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Rubber-toughening of plastics

Part 4 *Creep mechanisms in ABS emulsion polymer*

C. B. BUCKNALL, I. C. DRINKWATER
Department of Materials, Cranfield Institute of Technology, Bedford, UK

Mechanisms of deformation in an ABS emulsion polymer were studied quantitatively by a uniaxial tensile creep method. Craze formation was measured in terms of volume strain, which was calculated from simultaneous observations of longitudinal and lateral strains, and shear deformation was measured in terms of lateral strain. The experiments showed that shear deformation predominated during the early stages of creep, but that the rate of shear deformation fell with time. At stresses below 27 MN m^{-2}, specimens reached extensions of 5% without significant craze formation: at higher stresses, crazing was observed at strains above about 2½%. Rates of crazing increased with time and with stress, so that the contribution of crazing to creep was greatest during the later stages of the test, and at the higher stresses. The relevance of these results to engineering applications of ABS polymers is discussed.

1. Introduction

The methods available for studying mechanisms of rubber-toughening are reviewed in an earlier paper [1]. Microscopy has played an important part in identifying mechanisms: Bucknall and Smith used optical microscopy to show that crazing is the dominant mechanism of deformation in high-impact polystyrene (HIPS) [2], and Matsuo used electron microscopy to show that crazing also contributes to toughening in acrylonitrile-butadiene-styrene (ABS) polymers [3, 4]. More recently, Bucknall and co-workers have studied the role of shear bands in controlling fracture resistance of some rubber-toughened plastics, using both transmission and scanning electron microscopy [5]. In addition to microscopy, differences in the failure envelope have been employed by McGarry and Oien to distinguish materials failing by craze formation from those failing by shear under multiaxial tensile loading [6].

Studies of this kind form the basis for a more quantitative approach to rubber-toughening. Since crazes contain a high proportion of voids [7], crazing can be followed by measuring volume increases. Furthermore, in tensile tests on isotropic materials, crazing does not cause lateral contraction. By contrast, shear processes such as shear band formation may be assumed to cause lateral contraction without affecting volume, so that the contributions to deformation from the two mechanisms can readily be distinguished by plotting volume strain at a given time against the corresponding longitudinal strain [5]. The slope of the line indicates the contribution of crazing to the deformation: unit slope means 100% crazing, zero slope indicates no crazing, and a slope of 0.5 shows that 50% of the deformation is due to crazing.

Previous papers in this series describe the application of these ideas to HIPS and to blends of HIPS with poly(2,6 dimethyl-1,4-phenylene oxide) [1, 5, 8]. Volume strains were calculated from longitudinal and lateral strains, measured simultaneously in high-accuracy creep tests. The results showed that mechanisms and rates of creep are affected by a number of factors, including matrix composition and rubber particle size, and that interactions between crazes and shear bands significantly alter both creep and fracture behaviour. In the present paper, the analysis is extended to ABS polymers.

2. Experimental procedure

2.1. Material

The material used in this work was Cycolac T brand ABS polymer, manufactured by the Marbon Chemicals division of Borg-Warner Corporation. Cycolac T is a typical high-impact ABS emulsion polymer, i.e. a polymer made by charging styrene and acrylonitrile monomers to a vessel containing polybutadiene latex, and co-polymerizing the monomers in the presence of the rubber. The emulsion process produces an ABS with small rubber particles (between 0.05 and 1.0 μm in diameter) which have relatively little internal structure compared with polymers made by the alternative mass and suspension processes. Fig. 1 shows an ultrathin section of Cycolac T ABS, prepared by Kato's technique, in which the polybutadiene is hardened and stained by osmium tetroxide [9].

The ABS polymer, in the form of natural (unpigmented) moulding powder was compression-moulded at 180 °C into 2 mm thick sheets. Preliminary tests showed that the sheets were isotropic.

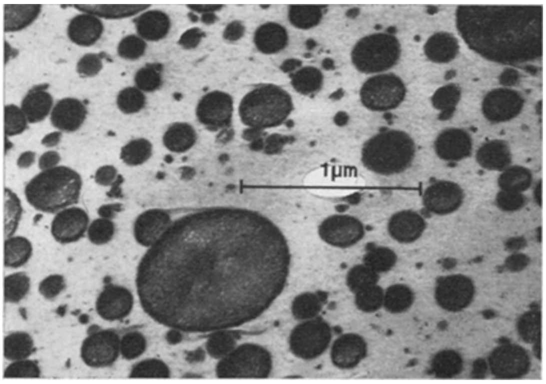

Figure 1 Transmission electron micrograph of an osmium-stained section of Cycolac T brand ABS.

2.2. Creep tests

Dumb-bell specimens with a parallel gauge portion 40 mm long and 5 mm wide were milled from the compression-moulded sheet and subjected to creep tests at 20 ± ½°C. Ten specimens were tested in uniaxial tension at stresses σ between 26.5 and 34.5 MN m^{-2}, using high-accuracy lever-loading rigs of the type developed by Darlington and Saunders [10]. Except where otherwise stated, the stresses quoted are nominal stresses, based upon the original cross-sectional area of the specimen. The tests were carried out at constant load rather than constant stress.

Longitudinal strain e_3 was measured in the central 20 mm of the specimen, and lateral strain e_1 was measured simultaneously, at the centre of the gauge portion; e_1 is, of course, usually negative in a tensile test. The volume strain $\Delta V/V$ was calculated from the expression:

$$\Delta V/V = (1 + e_3)(1 + e_1)^2 - 1.$$

Each long-term creep test was preceded by a loading-unloading programme at successively increasing loads, in order to obtain a 100 sec isochronous curve of tensile creep modulus against 100 sec longitudinal strain, within the low strain region [11]. During this preliminary programme, stress levels were kept well below those used for long-term testing. Long-term tests were terminated when e_3 reached a value of about 5%, and the specimen was then unloaded and allowed to recover. The loading-unloading programme was then repeated, in order to obtain another 100 sec isochronous curve, to illustrate the effects of a creep history upon the ABS.

3. Results

Results obtained at 26.5 and 34.5 MN m^{-2} are presented as fully as possible in this section, to illustrate the range of creep behaviour observed. Data obtained at intermediate stresses are included where appropriate.

3.1. Creep data

Fig. 2 shows that the pattern of creep and recovery varies with applied stress. At 26.5 MN m^{-2}, there is little change in volume, except for the initial elastic response to the applied hydrostatic component of stress, and the volume strain is recovered immediately when the specimen is unloaded at 1.8×10^6 sec. Creep takes place almost entirely by shear mechanisms, so that the decrease in cross-sectional area with time equals the increase in e_3, within the limits of experimental error. The creep rate is high at first, decreasing to an approximately constant value which is maintained for most of the test. Just before unloading, there is a slight increase in rate. Because of the decrease in cross-sectional area, the true stress increases by 3.8% between the first and last measurement of e_3 under load, and it appears likely that the creep rate would continue to drop slightly if the test were carried out at constant true stress rather than constant load.

At 34.5 MN m^{-2}, the pattern of a decelerating creep rate, dominated by the contribution of

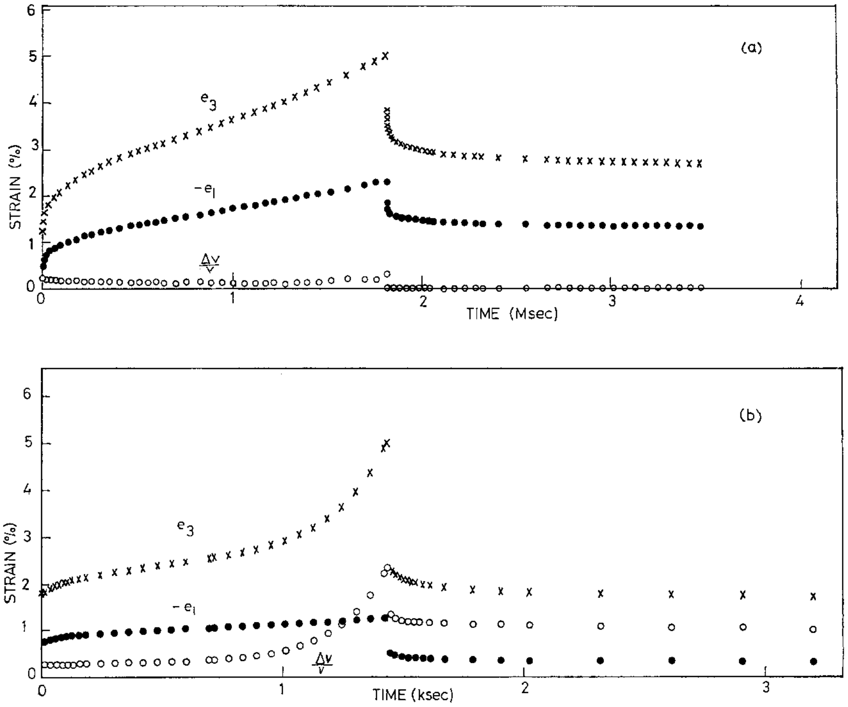

Figure 2 Creep and recovery curves showing e_3 (×), $-e_1$ (●), and $\Delta V/V$ (○) at two stresses: (a) 26.5 MN m^{-2}; and (b) 34.5 MN m^{-2}.

shear deformation, is also observed during the first half of the test. However, after about 800 sec, there is a rapid increase in volume, which is reflected in an increase in overall creep rate $\dot{e}_3$. In this test, the change in true stress with time is approximately 1%. The increase in creep rate during the second part of the test is clearly due to crazing. As in HIPS, craze formation is observed only after a substantial induction period [1]. In contrast with the results at 26.5 MN m^{-2}, the volume strain is not recovered completely upon unloading, and crazing makes the major contribution to e_3 in recovery.

Fig. 3 includes data obtained at intermediate stresses. At all stresses studied, the volume remains approximately constant for a long period after initial loading. The rapid increase in volume strain towards the end of the creep test is observed at all stresses except 26.5 MN m^{-2}. During the later part of the test, the lateral strain rate $\dot{e}_1$ is approximately constant in any one test. The contribution of crazing to creep increases with increasing stress between 26.5 and 34.5 MN m^{-2}, with a corresponding increase in unrecovered volume strain during the recovery stage of the test.

Lateral strain data obtained at 26.5 and 34.5 MN m^{-2} are shown in more detail in Figs. 4 and 5. The results indicate that the shear mechanism is a viscoelastic process which includes a prominent flow term. Rates of deformation due to this flow term increase very rapidly with stress, indicating that the viscoelastic shear mechanism is highly non-linear. Since craze formation is also a highly non-linear deformation process, the rate of extension $\dot{e}_3$ exhibits major deviations from linear viscoelastic behaviour.

3.2. Creep mechanisms

The quantitative method for determining the contribution of crazing to creep, by plotting volume strain against longitudinal strain, is described in the introduction. Fig. 6 shows the relationships obtained in this way for Cycolac T ABS in creep at five different stress levels. It is clear that the mechanisms of creep change both with strain (i.e., with time under load) and with stress.

At a stress of 26.5 MN m^{-2}, the respective values of $\Delta V/V$ and e_3 are 0.25 and 1.25% immediately after loading. During the subsequent creep test, $\Delta V/V$ remains substantially

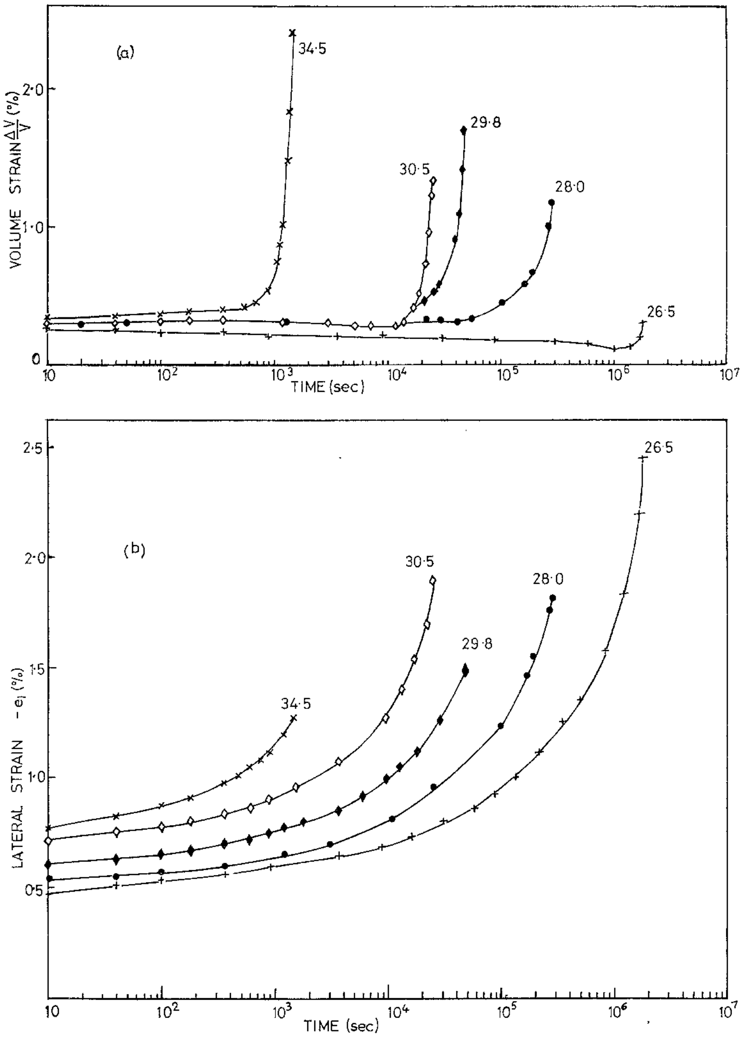

Figure 3 Creep curves showing (a) volume strain; and (b) lateral strain as functions of log t at five different stresses.

unchanged as e_3 increases to 5%, and the low slope of the line indicates that there is very little, if any, contribution from crazing.

At a stress of 34.5 MN m^{-2}, the initial values of $\Delta V/V$ and e_3 are higher because of the higher applied stress. The slope of the line is approximately 0.1 at low values of e_3, reflecting the small contribution from crazing during the early part of the creep test. However, at $e_3 > 3.2\%$, the slope is 0.86, which indicates that at the higher strains crazing contributes 86% to each increment in e_3, and shear mechanisms contribute the remaining 14%. The change in the principal mechanism of creep with time under load, and hence with e_3, is obvious in Fig. 2b, and is expressed quantitatively in Fig. 6.

Intermediate results are obtained at intermediate stresess. The upper curve in Fig. 7 shows the relationship between the maximum slope in the $\Delta V/V$ versus e_3 curve (i.e., the slope at $0.035 < e_3 < 0.05$) and the applied stress. On the basis of this criterion, the change in mechanism occurs at stresses between 26 and 31 MN m^{-2}.

3.3. Recovery mechanisms

The relationship between simultaneous values of $\Delta V/V$ and e_3 can be used in a similar manner to analyse the mechanisms contributing to recovery. Fig. 8 shows a selection of results obtained in the present study. The relationships are approximately linear within the time scale of the

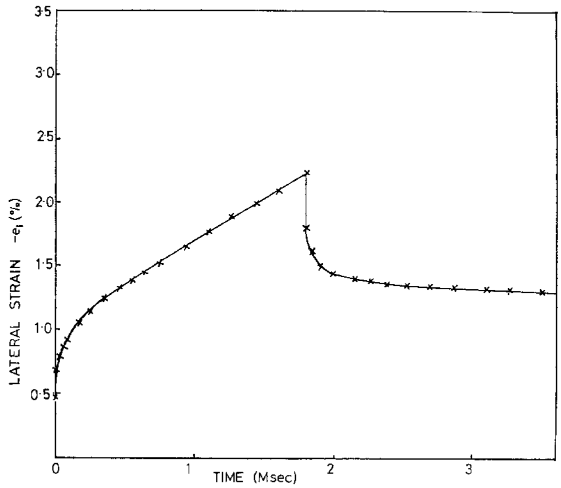

Figure 4 Lateral strain data obtained at 26.5 MN m^{-2}.

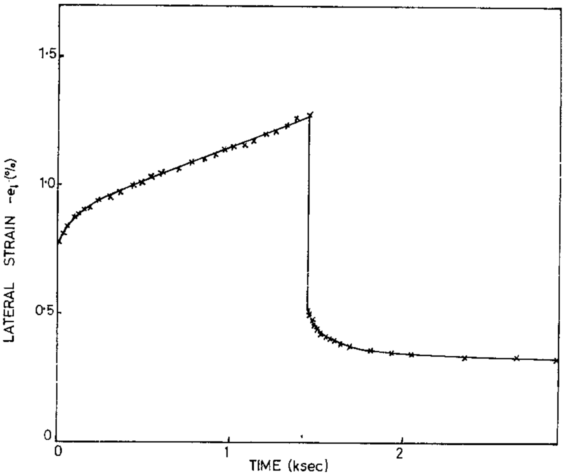

Figure 5 Lateral strain data obtained at 34.5 MN m^{-2}.

experiments, and the slopes of the lines are represented in the lower curve of Fig. 7. The slopes are lower in recovery than they are during the last stages of the preceding creep test on the same specimens, suggesting that rates of recovery are higher for the shear mechanisms than for crazing.

3.4. Creep rates

During each creep test, the rate of lateral contraction $\dot{e}_1$ is high at first, and decreases to a constant value which is maintained for most of the period under load. This constant, minimum, lateral contraction rate is a convenient means of characterizing the rate of deformation by shear mechanisms. Fig. 9 shows the relationship between the minimum $\dot{e}_1$ and σ; as expected, the rate of shear deformation increases with stress. Eyring activation volumes calculated from the slope of the log $\dot{e}_1$ versus σ curve decrease from 5000 Å^3 at lower stresses to 2500 Å^3 at the higher stresses.

Rates of crazing increase rapidly with time under load, showing no sign of levelling off, and it is, therefore, difficult to define a characteristic rate of crazing at each stress. As an alternative, we have arbitrarily defined the induction period for craze formation as the time at which the volume strain reaches 1.0%. This quantity is plotted against stress in Fig. 10. Since $\Delta V/V$ did not reach 1.0% in the specimen tested at 26.5 MN m^{-2}, the induction period has been estimated at this stress from the slight upturn in the $\Delta V/V$ versus log t curve (see Fig. 3). The induction period must be greater than 1.8×10^6 sec, and the estimated figure of 2.5×10^6 sec is probably a little low.

3.5. Isochronous curves

Fig. 11 shows isochronous curves of tensile creep modulus at 100 sec versus e_3 at 100 sec. The upper curve was obtained from specimens that had not been subjected to a long-term creep test. The lower curves illustrate the effects of long-term creep testing to a strain of 5.0% upon the 100 sec modulus. All three curves show a drop in modulus with strain, especially at $e_3 > 0.5$%, but the non-linearity is smaller than that observed in HIPS [8]. The extent of strain damage, as indicated by the drop in modulus caused by long-term creep testing, is also much smaller than that observed in HIPS.

4. Discussion

This work has shown that both crazing and shear mechanisms contribute to the deformation of ABS polymers, and has provided the basis for a fresh approach to understanding and exploiting the mechanical properties of this important class of materials. There are two main fields of practical interest: improved methods of materials selection and design using existing grades of ABS polymers, and the development of new ABS polymers with improved service performance. Both depend upon quantitative information concerning deformation mechanisms.

4.1. Engineering design

The engineer has the problem of selecting materials and designing components on the

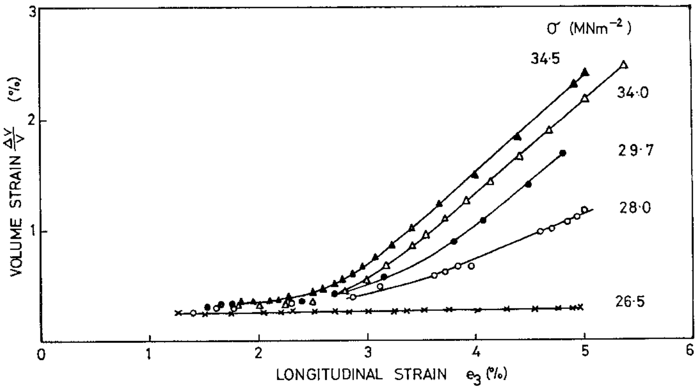

Figure 6 Relationship between $\Delta V/V$ and e_3, showing mechanism of creep as a function of strain at five different stresses.

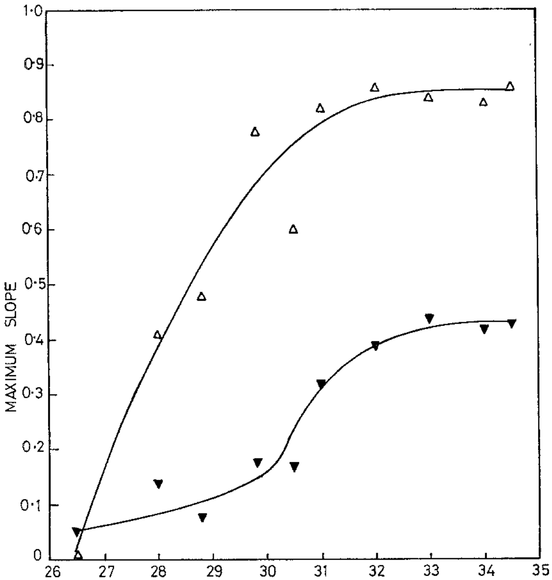

Figure 7 Maximum slope in $\Delta V/V$ versus e_3 curve as a function of stress. Upper curve (△) creep data from Fig. 6; lower curve (▽) recovery data from Fig. 8.

basis of a relatively small amount of data, usually from tests of shorter duration than the intended service life of the component. The problem is, therefore, to make each test as meaningful as possible. In the case of rubber-toughened plastics, inclusion of a lateral strain measurement in creep tests is a step in this direction. With the aid of this measurement, the engineer can now design to avoid significant craze formation in normal service, and can choose materials with this factor in mind. Since crazing is the first stage of fracture, and also causes a reduction in modulus, there are good reasons for avoiding it wherever possible. The relationship between the onset of crazing and the subsequent service performance of ABS is a subject that deserves further study now that the appropriate techniques are available.

Data of the type presented in Figs. 9 and 10 could perhaps be used to predict the long-term performance of ABS polymers under load, and to reduce the uncertainty involved in extrapolating curves obtained from short-term creep tests. The problem of predicting creep behaviour of ABS polymers by means of empirical equations fitted to short-term data is discussed by Bergen, who showed that curve-fitting equations can be developed for data obtained at 23 °C, but that problems arise if the temperature is increased [12]. The need to use extended expressions to fit the data at 23 °C, and difficulties encountered at higher temperatures, can now be seen to be due to the operation of at least two distinct creep mechanisms in ABS.

A comparison of the results presented above for ABS with those obtained previously for HIPS [1, 5, 8] illustrates the relevance of mechanism studies to engineering, particularly in the field of materials selection. In HIPS, there is very little shear deformation, so that creep takes place almost entirely by craze formation. If HIPS is subjected to an extension greater than about 1 %, crazes are formed, and there is a substantial drop in stiffness. In Cycolac T ABS polymer, on the other hand, shear mechanisms make an important contribution to creep, crazing becomes significant only at strains

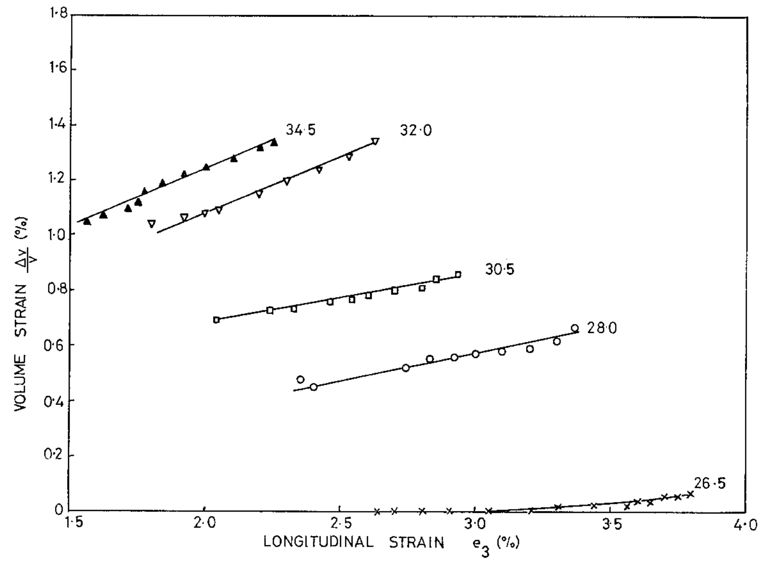

Figure 8 Relationship between $\Delta V/V$ and e_3 during recovery, showing mechanism of recovery from creep at five different stresses.

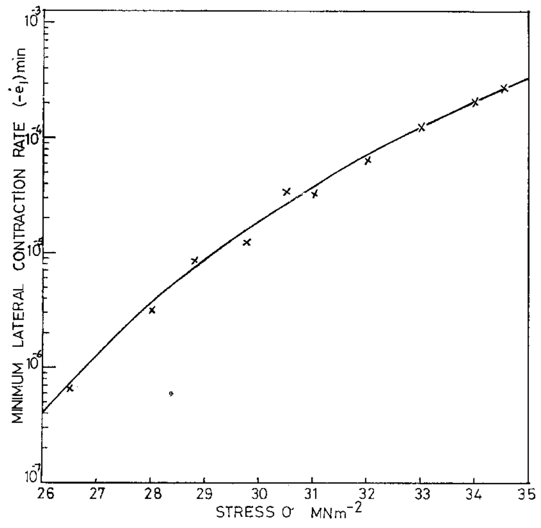

Figure 9 Stress-dependence of minimum lateral contraction rate during creep.

greater than $2\frac{1}{2}\%$, and the drop in stiffness is much smaller. Information of this type, though important, is not provided by standard creep tests. This is not simply a problem of a choice between two distinct classes of rubber-toughened polymer, however; similar differences are also observed between different members of the ABS family of polymers. Details of these differences will be published in a later paper.

4.2. Structure-property relationships

Only limited conclusions concerning structure-property relationships can be drawn from the present work, since only one ABS polymer has been studied. The main basis for comparison is the work on HIPS and HIPS blends presented previously in this series of papers. Nevertheless, the results do throw some light upon the factors affecting rubber-toughening.

Rubber particle size has long been recognized as an important structural parameter in HIPS and ABS polymers, and it is generally known in the industry that rubber particles under about 1 μm in diameter are ineffective in toughening polystyrene. In ABS polymers, the critical particle size appears to be about 0.3 μm. Evidence obtained in the present programme of work suggests that this effect is connected with the mechanism of termination of craze growth [5]: if the mechanism of termination is ineffective, large crazes are formed, leading to early fracture. The presence of large rubber particles, or, alternatively, of shear bands, is associated with effective craze termination and, therefore, with satisfactory fracture resistance.

If craze growth is controlled by an effective termination mechanism of this kind, the rate of crazing in a creep test should either remain constant or decrease with time under load. In Cycolac T ABS, which has a relatively small rubber particle size, the rate of crazing increases

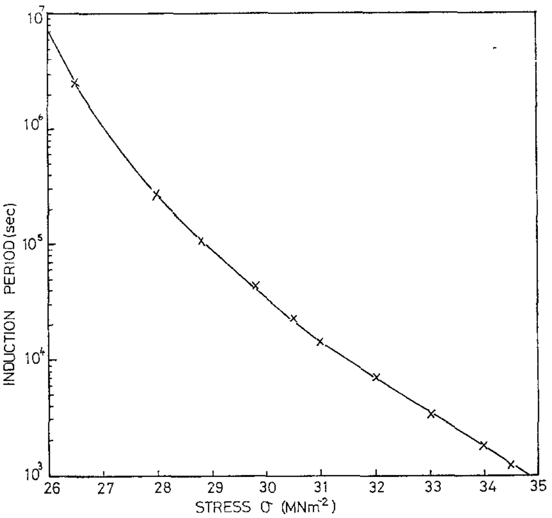

Figure 10 Stress-dependence of induction period for crazing, defined as time to reach 1.0% volume strain.

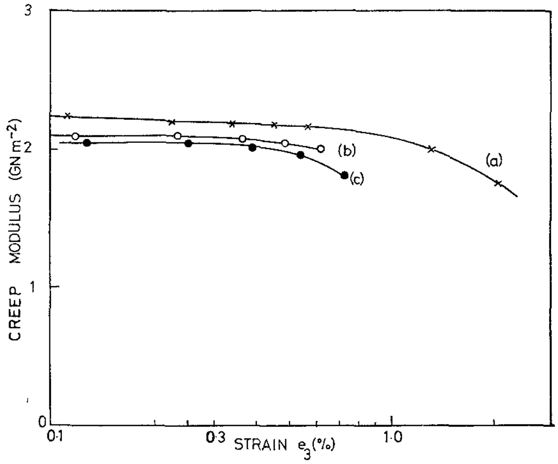

Figure 11 Effects of long-term creep upon stiffness: 100-sec isochrones for three conditions: (a) before long-term test; (b) after creep at 26.5 MN m^{-2} to 5% strain; and (c) after creep at 34.5 MN m^{-2} to 5% strain. The last two points on curve (a) were obtained from 100 sec data in long-term tests.

continuously with time under load at most of the stresses studied, especially at strains approaching 5%. This observation suggests that craze growth is not effectively controlled by the rubber particles, and that the shear processes operating at the same time do not provide a satisfactory alternative termination mechanism. A similar increase in rate of crazing with time was observed in a HIPS containing small rubber particles [5].

The difference in critical particle size between HIPS and ABS polymers is probably connected with the contribution of shear mechanisms to the deformation of ABS, which should have some effect upon craze growth, even if it is only a limited one. This argument is supported by the work of Grancio, who studied the effect of light rolling upon an ABS containing rubber particles approximately 0.1 μm in diameter, and found that elongations at break increased from under 10% to over 100% [13]. In this case, the rubber particles were too small to act as craze terminators, and it was necessary to introduce shear deformation by rolling in order to achieve satisfactory fracture resistance.

The main difference in structure between Cycolac T ABS and the polymers studied previously in this programme is in the composition of the matrix. The matrix in ABS materials is styrene-acrylonitrile copolymer, and the presence of the acrylonitrile group appears to increase the resistance of the copolymer to craze formation, so that higher stresses are required to produce crazing in ABS than in HIPS. At these higher stresses, rates of shear deformation are appreciable, with the result that both crazing and shear mechanisms contribute to creep. The change in mechanism with stress level can be regarded as the result of the decrease in craze induction period with increasing stress. As the induction period decreases, crazing is observed at lower strains, and makes a larger contribution to the total elongation of the specimen.

4.3. Nature of shear mechanism

The precise nature of the shear mechanism observed in this work remains in doubt. The alternatives are localized deformation in well-defined shear bands, or more general visco-elastic deformation. Attempts to distinguish between these alternatives by means of electron microscopy have so far proved unsuccessful. The shear mechanism would be expected to be more effective in terminating craze growth if it produced localized regions of high shear strain [5].

4.4. Limitations of test

The method employed in this work for measuring volume changes depends upon maintaining a uniform cross-section in the gauge portion of the specimen. Satisfactory lateral strain measurements cannot be made if the specimen is necking. For this reason, it is not possible to make meaningful measurements at longitudinal strains above about 5% on materials that undergo significant shear deformation. This is not a serious limitation, since engineers do not normally require creep data at higher strains than 5%. On the other hand, it would be interesting to analyse the deformation mechanisms at all strains up to the point of fracture.

A second limitation at present is the range of stresses and strain-rates over which measurements can be made. Work is now in progress to extend the method to higher stresses and strain-rates. The main problem is to obtain accurate lateral strain data under these conditions.

4.5. Relationship to standard tests

Because of accelerating craze formation, Cycolac T ABS polymer exhibits an increasing creep rate at constant stress. Conversely, there is a fall in true stress when the material is deformed at constant strain-rate in a standard tensile test. Visual observation of stress whitening confirms that crazing takes place near the yield point in ABS. Unlike HIPS, ABS usually necks in standard tensile tests at 23 °C, reflecting the greater contribution of shear processes to the deformation of ABS. By analysing deformation mechanisms quantitatively, the creep test provides a clearer understanding of these common observations.

Perhaps the most frequently quoted property of rubber-toughened plastics is impact strength. Whilst the conditions of the creep test are far removed from those of impact testing, it is interesting to note the trend in creep behaviour with stress: craze induction periods become shorter, and the contribution of crazing to deformation becomes more important. The trend suggests that crazing is more dominant under impact conditions than in creep in ABS polymers. A quantitative investigation of this point must await the development of new techniques.

5. Conclusions

This work has shown that creep of ABS polymers takes place by a combination of crazing and shear deformation. The combination of the two mechanisms changes with stress and strain. At low stresses there is very little crazing. Increasing stress shortens the induction period for crazing, so that crazing is observed at lower strains. Within the range of stresses studied, there is little crazing at strains below $2\frac{1}{2}\%$, and the dominant mechanism during the early stages of creep is shear deformation.

An insight into the mechanisms of deformation is of interest both to the design engineer and to the materials scientist. The additional data concerning mechanisms enable the engineer to choose materials and to develop design procedures which will avoid crazing under service conditions, and offer the materials scientist a fresh approach to structure-property relationships.

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