Rubber-toughening of plastics

Part 6 *Effects of rubber particles on the kinetics of creep in polypropylene*

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The kinetics of creep in polypropylene are compared with those in a rubber-toughened polypropylene "co-polymer" at 20° C. Rate coefficients, defined by fitting the data to the Andrade equation, are shown to increase exponentially with applied stress, in accordance with the Eyring equation. The activation volume for polypropylene is 2.45 nm^3. Addition of rubber particles accelerates creep by increasing the Eyring stress concentration factor, which has a value of 1.56 in the co-polymer. The dominant mechanism of creep in both polymers is shear yielding: there is no detectable dilatation in the homopolymer, but the co-polymer shows a small increase in volume with time under load.

1. Introduction

Polypropylene "co-polymer" is essentially a rubber-toughened material consisting of a polypropylene (PP) homopolymer matrix in which are embedded small particles of ethylene–propylene co-polymer rubber (EPR). Products of this type have been available commercially since the early 1960's, and are well established in applications requiring impact resistance. The "co-polymer" grade of PP is made by polymerizing propylene in the normal manner, preferably in a continuous reactor, and then transferring the product to a second reactor, which is fed with a mixture of ethylene and propylene [1]. The aim is to generate active PP chains in the first stage of reaction, which will form a block co-polymer with the EPR produced in the second stage. Since EPR is incompatible with PP, it forms a separate phase: spherical particles about 1 μm in diameter can be observed in the co-polymer by sectioning at low temperatures and etching with a suitable solvent [2], or by examining a molten sample in the phase contrast microscope.

Despite differences in the method of manufacture, there are obvious similarities in structure between this type of polypropylene co-polymer and ABS or HIPS (high-impact polystyrene). All three materials contain spherical rubber particles

that are chemically bonded to the matrix. However, significant differences are to be expected in the kinetics and mechanisms of toughening, since energy absorption takes place mainly by deformation of the matrix. In particular, a larger amount of shear yielding is to be expected in toughened PP than in HIPS.

Previous papers describe quantitative techniques for studying rubber toughening, based on creep tests in which crazing is measured by the time-dependent volume strain, and shear yielding is measured by the decrease in cross-sectional area. The tests show that multiple crazing is the principal toughening mechanism in HIPS [3], whereas a combination of crazing and shear yielding is responsible for the toughness of HIPS/PPO blends [4], and a transition from shear yielding to crazing occurs with increasing strain rate in ABS [5]. In the present study, similar techniques were applied to PP homopolymer and to the co-polymer, which will be represented by the abbreviation PP-b-EPR, to indicate that it contains block co-polymer.

2. Experimental procedure

2.1. Materials

Two general-purpose, medium-flow grades of Propathene supplied as natural, unpigmented

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granules by ICI Plastics Division, were used in this work: a PP homopolymer, and a PP-b-EPR containing approximately 16 vol % of EPR chains. These materials were compression-moulded at 190° C into 1.8 mm thick sheets.

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 sheets, and conditioned for four weeks at 20° C before being subjected to creep tests at $20 \pm 0.5°$ C, using high-accuracy lever-loading rigs of the type developed by Darlington and Saunders [6]. 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 the 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, ΔV, was calculated from the expression:

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

Each long-term creep test was preceded by a loading–unloading programme at stresses well below those used in long-term testing. Specimens were subjected to a small load for 100 sec, then unloaded for 500 sec before receiving a slightly higher load, in order to obtain a 100 sec isochronous curve of tensile creep modulus against 100 sec longitudinal strain [7]. The long-term tests were terminated when e_3 reached a value of about 0.05, and the specimen was then unloaded and allowed to recover.

3. Results

The 100 sec isochronous tests showed a marked difference in stiffness between the two polymers: at a strain of 0.25 %, Young's modulus was 1.50 ± 0.05 GPa for PP, compared with 1.03 ± 0.05 GPa for PP-b-EPR. The lower modulus is clearly due largely to the presence of rubber particles, although smaller contributions from other factors, such as differences in crystallinity, cannot be discounted.

Typical creep curves are shown in Fig. 1. The pattern is similar for the two polymers: the response to loading is initially rapid, but the creep rate then continuously decreases with time. The homopolymer shows no evidence of either visible whitening or a time-dependent increase in volume strain, whereas the co-polymer shows a small increase in volume with time, accompanied by a limited amount of whitening. The results clearly demonstrate that shear yielding is the dominant mechanism of deformation in both polymers, with a small contribution from crazing or other dilatational process in the co-polymer.

These observations on the creep of rubber-modified polypropylene are in sharp contrast to those previously recorded for HIPS, in which crazing is dominant. The difference between the two classes of materials is well illustrated in Fig. 2, which shows how volume-strain changes with elongation. A slope of unity is to be expected from a material deforming entirely by crazing, whereas a slope of zero indicates the absence of crazing or other dilatational processes [8]. The HIPS and PP-b-EPR specimens illustrated are close to these two extremes.

The strong dependence of creep rate upon applied stress in both PP and PP-b-EPR is shown in Figs 3 and 4, in which the creep extension e_3 is plotted against the cube-root of time. Writing e_0 for e_3 at time zero (immediately after loading) and e_t for e_3 at time t, the data can be fitted to the Andrade creep equation [9, 10]:

$$\epsilon = e_t - e_0 = bt^{1/3}. \qquad (2)$$

This empirical equation has been shown to correlate creep data for a wide range of materials, including mono- and poly-crystalline metals, ceramics, and polymers [9–13]. In the present work, the Andrade plots are linear for strains between 3 and 5 %, but show some deviation from linearity at lower strains, especially in the homopolymer. Nevertheless, the agreement is sufficiently good to characterize the parameter b in Equation 2, and thereby to define the relationship between creep rate and applied stress.

Fig. 5 shows that $\log b$ increases linearly with applied stress, σ, for both the homopolymer and co-polymer, the rate of increase being greater in the co-polymer. The two sets of data can be brought together onto a single line by plotting $\log b$ against $\gamma \sigma$, where the shift factor, γ, has the value 1.0 for PP and 1.56 for PP-b-EPR. The resulting master curve is shown in Fig. 6.

The observed creep processes are essentially viscoelastic in character. On unloading, at strains of approximately 5 %, the material begins to recover. A convenient method for presenting
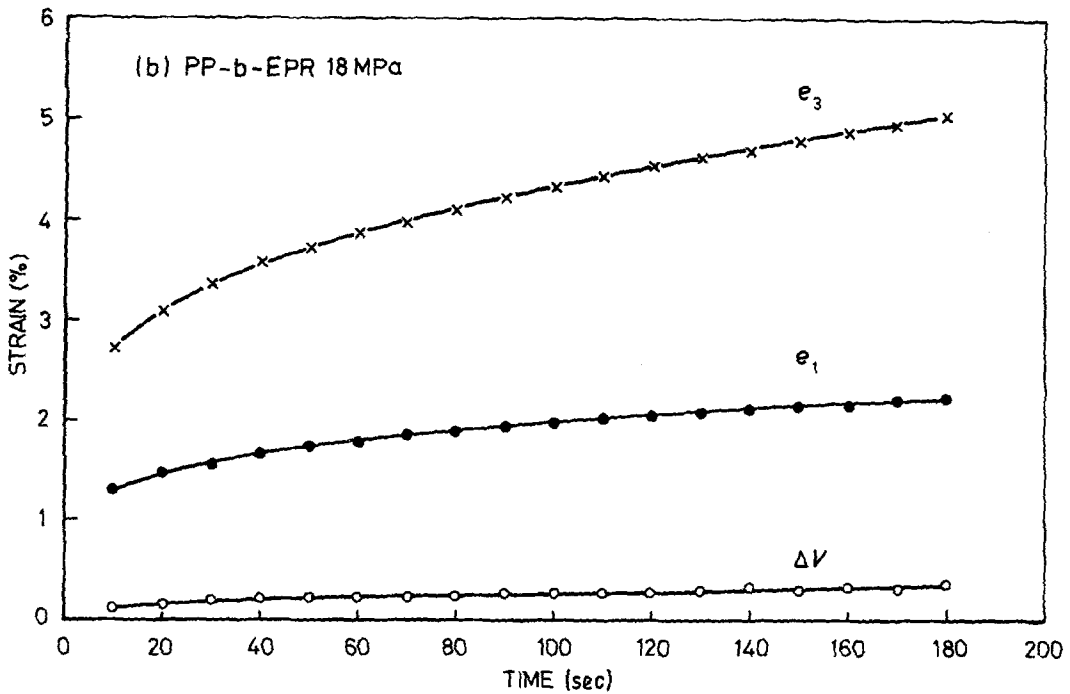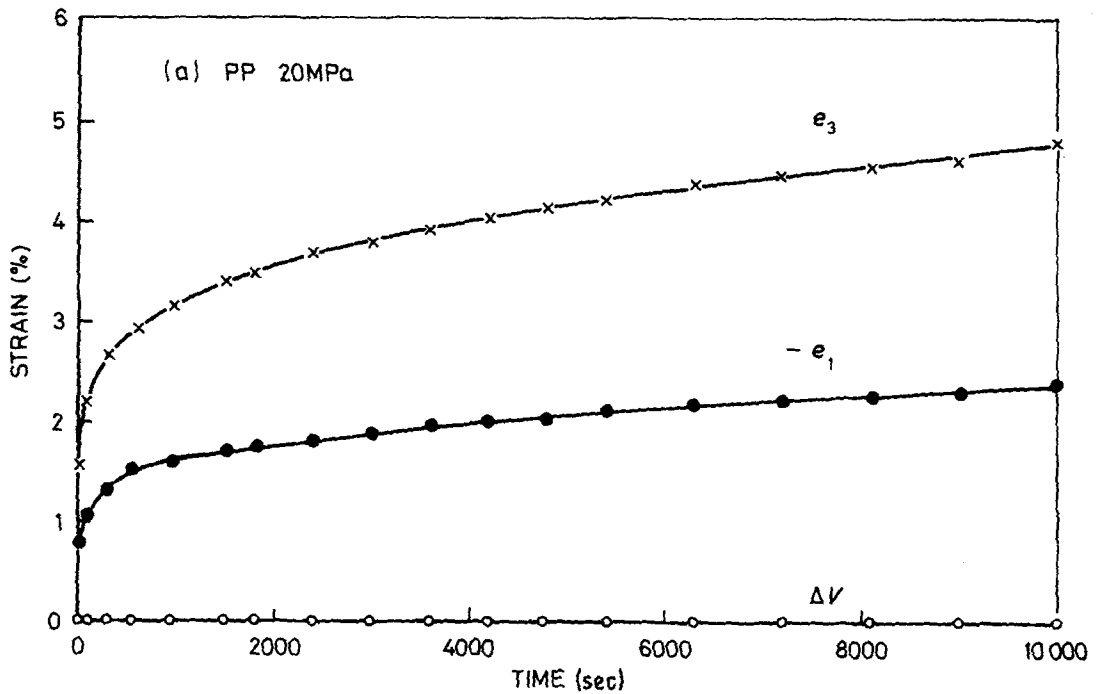
Figure 1 Typical creep curves showing extension (×), lateral contraction (●), and volume strain (○) for PP and PP-b-EPR.

the data is to plot fractional recovery against reduced recovery time, where fractional recovery is defined as strain recovered divided by maximum creep strain, and reduced recovery time is recovery time divided by creep time [14, 15]. Representative results are given in Fig. 7, which shows that

recovery occurs relatively more rapidly in specimens that have reached 5% strain in relatively short times.

4. Discussion
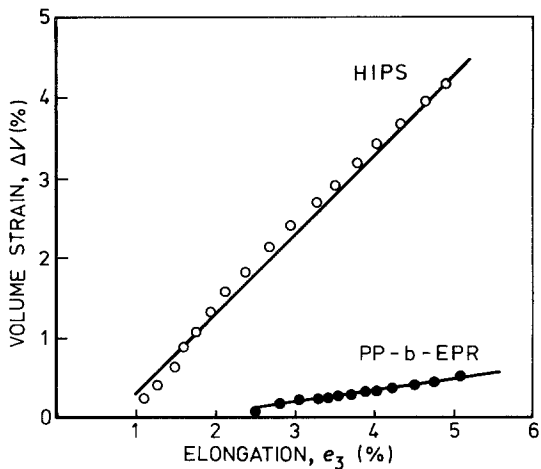This study has shown that there are significant

Figure 2 Relationship between volume strain and extension, showing the difference in creep mechanism between HIPS and PP-b-EPR.

quantitative differences in creep behaviour between polypropylene homopolymer and co-polymer, but that qualitative differences are relatively minor over the range of strains and strain rates studied. The co-polymer contains particles of EPR, which have lower shear moduli than the PP matrix, and therefore act as stress concentrators: the effective

stress acting on the matrix is higher than the applied stress, so that creep rates are higher than those observed in the homopolymer. The factor γ, used to correlate the data in Fig. 6, is the ratio of the average effective stress to the applied stress. In both homopolymer and co-polymer, creep is due largely to viscoelastic shear processes, with only a small contribution from crazing and other dilatational mechanisms. In this respect, the co-polymer differs from typical styrene-based rubber-toughened plastics such as HIPS and ABS. However, both the homopolymer and the co-polymer stress-whiten at the higher strains and strain rates obtained in standard tensile tests, the effect being particularly marked in the co-polymer, and it is clear from this and other evidence that dilatational mechanisms, including crazing, become significant as the strain rate is increased [16—18]. It was noted in Section 1 that ABS exhibits a similar change in deformation mechanism with strain rate.

Previous studies of deformation in polypropylene have shown that yielding and stress relaxation are activated processes which follow Eyring kinetics [19—22]. In its simplest form, the Eyring equation can be written [23, 24] as
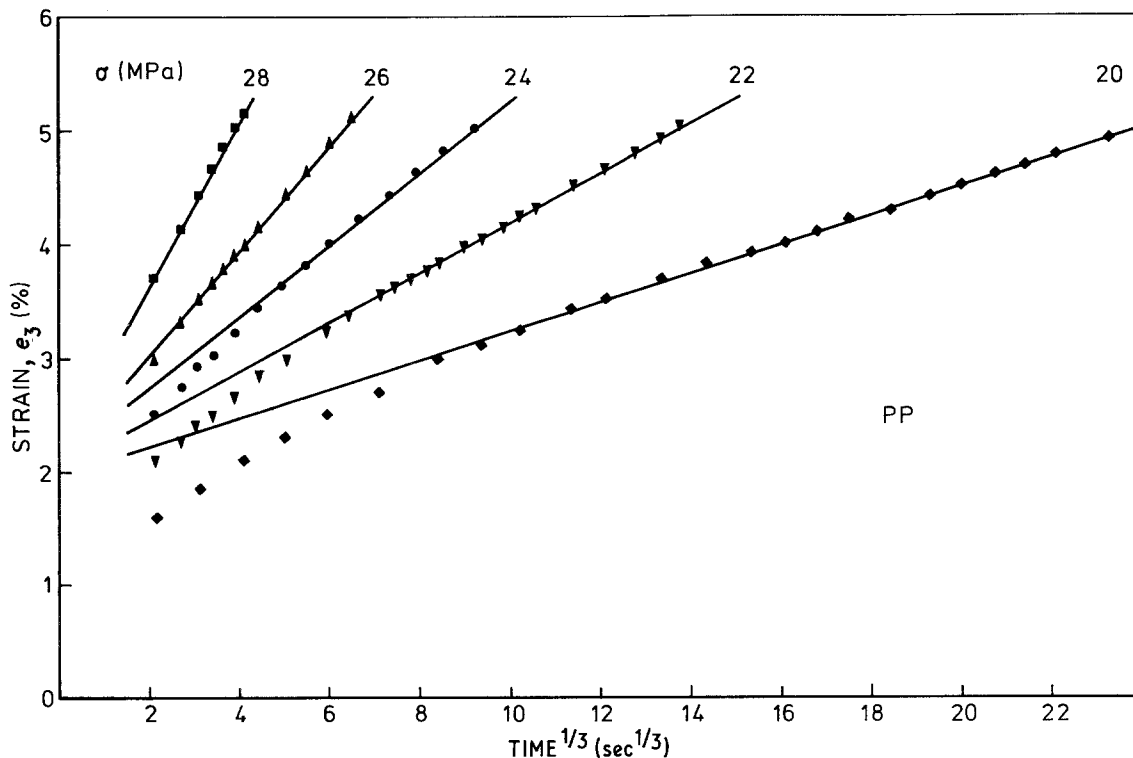

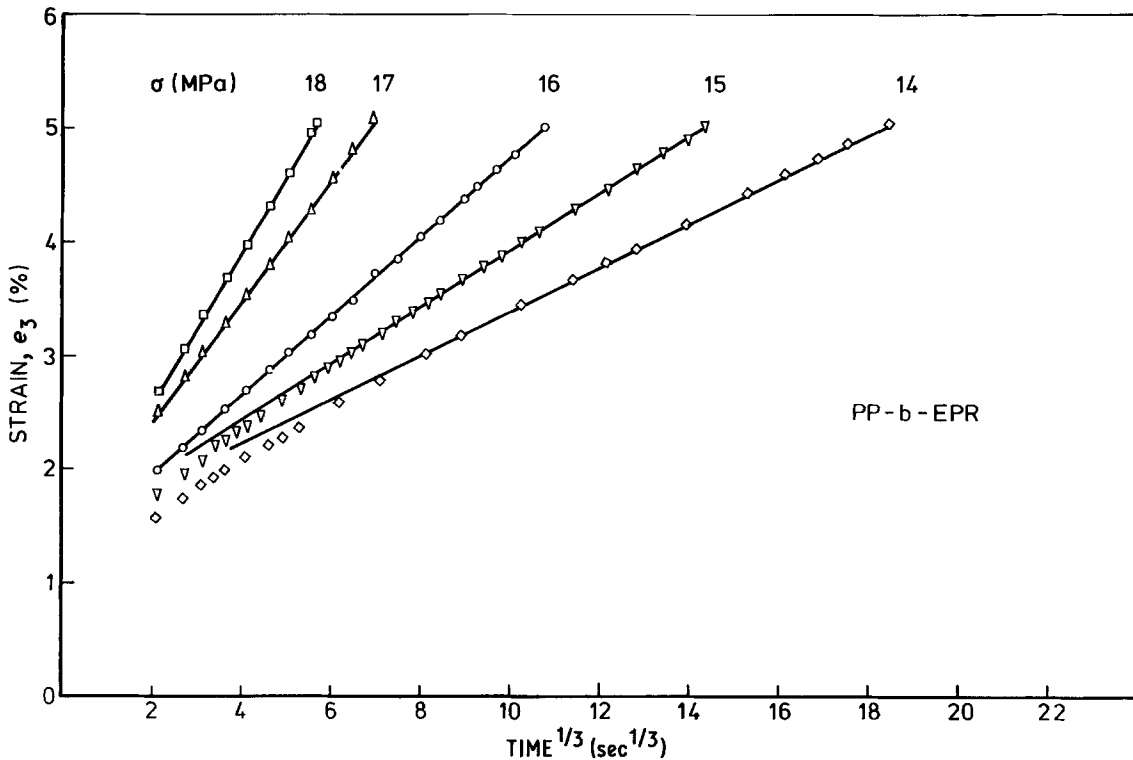*Figure 3* Andrade creep plots for PP over a range of stresses.

Figure 4 Andrade creep plots for PP-b-EPR over a range of stresses.

$$\kappa = 2A \sinh\left(\frac{\gamma V\sigma}{kT}\right) \simeq A \exp\left(\frac{\gamma V\sigma}{kT}\right), \quad (3)$$

where κ is the rate coefficient for flow, A is a constant at any given temperature T, k is Boltzmann's constant and V is the activation volume of the flow process. The Eyring equation defines γ more precisely than the definition given

above, as the ratio of the local stress acting on the molecule or molecular segment responsible for flow to the applied stress, σ. The basis of the Eyring theory is that energy barriers at the molecular level control the macroscopic rate of flow.

For many flow processes, the rate of deformation is constant provided that the stress and temperature are held constant, and the defor-
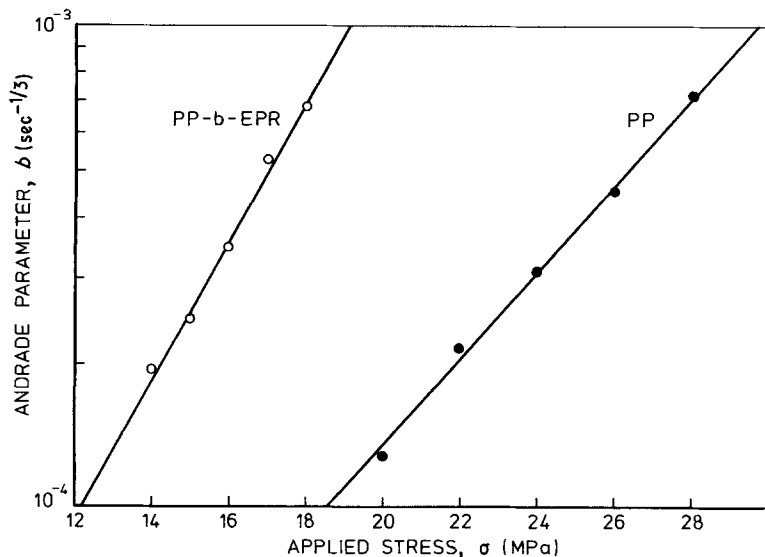

Figure 5 Eyring plots of $\log b$ against applied stress, σ, for PP and PP-b-EPR.
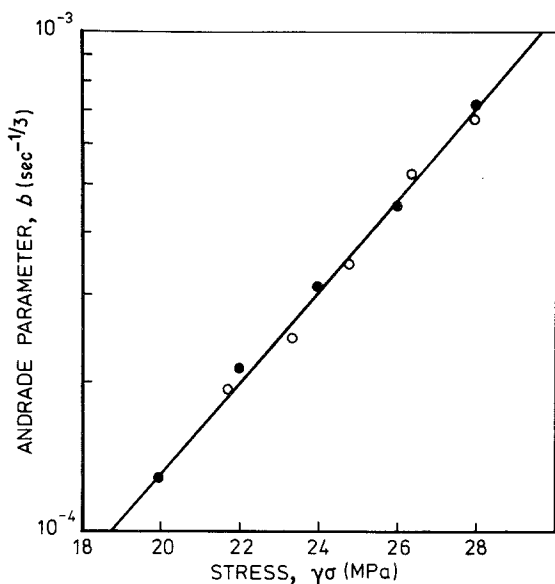
Figure 6 Eyring master plot of log b against $\gamma\sigma$ for PP (•) and PP-b-EPR (○).

mation rate can be used in place of the rate coefficient in the Eyring equation. However, in the present experiments the creep rate varies with time under load, and it is necessary to seek an alternative definition of κ. Differentiation of Equation 2 gives

$$\frac{d\epsilon}{dt} = \frac{b^3}{3\epsilon^2}, \qquad (4)$$

from which it can be seen that the rate coefficient for the process is $b^3/3$. Inserting this value into Equation 3 gives

$$\gamma V = 3kT \left(\frac{\partial \ln b}{\partial \sigma}\right)_T. \qquad (5)$$

An activation volume of $2.45\,nm^3$ for polypropylene homopolymer is obtained from Fig. 5, on the assumption that $\gamma = 1.0$ for this material. This result is in good agreement with the figure of $2.62\,nm^3$ obtained from the data of Roetling for the contribution of the α-process to yielding in PP [19]. Roetling concluded that the α-relaxation was associated with the glass transition in the non-crystalline component of PP, in which case an interlamellar slip mechanism is probably responsible [17, 18]. This line of reasoning leads to the conclusion that the rubber particles in the co-polymer accelerate creep by increasing the local stresses acting in the interlamellar regions of the PP matrix.

Discussions of stress concentrations in rubber-toughened plastics usually focus upon the zones of maximum stress, at the equators of the rubber particles, where γ values of two or more are to be expected. Clearly, these zones are the most probable sites for initiation of shear bands and crazes. However, the observation that $\gamma = 1.56$ for the co-polymer strongly suggests that the rate-controlling factor in the creep of polypropylene is not the maximum stress concentration, but the average stress concentration over the plane of the deformation band.

A simple calculation, based on the reduced area of matrix, suggests a stress concentration factor of $(1 - \phi)^{-1}$ in a material containing volume-fraction, ϕ, of holes or soft particles. However, Ishai and Cohen [25] have pointed out that deformation bands and cracks tend to follow minimum-area paths through the matrix, passing through the centres of spherical holes, so that significantly higher values of average stress concentration factor would be expected to determine rates of crack growth or yielding. Considering a unit cube of material, with a spherical hole of radius, r, at its centre, the minimum area of load-bearing matrix within the cube is $(1 - \pi r^2)$, from which the stress concentration factor is

$$\gamma = \left[1 - \pi \left(\frac{3\phi}{4\pi}\right)^{2/3}\right]^{-1}. \qquad (6)$$

Ishai and Cohen [25] measured yield stresses of epoxy resins containing 0 to 60 vol% voids, in uniaxial compression tests over a range of strain rates, and plotted yield stress against log (strain rate). They obtained a series of straight lines, as predicted by Equation 3, and showed that the slopes varied with ϕ in accordance with Equation 6. Experiments by Nicolais and co-workers [26–31] on tensile yielding and fracture of polymers containing unbonded glass beads have provided further support for the model of Ishai and Cohen.

Equation 6 predicts an average γ-value of 1.55 for polypropylene co-polymer containing 16 vol% EPR, in good agreement with the result obtained in the present study.

Models for Andrade creep kinetics have been proposed by Kennedy [11] and by Mott [12]. In Kennedy's model points in a viscous medium are connected by bi-stable links: as the shorter of the connections between two points breaks, creep takes place until the longer link becomes taut. Mott's model is based on the release of piled-up
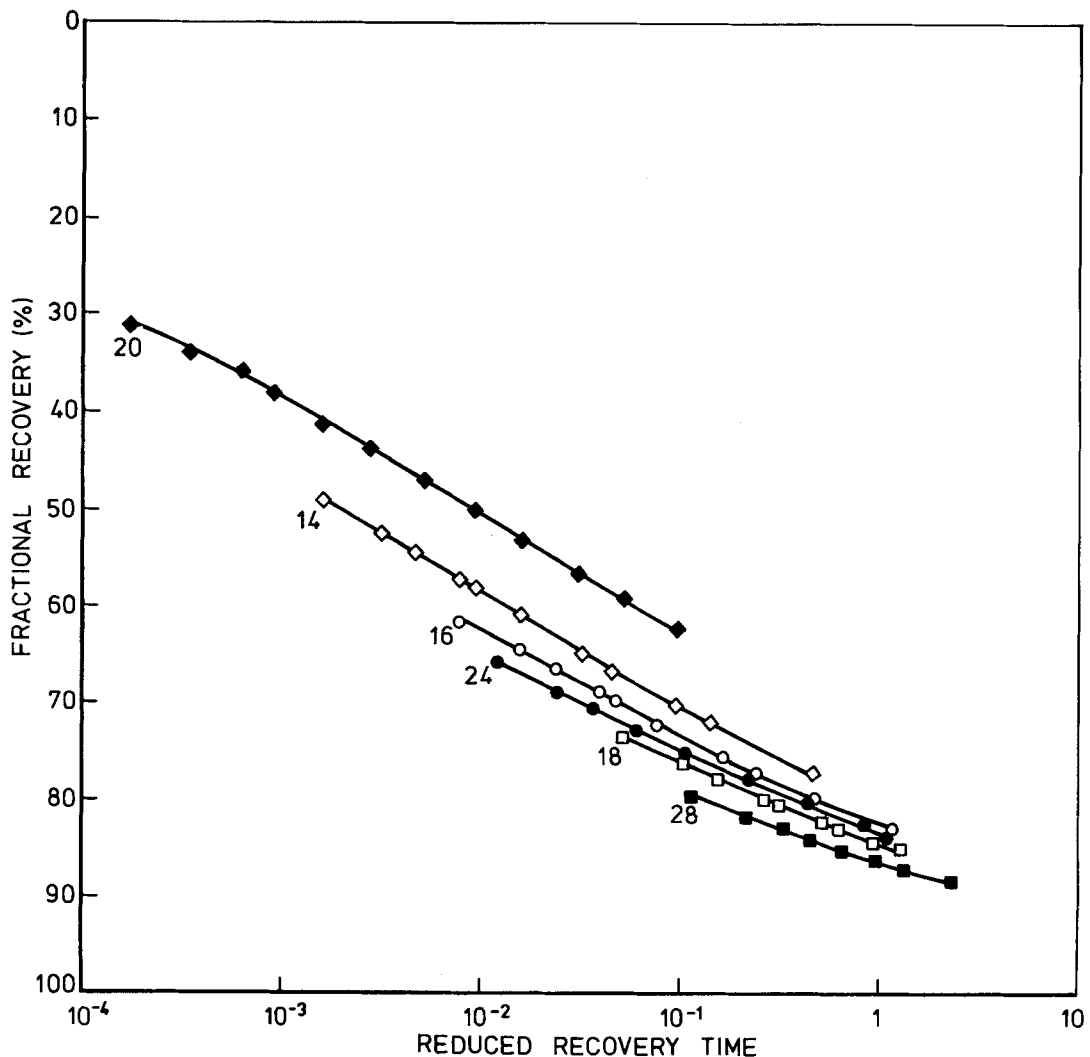
Figure 7 Recovery curves for PP (♦, ●, ■) and PP-b-EPR (◊, ○, □). Labels indicate the stress, in MPa, to which each specimen was subjected during creep.

dislocations in a crystal lattice. Neither explanation gives much understanding of the creep characteristics of polypropylene, and the following model, due to Atkinson [32], is proposed as a more relevant physical interpretation.

Creep is considered to be due to the formation of shear bands on three orthogonal planes, each at 45° to the applied tensile (or compressive) stress, the rate, Q, at which bands are initiated, per unit volume per second, being constant. The essential feature of Atkinson's model is that a growing shear band may not cross an existing shear band, so that the size that a band can attain decreases with strain, and thus with time. As creep proceeds, the material becomes divided into an increasing number of rectangular blocks.

If the number of blocks per unit volume is N, the average length of side of a block is x and the strain contributed by unit area of band is a, then:

$$N = \frac{1}{x^3} \qquad (7)$$

and the strain per band is ax^2, the strain per block is $3ax^2$ and the total strain, ϵ, is $3ax^2N$ or $3a/x$. Therefore,

$$\frac{d\epsilon}{dt} = Qax^2 = \frac{9a^3Q}{\epsilon^2}. \qquad (8)$$

Hence, from Equation 4,

$$Q = \frac{b^3}{27a^3}, \qquad (9)$$

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and the rate parameter, b^3, is interpreted as a measure of the rate at which shear bands are initiated.

Interactions between shear bands of the type proposed here have been observed in both glassy and semi-crystalline polymer [33–35]. Molecular orientation within a band creates a barrier to deformation on planes normal to the band, but not an absolute one: under a sufficiently high stress, a shear band will cross an existing band, usually producing a void at the point of intersection, and in some cases initiating a craze. Dense shear band formation has been observed in spherulitic polypropylene tested at low temperatures [35].

The effects of an additive upon the fracture resistance of polypropylene can best be discussed by referring to conditions at the tip of a sharp crack. In the homopolymer, a certain amount of yielding takes place at the crack-tip, and the crack extends through the yielded zone. Brittle fracture occurs, however, at high strain rates, low temperatures, and in thick sections, since each of these conditions restricts the extent of the yield zone. An important function of rubber particles is to reduce the yield stress, in the manner discussed above, thus increasing the amount of plastic deformation around the crack-tip. Where voids are formed as a result of deformation initiated by the rubber particles, yielding may be enhanced through the relief of plane-strain conditions. Factors affecting fracture resistance in polypropylene homopolymer and co-polymer are discussed in a recent paper by Fernando and Williams [36], which emphasizes the effects of temperature and crack-tip constraints on yielding. Equally important, on the other hand, are the effects of the additive upon the strength of the yielded zone. If the rubber is well bonded to the matrix, the stresses can become redistributed between the phases subsequent to yielding, so that the plastic zone is just as capable of resisting crack extension in the co-polymer as in the homopolymer. If, on the other hand, the particles are poorly bonded, the plastic zone in the co-polymer is weaker than the corresponding zone in the homopolymer, thus cancelling out the benefits to be derived from a reduction in yield stress.

Much of the interest in rubber toughening is directed towards impact strength, which involves considerably higher strain rates than those covered in the present programme. Some differences in the kinetics and mechanisms of deformation are to be expected, although they may not be large. It is interesting to note that at 30° C Roetling obtained [19] a linear relationship between yield stress and log (strain rate) over the range 10^{-5} to $10 \sec^{-1}$ in polypropylene, suggesting that a single mechanism controls the rate of yielding, despite the multiplicity of processes contributing to deformation. Even if there is a change in the dominant mechanism of deformation at high strain rates, there are good reasons for expecting Eyring kinetics to remain applicable, the difference in mechanism being marked by a change in the activation volume. Of more critical importance in rubber toughening is the effect of strain rate upon γ. Equation 6 is applicable provided that the shear modulus of the rubber is well below that of the matrix. At low strain rates, this means simply that the rubber must be above its glass transition temperature, T_g. At very high strain rates, on the other hand, the material may fracture before the rubber has had time to relax and generate stress concentrations, even at temperatures well above T_g [37]. This behaviour is an example of the well-known time–temperature superposition principle. In order to develop quantitative models for the impact behaviour of polypropylene "block co-polymer", it will be necessary to determine both the relaxation characteristics of the rubber and the kinetics of yielding in the matrix at high strain rates.

5. Conclusions

The following conclusions may be drawn from this study of creep in polypropylene homopolymer and "block co-polymer" at 20° C:

(a) The principal mechanism of deformation is shear yielding, with only a small contribution to the deformation being due to dilatational processes, which are more evident in the co-polymer than in the homopolymer.

(b) Under the conditions of these experiments, the rate coefficient of creep can be defined by means of an Andrade plot. The rate coefficient increases with stress, as predicted by the Eyring equation.

(c) The Eyring activation volume for creep in PP homopolymer is 2.45 nm^3.

(d) Rubber particles accelerate creep through their effect upon the Eyring stress concentration factor, γ.

(e) The observed stress concentration factor in the co-polymer is consistent with the minimum-area model of Ishai and Cohen.

Acknowledgement

References

1. C. B. BUCKNALL, "Toughened Plastics" (Applied Science Publishers, London, 1977) p. 88.
2. F. C. STEHLING, T. HUFF, C. S. SPEED and G. WISSLER, *J. Appl. Polymer Sci.* 26 (1981) 2693.
3. C. B. BUCKNALL and D. CLAYTON, *J. Mater. Sci.* 7 (1972) 202.
4. C. B. BUCKNALL, D. CLAYTON and W. E. KEAST, *ibid.* 7 (1972) 1443.
5. C. B. BUCKNALL and I. C. DRINKWATER, *ibid.* 8 (1973) 1800.
6. M. W. DARLINGTON and D. W. SAUNDERS, *J. Phys. E* 3 (1970) 511.
7. S. TURNER, *Trans. J. Plast. Inst.* 31 (1963) 60.
8. C. B. BUCKNALL, "Toughened Plastics" (Applied Science Publishers, London, 1977) p. 198.
9. E. N. da C. ANDRADE, *Proc. Roy. Soc.* A84 (1910) 1.
10. *Idem*, in "Creep and Recovery" (American Society for Metals, Metals Park, Ohio, 1957).
11. A. J. KENNEDY, *J. Mech. Phys. Sol.* 1 (1953) 172.
12. N. F. MOTT, *Phil Mag.* 44 (1953) 741.
13. C. D. POMEROY, "Creep of Engineering Materials" (Mechanical Engineering Publishers, London, 1978) p. 1.
14. S. TURNER, *Polymer Eng. Sci.* 6 (1966) 306.
15. I. M. WARD, "Mechanical Properties of Solid Polymers" (John Wiley and Sons, New York, 1971) p. 200.
16. H. G. OLF and A. PETERLIN, *J. Polymer Sci. Phys. Edn* 14 (1976) 1611.
17. R. J. SAMUELS, *J. Macromol. Sci.* B8 (1973) 41.
18. R. J. SAMUELS, "Structured Polymer Properties" (John Wiley and Sons, New York, 1974).
19. J. A. ROETLING, *Polymer* 7 (1966) 303.
20. H. N. YOON, K. D. PAE and J. A. SAUER, *J. Polymer. Sci. Phys. Edn* 14 (1976) 1611.
21. D. M. SHINOZAKI, G. W. GROVES and R. G. C. ARRIDGE, *Mater. Sci. Eng.* 28 (1977) 119.
22. E. PINK, V. BOUDA and H. BACK, *ibid.* 38 (1979) 89.
23. H. EYRING, *J. Chem. Phys.* 4 (1936) 283.
24. A. S. KRAUSZ and H. EYRING, "Deformation Kinetics" (Wiley Interscience, New York, 1975) pp. 40, 122.
25. O. ISHAI and L. J. COHEN, *J. Composite Mater.* 2 (1968) 302.
26. L. NICOLAIS, *Polymer Eng. Sci.* 15 (1975) 137.
27. L. NICOLAIS and M. NARKIS, *ibid.* 11 (1971) 194.
28. R. E. LAVENGOOD, L. NICOLAIS and M. NARKIS, *J. Appl. Polymer Sci.* 17 (1973) 1173.
29. L. NICOLAIS and M. NARKIS, *Polymer Eng. Sci.* 13 (1973) 469.
30. L. NICOLAIS, D. ACIERNO and J. JANACEK, *ibid.* 15 (1975) 35.
31. L. NICOLAIS and A. T. DiBENEDETTO, *Int. J. Polymer Mater.* 2 (1973) 251.
32. E. B. ATKINSON, private communication, 1966.
33. J. B. C. WU and J. C. M. LI, *J. Mater. Sci.* 11 (1976) 434.
34. C. C. CHAU and J. C. M. LI, *ibid.* 14 (1979) 1593.
35. K. FRIEDRICH, *ibid.* 15 (1980) 258.
36. P. L. FERNANDO and J. G. WILLIAMS, *Polymer Eng. Sci.* 20 (1980) 215.
37. C. B. BUCKNALL, "Toughened Plastics" (Applied Science Publishers, London, 1977) p. 295.