

The application of molecular simulation to the rational design of new materials: 2. Prediction of the physico-mechanical properties of linear epoxy systems*

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Molecular simulation was used to calculate the physico-mechanical properties of a linear epoxy system. Values of glass transition temperature (T_g) compare well with experiments as did elastic moduli. A correlation between hydrogen-bonding energy and T_g was derived indicating the importance of hydrogen-bonding in this system. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Epoxy resins are a very versatile family of polymers that may be converted (from polyfunctional monomers) to thermoset products through reaction with well over fifty classes of compounds¹. Bisphenol A and epichlorohydrin often form the basis of these widely used commercial resins which find application in such diverse areas as protective coatings and structural applications (e.g. laminates and composites, tooling and moulding, casting, construction, bonding and adhesives). As they have low molecular weights, these epoxide resins² need to be crosslinked to make them into useful products. Linear (primary and secondary) amines are generally used as low-cost and low-viscosity crosslinking agents (hardeners). Aromatic amines, however, have a much lower activity than the aliphatic amines, and are therefore used for higher temperature curing (usually at *ca.* 150°C) systems to produce cured resins with good strength and chemical resistance.

The amine-induced cure of epoxides and subsequent crosslinking chemistry is very complex, and a number of competing reactions have been identified^{3–5}. These reactions depend on the ratio of the amount of epoxy-containing moiety. Using stoichiometric amounts, addition reactions take place, which with multifunctional curing agents and epoxy moieties lead to three-dimensional, crosslinked networks. With catalytic amounts, the epoxy moieties undergo homopolymerization, but this reaction can also occur on raising the temperature of the previous systems. As part of our continuing interest in the structure and mechanisms of epoxy resins, we have studied the kinetics of the stoichiometric reaction by using a novel radiochemical method³, and are currently

studying the homopolymerization reaction with novel transition-metal-containing curing agents^{6–11}. Our previous work on the stoichiometric reaction³ was concerned with model chemical compounds that were unable to form the long chains that are characteristic of fully cured epoxy resins, and so the logical extension was to increase the complexity of the systems so as to enable chain formation, but also to prevent crosslinking which makes the system relatively intractable from a chemical analysis point of view. Hence, the curing agent, 1,2-dianiloethane (DAE), was chosen for this study (Figure 1) as it has two reactive hydrogens to complex, but lacks the ability to crosslink. The epoxy moiety chosen was Bisphenol A diglycidyl ether (BADGE), one of the most commonly used materials in aerospace applications. The study was performed on two fronts, which concerned both the chemical properties and a computational simulation of the polymeric materials. Earlier publications^{12,13} have concentrated on the changes in conformation of the epoxy moiety under compressive and tensile stresses and as a function of temperature. This paper concentrates on the computer simulation of the physical and mechanical properties of the linear epoxy system and the correlation with the mechanical measurements of the same. When considering the design of new materials by computer simulation an evaluation of the confidence limits between simulated and actual properties is vital for the wider application of these techniques.

EXPERIMENTAL

Materials

Bisphenol A diglycidyl ether, BADGE, (EPON[®]825, 99.5%) was obtained from Shell Chemicals. 1,2-Dianiloethane (DAE) *ex* Aldrich (99.5%) was recrystallized prior to use.

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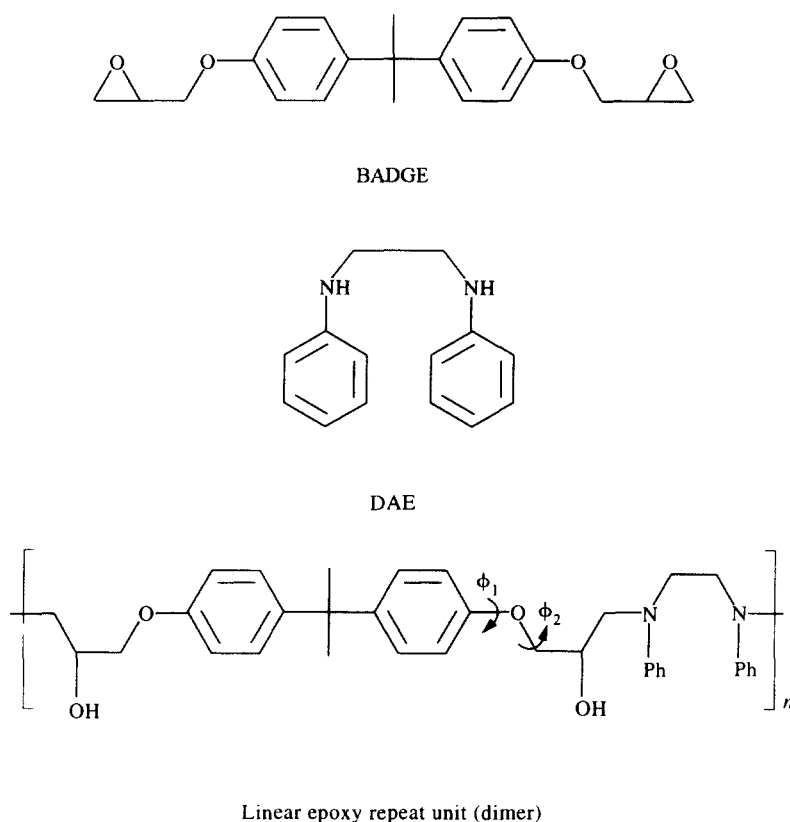


Figure 1 Structure of the linear epoxy polymer examined in this study

Table 1 'Instron' operating conditions used to measure the elastic constants in this work and the constants derived therefrom. Samples 1–4 refer to different experimental samples

Sample	Area (mm ²)	Crosshead speed (mm min ⁻¹)	Young's modulus (GPa)	Poisson's ratio
1	23.85	0.5	4.092	0.375
2	25.33	0.2	3.605	0.354
3	24.44	0.2	3.500	0.345
4	23.98	0.2	4.175	0.366
Mean (σ)			3.843 (± 0.340)	0.361 (± 0.013)

The confidence levels at 95% are ± 0.33 and ± 0.013 for Young's modulus and Poisson's ratio respectively

Equipment

¹H n.m.r. was performed at 298 K on a Bruker AC300 spectrometer operating at 300 MHz. Differential scanning calorimetry (d.s.c.) was performed on samples (7 ± 2 mg) using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyser. Measurements were made under nitrogen ($40 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate 10 K min^{-1} . All T_g determinations were calculated using Du Pont software. Thermomechanical analysis (t.m.a.) was performed on sample discs (1 cm diameter \times 2 mm deep) using a Du Pont 943 t.m.a. interfaced with a Du Pont 9900 computer/thermal analyser. Measurements were made at a heating rate of 2 K min^{-1} . All determinations were calculated using Du Pont software. The linear coefficient of thermal expansion (α) was also determined from the t.m.a. data. Gel permeation chromatography (g.p.c.) was performed on a Waters system comprising a model 510 pump/injection system, model 490 u.v. detector, and two columns (a Polymer Laboratories PLgel 3μ mixed-E and a Waters μ -STYRAGEL, pore size 10^4 \AA). The eluent was dichloromethane/methanol (95/5) and the

flow rate was $1 \text{ cm}^3 \text{ min}^{-1}$. The instrument was calibrated (at 354 nm) using polystyrene standards of known molecular weight and recalibrated using epoxy oligomers (prepared for g.p.c. analysis from DAE and phenyl glycidyl ether to form 1/1 and 2/1 adducts) at 254 nm. The densities of these samples were measured using a Mettler (model ME-33360) density determination kit. Samples were initially weighed in air and then in distilled water of a known temperature. All epoxy samples were tested on an 'Instron' Universal Testing Apparatus (model 1175) incorporating an electronically calibrated force measuring system with load cell strain gauges for detecting the load applied to a specimen under tension or compression. The 'Instron' conditions used to measure the elastic constants are tabulated in Table 1.

Theoretical property calculations

All property calculations were performed by two methods: (a) the group contribution (additive) method based on the work of van Krevelen¹⁴ and (b) by direct atomistic simulation.

Group contribution method. The density was calculated from

$$\rho(298 \text{ K}) = M / \sum_{i=1}^n V \quad (1)$$

where $M = 552$ (the molar mass of the repeat unit), values of V are the molar volumes of the individual groups and $i =$ number of groups. Using equation (1), the density of the linear epoxy was calculated to be 1.12 g cm^{-3} in the glassy state and 1.16 g cm^{-3} in the rubbery state.

Cohesive energy was obtained by a summation of each group contribution; the value of E_{cohesive} was calculated to be $59.71 \text{ kcal mol}^{-1}$ for the linear epoxy system. The Hildebrand solubility parameter was calculated from this cohesive energy using

$$\delta = [E_{\text{cohesive}}/V_m]^{1/2} \quad (2)$$

where V_m is the molecular volume in $\text{cm}^3 \text{ mol}^{-1}$. The value of $\delta = 12.22 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ was obtained for the linear epoxy system.

The bulk modulus was calculated using

$$B = \left[\sum_{i=1}^n U/M \right]^6 \rho \quad (3)$$

where U is the group contribution to Bulk modulus, M is the molar mass in the glassy state, ρ is the value calculated above and i is as above.

Direct atomistic simulation. All calculations were performed using POLYGRAF v.2.2 on a Stardent 'TITAN II' graphics minisupercomputer and on a CONVEX C3840 at the University of London Computing Centre. For some calculations professional POLYGRAF v.3.2 was used at the BP Research Centre, Sunbury and at Queen Mary and Westfield College, London. The force field used was DREIDING II¹⁵. The experimental density (1.17 g cm^{-3} at 300 K) was used to build models of the amorphous polymers using the amorphous builder in POLYGRAF v.2.2. Twenty structures were generated by Monte Carlo methods to obtain a representative number of configurations. Ten of the lowest energy structures were extended into infinite chains using the method of Weber *et al.*¹⁶, by extending the periodic boundary conditions and joining the head of the image to the tail of the chain. Molecular dynamics and energy minimization were used to remove high energy contacts resulting from this process. The scheme which was found to give the best results was as follows:

1. The periodic boundary cell was fixed and the molecule allowed to minimize to less than $0.1 \text{ kcal mol}^{-1}$.
2. Micro-Canonical Molecular Dynamics was used for 1000 steps from 600–300 K.
3. Repeat above procedure three times.
4. An adiabatic molecular dynamics (MD) algorithm (EPN) was applied from 100–300 K. Both the cell and the molecule were allowed to equilibrate. The run continued until the cell temperature reached the equilibrium temperature of 300 K.
5. Repeat step (1).
6. A canonical algorithm (TPN) was then applied at 300 K to the molecule in the periodic boundary cell

until a steady state volume was achieved. This typically took 15 ps.

7. A conformer from the later half of the run which had the lowest energy was extracted from the trajectory.
8. Energy minimization was applied to this conformation until energy convergence was reached.
9. This energy minimized conformation was used in the 'ELASTICA' module¹⁷ to give the mechanical properties.

Ten conformations were used to determine the mechanical properties and the results averaged.

Atomistic simulation of physical properties

Ten amorphous cells were built using the amorphous builder, the densities in each case were set to 1.17 g cm^{-3} as previously determined experimentally for the linear epoxy system. Typical cell constants were of the order of 10.23 \AA for a cell edge and the cell contained between 73 and 146 atoms. Ten cells of the following amine (A): epoxy (E) ratios were constructed: A:E amine:epoxy; (AE)₂ dimer of amine:epoxy; (A₂E) amine:epoxy:amine adduct; (AE)_∞ infinite periodic chain of amine:epoxy adduct.

The following procedures were used:

1. The polymer chain was energy minimized while the periodic boundary cell was fixed or until energy convergence was reached. This process was then repeated with the polymer chain fixed to give the starting volume of the cell at zero Kelvin;
2. the model with the lowest potential energy was extracted and the simulated temperature was raised from 0–500 K while the cell was fixed. This was typically carried out over a 15 ps period;
3. the temperature was lowered to 450 K and the volume of the cell and the molecule were allowed to reach equilibrium in the EPN ensemble over 100–150 ps period;
4. the temperature was lowered by 10 or 50 K depending on the model and the volume equilibration repeated until 100 K was reached.

Thermal expansion coefficients and specific volumes were calculated from these data and plotted vs temperature to determine the T_g as shown in Figure 2.

RESULTS AND DISCUSSION

Physical properties

The T_g values from experiment and simulation are given in Table 2. There is a trend towards higher T_g

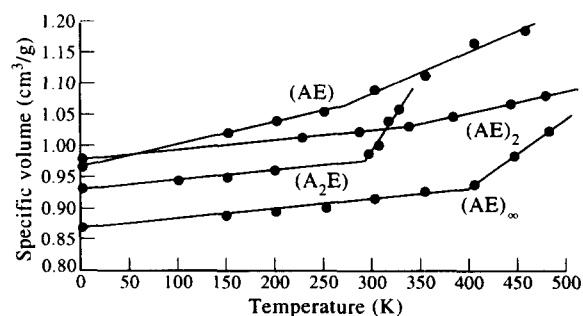


Figure 2 Graph of specific volume vs temperature for the systems: A:E amine:epoxy. (AE)₂ dimer of amine:epoxy. (A₂E) amine:epoxy:amine adduct. (AE)_∞ infinite periodic chain of amine:epoxy adduct

concurrent with oligomer length and this is reproduced well in the simulation. The graph of calculated specific volume vs temperature shows this trend. The T_g values from simulation are on average within 20 K of the experimental and this is well within the variations of T_g values from actual measurements. An interesting result from the simulation occurs if the hydrogen bonding energy is plotted vs temperature (Figure 3): the hydrogen bonding energy decreases with temperature and reaches a constant value at the T_g of the system. The hydrogen bond energy in this simulation is calculated from a specific 12,10 function with a smoothing cubic spline function to deal with cut-offs.

$$E_{hb} = \sum E_{hb} \cos^4(\theta_{AHD}) S(R_{AD}^2, R_{on}^2, R_{off}^2) \times S[\cos^2(\theta_{AHD}), \cos^2(\theta_{on}), \cos^2(\theta_{off})]$$

where D = H bond donors, A = H bond acceptors, $S() = 1$ for $R < R_{cut}$, $S() = (R_{on} - R)^2(R_{off} - 2R - 3R_{on}) / (R_{off} - R_{on})^3$ for $R_{on} < R < R_{off}$, $S() = 0$ for $R_{off} \leq R$, $R_{on} = 8.0 \text{ \AA}$, $R_{off} = 8.5 \text{ \AA}$, $R_{cut} = 9.0 \text{ \AA}$, $\theta_{on} = 65^\circ$, $\theta_{off} = 75^\circ$, and $\theta_{cut} = 90^\circ$.

$$E_{hb} = D_0 \{ 5[R_0/R]^{12} - 6[R_0/R]^{10} \}$$

where D_0 = hydrogen bond strengths in kcal mol^{-1} , $R = \text{A} \dots \text{D}$ distance (\AA), and R_0 = ideal $\text{A} \dots \text{D}$ distance (\AA).

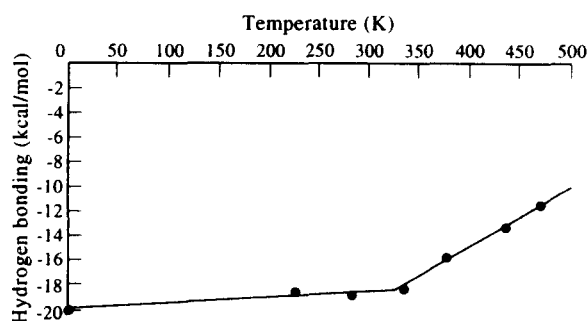


Figure 3 Graph of hydrogen-bonding energy vs temperature for the $(\text{AE})_\infty$ simulation

Table 2 Glass transition temperatures (T_g) in Kelvin

Oligomer	Experimental	Simulation
$(\text{AE})_\infty^a$	358	380
$(\text{AE})_2$	317	323
(A_2E)	302	288
(AE)	284	262

^a Group contribution values were calculated for this model (see Figure 1)

Table 3 Elastic constants (and standard deviations) derived from experimental, computer simulation and group contribution studies during the course of this work. These values were calculated from the model represented as $(\text{AE})_\infty$

	Experimental ^a	Simulation	Group contribution
Young's modulus, E (GPa)	3.84 (± 0.34)	5.84 (± 2.40)	4.15
Bulk modulus, B (GPa)	4.61 (± 0.12)	5.36 (± 2.68)	4.32
Poisson's ratio, ν	0.36 (± 0.01)	0.37 (± 0.09)	0.34
Lamé constant, μ (GPa)	1.41 (± 0.17)	2.05 (± 0.91)	1.55
Lamé constant, λ (GPa)	3.67 (± 0.01)	6.19 (± 2.94)	3.29

^a These data represent mean values of data presented in Table 1

It would be expected that in an epoxy resin system containing hydroxyl and amine groups there would be the possibility for hydrogen bonding. It is not unreasonable therefore to assume that the observed properties would depend to some extent on the hydrogen bonding taking place. It was gratifying to see from our simulation that this did seem to be the case. Before the onset of main chain motion, i.e. below the T_g , the hydrogen bonds are effectively frozen in place and cannot reorientate. Above the T_g there is a degree of main chain motion and the hydrogen bonding groups can reorientate. The elevated temperature in the simulation also provides the energy to break these bonds, so that total hydrogen bonding energy falls as the temperature rises. From the plot, Figure 3, this can be clearly seen and this therefore provides another method of estimating the T_g in this polymer system. The Hildebrand solubility parameter ($12.23 \pm 0.11 \text{ cal}^{1/2} \text{ cm}^{3/2}$) and cohesive energies ($59.81 \pm 4.86 \text{ kcal mol}^{-1}$) calculated from simulation are in excellent agreement with values calculated from group contributions.

Mechanical properties

The elastic constants calculated from theory, simulation and experiment are summarized in Table 3. All the results are directly comparable when the associated standard deviations are taken into account. However, there are a few factors that should be borne in mind when making such a comparison. Firstly, temperature plays a significant role in the magnitude of the elastic constants. The experimental and theoretical results show closer agreement because both procedures represent results taken at 298 K. The simulation values, however, were calculated at zero Kelvin, thus giving the elastic constants higher values than expected. Secondly, the size of the model used in the simulation experiment must be considered. The program has a 200 atom limit and only ten models were constructed. If it was desired to perform a simulation that gave mechanical and physical properties as accurately as possible, it would be necessary to simulate a much larger model, e.g. a chain of 200 atoms or more. This would then be a more representative model of the polymer and allow for the flexibility of the chain to be variable. However, these types of simulation are very demanding on computer time and suffer from the inherent problems of all models, in that the results obtained are only as accurate as the model used, i.e. there may be some feature of the polymer that is still overlooked in a much larger model.

It was our intention in this paper to investigate the potential for using molecular modelling in conjunction with experimental data. Hence, the simulations must be fast enough to be on the same timescale as the

experimental work. If it takes much longer to simulate the polymer than to make cast resin plaques and test them, then this approach is invalid. An additional constraint was imposed on us by the 200 atom limit in the version of the POLYGRAF software used.

$$\begin{aligned} \text{Elasticity tensor} = U &= U_0 + \sum_i (\partial U / \partial \epsilon) \epsilon_i \\ &+ 1/2 \sum_j (\partial^2 U / \partial \epsilon_i \partial \epsilon_j) \epsilon_i \epsilon_j \\ &+ \text{higher order terms} \end{aligned}$$

where U_0 = equilibrium energy, ϵ = strain, compliance matrix $C_{ij} = \partial^2 U / \partial \epsilon_i \partial \epsilon_j$, and stiffness matrix $S = C^{-1}$.

The mechanical properties are calculated from the stiffness matrix, which is the inverse of the compliance matrix. The latter is derived from the second derivative of the molecular mechanics potential energy with respect to the simulated applied strain. The storage of the compliance matrix, as it is the matrix of second derivatives requires large amounts of memory, hence the 200 atom limit. The current version of the software, which has only recently been released has overcome this constraint. This atom limit allowed defined the upper size limit for the models used in our simulations.

We judged these simulations to be successful if the physical and mechanical properties calculated were at least of the same order of magnitude as the experimental properties. In practice they turned out to be much better than expected, providing some degree of confidence in the ability to provide guidance to the expected physical and mechanical properties of polymers from limited molecular simulation. We have also simulated linear polyarylethersulfones¹⁸ and polycyanurates¹⁹ using similar procedures and a recent review of this work has recently been published²⁰. Ideally, an isotropic model should be built, but the probability of building an amorphous model that displays some anisotropic behaviour is quite high, even after relaxing the system using molecular mechanics (MM) and MD algorithms. Therefore, the elastic constants will vary from one model to another depending on the degree of anisotropy. This results in relatively large standard deviations between elastic constant values. Finally, one important factor that has not been accounted for in the model is the influence of macroscopic defects (e.g. voids and structural defects such as cracks, phase separation, incomplete cure, etc.). Our model represents an ideal system with ideal interactions between atoms and molecules, leading to simulated elastic constants with unexpectedly high experimental values. By considering these three factors it can be concluded that the simulation results represent the upper limits of the elastic constants.

With limited simulation such as we have carried out in this paper, the question of the significance of the results is always paramount. With the mechanical property simulation this is less important because the results are the statistical average of the ten model polymers simulated. This point, however, becomes more important with regard to the glass transition temperature (T_g) values. Owing to the computationally intensive nature of molecular dynamics simulation, it was not feasible (with the facilities available to use at the time of performing this work) to carry out a statistical average of the T_g simulation. Hence, the question of whether the results

are a fortunate coincidence remains; it would have been better to repeat the simulation with several models to gain confidence in the results. The T_g simulation is of course repeatable and reproducible because it is the nature of molecular dynamics that the same model starting with the same random number seed will give the same trajectory.

CONCLUSIONS

The molecular simulation of linear epoxy systems gives mechanical and physical properties that are in reasonable agreement with experimentally determined values indicating the potential of molecular simulation for the prediction of polymer properties. Additionally, the molecular simulation is able to provide information about interactions occurring in the system that influence these properties, viz. the good correlation of hydrogen bonding energy with T_g . In a system such as epoxy resins where many potential hydrogen bonding sites are available this is particularly encouraging.

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APPENDICES

Appendix 1 Preparation of epoxy sheets

Equimolar mixtures of BADGE and DAE were dissolved in chloroform. The resulting solution was then filtered through a sinter funnel and the bulk of the solvent was removed using a rotary evaporator at a temperature of *ca.* 50°C. The solution was then transferred to a vacuum oven (set at 100°C) for 1 h, during which time the chloroform was completely removed. ¹H n.m.r. was employed to determine the extent of residual chloroform (from its characteristic singlet at δ 7.25 ppm). A mould (Figure A1) was

constructed by applying silicone grease evenly over one side of two glass plates. A strip of pink 'melonex' (containing a fine coating of silicone) was cut and placed over the greased surface and a metal strip covered in tissue paper was used to remove air bubbles from the surface of the 'melonex'. Metal separators were used to maintain the required 3 mm distance between the glass plates when clamped, while a silicone rubber tube (*ex* BDH-Merck, i.d. 1.6 mm, o.d. 4.9 mm, tube size 14) was used as the mould. The sample was transferred by syringe into the completed mould and subsequently polymerized in a normal oven at 100°C for a 12 h period. The sample was allowed to cool overnight before being removed from the mould.

Appendix 2 Preparation of mechanical test pieces

The polymerized epoxy plates were cut into strips (50 × 8 × 3 mm³) using a water-cooled diamond wheel. The strips were lightly sanded to remove ripples on the surface and any silicone release agent from the 'melonex', while the dust was wiped off with a cloth dampened with aqueous methanol. Aluminium tabs were cut (12 × 8 × 1.5 mm³) and lightly abraded on both sides. The surface was then wiped with a cloth dampened with aqueous methanol. To one side of the tabs and the test sample was applied a coating of cyanoacrylate adhesive ('superglue'). The two surfaces were then placed together and a weight placed upon them to assist adhesion (Figure A2). All samples were left for a minimum of 24 h (under load) to harden, before testing commenced. Two 5 mm strain gauges (Tokyo Sokki Kenkyujo Co.) were placed on the strips (using cyanoacrylate adhesive), one parallel to the length of the samples (Young's modulus) and one perpendicular to it (Poisson's ratio).

The density, which is the reciprocal of specific volume, was determined experimentally using the following formula:

$$\rho_T = W_{(air)} / [W_{(air)} - W_{(H_2O)T}] \rho_{(H_2O)T}$$

where ρ_T is the density of the sample at temperature *T*, $W_{(air)T}$ is the weight of the sample in air, $W_{(H_2O)}$ is the weight of the sample in water at temperature *T* and $\rho_{(H_2O)T}$ is the density of distilled water at temperature *T*.

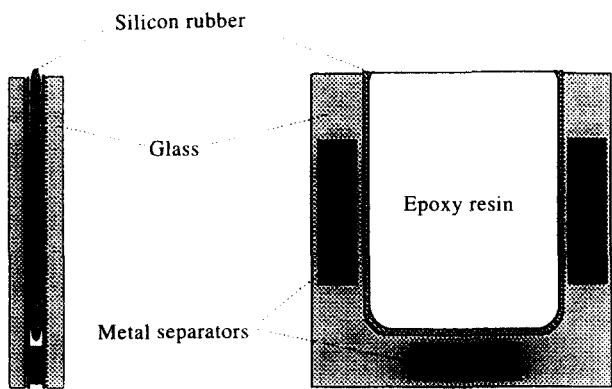


Figure A1 Schematic of the mould used to prepare the cast resin samples for physico-mechanical testing

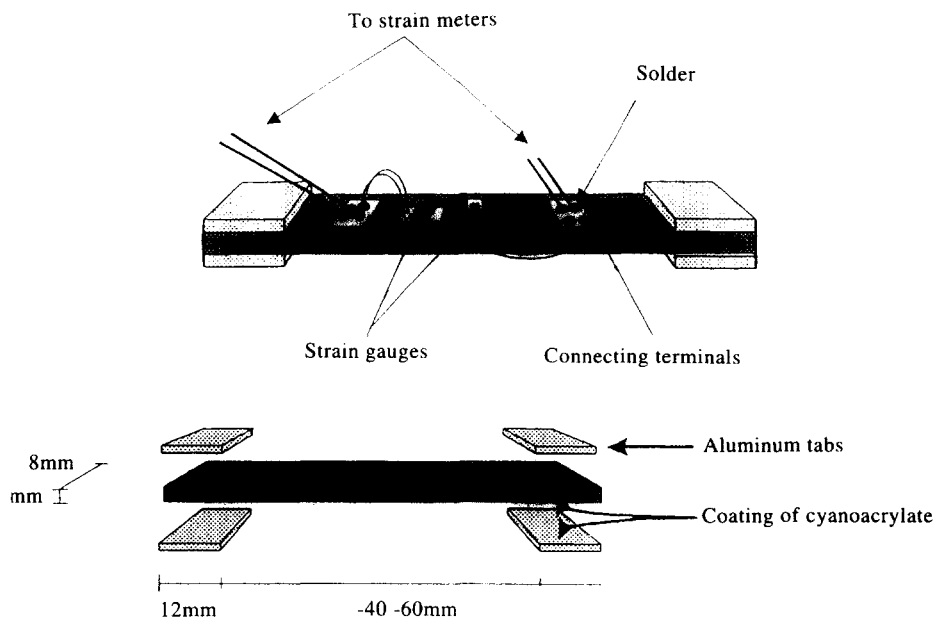


Figure A2 Preparation of cast resin samples for mechanical testing