Kinetics and Mechanisms of Fatigue Damage in Rubber-Toughened Poly(methyl Methacrylate) (RTPMMA)

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Synopsis

Specimens of RTPMMA were subjected to fully reversed tension–compression cycling under load control, at a frequency of 0.5 Hz and an ambient temperature of 21°C. Modulus, hysteresis, and temperature of the polymer were monitored continuously. Significant changes were observed at stress amplitudes greater than half the short-term yield stress. Temperature rises of between 5°C and 20°C account for the initial increases in compliance and hysteresis, which subsequently continue to increase, at approximately constant temperature. It is concluded that shear yielding is responsible for this second stage of the softening process. The rate of shear yielding increases exponentially with stress amplitude.

INTRODUCTION

Fatigue crack propagation takes place under loadings that would not be sufficient to cause crack growth under static conditions. In order to analyze this fatigue effect theoretically, it is necessary to develop a model for the accumulation of damage in the plastic zone at the crack tip. Williams has advanced such a model for polymers, based on the formation of a linear crazed zone ahead of the crack: crazed fibrils are assumed to weaken or fail under repeated loading and unloading, thus causing stress–relaxation.[1] The applicability of this model to rigid PVC has been demonstrated by Williams and Osorio.[2]

The observation of discontinuous crack growth in a number of polymers[3] provides further evidence of the importance of fatigue damage. The crack front may remain stationary for several hundred loading cycles before advancing as a result of fracture of an existing craze. The craze grows continuously during each arrest period. Discontinuous crack growth is observed in PMMA when the molecular weight is below about 300,000.[3,4]

The aim of the present program is to determine the factors that control rates of fatigue damage in thermoplastics, and especially in impact-resistant plastics, since toughness in impact does not necessarily ensure good fatigue properties, and vice versa. An earlier study showed that multiple crazing is the principal mechanism of fatigue damage in HIPS, but that shear yielding may be more important in some grades of ABS.[5] Both mechanisms cause an increase in compliance and hysteresis, but crazing may be distinguished by its disproportionate effect upon tensile properties. The increasing hysteresis accelerates

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internal heating of the material, and adds to the difficulties of analyzing the kinetics. The results presented below were obtained in a series of experiments on a transparent rubber-toughened PMMA, in which crack initiation and the onset of stress whitening could readily be detected.

EXPERIMENTAL

Material

The material was a transparent rubber-toughened thermoplastic supplied by ICI, and consisting of an injection-moulding grade PMMA [poly(methyl methacrylate)] matrix containing approximately 32 vol % of three-layered composite acrylic rubber particles with an average diameter of about 0.2 μm. The polymer was compression molded at 190°C into 6-mm sheets, which were water-cooled over 5–10 minutes before removal from the press. Specimens of the type illustrated in Figure 1 were milled from the sheet and carefully polished within the gauge portion. For temperature studies, a 0.8 mm diameter wire was molded into a waisted specimen, as illustrated, and then extracted, leaving a channel for a chrome–alumel thermocouple, which was positioned with the junction at the center of the specimen. Tests showed that the channel did not affect the fracture behavior of the specimen.

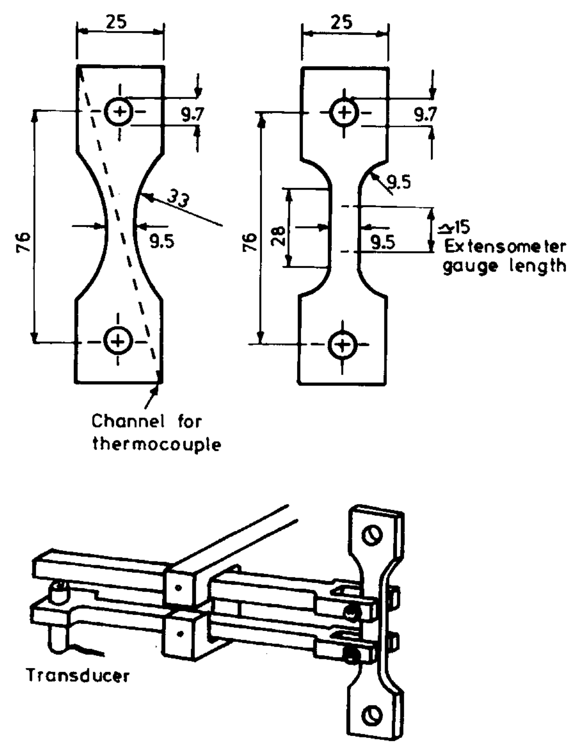

Fig. 1. Specimens and extensometry used in the fatigue experiments. All dimensions in mm.

Test Methods

Fatigue tests were carried out on a multistation closed-loop servo-hydraulic machine designed and built at Cranfield. Specimens were subjected to sinusoidal tension–compression cycling, under load control, with a mean stress of zero. Except where otherwise stated, all measurements were made at a test frequency of 0.5 Hz and an ambient temperature of 21 ± 1°C. In order to monitor mechanical properties during the fatigue test, an extensometer was attached to the specimen, as illustrated in Figure 1, using small pins to make light contact with the specimen. Load and displacement data were fed to a minicomputer, where they were analyzed to determine peak stress and strain, secant modulus and hysteresis in both tension and compression. The number of cycles to fracture was recorded in each case, and the fracture surfaces were examined by means of a traveling microscope, to measure the size of the fatigue crack at failure and the extent of the associated plastic zone. A very small number of specimens fractured as a result of cracking initiated at the extensometer pins; data from these specimens are omitted from the curve of fatigue lifetime as a function of stress amplitude.

In addition to the fatigue studies, tensile tests were carried out over a range of strain rates and temperatures.

Results

Tensile measurements were made between 20°C and 40°C. Over this temperature range, the material is ductile. Whitening is first observed at a strain of approximately 3%, and becomes dense at the yield point, which occurs at about 5% strain. Except at the lowest strain rates, the load decreases as the material extends beyond the yield point. The mechanism of yielding appears to be essentially shear deformation: bands lying at 45° to the tensile axis are observed at the end of the whitened zone, and earlier work by Ward[6,7] and by Hooley and co-workers[8] has conclusively demonstrated that shear yielding is the dominant mechanism of deformation in this type of rubber-toughened PMMA. The whitening must therefore be attributed to the shear process rather than to extensive crazing, although its exact cause has not been clearly established.

Data from the tensile tests are presented in Figure 2. Both modulus and yield stress fall rapidly between 20°C and 30°C, and thereafter decrease more slowly. These results show that there is a transition in mechanical properties in the region of room temperature. A similar transition occurs in PMMA itself, but is more difficult to study because the polymer is brittle at lower temperatures and high strain rates.

Hysteresis loops obtained in fatigue tests at a stress amplitude of 32 MPa are illustrated in Figure 3. The loops increase in area as the test proceeds, while retaining their original elliptical shape. Similar behavior, associated with the formation of shear bands, was previously observed in an emulsion ABS polymer.[5] By contrast, multiple craze formation in HIPS resulted in an expansion and change in shape of the tensile portion of the loop, which was not matched in the compressive portion.

The difference in fatigue behavior between ABS and HIPS was emphasized in the earlier paper by plotting the area of the hysteresis loop in tension against

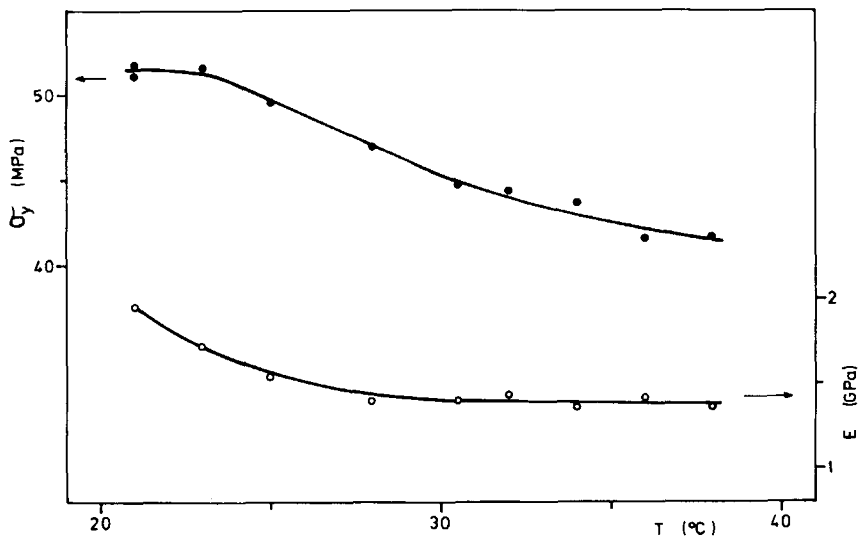

Fig. 2. Young's modulus at small strains and yield stress of RTPMMA determined in tensile tests at a strain rate of 3×10^{-3} s^{-1} over a range of temperatures.

the area of the same loop in compression; ABS gave a straight line of slope 0.8, whereas HIPS gave a slope of 5.0. Results obtained in the present study, at a range of stress amplitudes, are plotted in Figure 4. The data all lie on the same straight line, which has a slope of 1.1.

The increase in hysteresis is accompanied by a decrease in modulus, which is defined in the present study as the secant modulus, measured between the intercept on the stress axis and the subsequent peak stress, as illustrated in Figure 3. The tensile compliance J, obtained by taking the reciprocal of this secant modulus, increases relatively rapidly at the beginning of the fatigue test, and then becomes approximately linear with the number of cycles, as shown in Figure 5. The rate of change of compliance is a strong function of stress amplitude.

Temperature rises both internally and at the surface of a fatigue specimen are shown in Figure 6. Although these temperature rises are not large enough to cause thermal failure, they have a significant effect on modulus and yield stress, as indicated in Figure 2. Under the conditions employed in the present work,

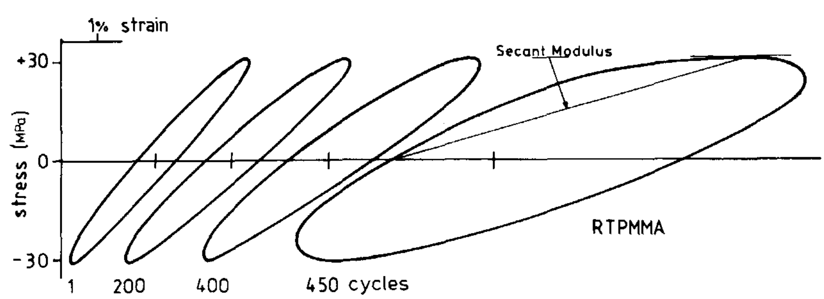

Fig. 3. Hysteresis loops obtained from a fatigue test at stress amplitude 32 MPa and frequency 0.5 Hz. Origin for each loop shifted as indicated.

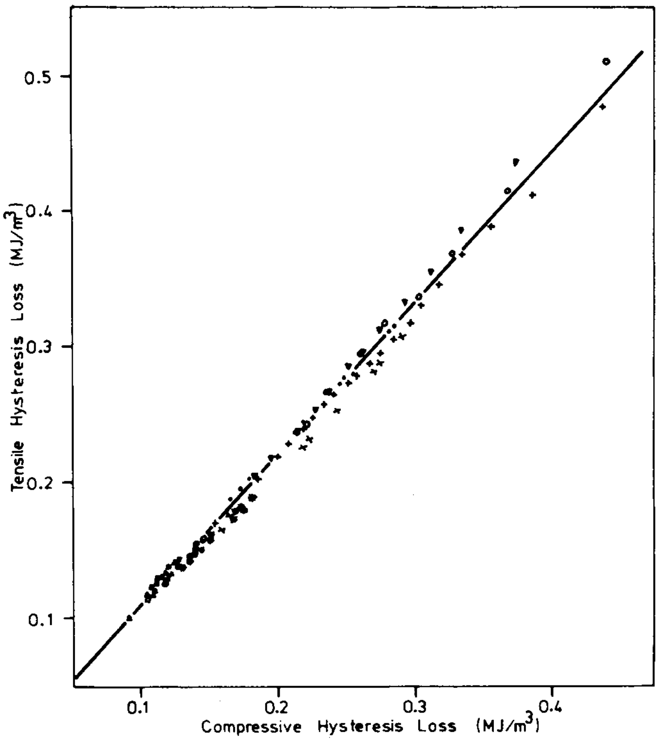

Fig. 4. Comparison of hysteresis half-loop areas in RTPMMA over a wide range of stress amplitudes (MPa): (△) 24; (□) 25; (⊙) 26; (*) 29; (X) 30; (●) 30; (+) 31; (▽) 32; (O) 33.8.

the specimens tend towards a steady state, in which the rates of heat generation due to hysteresis and heat loss to the surroundings become equal. The factors affecting the steady state temperature are discussed by Crawford and Benham.[9] An accurate theoretical prediction is difficult to achieve. Experimental measurements of the maximum temperature rise in RTPMMA ranged from 5°C at 24 MPa to 20°C at 33.8 MPa.

In order to distinguish between mechanical fatigue damage and changes in properties due simply to the temperature rise, it is necessary to have accurate information about the variation of secant modulus with temperature. Tensile test data are unsuitable for this purpose because of the differences in strain rate and method of measurement. Fatigue tests were therefore conducted at a frequency of 0.5 Hz over a range of ambient temperatures, using the low stress amplitude of 12.5 MPa in order to avoid heating effects and mechanical damage. The results are given in Figure 7. Both tensile hysteresis and compliance increase approximately linearly between 20°C and 50°C. Checks showed that the properties were independent of thermal and mechanical history at this stress amplitude, over the temperature range of the tests.

In Figure 8, curve 1 shows the observed increase in tensile compliance of RTPMMA at a stress amplitude of 30 MPa. Data on the internal temperature as a function of number of cycles were used to construct curve 3, which shows how compliance measured at a stress amplitude of 12.5 MPa would vary as the temperature increased. The difference between the two curves represents the

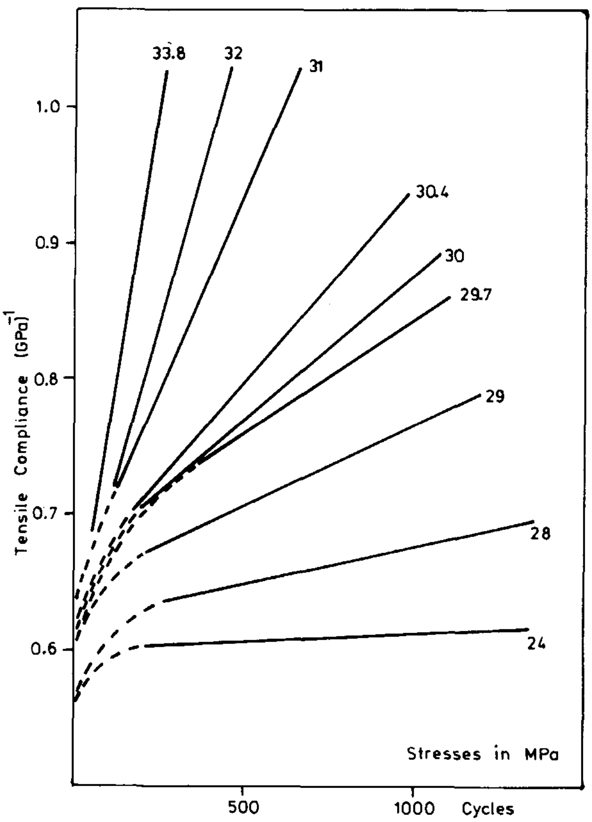

Fig. 5. Effects of stress amplitude on rate of fatigue damage in RTPMMA.

effect of the higher stress upon the mechanical response of the material. There are two basic mechanical effects: first, the initial compliance is higher at 30 MPa, indicating significant nonlinearity in the elastic properties; second, the compliance increases with cycling at the higher stress. Curve 2 is an estimate of the

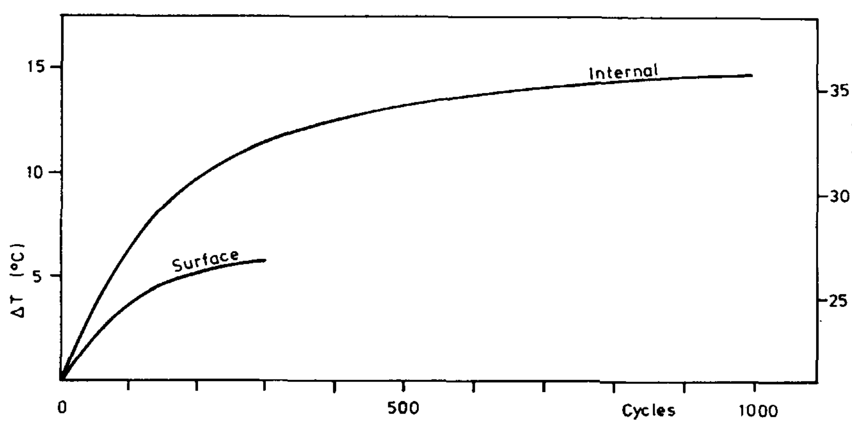

Fig. 6. Surface and internal temperature rises at 0.5 Hz and 30 MPa.

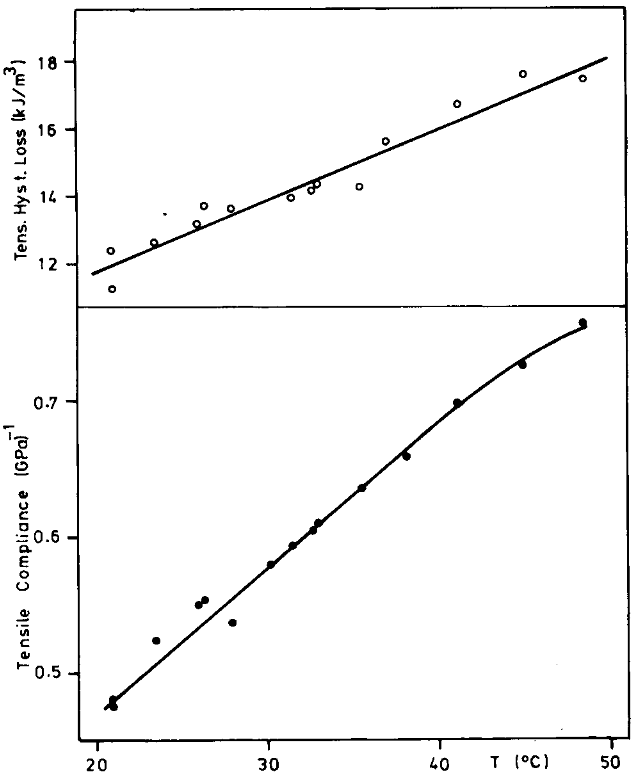

Fig. 7. Effect of temperature on secant modulus and hysteresis of RTPMMA, measured on the tensile half of the fatigue cycle at a stress amplitude of 12.5 MPa and 0.5 Hz.

way in which compliance varies with number of cycles, simply as a result of mechanical damage, after allowing for the effects of the temperature rises.

Progressive whitening of the specimen, which first becomes apparent shortly after the beginning of the test, confirms that mechanical damage is taking place. At a stress amplitude of 30 MPa, whitening is first observed as the specimen reaches peak tensile stress, at about 150 cycles. Between 150 and 800 cycles, the density of whitening under tensile loading increases, but the specimen becomes transparent in compression. Finally, the extent of damage reaches the stage at which a small amount of whitening is also observed in compression.

The relationship between the rate of damage dJ/dN and the stress amplitude σ, shown in Figure 9, can be represented approximately by the Eyring equation:

$$\frac{dJ}{dN} = \frac{1}{f}\frac{dJ}{dt} = A \exp \frac{\gamma V \sigma}{kT} \tag{1}$$

where t is time, f is frequency, N is number of cycles, A is a constant, V is the activation volume, γ is a stress concentration factor, k is Boltzmann's constant, and T is temperature. The apparent activation volume of γV calculated from the slope of the line is 2.2 nm^3, which is very close to the value of 2.0 nm^3 obtained by Ward from creep experiments on the same polymer.[6]

Figures 10 and 11 show the relationship between stress amplitude and the

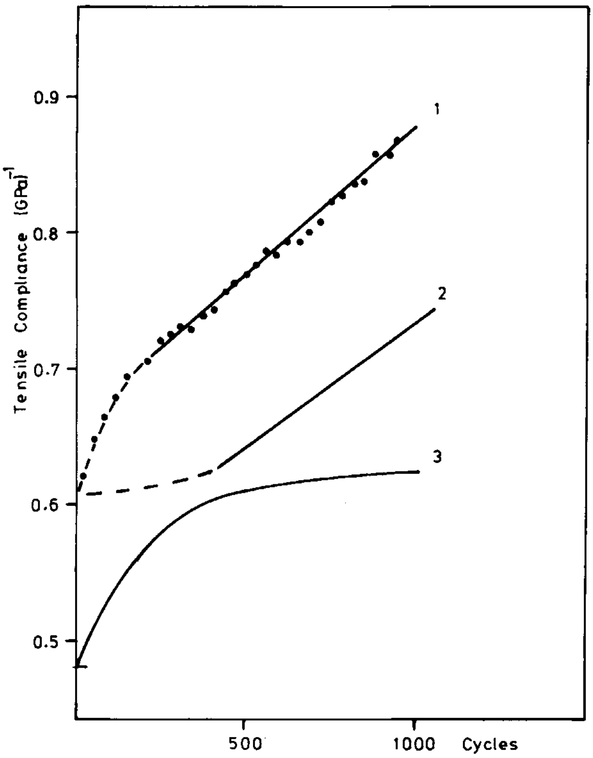

Fig. 8. Comparison between compliances: (1) observed experimentally in fatigue test at 0.5 Hz and 30 MPa; (2) compensated for temperature rise; (3) due to temperature rise alone (data from 12.5 MPa test).

fatigue damage, as measured by the area H under the tensile portion of the hysteresis loop. Measurements were made by cycling the specimen at low stress amplitude for 250 cycles and then allowing a period equal to five times the duration of the fatigue loading (i.e., about 1.25 h) before resuming the test at a higher amplitude. This procedure was repeated up to the point of fracture. In a linearly viscoelastic material, the energy H dissipated in each cycle through mechanical hysteresis is proportional to the square of the stress amplitude σ^2, and H/σ^2 is independent of σ. This type of behavior was observed in a sample of ABS mass-polymerized material, but the RTPMMA material showed strong deviations from linearity. In ABS, the hysteresis remained unchanged between 50 and 250 cycles at a given stress amplitude, whereas there is a steady increase in the case of RTPMMA, as shown. The deviations are particularly marked at higher stress amplitudes; again, there are contributions from both heating and mechanical damage.

An S–N curve of stress amplitude against fatigue endurance is presented in Figure 12. The highest σ tested was 33.8 MPa, which is approximately two-thirds of the short-term yield stress σ_y. The material shows a fatigue endurance limit between 8 and 9 MPa, i.e., at about 0.15 σ_y. Out of 43 specimens tested, eight fractured from cracks initiated internally, and the remaining 35 from cracks originating at the surface. The fatigue crack surfaces show a clear pattern of concentric striations, but little or no evidence of whitening. The edge of the

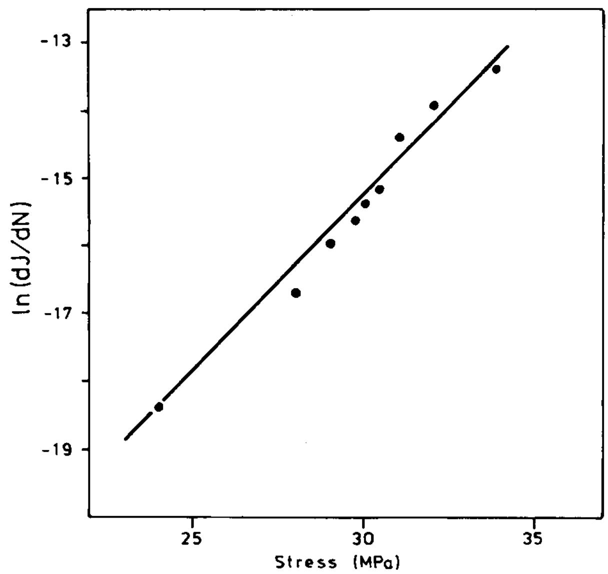

Fig. 9. Eyring plot of rate of change of compliance per cycle against stress amplitude.

fatigue crack is bordered by a whitened yield zone formed during the final load cycle. At low stress amplitudes, where the critical crack is relatively large, the remainder of the fracture surface is rough and essentially unwhitened. At high stress amplitudes, on the other hand, yielding occurs across the remaining liga-

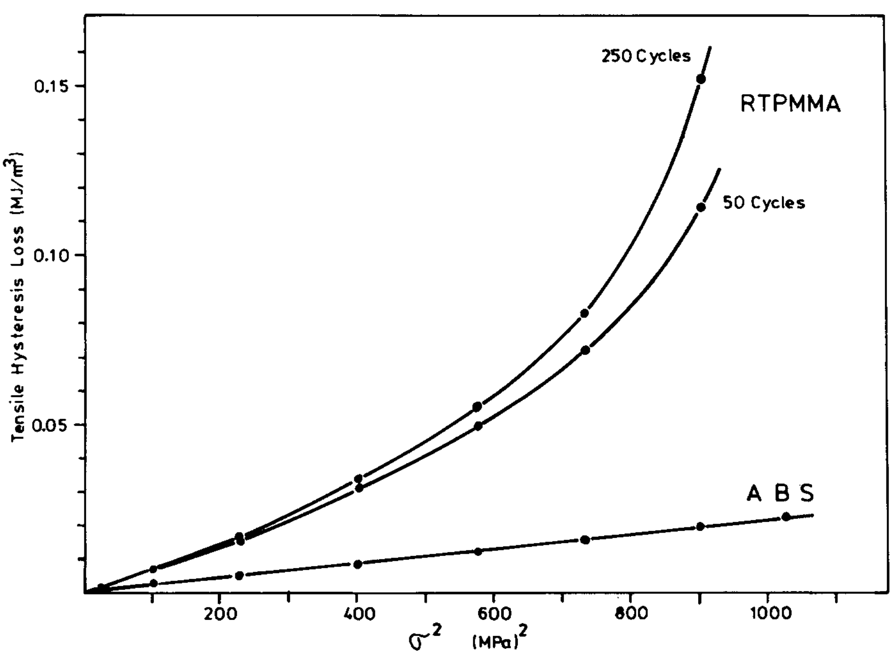

Fig. 10. Test of linearity between hysteresis and square of stress amplitude in ABS and RTPMMA.

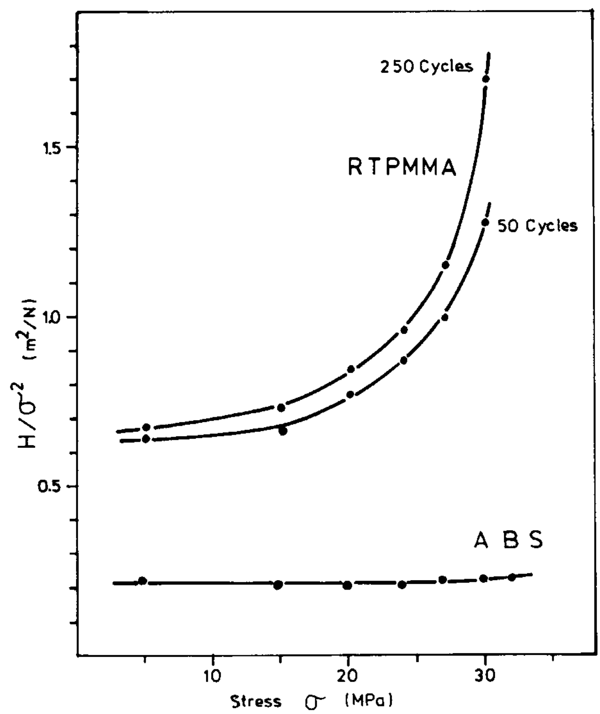

Fig. 11. Nonlinearity of reduced hysteresis H/σ^2 in RTPMMA.

ment during the final stage of the test, and dense whitening is observed up to 5 mm from the fracture surface.

The fracture toughness K_{IC} of the RTPMMA was calculated from the critical crack size and the peak tensile stress, using data from specimens tested at low stress amplitude, in which the crack radius a was large and the extent r of the associated plastic zone was small. For a penny-shaped crack originating at a corner[10]:

$$K_{IC} = 2.4\,\sigma\,\sqrt{a/\pi} \tag{2}$$

In the more general case of an elliptical crack having semiaxes of length a and c,

$$K_{IC} = (1.12\sigma/\Phi)\,\sqrt{\pi a^2/c} \tag{3}$$

where $\Phi = 3\pi/8 + \pi a^2/8c^2$. These measurements gave a value of 2.4 ± 0.2 MPa·m$^{1/2}$ for K_{IC}. Plastic zone sizes were in satisfactory agreement with those predicted by the Dugdale model, using yield stresses taken from tensile test data.

DISCUSSION

This study has shown that thermal and mechanical effects combine to produce an increase in compliance and hysteresis in rubber-toughened PMMA under fatigue loading. Thermal effects predominate during the early stages of the test, but mechanical damage becomes more important after this initial period.

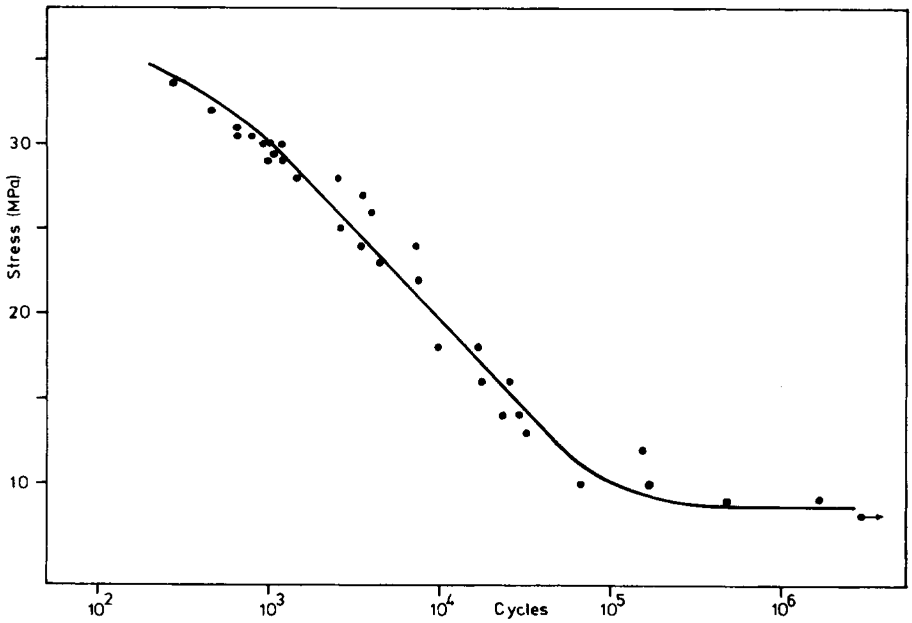

Fig. 12. Fatigue endurance curve for RTPMMA. Arrow indicates unbroken specimen.

A comparison of tension and compression portions of the hysteresis loop indicates that the principal mechanism of mechanical response is shear deformation. This process is accompanied by stress whitening in tension, which disappears when the material is compressed, except during the later stages of the fatigue test, when the whitening is particularly dense; compression then reduces the opacity of the specimen, but does not completely restore transparency. Previously reported measurements of volume strain in tensile creep tests.[6,7] and in tensile tests at constant strain rate[8] show that very little dilation takes place in RTPMMA under these loading conditions and, therefore, that shear yielding is the dominant mechanism of deformation. As in the case of fatigue, shear yielding is accompanied by stress whitening. Microscopy studies on each of these three types of specimen have so far failed to reveal any evidence for crazing. A possible explanation of the whitening is the interaction between the shear bands and the rubber particles. Small changes in the refractive index of the rubber are sufficient to cause opacity, as can be demonstrated by heating the polymer to 100°C: differential expansion produces a mismatch in refractive index between rubber particles and matrix. Relatively small dilatational strains imposed on the particles as a result of shear band formation could have a similar effect.

Another connection between fatigue behavior and creep and tensile response is found in the relationship between rate of deformation and applied stress. The Eyring equation is applicable in all three cases and gives almost identical values of apparent activation volume V, viz., 2.2 nm^3. However, the detailed kinetics appear to be different. In a creep test, the rate of deformation decreases continuously with time, whereas, under fatigue loading at a constant stress amplitude, the rate of increase in compliance becomes effectively constant. It is not clear whether the rate would be constant if the fatigue specimen were tested under truly isothermal conditions, should such conditions be attainable, but curve 2 of Figure 8 suggests that a linear relationship between compliance and number of cycles is a good approximation to the fatigue behavior under these conditions.

When a shear band is formed, a small volume of the polymer deforms to a large shear strain. The sense of this strain is reversed when the stress is reversed, as in the tension–compression testing employed in the present program. The increasing compliance and hysteresis during fatigue cycling confirm that the shear bands behave as regions of high compliance compared with the bulk of the material. The system can be treated as a composite in which layers of shear bands are sandwiched between blocks of unyielded polymer. According to this model, the increase in compliance under isothermal conditions reflects the continuous conversion of unyielded material into the sheared condition. Because the properties of the two forms of the polymer are so different, the depletion of the harder unyielded material can be neglected at total strains of a few percent and the changes in properties can be regarded as due to the addition of sheared layers to the composite.

At low stress amplitudes, or in the presence of an introduced sharp crack, yielding is confined to the region of the crack tip. The same deformation processes appear to occur here as in the bulk specimen. The experiments described in this paper, therefore, provide an insight into the mechanical response of the crack tip region, which has an important influence upon the rate of fatigue crack propagation. Similar studies on other polymers are in progress. The ultimate aim of the work is to develop a better understanding of the relationship between structure and fatigue resistance in polymers. In the case of rubber-toughened PMMA, the two major factors appear to be the beta transition in the PMMA matrix, which causes both the heating effect and the reduction in compliance, and the presence of rubber particles, which accelerate the shear deformation and thus lower yield stress.

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