Evaluation of adhesive bond Young’s modulus during crosslinking using a mechanical method and an ultrasound method

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Abstract. The strength and stability of adhesive bonded structures are related to polymer curing, when crosslinking occurs and leads to adhesive strength, stiffness and durability. Depending on the resin and curing agent used, cure time can vary from minutes to weeks. Methods based on dynamic mechanical analysis (DMA) or calorimetric techniques (DSC, DTA) are valuable for evaluating mechanical properties of adhesives, but are devoted specifically to the polymers alone, and not in situ in adhesive bonds. In this contribution, we have monitored - during crosslinking - the Young’s modulus of a slow-curing DGEBA - PAMAM adhesive system, with two non-destructive, in situ, methods used for the characterisation of the adhesive in a bonded system. The first method is based on measurements obtained from strain gauges mounted on one bonded adherend. The second method uses an ultrasound technique based on the through-transmission. Both methods suggest the same curing kinetics.

1. Introduction
Adhesive bonding is a fast developing method of joining structural parts together, giving advantages of reducing weight by eliminating rivets or bolts, and reducing local stresses when using large bonding surfaces. Many structural adhesives (and also composite materials) are based upon epoxy resins. The mechanical properties and chemical stability of epoxies in their final, as-used, form are due to chemical crosslinking. This reaction is achieved using a variety of crosslinking agents of which amines (for room temperature curing), and imidazoles (for high temperature) are good examples. The essential problems of such cured adhesives are their fragility (relatively low fracture toughness) and, to some extent, their toxicity. Due to the high toxicity of amine and imidazole curing agents, substitutes are sometimes used. PolyAMidoAMines (PAMAM) curing agents can help with both the above-mentioned weaknesses of epoxy-based structural adhesives. However, one of the major disadvantages of PAMAM agents is their longer curing time compared to amines or imidazoles. PAMAMs are low-volatility, low-toxicity curing agents, which mix easily with standard Di-Glycidyl Ether of Bisphenol A (DGEBA, or BADGE) epoxy resins [1, 2]. DGEBA-PAMAM systems are cured at room temperature, resulting in low final shrinkage. The proportion of resin-to-agent can be widely changed in order to obtain the required reaction kinetics and final bulk properties.
We have monitored the crosslinking of a DGEBA-PAMAM system with two, essentially different, non-destructive methods. The first is based upon strain gauge measurements obtained from one of the bonded substrates. The second method is based on the measurement of ultrasonic transmission through a tested material and the use of transmission spectra to infer its mechanical properties. These methods present the impact of crosslinking time on important mechanical properties of bonded structures, particularly the adhesive Young’s modulus. In addition, they are applied directly to adhesive joints, thus are potentially attractive for industry (e.g. for minimising the danger of leaving adhesive uncured in real, bonded structures).

2. Wedge test/strain gauge technique

The evaluation of mechanical properties of the adhesive, in situ in a bond, is made using the so-called wedge test (figure 1), in which a flexible, rectangular adherend is bonded to a second substrate, either also flexible or, in the present case, essentially rigid. A wedge, of thickness $\Delta_w$, is inserted at the unbonded end (produced by prior insertion of a non-sticking spacer). Curvature of the elastic, bent member(s) leads to stored strain energy, and as a fracture front progresses, either within the adhesive or at an interface, this energy is liberated and becomes the fracture energy of the adhesive joint. In 1867, Winkler [3] studied the problem of a beam on an elastic foundation, in order to study effects of the loads acting on rails lying on different soils. Previously, some of us have derived and employed this model to analyse the adhesive wedge test [4,5]. An advantage of the Winkler treatment is that changes in the elastic properties of the adhesive layer may be monitored, since apparent changes in crack length are attributable to strain within the adhesive layer, if actual crack length is constant. The Winkler model is derived from two differential equations, corresponding respectively to the bonded zone and the free zone. The differential equation for the part of the beam in the bonded zone is:

$$\frac{d^4 z}{dx^4} + \frac{\bar{k}}{EI} z = 0, \quad a < x < +\infty,$$

where $E$ is Young’s modulus of the plate bent and $I$ is the second moment of inertia of the beam section area ($I = bh^3/12$ in our case). To a good approximation, the foundation stiffness is given by

$$\bar{k} \approx \frac{E_A}{e} b,$$

where $E_A$ is Young’s modulus of the adhesive, $e$ its thickness and $b$ is joint width. The general solution of differential equation (1) involves four arbitrary constants, but parts of the solution are physically unrealistic. Terms in $e^{\lambda(x-a)}$ are thus neglected, leading to:

$$z(x)\big|_{a}^{\infty} = e^{\lambda(a-x)} [A_1 \cos \lambda(a-x) + B_1 \sin \lambda(a-x)].$$

In the free zone, the equation

$$\frac{d^4 z}{dx^4} = 0$$

applies, since there is no reaction from the adhesive, and this has a straightforward polynomial solution:

$$z(x)\big|_{0}^{\infty} = A_2 x^3 + B_2 x^2 + C_2 x + D_2.$$

In both equations (3) and (5), capital letters refer to integration constants given explicitly in reference [4].
Figure 1. Geometry of asymmetric wedge test and schematic representation of adhesive joint using the Winkler model.

In the instrumented wedge test technique, an expression is required for the upper surface strain of the flexible adherend $\varepsilon_S$. For the bonded zone the (absolute value of) strain can be written [4]:

$$\varepsilon_S(x) = \frac{h}{2R} \frac{d^2z}{dx^2} = \frac{3\Delta h \lambda^2 e^{\lambda(a-x)}(-\sin \lambda(a-x) + \lambda a(\cos \lambda(a-x) - \sin \lambda(a-x)))}{(3 + 6\lambda a + 6\lambda^2 a^2 + 2\lambda^3 a^3)}$$

(6)

where $R$ is the local radius of curvature of the adherend. This expression is derived from the 2nd derivatives of equations (3) and (5), using values of constants from reference [4]. In the free zone, the absolute value of strain is:

$$\varepsilon_S(x) = \frac{3\Delta h \lambda^3 x}{(3 + 6\lambda a + 6\lambda^2 a^2 + 2\lambda^3 a^3)}$$

(7)

In equations (6) and (7), the parameter $\lambda$, which we term the “wave number”, is given by:

$$\lambda = \frac{\sqrt{2}}{2} \left( \frac{\bar{K}}{EI} \right)^{1/4}$$

(8)

Thus, from equations (6) and (7), when $a =$ constant, any change of the actual strain can only be caused by a change of $\lambda$, which in turn indicates a change of $E_A$ (and possibly adhesive Poisson’s ratio $\nu_A$, but to a lesser extent), other parameters being constant (cf. equation (2)).

To take full advantage of the relations presented, in this Winkler Non-Destructive (ND) mode, six strain gauges were attached to the outer surface of the flexible plate: three in the free zone, and three in the bonded zone. The wedge test technique used here was asymmetric and employed in the newly introduced ND modes.

The thin, or flexible, adherend was made from 8-ply CFRP (carbon fibres in an epoxy matrix – Hexcel, Berkeley, CA, USA) composite with a [0°/90°]2s stacking sequence and $1.17 \pm 0.02$ mm thickness. In order to decrease flexural rigidity of the plate, thus increase strain recorded at the upper skin of the adherend, the composite plate was initially abraded using 320 grit paper. The final thickness achieved was $h = 0.96 \pm 0.02$ mm. An aluminium plate of Hydronalium AA 5754, with thickness $H = 5.4 \pm 0.02$ mm, constituted the rigid substrate. The flexible adherend of length, $l = 120$ mm, was bonded to the rigid one, of length $L = 180$ mm, along a bonded zone of length $l_{\text{adh}} = 45$ mm, making an unbonded zone length of $65 \pm 0.2$ mm. The width $b$ of both adherends was 25 mm.

Prior to bonding, the aluminium surface was abraded with 320 grit emery paper, sand blasted with carborundum (SiC) particles of average diameter $60 \mu m$, and washed in an ultrasound bath (in

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**Figure 1.** Geometry of asymmetric wedge test and schematic representation of adhesive joint using the Winkler model.
ethanol). The CFRP plate was cleaned with ethanol. Subsequently, the plates were bonded with an epoxy-based adhesive resin: Araldite GY784BD (modified DGEBA, epoxy equivalent weight 196 - 208 g/eq.) crosslinked with Aradur 125 high viscosity polyamidoamine (PAMAM) hardener, supplied by Huntsman (Huntsman, Fullertone, CA, USA). The adhesive was prepared by mixing resin and hardener in a ratio of 2:1 by weight, respectively, following the supplier’s recommendation. Ambient conditions during the test, as for the crosslinking, were ca. 23 ± 2°C, ca. 55 ± 5 % relative humidity and 100kPa pressure. Two PTFE strips, of thickness 0.2 mm, placed on the bonded zone extremities, were used to assure sharply defined bonded zone edges (sharp crack front with a constant value of crack length). To provide a homogenous bondline thickness, the epoxy resin was filled (by the supplier) with glass beads of 0.2 mm diameter. Their presence, as well as that of the PTFE spacers placed at the extremity, resulted in a bondline of thickness $e = 0.2 ± 0.01$ mm as measured with a digital microscope system (Dino - Lite Pro-IS Production S.A., 01633 St. Genis Pouilly, France).

The procedure used for the ND wedge test can be summarised as follows. A tapered asymmetric wedge of thickness, $\Delta w = 0.9$ mm, is inserted to the desired position at the open bond end. To assure that the value of initial crack length is constant in all tests, two wedge positioning (stopping) pins are adjusted in the set up (placed at 61.5 mm from the crack front towards the unbonded zone). Since the aluminium wedge used has a tapered attacking edge (to allow smooth insertion), the crack length, defined as the distance between the line of contact of the wedge with the flexible adherend and the crack front was measured as $a = 62.0 ± 0.05$ mm. Measurements being made, then the wedge is removed after each test. Overall, the time taken for each of the measurements was a maximum of ca. 10s. No crack propagation was observed in this short time, as verified by microscopic examination of the side of the sample.

3. Ultrasonic air-coupled through-transmission technique

Ultrasonic measurements represent a useful and easy way to characterize material properties of a single component [6], as well as layered structures [7, 9]. Here, a through-transmission method was employed to infer elastic properties of the adhesive during crosslinking. Air-coupled transducers are used to follow advancing crosslinking of the adhesive joint at atmospheric pressure and ambient temperature. Transmitted waveforms through the sample are collected for several wave incidence angles $\theta$ and frequencies $f$ (figure 2). In the classic, direct problem of plane wave transmission, the complete transmitted acoustic field, including internal echoes, is a function of the incident angle $\theta$ and frequency $f$. The transmitted spectra modulus at each incidence angle $|A_{T}(f,\theta)|$ are calculated by multiplying the plane wave transmission coefficients $T(f,\theta)$ by the frequency spectrum $A_{I}(f)$ of the real wave measured with no sample between the transducers:

$$|A_{T}(f,\theta)| = |T(f,\theta)A_{I}(f)|.$$  (9)

In this manner, the effect of noisy experimental data, being in the wings of the frequency distribution due to the limited frequency bandwidth of the transducers, will be considerably reduced during the inversion process. The transmission coefficient is predicted using the surface impedance matrix method [8], which permits both fast and stable computations. This model takes into account the anisotropy and viscoelasticity of materials by using the concept of heterogeneous plane waves and complex viscoelasticity moduli, $C_{ij} = C'_{ij} + iC''_{ij}$ [9]. The plane wave condition considerably simplifies computations. Finite fields, on the other hand, would require the summation of plane waves over an angular aperture corresponding to that of ultrasonic transducers. As a result, the plane wave consideration has an important advantage for solving the inverse problem. The inversion scheme determines values of the viscoelastic coefficients, $C_{ij}$, of the material giving the best fit between theoretically predicted and measured transmission frequency spectra (figure 3), by using the Simplex method. The problem and procedure are covered in references [9, 10] and the method has been applied to infer both elastic and viscoelastic properties of materials. However, this application
to adhesive joints, specifically when change of the adhesive properties is expected with time, is, to our knowledge, novel. The main advantage over the method already used to study changes in the state of bonding agents [11], is gaining values of engineering constants (such as Young’s modulus). Therefore, the ultrasonic method presented is potentially both a qualitative and a quantitative tool.

In the adhesive joint, shown schematically in figure 2, two of the constituents, the adherends (in the present case, composite CFRP and aluminium AA5754), are preliminary characterised separately by using through-transmission measurements and the inversion technique. Also, the required thicknesses and densities of the assembled plates were measured before adhesive bonding was realised. These characteristics are used for calculations of the theoretical spectra of transmitted waves through the adhesive assembly. Therefore, only the viscoelastic properties of the adhesive are unknown in the theoretical model, and only their change in time can lead to changes in the transmitted wave field. In this paper we consider only the real part of the $C_{ij}$ moduli in order to compare results with the wedge test method. The adhesive material is assumed to be isotropic and can be characterised by elastic coefficients $C_{11}$ and $C_{66}$.

3.1. Ultrasound setup

In the case of ultrasonic inspection, the sample was made from the same materials as in section 2, whilst the geometry used was necessarily different. The CFRP composite plate, the same as for the wedge test, but now of dimensions 150 x 150 x 1.17 mm$^3$, was bonded to a rectangular aluminium alloy plate 150 x 150 x 3 mm$^3$. Surface preparation for the aluminium was kept as before. However, preparation of the CFRP in this case was limited to cleaning with ethanol and drying before bonding. Since a vertical orientation of the plate is required in this test, special spring jigs were used to prevent any relative movement between the composite and aluminium plates. PTFE spacers at the joint extremities were not used here. This had, as a consequence, a reduced bondline thickness, compared to the wedge test. Measured bondline thickness was $e = 0.16 \pm 0.01$ mm (calliper gauge and dial gauge).

An air-coupled transmitter was excited with a chirp frequency range of 250 kHz to 450 kHz. The reference signal is transmitted directly to an air-coupled receiver without a sample in between. This was measured with low voltage amplification on the transmitter and a low gain on the receiver, to

![Figure 2. Schematic representation of air-coupled ultrasound through-transmission method for characterisation of adhesive elastic coefficients.](image)

![Figure 3. Optimisation of $C_{ij}$ coefficients by minimising cost function between theoretical (—) and experimental (○) spectra of transmitted waveform.](image)
prevent saturation of the signal. The bonded sample was placed between both transducers on a
motorised goniometer, and parallelism between sample plate and transducers was carefully adjusted.
Wave coupling between air and the solid medium is expected to be very poor and consequently
acoustic energy transmitted through the sample to be very low. Therefore, both amplification voltage
excitation and reception gain must be increased significantly to get signals transmitted through the
sample (this can be done with the assumption that the frequency response of the instrumentation is
constant and independent of the gain). In addition, signals were averaged over 2000 acquisitions in
order to remove any additional noise from instrumentation and obtain a high signal-to-noise ratio.

Subsequently, through-transmission signals were collected at different times during the
crosslinking period of the epoxy adhesive, and at several angles of incidence, \( \theta \), between 0° and 12°
with a 2° step, in order to optimise values of the elastic moduli \( C_{11} \) and \( C_{66} \). In the optimisation
process, transmission spectra are normalised to overcome the gain discrepancy between the reference
signal and through-sample signals (low gain for the reference signal and high gain for through-
sample signals). Values of elastic moduli are optimized so that predicted transmitted fields fit at best
those measured, over every incidence angles.

4. Results and discussion

4.1. Crosslinking evolution

Crosslinking occurs in three basic stages, during which the polymer transforms from a viscous liquid
to a rigid solid viz. resol-resitol-resit [12]. Resol is a polymer in which no crosslinking has yet
occurred and is within its gel time. Resitol corresponds to a partially crosslinked, partially unreacted
polymer. Finally, resit consists of (mostly) crosslinked adhesive, since completing crosslinking at

![Figure 4. Data obtained from ultrasound technique representing change in C11, on a logarithmic time scale.](image)

![Figure 5. Variation of characteristic parameter \( \lambda \), during crosslinking on a logarithmic time scale. Points indicate optimised \( \lambda \) values from experimental results and using the Winkler model. Three stages can be identified.](image)

room temperature is very hard to achieve because the reaction of secondary (or tertiary) amine
groups may be blocked (correct mixing ratio is crucial), and leads to residual, unreacted epoxy
groups, therefore the final resin state of the adhesive is rarely achieved.

We address first the influence of the evolution of crosslinking on parameters $\lambda$ and $C_{11}$ from both
the wedge and ultrasound measurements. Evolution of the measured parameters appears smooth with
no particular discontinuity occurring. As can be seen, the results obtained with the two different
approaches present the same trend of crosslinking kinetics. The three expected stages can be
identified from the wedge test data (figure 5): an initial, slow reaction (resol), acceleration (resitol),
and deceleration (resit) leading to (the same) final curing time. From the ultrasound data (figure 4)
the resol stage cannot be identified, because early crosslinking data are not available. Regarding the
resitol and resit stages, data from both techniques show the same trend of deceleration and plateau
reaching, which is associated with the decreasing rate of the crosslinking reaction. Therefore, the use
of the wedge test and Winkler model, which shows the change in elastic properties of the adhesive
with time at constant crack length, seems to be a suitable and meaningful way of estimating curing
time as well as monitoring adhesive properties.

4.2. Comparison of Young’s modulus obtained from both methods

Although parameters $C_{11}$ and $\lambda$ are both sensitive to crosslinking kinetics, and follow a similar trend,
they cannot be compared directly to a mechanical property. From both techniques presented in this
paper, it is possible to obtain the Young’s modulus, which is a standard parameter related to
mechanical properties of the bonded joint.

To obtain Young’s modulus of the adhesive $E_A$, from the ultrasound method, the modulus $C_{66}$
(which is equal to the shear modulus $G_A$) should also be estimated, because it is required together
with $C_{11}$ [13], since Young’s modulus can be expressed as

$$E_A = C_{66} \frac{3C_{11} - 4C_{66}}{C_{11} - C_{66}}. \quad (10)$$

The normal incidence signal is used for the characterisation of the $C_{11}$ coefficient, since the
longitudinal wave is insensitive to $C_{66}$ for that angle. Angles of incidence above $0^\circ$ are expected to
generate both longitudinal and shear wave modes inside the sample, shear wave modes being used
for characterisation of $C_{66}$.

From the wedge test method, having established the value of the wave number $\lambda$, it is then
possible to estimate Young’s modulus of the adhesive. Wave number is essentially a function of one
variable during crosslinking, the rest remaining constant: $\lambda = f(E_A) \propto E_A^{1/4}$ (see equations (8)
and (2)).
Values of Young’s modulus calculated from both techniques are compared in figure 6. Clearly, there is good agreement between the two methods for values of modulus obtained towards completion of chemical reaction, but this is less good near the start of the crosslinking. The discrepancy between ultrasound method and wedge method during the first phase of crosslinking could be explained by a low sensitivity of ultrasound due to high viscosity at the first stages of crosslinking. As a result, the uncured adhesive has a low shear stiffness, and we observe a poor sensitivity of the transmission spectra when optimising $C_{66}$ values, this unsensitivity probably being reinforced by the very low thickness of the adhesive bond. High uncertainty on $C_{66}$ values results directly from high uncertainty on Young’s modulus. In addition, high frequencies used with the ultrasound method (dynamic regime) are expected to give a higher value of Young’s modulus compared to the wedge Young’s modulus (quasi-static regime), this is observed during crosslinking. When the rate of crosslinking is maximal and reaches a plateau, we observe that both methods give a very good agreement of $E_{\text{wedge}} = 1.36$ GPa and $E_{\text{US}} = 1.40$ GPa at $t = 100$ hours. The ultrasound method also gives the shear modulus $G = C_{66} = 0.51$ GPa. For the characterisation of the cured adhesive, which represents the most frequent cases, both methods give consistent results and present a great interest for non-destructive evaluation of mechanical properties of adhesive bonds.

5. Conclusions
The curing of a DGEBA-PAMAM adhesive has been studied with two non-destructive approaches. One was based on an instrumented, asymmetric, wedge test technique, where changes of strain measured on the bent substrate during wedge insertion (without causing fracture) reveal the state of the adhesive. The second was based on an ultrasound through-transmission method, where changes of optimized transmitted spectra yield the adhesive properties. The main conclusions are as follows:

- Application of the Winkler model to the adhesive joint allows quantitative estimation of the adhesive properties, changing with time, as well as curing time itself.
- The ultrasonic through transmission method using inverse problem solution allows estimation of curing time and adhesive properties during crosslinking, when an actual adhesive joint is used.
- The final properties of the DGEBA-PAMAM system in question, as obtained with wedge test and ultrasonic experiments, are: $E_A = 1.38$ GPa as an average from both methods, and $G_A = 0.51$ GPa given by the ultrasound method.

The problem of non-destructive evaluation of curing time is particularly important in structural applications. Thus, these methods could allow in situ, non-destructive measurements to be made on a
structure in service. On the contrary, standard techniques, such as thermogravimetry (TG or TGA), calorimetric spectroscopy (CSC) and dynamic mechanical and thermo-mechanical analysers (DMA or DMTA) tend to be destructive and/or do not give the opportunity for use on working structures. In addition, they are devoted to polymers alone. This study shows the potential of the two techniques presented to be developed together, or separately, for applications in non-destructive testing (NDT), and for monitoring the development of strength in situ of structural adhesive bonding.

Acknowledgments
We would like to thank the company Rescoll for free supplying of the adhesive components. The work on the ultrasound method has been done in the framework of INMAT2 project.

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