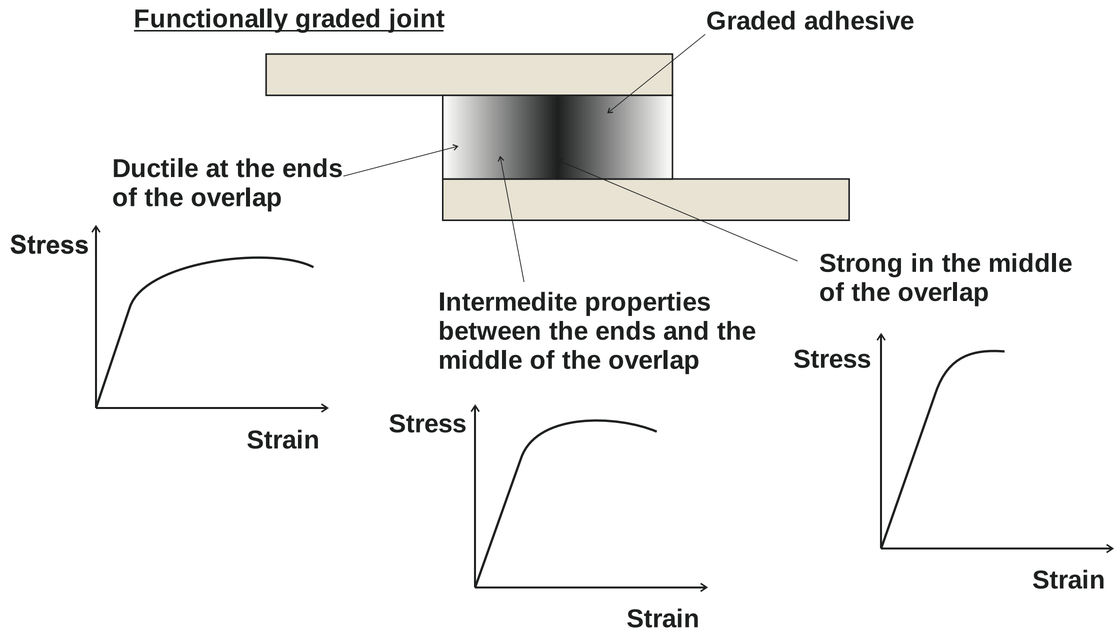
Functionally graded joint
Graded adhesive
Ductile at the ends of the overlap
Stress
Strain
Intermedite properties between the ends and the middle of the overlap
Stress
Strain
Strong in the middle of the overlap
Stress
Strain

FIG. 4

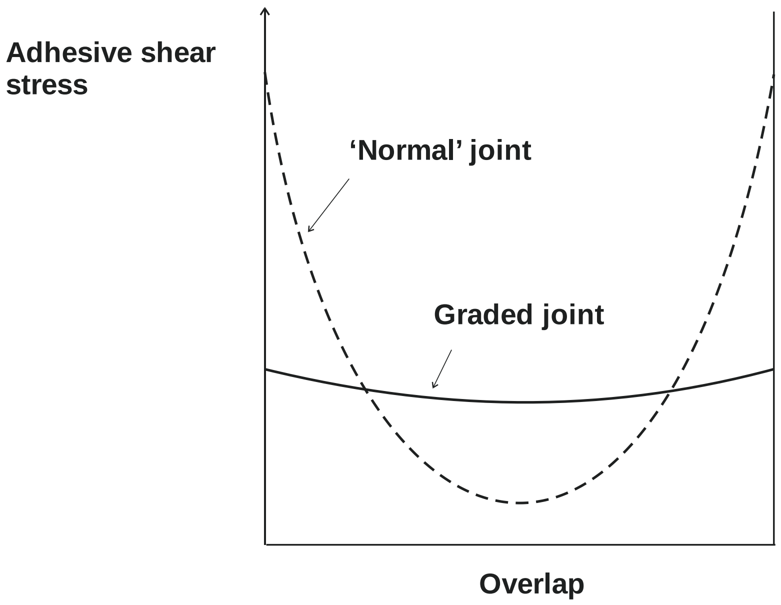
Adhesive shear stress
'Normal' joint
Graded joint
Overlap

FIG. 5

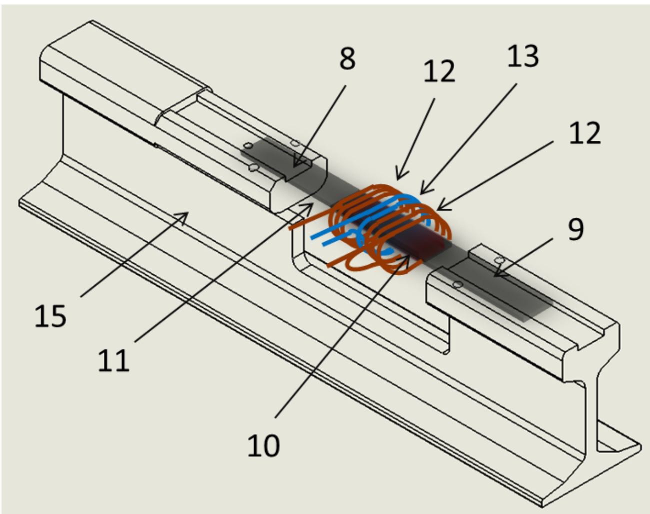
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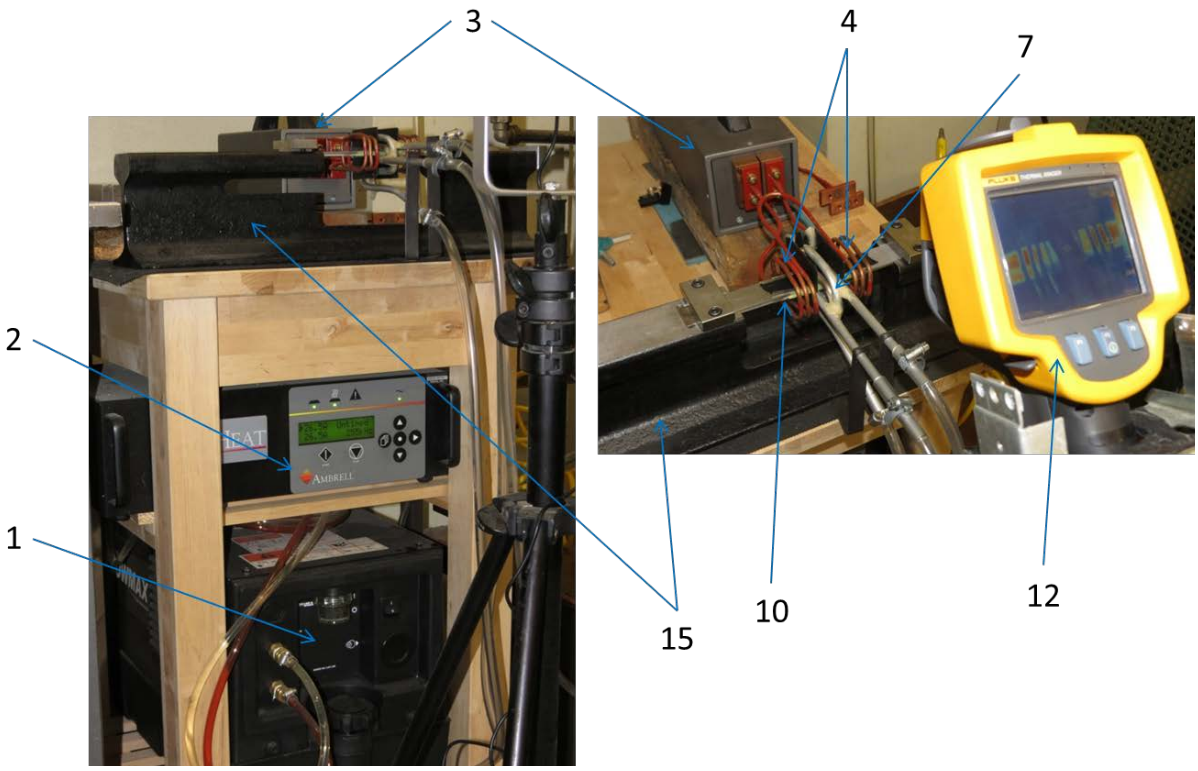
FIG. 6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2
1
15
10
12

FIG. 7

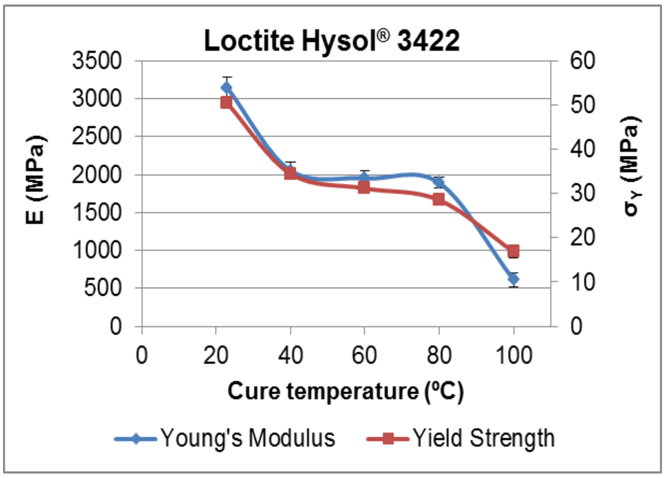
Loctite Hysol® 3422
E (MPa)
σ_Y (MPa)
3500
3000
2500
2000
1500
1000
500
0
60
50
40
30
20
10
0
0
20
40
60
80
100
Cure temperature (ºC)
Young's Modulus
Yield Strength

FIG. 8

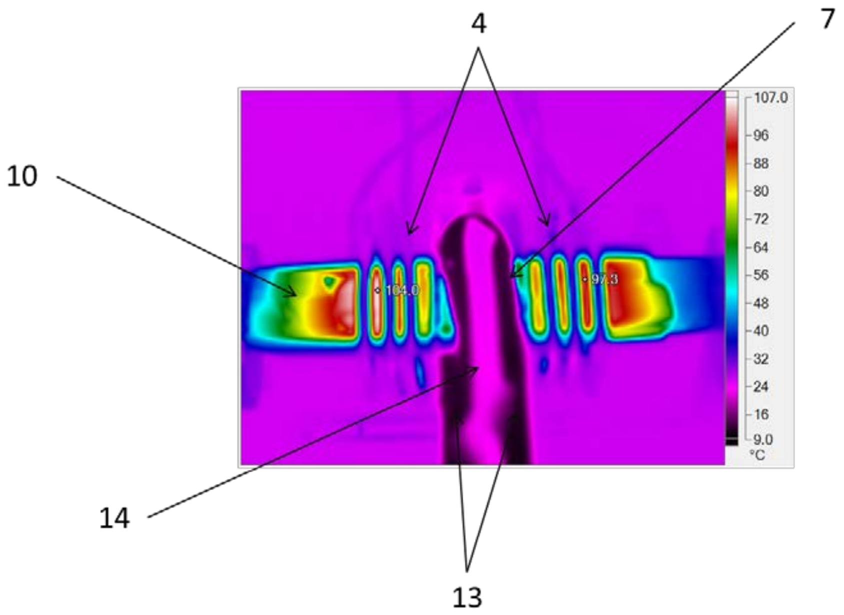

FIG. 9

1. Description

1.1. Field of the invention

This invention relates in general to an improved method and apparatus for bonding a structural assembly and more particularly to bonding joints where the adhesive is cured by induction heating.

The main objective is to develop a technique to obtain an adhesive functionally modified in order to have mechanical properties that vary gradually along the overlap. This allows for a stronger and more efficient adhesive joint due to a uniform stress distribution along the overlap reducing the typical stress concentrations at the ends of the overlap [1].

1.2. Background of the invention

In the 1940's, mechanical fasteners dominated the assembly industry, and adhesives were not as important to industry during this period. In the 1950's, the modern adhesives industry began to develop with the early work of de Bruyne on the modification of phenolics with vinyl, which enabled improved toughness [2]. Over the past 70 years adhesive joints have been intensively investigated and are increasingly being used due to their improved mechanical performance when compared with classical mechanical fixing methods. Currently there is a good understanding of the mechanics of failure of adhesive joints. The main advantage of adhesive joints is that the stress distribution is more uniform than with the other traditional methods of fastening such as bolts or rivets. This permits to work with smaller load bearing areas leading to weight savings. That is the main reason why adhesives were initially used in the aeronautical industry where the weight is a crucial matter. Nowadays, adhesives are used in other industries being the automotive industry one of the most growing market. That is obviously because the car industry is looking at ways to reduce fuel consumption by a weight reduction [3].

One of the most common types of joints is the single lap joint, due to its simplicity and efficiency. When analysing this type of joint, the main problem associated is the stress distribution (peel and shear) in the adhesive along the overlap which is in fact not uniform, being concentrated at the ends of the overlap. That is why one of the main areas of investigation in the field of adhesive bonding is to develop ways of reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings. In the literature, several methods have been proposed but none gives a uniform stress distribution in the adhesive [4-5].

Currently, there are strong investigations in joint strength improvement. This strength improvement has been obtained through modification of the adherend geometry by inclusion of a taper in the adherend, by rounding the adherend corners, or by modifications of the joint end geometry with a spew fillet. Another technique to improve the joint strength is by the use of more than one adhesive (so-called mixed adhesive joints) which consists in using a stiff and strong adhesive in the middle of the overlap and a flexible and ductile adhesive at the ends of the overlap. More recently, there are several investigations making use of functionally graded materials, and functionally graded bondlines for improved joint strength. Currently, this functionally modification of the adhesive is achieved by doping particles to modify gradually the bondline [6-7]. These techniques of joint strength improvement can be considered a rough version of functionally graded joints. The present invention creates a true continuously functionally modified adhesive along the overlap length of the joint by induction heating.

Induction heating is a fast heating method because it focuses heat at or near the adhesive bondline. The most important advantages of induction heating are assembly speed and the fact that an entire assembly does not have to be heated to cure only a few grams of adhesive (the confined area). This technique can be easily implemented in the industry and is very efficient (fast bonding, heating only the area of interest, curing equipment more compact, decreasing of the energy consumption). Induction heating is an electromagnetic heating method in which electrically conductive bodies absorb energy from an alternating magnetic field, generated by an induction coil. Induction heating is a technique very efficient since the heat is actually generated inside the workpiece. This technique uses high frequency electricity to heat materials that are electrically conductive, and does not contaminate the material being heated since it is a non-contact technique. The workpiece (e.g. joint) to be heated is placed within the intense alternating magnetic field, but the joint must be capable of being heated by an electromagnetic field. For induction heating to work, it is necessary that the joint be composed by metallic adherends or by an adhesive filled with ferromagnetic particles. The use of induction heating for bonding adhesive joints is significantly limited when bonding a non-ferromagnetic adherend to another non-ferromagnetic adherend. Such joints exist not only in the automotive field but in countless other fields such, as aeronautic, aerospace, marine industries or in some civil applications.

Since there is little if any molecular action within polymers induced by an alternating field which can generate heat, to bond adherends of polymers or composites or dissimilar adherends by induction heating, it is necessary to dope the adhesive with small ferromagnetic particles so that the adhesive can be inductively heated. The main problem of this technique is thermal bond between dissimilar components (adherends). In such applications, the induced flux tends to heat more the component with high conductivity than the other component with less conductivity. This in turn requires the positioning of the coil and the frequencies at which the induction coil operates to be closely controlled to regulate the depth and the magnetic field intensity of heating affected by the coil. The approach of adhesives doped with particles has been used recently to achieve a non-uniform dispersion within the adhesive resulting in uneven mechanical properties of the adhesive along the overlap thus reaching a rough graded joint. The same approach can be used for functionally graded joints by induction heating, where the adhesive is doped by metal particles, thus the gradient of temperatures along the bondline can be controlled by the dispersion of particles. However this approach needs the extra work of dispersion, but is a solution for components which are non-ferromagnetic.

2. Summary of the invention

The invention provides a method/apparatus and technological process to obtain an adhesive functionally modified in order to have mechanical properties that vary gradually along the bondline.

The joints obtained by this invention show a more uniform stress distribution along the overlap length and the stress concentrations at the ends of the overlap of the joints are reduced. This allows for a stronger and more efficient adhesive joint. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap. This functionally graded modification of the adhesive is achieved by the use of a differentiated cure process. The adhesive is modified to show a variation of the stiffness along the overlap.

In order to achieve a differential cure along the bondline, an induction coil was designed. A suitable design of the heating coil was made in order to obtain the desired temperature distribution along the length of the overlap (to achieve a gradual degree of cure so that the mechanical properties vary along the overlap). In order to ensure that the temperature gradient is obtained, a cooling system was developed, consisting of a cooling coil that cools the bondline area where it is necessary to ensure low cure temperatures. The induction coil was located in the bondline area where it is necessary to ensure high cure temperatures. The graded heating (temperatures) obtained along the overlap length with this invention, between the middle and the ends of the overlap, can be modified by changing the parameters of the alternating magnetic field (e.g. frequency and/or power), changing its induction heating. On the other hand, it is also possible to change the gradient of the temperature between the middle and the ends by changing the parameters of cooling (e.g. flow and/or coolant), changing its cooling.

3. Brief description of the drawings

The invention may take physical form in certain parts and arrangements of parts, preferred embodiments of which will be described in detail and illustrated in the accompanying drawings which will form a part hereof and wherein:

FIG. 1 is a schematic view illustrating the induction heating system and the cooling system;

FIG. 2 is a typical joint (single lap joint) that can be used with this invention;

FIG. 3 is a schematic view in detail illustrating the induction coil, the cooling coil and the joint to be cured gradually;

FIG. 4 is a schematic view of the mechanical properties distribution along the overlap of the functionally graded joint.

FIG. 5 is a typical shear stress distribution.

FIG. 6 is a schematic view in detail illustrating the mould and the position of the joint as well as the heating and cooling coils;

FIG. 7 is a picture of the invention prototype configured for a particular case to obtain a functionally graded joint;

FIG.8 is the mechanical properties of the adhesive Loctite Hysol® 3422 as a function of the cure temperature [8];

FIG. 9 is a thermographic picture of a functionally graded joint being heated by the induction heating equipment.

4. Detailed description of the invention

The term "adhesive" means adhesives, structural adhesives or non-structural adhesives like sealants. As used herein, "adhesive" is any which may be hardened or cured at least partially by the application of heat even if hardening or curing of the adhesive would occur solely by the lapse of time. The adhesive and this type of joint in and of itself do not form a part of this invention, but the technique to achieve an adhesive functionally modified.

Referring now to the drawings wherein, the showings are for the purpose of illustrating preferred embodiments of the invention only and not for the purpose of limiting the same. FIG. 1 shows the induction heating system and the cooling system. Generally, the induction heating is constituted by cooler 1, remote heat station 2, induction power supply 3, and heating coil 4. The cooling system is generally constituted by cooler 5, remote cold station 6, and cooling coil 7.

The adhesive joint represented in FIG. 2 is the joint most studied in the literature and very common in practice, the single lap joint (SLJ), due to its simplicity and efficiency. This type of joint may be formed by similar or dissimilar material adherends 8 and 9, any suitable material that can be bonded to another material by the use of adhesives.

The adherends can be metallic (including ferrous and non-ferrous) or non-metallic (including polymers and composites) that can be adhesively bonded by adhesives 10.

Referring now to FIG. 3, the joint 11 adhesively bonded (constituted by two adherends 8 and 9 metallic or non-metallic is bonded by adhesive 10 doped with or without ferromagnetic particles) is involved by the turns of the coils 12 and 13.

FIG. 4 shows the illustrative representation of the adhesive mechanical property variation along the bondline, with maximum stiffness in the middle and minimum stiffness at the ends. The aim is to achieve a joint where the adhesive properties vary gradually along the bondline, allowing a more uniform stress distribution along the overlap.

Two typical adhesive shear stress curves are represented in FIG. 5. The ‘normal’ joint (cured isothermally) shows a high stress concentration at the ends of the bondline. The graded joint (cured gradually) shows a more uniform stress distribution leading to a more efficient adhesive joint strength.

A mould 15 represented in FIG. 6 was made to ensure the correct alignment, bondline thickness and to accommodate the induction coil 12 and cooling coil 13 to achieve a graded cure of the joint 11.

FIG. 7 shows a particular case to obtain a functionally graded joint 11. The joint considered was a SLJ with a width of 25 mm, adherend of high strength steel with thickness of 2 mm, adhesive thickness of 1 mm and overlap length of 50 mm. The adhesive used was Loctite Hysol® 3422 (Henkel, Dublin, Ireland) which mechanical properties as a function of cure temperature are well known [8]. The induction heating equipment (1, 2, 3 and 4) used in this study was the equipment EasyHeat model 0224 from Ambrell (New York, USA), which operates at a frequency range of 150-400 kHz and with a maximum power of 2.4 kW. In order to obtain the desired temperature distribution along the length of the overlap (achieve a gradual degree of cure), a suitable heating coil was designed (4).

Referring now to FIG. 8, the mechanical properties of an epoxy adhesive (Loctite Hysol® 3422) are represented as a function of the cure temperature [8]. The adhesive shows ductile behaviour when cured at high temperature (100ºC) and a brittle behaviour when cured at low temperature (23ºC). For the functionally graded joints, the adhesive is modified gradually along the overlap. So that, the adhesive stiffness becomes maximum in the middle and minimum at the ends of the overlap, to achieve a uniform load transfer and uniform stress distribution along the overlap. Induction coil 12 design was developed to achieve this temperature gradient. In order to ensure that the temperature gradient is obtained, a cooling system was developed, consisting of cooling coil 13 that cools the joint in the middle of the overlap. Induction coil 12 is located at the ends of the bondline thickness to obtain an adhesive with ductile properties, and cooling coil 7 is located at the middle of the bondline thickness, to obtain a stiff adhesive. The temperature distribution along the bondline was monitored by a thermographic camera 12, Fluke model Ti25 (Eindhoven, The Netherlands).

FIG 9 shows a thermographic picture of functionally graded joint 11, bonded with Loctite Hysol® 3422 FIG 5. For this example, induction heating coil 4 was positioned at the ends of the bondline and cooling coil 7 was positioned in the middle of the bondline. The graded heating obtained along the bondline with this equipment was achieved for a power of 26.5 amps and with a cooling system of cold water 13 and forced air 14. The gradient of the temperatures between the middle and the ends can be modified by changing the parameters of the alternating magnetic field (e.g. frequency and/or power), or the parameters of cooling (e.g. flow and/or coolant). The mechanical analysis of the functionally graded joints bonded with Loctite Hysol® 3422 is presented in Carbas *et al.* [9].

Having thus described our invention, it is apparent that many modifications may be incorporated into the arrangement disclosed without departing from the spirit or essence of our invention. For example, the invention shows a particular experimental case to obtain a functionally graded joint, but any induction heating equipment can be used. Also, the power needed to produce the induction heating depends on the material to heat, as well as the intended gradient of temperature to achieve. This particular cooling system uses cool water and forced air to cool the area needed, but for certain applications cooling may not be required. In other cases, the use of other liquid coolant may be needed (e.g. liquid nitrogen), as well as other configurations of the cooling system, or different diameter or section of the cooling circuit. It is our intention to include such available modification of cooling system within the scope of our invention. Other applications may require a new design for the induction heating coil and a new design for the cooling coil, because this invention may be applied in other types of joints or implemented in assembly lines. It is our intention to include all such modifications and alternative arrangements within the scope of our invention.

5. Claims

Having thus described the invention, it is hereby claimed:

1. A method of bonding together an assembly of two adherends, each adherend having a face surface adjacent to the other adherend and an adhesive which can be thermally cured interposed between the face surfaces, the apparatus comprising:

(a) providing an adhesive that cures thermally, of a portion of at least one of the adherend's face surfaces;

(b) for adherends non-metallic, mixing a plurality of particles having magnetic characteristics with said adhesive;

(c) a plurality of small metallic particles interposed between the face surfaces and within the adhesive;

(d) means for inductively heating of the particles whereby the adhesive is thermally cured;

(e) pressing the face surfaces together to cause the adhesive layer uniform and without any air bubbles;

(f) a mould or positioning system to maintain the adherends in order to ensure the correct position, alignment, geometry and thickness adhesive layer; and

(g) heating of the adherends or particles by induction heating whereby the adherends or particles conveys sufficient heat to the adhesive and bond the members to one another.

2. Apparatus of claim 1 wherein the induction heating includes an induction coil and wherein the cooling means includes a cooling coil.

3. The method of claim 1 wherein means for inductively heating are operated at radio frequencies.

4. The method of claim 1 wherein the induction heating and cooling and ensures the gradual cure of the adhesive along the bondline. The induction heating is controlled so that the adherends or particles are not heated in excess of the cure temperatures of the adhesive that achieve the ductile or brittle behaviour (depends on the adhesive and is a function of cure temperature). The cooling is controlled so that the bond area to be cooled achieves the low temperature needed in order to ensure the functionally gradually modification of the adhesive and achieve the functionally gradually joint.

5. The method of claim 4 wherein the induction heating and cooling means includes a pair of induction coils (induction heating coil and cooling coil). For induction heating an electrically conductive metal is surrounding the area to be bonded at high temperature and a power supply producing an alternate current having a frequency high enough to heat said adherends or the particles to a temperature of at least equal to the curing temperature of said adhesive. For cooling a conductive material (with different conductivity of the adherend or particles to be heated) the area to be bonded at low cure temperature is surrounded by cooling coil, in order to ensure that the adhesive cure at low temperature.

6. The method of claim 1 wherein the induction coil for the induction heating is positioned on the bondline area (middle or ends) of the joint to be heated.

7. The method of claim 1 wherein the cooling coil for the cooling is positioned on the side of the bondline are (middle or ends) of the joint to be cooled.

8. The method of claim 13 wherein the adhesive is an adhesive with thermal cure which mechanical properties vary as a function of the cure temperature. The adhesive can be doped with particles (for the non-metallic adherends) or not (for the metallic adherends).

9. The method of claim 1 wherein two adherends are non-metallic.

10. The method of claim 8 wherein the adhesive is doped with particles when adherends non-metallic is used.

11. The method of claim 9 wherein the particles are metallic.

12. The method of claim 1 wherein one or two adherends are metallic.

13. The method of claim 11 when the other adherend is metal and the adhesive does need to be doped with particles.

14. The induction heating and cooling provide a bondline functionally graded to obtain a functionally graded joint.

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Paper 5

Experimental results of functionally graded joints obtained by induction heating

Adhesively bonded functionally graded joints by induction heating

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Abstract

The main objective of this work was to develop an adhesive functionally modified in order to have mechanical properties that vary gradually along the overlap, allowing a more uniform stress distribution along the overlap and to reduce the stress concentrations at the ends of the overlap. This allows for a stronger and more efficient adhesive joint. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap.

In this study, grading was achieved by induction heating, giving a graded cure of the adhesive along the joint. The functionally graded joint was found to have a higher joint strength compared to the cases where the adhesive is cured uniformly at low temperature or at high temperature. Analytical analysis was performed to predict the failure load of the joints with graded cure and isothermal cure.

Keywords: Epoxy adhesives, induction heating, functionally graded joints, analytical analysis.

1. Introduction

The main advantage of adhesive joints is that the stress distribution is more uniform than with the other traditional methods of fastening such as bolts or rivets. This permits to work with smaller load bearing areas leading to weight savings. That is the main reason why adhesives were initially used in the aeronautical industry where the weight is a crucial matter. Nowadays, adhesives are used in other industries being the automotive industry one of the most growing market. That is obviously because the car industry is looking at ways to reduce fuel consumption by a weight reduction [1].

One of the most common types of joints is the single lap joint, due to its simplicity and efficiency. When analysing this type of joint, the main problem associated is the stress distribution (peel and shear) in the adhesive along the overlap which is not uniform, being concentrated at the ends of the overlap. That is why one of the main areas of investigation in the field of adhesive bonding is to develop ways of reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings. In the literature, several methods have been proposed but none give a uniform stress distribution in the adhesive [2].

The joint strength optimization can be obtained through modifications of the adherend geometry, the adhesive spew fillet geometry, mixed adhesive joints, or adhesive joints with functionally graded materials. An important factor that affects the critical stresses is the geometry of the adherend corners at the ends of the overlap. Adherends with geometric modifications by inclusion of a taper in the adherend is a way to decrease the stress concentration at the ends of the overlap; the concentrated load transfer can be more uniformly distributed if the local stiffness of the joint is reduced and the strength of the joint increases substantially [3-5]. Joints with rounded adherends at the ends of the overlap reduce significantly the shear and peel [6-9]. Also, modifications of the joint end geometry with a spew fillet provides a great reduction in the adhesive stresses (shear and peel) concentration, gives a smoother load transfer over a larger area and alters the stress intensity factors [10-14]. However, the complexity of the geometry increases and that is not always possible to realize in practice.

The use of more than one adhesive has been proposed to modify the mechanical properties of the adhesive along the overlap. This technique consists in using a stiff and strong adhesive in the middle of the overlap and a flexible and ductile adhesive at the ends of the overlap to relieve the high stress concentrations at the ends of the overlap [4-5, 15-18]. This allows to have a more uniform stress distribution which leads to joint strength increases in relation to a stiff adhesive alone [15, 19-23]. Although this approach has been discussed theoretically, there have been relatively few published experimental demonstrations of a practical method that yields significant improvements in the joint performance. Fitton and Broughton [15] studied theoretically and experimentally that the variable modulus adhesive is an effective way of reducing stress concentration and especially peel. The study has shown that variable modulus bondlines can reduce stress concentrations, increasing joint strength and change the mode of failure. da Silva and Adams [13] investigated theoretical and experimental dual adhesive metal/composite joints and showed that there is a real improvement in joint strength, especially if the difference of coefficients of thermal expansion is high. Marques and da Silva [5], da Silva and Lopes [18] and Marques *et al*. [24] have shown that the mixed adhesive technique gives joint strength improvements in relation to a brittle adhesive alone in all cases. If the ductile adhesive has a joint strength lower than that of the brittle adhesive, a mixed adhesive joint with both adhesives gives a joint strength higher than the joint strength of the adhesives used individually. The mixed adhesive joint technique can be considered a rough version of a functionally graded material.

The ideal would be to have an adhesive functionally modified with properties that vary gradually along the overlap allowing a true uniform stress distribution along the overlap. Ganesh and Choo [25], Boss *et al*. [26] and Apalak and Gunes [27] have used functionally graded adherends instead of functionally graded adhesives. Ganesh and Choo [25] and Boss *et al*. [26] used a braided preform with continuously varying braid angle and the variation of the braid angle measured to realistically evaluate the performance of adherend modulus grading in single-lap bonded joint. An increase of 20% joint strength was obtained due to a more uniform stress distribution. Apalak and

Gunes [27] studied the flexural behaviour of an adhesively bonded single lap joint with adherends composed of a functionally gradient layer between a pure ceramic (Al_2O_3) layer and a pure metal (Ni) layer. The studies are not supported with experimental results and the adhesive stress distribution was not hugely affected.

There have been some attempts to modify the adhesive along the overlap. Sancaktar and Kumar [28] used rubber particles to modify locally the adhesive at the ends of the overlap and with this technique increase the joint strength. More recently, Stapleton *et al*. [29] used glass beads strategically placed within the adhesive layer in order to obtain different densities and change the stiffness along the overlap. In this study it was showed that with this technique a significant reduction in peel stress is obtained. The mixed adhesive and the physical modification of the adhesive with adhesive doped by rubbery particles or glass beads, can be considered a rough version of a functionally graded material. However, the dispersion of particles (rubber particles or glass beads) throughout the adhesive layer is a complex bonding technique which is inconvenient to perform in practice.

In this study a technological process to functionally modify the adhesive along the overlap allowing a true uniform stress distribution was developed. The adhesive stiffness varies along the overlap, being maximum in the middle and minimum at the ends of the overlap for a uniform load transfer. This functionally graded adhesive was achieved based on a differentiated cure process. Adhesives are generally cured in an oven or in a hot press uniformly giving an adhesive with uniform properties along the overlap area. If the adhesive can have several degrees of cure, then a gradient in the rigidity of the adhesive along the overlap can be obtained, as was recently shown by Carbas *et al.* [30-31]. The localised heating was done with induction heating. Induction heating is a fast heating method because it focuses heat at or near the adhesive bondline. The most important advantages of induction heating are assembly speed and the fact that an entire assembly does not have to be heated to cure only a few grams of adhesive (the confined area). This technique can be easily implemented in the industry and very efficient (fast bonding, heating only the area of interest, curing equipment more compact, decreasing of the energy consumption).

The present study demonstrated the high performance of functionally graded joints obtained by induction heating when compared with adhesive joints cured isothermally at low or high temperature. In order to predict the failure load value of joints cured isothermally, simple numerical analysis were used (as Volkersen´s analysis [32] and global yielding criterion [33]). A simple analytical analysis proposed by Carbas *et al.* [34] was performed to predict and assess the possible effectiveness of a graded joint concept.

2. Experimental details

2.1. Materials

According to previous studies [30-31], adhesives were selected in order to have an adhesive with a high variation of the mechanical properties as a function of the cure temperature. The adhesives selected are two bi-component epoxy adhesives which mechanical properties were determined as a function of the cure temperature by Carbas *et al.* [30-31].

The first adhesive studied was Araldite® 2011 (Huntsman, Basel, Switzerland). The chemical formulation of this adhesive is bisphenol A for the epoxy resin and polyaminoamide for the hardener.

The second adhesive studied was Loctite Hysol® 3422 (Henkel, Dublin, Ireland). The chemical formulation of this adhesive is bisphenol A diluted with bisphenol F in for the epoxy resin, and 3-Aminopropylmorpholine and polyoxypropylene diamine for the hardener.

Typical stress-strain curves of the adhesives Araldite® 2011 and Loctite Hysol® 3422 as a function of the cure temperature are shown in Figure 1.

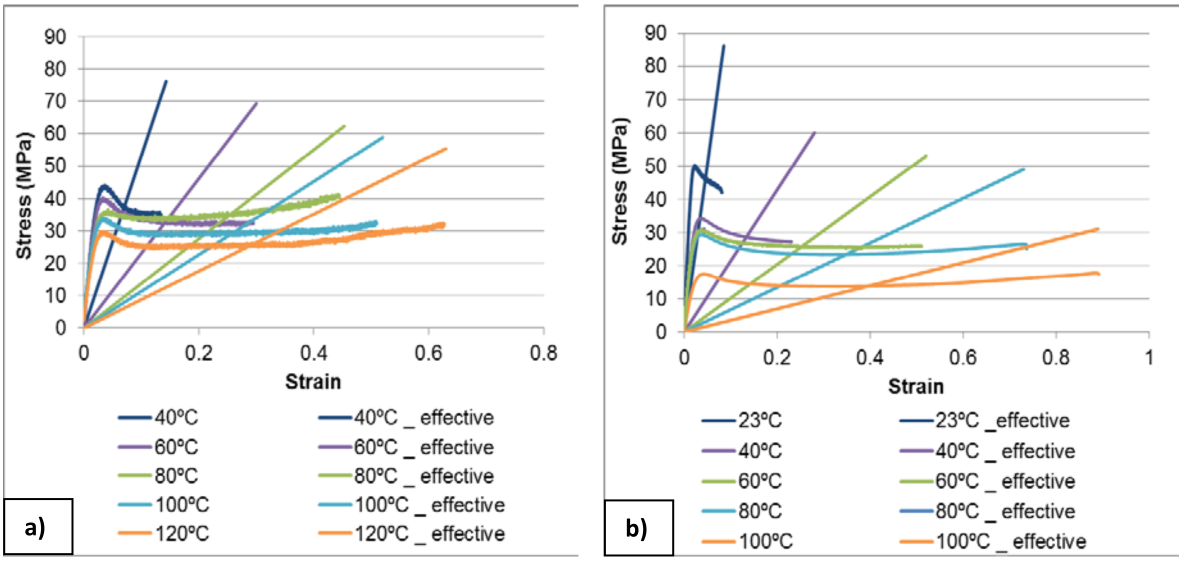

Figure 1 – Tensile stress-strain curves of Araldite® 2011 a) and Loctite Hysol® 3422 b) adhesives as a function of the cure temperature.

The adherend selected was a high strength steel (DIN C65 heat treated) with (tensile strength of the adherend) σ_{ys} = 1260 MPa and E = 210 GPa to avoid plastic deformation of the adherend [35 - 37].

2.2. Single lap joint (SLJ) test

The geometry and dimensions of the SLJ are detailed in Figure 2. The dimensions selected for this work were an adherend thickness of 2 mm, an adhesive thickness of 1 mm and an overlap length of 50 mm. The bonding surfaces were subjected to a passive surface treatment by grit blasting, followed by cleaning with acetone. In this study two different curing processes were performed: a graded cure obtained by induction heating and an isothermal cure. The isothermal cure process was used as a reference for comparison with the joints obtained by a graded cure.

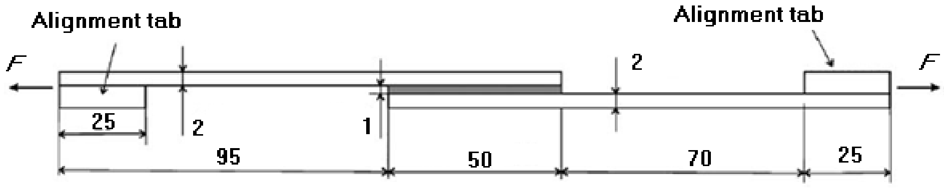

Figure 2 – Geometry of the SLJ test specimens (dimensions in mm).

2.2.1. *Isothermal cure*

A mould was used to ensure the correct alignment of the substrates and the bondline thickness with packing shims, as shown in Figure 3. Release agent was applied to the mould prior to manufacturing the specimens. Two different cures in a hot press were performed for each adhesive, one cure in order to achieve stiff, but strong brittle properties of the adhesive and another cure in order to obtain ductile properties of the adhesive. For adhesive Araldite® 2011, to achieve brittle properties, the adhesive joints were cured for 30 min at 40 ºC, and to achieve ductile properties, the adhesive joints were cured for 30 min at 100 ºC. For adhesive Loctite Hysol® 3422 to achieve brittle properties, the adhesive joints were cured for 1 hour at 23 ºC, and to achieve ductile properties, adhesive joints were cured for 1 hour at 100 ºC. After cure, the joints were removed from the mould and the excess of adhesive outside of the bonded area was cleaned.

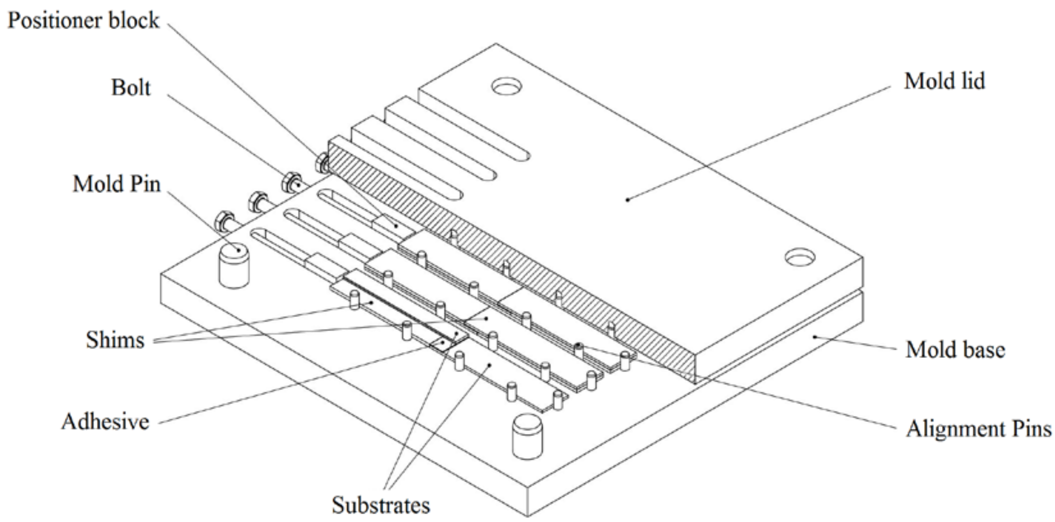

Figure 3 – Mould with SLJ specimens.

2.2.2. Graded cure

Induction heating is an electromagnetic heating method in which electrically conductive bodies absorb energy from an alternating magnetic field, generated by an induction coil. The advantages of induction heating technique are assembly speed and the fact that an entire assembly does not have to be heated to cure only a few grams of adhesive. Induction heating is a fast heating method because it focuses heat at or near the adhesive bondlength. Induction heating is a technique very efficient since the heat is actually generated inside the workpiece. This technique uses high frequency electricity to heat materials that are electrically conductive, and does not contaminate the material being heated since it is a non-contact technique. The workpiece (e.g. joint) to be heated is placed within the intense alternating magnetic field, but the joint must be capable of being heated by an electromagnetic field. For induction heating to work, the joint has to be composed by metallic adherends or by an adhesive filled with ferromagnetic particles [38-40].

A mould was made to ensure the correct alignment, bondline thickness and to accommodate the induction coil to achieve a graded cure of the joint. The mould and the induction coil design are detailed in a patent under preparation [41].

With the mechanical properties of the epoxy adhesives as a function of the cure temperature [30-31], we have the full knowledge of the adhesive behavior for different degrees of cure. Adhesives Loctite Hysol® 3422 and Araldite® 2011 show similar mechanical properties behavior as a function of the cure temperature, i.e. for high temperatures of cure (100 and 120 ºC, respectively) the adhesive shows ductile properties and for low temperatures of cure (23 and 40 ºC, respectively) the adhesive shows brittle properties.

The induction heating system enables to obtain a graded cure with a focus temperature at the ends of the overlap and gradually decreasing the temperature up to the middle of the overlap by positioning the induction heating at the ends of the overlap and the induction cooling in the middle. The temperature distributions along the overlap for both adhesives with this technique are presented in Figure 4 and were measured by a thermographic camera. The temperature gradient is that which is compatible with a suitable grading of the mechanical properties.

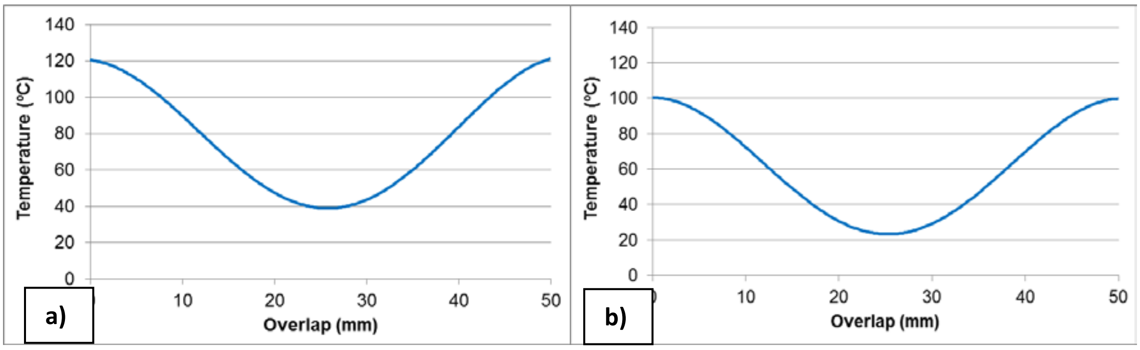

Figure 4 – Cure temperature distribution of Araldite® 2011 (a)) and Loctite Hysol® 3422 (b)).

3. Experimental results

The joints cured isothermally were compared with the joints cured gradually in order to compare the strength of the joints. The cure temperature values applied to the ends and to the middle of the overlap in the graded joint are the same values used to cure the isothermally cured joints.

SLJ tests were performed using a MTS servo-hydraulic machine (Minneapolis, USA), at a constant displacement rate of 1 mm/min. A load cell of 100 kN was used and the loads and displacements up to failure were recorded. For each case five specimens were tested in laboratory ambient conditions (room temperature of 23ºC, relative humidity of 55%).

3.1. Load-displacement curves

Typical load-displacement curves obtained by tensile tests of the SLJ specimens are represented in Figure 5. Figure 5a) shows the load displacement curves of the joints cured isothermally and gradually for adhesive Araldite® 2011, and Figure 5b) for adhesive Loctite Hysol® 3422.

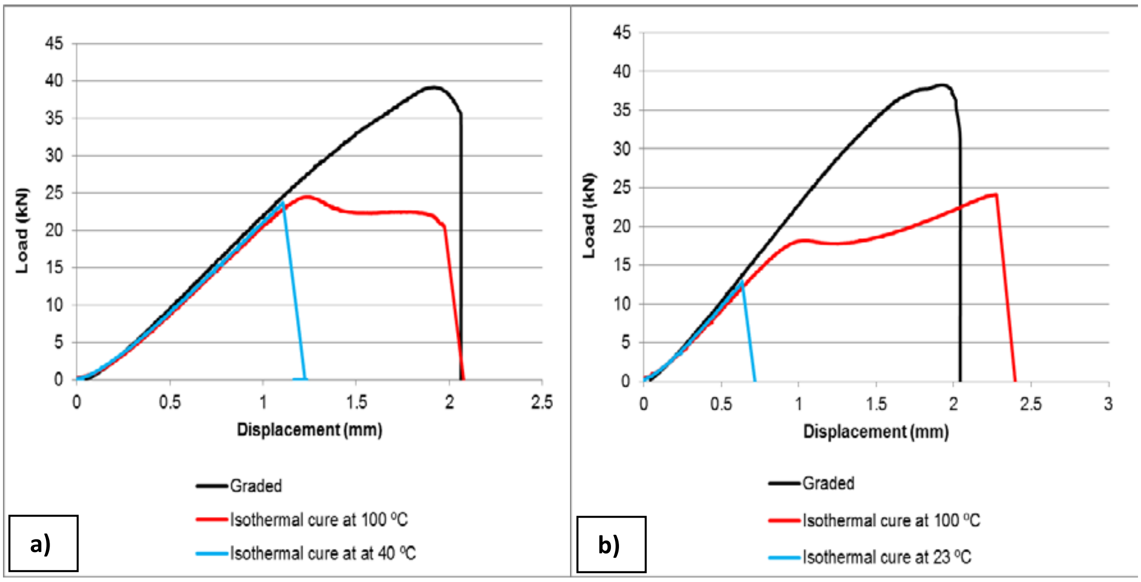

Figure 5 – Typical load-displacement curves of joints with isothermal cure and graded cure for adhesives Araldite® 2011 (a) and Loctite Hysol® 3422 (b).

The experimental values of the failure load of graded joints and the joints cured isothermally are shown in Figure 6.

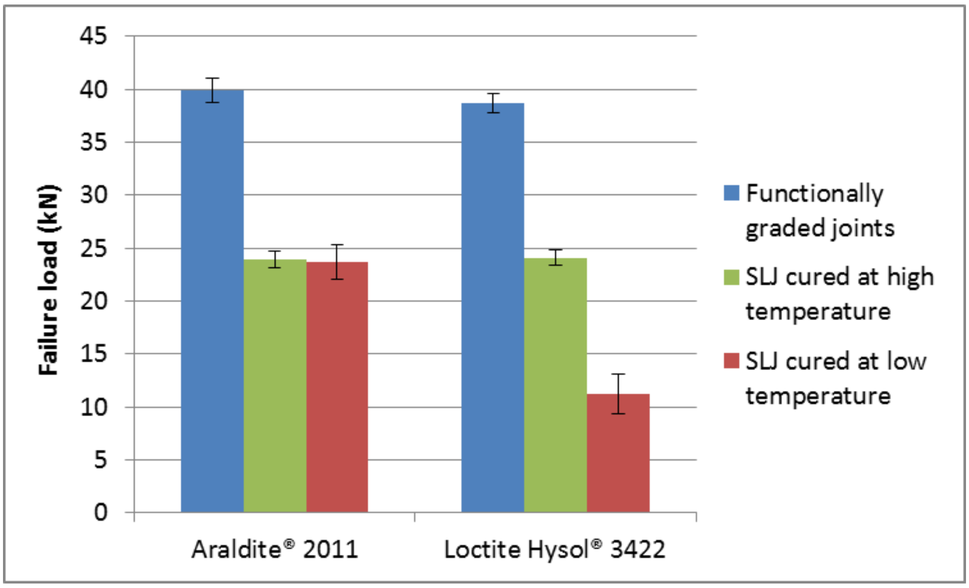

Figure 6 – Experimental failure loads of SLJs.

As expected, the joints with a graded cure show the highest failure load, compared to the joints cured isothermally, and this happens for both adhesives. The joints gradually cured by induction heating are stronger and with a larger displacement, thus it can be concluded that these joints have higher energy absorption. The joints cured isothermally at low temperature (brittle behaviour) show the lowest value of failure load. This is explained by the high stress concentration of the joint at the ends of the overlap due to its high stiffness and brittleness of the adhesive. The adhesive usually has a rather brittle behavior which does not permit the adhesive to deform plastically all over the overlap and the failure strain of the adhesive is reached at the ends of the overlap before there can be global yielding of the adhesive along the whole overlap [42].

The performance gains of the graded joints in relation to the joints cured isothermally are shown in Table 1. The functionally graded joints are at least 60% stronger than the joints cured isothermally which represents an important joint strength improvement.

Table 1 – Performance gains of the functionally graded joints in relation to the joints cured isothermally.

	Isothermal cure at low temperature	Isothermal cure at high temperature
Functionally graded joints bonded with Araldite® 2011	+ 68.4 %	+ 67.0 %
Functionally graded joints bonded with Loctite Hysol® 3422	+ 245.5 %	+ 60.6 %

3.2. Failure mechanism

Typical failure surfaces of the joints cured isothermally and gradually are presented in Figure 7 (Araldite® 2011) and Figure 8 (Loctite Hysol® 3422). In Figure 7a), a typical failure surface of a joint cured isothermally at low temperature (brittle behaviour) is presented and the failure is of the adhesive type (or interfacial). In Figure 7b), a typical failure surface of a joint cured isothermally at high temperature (ductile behaviour) is presented and the failure surface is cohesive in the adhesive but close to the interface. In Figure 7c), a typical failure surface of a joint cured gradually is presented and the failure surface is also cohesive in the adhesive, close to the interface.

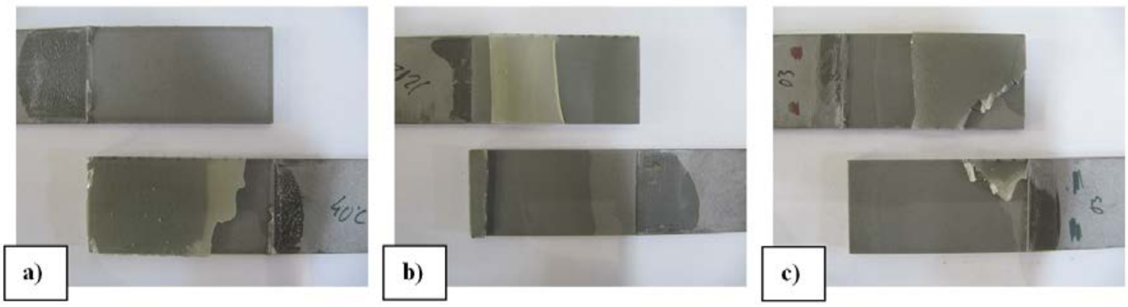

Figure 7 – Typical fracture surfaces of SLJ specimens bonded with Araldite® 2011: a) isothermal cure at low temperature, b) isothermal cure at high temperature, c) graded cure.

Figure 8a) presents a typical failure surface of a joint cured isothermally at low temperature (brittle behaviour) and the failure is of the adhesive type. In Figure 8b), a typical failure surface of a joint cured isothermally at high temperature (ductile behaviour) and the failure is cohesive in the adhesive but close to the interface. In Figure 8c), a typical failure surface of a joint cured gradually is presented, the failure is cohesive in the adhesive with an irregular shape and whitening of the adhesive, indicating plastic deformation of the adhesive along the whole overlap.

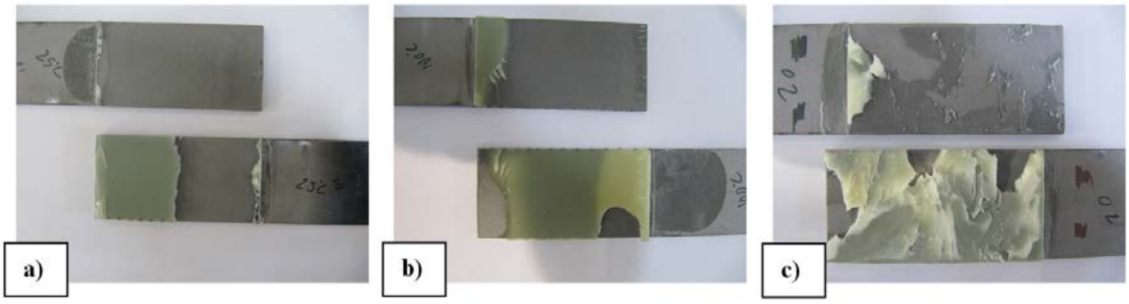

Figure 8 – Typical fracture surfaces of SLJ specimens bonded with Loctite Hysol® 3422: a) isothermal cure at low temperature, b) isothermal cure at high temperature, c) graded cure.

4. Failure load prediction

4.1. Isothermal cure

For joints cured isothermally at high temperature (ductile behaviour), the failure load was predicted using the global yielding criterion [33]. The load corresponding to the total plastic deformation of the adhesive is given by

$$F_a = \tau_y \, w \, l \qquad (1)$$

where F_a is the failure load of the adhesive, τ_y the shear yield strength of the adhesive, w the joint width and l the overlap length.

For joints cured isothermally at low temperature (brittle behaviour), the failure load was predicted with the Volkersen's model [32]. The failure occurs when the maximum shear stress at the ends of the overlap exceeds the shear strength of the adhesive. The following equation was used:

$$P = \tau_r \frac{2bl\sinh(\lambda l)}{\lambda l\left[(1+\cosh(\lambda l)\right]} \quad (2)$$

where

$$\lambda^2 = \frac{G}{t_a}\left(\frac{2}{Et_s}\right) \quad (3)$$

b is the joint width, t_a is the adhesive thickness, t_a is the adherend thickness, τ_r is the adhesive shear failure strength, G the adhesive shear modulus and E the adherend Young's modulus. This failure criterion works well when the adhesive is brittle, the steel is elastic and the failure is cohesive as in all tests.

The experimental values of failure loads and the predicted failure loads, as well the errors of predictions for the joints cured isothermally are shown in Table 2.

Table 2 – Experimental and predicted failure loads of single lap joints.

	Araldite® 2011			**Loctite Hysol® 3422**		
	Experimental (kN)	**Predicted (kN)**	**Error (%)**	**Experimental (kN)**	**Predicted (kN)**	**Error (%)**
SLJ cured at low temperature	23.7	18.5	21.9	11.2	16.2	44.6
SLJ cured at high temperature	23.9	21.9	8.4	24.1	22.0	8.7
Functionally graded joints	39.9	37.7	5.5	38.7	36.5	5.7

For joints cured isothermally at high temperature (ductile behaviour), the global yielding criterion [33] gives a good prediction of the failure load. The error of predictions with this technique was 8.4 % for Araldite® 2011 and 8.7 % for Loctite

Hysol® 3422. For joints cured isothermally at low temperature (brittle behaviour), the Volkersen's analysis [32] was used. The error of predictions with Volkersen's analysis was 21.9 % for Araldite® 2011 and 44.6 % for Loctite Hysol® 3422. It is known that Vokersen's model does not give good predictions for thick bondlines [42].

4.2. Graded cure

A simple analytical analysis proposed by Carbas *et al.* [34] was carried out in order to predict the maximum failure load of the functionally graded joint. The development of this analytical model, based on Volkersen's analysis [32], was solved with power series expansion for a reduced number of expansion terms (21 terms). Equation (4) represents the adhesive shear stress ($\tau(x)$) distribution along the bondline for only 2 terms of the power series expansion and for a linear adhesive shear modulus variation along the bondline. For high order of terms the equation becomes more complex but there is also a repetition of terms with an increase of order.

$$\tau(x)=\frac{32\cdot P\cdot\left(6\cdot l\cdot x\cdot\frac{2}{t_S\cdot t_a\cdot E}\cdot K-8\cdot x^3\cdot\frac{2}{t_S\cdot t_a\cdot E}\cdot m+x^2\cdot\left(\frac{2}{t_S\cdot t_a\cdot E}\right)^2\cdot K^2\cdot l-24-12\cdot x^2\cdot\frac{2}{t_S\cdot t_a\cdot E}\cdot K+3\cdot x^2\cdot\frac{2}{t_S\cdot t_a\cdot E}\cdot m\cdot l\right)}{b\cdot t_a\cdot l\cdot\left(-768+16\cdot l^2\cdot\frac{2}{t_S\cdot t_a\cdot E}\cdot K+l^4\cdot\left(\frac{2}{t_S\cdot t_a\cdot E}\right)^2\cdot K^2\right)} \quad (4)$$

where P is the applied load, m is the slope and K is the constant (y-intercept) of the linear adhesive shear modulus variation along the bondline.

This model was shown to be a valid tool to predict the shear stress distribution along the overlap length. It is a simple analytical model of functionally graded joints that allows the use of different mechanical properties distribution along the overlap length. The failure occurs when the maximum shear stress exceeds the shear strength of the adhesive.

In order to take in to account the plastic deformation of the joint, a simple elastic-plastic analysis was considered. The simple elastic-plastic adhesive behaviour proposed Adams and Mallick [43] was used. Adams and Mallick [43] introduced the linear 'effective modulus' solution. This analysis consists in considering the energy under the stress-strain curve obtained through tensile test and this energy is used to construct a theoretical line (called the linear 'effective modulus' solution), which has the same shear strain energy and strain to failure of the full elastic-plastic curve (see Figure 9).

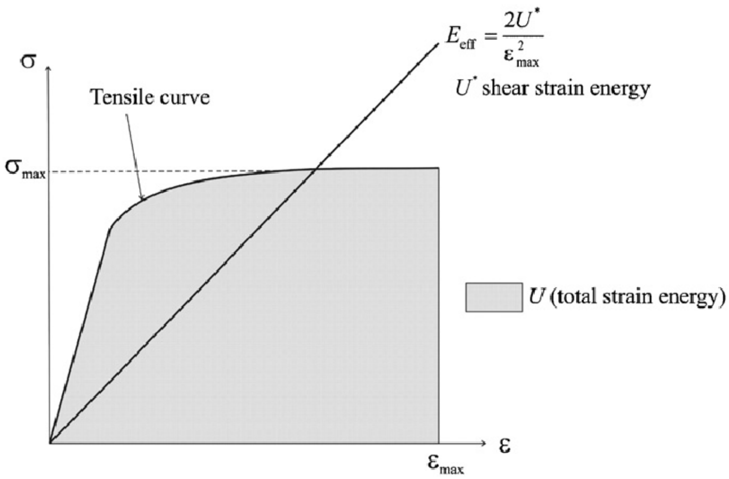

Figure 9 – 'Effective modulus' solution proposed by Adams and Mallick [43].

The shear stress of the adhesive was chosen for this analysis, as the shear stress distribution allows a quick and relevant assessment of the stress state in the functionally graded joint.

Figure 1 shows the 'effective modulus' for both adhesives and for each cure temperature used, these values were obtained through tensile tests carried out in a previous study [31], converted to true stress-strain values, that the mechanical properties vary as a function of the cure temperature. The $E_{eff.}$ were determined by making use of the the linear 'effective modulus' solution proposed by Adams and Mallick [43]. The shear stress was obtained from the tensile stress assuming that the adhesive obeys the von Mises criterion. This is not exactly true but was found accurate enough in this study. Figure 10 shows the effective modulus effective ($E_{eff.}$) is as well as the maximum shear stress effective ($\tau_{eff.}$) as a function of the cure temperature.

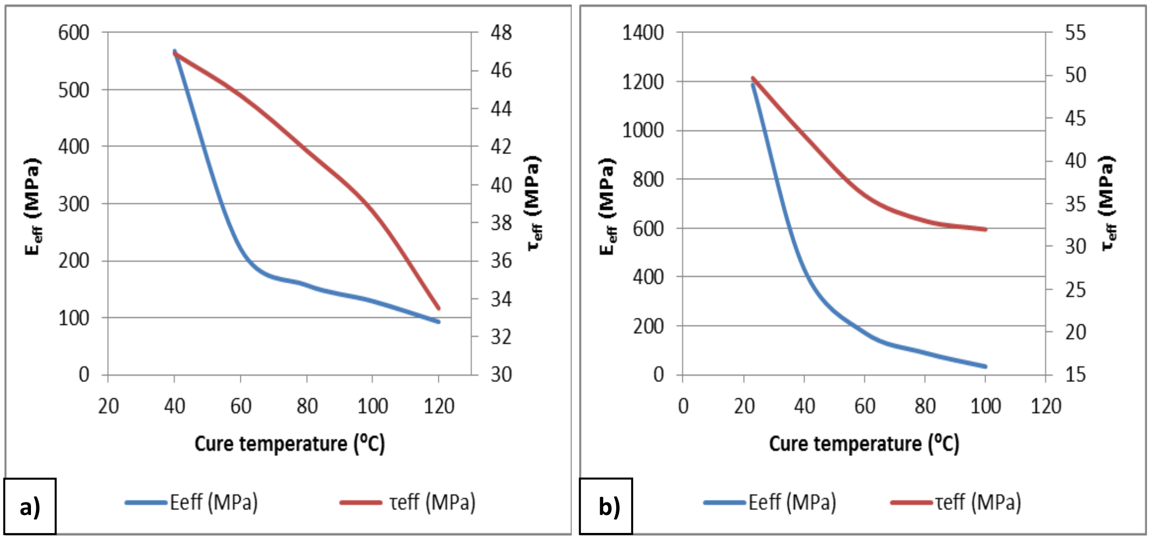

Figure 10 – Mechanical properties using the 'effective modulus' of adhesive Araldite® 2011a) and Loctite Hysol® 3422 b).

In the analytical analysis for the functionally graded joints, the equation used to represent the variation of adhesive mechanical properties along the overlap was of the exponential type [34] for both adhesives. Figure 11 shows the variation of the adhesive effective modulus along the overlap used to calculate the failure load prediction.

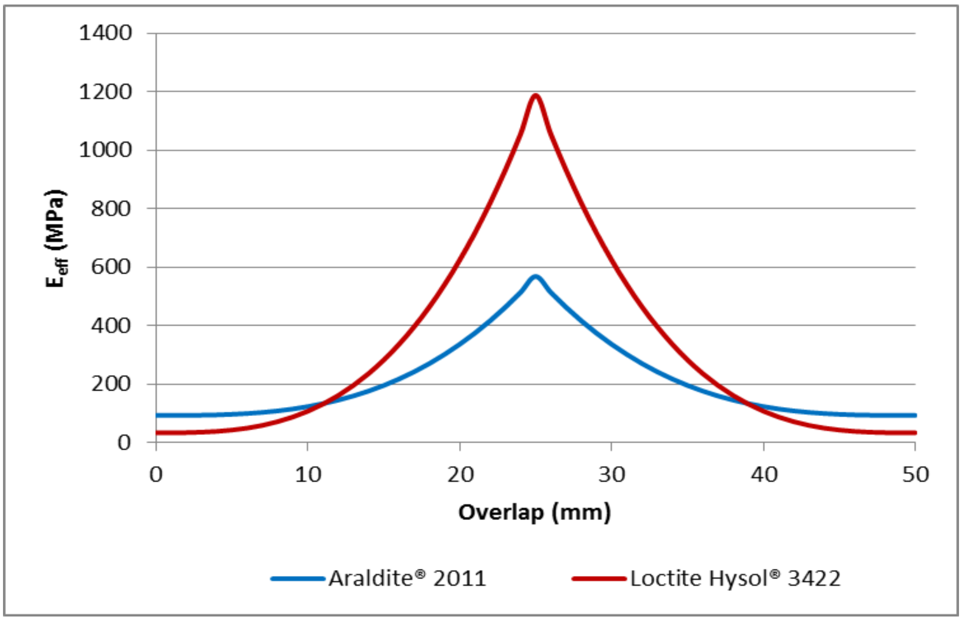

Figure 11 – Effective modulus distribution along the overlap.

The experimental values of failure loads and the predicted failure loads obtained by the analytical analysis, as well the errors of predictions, are shown in Table 2. The error of predictions with this technique is 5.5 % for Araldite® 2011 and 5.7 % for Loctite Hysol® 3422.

4.3. Influence of adhesive thickness

The joints cured gradually with 1mm adhesive thickness were compared with joints cured gradually with 0.2mm adhesive thickness in order to study the influence of the adhesive thickness. It is well known that for joints cured isothermally with uniform adhesive properties along the overlap, the strength decreases with increase in adhesive thickness [35, 44-45].

Figure 12 shows the influence of the adhesive thickness on the failure load of functionally graded joints. It is very interesting to note that a decrease of the adhesive thickness decreases the joint strength.

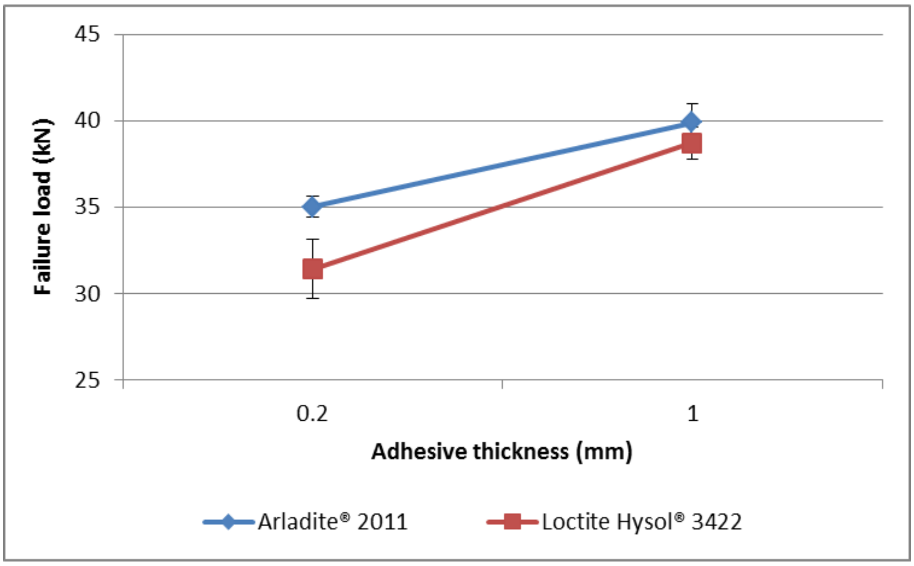

Figure 12 – Failure load behaviour as a function of the adhesive thickness.

The predictions with the analytical model (Table 3) follow the experimental results which validates the accuracy of the model for various bondline thicknesses.

Table 3 – Experimental failure loads and analytical prediction of functionally graded joints with 0.2 mm adhesive thickness.

	Experimental (kN)	Predicted (kN)	Error (%)
Functionally graded joints bonded with Araldite® 2011	35.0 ± 0.6	32.3	7.7
Functionally graded joints bonded with Loctite Hysol® 3422	31.4 ± 2.5	29.2	6.9

5. Conclusions

In this paper joints with the adhesive gradually modified along the overlap by induction heating were studied. The functionally graded joints were compared with joints cured isothermally at different temperatures (temperatures equal to those that the graded joints achieve in the middle and in the ends of the overlap). The following conclusions can be drawn:

1. The invention to obtain functionally graded joints was shown to be a viable technique to obtain a functionally graded joint with the adhesive gradually modified along the overlap. This invention demonstrated to be very versatile, because of the possibility to obtain different gradients of temperature along the bondline;

2. Compared to the joints cured isothermally, the functionally graded joints were found to have the best performance (highest failure load) and similar displacement than the joints cured isothermally at high temperature (ductile behavior);

3. The functionally graded joints bonded with Araldite® 2011 show a performance gain of approximately 70% in relation to the joints cured isothermally (at low temperature and high temperature);

4. The functionally graded joints bonded by Loctite Hysol® 3422 show a performance gain of approximately 210% in relation to the joints cured isothermally at low temperature (brittle adhesive behaviour) and approximately 62% in relation to the joints cured isothermally at high temperature (ductile adhesive behaviour);

5. The simple analytical analysis proposed by Carbas *et al.* [34] shown to be a valid tool to predict the maximum failure load of the functionally graded joint;

6. The linear ‘effective modulus’ solution proposed by Adams and Mallick [43] to simulate the elastic-plastic adhesive behavior was shown to obtain a good prediction of the failure load for functionally graded joints;

7. For the joints cured gradually, the strength increase with an increase of the adhesive thickness.

Acknowledgments

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Paper 6

Effect of post-cure on the performance of the functionally graded joints

Effect of post-cure on adhesively bonded functionally graded joints by induction heating

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Abstract

Functionally graded joints with an adhesive functionally modified by induction heating confer a more uniform stress distribution along the overlap and reduce the stress concentrations located at the ends of the overlap. The adhesive stiffness varies gradually along the overlap, being maximum in the middle and minimum at the ends of the overlap.

The effect of post-curing on functionally graded joints obtained by induction heating was studied in order to understand the performance of functionally graded joints when submitted to different post-cure temperatures. Three different post-curing conditions were considered, with temperatures above and below the glass transition temperature of the fully cured network, $T_{g\infty}$. The functionally graded joints (with and without post-cure) were compared with joints cured isothermally (with and without post-cure). The cure temperature values applied to the ends and to the middle of the graded joint are the same temperatures used to cure the isothermally cured joints. Analytical modelling to assist with the prediction and assessment of the possible effectiveness of a graded joint concept. The functionally graded joints subjected to post-cure at low temperatures (below $T_{g\infty}$) show a slight decrease of the strength and the joints cured isothermally show a slight increase of the strength. With increase of the post-cure temperature (above $T_{g\infty}$) the functionally graded joints exhibit strength similar to that of the joints cured isothermally. However, even for the highest post-cure temperatures, the functionally graded joints have a slightly higher strength.

Keywords: Epoxy adhesives, induction heating, functionally graded joints, post-cure, stress distribution, analytical analysis.

1. Introduction

The adhesive joint most studied in the literature and more common in practice is the single lap joint (SLJ), due to its simplicity and efficiency. But, the main problem associated to this type of joint is that the stress distribution (peel and shear) in the adhesive along the overlap is not uniform, being concentrated at the ends of the overlap. In the literature, we can find several methods for reducing these stress concentrations for a more efficient adhesive joint strength and additional weight savings, but none give a uniform stress distribution in the adhesive [1-2].

The joint strength improvement can be obtained through modification of the adherend geometry by inclusion of a taper in the adherend [3-5], by rounding the adherend corners [6-9], or by modifications of the joint end geometry with a spew fillet [10-15]. Another technique to improve the joint strength is the use of more than one adhesive (so-called mixed adhesive joints) which consists in using a stiff and strong adhesive in the middle of the overlap and a flexible and ductile adhesive at the ends of the overlap [16-26]. More recently, there have been several studies in the improvement of the joint strength by making use of functionally graded materials [27-29], and functionally graded bondline [30-31]. Sancaktar and Kumar [30] used rubber particles to modify locally the adhesive at the ends of the overlap to increase the joint strength. More recently, Stapleton *et al.* [31] used glass beads strategically placed within the adhesive layer in order to obtain different densities and change the stiffness along the overlap. These techniques can be considered a rough version of an adhesive functionally graduated along the bondline.

Recently, the authors proposed a patent [32], under preparation, that provides a differentiated cure process by induction heating. This technique provides an adhesive functionally modified along the overlap, without any particles mixed with the adhesive. The authors have shown a substantial improvement of joint strength by the use of a functionally graded joint. The functionally graded joints were compared with joints cured isothermally [33].

Previously, the authors studied the mechanical behaviour of epoxy adhesives when cured at different cure temperatures [34] and, also, studied the effect of post-cure on the mechanical properties of epoxy adhesives [35]. This previous studies [34-35] are important to understand the gradient in the stiffness of the adhesive along the bondline when submitted to different conditions of cure. For the functionally graded joints to work well, it is necessary to ensure that the adhesive used shows a large variation of mechanical properties when cured at different temperatures. The adhesive should be stiff and strong in the middle and flexible and ductile at the ends of the joint.

In this work, the influence of the post-cure on the functionally graded cure was performed, to evaluate and understand the performance of functionally graded joints when subjected to different temperatures after production. For example, in the assembly lines of the automobile industry, structural adhesives used to bond the different parts of the automobile are subjected to post-cure conditions; the post-cure occurs during the painting process where the entire body is subjected to high temperature to cure the paint.

The functionally graded joint obtained by induction heating was compared with adhesive joints cured isothermally at low or high temperature, being all the joints subjected to the same post-cure. Three different post-curing conditions were considered. In the first set, the joints (cured gradually, cured isothermally at high and low temperatures) were not subjected to any post-curing process; in the second set, the joints were subjected to a post-cure performed at a temperature below the glass transition temperature of the fully cured network ($T_{g\infty}$), and in the third set, the joints were subjected to a post-cure performed at a temperature above the $T_{g\infty}$. In order to predict the failure load value of joints cured isothermally, a simple numerical analysis was used (Volkersen´s analysis [36] and global yielding criterion [37]). A new analytical model for graded joints was used to assist with the prediction and assessment of the possible effectiveness of a graded joint concept.

2. Experimental details

2.1. Materials

Two bi-component epoxy adhesives were used: Araldite® 2011 (Huntsman, Basel, Switzerland) and Loctite Hysol® 3422 (Henkel, Dublin, Ireland). The chemical formulation of this adhesive is bisphenol A for the epoxy resin and polyaminoamide for the hardener. The chemical formulation of this adhesive is bisphenol A diluted with bisphenol F for the epoxy resin, and 3-Aminopropylmorpholine and polyoxypropylene diamine for the hardener.

The effect of post-cure on these two adhesives was studied previously [35]. Adhesives Loctite Hysol® 3422 and Araldite® 2011 show similar mechanical properties behaviour as a function of the cure and post-cure temperatures. For all post-cure conditions, when cured at high temperatures (100 and 120ºC, respectively) the adhesives show ductile properties and for low temperatures of cure (23 and 40ºC, respectively) the adhesives show brittle properties. Typical stress-strain curves of the adhesives Araldite® 2011 and Loctite Hysol® 3422 without any post-cure condition, as a function of the cure temperature are shown in Figure 1.

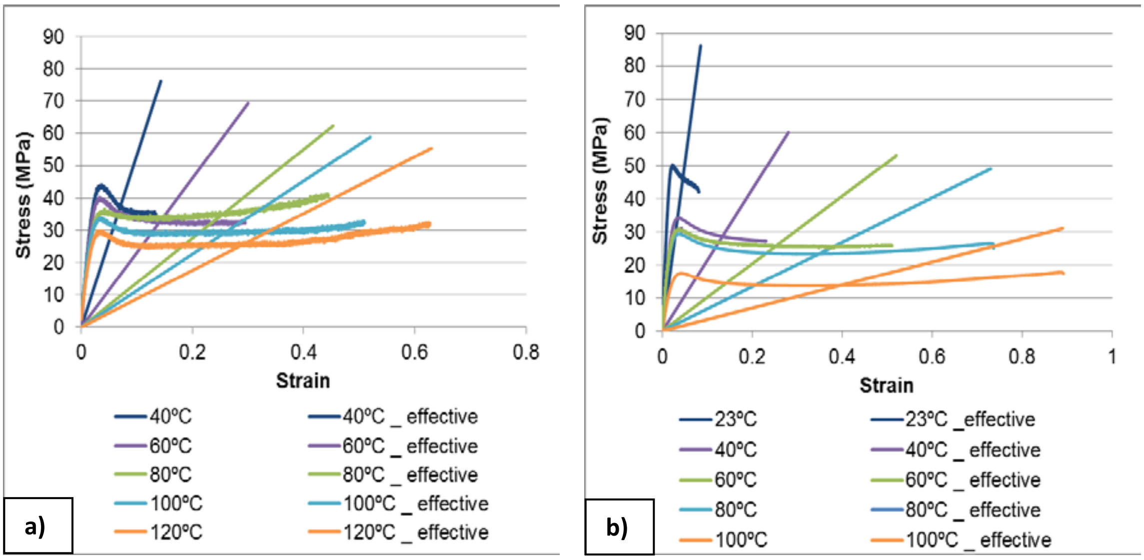


Figure 1 – Tensile stress-strain curves of Araldite® 2011 a) and Loctite Hysol® 3422 b) adhesives without post-cure, as a function of the cure temperature.

The variation of $T_{g\infty}$ of adhesives Araldite® 2011 and Loctite Hysol® 3422 as a function of the post-cure temperatures is shown in Figure 2.

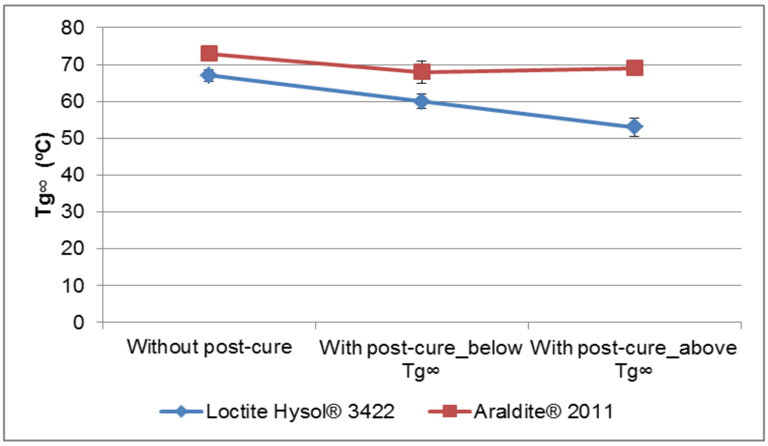
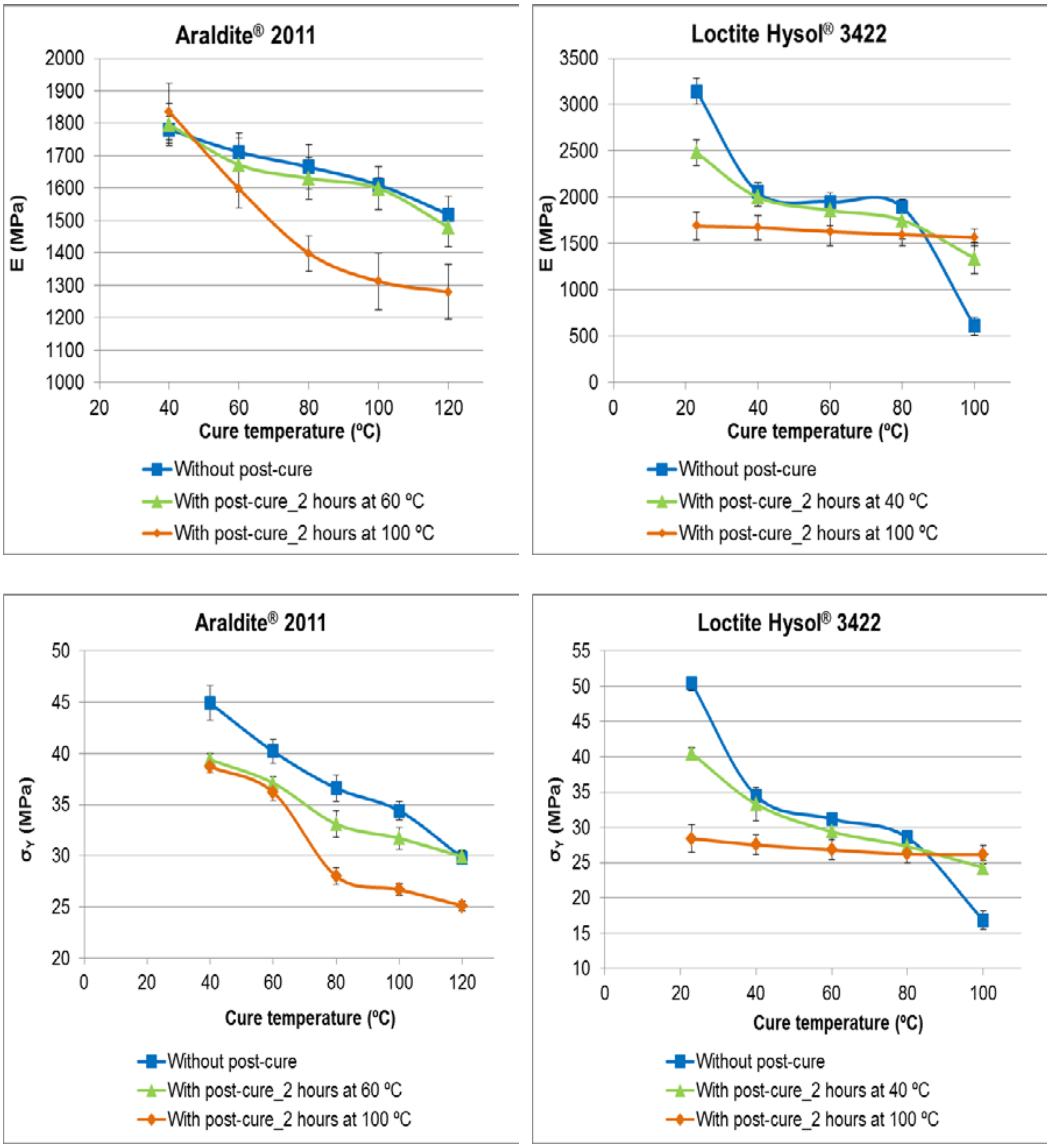


Figure 2 – The variation of $T_{g\infty}$ of adhesives Araldite® 2011 and Loctite Hysol® 3422 as a function of the post-cure temperatures.

The variation of the mechanical properties (Young's modulus (E), tensile yielding stress (σ_y) and failure strain (ε)) of adhesives Araldite® 2011 and Loctite Hysol® 3422, submitted to different post-cure temperatures as a function of the cure temperature is shown in Figure 3.



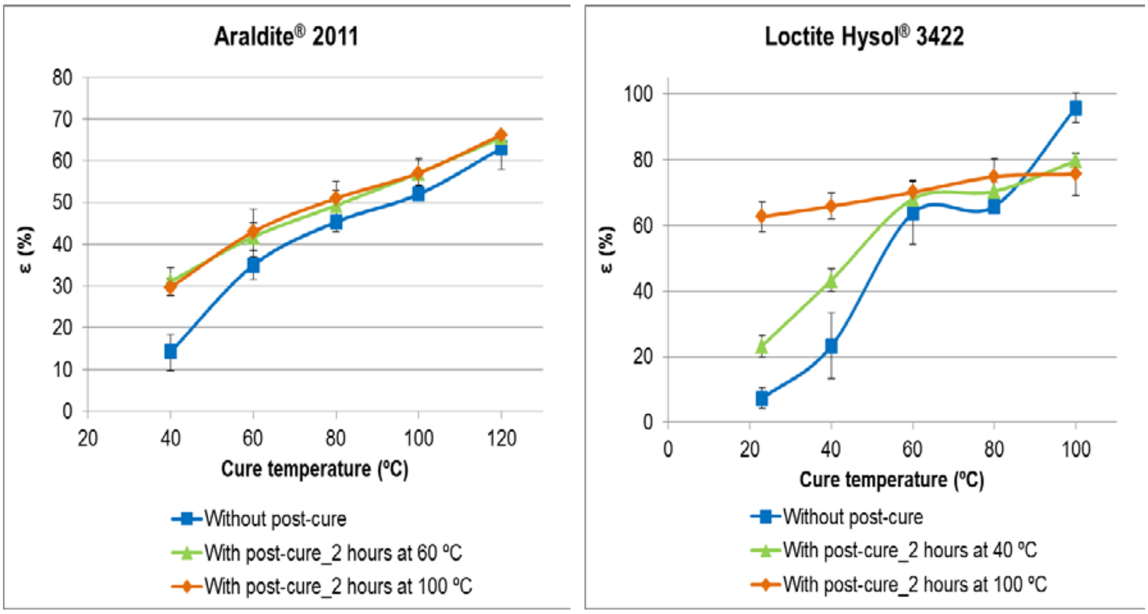


Figure 3 – Mechanical properties of the two epoxy adhesives subjected to different post-cure conditions as a function of the cure temperature

The adherend selected was a high strength steel (DIN C65 heat treated) with (tensile strength of the adherend) σ_{ys} = 1260 MPa and E = 210 GPa to avoid plastic deformation of the adherend [38 - 40].

2.2. Single lap joint (SLJ) test

The SLJs had an overlap of 50 mm and width of 25 mm, see geometry in Figure 4. The adherend thickness was 2 mm and the adhesive thickness was 1 mm. The joint surface of all substrates was grit blasted and degreased with acetone prior to the application of the adhesive.

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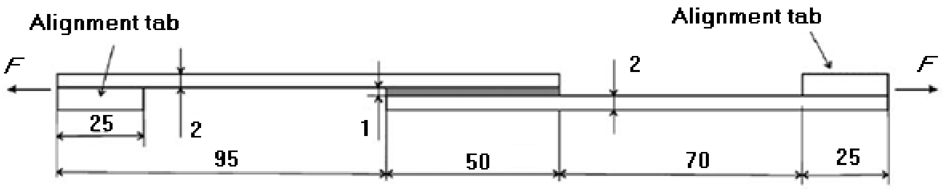

Figure 4 – Geometry of the SLJ test specimens (dimensions in mm).

Two different curing processes were performed: a graded cure obtained by induction heating and an isothermal cure. The isothermal cure process was used as a reference for comparison with the joints obtained by a graded cure.

2.2.1. Isothermal cure

A mold with spacers for correct alignment of the substrates was used to produce the SLJ specimens [33]. For adhesive Araldite® 2011, to achieve brittle properties, the adhesive joints were cured for 30 min at 40 ºC, and to achieve ductile properties, the adhesive joints were cured for 30 min at 100 ºC. For adhesive Loctite Hysol® 3422 to achieve brittle properties, the adhesive joints were cured for 1 hour at 23 ºC, and to achieve ductile properties, adhesive joints were cured for 1 hour at 100 ºC.

2.2.2. Graded cure

Induction heating is an electromagnetic heating method in which electrically conductive bodies absorb energy from the passage of current through the induction coil generates a very intense and rapidly changing magnetic field in the space within the work coil [33].

The mould used to ensure the correct alignment and bondline thickness, as the induction and cooling coils design are detailed in a patent under preparation [32].

The induction heating system enables to obtain a graded cure with a focused temperature at the ends of the overlap and gradually decreasing the middle of the overlap by positioning the induction heating at the ends of the overlap and the induction cooling in the middle. The temperature distributions along the overlap for both adhesives with this technique are presented in Figure 5.

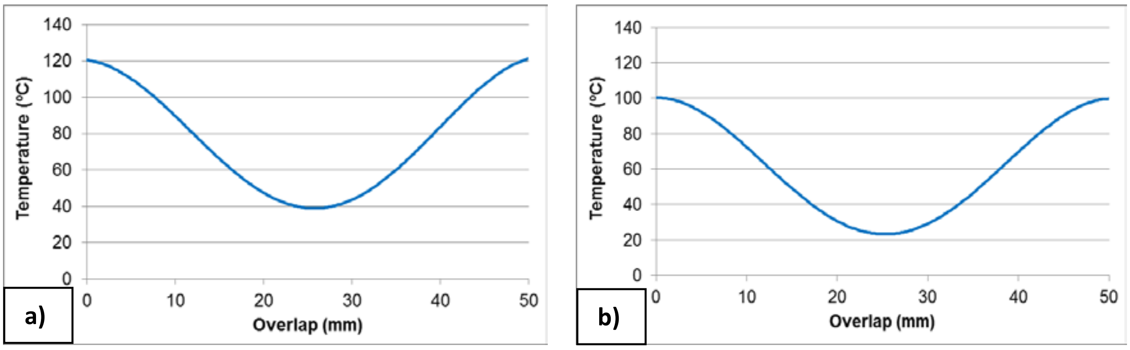

Figure 5 – Cure temperature distribution of Araldite® 2011 (a) and Loctite Hysol® 3422 (b).

The cure temperature values applied to the ends and to the middle of the overlap in the graded joint are the same values used to cure the isothermally cured joints.

2.3. Post-cure conditions

Three different post-curing procedures were considered (Figure 6). In the first set, the joints were only subjected to a curing process; in the second set, the joints were subjected to a curing process followed by a post-cure performed at a temperature below $T_{g\infty}$; and in the third set, the joints were subjected to a curing process followed by a post-cure performed at a temperature above $T_{g\infty}$.

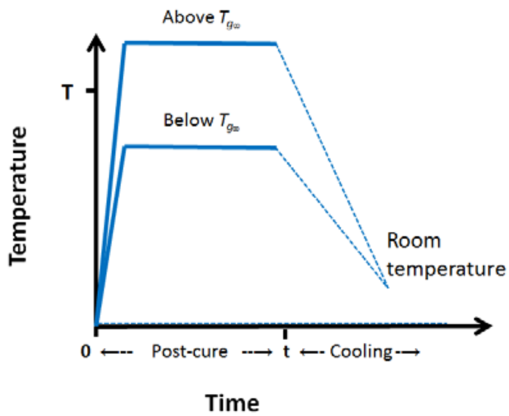

Figure 6 – Diagram of the post-cure used.

The temperatures used for the post-cure below $T_{g\infty}$, for joints bonded with Araldite® 2011 was 60ºC and for the joints bonded with Loctite Hysol® 3422 was 40ºC. The post-cure at high temperature (above $T_{g\infty}$) used for both adhesives was 100 ºC. The time of post-cure at which the adhesives were exposed was 2 hours. The reason for this post-cure, below and above the $T_{g\infty}$, is to understand the effect of the post-cure at temperatures of the glassy and rubbery region, respectively, on the mechanical behaviour of the adhesive joints. Reference samples were used, subject to similar cure conditions but without a post-cure.

3. Experimental results

SLJ tests were performed using a MTS servo-hydraulic machine (Minneapolis, USA), at a constant displacement rate of 1 mm/min. A load cell of 100 kN was used and the loads and displacements up to failure were recorded. For each case five specimens were tested in laboratory ambient conditions (room temperature of 23ºC, relative humidity of 55%).

3.1. Load-displacement curves

Typical load-displacement curves obtained by tensile tests of the SLJ specimens without post-cure are represented in Figure 7.

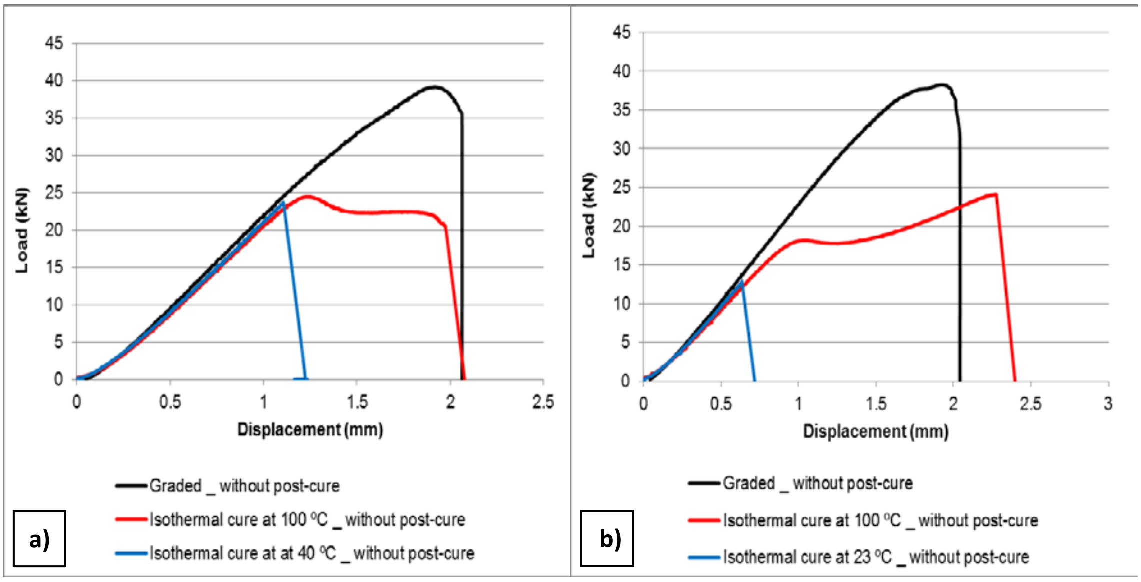

Figure 7 – Typical load-displacement curves of joints (isothermal cure and graded cure) without post-cure, for adhesives Araldite® 2011 (a) and Loctite Hysol® 3422 (b).

Figure 8 shows typical load-displacement curves obtained by tensile tests of the SLJ specimens with a post-cure below $T_{g\infty}$.

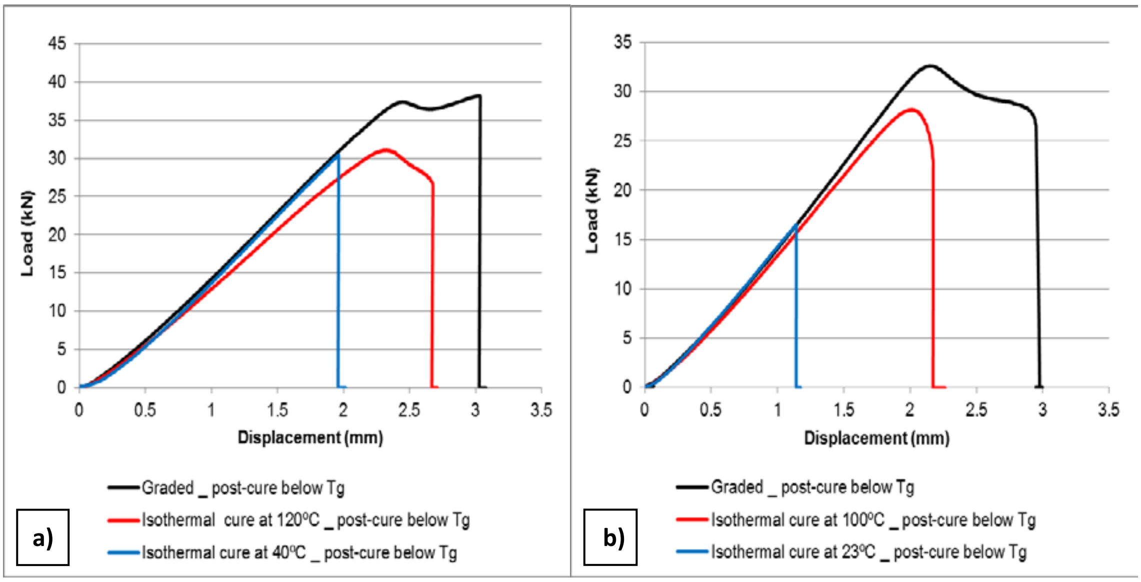

Figure 8 – Typical load-displacement curves of joints (isothermal cure and graded cure) with a post-cure below $T_{g\infty}$, for adhesives Araldite® 2011 (a) and Loctite Hysol® 3422 (b).

Typical load-displacement curves obtained by tensile tests of the SLJ specimens with a post-cure above $T_{g\infty}$ are represented in Figure 9.

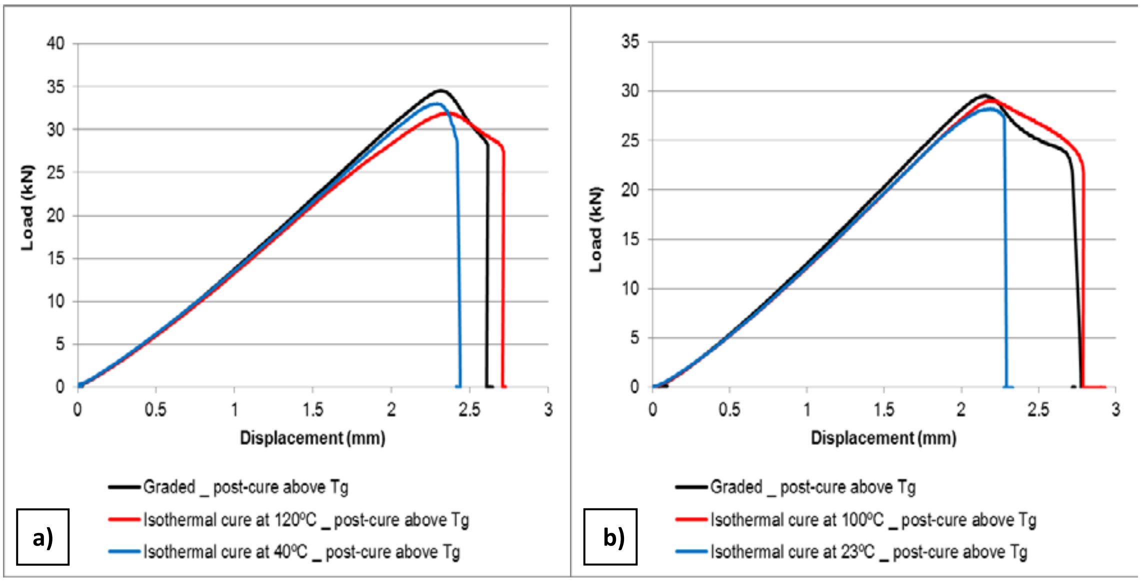

Figure 9 – Typical load-displacement curves of joints (cure isothermal and graded cure) with post-cure at above $T_{g\infty}$, for adhesives Araldite® 2011 (a) and Loctite Hysol® 3422 (b).

As expected, the joints with a graded cure show the highest failure load, compared to the joints cured isothermally [33], this happens for all post-cure conditions and for both adhesives. For all post-cure conditions, the joints gradually cured are stronger and with a larger displacement, thus it can be concluded that these joints have higher energy absorption. The joints cured isothermally at low temperature without post-cure show the lowest value of failure load. But with an increase of the post-cure temperature the strength of joints cured isothermally at low temperature increases. For the post-cure at high temperature (above $T_{g\infty}$) the joints cured isothermally and gradually show similar strength and displacement.

The experimental values of the failure loads when submitted to different post-cure conditions are shown in Figure 10.

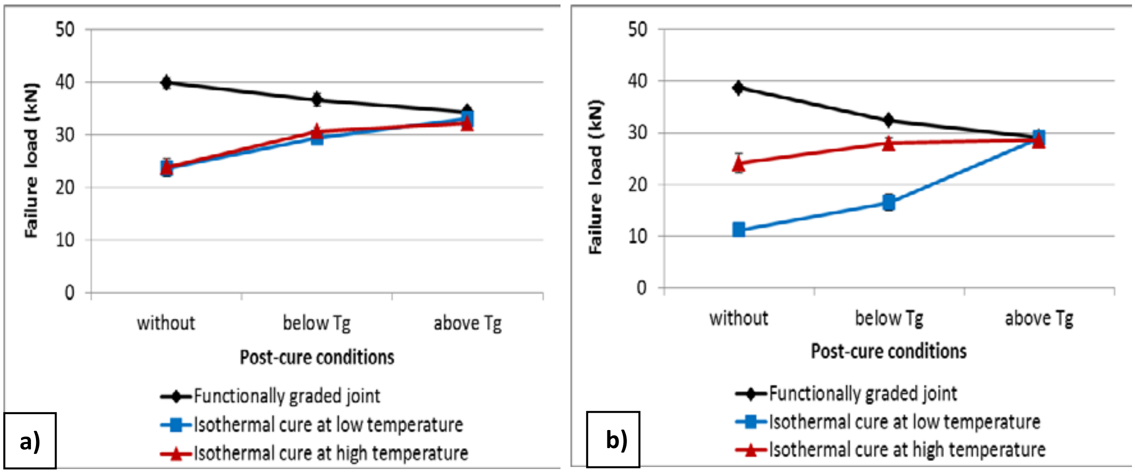

Figure 10 – Failure loads of joints cured isothermally and gradually, bonded with adhesives Araldite® 2011 a) and Loctite Hysol® 3422 b), as a function of post-cure conditions.

The performance gains of the graded joints in relation to the joints cured isothermally are shown in Table 1.

Table 1 – Performance gains of the functionally graded joints in relation to the joints cured isothermally when submitted to different post-cure conditions.

	Isothermal cure at low temperature	Isothermal cure at high temperature
	Without post-cure	
Functionally graded joints bonded with Araldite® 2011	+ 68.4 %	+ 67.0 %
Functionally graded joints bonded with Loctite Hysol® 3422	+ 245.5 %	+ 60.6 %
	Post-cure – below $T_{g\infty}$	
Functionally graded joints bonded with Araldite® 2011	+ 24.4 %	+ 19.5 %
Functionally graded joints bonded with Loctite Hysol® 3422	+ 96.4 %	+ 15.7 %
	Post-cure – above $T_{g\infty}$	
Functionally graded joints bonded with Araldite® 2011	+ 3.9 %	+ 6.8 %
Functionally graded joints bonded with Loctite Hysol® 3422	+ 0.7 %	+ 2.5 %

The performance of the functionally graded joints is higher than either joints cured isothermally, for all post-cure conditions. However, the higher performance of the functionally graded joints when compared to the joints cured isothermally is more evident for the joints that were not submitted to any post-cure conditions. A post-cure below $T_{g\infty}$ does not affect much the joint strength being the graded joints still much stronger than the joints cured isothermally. This means that for the graded joints to be stronger than the isothermal joints, they should never be subjected to temperatures above $T_{g\infty}$.

The functionally graded joints submitted to a post-cure above $T_{g\infty}$ have a strength similar to that of the joints cured isothermally (at high and low temperature). This is because the mechanical properties of the graded adhesive bondline become uniform after a post-cure. The graph of the variation of mechanical properties as a function of the post-cure for the adhesives studied (Figure 3) show that with an increase of the post-cure temperature, the mechanical properties variation tends to a constant behaviour, independently of the cure temperature. With an increase of the post-cure temperature the two epoxy adhesives show a ductile behaviour and the graded properties along the overlap of the graded joints disappear.

4. Analytical analysis

4.1. Isothermal cure

For joints cured isothermally with a ductile type behaviour, the failure load was predicted using the global yielding criterion [37]. The load corresponding to the total plastic deformation of the adhesive is given by

$$F_a = \tau_y \, w \, l \quad (1)$$

where F_a is the failure load of the adhesive, τ_y the shear yield strength of the adhesive, w the joint width and l the overlap length.

For joints cured isothermally with a brittle type behaviour, the failure load was predicted with the Volkersen's model [36]. The failure occurs when the maximum shear stress at the ends of the overlap exceeds the shear strength of the adhesive. The following equation was used:

$$P = \tau_r \frac{2bl \sinh(\lambda l)}{\lambda l[(1+\cosh(\lambda l)]} \tag{2}$$

where

$$\lambda^2 = \frac{G}{t_a}\left(\frac{2}{Et_s}\right) \tag{3}$$

τ_r is the shear failure strength of the adhesive, t_a is the adhesive thickness, G the adhesive shear modulus and E the adherend Young's modulus. This failure criterion works well when the adhesive is brittle, the steel is elastic and the failure is cohesive as in all tests.

4.2. Graded cure

A simple analytical analysis proposed by Carbas *et al.* [41] was carried out in order to predict the maximum failure load of the functionally graded joint. The development of this analytical model, based on Volkersen's analysis [36], was solved with power series expansion for a reduced number of expansion terms (21 terms). Equation (4) represents the adhesive shear stress ($\tau(x)$) distribution along the bondline for only 2 terms of the power series expansion and for a linear adhesive shear modulus variation along the bondline. For high order of terms the equation becomes more complex but there is also a repetition of terms with an increase of order.

$$\tau(x) = \frac{32 \cdot P \cdot \left(6 \cdot l \cdot x \cdot \frac{2}{t_s \cdot t_a \cdot E} \cdot K - 8 \cdot x^3 \cdot \frac{2}{t_s \cdot t_a \cdot E} \cdot m + x^2 \cdot \left(\frac{2}{t_s \cdot t_a \cdot E}\right)^2 \cdot K^2 \cdot l - 24 - 12 \cdot x^2 \cdot \frac{2}{t_s \cdot t_a \cdot E} \cdot K + 3 \cdot x^2 \cdot \frac{2}{t_s \cdot t_a \cdot E} \cdot m \cdot l\right)}{b \cdot t_a \cdot l \cdot \left(-768 + 16 \cdot l^2 \cdot \frac{2}{t_s \cdot t_a \cdot E} \cdot K + l^4 \cdot \left(\frac{2}{t_s \cdot t_a \cdot E}\right)^2 \cdot K^2\right)} \quad (4)$$

where P is the applied load, m is the slope and K is the constant (y-intercept) of the linear adhesive shear modulus variation along the bondline.

This model was shown to be a valid tool to predict the shear stress distribution along the overlap length for linear-elastic behaviour of the adhesive. It is a simple analytical model of functionally graded joints that allows the use of different mechanical properties distribution along the overlap length. The failure occurs when the maximum shear stress exceeds the shear strength of the adhesive.

In order to take into account the plastic deformation of the joint, a simple elastic-plastic analysis was considered. Adams and Mallick [42] introduced the linear 'effective modulus' solution. This analysis consists in considering the energy under the stress-strain curve obtained through tensile tests and this energy is used to construct a theoretical line (called the linear 'effective modulus' solution), which has the same shear strain energy and strain to failure of the full elastic-plastic curve (see Figure 11).

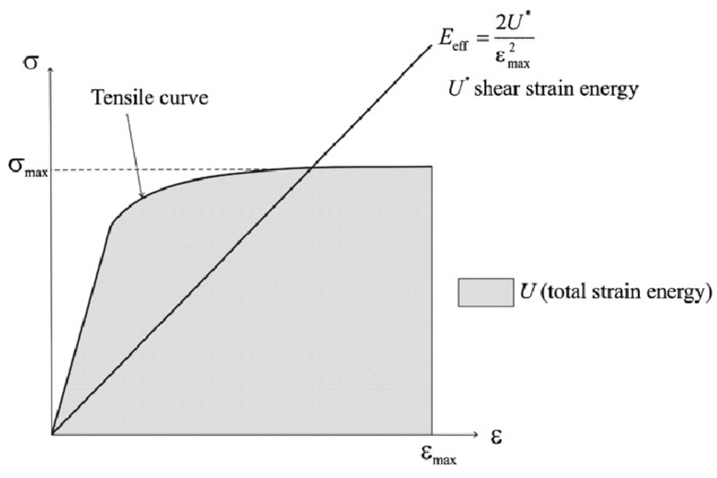

Figure 11 – 'Effective modulus' solution proposed by Adams and Mallick [42].

The shear stress of the adhesive was chosen for this analysis as the shear stress distribution allows a quick and relevant assessment of the stress state in the functionally graded joint. It was considered that failure occurs when the maximum shear stress exceeds the effective shear strength of the adhesive along the overlap.

Figure 1 shows the 'effective modulus' for both adhesives and for each cure temperature used subjected at different post-cure conditions. In Figure 12 the Young's modulus effective ($E_{eff.}$) is shown as well as the effective shear strength ($\tau_{eff.}$) as a function of the cure temperature and for different post-cure conditions.

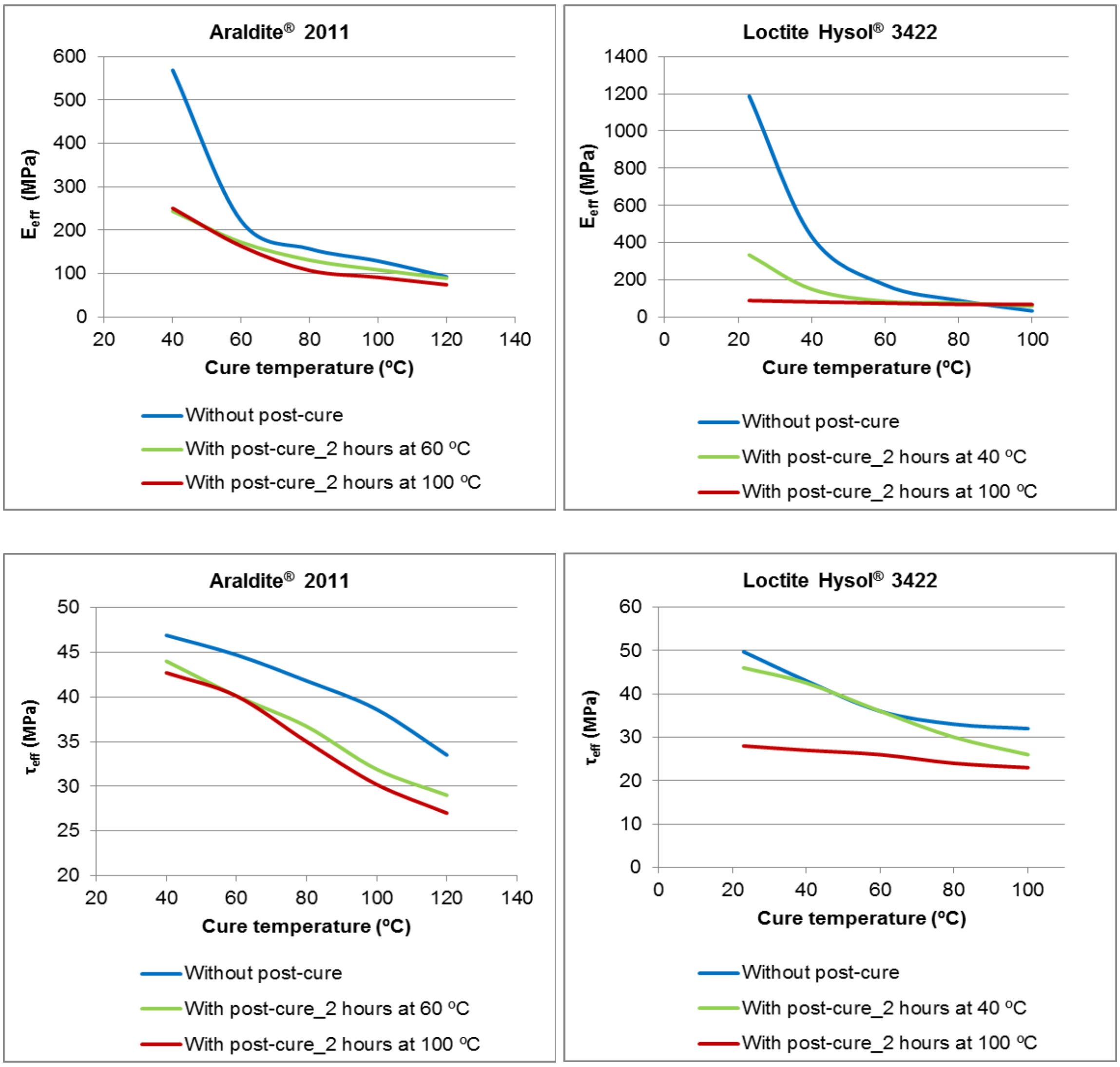

Figure 12 – Mechanical properties using the 'effective modulus' of epoxy adhesives when submitted to different post-cure conditions.

In the analytical analysis for the functionally graded joints, the equation used to represent the variation of adhesive mechanical properties along the overlap was of the exponential type (Carbas *et al.* [41]) for all post-cure except for adhesive Loctite Hysol® 3422 post-cured at high temperatures where a linear distribution was used for the mechanical properties distribution along the overlap. This variation of the adhesive effective modulus along the overlap was used in order to better approximate the real behaviour of the adhesive. Figure 13 shows the variation of the adhesive effective modulus along the overlap used to calculate the failure load prediction.

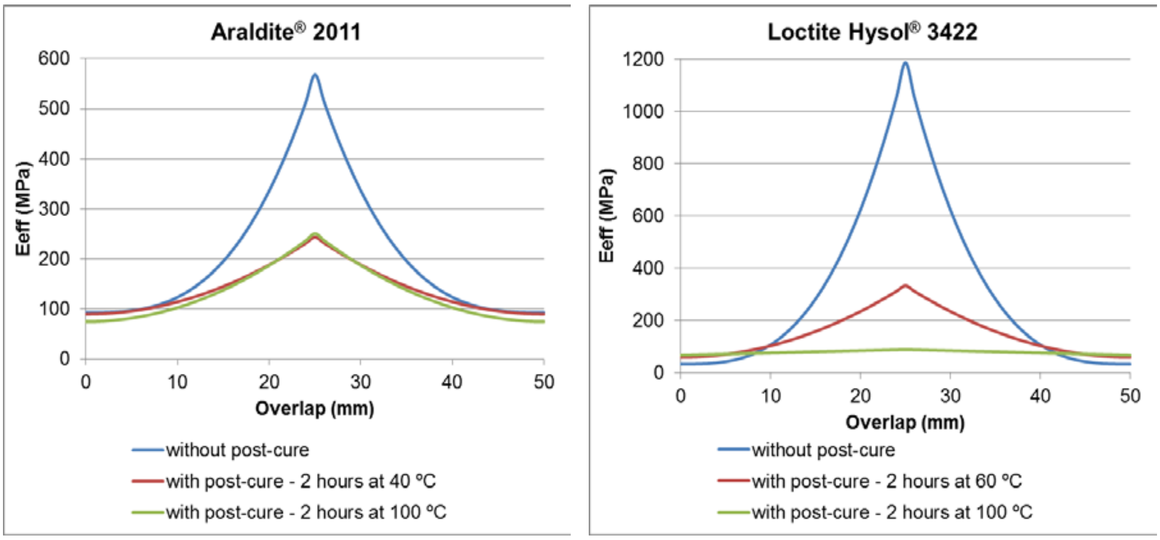

Figure 13 – Effective modulus distribution along the overlap length.

The experimental values of failure loads and the predicted failure loads obtained by the analytical analysis, as well the errors of predictions subjected at different post-cure conditions, are shown in Table 2.

Table 2 – Failure loads obtained experimentally and predicted for the joints cured isothermally and gradually, and submitted to different post-cure conditions.

Without post-cure

	Araldite® 2011 Experimental (kN)	Araldite® 2011 Predicted (kN)	Araldite® 2011 Error (%)	Loctite Hysol® 3422 Experimental (kN)	Loctite Hysol® 3422 Predicted (kN)	Loctite Hysol® 3422 Error (%)
Functionally graded joints	39.9	37.5	5.5	38.7	36.5	5.7
Isothermal cure at low temperature	23.7	18.5	21.9	11.2	16.2	44.6
Isothermal cure at high temperature	23.9	21.9	8.4	24.1	22.0	8.7

With post-cure – below $T_{g\infty}$

	Araldite® 2011 Experimental (kN)	Araldite® 2011 Predicted (kN)	Araldite® 2011 Error (%)	Loctite Hysol® 3422 Experimental (kN)	Loctite Hysol® 3422 Predicted (kN)	Loctite Hysol® 3422 Error (%)
Functionally graded joints	36.7	34.6	5.7	32.4	31.1	4.0
Isothermal cure at low temperature	29.5	28.9	2.0	16.5	16.3	1.2
Isothermal cure at high temperature	30.7	28.2	8.1	28.0	26.3	6.1

With post-cure – above $T_{g\infty}$

	Araldite® 2011 Experimental (kN)	Araldite® 2011 Predicted (kN)	Araldite® 2011 Error (%)	Loctite Hysol® 3422 Experimental (kN)	Loctite Hysol® 3422 Predicted (kN)	Loctite Hysol® 3422 Error (%)
Functionally graded joints	34.4	32.5	5.5	29.2	28.0	4.1
Isothermal cure at low temperature	33.1	31.3	5.4	29.0	27.5	5.2
Isothermal cure at high temperature	32.2	29.9	7.1	28.5	26.9	5.6

The failure criterion used for each joint and for each post-cure condition showed a good failure load prediction. The errors in the predictions obtained by the new analytical model developed for graded joints were very small (less than 5.7%). The Vokersen's model used to predict the joint strength of joints cured isothermally with a brittle behaviour did not perform very well in some cases (error up to 44.6%), but it is known that this model has a limited applicability for thick bondlines (1mm) [38].

5. Conclusions

In this paper, joints with the adhesive gradually modified along the overlap by induction heating and submitted at different post-cure conditions were studied. The functionally graded joints were compared with joints cured isothermally at different temperatures. The following conclusions can be drawn:

The analytical analysis proposed by Carbas *et al.* [41] for functionally graded joints was shown to be a useful tool to predict the failure load and shear stress distribution of the functionally graded joints (submitted or not at any post-cure conditions);

The linear 'effective modulus' solution proposed by Adams and Mallick [42] used in the analytical analysis for functionally graded joints, showed to be a good approach to simulate the elastic-plastic adhesive behaviour.

For the same post-cure conditions, the functionally graded joints show a better performance (highest failure load) and similar displacement than the joints cured isothermally at high temperature (ductile behaviour);

The functionally graded joints bonded with Araldite® 2011 and Loctite Hysol® 3422 showed a high performance gain when not submitted to any post-cure conditions in comparison to the joints cured isothermally at low or high temperatures;

For post-cure below $T_{g\infty}$, the joints cured gradually show a slight decrease of the failure load and those cured isothermally show an increase of the failure load value;

With an increase of the temperature of post-cure (above $T_{g\infty}$), the joints cured gradually and isothermally tend to show similar failure load values;

Therefore it can be concluded that the functionally modified adhesive properties are lost when the joint is subjected to a post-cure above the $T_{g\infty}$. To ensure that a functionally graded joint is obtained, the temperature of post-cure that it is subjected must be below $T_{g\infty}$.

Acknowledgments

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Paper 7

Functionally graded adhesive applied in civil applications

Functionally Graded Adhesive Patch Repairs in Civil Applications

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Abstract

Several investigations have been made concerning the fracture behaviour of scaled specimens of wood beams repaired with adhesively bonded carbon fibre reinforced plastic. However, one of the problems associated to these joints is the fact that the stress distribution (shear and peel) is concentrated at the ends of the overlap, leading to premature failure of the joint. Some solutions to this problem have been developed, such as hybrid joints, adherend shaping, adherend rounding and fillets at the ends of the overlap. Some of these methods tend to increase the weight of the structure and others are very expensive due to its complex manufacturing process.

The stress concentration can be reduced with use of a functionally graded adhesive, in which the mechanical properties vary along the bondlength. This can be achieved with a graded cure, in which the temperature varies along the bondlength. In order to perform a graded cure, induction heating was used. This technique has already been successfully tested in single lap joints to obtain a more uniform stress distribution along the bondlength, increasing the strength of the joint. In this project, the repair of wood structures with Carbon-Fibre Reinforced Plastic (CFRP) was made using a homogeneous cure and a graded cure.

Two common types of defects on beams under bending solicitations were analysed. Scaled specimens of damaged wood beams were repaired and tested under four point bending. The results show that the beams repaired with a graded bondline were able to withstand higher loads.

Keywords: Composites, Wood, Fracture mechanics, Repair, Finite element analysis, Damage mechanics, Functionally graded cure, Civil engineering.

1. Introduction

Wood is an inexpensive building material that can provide easy to build structures. Its thermal conductivity is low, providing good thermal isolation. It is also a good acoustic isolator. It has good specific mechanical properties (divided by its weight). However, if not properly preserved, it is easily degraded by atmospheric and biological agents, such as fungus and insects. It is also susceptible to moisture changes and fatigue for low stress levels [1]. Little pollution is created during wood production. It is a renewable and recyclable product.

Replacements of large timber sections are very expensive due to the complexity of the process and the limited availability of the material. When possible, timber beams should be repaired rather than replaced. Timber structures repairs using structural adhesives are both economically and structurally efficient. Among the several types of adhesives, epoxy adhesives are the best for this kind of joint as they do not require high pressure during application, they exhibit good adhesion to wood and several other materials (such as CFRP), little shrinkage during cure and are highly resistant to moisture and chemical products [2].

Several authors have witnessed the considerable improvement of the strength and stiffness of timber beams repaired with bonded CFRP patches [3-6]. However, one of the problems associated with this kind of joint is the stress concentration in both the adherends and the adhesive, which causes the premature failure of the joint [7]. In the literature we can find several techniques that have been developed in order to reduce this problem, such as through modification of the adherend geometry by inclusion of a taper in the adherend [8-10], by rounding the adherend corners [11-14], by modifications of the joint end geometry with a spew fillet [15-20], by the use of more than one adhesive (so-called mixed adhesive joints) [21-30], and or by the use of functionally graded materials [31-33]. These techniques are usually very expensive to implement due to the excessive steps in the manufacture process and tend to increase the weight of the structure, or due to the complexity of the bonded technique.

It is known that graded adhesives can provide a significant improvement in the strength of adhesive joints [34-36]. Some epoxy adhesives have different properties depending on their temperature of cure [37, 38]. Recently, Carbas *et al*. [39-41] showed the highest strength of the joints functionally cured along the overlap, when compared with joints cured isothermally. The functionally graded adhesive joint showed a gradient in the stiffness of the adhesive along the overlap and this was obtained by differentiated cure along the bondline. This differentiated graded cure was obtained by induction heating [42].

In this work, experimental and numerical studies were performed on the repair of wood beams of the Portuguese *Pinus Pinaster* species with adhesively-bonded CFRP patches. Two different wood beams damage were studied, by cross-grain and compression failure. The repaired wood beams were cured at three different ways, cured isothermally at room temperature, cured isothermally at high temperature and cured gradually. Two patch lengths for each type of wood beams damage were tested under a four-point bending load. A numerical procedure by Finite Element Method (FEM) was developed to predict the fracture behaviour for adhesively-bonded wood repairs. Cohesive zone models (CZM's) were employed to simulate these fractures, whose adhesive toughness properties were calculated by Double Cantilever Beam (DCB) and End Notched Flexure (ENF) specimens.

2. Characterization of the adhesive

The adhesive studied was Loctite Hysol® 3422 (Henkel, Dublin, Ireland). The chemical formulation of this adhesive is bisphenol A diluted with bisphenol F in for the epoxy resin, and 3-Aminopropylmorpholine and polyoxypropylene diamine for the hardener. Carbas *et al*. [38] studied the mechanical properties of the adhesive Loctite Hysol® 3422 as a function of the cure temperature.

In order to accurately simulate the behaviour of the repaired wood specimens, the fracture toughness of the adhesive in pure modes I and II for three temperatures of cure was determined. For this, the DCB (pure mode I) and the ENF (pure mode II) tests were used.

2.1. Specimens fabrication

Steel adherends were used for the DCB and ENF specimens. The joint surfaces of the adherends were grit blasted and degreased with acetone. In order to guarantee a 0.2 mm adhesive thickness, one spacer was inserted at each end. On the end where the crack is supposed to propagate, the spacer was constituted by a 0.1 mm razor blade inserted between two 0.05 mm plates. This allows the stress concentration factor to increase, making it easier for a crack to be created. The schematic geometry of the DCB and ENF specimens is represented in Figure 1.

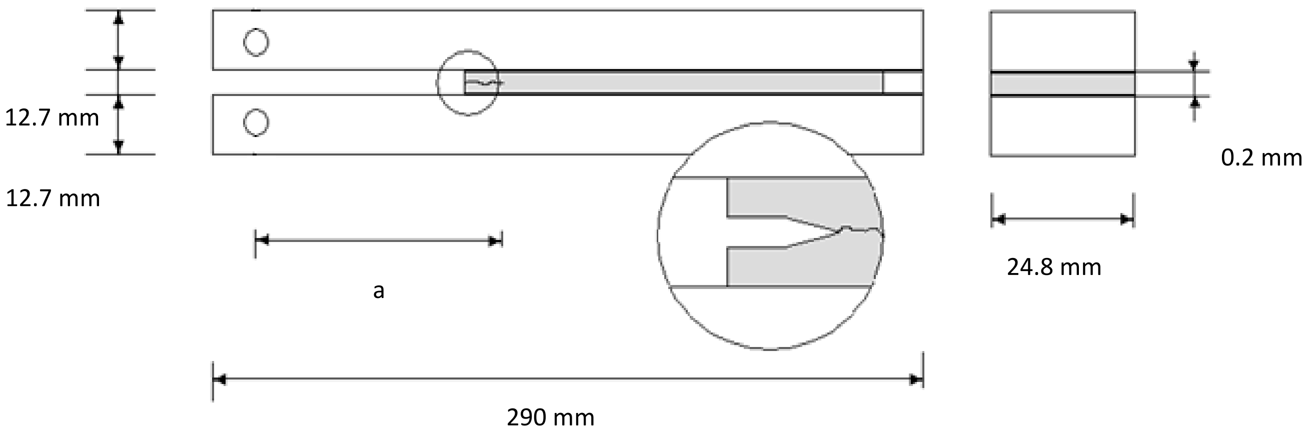


Figure 1 – DCB and ENF specimen geometry.

Three different temperatures of cure (23, 60 and 100 ºC) for 1 hour, were performed. Prior to the testing of the specimens, in order to avoid a blunt crack a pre-crack was created by loading each specimen in pure mode I.

2.2. Pure mode I toughness

The determination of G_{IC} was done with the use of DCB specimens. This test consists on the mode I solicitation of the adhesive. During crack propagation, the values of force (P) and displacement (δ) are recorded. In order to calculate the fracture toughness, the compliance based beam method (CBBM) was used. This is a technique that has recently been developed by de Moura *et al*. [43].

2.2.1. Data analysis

The specimens were tested in a MTS® model 312.31 servo-hydraulic machine with a capacity of 250 kN (Eden Prairie, Minnesota, USA) at room temperature. The specimen with the adhesive cured at room temperature was tested at a displacement rate of 0.1 mm/min, however, due to the brittleness of the adhesive, unstable crack propagation was observed in all specimens, making it impossible to determine the mode I fracture toughness. The specimens with the adhesive cured at 60 ºC and 100 ºC were tested at a displacement rate of 0.2 mm/min. The mode I fracture energy of the adhesive cured at 100°C and 60°C was about 4.90 N/mm and 3.08 N/mm respectively, which is consistent with the studies made by Carbas *et al*. [38].

2.3. Pure mode II toughness

The determination of G_{IIC} was done with the use of ENF specimens. The schematic geometry of the specimens used is shown in Figure 1. Two steel adherends are adhesively bonded and tested under three point bending. This allows the adhesive to be under a pure mode II solicitation. During crack propagation, the values of force (P) displacement (δ) are recorded.

In order to calculate the critical energy release rate in mode II, G_{IIC}, the CBBM was used [43]. In this method, an equivalent crack length is computed based only on the P-δ curve during the crack propagation, which means the crack length measurement during the test is not required.

2.3.1. Data analysis

The specimens were tested in an INSTRON® model 3367 universal test machine with a capacity of 30 kN (Norwood, Massachusetts, USA), at room temperature and constant displacement rate of 0.5 mm/min. For the cures performed at 60 ºC and 100 ºC, due to the high ductility of the adhesive, the crack did not propagate. For this reason, no information could be recovered about the mode II fracture toughness of the adhesive.

Figure 4 shows the results concerning the specimens with the adhesive cured at room temperature. The results show that the mode II fracture toughness of the adhesive cured at 23 ºC is about 12.47 N/mm.

2.4. Discussion and results

The fracture toughness values are graphically represented, of the Loctite® Hysol 3422 adhesive in modes I and II, in Figure 2. Since the mode I toughness of the adhesive cured at 23 ºC and the mode II toughness of the adhesive cured at 60 ºC and 100 ºC could not be determined, these values were extrapolated.

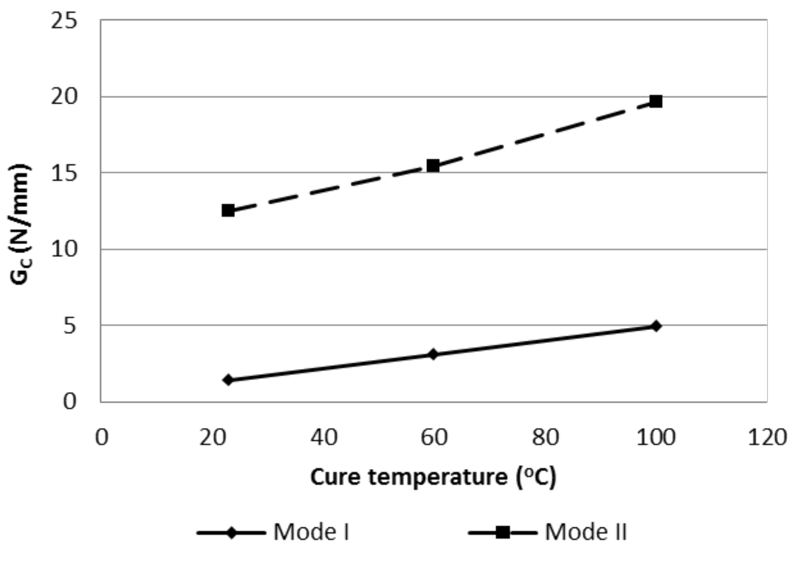


Figure 2 – Toughness in modes I and II as a function of the temperature of cure.

3. Experimental details

3.1. Mechanical properties of the Pinus Pinaster wood

On the macroscopic scale, wood is an orthotropic material with three orthogonal directions of symmetry, as can be seen in Figure 6. Six propagation systems are distinguished for each propagation mode (I, II and III): TL, RL, LR, TR, RT, and LT. The first letter refers to the normal direction to the crack plane and the second letter to the direction of crack growth [44, 45].

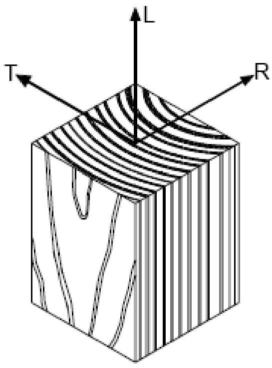


Figure 3 – Orthogonal directions of symmetry of wood.

Wood failure in two propagation systems in modes I and II were considered. The elastic and fracture properties of the *Pinus Pinaster* wood are in Tables 1 and 2 respectively. Because wood is a biological product, these values vary greatly from specimen to specimen, depending on the environment the tree grew in, among other factors.

Table 1 – Elastic properties of the *Pinus Pinaster* wood [44].

E_L= 15.13 GPa	ν_{LR}= 0.47	G_{LR}= 1120 MPa
E_R= 1910 MPa	ν_{LT}= 0.51	G_{LT}= 1040 MPa
E_T= 1010 MPa	ν_{RT}= 0.59	G_{RT}= 170 MPa

Table 2 – Cohesive properties of the *Pinus Pinaster* wood for two propagation systems [5].

	RL Plane		LR Plane	
Pure mode	**I**	**II**	**I**	**II**
$\sigma_{u,i}$ (MPa)	16	16	65	16
G_{iC} (N/mm)	0.2	1.2	25	1.2

Table 3 summarizes the mechanical properties of adhesive Loctite Hysol® 3422 [38].

Table 3 – Mechanical properties of adhesive Loctite Hysol® 3422.

Temperature (°C)	23	60	100
E (MPa)	3415.0	1952.0	611.5
G (MPa)	1182.3	733.8	229.9
σ (MPa)	50.4	31.2	16.8
τ (MPa)	29.1	18.0	9.7
G_{IC} (N/mm)	1.4	3.1	4.9
G_{IIC} (N/mm)	12.5	15.4	19.6

3.2. Mechanical properties of the CFRP patches

The wood beams were repaired using CFRP patches. This is an orthotropic material, whose elastic mechanical properties can be seen in Table 4.

Table 4 – Elastic properties of the CFRP patches [46].

E_x = 1.09E5 MPa	ν_{xy} = 0.342	G_{xy} = 4315 MPa
E_y = 8819 MPa	ν_{xz} = 0.342	G_{xz} = 4315 MPa
E_z = 8819 MPa	ν_{yz} = 0.380	G_{yz} = 3200 MPa

3.3. Geometry

Scaled specimens of *Pinus Pinaster* beams were repaired with bonded CFRP patches and tested under bending. These specimens were designed to simulate two common types of failure of wood beams under bending loads: compression failure (Figure 4) and cross grain tension failure (Figure 5).

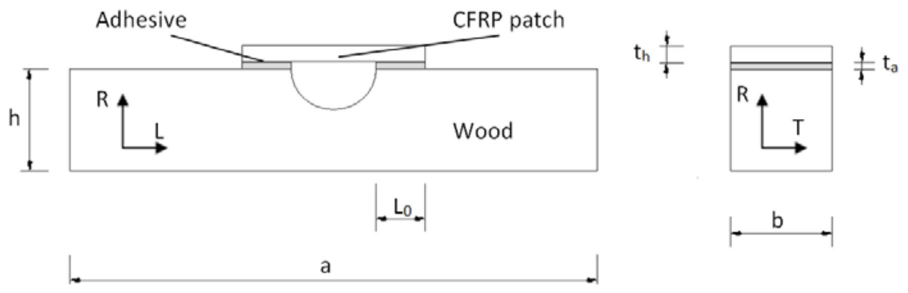


Figure 4 – Schematic representation of the compression damage specimen.

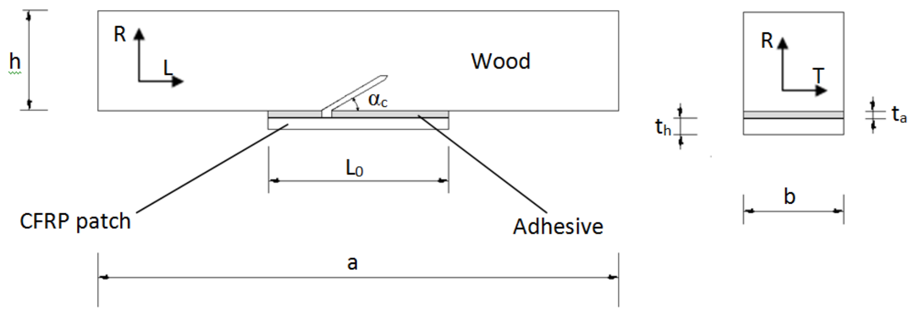


Figure 5 – Schematic representation of the cross grain tension specimen.

Table 5 shows the dimensions of the compression and cross grain specimens.

Table 5 – Geometry of the compression and cross grain tension specimens.

Compression failure specimen					
a = 300 mm	b = 20 mm	h = 20 mm	t_a = 0.2 mm	t_h = 1.2 mm	
Cross grain tension failure specimen					
a = 300 mm	b = 20 mm	h = 20 mm	t_a = 0.2 mm	t_h = 0.6 mm	α_c = 15°

For each kind of damage beam, two bonded lengths were considered (L_0): 20 and 30 mm for the compression damage and 40 and 60 mm for the cross grain tension damage.

3.4. Cure process

The cure of the adhesive was performed in two different ways, the isothermal and graded cure.

3.4.1. Isothermal cure

In order to guarantee the correct adhesive thickness, two spacers were used. The pressure was applied through the use of grips. Two different cures were performed, one cure in order to achieve stiff, but strong brittle properties of the adhesive and another cure in order to obtain ductile properties of the adhesive. To achieve brittle properties, the adhesive joints were cured for 1 hour at 23 ºC, and to achieve ductile properties, adhesive joints were cured for 1 hour at 100 ºC.

3.4.2. Graded cure

Induction heating was used to raise the temperature of the adhesive at the ends of the overlap, where the stress concentration exists. As this adhesive is flexible when cured at high temperatures, this allows the stresses in the joint to be more uniform. This technique has already been successfully used in single lap joints by Carbas *et al*. [39, 40]. A recently invented apparatus was used to locally heat the adhesive and perform a graded cure [42].

Figure 6 shows the approximated distribution of temperature along the overlap length for the compression and cross grain tension specimens, obtained by the apparatus of induction heating localized [42]. The temperature was monitored using a thermographic camera.

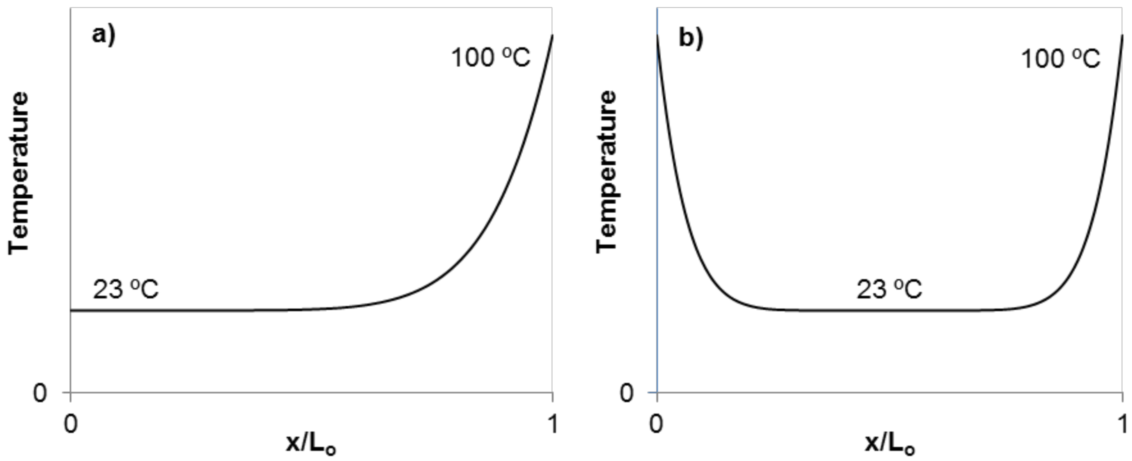


Figure 6 – Approximated temperature distribution during the graded cures: a) compression specimens (half of the beam); and b) cross grain tension specimens.

At the ends of the overlap there is a greater gradient in the stress than in the middle. In order to obtain a more uniform distribution, these areas must also receive a considerable gradient in the rigidity. To achieve this, a great gradient in the temperature of cure was used at this area. At the middle of the overlap there is not a great variation in the stress. This is why a small gradient in the temperature of cure was used here.

3.5. Specimens testing

The specimens were tested under four point bending in an INSTRON® model 3367 universal test machine with a capacity of 30 kN. This allows a constant bending moment to be created on the repaired area (at the middle of the beam), as is shown in Figure 10. The displacement rate was 2 mm/min. The specimens were placed with the repaired area at equal distances from the rollers. The compression specimens had the patch on the upper side (compression face of the beam) and the cross grain tension specimens were placed with the repaired area on the bottom side of the beam (tensile face). Five specimens were manufactured for each kind of repaired beam. Only the valid tests were considered in the analysis of results.

4. Numerical analysis

CZM can predict the formation and propagation of cracks [46, 47]. The triangular CZM, due to its simplicity, is very widely used and provides good results for most of the real situations [48]. This cohesive law has an initial elastic behaviour. After the maximum stress is achieved, linear softening initiates. When the stress reaches the value of zero, no load can be transmitted, which is the same as saying that a crack has been created.

4.1. Finite element model

The FEM analyses were performed in ABAQUS 6.10 program (Dassault Systèmes Simulia Corp. Providence, RI, USA) using CZM. 2D models were used. The CFRP patch and the wood beam were modelled with 4 node solid elements (CPS4R). The adhesive was modelled with 4 node cohesive elements (COH2D4). Cohesive layers were also added to the beam (Figure 7), so that the crack initiation and propagation could be simulated. In this study, every simulation was carried out with the use of a triangular cohesive zone model.

Due to the symmetry of the compression specimen, in order to decrease the computational effort, only half of the beam was numerically simulated. The boundary conditions, as well as the place where each layer of cohesive elements was created are represented in Figure 7.

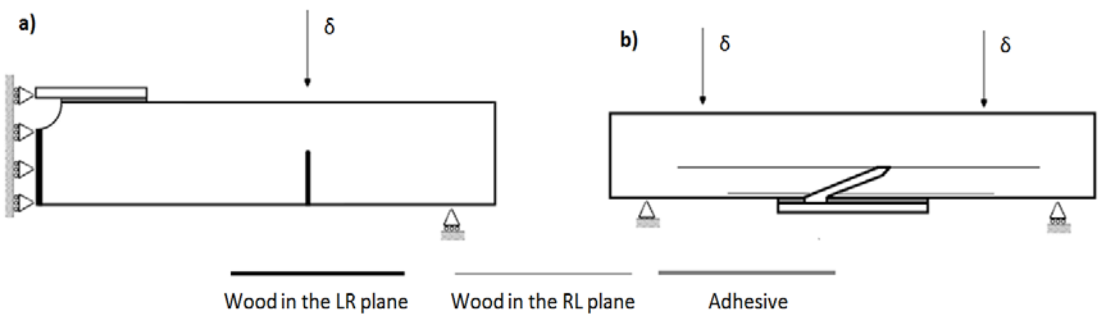


Figure 7 – Boundary conditions and cohesive elements location: a) compression failure and b) cross grain tension failure.

In the compression specimens, to simulate failure at the symmetry axis of the beam and bellow the loading cylinder, cohesive layers of wood were added to these locations. In the cross grain tension specimens, cohesive layers of wood in the RL plane were used in order to simulate the propagation of the pre-crack and the failure of the wood-adhesive interface. In all cases cohesive elements were used in the adhesive.

In order to simulate graded adhesive properties, 50 partitions were made in the adhesive layer so that the transition between divisions (mechanical properties) became the smoothest possible. Different properties were assigned to each partition. These are the properties of the adhesive cured at different temperatures. This way it was possible to create an approximation to a graded bondline. Figure 8 shows a schematic representation of the Young's modulus of the adhesive in the numerical model along the overlap length. A considerable gradient in the Young's modulus is introduced in the stress concentration zone at the ends of the overlap. These areas received a greater gradient in the rigidity, so that the stress distribution could be as uniform as possible. At the middle of the overlap there is not a great variation in the stress. This is why a small gradient in the rigidity was assigned to this area.

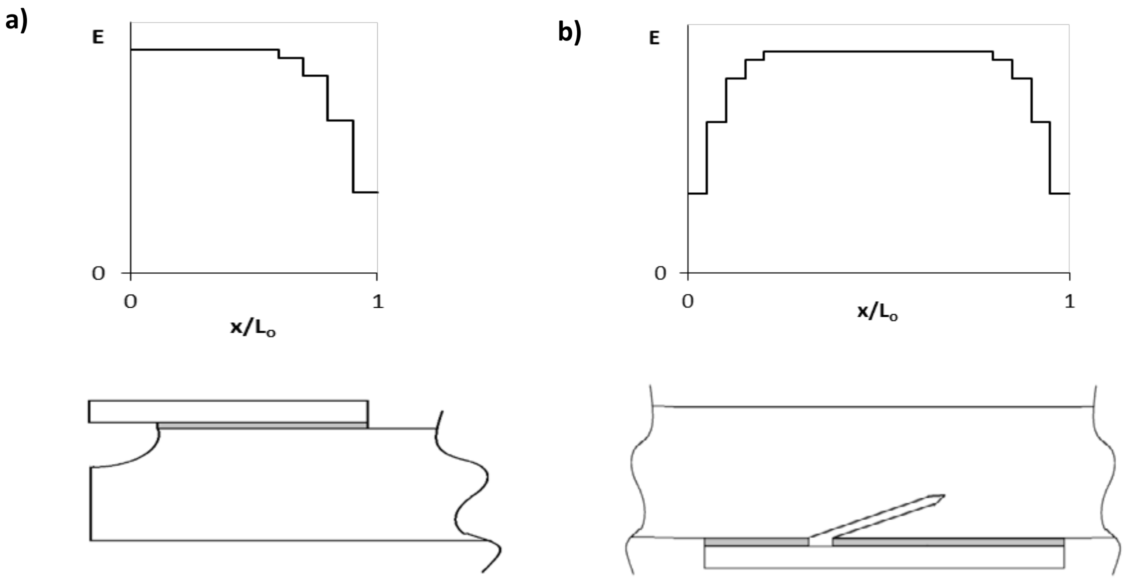


Figure 8 – Schematic representation of the Young's modulus along the overlap length: a) compression specimens and b) cross grain tension specimens.

However, this is not a perfect approximation. The stress distribution that is computed, as a result of discontinuous adhesive properties along the overlap, is not a continuous line. For this reason, the stress distributions regarding the graded cures were approximated by a six degree polynomial function.

4.2. Stress distribution in the adhesive layer

In this section the stress distribution in the adhesive (shear and peel) in the compression and cross grain tension specimens under 4PB are presented. All the figures refer to the elastic domain.

4.2.1. Compression specimens

Figure 9 shows the adimensionalised shear and peel stress $\left({}^{\tau}/_{\tau_{avg}} \text{ and } {}^{\sigma}/_{\tau_{avg}}\right)$ of the compression specimens over the overlap length for a 20 mm repair.

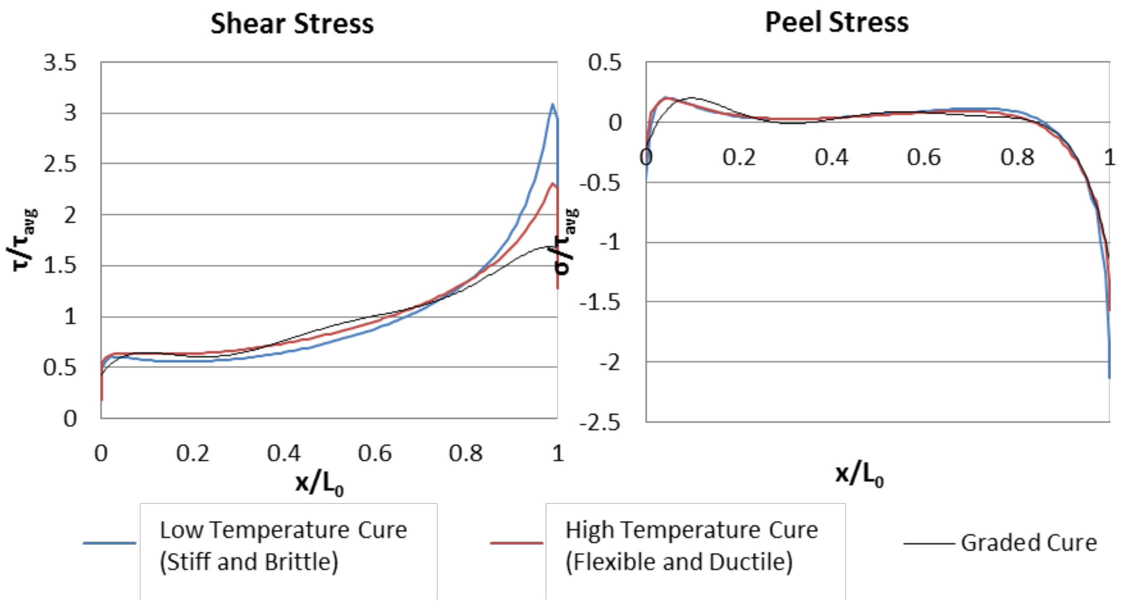


Figure 9 – Shear and peel stress distribution in the 20 mm repair compression specimen.

In the repaired compression specimens, both the peel and the shear stresses are maximum at the ends of the overlap.

The highest stress concentration factor belongs to the adhesive cured at room temperature, as its Young's modulus is the highest. If this adhesive is cured at 100 ºC, its Young's modulus gets lower, and is able to provide a more uniform stress distribution. The graded cure was able to significantly decrease the stress concentration factor at the ends of the overlap when compared with the adhesive cured at high and low temperature.

4.2.2. Cross grain tension specimens

Figure 10 shows the stress distribution along the overlap of the cross grain tension repairs specimens for a 40 mm repair.

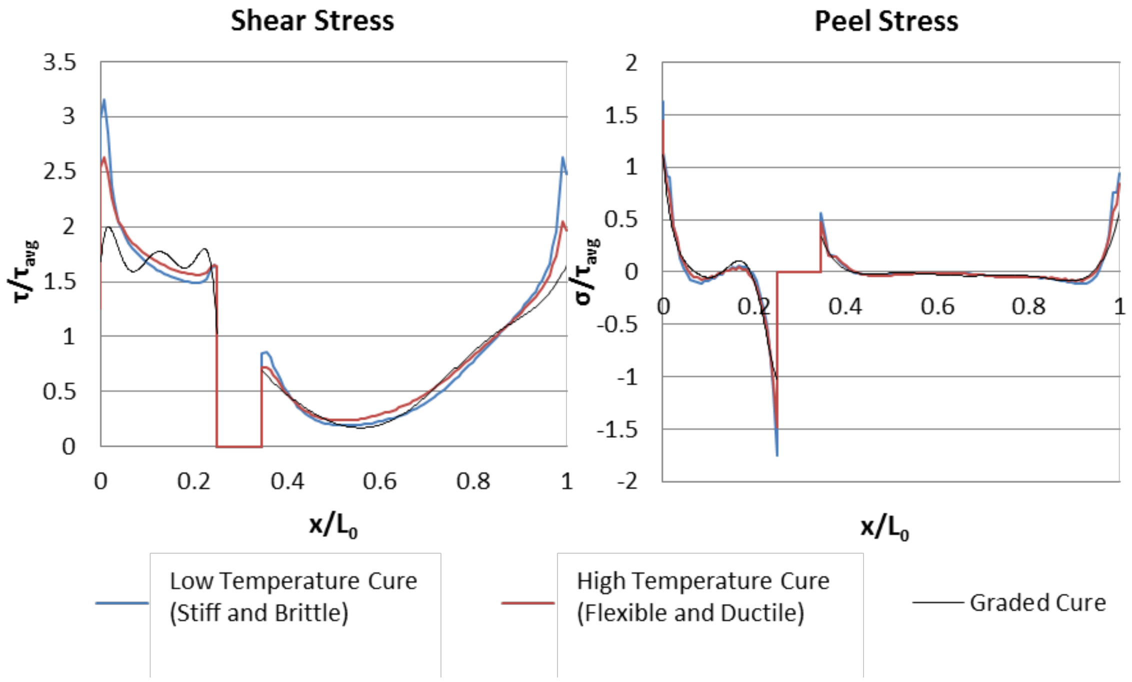


Figure 10 – Shear and peel stress distribution in the 40 mm repair cross grain tension specimen.

Figure 10 shows that the maximum stress (both peel and shear) occur at the ends of the overlap. The stress concentration factors are also higher for the adhesive cured at low temperature. The graded cure was able to create the most uniform stress distribution.

5. Strength results

5.1. Undamaged beam

Two fracture mechanisms were observed in the undamaged beam: pure tension (Figure 11 a) and cross grain tension (Figure 11 b). The cracks that were initiated by pure tension started to propagate in the RL plane. Only the specimens whose fibres were not exactly aligned failed by cross grain tension. All the others failed by simple tension bellow one of the loading cylinders.

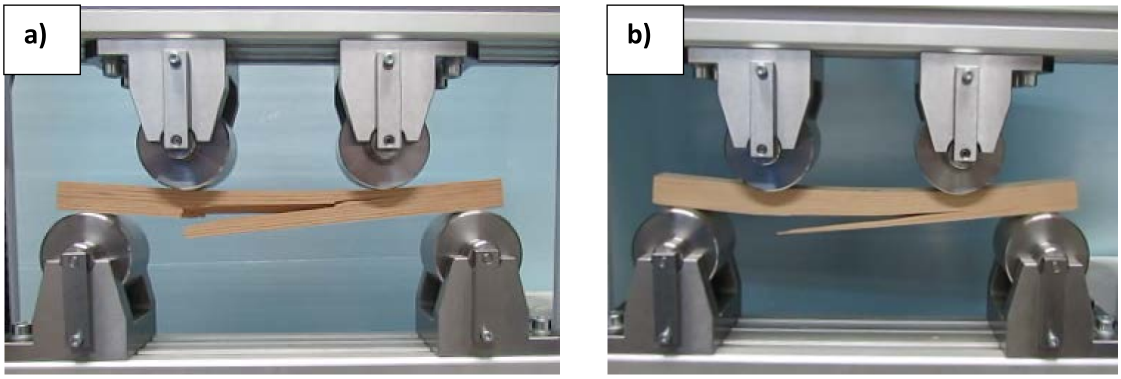


Figure 11 – Failure mechanisms observed in the undamaged beam: a) simple tension and b) cross grain tension.

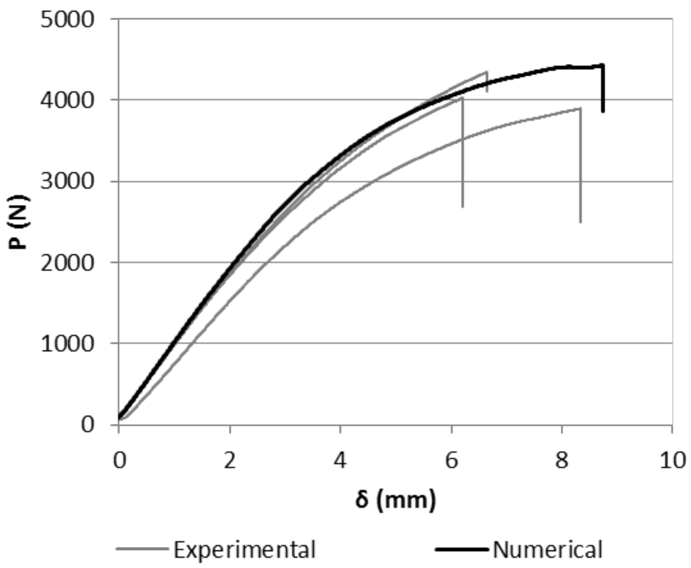


Figure 12 – Experimental and numerical *P*-*δ* curves of the undamaged beam.

Figure 12 shows the experimental and numerical P-δ curves of the specimens. Failure occurred when P reached about 4171 N. The numerical simulation was able to accurately predict the strength of the beam. As in the numerical model the grain is perfectly aligned, the numerical failure, like the experimental failure, occurred by simple tension under a loading cylinder.

5.2. Compression damage specimens

The unrepaired compression failure specimens failed in the wood mostly in the symmetry plane by pure tension (Figure 13 a). The specimens that exhibited a slight cross graining failed by cross grain tension (Figure 13 b).

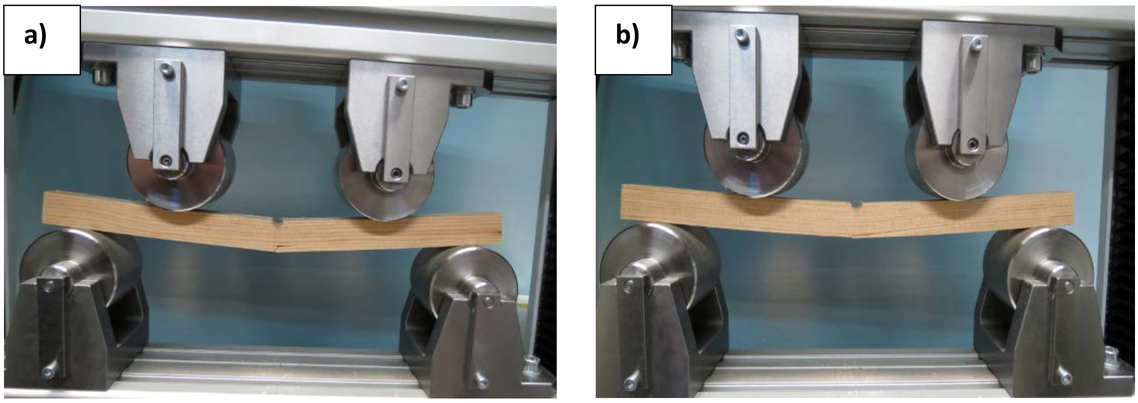


Figure 13 – Failure mechanisms observed in the unrepaired compression damage specimens: a) simple tension and b) cross grain tension.

Figure 14 shows the experimental and numerical P-δ curves of the unrepaired compression specimens. The average strength of the beams was about 2852 N.

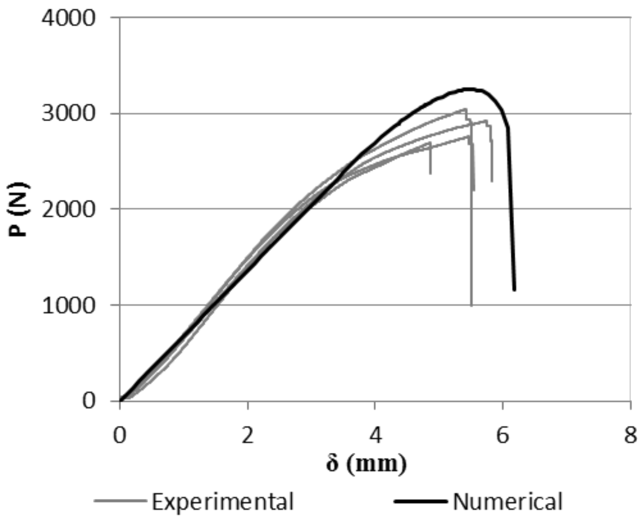


Figure 14 – Experimental and numerical *P-δ* curves of the unrepaired compression specimen.

The failure mechanisms reported for both the 20 mm repair and for the 30 mm repair were similar. Fracture occurred away from the repaired region, either by simple tension or, in the beams that exhibited slight cross graining, by cross grain tension. The failure of the 20 mm patch specimens that failed by simple tension initiated in the symmetry axis of the beam, while the 30 mm patch's started under one of the loading cylinders. As failure occurred away from the repaired area, no conclusions could be made about the effectiveness of the different kinds of cure in the performance of the beams.

Figure 15 shows the experimental and numerical *P-δ* curves of the repaired compression damage specimens with the patch length of 20 and 30 mm. These specimens were cured isothermally (room temperature and 100 ºC) and also cured gradually.

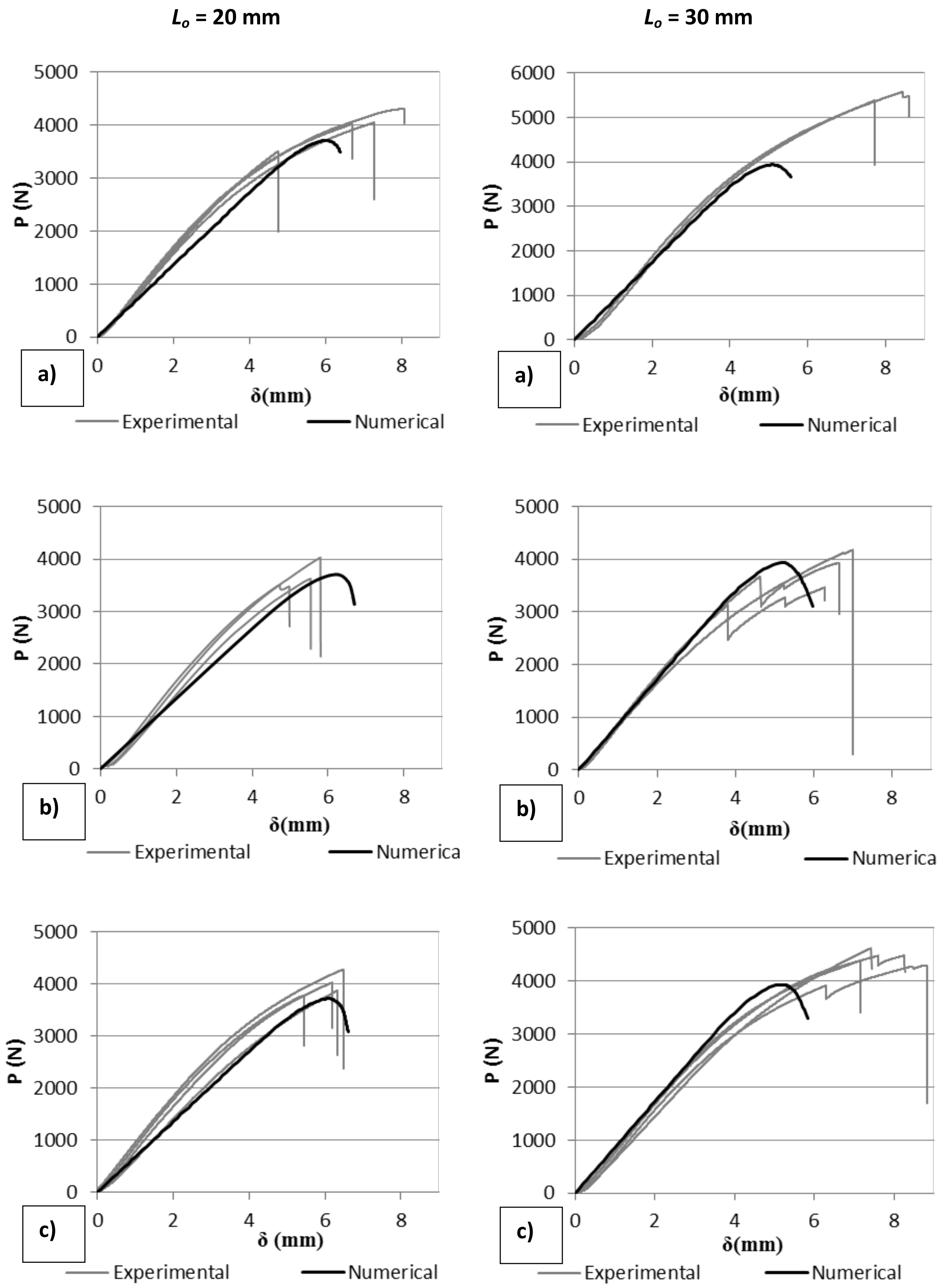


Figure 15 – Experimental and numerical *P-δ* curves of the repaired compression damage specimens: a) cured at 23 ºC, b) cured at 100 ºC and c) cured gradually.

In the 20 mm and 30 mm compression failure specimens, failure occurred in the wood. The strength of the 20 mm compression failure specimens was lower than the strength of the 30 mm compression failure specimens because fracture occurred in the symmetry axis of the beam, influenced by the damaged area. The FEM failure also shows the fracture occurring in the wood beam by simple tension in the symmetry axis of the beam for the 20 mm repair and below the loading cylinder for the 30 mm repair.

The beams repaired with the adhesive cured at 100 ºC are slightly more compliant, as the adhesive cured at this temperature is more flexible. The numerical results regarding the 23 ºC and the graded cure 30 mm patch repairs did not match exactly the experimental results. As all other simulations were reasonably accurate, this is probably due to the natural variability of wood mechanical properties.

5.3. Cross grain tension specimens

The damage in the unrepaired cross grain tension specimens initiated in the RL plane, on path 1 (Figure 16). Despite the drop in the stiffness of the beam, *P* continued to rise until a crack appeared on path 2 (Figure 16), leading to a drop in *P*. This is visible in the *P*-δ curves (Figure 17).

Numerical failure also occurred first on path 1, with the consequent loss of stiffness, and then on path 2.

Figure 16 – Schematic representation of paths 1 and 2.

Figure 17 shows the experimental and numerical *P*-δ curves of the unrepaired cross grain tension specimens. The average strength of the beams was about 2485 N.

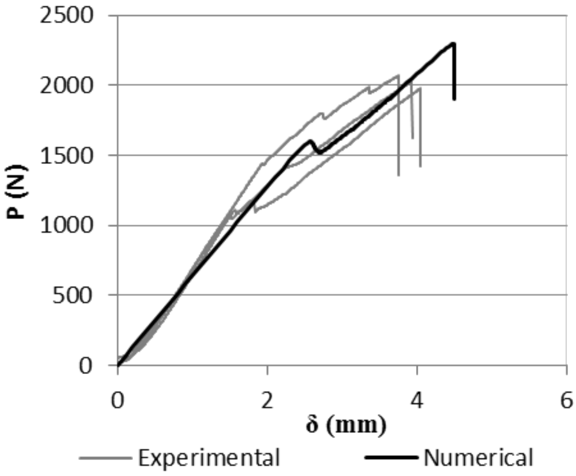
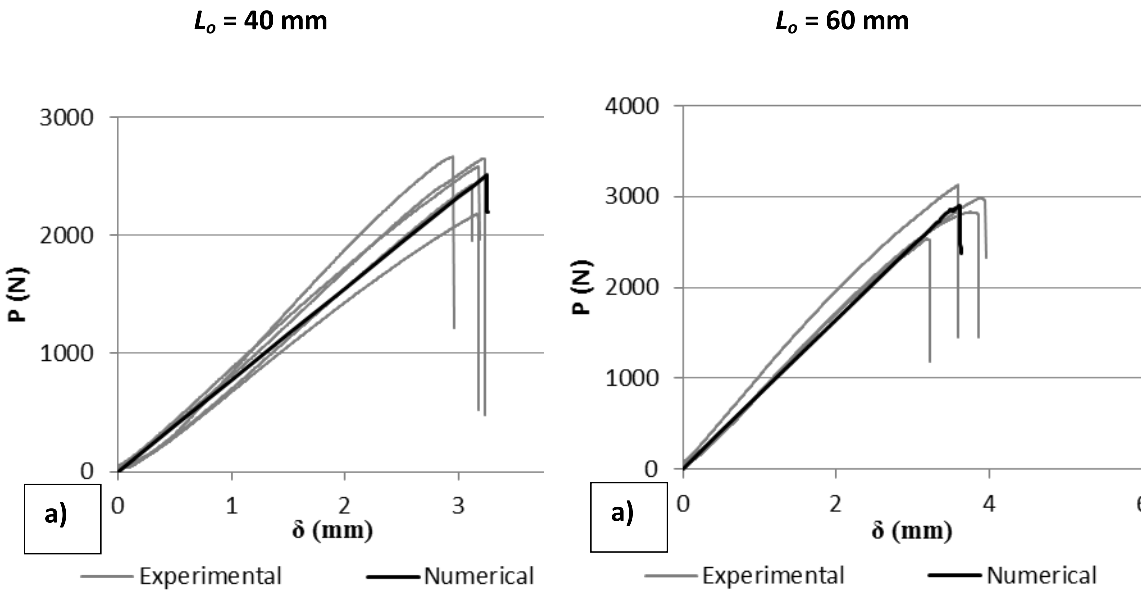


Figure 17 – Experimental and numerical *P-δ* curves of the unrepaired cross grain tension specimens.

Failure in the repaired beams (for both the 40 mm patch and the 60 mm patch specimens) occurred suddenly. Cracks appeared instantly, at the same time, in the adhesive-wood interface and paths 1 and 2 (Figure 16).



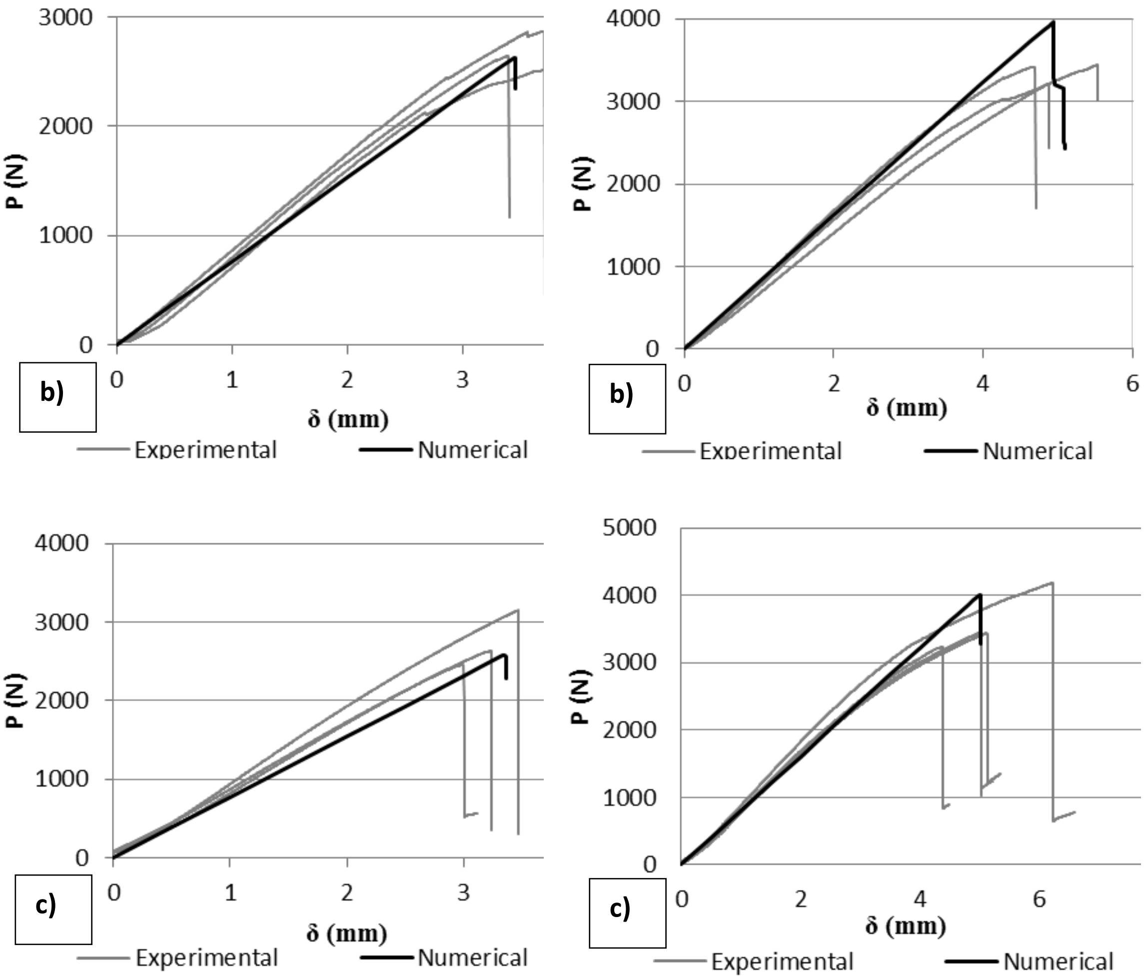


Figure 18 – Experimental and numerical *P-δ* curves of the repaired compression damage specimens: a) cured at 23 ºC, b) cured at 100 ºC and c) cured gradually.

Figure 18 shows that the strength of the beam increases with the patch length (L_0). The beams repaired with the ductile adhesive were stronger than the beams repaired with the brittle adhesive. The strongest beams were those repaired with the graded adhesive. Numerical failure started in the adhesive-wood interface. At this stage, a drop in P occurred. The crack propagated first to path 1 and then to path 2.

6. Discussion

Table 6 summarizes the results of the 4PB tests.

Table 6 – Failure load values of the repaired specimen.

Specimen	L_0	T_{cure}	P_{max} [N]
Compression Specimen	*20 mm*	23°C	3974 ± 467
		100°C	3734 ± 303
		Graded	3982 ± 289
	30 mm	23°C	4927 ± 647
		100°C	3860 ± 393
		Graded	4447 ± 149
	Unrepaired		2852 ± 191
Cross Grain Tension Specimen	*40 mm*	23°C	2505 ± 321
		100°C	2677 ± 1929
		Graded	2745 ± 403
	60 mm	23°C	2872 ± 330
		100°C	3391 ± 176
		Graded	3580 ± 609
	Unrepaired		2485 ± 174
Undamaged Beam	-		4171 ± 277

Finite element analyses show that there is no great difference between the kind of adhesive cure in the compression specimens. However, experiments have shown distinct values for all kinds of cure. As fracture occurred always in the wood, this might be due to the high dispersion of results expected to happen on wood specimens. The failure of the specimens is conditioned by the existence of defects in the wood. As wood is a biological product, these defects have a wide dispersion. Some beams have many defects, others have very few defects. This reflects on the dispersion of results.

The adhesive cured at high temperature (flexible behaviour) was more efficient in repairing wood beams damaged by cross grain tension than the adhesive cured at low temperature (brittle behaviour). The specimens repaired with a graded bondline showed the greatest strength and are the best choice when repairing wood structures. However, as failure occurred in the repaired region, these patches were not able to restore the full strength of the beam, as can be seen in Figure 30. In order to fully repair the cross grain tension wood beams, longer patches should be used. As fracture occurred always in the repaired area, the fracture is conditioned by a single defect that is almost equal for every specimen. This might be the reason why the dispersion of results is wider in the compression specimens than in the cross grain tension specimens.

The great advantage of the graded joint is that the adhesive is ductile where there is great stress concentration and resistant where the stress concentration factor is low, however, as fracture occurred in the wood-adhesive interface, the adhesive was not allowed to develop its full ductility or strength. The improvement on the strength of the beams was due to the more uniform stress distribution, obtained with this kind of bondline.

7. Conclusion

This study focused on the patch repair of wood structures with a functionally graded bondline. Two common types of defects of wood beams under bending loadings, cross grain tension and compression failure, were analysed. CFRP patches were bonded to the damaged area using the Loctite® Hysol 3422 adhesive. The effect of the cure processes of the adhesive in the effectiveness of the repair was assessed. Two different cure processes were studied: isothermal cure and graded cure. For the isothermal cure two different cures were performed, one cure ta low temperature cure in order to achieved an adhesive with stiff and brittle properties, another cure at high temperature cure in order to achieved an adhesive flexible and ductile properties. The graded cure ensures gradual adhesive properties along the bondline, an adhesive with ductile behaviour where there is greater stress concentration and strong adhesive behaviour where high strength is required.

These repairs were simulated with the FEM. CZM were used to simulate the crack initiation and propagation. In order to be able to simulate the fracture behaviour of the adhesive layer, DCB and ENF tests were performed and the toughness of the adhesive in modes I and II for different temperatures of cure was determined.

The results concerning the bending tests on the wood beams showed that graded joints can be used to improve the strength and reliability of repaired beams. The numerical simulations were able to predict the behaviour of the wood specimens, including the specimens repaired with a graded bondline.

Acknowledgments

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ERRATA

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This is an Errata for the thesis: **Adhesively Bonded Functionally Graded Joints**.

Page 2, line 20	Remove one ‘that’
Page 12, line 10	Presently reads: Abstract of Paper 6 Change to: Abstract of Paper 7
Page 22, Figure 12	Height of wood specimen Presently reads: 0.2 mm Change to: 20mm
Page 185, line 4	Presently reads: Figure 6 Change to: Figure 3
Page 202, line 26	Presently reads: ta Change to: at