

Evaluation of a Multi-Functional Adhesives Test Station

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Project PAJ1: Failure Criteria and their Application to Visco-Elastic/Visco-Plastic Materials.

Report No 12
(Milestone 4)

April 1999

SUMMARY

Development of a multi-purpose test instrument capable of characterising the properties of flexible adhesives in the liquid state, during cure and in the solid state would significantly simplify adhesives testing. Modern rheometers have sophisticated measurement capabilities and offer promise as a multi-functional technique. The oscillatory measurement functions enable measurement of the visco-elastic properties of adhesives. The multi-frequency and temperature scanning capabilities allow determination of transitions in material properties.

However, the stiffness of the instrument is a major source of error in measurements on solid materials. Techniques have been developed for correcting results for the instrument compliance. The correction factor increases as the stiffness of the sample increases. It is essential that corrections are applied when measuring 'solid' adhesives. Despite modifications to increase the rheometer's stiffness, it is still too compliant to accurately determine the properties of materials with shear moduli greater than 500 MPa. However, the instrument appears to be suitable for studying lower modulus materials, such as flexible adhesives above the glass transition temperature. The high sensitivity of the measurement and control functions of the instrument may offer advantages over conventional tension or DMTA methods for low modulus materials.

The modified Carrimed CSL500 rheometer is capable of operating as a multi-functional test station for flexible adhesives. The instrument is able to measure the flow properties of adhesive resins, their curing behaviour and their mechanical properties.

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ISSN 1361-4061

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Approved on behalf of Managing Director, NPL by Dr C Lea,
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1. INTRODUCTION

Rheological measurement methods are widely used for characterising the flow and dispensing behaviour of adhesives. This information is required for adhesive formulation development and the design of processing equipment. The basic measurement techniques for characterising shear flow rheology were described in an earlier report⁽¹⁾. A previous project demonstrated the use of oscillatory rheometers to monitor the development of the mechanical properties of an adhesive as it cures⁽²⁾.

Development of a multi-purpose test instrument capable of characterising the properties of flexible adhesives in the liquid state, solid state and intermediate states during cure would significantly simplify adhesives testing. One of the aims of Project PAJ1 of the DTI Materials Metrology Programme - Performance of Adhesive Joints - was to establish the feasibility of developing such an instrument. The controlled stress rheometer used in the earlier work on cure monitoring was used as the starting point for this work. The accuracy of measurements in the final stages of the cure was compromised by the compliance of the rheometer. A significant proportion of the measured angular rotation was occurring through deformation of the shaft of the rheometer rather than in the specimen. To improve the capability for testing solids, modifications were made to the rheometer which reduced the compliance from, at best, 1.96 mrad/Nm (stiffness $K = 510 \text{ Nm/rad}$) to 1.64 mrad/Nm ($K = 610 \text{ Nm/rad}$). These modifications are described elsewhere⁽³⁾. Methods for correcting for the remaining compliance in the instrument were also developed and these are outlined in Appendix I.

The aim of this report is to assess the modified instrument's capability for measuring the mechanical properties of flexible adhesives. The modes of operation studied were:

- 1) oscillatory measurements at a constant torque or displacement amplitude (using the frequency sweep and temperature sweep functions) - analogous to dynamic mechanical thermal analysis⁽⁴⁾, commonly known as DMTA;
- 2) torque sweep using increasing oscillation amplitudes - to mimic shear stress-strain measurements (e.g. a butt torsion test).

Further assessment of the instrument using transient methods (creep and stress relaxation) will be described in a subsequent report⁽⁵⁾.

2. EXPERIMENTAL

2.1 APPARATUS

2.1.1 Controlled Stress Rheometer

The Carrimed CSL 500 controlled stress rheometer is shown in Figure 1. Modifications made to the standard equipment are detailed elsewhere⁽³⁾. Figure 2 shows the modified, splined shaft adaptation to increase the stiffness of the instrument. The instrument is capable of high precision measurements. The angular displacement resolution is 1×10^{-5} rad and the torque resolution is $1 \mu\text{Nm}$ (full range is $49,999 \mu\text{Nm}$). The gap can be set to within $\pm 2 \mu\text{m}$. The measurement geometry used was a 10 mm diameter parallel plate system. The measurement gap was set to 1 mm. Thus, from the measurement geometry dimensions⁽¹⁾, strain is measured to $\pm 5 \times 10^{-5}$ and stress is measured to $\pm 0.08 \text{ Pa}$. Temperature is controlled using either the standard Peltier temperature control system or an optional extended temperature module (ETM) system. The Peltier system controls the temperature by directly heating or cooling the specimen plate. It provides a relatively fast response time to changes in temperature. It can, however, only operate over a limited range of temperatures (0 to 80°C). The ETM system enables tests to be carried out over a wider range of temperatures, ranging from -120°C to over 300°C . The extended temperature module consists of two parts. There is a heating coil that surrounds the specimen. The two plates which clamp the specimen contain channels that allow circulation of liquid nitrogen coolant. The ETM can operate over a wider range of temperatures but does not give as stable temperature control as the Peltier system. Temperature is measured using a PT100 platinum thermocouple that is embedded just beneath the surface of the lower plate.

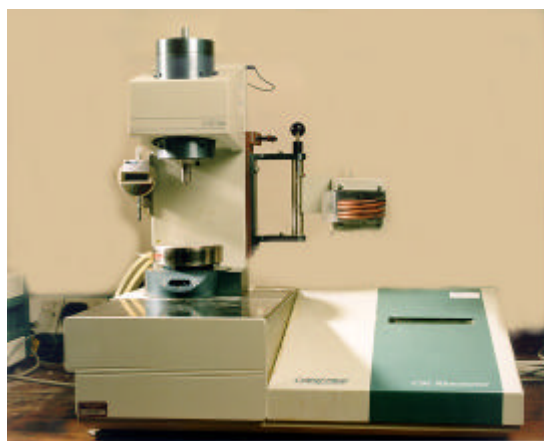


Figure 1: CSL Rheometer



Figure 2: Close-up of splined shaft

The software supplied with this instrument allows a number of different measurement modes to be used - including steady shear flow, oscillation and creep. The steady shear flow measurement mode is inappropriate for solid samples. Oscillatory measurements are more suitable for obtaining mechanical property data.

2.1.2 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were made using a Polymer Laboratories instrument. This equipment was used in single-cantilevered, flexure mode. Thermal expansion effects can cause problems with double-cantilevered measurements when a large temperature range is scanned. DMTA allows a large amount of data to be gathered easily at several frequencies and over a large range of temperatures. The accuracy of DMTA measurements is not always as good as desired for design purposes⁽⁴⁾. Length corrections are required to account for movement in the grips. Shear corrections are needed to account for shear deformations in the flexural mode. These are rarely carried out due to the extra experimental complexity. Uncertainties in the measured moduli can be $\pm 15\%$ or more. However, DMTA does enable determination of transitions in state (e.g. the glass-rubber transition) which may lead to problems in service use. DSC may also be used to locate transitions. However, this technique relies on the measurement of thermal rather than mechanical properties.

2.1.3 Tensile Tests

Tensile tests were carried out using an Instron Universal Test Machine to ISO 527-2 (except for the measurement of strain). Dumbbell specimens (corresponding to specimen type B1 in ISO 527-2:1993(E)) with a 5 mm wide by 1 mm thick gauge sections were used. Strains were measured using a video extensometer to enable the determination of large strains at failure. The test speed was 4 mm per minute. The test temperature was controlled using a temperature cabinet.

2.2 ADHESIVES

The three adhesives selected for this work correspond to the adhesives whose mechanical properties were investigated elsewhere in the project. The adhesives are described in Table 1.

Table 1: Adhesives

Adhesive	Supplier	Type	Cure
DP609	3M	2-part polyurethane	room temperature, > 8 hours
M70	Evode	1-part polybutadiene (elastomeric)	200 °C, 45 minutes
3289Y5000	PPG	1-part epoxy-butadiene	190 °C, 20 minutes

The cure regimes selected for bulk adhesive specimens are thought to be typical of those that are used in a manufacturing environment. Measurements made on DP609 using the oscillatory rheometer, such as those shown in Figure 3, show that the modulus of the adhesive is still increasing after the nominal cure time. It was noticeable that properties continued to change well after the nominal cure time. Bulk test specimens were stored for several weeks prior to testing. This was to ensure that the cure was far advanced and that any rate of further change in the properties was minimal. However, in the tests carried out using the rheometer, it was impracticable to

leave specimens curing for this length of time. This may cause differences between the bulk specimen and the rheometry data.

The two adhesives cured at high temperatures do not present a significant problem with changes to mechanical properties with ageing after cure. However, the final properties of the adhesives depend on their curing regime. The PPGY5000, in particular, was extremely sensitive to the cure time (Figure 4). Minor changes in the cure time can produce dramatic differences in the final properties (the glass transition temperature, T_g , can vary by 80 °C or more). A longer cure time can give a stiff, glassy material whilst a shorter cure time can give a weak, rubbery material. The final cured properties depend on the thermal history, which depends on the thermal capacity of the system in contact with the adhesive. It may be difficult to obtain the same degree of cure in small bonded plates as in a bulk sheet.

Figure 3: Storage modulus of DP609 during a 60 hour cure at 20°C

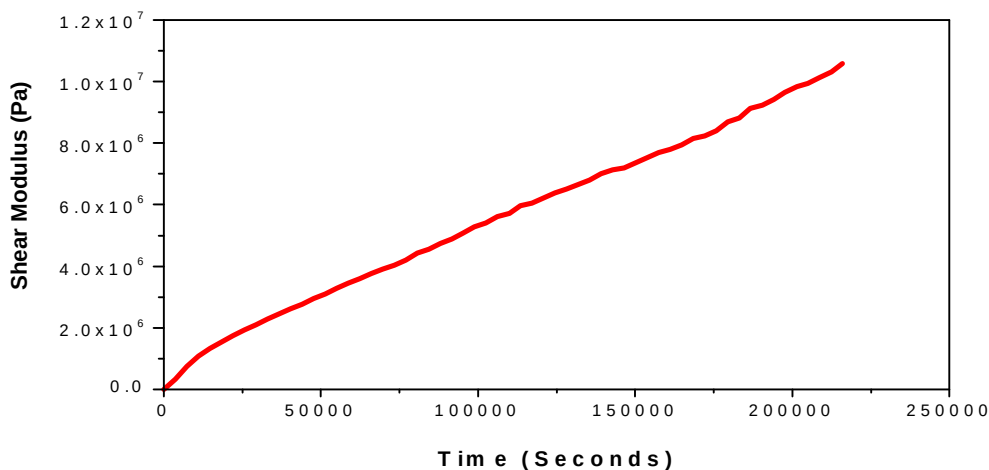
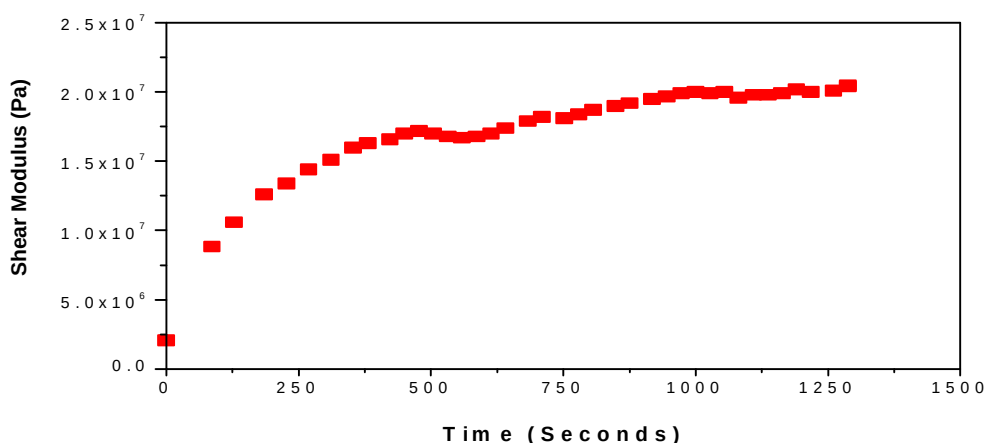


Figure 4: Storage modulus during the cure of PPGY5000 at 190°C



2.3 RHEOMETRY PROCEDURES

2.3.1 Specimen Preparation

Specimens were prepared by curing a 1 mm thick layer of adhesives between two parallel plates 10 mm in diameter. For experiments conducted at or near ambient temperature disposable metal studs were used instead of the conventional plates. This allowed the adhesive to be cured outside the rheometer, thereby increasing the rate at which specimens could be prepared. To prepare the specimens the studs were aligned in the rheometer and then held together with a Unex grip (Figure 5). This allowed the studs to be removed from the rheometer and the adhesive cured in a conventional air circulated oven. Once the adhesive had been cured the specimens were removed from the Unex grips and any excess adhesive removed from the outside of the studs.

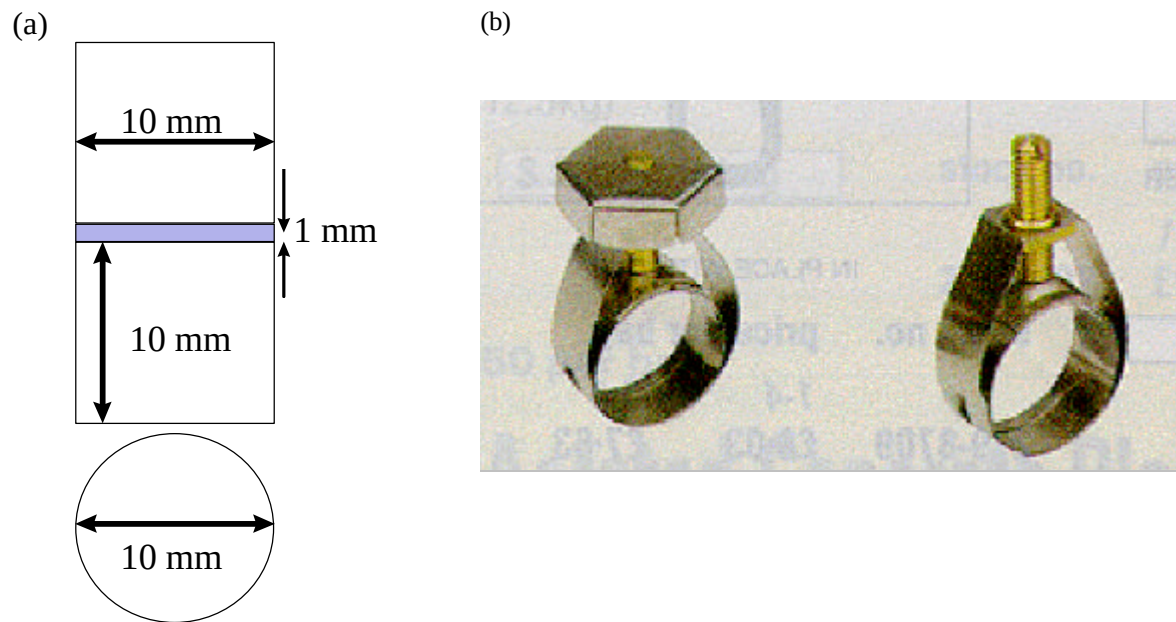


Figure 5: (a) Schematic of bonded studs specimens used in this work;
(b) Examples of the type of Unex grip used to hold the studs together outside the rheometer.

Specimens cannot, however, be prepared outside the rheometer if the Extended Temperature Module (ETM) is used. The reason for this is that the specimens have to be bonded onto the ETM plate while the plate is still in the rheometer. To prepare these specimens the upper plate was bonded to the ETM plate. To ensure the adhesive was cured for the correct length of time (Table 1) the plates were both preheated to the required curing temperature before the adhesive was applied. Once the adhesive had cured the whole system was rapidly quenched to room temperature using the liquid nitrogen ETM cooling facility to terminate the curing process.

2.3.2 Dynamic Properties Measurement

Dynamic mechanical properties for the adhesives were obtained using the oscillation software in the TA Instruments' Rheology Solutions software package for the CSL rheometer. For each adhesive the shear modulus was determined at frequencies of 0.1, 1 and 10 Hz over a range of temperatures from -60 to 80 °C. To avoid the adhesive curing or degrading at high temperatures the tests were conducted from low to high temperature and a new specimen used for each test. In each experiment the temperature was ramped from -60 to 80°C over a period of 2 hours using the ETM system. The ETM system was set to control the temperature to within ± 0.3 °C. However, independent external measurements indicated that the temperature varied by up to ± 1.5 °C. To ensure the experiments were conducted within the linear visco-elastic region of the adhesive the displacement of the oscillations was set at 1×10^{-4} rad for the M70 and PPGY5000 specimens. For the DP609 specimens, however, the oscillations were controlled using a 49999 μNm torque rather than a fixed displacement. The oscillations were monitored during the experiment using an on-screen display to ensure the oscillations were sinusoidal thereby confirming linear visco-elastic behaviour. Data were collected using the software and corrections were made for machine compliance using the method given in Appendix 1.

2.3.3 Stress-Strain Measurement

Stress-strain measurements were obtained using the stress sweep facility in the oscillation module software. This allowed the strain to be measured in each of the adhesives over a range of stresses from 5 to 25000 Pa. To examine the effect that temperature has on the stress-strain curves, tests were conducted at three different temperatures (20, 40 and 60 °C) for each of the adhesives. Temperature was controlled in each of the experiments using the ETM system. Oscillations were monitored using the on-screen display and the data corrected using the formulae shown in Appendix I.

3. DYNAMIC MEASUREMENT RESULTS

Dynamic measurements were made on each material using both the oscillatory rheometer and DMTA. One significant difference between the measurements is that the rheometer gives shear moduli (G) and the DMTA gives tensile moduli (E). Shear and tensile moduli are related through Poisson's ratio (ν):

$$G = \frac{E}{2(1+\nu)} \quad \text{Equation 1}$$

Since ν will typically have a value between 0.3 and 0.5, taking $\nu = 0.4$ gives an approximate relationship that $E = 2.8G$ (within $\pm 10\%$).

Dynamic oscillation or vibration measurements on visco-elastic materials result in a phase difference between the applied stress and resultant deformation. Purely elastic materials have a 0° phase difference; purely viscous materials a 90° phase difference. The ratio between maximum stress amplitude and maximum strain amplitude defines

the complex tensile modulus E^* (or G^* for shear) which contains elastic (storage) and viscous (loss) components. From E^* and the phase difference (δ) the elastic modulus [$E' = E^* \cos(\delta)$] and viscous modulus [$E'' = E^* \sin(\delta)$] can be determined.

3.1 3M DP609

Typical dynamic measurements for the polyurethane adhesive DP609 obtained using the DMTA and the CSL rheometer are shown in Figures 6 and 7 respectively. Values of E' and E'' were determined using DMTA. Values for G' and G'' determined using the rheometer are shown uncorrected for instrument compliance. Due to the large range of values of these quantities, the $\log_{10}$ value of each quantity is plotted (this is the normal practice for such measurements). Table 2 shows values for the elastic modulus and viscous modulus (taken from these data at -50°C). T_g values were estimated from the location of the peak in the viscous modulus. These results show that there are large differences between the DMTA data and the uncorrected rheometer data. However, the T_g values are in reasonable agreement.

Figure 6: Tensile DMTA Properties of DP609

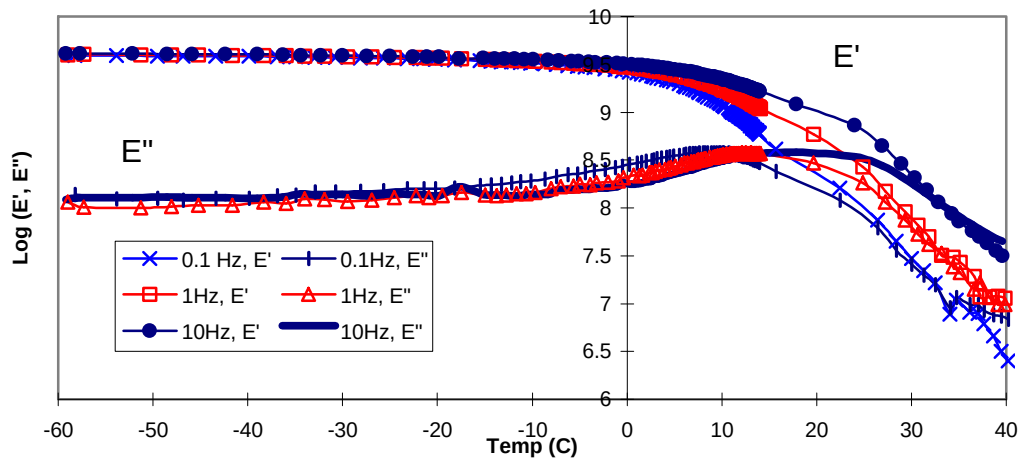


Figure 7: Shear Moduli for DP609 from the Rheometer

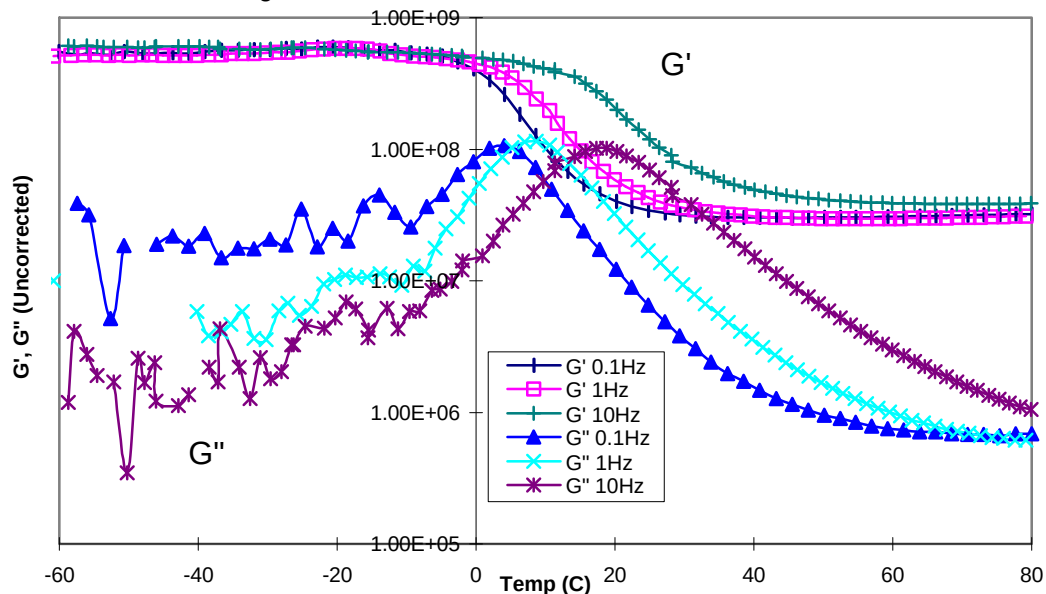
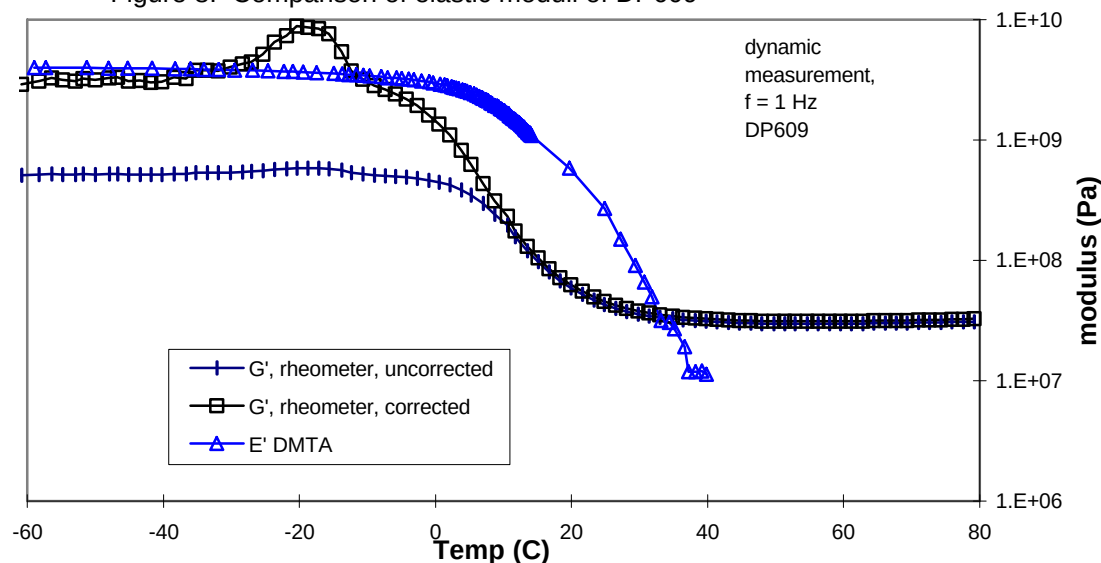


Table 2: Dynamic Materials Property Data for DP609

Frequency	DMTA (-50 °C)			Oscillatory Rheometer (-50 °C) (uncorrected)		
	E' (GPa)	E'' (GPa)	T _g (°C)	G' (GPa)	G'' (GPa)	T _g (°C)
0.1 Hz	3.86	0.126	9.4	0.53	0.0186	4.1
1.0 Hz	3.98	0.100	12.5	0.57	0.0000	8.7
10.0 Hz	4.07	0.130	17.8	0.59	0.0003	17.3

Figure 8: Comparison of elastic moduli of DP609



A direct comparison between the elastic moduli measured using DMTA and the rheometer at a single frequency (1 Hz) is shown in Figure 8. Also included are moduli from the rheometer that have been corrected for the instrument compliance. The compliance correction increases the determined low temperature modulus by a factor of around 6. Above room temperature, the compliance correction is negligible. The reason that the compliance correction is so large at low temperatures is that the stiffness of the instrument and sample is a significant proportion of the stiffness of the instrument alone. The higher modulus of the adhesive below T_g increases the stiffness of the system to more than 500 Nm/rad (Figure 9). This is close to the stiffness of the instrument (610 Nm/rad). Therefore, much of the deformation is taking place in the instrument shaft and not the sample. The angular displacement of the sample is only a fraction of the total measured displacement as shown in Figure 10. Since the stress amplitude is constant, the modulus is inversely proportional to the displacement.

Where the measured stiffness of the sample and instrument is large in comparison with the instrument stiffness, the correction factor for the modulus will be extremely sensitive to small changes in the measured stiffness. Under these conditions, the corrected modulus values will also strongly depend on the determined instrument stiffness. Therefore, there will be large uncertainties in the corrected modulus values calculated. However, without this correction the determined modulus could be 5 to 10 times too small.

Figure 9: Measured stiffness of rheometer and sample

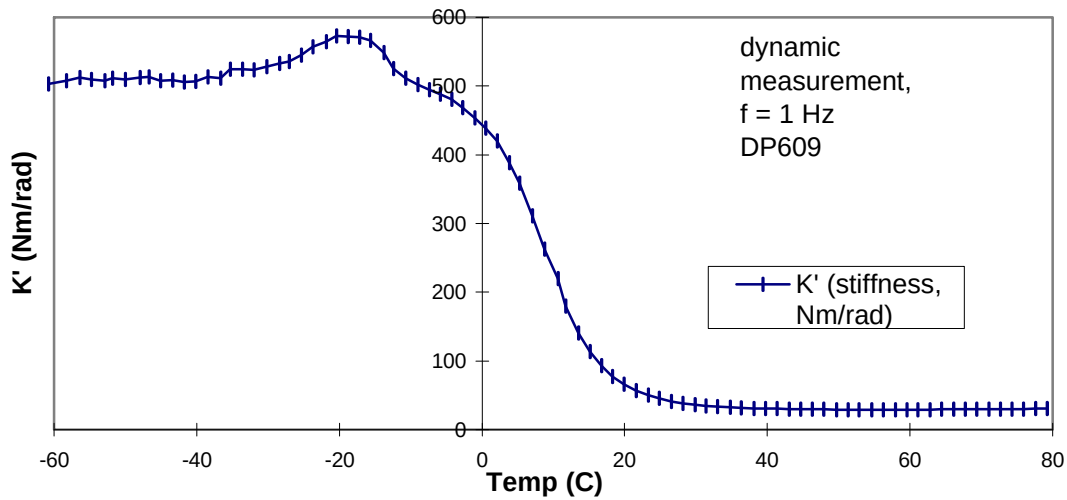


Figure 10: Sample displacements in rheometer

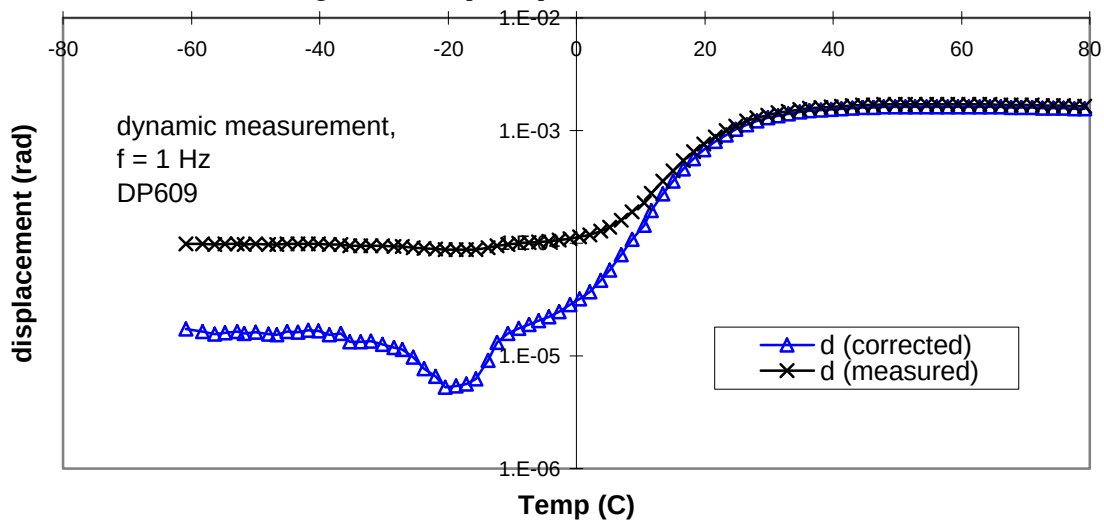
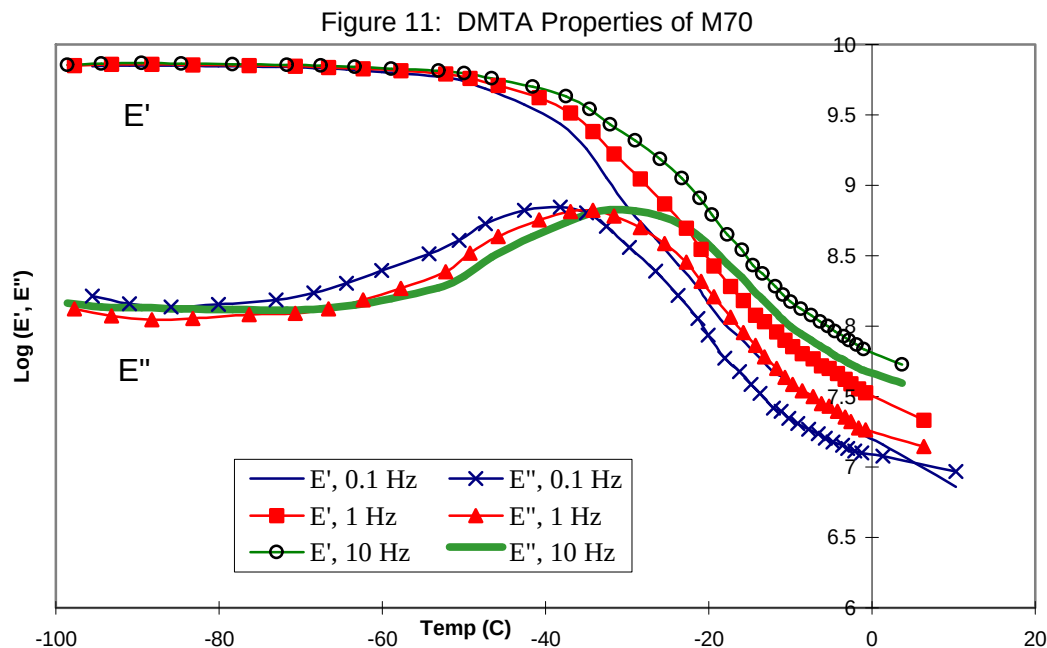


Figure 8 shows a peak in the elastic modulus G'' determined using the rheometer around $-20\text{ }^{\circ}\text{C}$. This is thought to be an artefact of the measurement (possibly due to thermal expansion causing a compressive, hydrostatic stress). This peak is not observed with other measurement methods. This peak is present in the measured stiffness (Figure 9). When the corrected moduli were calculated, the small increase in the measured stiffness was magnified due to the high sensitivity of the modulus to stiffness. Ignoring this peak, the agreement between the corrected rheometer data and the DMTA is good at low temperatures. The rheometer gives a shear modulus and the DMTA a tensile modulus. Therefore the DMTA modulus would be expected to be some 2.5 to 3 times greater than the rheometer modulus. However, in these measurements at $-50\text{ }^{\circ}\text{C}$, the corrected G' (3.15 GPa) is close to the DMTA E' measurement (3.98 GPa). As discussed above, there is likely to be a large uncertainty in the correction to the rheometry data. The DMTA method is also subject to large uncertainties and requires corrections to the data (shear correction and length correction in flexure) to obtain accurate values.

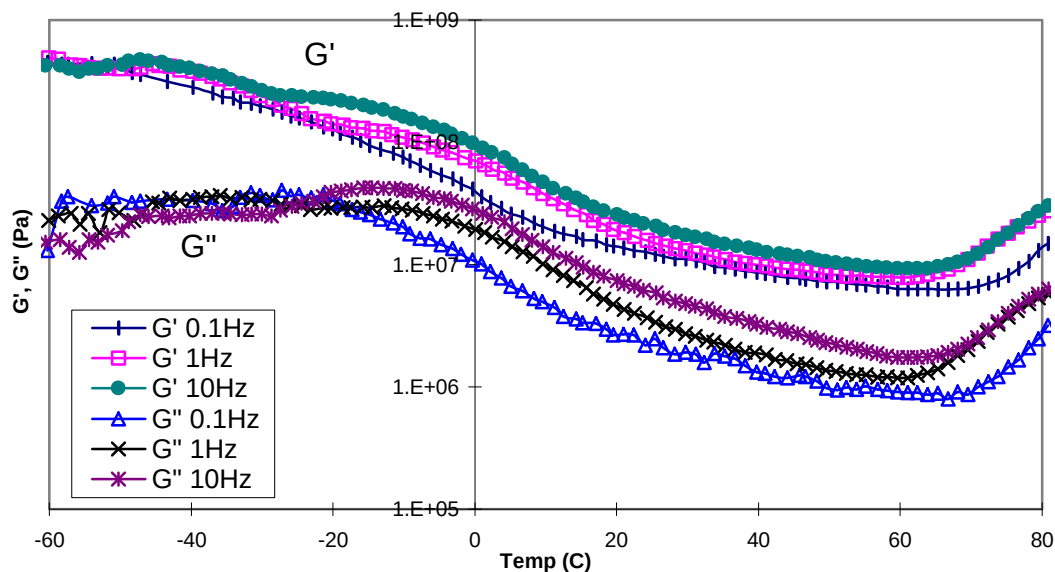
3.2 EVODE M70

Figures 11 and 12 show dynamic properties data for M70 adhesive obtained from the DMTA and rheometer respectively. The rheometer data have been corrected for the instrument compliance. The mechanical properties extracted from these curves are presented in Table 3. There is a large degree of uncertainty in determining the T_g values due to the broad peaks in the loss moduli.



These data indicate that there are considerable differences between the two techniques at low temperatures. This is shown more clearly in Figure 13. The shear moduli are approximately 15 times lower than the DMTA tensile moduli. The DMTA moduli (ca. 6 GPa) seem reasonable values to expect from a polymer in the glassy state. The

Figure 12: Shear Moduli for M70 from the Rheometer



rheometer moduli (< 1 GPa) appear to be too small. This seems to be too large a

difference to account for through measurement uncertainties. Differences in the way in which the oscillation amplitudes were controlled for tests on these two materials are discussed below. The rise in modulus found at high temperature is thought to be another artefact of the measurement possibly due to thermal expansion.

Figure 13: Elastic moduli of M70

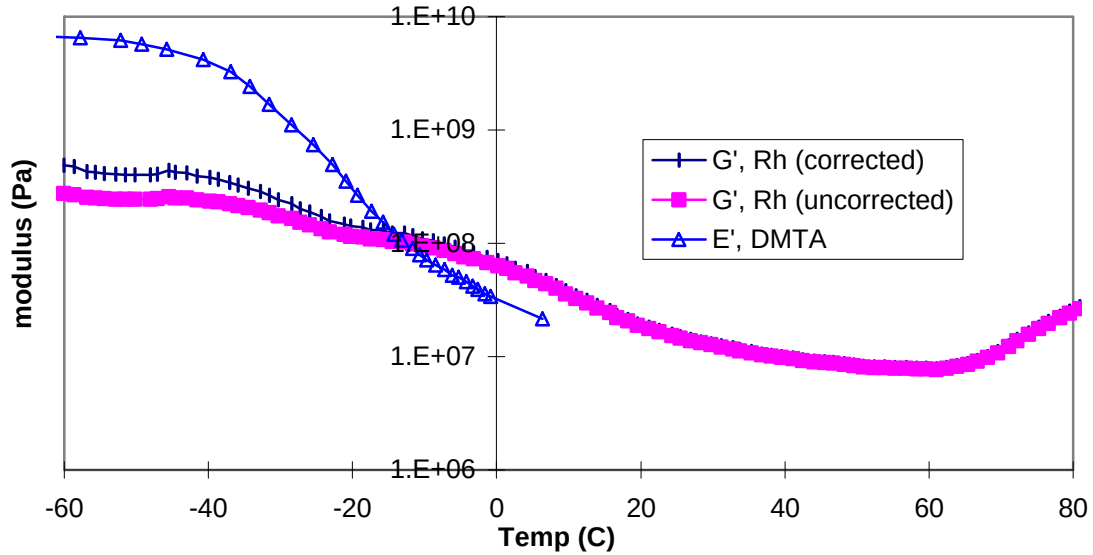


Table 3: Dynamic Materials Property Data for M70

Frequency	DMTA (-60 °C)			Oscillatory Rheometer (-60 °C)		
	E' (GPa)	E'' (GPa)	T _g (°C)	G' (GPa)	G'' (GPa)	T _g (°C)
0.1 Hz	6.38	0.248	-38.4	0.45	0.013	-50.9
1.0 Hz	6.72	0.153	-34.2	0.49	0.023	-35.9
10.0 Hz	6.91	0.148	-32.0	0.51	0.015	-14.5

3.3 PPGY5000

Dynamic properties data for PPGY5000 obtained using the DMTA and rheometer are shown in Figures 14 and 15 respectively. Values extracted from these graphs are shown in Table 4. The shear moduli determined from the rheometer have been corrected for instrument compliance. The comparability between the results is similar to that of the M70 adhesive.

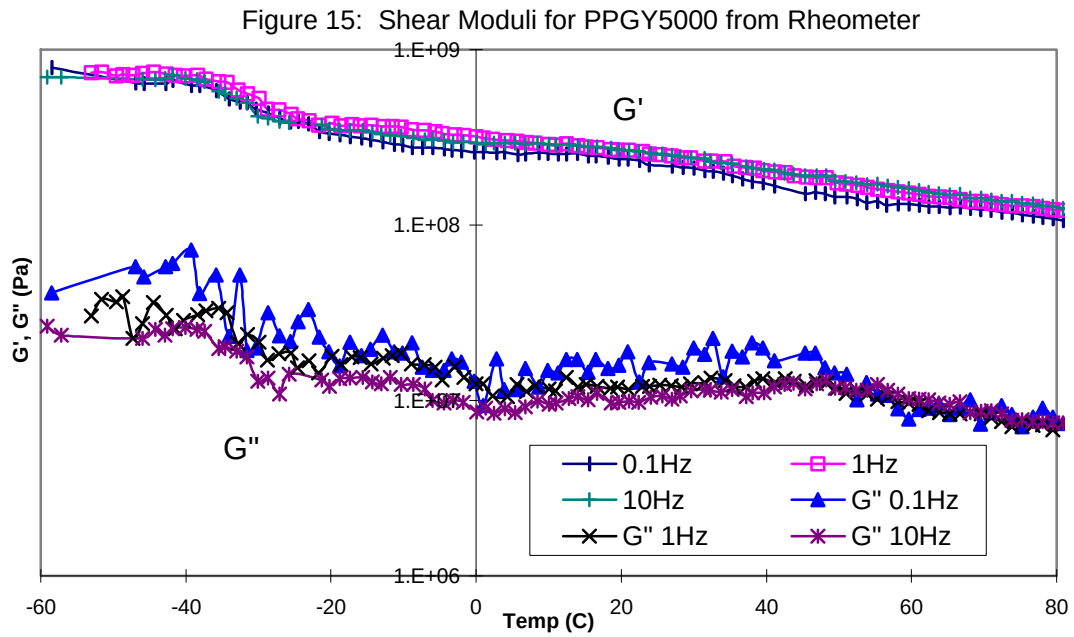
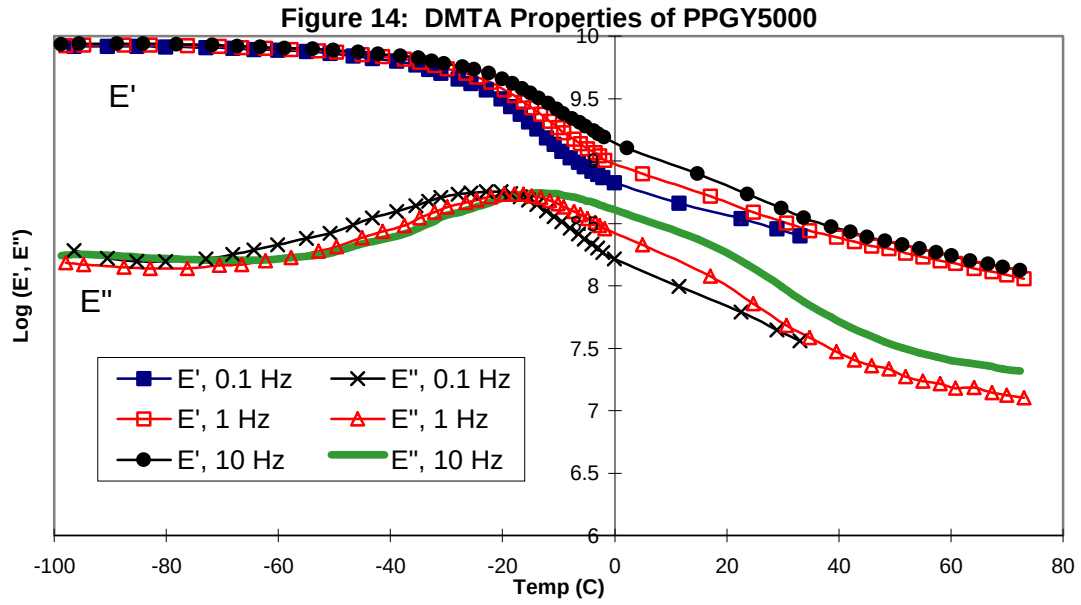


Table 4: Dynamic Materials Property Data for PPGY5000

Frequency	DMTA (-60 °C)			Oscillatory Rheometer (-60°C)		
	E' (GPa)	E'' (GPa)	T _g (°C)	G' (GPa)	G'' (GPa)	T _g (°C)
0.1 Hz	7.67	0.212	-22.8	0.64	0.04	-39.3
1.0 Hz	7.97	0.157	-17.9	0.73	0.03	-48.7
10.0 Hz	8.03	0.165	-13.5	0.69	0.02	-40.1

3.4 DYNAMIC MEASUREMENTS DISCUSSION

3.4.1 Low Temperature Results

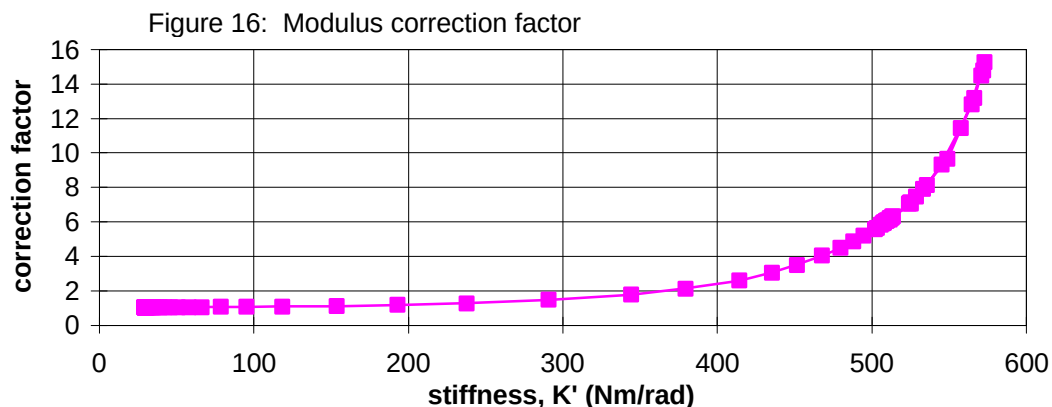
The dynamic properties of three adhesives have been measured using established DMTA equipment and the modified oscillatory rheometer. There are significant differences between the data determined using the DMTA and the rheometer. These are worst for the low temperature properties where the adhesive is 'glassy' and the modulus is relatively large. As the data determined for the DP609 polyurethane adhesive show, applying corrections to the measured data to account for the compliance of the rheometer can greatly improve the correlation between the two techniques.

However, the data measured for the M70 and PPGY5000 adhesives show that, even with the compliance correction, the low temperature modulus values determined with the rheometer are around an order of magnitude too small.

There were differences between the techniques used to control the instrument for tests on DP609 and the tests on the other two adhesives. In an attempt to reduce the differences between the DMTA and rheometry results seen with M70 and PPGY5000, the DP609 tests were carried out using a set torque to control the oscillation. The oscillation displacement was the quantity measured. The torque used was the maximum for the instrument (49999 μNm) in order to maximise displacements (and hence sensitivity) when the sample modulus was highest. In contrast, the tests on M70 and PPGY5000 were performed with the instrument controlling the displacement amplitude (10^{-4} rad) and varying the torque. Dynamic tests on the DP609 adhesive using the displacement control method used for M70 and PPGY5000 showed similarly large discrepancies from the DMTA data at low temperatures.

The tests run using the torque control give much better agreement with the low temperature DMTA results than the tests run with displacement amplitude control. The reasons why this should occur are unclear. The device is designed to control the torque from the drive shaft. Hence, it may be that the displacement control, despite being an option in the control software, is not suitable for stiff specimens. Instrument control developments may improve the suitability of the displacement control function in newer rheometers. Results produced by displacement control measurements should be compared with those from torque control measurements in order to establish the most suitable control mode.

One difference between the two control methods is that the displacement oscillation amplitude increases significantly as the material softens in the controlled torque mode. The displacement amplitude and, hence the strain in the DP609 specimens increases by approximately 100 times between the two temperature extremes. The strain amplitude increases from 0.005 % to 0.5 %. The high temperature strains are not excessive for the material but are relatively large for a dynamic measurement. The larger strains may be outside the linear visco-elastic region for the specimen. In the controlled amplitude test the strain will change by a lesser amount as the instrument deformation decreases.



Under displacement control the measured stiffness of the instrument and sample did not exceed around 300 Nm/rad with any of the adhesives. At this stiffness, the corrected sample modulus is approximately twice the apparent modulus. This stiffness equates to a shear modulus of 500 MPa for the measurement geometry used. In torque control mode, measured stiffness values exceeding 500 Nm/rad were easily obtained. Therefore, the corrected modulus was in excess of five times the apparent modulus. Figure 16 shows the relationship between correction factor and measured instrument stiffness for the rheometer used in this work. The correction factor increases rapidly as the stiffness of the sample and instrument approaches that of the instrument (610 Nm/rad).

With the equipment and parallel plate geometry used here (10 mm diameter, 1 mm gap), the correction factor is around 1.05 for samples with shear moduli around 1 MPa and rises rapidly after 100 MPa. It is essential to apply the compliance correction to all measurements, especially when the apparent shear moduli are greater than 100 MPa, to avoid gross errors in the data. However, the compliance correction factor becomes increasingly sensitive to the measured stiffness as the sample modulus increases. The uncertainties in the corrected modulus values are magnified as the sample becomes stiffer. Measurements where the correction to the data is several times the magnitude of the measured data are inherently inaccurate and should be treated with great caution.

The compliance correction is reduced if the sample stiffness is smaller. For a given material modulus, this could be achieved through smaller diameter plates and/or a larger gap. The calculation of the modulus from the measured torque and displacement depends on the fourth power of the plate diameter. Thus, the uncertainty in the modulus is extremely sensitive to the plate diameter. The presence of any adhesive fillet will have increasingly significant effects on the results as the plate size reduces. Reducing the plate size increases the relative size of the measurement uncertainties. Plate alignment becomes more difficult as the diameter decreases. The 10 mm diameter plates are thought to be a reasonable compromise between measurement accuracy and unacceptable stiffness. Increased measurement gaps reduce the sensitivity of the strain measurement (which is inversely proportional to the gap). It is also more difficult to prepare and align specimens with large plate separations. The 1 mm gap used is relatively large for rheometry but is comparable to bond line thicknesses.

3.4.2 High Temperature Results

Where the rheometer does seem to show significant promise is in the measurement of the material properties above the glass transition temperature. The shear moduli of the samples are sufficiently low that the compliance corrections are small (around 1.05 times the apparent modulus) and the uncertainties in the corrections are low. The high sensitivity of the instrument (designed for the study of viscous liquids rather than stiff solids) ought to allow accurate measurement of the material properties.

The rheometer results for each adhesive are closer to the DMTA results at temperatures above the T_g than they are below T_g . At the higher temperatures, there are still some differences between the DMTA and rheometry measurements. However, in this region the problems are thought to lie more with the DMTA. The measurement capability of the DMTA for low stiffness specimens ($E' < 10$ MPa) is poor. For the DP609 and M70 adhesives, the DMTA ceased being capable of continuing to make measurements soon after T_g (e.g. Figures 8 and 13). Measurements made close to temperature where the test ceased should also be considered suspect. The PPGY5000 adhesive showed a larger high temperature modulus ($E' > 100$ MPa) and the DMTA functioned until the end of the test (Figure 14). The limitations of the DMTA could be overcome through the use of thicker test specimens to give higher stiffness in the rubber region. However, there may be differences between the properties of thick and thin specimens due to differences in cure state.

3.4.3 Glass Transition Temperature Measurements

Dynamic measurements of this nature rarely give accurate moduli. However, they are extremely useful in determining the location of transitions in the phase of the solid. For the PPG 3289Y5000 adhesive the glass transition temperature T_g obtained from the rheometer is much lower than that obtained using the DMTA. However, for the DP609 and M70 adhesives the T_g for the 1 Hz measurement appears to be in agreement between the two techniques. However, the rheometer results are more frequency dependent than the DMTA results. It is unclear why there should be greater frequency dependence in the rheometry data. The G'' (loss) peaks are not as sharp as the E'' (loss) peaks measured in DMTA. This is much more noticeable in the data corrected for the instrument compliance. Hence, there is more uncertainty in the location of the peak that is used to determine T_g .

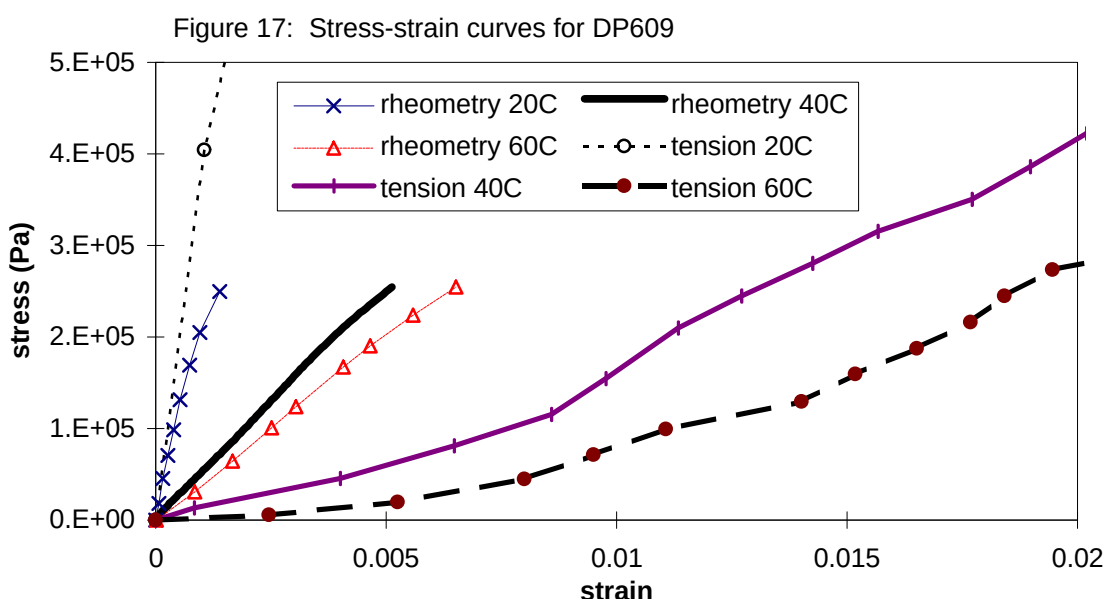
In the PPGY5000 adhesive it appears that there are two different relaxation peaks in the rheometer data compared with only one peak in the DMTA data. The shear modulus obtained from the rheometer is lower than that obtained from the DMTA results. There is a large decrease observed in the storage modulus at the low temperature peak in G'' . Hence, it would appear reasonable to assume that the low temperature peak in the rheometer results is due to the glass transition.

As described earlier, the PPGY5000 is extremely difficult to cure reproducibly. The samples tested in the rheometer may have had a lower degree of cure than the bulk specimens tested in the DMTA. The bulk specimens were prepared several months before testing compared with the rheometer samples which were prepared immediately prior to testing. The bulk specimen may have aged after curing. It is also possible that

the adhesive resin may have changed between the manufacture of the bulk specimens and the rheometry samples.

4. STRESS-STRAIN MEASUREMENTS

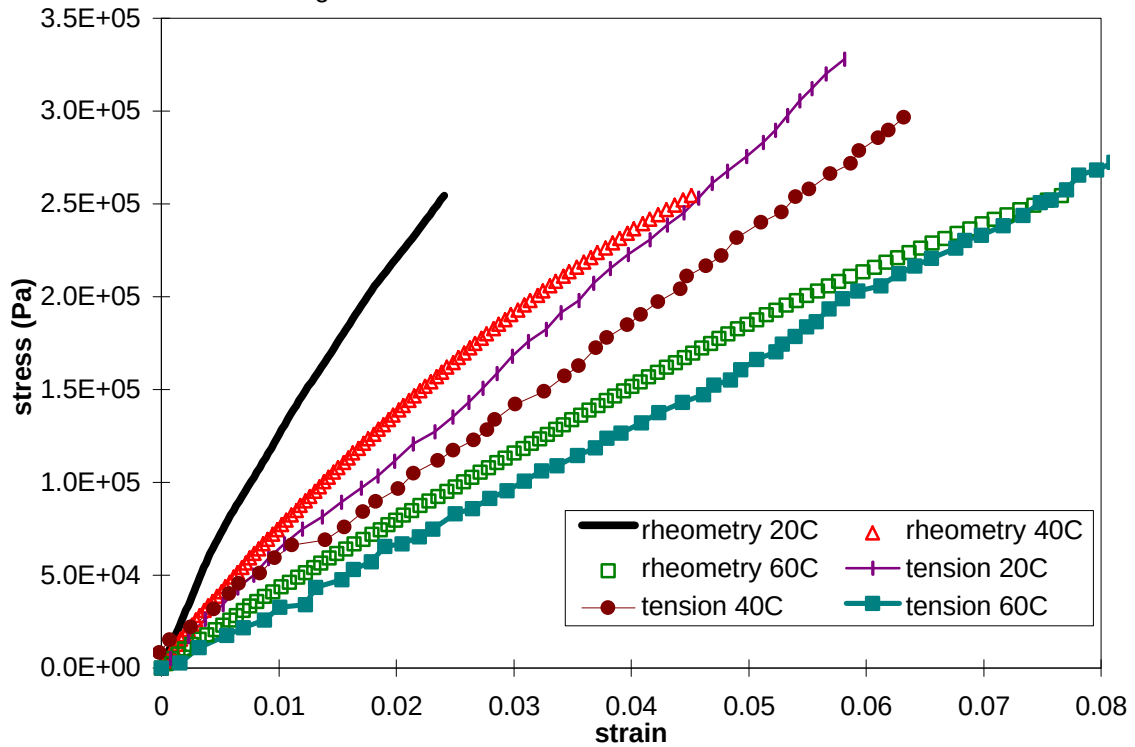
The rheometer software supplied with the instrument was incapable of applying a constant rate of deformation to the sample in the manner of a mechanical test measurement. The only option available was to carry out a torque sweep measurement - oscillatory tests applying ever greater input torque and measuring the rotation or strain as a function of torque or stress. If the torque sweep is performed at a constant frequency, the applied rate of strain must increase as the torque amplitude and, hence, maximum strain increases. Stress-strain measurements obtained using tensile testing and using the rheometer are shown in Figures 17, 18 and 19.



In both the rheometer and the tensile results for the DP609 adhesive (Figure 17) it can be seen that there is a significant decrease in the gradient of the stress-strain curves as the temperature is increased from 20 to 40°C. By comparing these results to the values of T_g that have been obtained in Table 2 it can be seen that these changes in the properties of the adhesive coincide with the glass transition.

Such dramatic effects were not observed in the stress-strain curves obtained from M70 and PPGY500 adhesives as their glass transition temperatures are considerably lower than that of DP609. It can, however, be seen in Figure 19 that the gradient of the rheometry stress-strain curve for PPGY5000 decreases significantly as the temperature is increased from 40 to 60°C. This change in the properties of the adhesive appears to coincide with the additional loss peak that is observed at approximately 40°C in PPGY5000 adhesive (Figure 15).

Figure 18: Stress-strain curves for M70



The stress-strain curves for all the adhesives appear similar in tension and shear. In many cases the shear tests seem to give the greater moduli. The expectation would be that the shear moduli should be smaller than the tensile moduli. These discrepancies could be an effect of the differences in the methods. The rheometry data were obtained from increasing amplitude oscillations at a constant frequency. The rate of shear in the rheometer samples will increase significantly as the amplitude is increased. This would tend to reduce the curvature of the stress-strain curve owing to the rate dependence of the modulus.

Figure 19: Stress-strain curves for PPGY5000

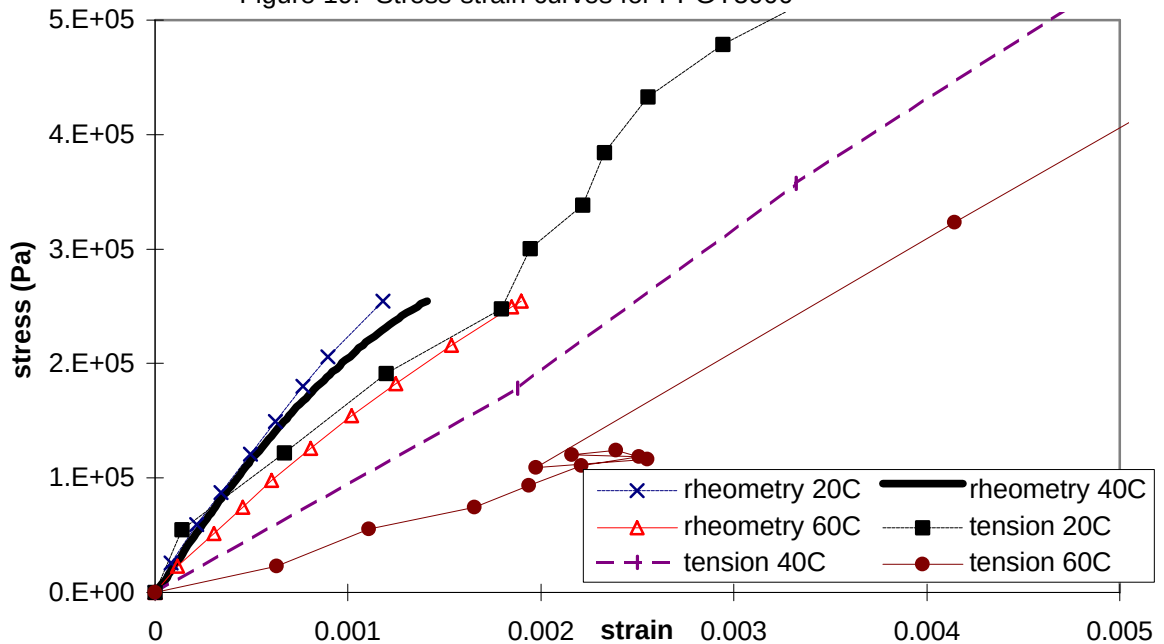


Table 5: Elastic moduli from stress-strain curves

Adhesive	T (°C)	Tensile Modulus, E (MPa)	Shear Modulus, G (MPa)
DP609	20	251	265
	40	20.5	52.0
	60	14.0	39.0
M70	20	5.7	14.0
	40	4.2	7.6
	60	3.2	4.0
PPGY5000	20	181	262
	40	100	238
	60	83.9	166

Figures 17-19 show that the rheometry data are much smoother than the tension data. This is probably due to differences in the sensitivity of the instrumentation used. The tension data were taken from measurements made to failure. Since specimen failure was expected to occur at large strains (e.g. > 1) the video extensometer was configured to measure over a large range of strain. Consequently, the resolution of the instrument was poor at low strain. Also initial forces are small and the resolution of the force transducer will cause significant uncertainties. The initial part of the tensile stress-strain curve will include events other than tensile deformation of the specimen such as straightening of the specimen and take-up of slack in the grips. Therefore, the tensile test configuration for determining stress-strain to failure will not be particularly accurate at low strains. In contrast, the rheometer has good resolution at low displacements and low forces.

The measurement range of the rheometer is limited by the maximum torque available from the drive motor. For the Carrimed CSL500 this was 49999 μNm . Thus, in the 10 mm diameter parallel plate measurement system the maximum stress applied was 0.25 MPa. Consequently, only the initial parts of the stress-strain curve can be measured. Large strain data cannot be measured. Furthermore, since the technique is oscillatory only complete oscillations are analysed. The raw data for each cycle are not available. Hence, failure of the specimens could not be determined in oscillatory tests even if sufficient torque was applied.

5. CONCLUSIONS

The modified Carrimed CSL500 rheometer is capable of operating as a multi-functional test station for low modulus, flexible adhesives. The instrument appears able to measure the flow properties of adhesive resins, their curing behaviour and their mechanical properties. However, the accuracy is limited for moduli above 100 MPa.

The oscillatory rheometer is suited to the measurement of materials with low moduli (e.g. < 100 MPa) such as flexible adhesives above their glass transition temperature. The high sensitivity of the measurement and control systems may give advantages over conventional tensile and DMTA techniques for flexible materials. However, the torque range limits the measurements to relatively low strains.

The method of test control can influence the results obtained. The work performed in this study suggests that the displacement control function of the rheometer evaluated does not give as reliable measurements as the torque control function.

It is essential to correct the results for the instrument compliance to obtain accurate shear moduli. However, even after modifications to increase the rheometer's stiffness, the compliance is still too large to enable accurate modulus determination with stiff, glassy adhesives. Where G' is greater than 500 MPa, the correction to the modulus is larger than the measured modulus. Relative uncertainties will increase as the correction factor increases. To improve the accuracy of the instrument significantly for higher modulus adhesives would require an increase of an order of magnitude in the instrument stiffness. This is unlikely to be achieved without major changes to the design of the rheometer.

Measurements can be made over a wide range of temperatures and frequencies. This enables transitions in material properties to be determined even if the accuracy of measurements in the glass region is poor.

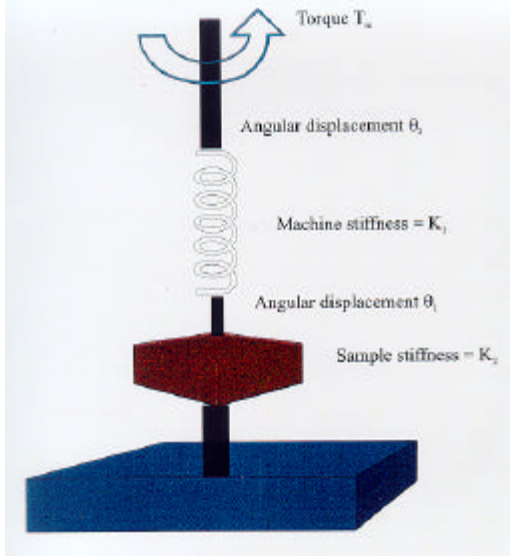
6. ACKNOWLEDGEMENTS

This work was funded by the DTI Materials Metrology Programme Performance of Adhesive Joints. The authors wish to thank Abayomi Olusanya, Roger Hughes, Crispin Allen and Martin Rides for their assistance during this work.

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APPENDIX I: COMPLIANCE CORRECTIONS



Compliance of Rheometer

The theory behind the compliance correction was described in an earlier report⁽²⁾. Since the rheometer is not infinitely stiff, some of the angular displacement must occur in the measuring shaft of the rheometer as well as in the sample. Thus, angular displacements and strains for the sample will be over-estimated. This extra displacement is assumed to be elastic and linearly dependent on the applied torque. The 'stiffness' of the instrument is found from the slope of applied torque against displacement. This is measured by testing an infinitely stiff sample (e.g. locked plates). Once this stiffness value (K_∞) is found, all measured angular displacements can be corrected to give the true sample displacement.

The elastic and the viscous parts of the measured stiffness ($K = K' + K''$) are defined from the measured torque (T), angular displacement (θ_m) and phase difference (δ_m).

$$K' = \frac{T}{q_m} \cos \delta_m \quad \text{and} \quad K'' = \frac{T}{q_m} \sin \delta_m$$

The true stiffness of the sample, denoted by the subscript t, can be calculated:

$$K'_t = \frac{K_\infty}{(K_\infty - K')^2 + (K'')^2} \{K'(K_\infty - K') - (K'')^2\}$$

$$K''_t = \frac{K_\infty}{(K_\infty - K')^2 + (K'')^2} \{K''(K_\infty - K') + K'K''\}$$

$$\tan \delta_t = \frac{K''_t}{K'_t}$$

K'_t and K''_t can be used in conjunction with the conversion factor for the measurement geometry to calculate the actual sample moduli G'_t and G''_t . For the parallel plate geometry used in this work:

$$G = \frac{2L}{pR^4} K \quad \text{where } L \text{ is the plate separation and } R \text{ is the plate radius.}$$