Rubber-toughening of plastics

Part 3 *Strain damage in HIPS and HIPS/PPO blends*

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The effects of stress- and strain-history upon the mechanical properties of HIPS (high-impact polystyrene) and of blends containing HIPS and PPO[R] resin* have been studied in a number of different tests, including repeated creep testing of individual specimens and repeated tensile tests at constant strain-rate upon individual specimens. The results show that craze formation increases volume and lowers Young's modulus in specimens subjected to tensile strain, and that strained specimens recover only slowly towards the properties of the unstrained material. Recovery is accelerated by heating, or by immersion in alcohols. A given initial strain produces a greater reduction in modulus in HIPS, which deforms almost entirely by crazing, than in HIPS/PPO blends, which deform by a combination of crazing and shear band formation. The properties of strained specimens are dominated by the distinctive non-linear mechanical behaviour of crazes, and the problems of constructing models to represent this behaviour are discussed.

1. Introduction

The effects of stress and strain history upon the mechanical properties of materials are of interest both to the engineer and to the materials scientist. In rubber-toughened plastics, quite striking effects are observed as a result of craze formation under tensile stress: modulus decreases, mechanical hysteresis increases, and the strained composite material behaves macroscopically in a manner similar to that observed microscopically in individual crazes [1-3]. In terms of engineering applications, these strain-damage effects are amongst the most important consequences of the multiple-craze mechanism of rubber-toughening [1, 4-6].

This paper considers a number of the factors that affect the mechanical properties of previously-strained specimens of rubber-toughened plastics, including the level of the initial strain, the duration of the subsequent recovery period, the temperature during recovery, the presence of active liquids during recovery, and the composition of the material. The work forms part of a quantitative study of deformation mechanisms in rubber-toughened plastics; and the initial response of these materials to an applied stress is discussed in an earlier paper [6]. The two parts of the study, deformation and recovery, are equally important in developing an understanding of deformation mechanisms and of the limitations of the materials in engineering applications.

2. Experimental

All experiments followed the same pattern: a dumb-bell specimen was deformed in uniaxial tension, unloaded and allowed to recover, then retested in tension. This pattern of testing was used in two ways: firstly, to study the effects of environment upon the recovery of HIPS; and secondly, to study the relationship between polymer structure and recovery in HIPS/PPO blends. An Instron tensometer was used for the first set of experiments, and a high-accuracy creep rig was used for the second set.

2.1. Materials

The Instron tests were carried out on white, pigmented Bextrene XL750, which was obtained in the form of 0.15 cm extruded sheet. Bextrene XL750 is a HIPS mass polymer, formerly manufactured by Bakelite-Xylonite Ltd, contain-

*PPO[R] is a registered trade-mark of the General Electric Company. The material used is poly (2, 6-dimethyl-1, 4-phenylene oxide), hereafter referred to simply as polyphenylene oxide.

ing approximately 10% of polybutadiene in the form of composite rubber particles between 1 and 5 μm in diameter. Preliminary tests showed that the sheet was isotropic.

The other HIPS polymer used was X600, an experimental polymer made by Sterling Moulding Materials. A micrograph illustrating the microstructure of this polymer is included in the preceding paper of this series [6]. The polybutadiene content is approximately 30%, and the particle size distribution is bimodal: a few particles are between 1 and 3 μm in diameter, but most are between 0.1 and 0.3 μm.

The creep tests were carried out on five blends, each of which contained 50% by weight of X600 grade HIPS. The remaining 50% consisted of polystyrene (PS) and polyphenylene oxide in various proportions. The polyphenylene oxide contents of the five blends were 0, $12\frac{1}{2}$, 25, $37\frac{1}{2}$ and 50%. Blends were made by mixing solutions of the polymers in chloroform, precipitating in methanol, drying and compression moulding. Further details of the materials and of the blending procedure are set out in reference [6].

2.2. Instron tests

Dumb-bell specimens with a parallel gauge portion 7.5 cm long and 1.25 cm wide were milled from the extruded HIPS sheet. These specimens were deformed in uniaxial tension at $20 \pm \frac{1}{2}$ °C, using an Instron tensometer with a constant crosshead speed of 0.5 cm min^{-1}. The direction of travel of the crosshead was reversed when the specimens reached an elongation of 40%, and the stress was reduced to zero, again at a crosshead speed of 0.5 cm min^{-1}.

After this standardized initial loading programme, the specimens were allowed to relax under specified conditions, and then retested in the Instron tensometer at 20°C and 0.5 cm min^{-1} crosshead speed, in order to study the effect of deformation and subsequent relaxation upon yield behaviour.

Specimens were allowed to relax in three ways: (i) in air at 20°C; (ii) in an alcohol at 20°C; and (iii) in an evacuated oven at a temperature between 20°C and the glass temperature of polystyrene. The alcohols chosen for this work were methanol, ethanol, isopropanol, n-butanol, and cyclohexanol. Specimens were immersed in the alcohol for 24 h, then dried and placed in a vacuum chamber at 20°C for 24 h, in order to remove absorbed alcohol. Weighing experiments indicated that some alcohol remained in the

specimens, so that this procedure was not entirely satisfactory. Nevertheless, some useful information was obtained. The effects of the residual alcohol upon the results are discussed below. The reason for using an evacuated oven for the heating experiments was to avoid oxidation problems.

2.3. Creep tests

Creep tests were carried out upon the HIPS/PS/PPO blends at 20°C. Each specimen was first subjected to a short-term programme of loading and unloading at relatively low stresses, in order to obtain 100-sec isochronous curves of modulus against strain in the strain range 0.1 to 0.7%. Each period of 100 sec under load was followed by 600 sec under zero load. The cycle was then repeated, using a higher stress level. Strains were limited to 0.7% in order to avoid crazing and shear-band formation at this stage of the test.

This short-term creep programme was followed by a long-term creep test at a substantially higher load. The 100-sec reading from this part of the programme was included in the isochronous modulus-strain results. Specimens were unloaded at elongations between 5 and 6%, and allowed to recover under zero load.

The time allowed for recovery was between one and eighty times as long as the period of the long-term creep test. At the end of the recovery period, the specimen was again subjected to a short-term loading and unloading programme at relatively low stresses, as described above, and a second isochronous curve was obtained.

The tests were carried out in high-accuracy lever-loading rigs of the type developed by Darlington and Saunders [7]. Longitudinal strain e_3 and thickness strain e_1 were monitored at each stage of the test, and volume strain was calculated from the expression:

$$\frac{\Delta V}{V} = [(1 + e_3)(1 + e_1)^2 - 1].$$

3. Results and discussion

Previous papers have established that crazing is the dominant mechanism of tensile deformation in HIPS, and that both crazes and shear bands contribute to the tensile deformation of HIPS/PPO blends [5, 6]. Recovery of crazes, which is usually described as craze "healing", is an important part of the recovery process in both types of polymer, but in the PPO polymer blends, there is the additional possibility of a contribu-

tion from recovery of shear bands. The present study therefore covers two separate problems: the effects of environment upon the recovery of crazes in HIPS, and the quantitative contributions of crazes and shear bands to the recovery of HIPS/PPO blends.
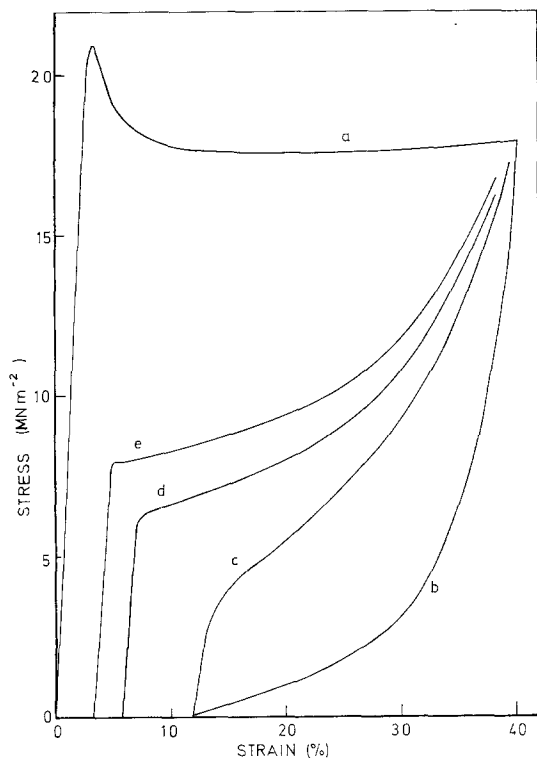

Figure 1 Instron tensometer curves for Bextrene XL750 HIPS: (a) initial tensile test; (b) recovery curve; (c) immediate tensile re-test; (d) re-test after 2×10^4 sec at 20°C; (e) re-test after 2×10^6 sec at 20°C. Crosshead speed 0.5 cm min^{-1}. Test temperature 20°C.

3.1. Instron tests
3.1.1. Temperature and recovery
Immediately after the initial loading and unloading cycle in the tensometer, the HIPS specimens exhibited very different properties from those shown during the first part of the loading cycle. Fig. 1 illustrates this strain-damage effect. Whereas the specimen originally yielded at 21 MN m^{-2}, the curve obtained immediately after the initial loading cycle showed no clear yield point. Instead, there was a knee at about 4 MN m^{-2}. In analysing the results, the point of

maximum curvature was taken as the effective yield point.

Over a period of time, the properties of the crazed specimens returned towards those of the unstrained material. Curves obtained after 2×10^4 and 2×10^6 sec at 20°C, which are included in Fig. 1, illustrate the trend; the yield point of the crazed specimens became higher and more clearly defined as the recovery period increased.
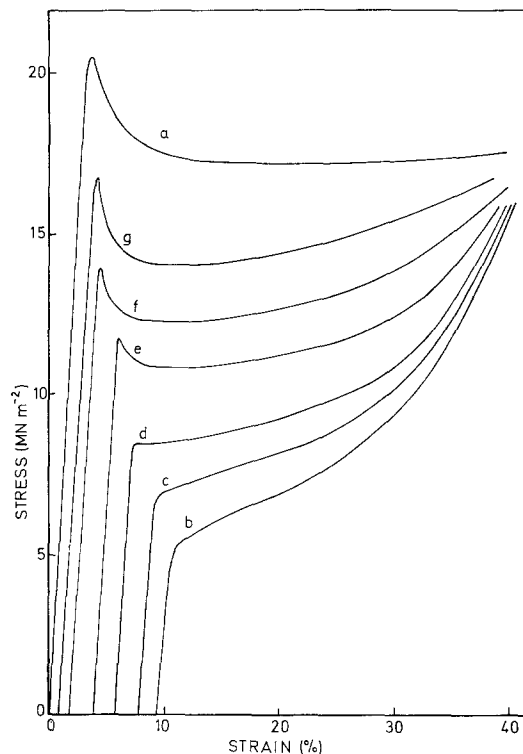

Figure 2 Instron tensometer curves for Bextrene XL750 HIPS: (a) initial tensile test. Re-tested after 30 min at (b) 20°; (c) 31°; (d) 45°; (e) 57°; (f) 64°; and (g) 69°C. Crosshead speed 0.5 cm min^{-1}. Test temperature 20°C.

The recovery of the crazed specimens was accelerated by heating. Fig. 2 shows the effect of conditioning for 30 min at temperatures between 20 and 69°C upon the stress-strain behaviour of the crazed material. The increase in the yield stress with increasing temperature is clearly illustrated.

A convenient measure of the recovery of the HIPS is the "recovered yield stress" Y, which we define as the yield stress of the conditioned crazed specimen divided by the original yield
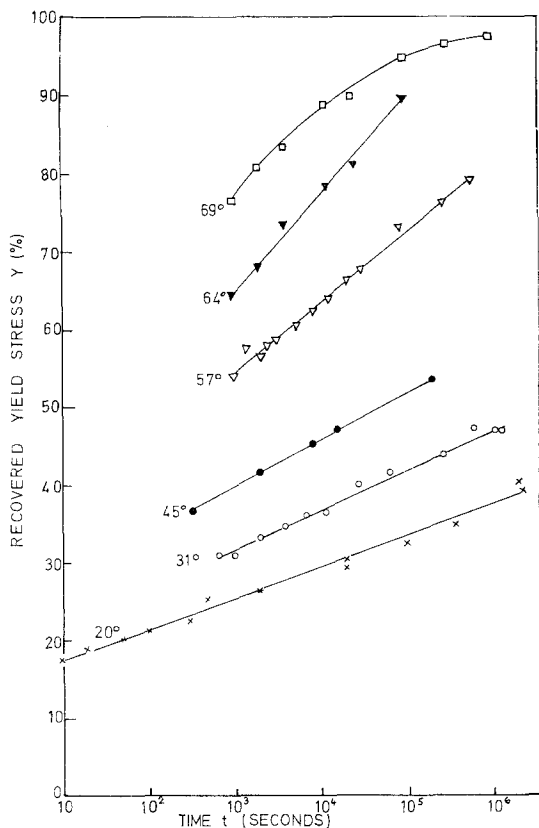
Figure 3 Relationship between recovered yield stress, Y, and recovery time, t, for Bextrene XL750 HIPS at six different temperatures.

stress of the specimen. Fig. 3 shows the relationship between yield stress and recovery time for each of the temperatures studied. Except for the results obtained at 69° C, the recovered yield stress increased approximately linearly with log (recovery time) at each temperature:

$$\frac{dY}{d \ln t} = K \text{ (constant)} \qquad (1)$$

whence

$$\frac{dY}{dt} = K t^{-1}. \qquad (2)$$

The equations show that the recovery process becomes progressively slower throughout the conditioning period, and this conclusion is supported by the creep-recovery results presented below.

It is clear from Fig. 3 that recovery is a thermally activated process. Activation energies were estimated by extrapolating the isothermal

lines, and determining the time t taken to reach a given recovered yield stress at each temperature T. Equation 2 shows that t^{-1} is a measure of the rate of recovery of the HIPS at the specified level of recovered yield stress, and the activation energy of recovery can therefore be determined by plotting $\log(t^{-1})$ against T^{-1}. Fig. 4 shows two Arrhenius plots of this type, for intercepts at the 40 and 50% levels of recovered yield stress. The calculated activation energies obtained from Fig. 4 were 56 kcal mol^{-1} at 40% recovery (Y_{40}), and 70 kcal mol^{-1} at 50% recovery (Y_{50}).
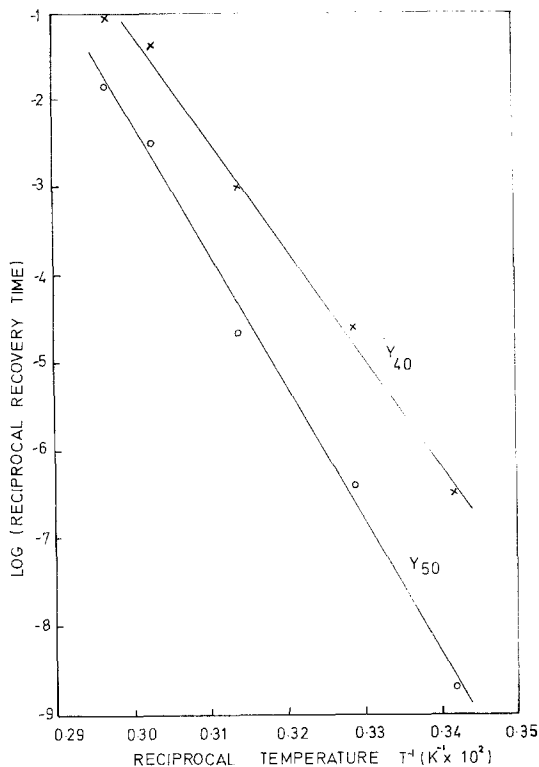

Figure 4 Arrhenius curves of log (recovery rate) against T^{-1}; results from Fig. 3. (Y_{40}) intercepts at $Y = 40\%$; (Y_{50}) intercepts at $Y = 50\%$.

Since crazing is the dominant mechanism of tensile deformation in HIPS [5], it follows that the recovery behaviour described above is due largely to healing of crazes, although the process is complicated to some degree by the presence of rubber particles embedded in the crazed polymer. The similarity between the macroscopic mechanical properties of crazed HIPS and the microscopic mechanical properties of individual crazes in polycarbonate has already

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been noted. Healing of crazes is a familiar phenomenon, exemplified by the fading of interference colours on fracture surfaces of glassy polymers, especially poly(methyl methacrylate), and by the partial or complete disappearance of crazes in glassy polymers upon removal of applied stress. The results of the present work provide further information about the healing process.

The forces responsible for craze healing may be taken to be of two types: cohesive forces, tending to reduce the area of free surface in the expanded craze layer, and quasi-rubber-like retractive forces, tending to decrease molecular orientation in the fibrils of the crazes. Cohesive forces become increasingly important as the material approaches the density of the bulk polymer, whereas rubber-like retractive forces are dominant during the early stages of healing, and decrease as the recovery process proceeds. Consequently, it is probably the rubber-like forces that are mainly responsible for the healing of crazes, except at very high levels of recovery.

Figs. 3 and 4 show that the apparent activation energy of healing increases as the crazes recover. The isothermal lines in Fig. 3 converge at low values of recovered yield stress, indicating that the energy barriers to recovery at this stage of healing are extremely low. Activation energies are approximately proportional to recovered yield stress.

Interpreting these results is by no means an easy task. The healing process is clearly rather complex, and it would be unwise to attempt an elaborate interpretation upon the basis of the evidence available at present. Nevertheless, it is possible to develop some general principles relating to healing of crazes, provided that the limitations of the treatment are recognized.

Clearly, craze healing is both a stress- and a temperature-activated process. Therefore, instead of using the ordinary Arrhenius equation, it is more appropriate to use the Eyring equation [8], in the form:

$$\text{Rate} = 2A \exp\left(-\frac{E}{kT}\right) \sinh\left(\frac{\gamma v \sigma}{kT}\right)$$
$$\simeq A \exp\left(\frac{\gamma v \sigma - E}{kT}\right) \quad (3)$$

where A = constant, E = activation energy, k = Boltzmann's constant, γ = stress concentration factor, v = activation volume, and σ = stress.

It follows from Equation 3 that the slopes obtained in Fig. 4, by plotting log (rate), or $\log (t^{-1})$, against T^{-1}, are measures not simply of activation energy E, but of $(E - \gamma v \sigma)$, and that it is this quantity that increases as the crazes recover. The stress σ is an internal one in the present case, and the considerations outlined above suggest that its magnitude decreases as the crazes heal, except in the final stages of the recovery process, when cohesive forces become important. The difference in slope between the two Arrhenius plots shown in Fig. 4, and the related divergence of the isothermal lines in Fig. 3, can therefore be attributed to a reduction in σ, and a consequent increase in $(E - \gamma v \sigma)$, as the crazes recover. However, this conclusion does not exclude the possibility that E also varies and that an increase in activation energy E with degree of recovery contributes to the observed effects.

To sum up, the recovery of crazes towards the properties of the bulk polymer can be described in terms of a thermally-activated flow process taking place under the influence of rubber-like retractive forces. A combination of rubber-like elasticity theory and the Eyring flow equation is suggested as a basis for analysing the deformation and recovery of crazes, except at densities approaching that of the bulk polymer, where cohesive forces become important.

3.1.2. Alcohols

The lower alcohols are well known as "solvent" crazing agents for polystyrene [9], which means that crazes form at lower stresses in the presence of an alcohol than in air. Bernier and Kambour [10] have shown that liquids promote crazing in two ways: by acting as plasticizers, and by reducing the surface energy of craze voids. Methods for distinguishing between these two mechanisms are obviously of interest in studying this important phenomenon.

The recovery test offers such a method, since liquids that act as plasticizers should accelerate recovery, whereas those that reduce surface energy, and stabilize the craze voids, should have the opposite effect.

Each of the alcohols studied increased the rate of recovery, as measured by the recovered yield stress, in comparison with recovery in air. Values of recovered yield stress varied from 66%, after immersion in methanol, to 40%, after immersion in cyclohexanol. A specimen conditioned in air for a comparable period had a recovered yield stress of 33%. However, these figures should be
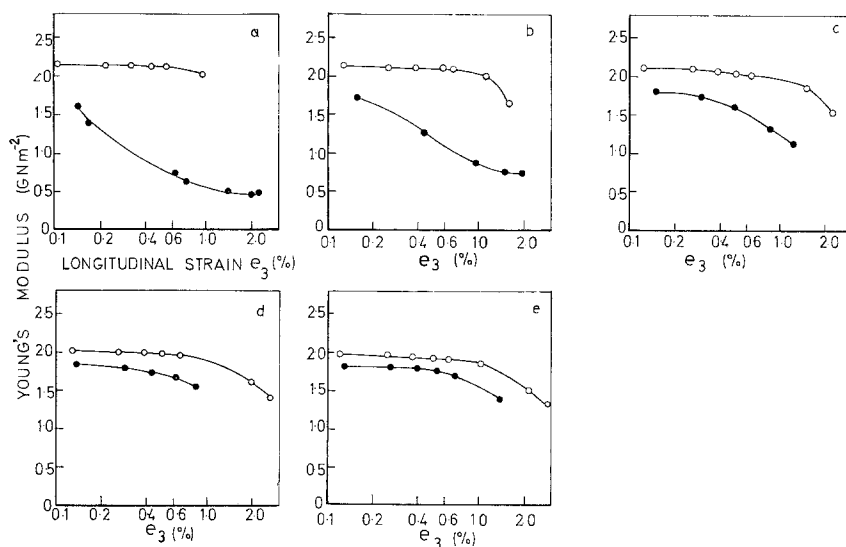
Figure 5 Young's modulus before (○) and after (●) creep to 5% elongation: 100-sec isochrones for HIPS/PS/PPO blends containing 50% X600 HIPS. Polyphenylene oxide contents: (a) 0%; (b) 12½%; (c) 25%; (d) 37½% and (e) 50%.

treated with caution, since absorbed alcohol was not completely removed under vacuum, and the recovered yield stress values for specimens immersed in alcohols must therefore be regarded as low. The alcohols that are absorbed most readily, and are therefore most difficult to remove under vacuum, are also the most effective crazing agents [9], and both factors tend to lower the recovered yield stress. This argument could explain why the most active solvent-crazing agents appeared to have the least effect upon the recovery process.

3.2. Creep tests
3.2.1. Isochronous creep curves
Isochronous curves of 100-sec modulus against 100-sec longitudinal strain are shown in Fig. 5 for each of the blends containing 50% X600 grade HIPS. Results obtained before and after long-term creep deformation are plotted for each blend, and it is clear that a creep test to 5% elongation reduces modulus, especially in blends containing a low proportion of polyphenylene oxide. This reduction in modulus is a further example of strain damage associated with craze formation in rubber-toughened plastics.

The initial isochronous curves show only a small reduction in modulus with strain in the strain range 0.1 to 0.6%. This observation is especially applicable to the blends containing a high proportion of polystyrene. At higher strains, however, there is a marked drop in modulus, owing to the formation of a significant number of crazes within the 100-sec loading period. The sharpness of this drop is greatest in the blends containing a high proportion of polystyrene, and becomes progressively less severe as the polyphenylene oxide content of the blend is increased. Consequently, the blends with the highest moduli at low strains have the lowest moduli at high strains.

After the initial isochronous testing, each of the specimens represented in Fig. 5 was extended to 5.6 ± 0.1% longitudinal strain in a long-term creep test. The results of these long-term tests are presented and discussed in a previous paper [6]. The specimens were allowed to recover, as described in Section 2.3, and then subjected to a second isochronous test.

Whereas the initial isochronous tests showed an approximate linearity between stress and strain in the low-strain region, the second set of isochronous tests revealed distinct non-linearity, especially in the HIPS/PS blend. The non-linearity, demonstrated as the fall of modulus with strain, became less pronounced as the proportion of polyphenylene oxide in the blends increased, and the 50/50 HIPS/PPO blend was approximately linear at strains below about 0.5%. In all cases, the long-term creep test

TABLE I Analysis of maximum strains reached during creep of HIPS/PS/PPO blends

Composition of blend (wt %)			Stress (MN m^{-2})	Contribution to strain e_3 (in elongation %)			
HIPS	PS	PPO		Elastic	Crazing	Shear bands	Total e_3 (%)
50	50	—	19.7	0.9	4.6	—	5.5
50	37½	12½	29.5	1.5	3.8	0.3	5.6
50	25	25	33.6	1.8	3.2	0.5	5.5
50	12½	37½	36.2	2.1	2.2	1.4	5.7
50	—	50	38.8	2.2	2.0	1.4	5.6

resulted in a reduction in the modulus of the specimen at any given strain. This effect was also most apparent in blends containing a high proportion of polystyrene, and became smaller as the proportion of polyphenylene oxide was increased.

The modulus-strain behaviour represented in the lower curve of Fig. 5a is similar to that exhibited by individual crazes [3], and therefore provides additional support to the view that the strain-damage effects are largely or wholly due to craze formation. The variations in behaviour between blends of different compositions can be attributed to two possible causes: firstly, differences in the amount of crazing taking place during long-term creep testing, and secondly, differences in the deformation behaviour of individual crazes of differing composition. Other possible factors include the length of the recovery period, the duration of the long-term creep test, and the stress level during the long-term test, but none of these factors appeared to be important in the present series of isochronous tests. Specimens of each blend were compared after subjection to differing stress and strain histories, and it was found that the isochronous modulus-strain curves were identical provided that the maximum strain reached in the long-term test was the same in each case. As expected, the reduction in modulus, between the initial and final isochronous test, became larger as the maximum long-term strain level was increased.

Table I presents an analysis of the mechanisms contributing to the creep strain in the blend specimens at the point of unloading. In making the analysis, the instantaneous (10-sec) elastic strain was first subtracted from the total strain, leaving the time-dependent component, which was then further divided into strain due to crazing, and strain due to shear-band formation, using data obtained from Fig. 6 of [6]. This

diagram shows that there is a linear relationship between volume strain and longitudinal strain for each of the blends. The principle of the analysis is that the slopes of the lines are measures of the contribution of crazing to creep: a line of zero slope (no time-dependent volume change) indicates no crazing, and therefore 100% shear deformation, whereas a line of unit slope (increments of volume strain and longitudinal strain equal, hence no change in cross-sectional area) indicates 100% crazing, and therefore no shear deformation. A line of intermediate slope x indicates a fractional contribution x from crazing and $(1 - x)$ from shear yielding during the period under consideration.

It is clear from Table I that there are differences in the degree of crazing in the strained specimens that are sufficient to account for at least part of the observed differences in strain damage illustrated in Fig. 5. Variations in mechanical properties of crazes with composition are also to be expected, but it is difficult to quantify this effect at present, especially in view of the probable interaction between crazes and other features of the structure, including shear bands and rubber particles.

The effects of uniaxial creep testing upon the subsequent mechanical properties of the blends were strongly anisotropic, essentially affecting only the tensile direction. Fig. 6 shows that, for the most of the blends, the long-term creep test had little effect upon the 100-sec lateral compliance s_{13} (defined as e_1/σ_3, where σ_3 is the longitudinal applied stress), which was virtually independent of longitudinal strain in the low-strain region, and began to rise only when the longitudinal strain exceeded 2.0%. These observations are consistent with the view expressed earlier, that crazing is responsible for most of the observed strain-damage effects, since crazing should not affect the properties of the
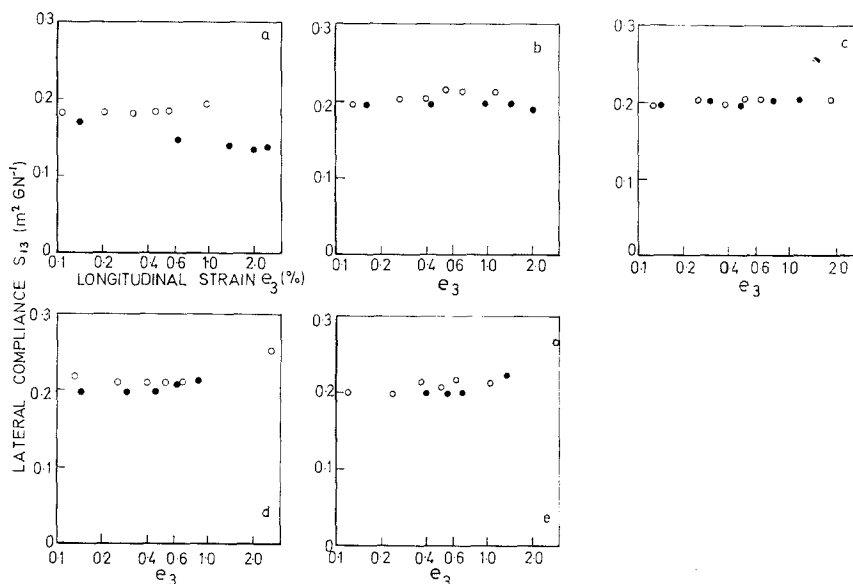
Figure 6 Lateral compliance before (○) and after (●) creep to 5% elongation: 100-sec isochrones for HIPS/PS/PPO blends containing 50% X600 HIPS. Polyphenylene oxide contents: (a) 0%; (b) $12\frac{1}{2}$%; (c) 25%; (d) $37\frac{1}{2}$% and (e) 50%.

creep specimens in the lateral directions.

The low values of s_{13} shown in Fig. 6a, for a strained specimen of the 50/50 HIPS/PS blend, were probably due to a slight distortion of the surface. It was reported in Section 4.1 of [5] that minute bulges approximately 1 μm high appear on the surface when crazed HIPS specimens are subjected to tensile stress. These bulges, which are sufficient to account for the fall in s_{13}, have not been observed in blends containing polyphenylene oxide.

3.2.2. Long-term recovery

Long-term creep and recovery results for two of the blends are presented in Figs. 7 and 8. Despite major differences in creep behaviour under load, the two specimens shared several features in their recovery behaviour. In both cases, the longitudinal strain e_3 fell from about 5.6 to 2.6% upon unloading, and decreased by a further 0.7% over a recovery period of 2500 sec, which was the approximate duration of the creep test. A residual strain of over 1.5% remained in the specimens at the end of this period. Similar results were obtained from the other blends, and at different stress levels.

The main differences in recovery behaviour between the blends arise from differences in the mechanisms of deformation. The 50/50 HIPS/PS

blend, illustrated in Fig. 7, deformed by instantaneous elastic deformation, followed by crazing. The absence of shear deformation mechanisms is marked by the fact that lateral strain e_1 was virtually independent of time, whilst the presence of crazing is indicated by the increase of volume strain with time. When the specimen was unloaded, e_1 fell immediately almost to zero, again indicating that this component of strain was due to elastic deformation. By contrast, the residual volume strain was relatively high, and almost equal to the residual longitudinal strain e_3. This observation shows that the presence of unrecovered crazes was responsible for the high values of e_3 in this specimen during the recovery period.

Both crazes and shear bands contributed to the creep of the $50/37\frac{1}{2}/12\frac{1}{2}$ HIPS/PPO/PS blend illustrated in Fig. 8, and residual strain contributions from both mechanisms were observed during recovery. During the latter half of the recovery period in Fig. 8, e_3 had a value of 1.7%, which was made up of 1.0% volume strain, due to unrecovered crazes, and 0.7% area strain, due to shear bands.

Within the range of blends studied, the residual lateral strain e_1 in the specimens, at the end of a standard creep and recovery cycle, increased with polyphenylene oxide content to a maximum in
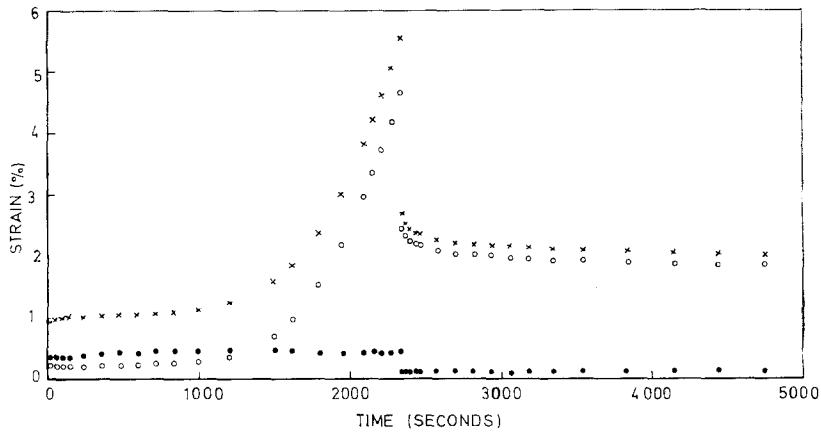
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Figure 7 Creep and recovery of 50/50 HIPS/PS blend specimen at 20°C. Stress 19.7 MN m⁻² unloaded after 2340 sec; (×) longitudinal strain e_3; (●) lateral strain e_1; (○) volume strain $\Delta V/V$.
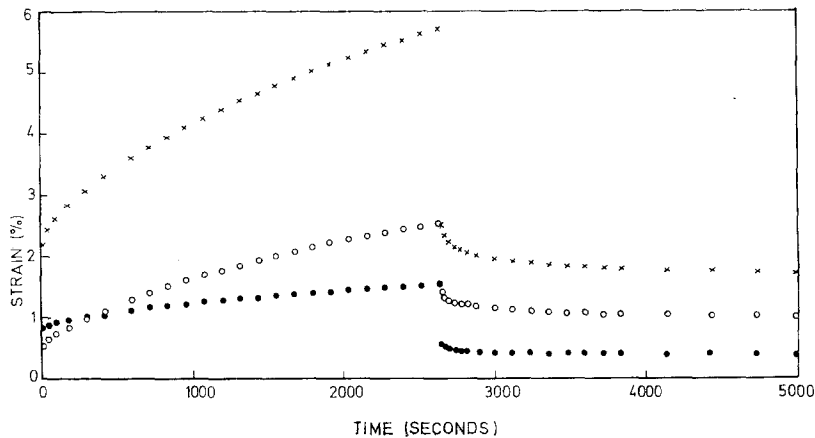

Figure 8 Creep and recovery of 50/37½/12½ HIPS/PPO/PS blend specimen at 20°C. Stress 36.2 MN m⁻² unloaded after 2640 sec; (×) longitudinal strain e_3; (●) lateral strain e_1; (○) volume strain $\Delta V/V$.

the 50/37½/12½ HIPS/PPO/PS blend, and then fell to a significantly lower value in the 50/50 HIPS/PPO blend. This observation suggests that the increase in the concentration of shear bands through the series is offset by an increased degree of recoverability in the shear bands as the polyphenylene oxide content of the matrix is increased. Further evidence in support of the view is presented below.

An interesting insight into the mechanisms participating in the recovery process is obtained by plotting the volume strain against the corresponding longitudinal strain, as in Fig. 9. The slopes of the lines measure the contribution of crazing to recovery. A line of unit slope means that the specimen is recovering entirely by craze healing, which does not affect cross-sectional area, so that the increments of volume and longitudinal strain are equal. On the other hand,

a line of zero slope means that there is no contribution from craze healing, so that the volume remains constant. A slope of 0.5 indicates that craze healing and shear-band recovery are contributing equally to the recovery in the longitudinal direction.

Each of the five blends is represented in Fig. 9. The slopes given by these blends, in order of increasing polyphenylene oxide content, were 0.95, 0.88, 0.78, 0.50 and 0.50. These results indicate that craze healing is responsible for almost all of the recovery in the 50/50 HIPS/PS blend, but only 50% of the recovery in the 50/50 HIPS/PPO blend. The slopes were all lower than those obtained in the corresponding creep extension experiments, which suggests that the rate of recovery of individual shear bands is higher than that of individual crazes.
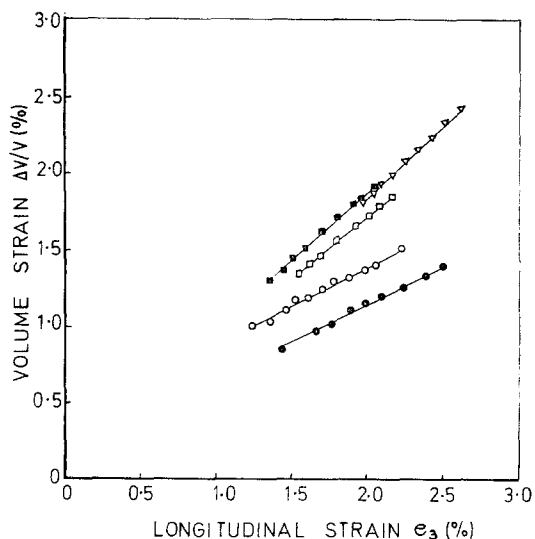
The linear relationships between volume and

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Figure 9 Relationship between volume and longitudinal strains during recovery of HIPS/PPO/PS blends from 5% creep elongation. Blends contain 50% X600 HIPS. Polyphenylene oxide contents and stresses during creep test (MN m⁻²): (∇) 0%, 19.7; (■) 12½%, 29.5; (□) 25%, 33.6; (●) 37½%, 36.2; (○) 50%, 38.8.

Figure 10 Relationship between volume strain and reduced recovery time for HIPS/PPO/PS blends containing 50% X600 HIPS. Polyphenylene oxide contents and stresses during creep test: (∇) 0%, 19.7; (■) 12½%, 29.5; (□) 25%, 33.6; (●) 37½%, 36.2 and (○) 50%, 38.8.

longitudinal strains shown in Fig. 9 indicate that the mechanisms of recovery do not change with strain, so that craze healing makes a constant fractional contribution to the rate of recovery of an individual specimen throughout the period of the measurements. The results also show that rates of change of longitudinal, lateral, and volume strain with time are linearly related.

Fig. 9 also provides some evidence about the nature of the recovery processes operating in the 10 sec interval between unloading the specimen and making the first recovery measurement. Figs. 7 and 8 show that the longitudinal recovery during this interval was approximately 3.0%, well in excess of the instantaneous elastic strain produced upon initial loading of the specimen. Similar results were obtained from the other blends. The results presented in Fig. 9 suggest that linear extrapolations are possible to shorter recovery times and higher residual strains. It would follow that the same mixture of craze healing and shear band recovery took place during the first 10 sec after unloading as during the later stages of recovery, and that both processes contributed to the large initial reduction in longitudinal strain.

In each of the five blends studied, strain fell approximately linearly with log (recovery time). Fig. 10 illustrates the relationships between
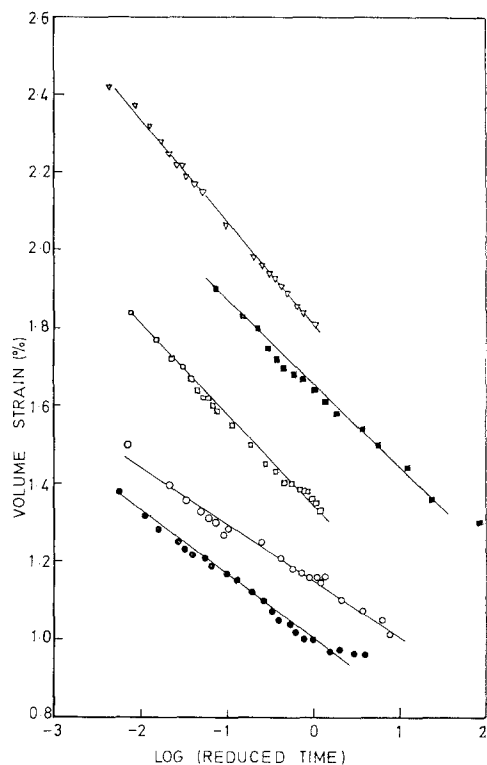
volume strain and log (reduced time), where reduced time is defined as the elapsed recovery time divided by the time taken to reach 5.0% creep extension. Similar relationships were obtained for lateral and longitudinal strain. The relationships are similar in form to those contained in Fig. 3, which showed that recovered yield stress was linearly related to log (recovery time), and it is clear that the two methods of studying recovery measure closely related properties of the strained material. Equations 1 and 2 apply, approximately, in both cases. The value of the constant K in these equations was found to change not only with composition but also with the stress level during the tensile creep stage of the test.

3.3. Composite materials approach

It is clear from this work that the mechanical properties of HIPS and related polymers change drastically at elongations above about 1%, and that the changes are due mainly to the formation

of crazes. The crazed specimen is effectively a composite structure, consisting of layers of bulk polymer and crazes in series, with the layers lying normal to the direction of the applied stress. Both types of layer are themselves composites of glassy polymer and rubber particles, but that is a separate problem.

In discussing the mechanical properties of a layered composite of the type described above, the main problem concerns the crazes, since the properties of the rubber-modified bulk polymer can be expressed in reasonably adequate terms by a Young's modulus and Poisson's ratio. In comparison with the crazes, any strain- or time-dependence of stiffness in the bulk polymer can be ignored, provided that no further crazing or shear-band formation takes place.

Crazes have distinctive mechanical properties. The low moduli, high hysteresis, capacity to undergo large and partially-reversible deformations, and the shape of their stress-strain curves suggest a rather viscous rubber. The combination of rubber-like elasticity with Eyring flow, which was mentioned in Section 3.1.1, has been used successfully by Haward and Thackray [11] to describe large recoverable deformations in PVC and cellulosic polymers below the glass temperature, and is perhaps the most suitable available model for craze deformation. Further work is now needed to examine the validity of this approach.

Discussion of creep recovery in HIPS and its blends is further complicated by the fact that crazes and shear bands are formed throughout the creep test, so that the composition of the layered craze-bulk polymer composite changes continuously with time under load, and the recovery contains contributions from crazes formed at widely differing times, and hence having differing stress histories. Experiments to determine the properties of crazes must take account of these factors.

A quantitative understanding of the recovery processes described in this paper depends upon the development of an adequate model along the general lines indicated above. The problem is difficult, but is of fundamental importance in the study of deformation in glassy polymers.

4. Conclusions

This work has shown that tensile strains in excess of 1 % are not fully recoverable in HIPS and HIPS/PPO blends. In HIPS, the residual strain is due to the presence of crazes. In blends containing polyphenylene oxide, shear bands also contribute to the residual strain. The presence of incompletely recovered crazes is observed as a residual volume strain, which decreases linearly with log (recovery time). Longitudinal and lateral strains follow similar relationships. The decrease in volume strain results in an increase in the yield stress of the crazed specimen, from an initially low value.

Recovery processes in the crazed specimens are accelerated by heating, and by immersion in stress-crazing agents, which appear to act as plasticizers.

In considering rubber-modified plastics for engineering applications, it is important to note the connection between craze formation and strain damage: crazing is a type of failure, which results in a major reduction in modulus. Strain-damage effects are more pronounced in HIPS/PS blends, which deform by crazing alone, than in HIPS/PPO blends, which deform by a combination of crazing and shear band formation. This observation emphasizes the importance of quantitative studies of deformation mechanisms, the main theme of the present series of papers, in understanding the engineering properties of rubber-modified plastics.

Acknowledgements

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