JOURNAL OF MATERIALS SCIENCE 7 (1972) 1443–1453

Rubber-toughening of plastics

Part 2 *Creep mechanisms in HIPS/PPO blends*

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The effects of matrix ductility upon mechanisms of rubber toughening have been studied in a set of materials having identical rubber contents, but differing in matrix composition. The materials were made by solution blending 50% of HIPS (high-impact polystyrene) with polystyrene and PPO®† poly-(2, 6-dimethyl-1, 4-phenylene oxide) in varying proportions. Crazing was studied quantitatively by measuring volume changes during creep. Analysis showed that in blends of HIPS with polystyrene, crazing is the only significant mechanism of tensile creep, whereas in blends containing polyphenylene oxide, shearing mechanisms are also important, and the contribution of crazing to creep deformation can be as low as 30%, depending upon matrix composition. Scanning electron microscopy showed that both crazes and shear bands were present in strained HIPS/PPO blends. Shear band formation appears to be responsible for the increased fracture resistance of blends containing a high proportion of polyphenylene oxide. A theory of toughening is proposed for these blends.

1. Introduction

The principle of measuring volume change during tensile creep, as a means of studying crazing in rubber-modified plastics, was introduced in earlier papers [1, 2]. This principle was used in the first paper of the present series, which showed that crazing was responsible for over 95% of the observed time-dependent elongation of HIPS specimens, and which presented information about the kinetics of craze formation [2]. In analysing the results, it was assumed that the instantaneous increase in volume upon loading was the ordinary elastic response to the hydrostatic component of stress, and that the subsequent time-dependent volume increases were due entirely to craze formation. These assumptions are based upon the work of Maxwell and Rahm [3], who showed that crazing is a time-dependent phenomenon in glassy polymers; of Kambour [4], who showed that crazes contain roughly equal volumes of voids and polymeric material; and of Bucknall and Smith [5], who demonstrated the importance of multiple craze formation as a deformation mechanism in rubber-modified plastics.

Although crazing appears to be the only important mechanism of tensile creep in HIPS at room temperature, there is a good evidence that additional mechanisms operate in other rubber-modified plastics at room temperature, and in HIPS at higher temperatures. For example, marked reductions in cross-sectional area are often observed, although craze formation, like crack opening, should have little or no effect upon area. Measurements of lateral strains during a creep test provide direct information about these additional mechanisms, which are assumed to take place at constant volume, and to involve local or general shear yielding. Examples of such shear yielding mechanisms include micro shear band formation, and general cold drawing. An important feature of the present study is that the creep elongation is analysed into three separate components: (i) instantaneous elastic response; (ii) crazing; (iii) shear yielding, so that the kinetics of crazing and shear yielding can be analysed separately.

Instantaneous elastic strains are obtained by extrapolating back to zero time. When the initial creep rate is very low, the strains at 10 sec are taken as the instantaneous strains. The instantaneous volume strain is obtained from the expression:

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$$\left(\frac{\Delta V}{V}\right)_{\text{elastic}} = [\lambda_3(0)]\,[\lambda_1(0)]^2 - 1$$

where $\lambda_3(0)$ and $\lambda_1(0)$ are the instantaneous values of longitudinal and lateral extension ratio.

The subsequent time-dependent volume changes are then taken as a measure of craze formation:

$$\left(\frac{\Delta V}{V}\right)_{\text{crazing}} = [\lambda_3(t)]\,[\lambda_1(t)]^2 - [\lambda_3(0)]\,[\lambda_1(0)]^2$$

The rate of crazing is simply the rate of change of volume strain, $(1/V)(\mathrm{d}V/\mathrm{d}t)$ and the fractional contribution of crazing to an incremental extension de_3 is given by $(1/V)(\mathrm{d}V/\mathrm{d}\lambda_3)$, or $(1/V)(\mathrm{d}V/de_3)$. The contribution of shear deformation to the incremental extension is given by $de_3 - (\mathrm{d}V/V)$, which is approximately equal to $-\,2de_1$, where e_1 is the lateral strain. The fractional contribution of shear deformation to de_3 is therefore

$$1 - (1/V)\,(\mathrm{d}V/de_3)\,.$$

The aim of the work described in this paper was to study the effects of matrix composition upon deformation mechanisms in rubber-modified plastics, using the creep tests outlined above. In order to eliminate any effects due to changes in the rubber component, a set of materials was made in which the concentration, composition, structure, size and size distribution of the rubber particles were identical, so that all variations in mechanical behaviour could be attributed to differences in the composition of the matrix.

The system HIPS/PS/PPO is ideally suited to such a study. Recent research has shown that PS and PPO are compatible [6-8], and it follows that matrix composition can be varied independently of rubber content by blending a fixed amount of HIPS with different mixtures of PS and PPO. Furthermore, polyphenylene oxide is considerably more ductile than polystyrene under the test conditions, so that the variations in matrix compositions should give rise to marked variations in mechanical behaviour.

2. Experimental

2.1. Materials

The general purpose polystyrene used in this work was Monsanto HH-101. PPO® polymer is manufactured by the General Electric Company, and is a trade name for poly(2, 6-dimethyl 1,4-phenylene oxide), hereafter referred to simply as polyphenylene oxide. Two grades of HIPS were used. Initial experiments were carried out on Monsanto HT-91, a typical mass or suspension polymer with a particle size of between 1 and 2 µm. A section showing the structure of this material appears in a recent paper by Kambour and Russell [9]. Most of the experiments were carried out on X600, an experimental polymer made by Sterling Moulding Materials. The structure of this material is illustrated in Fig. 1, which is an osmium-stained section prepared by Kato's method [10] from a blend containing 50% of X600. The particle size distribution is bimodal: a few particles are between 1 and 3 µm in diameter, but most are between 0.1 and 0.2 µm. Both types of particle are composite in structure, the larger particles being typical of a mass polymer, whereas the smaller ones are typical of an emulsion polymer.

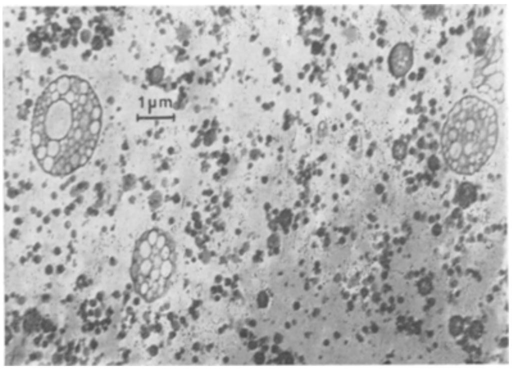

Figure 1 Osmium stained section of 50/50 X600 HIPS/PPO blend. Transmission electron micrograph.

2.2. Blending

Blends were made by mixing separate 10% solutions of the polymers in chloroform. Each blend contained ¼% of tricetyl borate and ¼% of acetyl phenyl hydrazine as stabilizers. After thorough stirring, the blends were precipitated in 10 volumes of methanol, sprayed with 1% of a phenolic antioxidant in methanol solution, and dried in air at room temperature for two days. The remaining methanol was removed in a heated vacuum oven.

The open mat of polymer obtained in this way was compacted, and then compression moulded at temperatures between 180 and 270°C, depending upon the ratio of polystyrene to polyphenylene oxide. Electron microscope examination of ultrathin sections showed that the solu-

TABLE I Composition of HIPS/PS/PPO blends

HIPS (X600)	50	50	50	50	50
PS (HH-101)	50	37½	25	12½	0
PPO	0	12½	25	37½	50

tion blending method was successful in producing a good dispersion of the rubber particles without affecting their size or structure: the rubber particles were uniformly distributed in all of the blends made by this procedure.

Preliminary experiments, including most of the microscopy, were carried out on a 50/50 blend of HT-91 HIPS with PPO polymer. The main part of the work was carried out on five blends each containing 50% by weight of X600 HIPS. The composition of these blends is shown in Table I.

2.3. Creep tests

The procedure for creep testing is described in an earlier paper [2]. Dumb-bell specimens were tested in uniaxial tension at 20°C, using high-accuracy lever-loading creep rigs of the type developed by Darlington and Saunders [11]. Each specimen was first subjected to a loading-unloading programme at successively increasing loads in order to obtain 100 sec isochronous curves of modulus against strain [12]. The main purpose of this preliminary test was to ensure satisfactory mounting and response of the specimen under load. Stresses were chosen to give elongations of less than 0.7% at 100 sec, so that a negligible amount of crazing and shear deformation occurred at this stage of the test.

The long term creep test was then carried out: a higher load was applied to the specimen, which was allowed to creep to an extension of 5% before being unloaded and allowed to recover. Longitudinal strain e_3 and thickness strain e_1 were simultaneously monitored throughout the creep and recovery stages of the test, and volume strain $\Delta V/V$ was calculated from the expression $[(1 + e_3)(1 + e_1)^2 - 1]$. The loading-unloading programme was then repeated in order to obtain another 100 sec isochronous curve, showing the effects of stress history upon the specimen. The results of the recovery and reloading experiments will be reported in a later paper.

2.4. Microscopy

The uniformity with which the rubber particles were dispersed by the blending procedure was checked in undeformed specimens by Kato's method [10], in which ultrathin sections cut from an osmium-stained block are examined in the transmission electron microscope. This method can also be used to reveal the presence of crazes [13] and shear bands, in deformed specimens but is less reliable in this role: sections often fail to show crazes even when these features are known to be present. For this reason, alternative methods for studying deformation mechanisms were sought.

The most successful alternative method is described in a paper by Bucknall, Drinkwater, and Keast [14]: blocks cut from deformed tensile specimens were sectioned in the ultramicrotome to produce perfectly flat planed surfaces, and then immersed in an oxidizing acid solution for about a minute at 70°C in order to etch the planed surface. A typical etch solution contained 400 ml H_2SO_4, 130 ml H_3PO_4, 125 ml H_2O, 20 g CrO_3. Rubber particles, crazes and shear bands were etched preferentially and could be examined by optical, scanning-electron, or transmission electron microscopy. In the present series of experiments, some etched blocks were coated with a thin layer of platinum/gold and examined in the scanning electron microscope; others were replicated by a two-stage process, using polyvinyl alcohol and carbon with platinum shadowing, and examined by transmission electron microscopy.

2.5. Fracture in tension

Dumb-bell specimens milled from compression-moulded sheet were tested to failure in tension in the Instron tensometer. All tests were carried out at 20°C at a constant crosshead speed equivalent to a strain rate, based upon original gauge length, of 2.5% per min.

3. Results

The results are presented below under two headings. The first covers the preliminary investigation of the mechanisms of tensile deformation in HIPS/PPO blends, using a 50/50 blend containing HT-91, which contains relatively large rubber particles. The second covers the subsequent study of the effects of matrix composition upon the kinetics and mechanism of tensile creep. The blends used in this later work contained X600, which has a smaller rubber particle size than HT-91.

3.1. Creep mechanisms

Creep data for the HT-91/PPO blend are presented in Fig. 2, in which longitudinal, lateral, and volume strains are plotted against

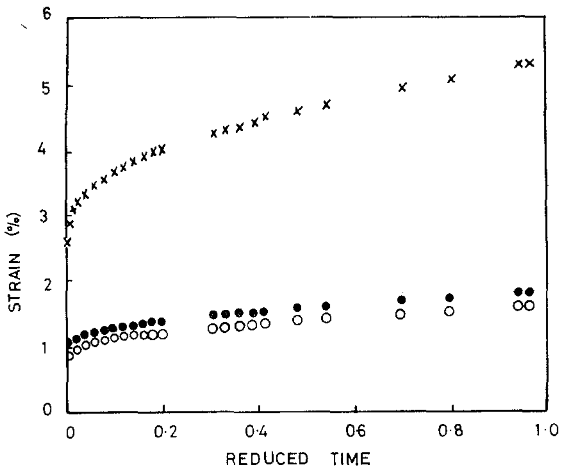

Figure 2 Longitudinal strain e_3 (×), lateral strain — e_1 (●) and volume strain $\Delta V/V$ (○), plotted against reduced time for a 50/50 HT-91 HIPS/PPO blend under a load of 49.1 MN m^{-2}.

reduced time, where reduced time is defined as the elapsed time divided by the time taken to reach 5% extension. The results illustrated were obtained at a nominal stress of 49.1 MN m^{-2}.

The first measurements were made after 25 sec, when $e_3 = 2.56\%$, $e_1 = -0.88\%$, and $\Delta V/V = 0.77\%$. The specimen reached an extension of 5% after 15100 sec. The creep rate was relatively high at first, but fell continuously throughout the experiment. This fall can be attributed to two factors: a decreasing rate of craze formation, as indicated by the volume strain results, and a decreasing rate of shear deformation, as indicated by the lateral contraction measurements. The results show that both crazing and shear deformation contribute significantly to the time-dependent part of the total elongation.

This point is demonstrated more clearly in Fig. 3, which presents the same data in the form of a graph of volume strain at a given stress and time against the corresponding longitudinal strain, and compares them with results for HT-91 grade HIPS taken from previous work [1, 2]. At a stress of 49.1 MN m^{-2}, the results for the blend lie on a straight line of slope 0.33, and at a stress of 47.9 MN m^{-2}, a similar straight line is obtained, of slope 0.28. These results are in marked contrast to those for the HIPS itself, which can be represented, over a range of stresses, by a single line of unit slope.

The conclusion to be drawn from Fig. 3 is that crazing is responsible for only about 30% of the observed time-dependent elongation of the HIPS/PPO blend, and that the remaining 70% is due to shear deformation processes. There is some evidence that in this blend the contribution of crazing to any given extension falls with stress. In HIPS, on the other hand, volume and longitudinal strains increase at the same rate, indicating that crazing is entirely responsible for the time-dependent portion of the extension. Within the range of stresses studied, there is

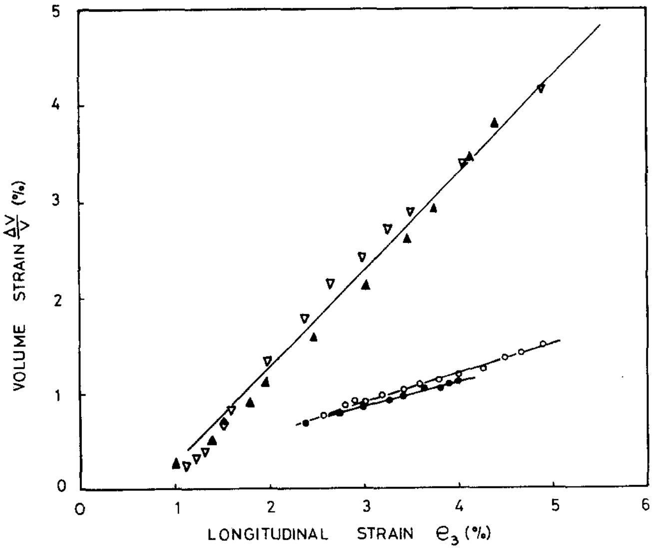

Figure 3 Volume strain plotted against corresponding e_3 for HT-91 grade HIPS at 23.3 MN m^{-2} (▽) and at 21.6 MN m^{-2} (▲), compared with 50/50 HT-91/PPO blend at 47.9 MN m^{-2} (●) and 49.1 MN m^{-2} (○).

little evidence of a change of mechanism with stress in HIPS.

The creep test distinguishes between classes of deformation mechanisms, namely volume change and shear deformation (i.e. constant volume) mechanisms, rather than between specific mechanisms. In order to identify the particular processes operating in a specimen, it is necessary to use microscopy or other techniques. There is ample evidence from previous work [5, 9, 13] that the volume increases are substantially due to crazing, but relatively little relating to the nature of possible shear deformation processes.

The etch method described in Section 2.4 provides direct evidence on this point. Etched specimens of the blend show the presence of both crazes and micro-shear bands. Fig. 4 compares a scanning electron micrograph with a transmission electron micrograph of a replica taken from the same tensile specimen. Both show the same features: the rubber particles are removed by the etch, leaving hemispherical cavities; the crazes appear as deeply etched planar fissures lying normal to the direction of applied stress and to the plane of the micrograph; the shear bands are less deeply etched, and lie at approximately 45° to the applied stress.

In summary, the blend of HT-91 with polyphenylene oxide has a much higher creep resistance than HT-91 itself: the stress needed to produce 5% extension in a given time is over twice as high for the blend as for the HIPS. There are major differences in the mechanisms of creep. The blend deforms by a combination of crazing and shear band formation, whereas HIPS creeps by crazing alone. Finally, the kinetics of deformation are significantly different. The creep rate decreases with time under load in the case of the blend, but increases with time in the case of the HIPS.

The effects of matrix composition upon creep behaviour in blends containing 50% X600 grade HIPS are shown in Figs. 5 and 6, and Table II. The general trends are the same as those described above. As the proportion of polyphenylene oxide in the blends increases, the creep rate at a given stress decreases, shear processes become relatively more important, and the individual creep curves change from an acceleration to a deceleration with time. All of these changes can be attributed to the matrix composition, since the rubber content is the same for all blends in the series.

TABLE II Time (sec) taken to reach 5.0% longitudinal strain.

Stress (MN m^{-2})	Ratio X600/PS/PPO				
	4/4/0	4/3/1	4/2/2	4/1/3	4/0/4
38.8					710
36.2				1800	7500
33.6			1260	25 000	41 700
31.5			28 800	308 400	
29.5		126	69 000		
25.1		3210			
22.5		121 800			
19.7	2270				
18.9	4450				
18.0	5320				
17.2	15 900				

The increase in creep resistance with polyphenylene oxide content is evident in Table II. Where possible, creep tests were carried out on two blends at the same stress for purposes of comparison. The results show that the most marked changes in creep rate occurred between the first blend, containing no PPO, and the second, containing $12\frac{1}{2}\%$ PPO. Each successive substitution of polyphenylene oxide for polystyrene in the matrix produced a smaller effect upon the time taken to reach 5% extension.

The curves plotted in Fig. 5 are representative of the results for each blend. Curves obtained at different stresses are similar in shape to those in the illustration, but do not superpose exactly. Strictly, the basis for comparison should be a graph of compliance against reduced time. On that basis, the curves for the 50/50 HIPS/PS blend are in close agreement, but those for the other blends show small but significant variations in shape with stress. Variations are to be expected where two different mechanisms, each with a different stress-dependence, are contributing to creep.

The creep curves can be represented to a good approximation by a power law of the form:

$$x = k\,t^n + x_0$$

or

$$\mathrm{d}x/\mathrm{d}t = k\,n\,t^{n-1}$$

where x = strain (e_3, e_1, or $\Delta V/V$), k is a constant, t = reduced time, and x_0 is the instantaneous elastic strain. The value of the exponent falls with increasing polyphenylene oxide content, from $n \simeq 5$ for the four 50/50 HIPS/PS blend specimens, through $n \simeq 1$ for the 50/25/25 HIPS/PS/PPO blend specimens, to

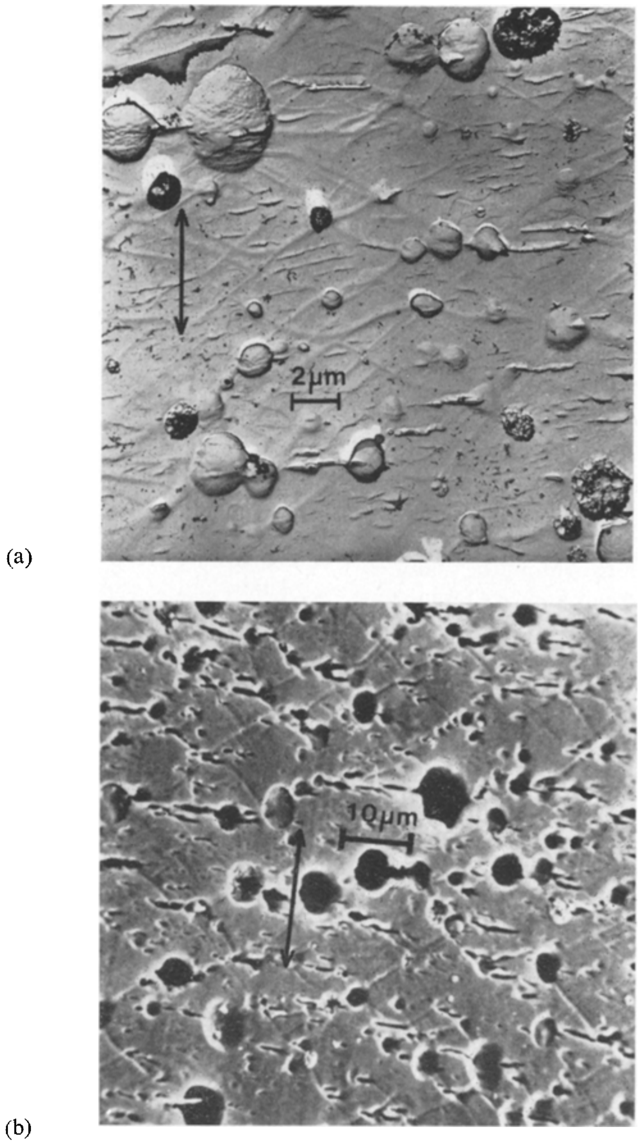

Figure 4 Etched surface of 50/50 HT-91/PPO blend after tensile creep test. Arrows indicate stress direction; (a) transmission electron micrograph of replica; (b) scanning electron micrograph of Pt/Au coated surface.

$n \simeq \frac{1}{2}$ for the 50/50 HIPS/PPO blend specimens. For any given blend, the value of k is different for the longitudinal, lateral, and volume strain relationships, and in the case of the HIPS/PS blend $k \simeq 0$ for the lateral strain e_1.

Although the relationships between creep strain and time are rather complex, the relationships between volume strain $\Delta V/V$ and longitudinal strain e_3 are relatively simple. Fig. 6 shows that ΔV is linearly related to e_3 for each of the blends. The slope of the line decreases with increasing polyphenylene oxide content: the values are 1.00, 0.93, 0.88 0.60 and 0.60 for the five blends in order. As explained earlier, the slope measures the fractional contribution of crazing to the time-dependent portion of the elongation, and hence to the overall strain rate de_3/dt. Conversely, the contributions of shear deformation to the incremental strain Δe_3 and to the strain rate de_3/dt are 0, 7, 12, 40 and 40% for the five blends in order of increasing polyphenylene oxide content. As in Fig. 3, the lines are

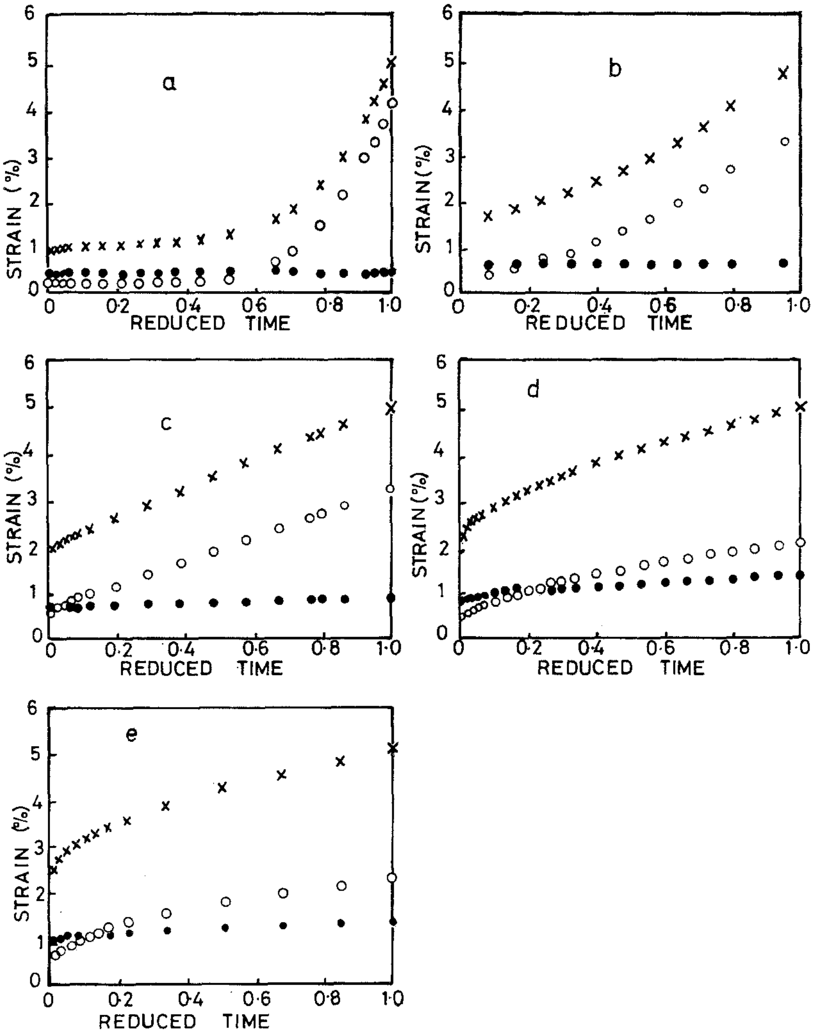

Figure 5 Longitudinal strain e_3 (×), lateral strain — e_1 (●) and volume strain $\Delta V/V$ (○) plotted against reduced time for blends containing 50% X600 HIPS, remainder PS plus PPO. Concentrations of PPO, and stress levels (MN m^{-2}): (a) 0%, 19.7; (b) 12½%, 29.5; (c) 25%, 33.6; (d) 37½%, 36.2; (e) 50%, 38.8.

straight, so that their slopes are independent of strain, indicating that the relative importance of each contributing mechanism is independent of strain within the range of the creep measurements. In other words, although the rates of crazing and shear band formation are functions of time, both appear to vary in the same way, so that both contribute a constant proportion to the total creep extension.

The increase in creep resistance with polyphenylene oxide content is reflected in an increase in yield stress in the Instron test. Fig. 7 shows that at a constant strain rate, yield stress increases from 29 to 46 MN m^{-2} for the series of blends. The shape of the Instron curves also correlates well with the creep results: a decrease in stress at constant strain rate (i.e. a yield drop) corresponds to an increase in strain rate at constant stress (accelerating creep); conversely, an increase in true stress at constant strain rate corresponds to a decrease in strain rate at constant stress (decelerating creep).

Increasing the polyphenylene oxide content of the blends not only raised the yield stress, but also increased the ultimate elongation in the standard Instron test. The values of elongation

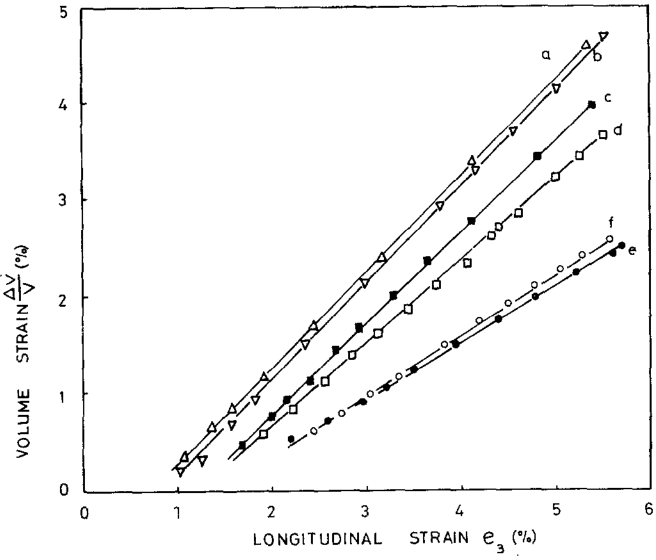

Figure 6 Volume strain plotted against e_3 for blends containing 50% X600 HIPS, remainder PS plus PPO. Concentrations of PPO, and stress levels (MN m^{-2}): (a) 0%, 18.8 (Δ); (b), 0%, 19.7 (▽); (c) 12½%, 29.5 (■); (d) 25%, 33.6 (□); (e) 37½%, 36.2 (●); (f) 50%, 38.8 (○).

recorded for the series were 5, 30, 31, 60 and 71%, in order of increasing polyphenylene oxide content. The increases in both yield stress and elongation combine to produce a very large increase in work-to-break over the series.

The exact composition of the matrix has not been determined for any of the polyphenylene oxide blends used in this work. Nevertheless, there is clear evidence that the polyphenylene oxide content of the matrix is higher in the 50/50 X600/PPO blend than in the corresponding 50/50 HT-91/PPO blend. Microscopy shows that the volume fraction of rubber is higher in X600 than in HT-91, and this conclusion is confirmed by the 100 sec isochronous creep value of Young's modulus, which at strains between 0.1 and 0.6% was 1.3 GN m^{-2} for X600, and 2.2. GN m^{-2} for the 50/50 X600/PS blend, compared with 2.2 GN m^{-2} for HT-91. A given quantity of X600 therefore contributes less polystyrene to the matrix of a blend than does a similar quantity of HT-91.

4. Discussion

This work has shown that at least two important deformation mechanisms – crazing and shear band formation – operate in HIPS/PPO blends under uniaxial tension, and that the relative importance of shear band formation increases with the polyphenylene oxide content of the matrix. Furthermore, the results show that in this case the presence of the extra deformation mechanism is associated with a decrease rather than an increase in creep rate at a given stress and also with a decrease of creep rate with time under load. Perhaps of even greater significance is the increase in toughness with polyphenylene oxide content in a series of blends containing a fixed percentage of rubber.

These facts lead us to suggest that the presence of shear bands reduces the rate at which crazes propagate, and vice versa. It follows from this suggestion that at a given stress, the rates of crazing and shear band formation will fall with time, and that both individual crazes and individual shear bands will be smaller than they would be if only one of the two mechanisms were operative. In fracture mechanics terms, a craze is an intrinsic flaw in the material, and a reduction in craze size should result in an increase in fracture resistance. The observed increase in work-to-break with polyphenylene oxide content can thus be related directly to the effect of shear bands upon the rate of craze propagation, and consequently upon craze dimensions.

The kinetics of crazing in the blends are clearly rather complex and it would not be profitable to attempt a full analysis at the present stage of the programme. Nevertheless, the results contain several novel features, which merit some

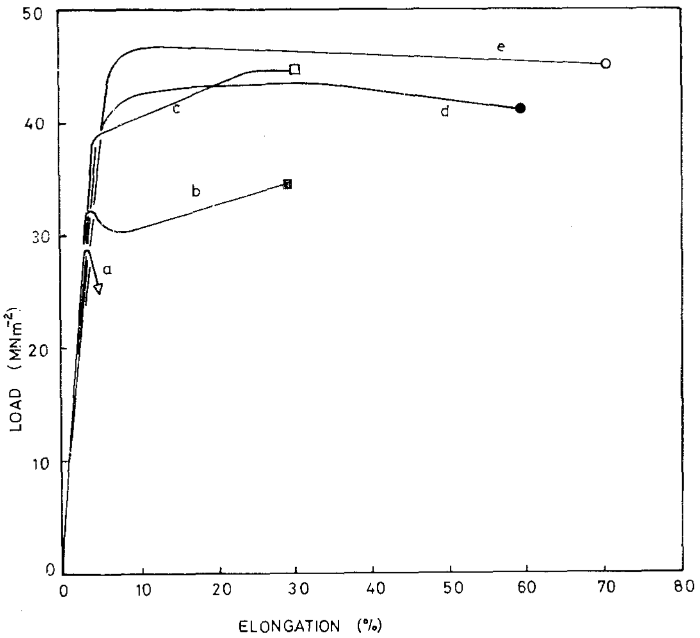

Figure 7 Instron load-elongation curves for tensile test at 20° C at constant crosshead speed equivalent to initial strain rate of 2.5% min^{-1}, on blends containing 50% X600 HIPS, remainder PS plus PPO. Concentration of PPO: (a) 0% (▽); (b) 12½% (■); (c) 25% (□); (d) 37½%, (●); (e) 50% (○).

discussion. In particular the differences in kinetics between the X600/PS blend and HT-91 are striking. The rate of crazing in HT-91 is initially proportional to time t, and becomes constant at the end of an induction period [2]. The rate of crazing in the blend, on the other hand, is proportional to t^4 throughout the creep test, since $n \simeq 5$ in the power law equation. On the assumption that the rate of initiation of crazes is constant during a creep test (i.e. that rates of initiation are functions of stress but not of time), this result implies that the volume of individual crazes in the blend increases as t^4, and that the termination mechanism proposed for HT-91 does not operate in the blend.

A termination mechanism involving interaction between a propagating craze and a rubber particle was invoked to explain the increase in creep rate to a constant value during the latter part of the creep tests on HT-91 [2]. There is no evidence for such a mechanism in the X600 blend. On the contrary, the evidence suggests an accelerating growth rate for the crazes, perhaps resulting from increasing stresses at the tip of each craze as it propagates.

The obvious structural difference between the two grades of HIPS is the size of the rubber particles. The evidence presented above is consistent with the view that particles of about 1 μm or more act as craze terminators, and control the rate of crazing, whereas particles under 0.3 μm in diameter do not act as effective terminators, and do not significantly affect the rate of craze propagation. A high concentration of crazes is observed with both types of particle, indicating that both are effective initiators of crazes. The failure of the termination mechanism would explain the well-known relationship between particle size and toughness in HIPS: the growth of individual crazes is unchecked if the particles are below a critical size, and fracture occurs prematurely.

The failure of the small particles to act as craze terminators is less serious if an alternative termination mechanism is available. Our evidence suggests that shear bands supply such a mechanism, by hindering craze propagation. The molecules in the shear bands are oriented towards the direction of the applied tensile stress, and therefore normal to the plane of the crazes. In this orientation they would be expected to hinder or stop craze propagation, as in the case of homogeneously oriented polymers [15, 16]. The effect of the shear bands upon the rate of crazing will increase, of course, with the number of shear bands present, and the rate of crazing should therefore fall with time during the creep test, as more shear bands are formed. An interaction of this sort would explain the fall in craze rate with time in the blends containing a high proportion of polyphenylene oxide. Intermediate effects are to be expected in the blends containing a lower proportion of polyphenylene oxide, in which lower concentrations of shear bands are formed.

The corresponding reduction in the rate of shear band formation with time can be explained in a similar way. A craze is an expanded layer of low modulus and high mechanical hysteresis sandwiched between two regions of bulk polymer, and can be expected to hinder the propagation of shear bands by dissipating the strain energy in the region surrounding the tip of the band.

These theories provide a basis for interpreting the Instron results contained in Fig. 7. The rubber particles are very small for all blends in the series, and do not provide a termination mechanism for the crazes. Large crazes are therefore formed rapidly, causing early fracture, unless an alternative termination mechanism is available. Shear bands, which are formed in increasing numbers as the polyphenylene oxide content is increased, provide such a mechanism, so that craze size is reduced, and ultimate elongation consequently increased. In addition, the mutual interference in the propagation process between crazes and shear bands reduces the rate of deformation due to both processes, with the result that yield stress increases along the series.

This theory could explain why the "critical particle size" for rubber-modified plastics varies so much from one material to another. Many commercial grades of toughened PVC, for example, contain very small particles, whereas relatively large particles are necessary in HIPS. Shear deformation is known to occur more readily in PVC than in polystyrene under tension, and shear band termination, or an equivalent process, is to be expected in a PVC matrix, in contrast to polystyrene.

The blend of HT-91 with PPO contains large rubber particles and forms shear bands under stress. Both rubber particle and shear band termination are therefore to be expected in this blend, and there is some evidence for both in the scanning electron micrograph shown in Fig. 4. However, the evidence is far from conclusive, and more work is needed in this area. The operation of both termination mechanisms would explain why crazing contributes only 30% to the creep deformation of the HT-91/PPO blend, compared with a 60% contribution in the corresponding X600/PPO blend, although the matrix of the latter blend is almost certainly richer in polyphenylene oxide, and would therefore be expected to favour shear band formation. The explanation is based upon the assumption that the large rubber particles terminate craze formation, but do not affect shear band propagation, so that shear band formation becomes the dominant mechanism of deformation.

An alternative explanation is that the higher rubber content of the X600 blend gives rise to a higher degree of triaxiality in the stress field in the matrix, because the rubber particles are closer together. An increase in the hydrostatic tensile component of stress relative to the stress deviator will favour cavitation processes in comparison with shear processes, and an increased proportion of crazing should follow from the increased triaxiality.

It should be noted that the above discussion applies to specimens under relatively high stresses, sufficient to cause extensions of at least 1% within a few seconds, and of 5% within a few days. There is another field of considerable interest, especially to the design engineer, in the behaviour of rubber-modified plastics under lower stresses. The results presented in the first paper of this series [2] show that the rate of crazing falls rapidly with decreasing stress, so that there is effectively a threshold stress for craze formation. Below this stress, the mechanical properties of rubber-modified plastics can be described in terms of viscoelasticity theory, rather than of crazing, which is essentially a failure mechanism. The properties of the blends at low strains will form the subject of a separate paper.

Another field of interest to the engineer is the change in properties resulting from deformation. Creep recovery and reloading results obtained in the present work reflect the lower modulus of crazes compared with the bulk polymer. The field is a complex one, and the results will be presented separately.

5. Conclusions

This study has shown that creep of HIPS/PPO blends takes place by a combination of crazing and shear band formation. The proportion of shear deformation in a given extension increases with the polyphenylene oxide content of the blend and is also affected by either the concentration or size of the rubber particles. Mutual interaction between crazes and shear bands reduces the rates of propagation of both, and hence increases the creep resistance with time under load and with polyphenylene oxide content. The principle is probably of general application both to other rubber-modified plastics and to glassy plastics. Shear bands strengthen the material by reducing craze sizes.

Acknowledgements

The authors thank the Science Research Council and the General Electric Company for grants in support of this work, Dr M. J. Bevis of the University of Liverpool for the scanning electron microscopy, Mr I. C. Drinkwater for assistance with experiments, and Sterling Moulding Materials for the gift of high-impact polystyrene.

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Received 13 April and accepted 2 May 1972.