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Rubber toughening of plastics

Part 5 *Fatique damage mechanisms in ABS and HIPS*

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Mechanisms of fatigue damage in ABS and HIPS polymers were studied by monitoring changes in mechanical properties under sinusoidal and square wave loading at a frequency of 0.033 Hz. Both materials exhibited a large increase in hysteresis and a decrease in modulus. In ABS, these changes occurred to approximately the same extent in tension and compression, whereas in HIPS the changes in tensile properties were much more pronounced. From the shape of the hysteresis loops, and from volumetric measurements, it was concluded that crazing is the dominent fatigue damage mechanism in HIPS, whilst shear yielding is responsible for most of the damage observed in ABS. Large increases in hysteresis caused substantial rises in temperature despite the low frequency, and thus accelerated fatigue damage accumulation.

1. Introduction

Rubber-modified plastics are designed for toughness under monotonic loading, especially in impact. In this respect, they have proved very successful, as testified both by the increasing use of HIPS (high impact polystyrene) and ABS, and by the application of the rubber toughening principle to an increasing number of thermoplastics and thermosetting resins. Much less attention has been devoted to the improvement of fatigue resistance, despite the obvious importance of fatigue in a wide range of applications, not all of them in the field of engineering. It is probable that fatigue failures occur more frequently than is generally recognized, since polymers are more likely to encounter fluctuating stresses than constant loading in service, and fracture surfaces often do not receive the close scrutiny necessary to identify fatigue cracks.

Fatigue failures have been recorded in a number of applications of ABS, including boat hulls [1], shoes, office equipment, bobbins, and seats. Similar problems occur in other rubber-modified plastics which have been designed for impact rather than fatigue. It is interesting to note in this connection that Bucknall *et al.* found ABS to be inferior to rigid PVC in fatigue tests at 20° C and 0.5 Hz [2]. An understanding of the differences in response to monotonic and cyclic loading would clearly be of value in improving the performance of rubber-modified plastics.

The literature on fatigue in plastics has been well reviewed by Manson and Hertzberg [3] and, more recently, by Sauer and Richardson [4]. These reviews describe the three principal methods available for studying fatigue: (i) determination of stress (S)–number of cycles (N) curves, using unnotched specimens; (ii) fracture mechanics measurements on sharply notched specimens; and (iii) monitoring of fatigue damage in unnotched specimens. The third method offers the best prospects for relating fatigue properties to polymer structure, and for this reason use of this method has been advocated by Beardmore and Rabinowitz [5]. In general, polymers undergo cyclic softening, characterized by a decrease in modulus and an increase in hysteresis, in contrast to the cyclic hardening observed in some metals.

The aim of the present work is to analyse the process of cyclic softening in ABS and HIPS polymers in order to distinguish between the contributions produced by crazing and by shear yielding. Previous studies have shown that the two polymers respond differently to monotonic

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loading: HIPS deforms predominantly by multiple crazing [6], whilst ABS exhibits both crazing and shear yielding [7]. Under cyclic loading, both mechanisms cause softening in tension, but only shear yielding would be expected to affect compressive properties, since crazes close under compression. This concept formed the basis for the present study.

2. Experimental procedure

2.1. Materials

The ABS chosen for this programme was Borg Warner Cycolac T, and the HIPS chosen was Dow Styron 461. Both polymers were supplied as natural unpigmented pellets, and were compression moulded at 190° C into sheets 6 mm in thickness, from which specimens of the type illustrated in Fig. 1 were milled. All four faces of each specimen were polished within the gauge portion using 600 grade emery paper. For temperature studies, a 0.5 mm diameter wire was moulded into a waisted specimen, as illustrated, and then extracted, leaving a channel for a chrome alumel thermocouple. Care was taken to ensure that the junction was positioned at the centre of the specimen. Tests showed that the presence of the channel did not affect the fracture behaviour of the specimens.

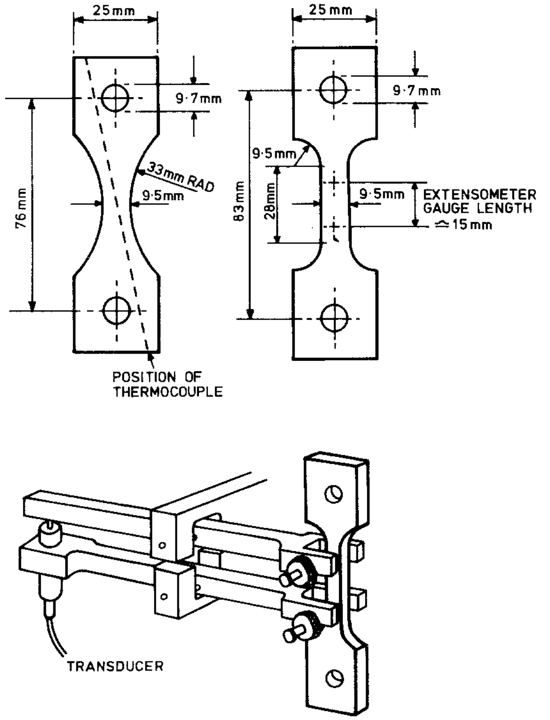

Figure 1 Specimens and extensometry used in the fatigue experiments.

2.2 Fatigue testing

Fatigue testing was carried out on an eight-station closed-loop servo-hydraulic machine designed and built at the Cranfield Institute by Mr. T. E. Clifton. The machine tests specimens in the push–pull tension–compression mode under either load or displacement control over the frequency range between 0.005 and 10 Hz, using a sine, a triangular or a square waveform. Upper and lower levels of load (or displacement) can be varied independently. Strain in the specimen is measured by an extensometer of the type illustrated in Fig. 1. The transducer is operated by lever arms which make light contact with the specimen through small pins. This technique has been used successfully for many years in creep measurements. A second, lateral extensometer was used in experiments to measure volume changes.

Load and displacement data from each specimen are fed to a mini-computer, where they are analysed and stored. The tensile and compressive portions of the hysteresis loop are recorded separately, in terms of the quantities defined in Fig. 2: peak stress, strain at peak stress, secant modulus, work done, and hysteresis loop area for the tensile and compressive halves of the cycle.

In the present work, all tests were performed under load control at a constant ambient temperature of 23° C. Load control was chosen in preference to displacement control after preliminary trials, which showed that a state of zero strain became extremely difficult to identify

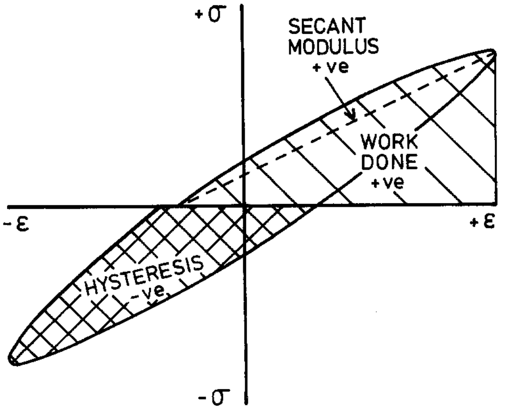

Figure 2 Definitions of quantities calculated from hysteresis loops.

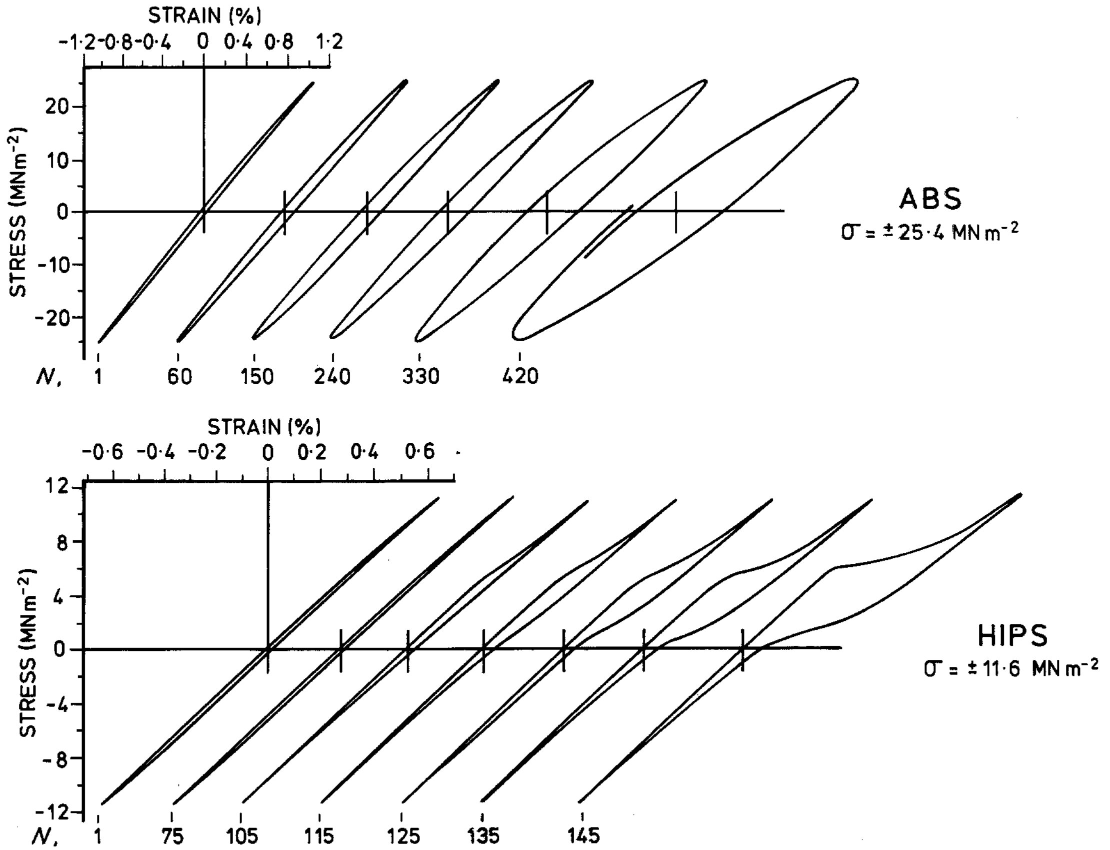

Figure 3 Hysteresis loops obtained by interrupting a square-wave loading test at intervals, and applying a single sine-wave cycle. Number of cycles, N, as indicated. Zero of strain is indicated for each loop.

once the material began to strain-soften, because of the possible difference between tensile and compressive properties. Specimens were cycled in fully-reversed tension–compression, using either sinusoidal or square-wave loading. In the case of square-wave loading, the test was interrupted at intervals, and a single sinusoidal cycle of the same amplitude was applied to the material in order to measure properties. A frequency of 0.033 Hz (2 cycles per minute) was employed as a precaution against overheating. Parallel-sided specimens were used for all of the mechanical measurements reported in this paper. Waisted specimens were used for the temperature measurements, in order to ensure that the thermocouple was located at the hottest part of the specimen; they were also used for fatigue endurance tests, which will be discussed in a later paper.

3. Results

These experiments confirmed that significant cyclic softening occurs in ABS and HIPS, especially at stress amplitudes greater than half the short-term yield stress. Analysis of the changes in properties shows quite clearly that different mechanisms operate in the two materials. Despite the low frequency of testing, both polymers exhibited substantial temperature rises.

3.1. Hysteresis and modulus changes

The differences between ABS and HIPS in their response to fatigue loading are well illustrated in Fig. 3. In ABS, the hysteresis loop is approximately elliptical, with the tensile and compressive portions similar in size and shape. In HIPS, on the other hand, the loop is irregular in shape, and the tensile portion increases in size far more rapidly than the compressive portion.

The distinctive shape of the developing tensile hysteresis loop for HIPS is characteristic of a crazed material. This type of loop was first observed by Kambour in experiments on a single craze in polycarbonate [8]. On application of a tensile stress, the craze is initially stiff, shows an

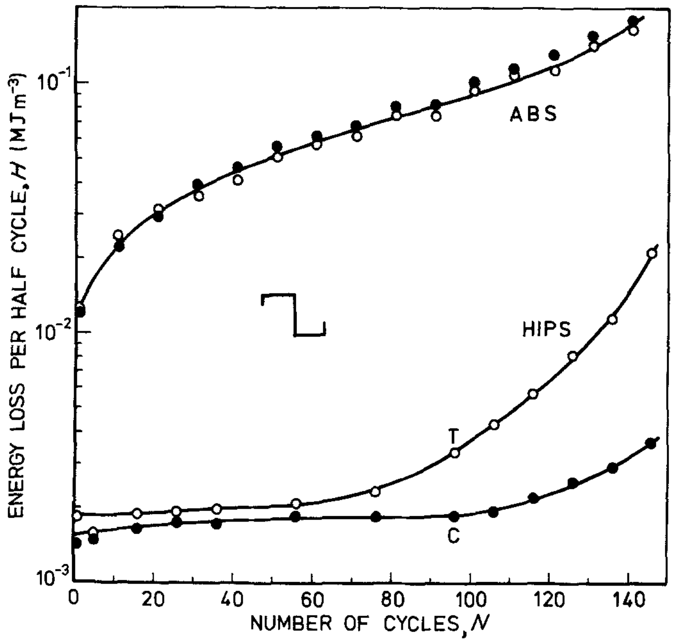

Figure 4 Energy losses in tension (○) and compression (●) for ABS and HIPS under square-wave loading at stress amplitudes of 27.6 and 11.6 MPa, respectively.

apparent softening as it extends, and then strain hardens at higher extensions as the molecules become orientated in the stress direction. On unloading, the viscoelastic character of a crazed polymer becomes apparent, as the strain lags behind the stress, tracing out a broad hysteresis loop. Similarly shaped tensile hysteresis loops have been reported in HIPS containing large numbers of crazes, where the properties of crazes can be observed on a macroscopic scale [9].

In the present fatigue tests, as in previous work, observation of dense stress whitening in the HIPS supports the view that the increase in tensile hysteresis is due to craze formation. Under compressive loading, the remaining craze voids close up, and the degree of whitening decreases, becoming barely detectable at peak load; the material then approaches the stiffness of the undeformed polymer. However, closure of the voids does not restore the material to its original condition: on re-application of a tensile stress, the crazes re-open. Further crazing occurs during the next cycle, so that the changes in properties are cumulative.

The ABS specimen, by contrast, shows no

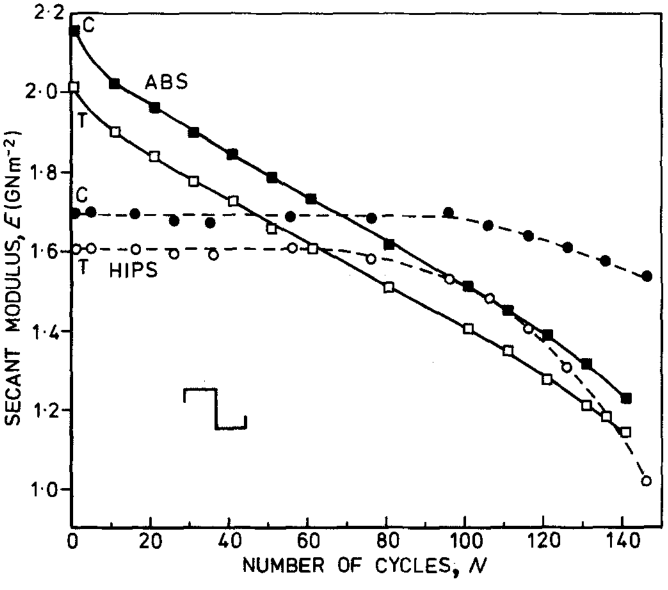

Figure 5 Modulus changes in tension (○) and compression (●) for the specimens illustrated in Fig. 4.

evidence of crazing until it reaches the final stages of its fatigue life. Except for the last few cycles before fracture, the material remains unwhitened, and the hysteresis loops are almost symmetrical. On this evidence, it must be concluded that crazing plays little part in the process, and that shear deformation is the dominant mechanism of fatigue damage. Since rubber particles produce an inhomogeneous strain field in the styrene acrylonitrile co-polymer (SAN) matrix, it is probable that the shear deformation is confined to discrete shear bands, as has been observed in HIPS/PPO blends [10].

The differences in fatigue behaviour between ABS and HIPS polymers are further emphasized in Figs. 4 and 5, where hysteresis and modulus are plotted against number of cycles. As in most polymers, moduli are higher in compression than in tension, but if allowance is made for the differences in initial values, it is clear that the hysteresis and modulus curves for tension are very similar to those for compression in the case of ABS, but quite different in the case of HIPS. Crazing causes the curves to diverge as the test proceeds. The initial hysteresis is much lower in the HIPS specimen because of the lower stress amplitude (hysteresis increases as the square of the amplitude). The stresses used in this comparison were chosen on the basis of separate fatigue endurance trials, which showed that fracture occurred after 200 cycles in both materials at the stress amplitudes indicated.

3.2. Volume changes

Shear deformation occurs essentially at constant volume, or perhaps with a slight densification, whereas crazing results in a substantial increase in volume. This principle, which has been used previously to distinguish between the two mechanisms in creep experiments [6, 7], was adapted to the present study: volume changes were monitored during the first fatigue cycle, and the

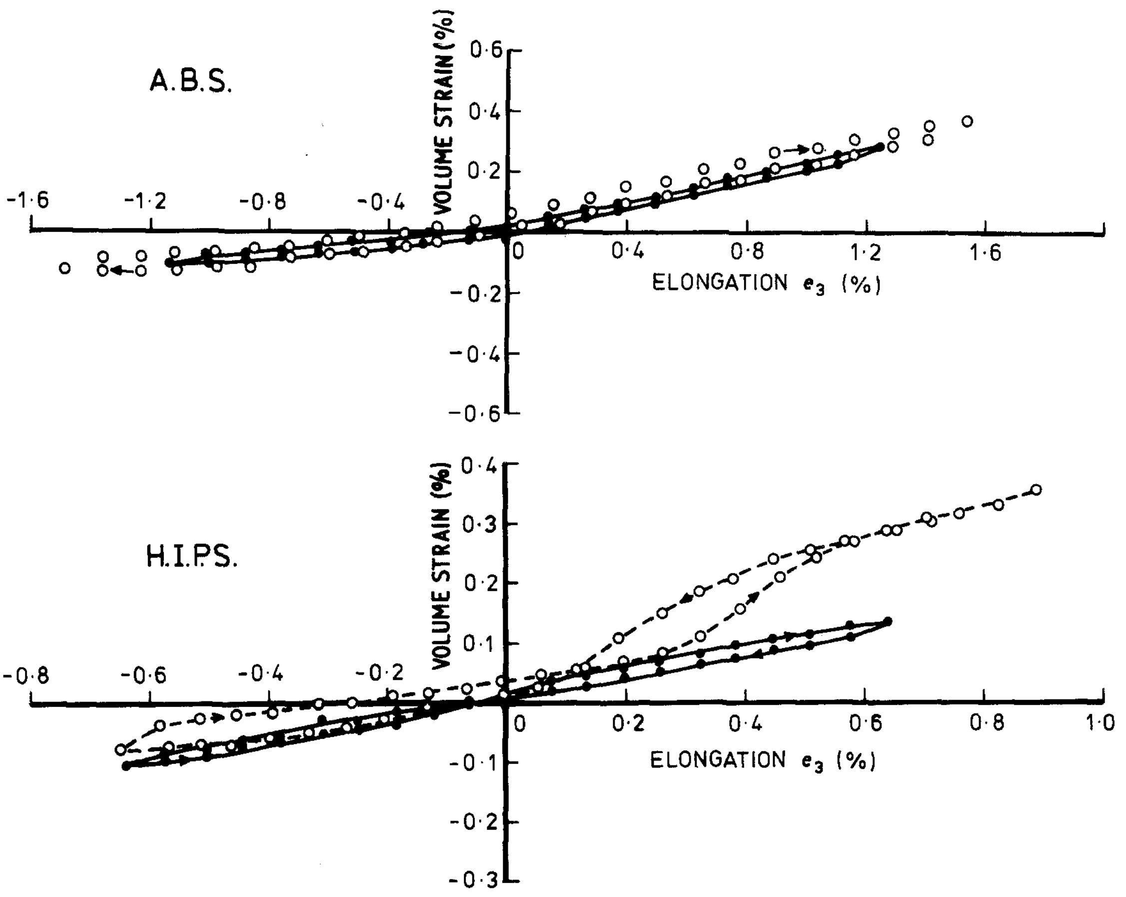

Figure 6 Relationship between volume strain and elongation before (●) and after (○) fatigue cycling of ABS and HIPS to tenfold hysteresis increase. Interrupted square-wave fatigue at 27.6 and 11.6 MPa, respectively.

measurement was repeated after sufficient cycling to increase the hysteresis by a factor of 10. The relationships between volume strain ΔV and elongation e_3 are presented in Fig. 6. During the first loading cycle, both HIPS and ABS respond in a similar manner, reflecting the bulk viscoelastic properties of the materials. The sinusoidal variation in stress σ produces corresponding changes in e_3 and ΔV, and there is little or no lag between the two strains. At this stage of the test, the volume strain can be treated as an essentially homogeneous bulk response to the hydrostatic component of stress. Even the rubber particles cause little inhomogeneity in volume strain, as the bulk modulus of rubber is comparable with that of polystyrene. On the first fatigue cycle, Poisson's ratio is 0.40 for both ABS and HIPS.

After prolonged load cycling, there is a marked change in the volumetric response of HIPS to tensile stress. As e_3 increases from 0.2 to 0.6 %, ΔV rises rapidly, before levelling off. This dilatation is clearly due to the opening of pre-existing crazes, and is followed by elastic extension of crazes and bulk polymer. On unloading, the uncrazed bulk polymer is first to recover: only when e_3 reaches 0.5 % does the volume begin to decrease more rapidly, as the crazes close. This part of the volume recovery is substantially complete at a strain e_3 of about 0.1 %. Comparison with the corresponding stress–strain hysteresis loops shows that $d\sigma/de_3$ is low over those parts of the cycle where dV/de_3 is high.

Under compression, the crazed HIPS shows a similar but not identical response to that observed in the first compression cycle. The specimen behaves as expected during the application of the compressive stress, but there is some irregularity in the volume strain on unloading, the reasons for which are not clear.

It is interesting to note that fatigue cycling at a constant stress amplitude has increased the peak extension e_3 by 0.26 %, and the peak volume strain ΔV by 0.23 %. Within experimental error, the two increments are equal, as expected in a material which is deforming by multiple crazing only.

The volumetric measurements on ABS support the evidence from modulus and hysteresis data: fatigue softens the polymer, allowing the peak values of e_3 and ΔV to increase, but the type of dilatation observed in HIPS does not occur. The data presented in Fig. 4 confirm the view that shear yielding is the dominant mechanism of fatigue damage in ABS.

3.3 Temperature changes

Significant rises in temperature were observed during fatigue tests, especially under square-wave loading, despite the low frequencies employed in this programme. As expected, the rate of heating increased with stress amplitude. A good example of the heating effect is shown in Fig. 7, which was obtained from an ABS specimen cycled at a stress amplitude of 37.5 MPa, equivalent to 84 % of the short-term yield stress. The temperature rose by 7 K during 20 cycles applied over a period of 10 minutes. The stored energy released when the specimen broke at approximately peak tensile load caused a further 7 K rise in temperature. Subsequent cooling was slow, owing to the low thermal conductivity of ABS and the large cross-sectional area of the specimen.

In addition to the general upward trend in

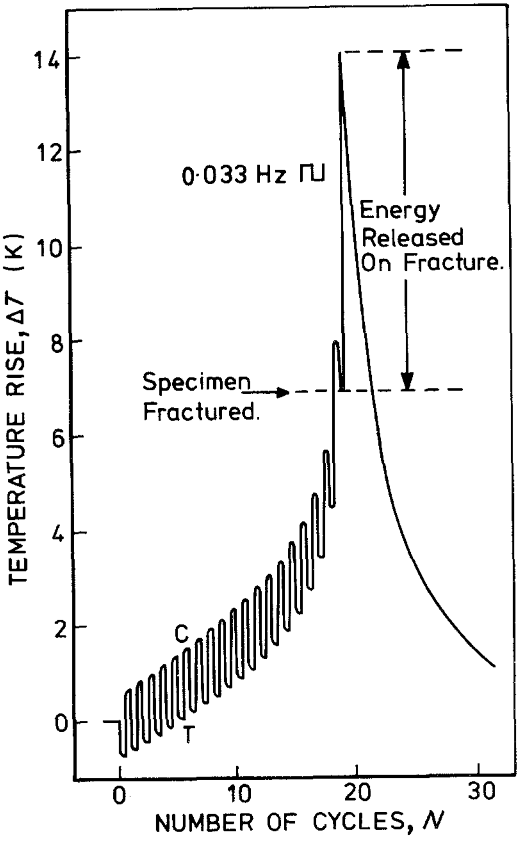

Figure 7 Thermocouple output showing temperature changes during square-wave fatigue of ABS at a stress amplitude of 37.5 MPa.

temperature due to energy dissipation, there is a marked cycling of temperature over each load cycle. The temperature falls sharply on application of tensile stress, and rises equally sharply when the material is compressed. These fluctuations are due to the thermoelastic effect, which has been extensively investigated in metals [11], and has also been observed in plastics [11, 12]. The temperature change ΔT obtained on applying a change in stress $\Delta\sigma$ is given by the Joule equation

$$\Delta T = -\frac{a\,T}{\rho\,C_\sigma}\Delta\sigma, \tag{1}$$

where a is the coefficient of linear expansion, ρ is the density, and C_σ is the specific heat at constant stress. In Fig. 7, ΔT on reversing the stress is approximately 1.2 K, which is in reasonable agreement with the theory.

4. Discussion

The evidence presented above points conclusively to crazing as the dominant mechanism of fatigue damage in HIPS. This is entirely to be expected, since crazing is known to be the dominant mechanism of tensile creep under the same conditions. Shear yielding is observed in HIPS at higher temperatures than those used in the present work, or in highly-drawn specimens, but at 23° C isotropic HIPS does not shear yield at the stresses employed in this work. Shear yielding in compression requires stresses of about 80 MPa [13]. The fatigue experiments show that crazing develops after an induction period, as in creep. At the end of this period, whitening becomes visible, dilatation can be observed on the tensile portion of the load cycle, and the tensile hysteresis loop shows the characteristic shape for a crazed material. Fatigue damage is also detectable on the compressive portion of the load cycle, but the effects are much smaller; the decrease in modulus and increase in hysteresis are clearly due to incomplete recovery of the crazes on removing the tensile stress. Nevertheless, these effects are large enough to complicate the problem of distinguishing between crazing and shear yielding. A drop in secant modulus or increase in hysteresis in compression is not necessarily an indication of shear yielding, so that some more sophisticated method of analysis is required in order to determine quantitatively the contributions from the two mechanisms. Experience with volumetric measurements indicates that they do not provide the ideal answer, even at low frequencies of fatigue cycling.

The evidence also shows clearly that shear yielding is the dominant mechanism of fatigue damage in isotropic ABS under the experimental conditions employed in this programme. Again, this result is not unexpected. In creep tests, the same ABS responds initially by shear mechanisms, and forms crazes only after prolonged loading [7]; at low stresses, elongations of 5% or more are reached by shear yielding alone. The shape of the hysteresis loop is perhaps the clearest indication that shear yielding is taking place in the fatigue test, and this evidence is supported by the absence of visible whitening, the volume strain data, and the similarity between secant moduli in tension and compression.

A complete description of fatigue damage requires not simply the identification of responsible mechanisms, but also quantitative information on the kinetics of each mechanism. In the present work, one mechanism predominates in each of the two materials investigated, so that the problem of analysing the damage into two components does not arise. However, both crazing and shear yielding will be present in the more general case, and it is therefore necessary to ask how the two mechanisms could be distinguished. A comparison of the data for ABS and HIPS suggests a number of ways in which this problem could be approached, using hysteresis, modulus and volumetric strain measurements.

One of the most striking comparisons is shown in Fig. 8, in which hysteresis loss in tension is plotted against hysteresis loss in compression for ABS and HIPS. The term "hysteresis loss" is here used to mean energy dissipated in hysteresis divided by work done, using the definitions given in Fig. 2. Both polymers show a linear relationship between the two loss factors, but the slopes of the lines are 0.8 and 5.0 respectively, reflecting the differences in mechanism of fatigue damage. The onset of crazing in ABS would be expected to cause an upturn in the curve, and the fact that the slope is constant is perhaps the best indication that crazing has not taken place during the period covered by the data. This type of plot could perhaps be used more generally to determine the mechanisms of deformation and damage in rubber-modified and other plastics. There is no obvious

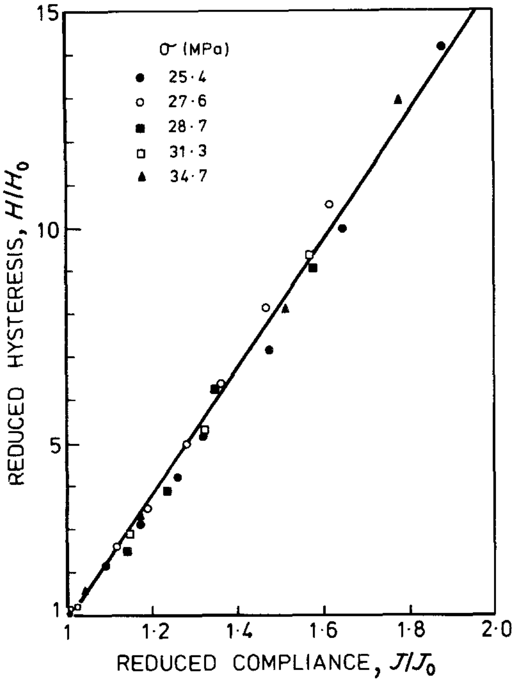

Figure 8 Relationship between tensile and compressive hysteresis for ABS and HIPS. Interrupted square-wave fatigue.

reason why the slope should be 0.8 in the absence of crazing, and 5.0 when crazing is the only mechanism, and it would therefore appear to be necessary to use some method such as volume measurements to assess the effect of degree of crazing upon the slope for a given material. Once suitable calibration curves of this type had been produced, the problem of determining the mechanisms of fatigue damage would be greatly reduced. Hysteresis measurements offer considerable practical advantages over the monitoring of volume strains.

The increase in hysteresis is one measure of the extent of fatigue damage in a material. The absolute value of energy loss is determined by the stress amplitude, and it is therefore more satisfactory to use a reduced hysteresis factor, defined as H/H_0, where H_0 is the hysteresis at the start of the test and H is the current value of hysteresis. Data obtained at different stress levels can be compared on this basis. Another measure of response to fatigue loading is the reduced compliance of the material J/J_0, where J and J_0 are the current and initial values for the reciprocal of the secant modulus. Fig. 9 shows that there is good correlation between these two quantities, at least in the case of ABS.

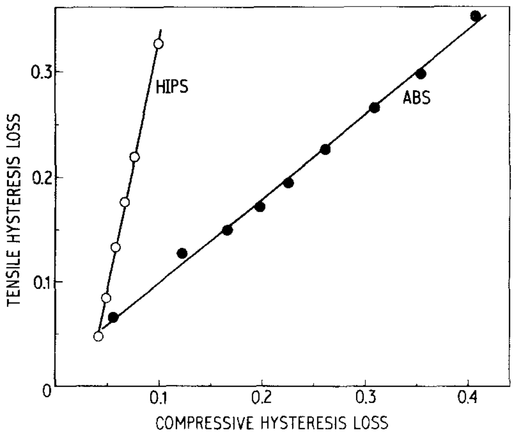

Figure 9 Relationship between reduced hysteresis and reduced compliance in ABS over a range of stress amplitudes. Tensile data from interrupted square-wave fatigue.

The formation of shear bands in the ABS provides a good explanation for both the increase in hysteresis and the increase in compliance. Little is known about the loss characteristics of shear bands, but there is good evidence for a low effective compliance. Polymers form shear bands at elastic shear strains of between 0.02 and 0.05, whereas the shear strains within the bands have been estimated as between 1.0 and 2.2 [14, 15]. These figures could be taken to indicate that the compliance of a shear band is between 20 and 100 times higher than that of the surrounding matrix. On this interpretation, the observed doubling in compliance could be caused by between 1 and 5% of the polymer forming shear bands. It would also follow that energy losses in the shear bands are 300 to 1500 times greater than in the equivalent volume of the surrounding material. This line of argument leads to the conclusion that enough heat could be generated within a shear band during a single load reversal to raise the temperature of the band above the glass transition temperature. The discussion is necessarily speculative on this point, as there is no available information about the strains within shear bands in ABS.

However the energy is dissipated, either locally within shear bands or in a more diffuse manner, it is clear that heating of the specimen plays an important part in the fatigue damage process. The temperature rises recorded are not sufficient to reduce the modulus of ABS directly to any significant extent, although they may have this effect within shear bands, as discussed above. The main result of the internal heating is to accelerate the processes of fatigue damage. Both crazing and shear yielding are activated processes, with relatively high activation energies, so that a rise of only one or two degrees is sufficient to cause an observable increase in rate. This effect, together with other aspects of the kinetics of fatigue damage, will be discussed more fully in a later paper.

The temperature rises recorded in this paper are average values for the material as a whole. In cases where a crack develops as a result of fatigue, or is present before cycling begins, a more localized heating at the crack tip is to be expected, becoming more pronounced as crazing and shear yielding occur in the region of maximum stress concentration. Damage zones of this type can be detected by means of scanning infra-red photography, as has been demonstrated with metal fatigue specimens [16], so that regions where fatigue cracks are likely to form can be identified. This method has also been used to determine the stage that has been reached in the fatigue life of a metal specimen, and the same technique could presumably be applied to plastics.

The ultimate aim of any fatigue study is to predict the endurance of the material under cyclic loading. Monitoring of fatigue damage shows promise in this direction. In one sense, the damage itself constitutes failure, since a component in which the modulus has fallen to one half of its original value can legitimately be said to have failed. Defining fatigue failure in the more usual way as fracture of the specimen, the results obtained to date in this investigation indicate a correlation between the rate of fatigue damage and the number of cycles to failure. However, the number of data points obtained is somewhat limited, especially in view of the scattered nature of the fatigue endurance results, and discussion of this topic will therefore be postponed.

The evidence obtained in this study shows that crazing and shear yielding, which are together responsible for the toughness of HIPS and ABS under monotonic loading, cause accelerating temperature rises in fatigue, either generally throughout the material, or more locally at stress concentrations. These effects are additional to the well known thermal effects due to viscoelastic energy dissipation in the material as a whole, and are considerably more severe because loss factors rise by an order of magnitude when fatigue damage accumulates. Accelerated internal heating offers one possible explanation for the problems encountered in the fatigue of rubber-modified glassy polymers such as ABS and HIPS.

5. Conclusions

This work has shown that crazing is the dominant mechanism of deformation in HIPS under fully-reversed tension–compression loading at 23° C. Shear yielding is the dominant mechanism in ABS, and crazing is observed only during the final stages of the fatigue life. Both mechanisms produce regions of high hysteresis in the polymer, with the result that substantial temperature rises occur even at low frequencies of loading. Internal heating affects the kinetics of fatigue damage, causing rates of crazing and shear yielding to increase during a fatigue test.

Acknowledgement

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