Thermomechanical Properties of Polymers at High Rates of Strain

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Abstract: The dissipation of mechanical energy within a polymer in a relatively short timescale can cause softening of temperature dependant materials and at high strain-rates this effect is more pronounced. In the present study, tests have been performed on a bisphenol A epoxy resin, LY-564, at strain-rates of approximately 2500s⁻¹ using a Split Hopkinson Pressure Bar in compression. Temperature measurement has been carried out using a fast response infra-red radiometer developed at Oxford which is able to measure the surface temperature rise of a material during high rate tests. The temperature data shows three distinct slopes. Significant rises in temperature of approximately 50°C have been recorded during high rate compression tests.

Résumé: La dissipation de l'énergie mécanique dans un polymère durant une courte période peut causer une diminution de dureté pour les matériaux qui dépendent de la température et à des vitesses de déformation élevée cet effet est plus prononcé. Dans la présente étude, des tests ont été effectués sur l'epoxy résine bisphénole A, LY-564, à des vitesses de déformation de 2500s⁻¹ en utilisant une barre de compression Hopkinson. Les mesures de température ont été effectuées en utilisant un radiomètre infrarouge à réponse rapide développé à Oxford capable de mesurer l'augmentation de température de surface d'un matériau durant les tests à haute température. Les données de température montrent trois pentes distinctes. Des augmentations significatives de température d'approximativement 50°C ont été enregistrées durant les tests de compression à vitesse élevée.

1. INTRODUCTION

There are two groups of plastics generally in use, namely thermoplastics - the largest group - and thermosets. Thermoplastic polymers are those that when heated, flow in the manner of a highly viscous liquid and do so reversibly time and time again on subsequently being heated and cooled. The latter group are heated to an appropriate temperature for a short time, so that they will flow as a viscous liquid. A slow chemical cross-linking reaction then causes the liquid to solidify to form an infusible mass.

Once the chemical cross-linking process has occurred, extensive flow is generally not possible even at high temperatures; only a small degree of chain mobility is possible. The dissipation of mechanical energy can raise the temperature within a polymer, causing significant heating effects which increase with strain rate.

The mechanical behaviour of polymers subjected to large strain deformations is primarily governed by the evolution of the polymer chain network with deformation state and temperature from that of an initially random configuration to a highly oriented state.

Cross-linked polymers can respond to stresses in three different ways, depending on the temperature, which influences the mobility of chain segments. Below T_g they behave like glasses. That is, their extension is due mainly to bending of valency angles and to bond extension. In this temperature range the modulus of the resin is high; the extension is instantaneous and fully recovers on the removal of the stress.

At a sufficiently high temperature thermal energy allows segmental rearrangements, involving bond rotation, to take place practically instantaneously. Above this temperature the resin behaves like a rubber. Its modulus is low, usually by several orders of magnitude lower than it was in the glassy region. The extension is again instantaneous and fully recoverable. Because of the chemical bonds linking neighbouring segments, cross-linked polymers cannot flow as linear polymers do at high temperature. In a cross-linked polymer the chains are joined chemically at tie points. The whole material is one giant molecular network. In the liquid

state the cross-links inhibit flow: they cause the polymer to be form stable and to possess properties typical of rubbers. Once the material is cross-linked its shape is fixed and can be 'frozen in' by cooling to a sufficiently low temperature. However, if the material is re-heated it will revert to the shape it had when the cross-links were introduced.

According to the theories of Robertson[1] & Argon[2], the onset of inelastic deformation in polymers is believed to occur once individual polymer chain segments overcome a local resistance to rotation. This initial yield depends on temperature, strain rate, and pressure. The continuing plastic flow is characterised by strain softening followed by strain hardening. This is considered to be the result of an evolving resistance to chain alignment arising from a decreasing entropy associated with the ordered network of oriented chains.

Constitutive equations attempt to explain the reason for observed behaviour and several have been suggested. Many workers have applied the formulation by Eyring to the study of polymers. Since yielding is pressure sensitive, a possible approach consists in taking one of the established criteria for metals and modifying it by introducing a term involving hydrostatic pressure. The Eyring model, including a pressure term, leads to the following:

$$\dot{\varepsilon}_y = \dot{\varepsilon}_0 \exp\left[-\left(\frac{\Delta H - p\Omega(p)}{kT}\right)\right]\exp\left(\frac{\tau_y V}{kT}\right) \tag{1}$$

where $\Omega(p)$ is a function called the "pressure activation volume" and ΔH represents the barrier height or the activation energy for the flow process at $p=0$, k is the Boltzmann constant, T is the absolute temperature. V is the activation volume. The equation relates the yield stress σ_y ($\sigma_y = 2\tau_y$) to the strain rate $\dot{\varepsilon}_y$ and temperature T. However, the proposed equations relate to quasi-static testing rates where the temperature may be assumed constant rather than to high rate tests where adiabatic conditions prevail and the temperature increases as deformation proceeds.

2. TESTING METHOD

2.1 Apparatus

The material used in this study is Araldite LY 564, a bisphenol A epoxy resin with hardener HY 2954. a cycloaliphatic amine hardener. The specimen was cylindrical with a diameter 9mm and length 5.5mm. Compression tests were performed at strain rates of approximately $2500s^{-1} \pm 200s^{-1}$.

One of the simplest and most widely used testing high rate testing techniques is that developed by Kolsky. In the Split Hopkinson Pressure Bar (SHPB), fig.1, a stress pulse is initiated at the upstream end of the input bar and travels towards the specimen at the elastic wave velocity. Initiation of the stress pulse is through a steel projectile, accelerated to a particular velocity using a reservoir of compressed air. When the compressive pulse in the incident bar reaches the specimen, a part is
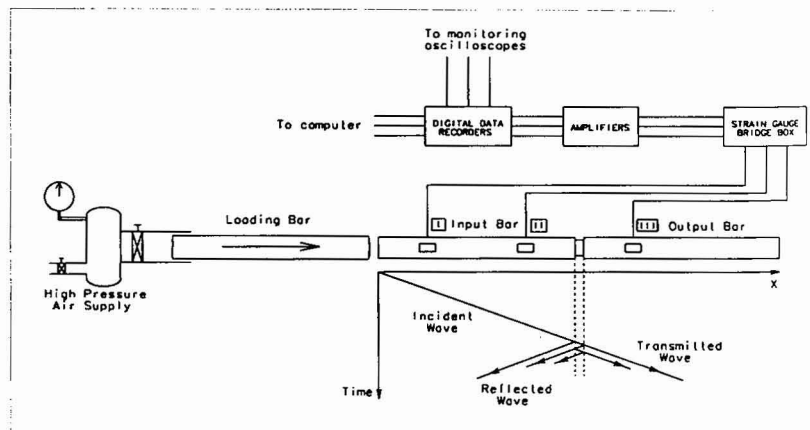

Fig.1 The Split Hopkinson Pressure Bar set-up

reflected because of mismatch in the cross-sectional area and acoustic impedance of the bar and the specimen, and a part is transmitted through the specimen. Strain gauges on both input and output bars monitor the stress wave before and after encountering the specimen.

A set of digital transient recorders were used to record the data from the SHPB for later analysis. In all cases, hydrocarbon based lubricants were used to aid homogeneous flow and to eliminate frictional stresses between the specimen and the anvils at all strain rates. Workers have shown that an enhancement in flow stress is obtained without sufficiently lubricated interfaces [3]

2.2 Verification of data

Data from strain gauges on the input and output bars was recorded and analysed using HOPBAR - an 'in-house' software capable of analysing strain gauge data from Hopkinson bars, either in tension, torsion or compression. Verification of HOPBAR was done in two ways: i) high speed photography, which also provided a visual insight into the specimens' deformation, and ii) a manual analysis of the strain gauge data.

A CORDIN 377 Rotating Prism camera operating at 100,000 frames/second was used, in an arrangement shown in fig.2, giving a sequence of photographs 10µs apart. By taking measurements from prints using a travelling microscope, a 'Strain vs Time' graph can be constructed. The strain-time characteristics, shown in fig.3, compare HOPBAR results with those calculated manually using standard wave analysis. The evidence from photographs shows a good correlation with the strain calculated using HOPBAR and from the 'manual analysis'
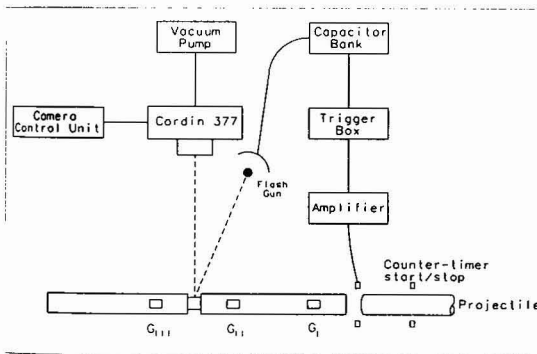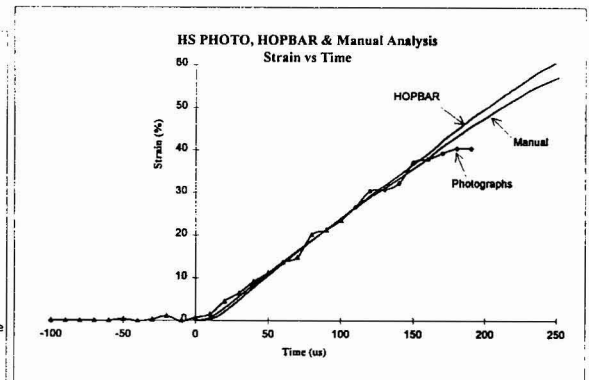

Fig.2 High Speed Photography set-up

Fig.3 Comparison of strain-time measurements

2.3 Temperature measurement

During the deformation of a material under whatever loading condition, some plastic work is converted into stored strain energy and the remainder evolves as heat. The ease of measuring the variation in temperature increases as the deforming process becomes slower, and so simpler measuring equipment may be used. For higher rate tests in the region of 2500s⁻¹, large increases in temperature can occur and the response time of the measuring equipment becomes a limiting factor. A radiometric non-contact method of surface temperature measurement has been developed within Solid Mechanics at Oxford, which can be split into two sections - the imaging system which gathers and focuses radiation from the surface of the material and the detector which reacts to the incident radiation. A schematic diagram of the imager and detector is shown in fig.4.

2.3.1 Detector details

A single element nitrogen cooled Mercury-Cadmium-Telluride (HgCdTe) detector of area $1mm^2$ (sensitive to light in the range $2\mu m$ - $5.5\mu m$) was used. This is combined with electronics giving a response time of $1.4\mu s$. The size of the detector limits its spatial resolution and it is useful only where uniform temperature rises occur. The detector is cooled with liquid nitrogen to improve performance by reducing thermal noise.

2.3.2 Imager

An ideal imaging system for the radiometer will gather 100% of the emitted radiation from a given region of the specimen and focus this onto the detector, without distortion. In practice, however, only a fraction of the emitted light can be gathered and some geometric aberration is inevitable. An initial design using two free standing parabolic mirrors, developed by Craig [4] has been improved upon, using a Cassegrain mirror arrangement, consisting of two annular uni-axial spherical mirrors. Zinc Sellenide coated Potassium Chloride lenses are placed in the centre of each mirror to correct for geometric aberrations. This optical system gathers about 5% of the available emitted light (ten times that of the previous arrangement) and causes minimal distortion of the light path ($\pm12.5\mu m$). This increase in light gathering power and reduction in distortion of the image has improved the performance of the detector considerably.
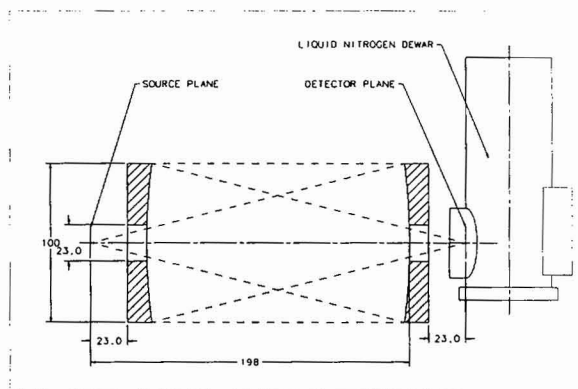

Fig.4 Temperature measurement apparatus

2.3.3 Calibration

In order to obtain useful temperature data, it is imperative that an accurate calibration be carried out relating the voltage output from the detector to the specimen surface temperature. This calibration is performed with the specimen *in situ* so that focussing errors between the calibration and the testing conditions are eliminated. The calibration technique involved heating the specimen to a known temperature whilst located in the test position and then measuring the radiometer output voltage. Since the electronics are only sensitive to a.c. signals, a chopper wheel was used to produce a pseudo a.c. signal. The chopping frequency had a lower limit of 10Hz, which eliminated errors arising from low frequency background radiation , and an upper limit of 145kHz, related to the response time of the detector and governed by the cut-off frequency, $f_c = 1/(2\pi\tau)$. To perform the calibration the specimen was heated using a hot-air gun to above the desired temperature and then allowed to cool. A thermocouple in contact with the specimen monitored its surface temperature. This was repeated at different temperatures until a full calibration curve was obtained, see fig.5.

3. RESULTS

In the calibration curve of fig.5 each point is the average of several readings. A polynomial curve was fitted to the calibration data and an equation obtained which was subsequently used to convert the detector output voltage into an actual value of temperature .
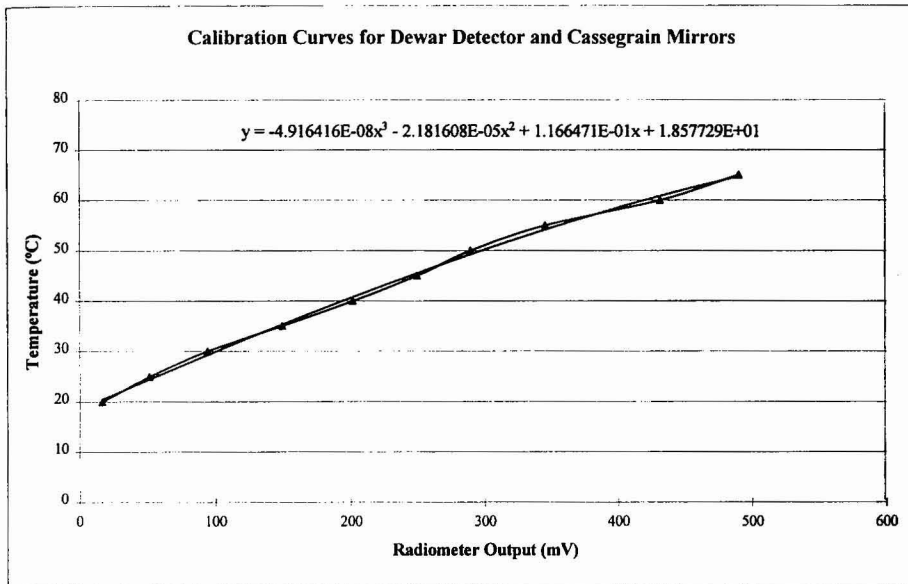
Fig.5 Calibration curve

Fig.6 shows the mean true stress-true strain curve and the corresponding rise in specimen temperature for five nominally identical compression tests. The mean strain rate was ~2500s^{-1}, as shown in fig.7. The experimental scatter in the measurement of stress, strain and temperature was of the order of ±5%.

The temperature profile shown in fig.6 is typical of all such tests and exhibits three distinct and totally reproducible regions. At true-strains less than ~15% there is a steady rise in temperature of ~37°C/ms. Between ~15% and ~60% strain this increases to ~147°C/ms until, at just over 60% strain, the specimen fractures and the rate of temperature increase jumps to ~833°C/ms.
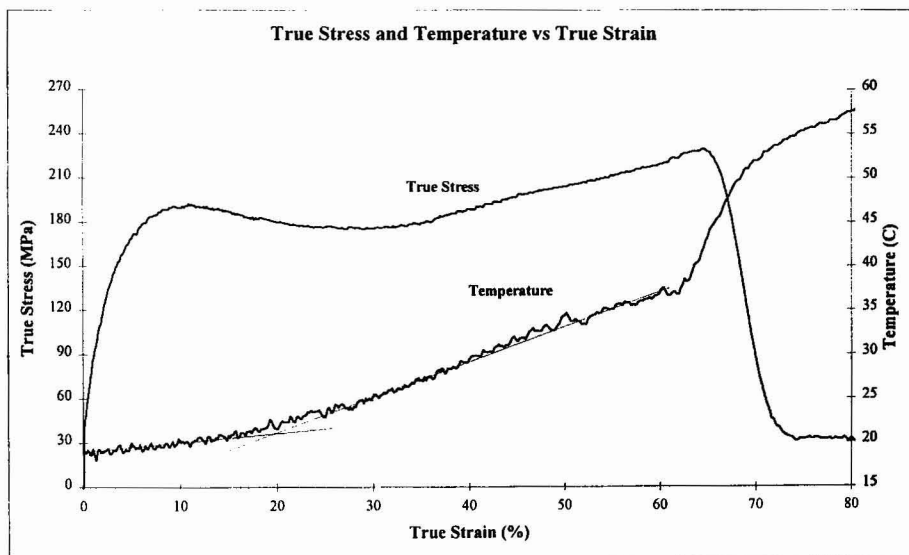

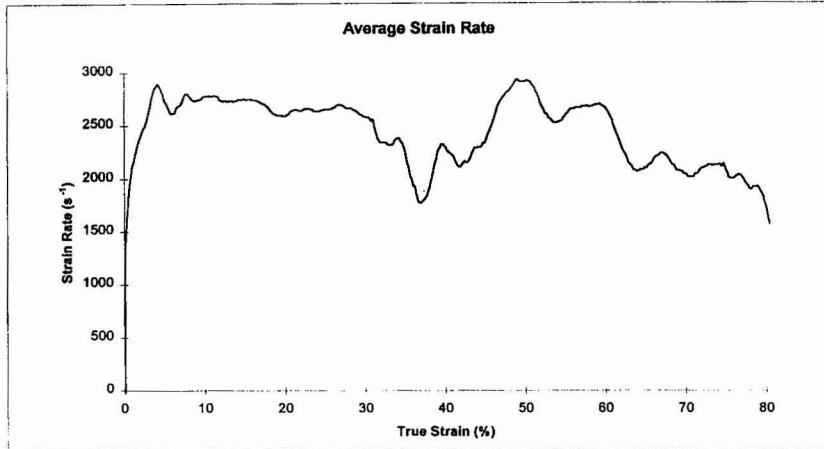
Fig.6 Stress and Temperature results

Fig.7 Average strain rate

4. CONCLUDING REMARKS

The first region of the temperature profile in fig.6, i.e. at strains up to ~15%, corresponds to the initial yield of the specimen and the subsequent slight drop in stress. In this region the rate of temperature increase is very small, possibly because the input energy is mainly used in the breaking of secondary bonds between the polymer chains rather than being stored as internal energy. In the second region, from ~15% to ~60% strain, both the flow stress of the specimen and its surface temperature increase at a significant rate. Here, therefore, it seems likely that most of the input energy is stored as internal energy in the specimen and a much smaller proportion is used in breaking bonds.

Finally, at a strain of ~65% and a temperature approaching 40°C, the specimen shatters into many pieces and an even more rapid rate of temperature increase is observed. This rapid increase in temperature associated with fracture is not limited to tests on polymeric specimens in high-rate compression but has also been seen in a variety of high-rate tests on a range of metallic materials, e.g. titanium alloy in high-rate torsion [5]. The reason for this behaviour is still open to question but there are a number of possibilities. In particular in the present tests, where the specimen shatters into many pieces at failure, it has not been possible to check whether there is any associated change in emissivity and hence in radiometer calibration leading to an overestimate of the true specimen temperature. Alternatively, if the observed rapid increase in temperature is valid it could be due to frictional effects between the shattered pieces of specimen as they are crushed following fracture or to the sudden release of stored strain energy resulting from fracture. Further investigations into these effects are currently being carried out.

5. ACKNOWLEDGEMENTS

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