

The mechanical properties of epoxy resins

Part 1 *Mechanisms of plastic deformation*

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The yield stress, σ_y , and Young's modulus, E , of a series of triethylenetetramine-cured epoxy resins have been measured as a function of resin composition and testing rate and temperature. It is found that for a given composition, both σ_y and E increase as the testing rate is increased and as the temperature is decreased. It is also found that under the same testing conditions, σ_y and E both decrease as the amount of curing agent in the resin is increased. The relationship between σ_y and E has been analysed using the theories of plastic deformation in glassy polymers of Argon and Bowden. Good agreement has been found with the Argon theory at low temperatures whereas the agreement with the Bowden theory is found to be good at all temperatures up to T_g . It appears therefore that the plastic deformation of epoxy resins which are thermosets is similar to that of glassy thermoplastics. The significance of the parameters derived from the two theories has been discussed in terms of the molecular structure of the resins.

1. Introduction

Epoxy resins are inherently brittle materials but under certain circumstances they can undergo a surprising degree of plastic deformation. The addition of plasticizing agent will allow plastic flow to occur at ambient temperature under a variety of test modes such as tension [1], compression [1, 2] or flexure [1]. Non-plasticized epoxy resins display rather more limited ductility but will undergo deformation in uniaxial compression because there is a large component of hydrostatic compression in this testing mode. The plastic deformation of glassy polymers has received considerable interest recently. Two important theories, based upon physical descriptions of plastic flow upon molecular level, have been developed by Bowden [3-5] and Argon [6-8]. Earlier approaches to this problem had been based upon modifications of viscoelastic models using the Eyring theory of viscous flow [9]. The Bowden and Argon theories, which are different from each other in approach, do not use the Eyring model and are both concerned with the thermal activation of the molecular displacements that take place during plastic flow. The two theories have been tested using plastic flow data from a variety

of glassy thermoplastic polymers such as polystyrene [4, 6] polymethylmethacrylate [4-6], polyethylene terephthalate [6] polycarbonate [6] and a series of aromatic polyimides [7, 8]. On the whole, both theories have met with a considerable degree of success, predicting the yield stresses of these polymers over a wide range of temperatures from very low temperatures to near T_g .

The relationship between plastic deformation and the microstructure is well-established in metals [10]. However, it is usually difficult to produce sufficient structural variations in glassy polymers to enable the parameters obtained from the theories to be related to the molecular structure. For example, the molar mass of the polymer has very little effect upon plastic deformation. There have been attempts to relate the plastic flow behaviour of glassy thermo-plastics to their chemical structure. Argon and Bessonov [7, 8] looked at the effect of introducing long stiff units into the molecules of aromatic polyimides. They assumed that this had the effect of increasing the spacing between the natural hinges on the polymer molecules and showed that it had the effect of causing the plastic deformation to become less local.

All of the work so far reported on the plastic

deformation glassy polymers has been concerned with thermoplastics. In this present study, we have looked at the plastic flow behaviour of epoxy resins which are cross-linked thermosetting polymers. With these materials it is possible to vary the structure, in particular the density and nature of the cross-links, using different quantities and types of curing agent and different cure schedules. In the first part of this presentation we report the effect of varying the amount of curing agent and post-cure temperature upon the plastic deformation of a commercial epoxy resin and interpret it in terms of the various theories that have been developed to explain the plastic deformation of glassy polymers. In the second part we show how crack propagation in these materials is controlled by the plastic deformation behaviour of the resin.

2. Experimental procedure

2.1. Moulding and specimen preparation

The resin used for this present study was a commercial diglycidyl ether of bisphenol A (DGEBA), Epikote 828 (Shell) cured exclusively with various amounts of triethylene tetramine (TETA), a mixed primary and secondary amine. Details of the moulding conditions are given in previous publications [11–13]. Four different quantities of the curing agent were used: 7.4, 9.8, 12.3, and 14.7 phr*. For all mouldings the initial hardening reaction was allowed to proceed for 24 h at room temperature before curing at elevated temperatures for different periods of time. The cast resins were in the form of sheets of two different thicknesses: 3.9 and 6.3 mm.

2.2. Young's modulus determinations

The 3.9 mm sheets of moulded resin were cut into rectangular plates 30 mm by 70 mm. The modulus of the resin was determined in three-point bending using an Instron mechanical testing machine operated at different cross-head speeds. The specimen loading is illustrated schematically in Fig. 1a.

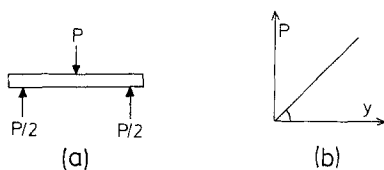


Figure 1 Young's modulus determination. (a) Three-point bend test, (b) schematic load–displacement curve.

*Parts by weight of hardener per 100 parts by weight of resin.

The relationship between the applied load, P , and the displacement of the centre of the specimen, y , was found to be linear as shown in Fig. 1b and the ratio P/y is related to the Young's modulus of the resin through the equation [14]

$$P/y = 4Ebh^3/L^3 \quad (1)$$

for a rectangular cross-section specimen of thickness h and breadth b . The distance between the supports is L and the modulus of the resin is E . The displacement y was determined from the movement of the cross-head taking into account corrections for machine softness. Tests were carried out at a variety of rates controlled by the cross-head speed used, and at different temperatures in an Instron environmental chamber. The temperature was controlled by electrical heating at elevated temperatures and using carbon dioxide at low temperatures, both to an accuracy of $\pm 2^\circ \text{C}$.

2.3. Yield stress measurement

Cylindrical specimens, 10 mm long and 5 mm diameter, were machined from the 6.3 mm plates of resin. They were deformed in uniaxial compression between polished lubricated steel plates in the environmental chamber of the Instron testing machine as shown in Fig. 2a. The nominal strain, e , was determined from the cross-head displacement, corrected for machine softness. The load, P , was converted into true stress σ_T using the initial cross-sectional area A_0 in the equation

$$\sigma_T = P(1 - e)/A_0 \quad (2)$$

which is derived assuming constant volume deformation. A typical stress–strain curve is shown in Fig. 2b. The yield stress has been taken as the maximum stress in such a curve.

3. Results

3.1. Young's modulus measurements

The variation of the Young's modulus of the epoxy resins with various material and testing

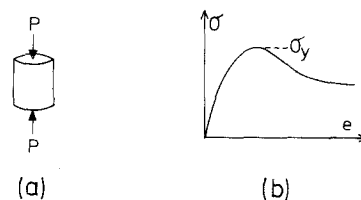


Figure 2 Yield stress measurement. (a) Uniaxial compression specimens, (b) schematic stress–strain curve.

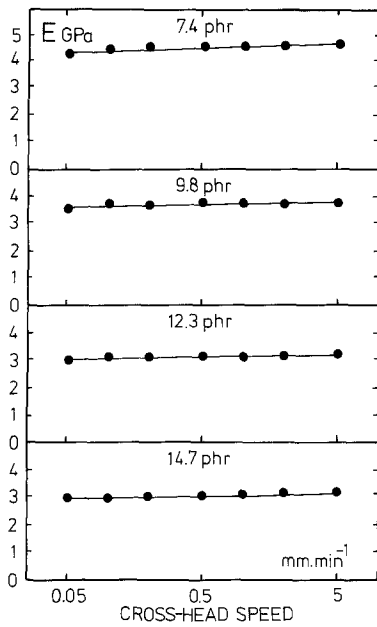


Figure 3 Variation of Young's modulus, E , with cross-head speed for a series of resins post-cured at 100°C for 3 h and tested at $22 \pm 2^{\circ}\text{C}$.

variables was determined. Fig. 3 shows the variation of E with curing agent content and cross-head speed (strain rate) for samples tested at room temperature ($22 \pm 2^{\circ}\text{C}$). In all cases the modulus increases slightly with increasing cross-head speed. It is also found to fall as the amount of hardener in the resin is increased. Fig. 4 shows the variation of E with cross-head speed for a series of resins containing the same quantity of hardener but cured at different temperatures for 3 h. They were

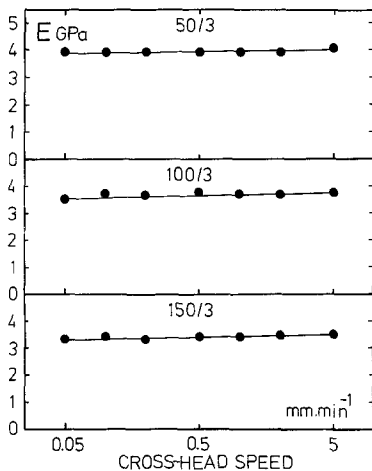


Figure 4 Variation of Young's modulus, E , with cross-head speed for a series of resins containing 9.8 phr of TETA and post-cured for 3 h at different temperatures.

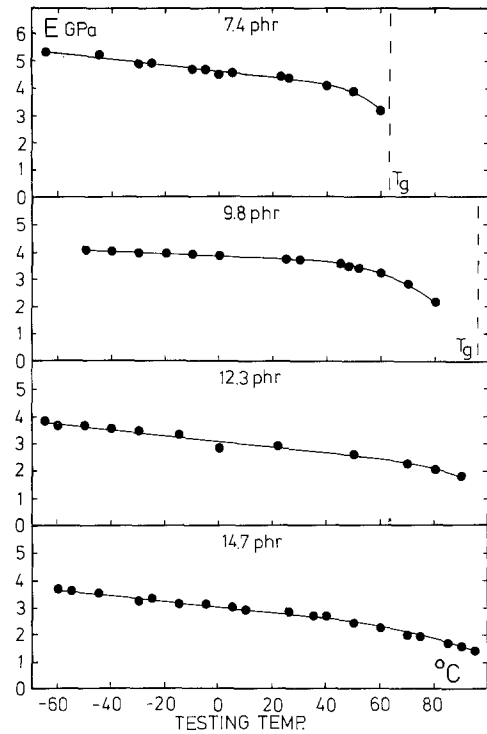


Figure 5 Variation of Young's modulus, E , with testing temperature for a series of resins containing different amount of TETA and post-cured at 100°C for 3 h. The cross-head speed used was 0.5 mm min^{-1} . The T_g s of the 12.3 and 14.7 phr resins are 102 and 109°C , respectively.

all tested at room temperature and it can be seen that modulus tends to increase with increasing cross-head speed and decreasing curing temperature.

The moduli of the epoxy resins were also measured at a constant cross-head speed using different testing temperatures. These results are given in Fig. 5. It can be seen that in each case the modulus of the resin decreases steadily as the testing temperature is increased. There is a more abrupt decrease as the glass transition temperature T_g of the resin is approached. The values of T_g were measured for each resin using differential scanning calorimetry, DSC [15].

3.2. Yield stress measurements

The yield stresses, σ_y , of the different resins were measured at similar cross-head speeds and temperatures to those used in Section 3.1. The variation of yield stress with cross-head speed for resins of different hardener content is given in Fig. 6. As for the modulus data in Fig. 3, it is found that the yield stress increases with increasing cross-head speed and decreases as the amount of hardener in the resin is increased. The effect of post-

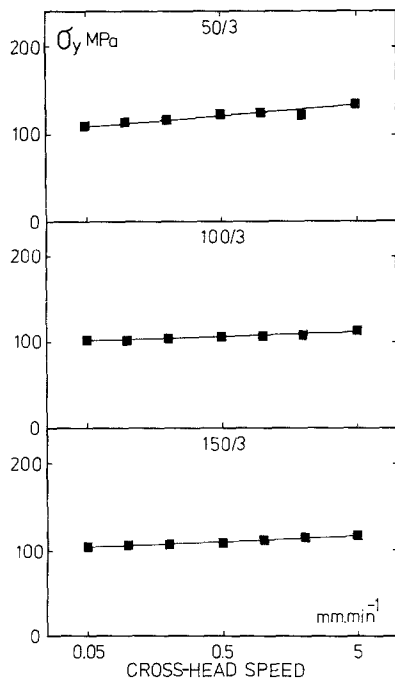


Figure 6 Variation of yield stress, σ_y with cross-head speed for a series of resins post-cured at 100°C for 3 h and tested at $22 \pm 2^\circ\text{C}$.

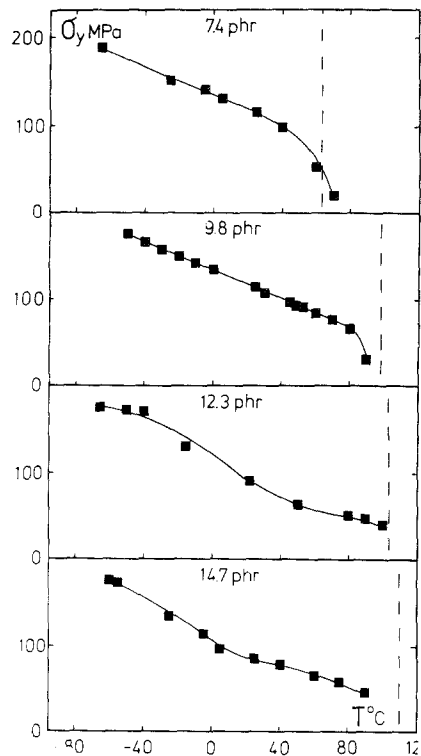


Figure 8 Variation of yield stress, σ_y , with testing temperature for a series of resins containing different amounts of TETA and post-cured at 100°C for 3 h. The cross-head speed used was 0.5 mm min^{-1} .

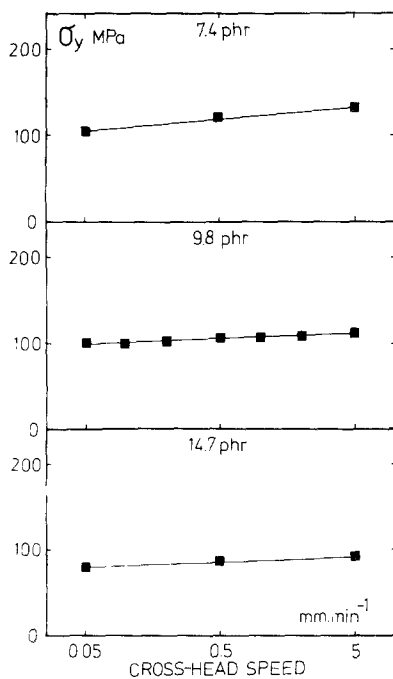


Figure 7 Variation of yield stress, σ_y with cross-head speed for a series of resins containing 9.8 phr of TETA and post-cured for 3 h at different temperatures.

cure temperature upon the yield stress of a resin containing 9.8 phr of hardener is shown in Fig. 7. Again the behaviour is similar to the corresponding variation in modulus.

The effect of testing temperature upon the yield stress of four different formulations of resin is shown in Fig. 8. The behaviour is again similar to that of the Young's modulus of similar resins (Fig. 5) but the drop in yield stress with increasing temperature is proportionately much more rapid than that of the modulus.

Specimens were sectioned after deformation and examined in a polarized light microscope. The deformation was found to be homogeneous with no evidence of shear band formation [16, 17].

4. Discussion

At first sight the variation of the modulus and yield stress of the epoxy resins with different testing variables shows a similarity to the behaviour of glassy thermoplastics. The epoxy resins appear to obey the empirical rules set out by Brown [18] some years ago governing the yield behaviour of glassy polymers. Any variable which

increases E also increases σ_y and the ratio of the yield stress to the modulus is in the range 1/60 to 1/30. It has been possible to successfully explain the yield behaviour of glassy polymers in terms of molecular theories [3–8] that have been put forward more recently. The critical test of such theories is to look at the relationship between E and σ_y over as wide a range of temperatures as possible when significant changes in the values of these parameters occur.

4.1. Argon's theory

The theory of yielding in glassy polymers put forward by Argon and Bessonov [6–8] proposes that this occurs by the thermally activated production of local molecular kinks which they modelled by the formation of wedge disclinations. The mathematical analysis is somewhat complex but the final equations predicting the relationship between the shear yield stress τ and the shear modulus μ are relatively simple. It can be shown [8] that

$$(\tau/\mu)^{5/6} = A - B(T/\mu), \quad (3)$$

where T is the absolute temperature. The constants A and B are given by

$$A = \left[\frac{0.077}{(1-\nu)} \right]^{5/6} \quad (4)$$

and

$$B = A \left[\frac{16(1-\nu)k}{3\pi \omega^3 a^3} \ln(\dot{\gamma}_0/\dot{\gamma}) \right], \quad (5)$$

where ν is Poisson's ratio, k Boltzmann's constant, ω the net angle of rotation of the molecular segment between the initial configuration and the activated configuration, and a the mean molecular radius. The shear strain rate is given by $\dot{\gamma}$, and $\dot{\gamma}_0$ is a pre-exponential frequency factor usually taken as about 10^{13} sec^{-1} . These equations predict that plots of $(\tau/\mu)^{5/6}$ against (T/μ) should be linear. Also since for most glassy polymers ν is of the order of 0.3 it is expected that they should all have a common intercept, A of the order of 0.16 as $T \rightarrow 0$.

In order to test the applicability of this theory to the data in Section 3 it is necessary to convert the moduli and yield stresses into the corresponding shear moduli and shear yield stresses. This can be done using the equations [8]

$$\mu(T) = E(T)/2(1 + \nu) \quad (6)$$

$$\tau(T) = \sigma_y(T)/\sqrt{3}. \quad (7)$$

The value of Poisson's ratio ν for the epoxy resins has been taken as 0.35 [11] and the relationship in Equation 3 is obtained by assuming that yielding obeys a von Mises criterion [19]. Strictly speaking, both $E(T)$ and $\sigma_y(T)$ should be measured at the same strain rate. In the calculations described below, the same cross-head speed has been used but it is not envisaged that significant error will be introduced.

Fig. 9 shows the variation of $(\tau/\mu)^{5/6}$ with T/μ for the resins of different formulation. The data used were taken from Figs. 5 and 8. The lines are drawn as a best fit of the low-temperature data. It can be seen that Equation 3 is obeyed at low temperatures but as the T_g of the resin is approached and the polymer becomes leathery, the data points tend to become parallel to the T/μ axis. This deviation was also observed by Argon and Bessonov [6–8] for a series of different glassy thermoplastic polymers. The deviation tends to be affected by the formulation of the resin. For the resin containing 7.4 phr hardener, Equation 3 is obeyed up to its T_g . The temperature to which the equation holds is reduced progressively as the amount of hardener is increased until, for the resin with 14.7 phr hardener, deviation occurs above 5° C which is over 100 degrees below the T_g of this strain.

The Argon theory is particularly useful for the

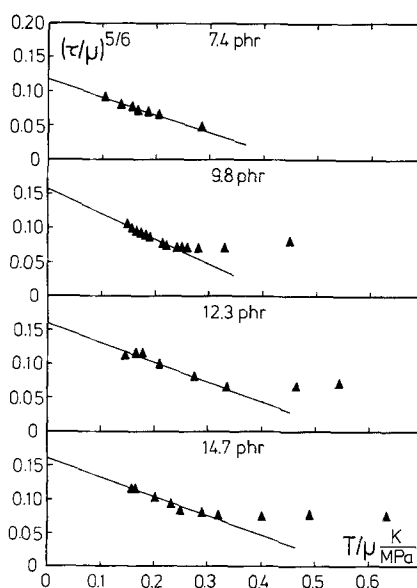


Figure 9 Variation of $(\tau/\mu)^{5/6}$ with T/μ derived from the data in Figs. 5 and 8. The straight lines have been plotted according to Argon's theory [6–8] and Equation 3.

TABLE I Values of the various parameters derived from Argon and Bowden's theories of plastic deformation in glassy polymers.

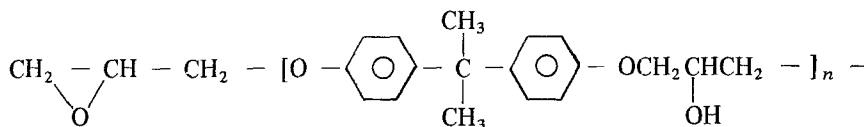
Polymer*	<i>A</i>	<i>B</i> (MPa K ⁻¹)	<i>a</i> (10 ⁻¹⁰ m)	<i>z</i> [*] (10 ⁻¹⁰ m)	<i>b</i> (10 ⁻¹⁰ m)
PC	0.176	0.129	5.77	11.6	4.25
PET	0.169	0.138	5.64	11.4	4.9
PS	0.180	0.480	3.72	7.44	2.8
PMMA	0.171	0.364	4.08	8.24	2.7
<i>Epoxy</i> s					
7.4 phr	0.120	0.258	4.10	8.97	3.0
9.8 phr	0.158	0.369	3.98	8.25	3.8
12.3 phr	0.160	0.289	4.34	8.97	4.2
14.7 phr	0.162	0.285	4.38	9.03	4.3

*The values for PC, PET, PS and PMMA have been taken from previous publications [3-7]. The parameters *a* and *z*^{*} are the mean molecular radius and critical separation of a pair of molecular kinks respectively, from Argon's theory. The Burgers vector *b* has been derived from Bowden's theory.

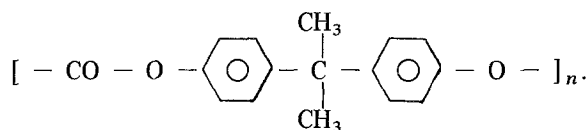
description of yield processes in glassy polymers as it allows molecular parameters to be determined from the values of *A* and *B* which are measured experimentally. Table I shows the values of *A* and *B* obtained for the four different formulations of resin along the measurements of *A* and *B* determined by previous investigators [6-8] for different glassy thermoplastics. It can be seen immediately that the values of the parameters for the epoxy resins are within the range of those obtained for other glassy polymers. Rearrangement of Equation 5 allows the mean molecular radius to be determined as

$$a^3 = \frac{A}{B} \frac{16(1-\nu)k}{3\pi\omega^2} \ln(\dot{\gamma}_0/\dot{\gamma}). \quad (8)$$

Values of *a* determined experimentally for the four formulations of resin are given in Table I using a value of $\omega = 2$ and $\dot{\gamma} = 4 \times 10^{-4} \text{ sec}^{-1}$. It can be seen that for all of the resins, *a* is of the order of $4.2 \pm 0.2 \text{ \AA}$ and similar to values obtained for other carbon chain polymers. Since the epoxy resin and PC are both derivatives of bisphenol A it might be expected that their molecular parameters may be similar. Even the uncured epoxy resin has a rather complex chemical structure



and curing produces a complicated network. On the other hand PC is a similar molecule but contains a smaller proportion of C atoms in the chain:



Since the PC molecule is bulkier than the epoxy molecule it would be expected that the mean molecular radius of the epoxy molecule would be less than that of the polycarbonate molecule. This is precisely what is found, *a* is 5.77 Å for PC and only ~ 4.2 Å for the epoxy resin.

Another parameter that can be determined for the polymer is *z*^{*}, which is the critical separation at yield of a pair of kinks (wedge disclinations) on the polymer molecule. This is given by absolute zero by [8]

$$(z/a)^*_{0K} = \left[\frac{45}{8(1-\nu)} \right]^{1/6} A^{-1/5}. \quad (9)$$

The value of *z*^{*} is not expected to vary significantly with temperature and it is found to be of the order of 9 Å for all the resins formulations studied. This value lies between that of the very flexible molecules with a C-C backbone such as PMMA and PS and stiffer molecules containing benzene rings in the chain such as PET and PC. The epoxy resin

contains a few widely-spaced benzene rings along a C-C chain and so this value of *z*^{*} is not unreasonable.

It is clear from Section 3 that under a given set of testing conditions both E and σ_y decrease as the curing agent content and post-cure temperature are both increased. This means that, rather surprisingly, E and σ_y both decrease as the degree of cure and hence cross-link density are both increased. However, it is perhaps more significant that, as can be seen from Table I, a and z^* do not vary significantly with the degree of cure. This may be because the yield process as conceived by Argon's theory is controlled by the main chain stiffness and so the degree of cross-linking has very little effect upon the value of the parameters that are measured.

4.2. Bowden's theory

An alternative model to predict the yield behaviour of glassy polymers was developed independently, at about the same time as Argon's theory was developed, by Bowden and co-workers [3–5]. This model is simple in concept and it envisages the critical step in the yield process as being the thermally activated nucleation under stress of small disc-shaped sheared regions in the polymer. The strain fields of the sheared regions are assumed to be analogous to those of dislocation loops with a Burgers vector equal to the shear displacement. It must be stressed that the dislocation concept is only an analogy and it is introduced because solutions for the energies of and stresses in dislocation loops are readily available and at no time is it suggested that dislocations are present in glassy polymers.

The energy of a dislocation loop of radius R and Burgers vector b in a solid with shear modulus of μ under an applied stress τ is given approximately by the relation:

$$U = (2\pi R)(Gb^2/4\pi) \ln(2R/r_0) - \pi R^2 \tau b, \quad (10)$$

where r_0 is the core radius of the dislocation. The energy of the loop U increases as R increases until it reaches a maximum value U_c at R_c which can be found by differentiating Equation 10 and is given by

$$U_c = (Gb^2 R_c/4)[\ln(2R_c/r_0) - 1]$$

at

$$R_c = (Gb/4\pi\tau)[\ln(2R_c/r_0) + 1]. \quad (11)$$

The core radius r_0 can be eliminated by assuming that at absolute zero τ reaches a critical value of $G/\sqrt{3\pi}$ [4] and this leads to a value of r_0 of $b\sqrt{3}/e(\approx b)$. Bowden assumed that yielding will

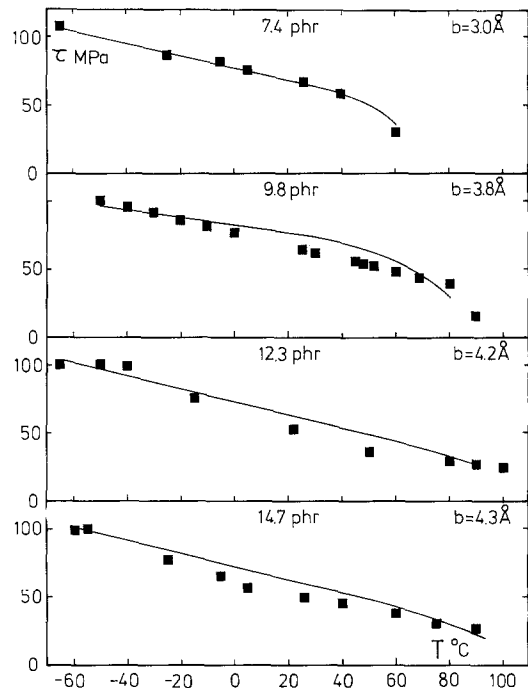


Figure 10 Variation of shear yield stress τ with testing temperature for resins of different formulations. The squares are the experiment points and the curves are the variation predicted from the modulus measurements using the Bowden theory [3–5] using the values of Burgers vector, b , indicated.

occur when U_c reaches an energy of $50 kT$, which should be available from thermal fluctuations. If this value of U_c is used, Equation 11 can be solved with suitably chosen values of b and experimental values of μ to predict the corresponding values of τ . The values of μ determined from the modulus data in Fig. 5 using Equation 6 have been used to predict the variation of τ with temperature represented as solid lines in Fig. 10. The measured values of τ , calculated using Equation 7 are also given in Fig. 10 and appropriate values of b have been chosen to fit the theoretical lines to the experimental points. The value of Burgers vector b increases as the amount of hardener in the resin is increased and it can be seen that the agreement between theoretical prediction and the experimental data over a wide range of temperature is extremely good. The theory appears to hold to very near T_g in contrast to Argon's theory (Section 4.1) which does not apply near T_g .

Table I compares the values of b determined for the epoxy resins with different amount of hardener with those found for other polymers [3–5]. It can be seen that, as with the parameters

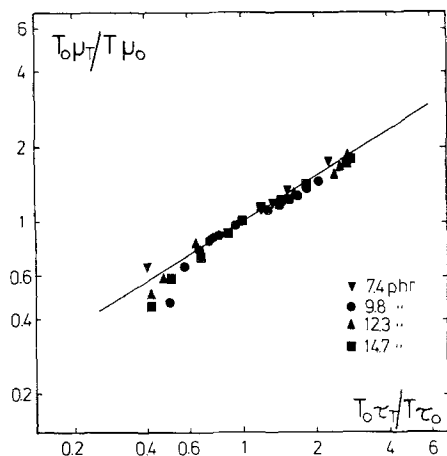


Figure 11 Master curve for the relationship between μ and τ plotted according to Equation 12 in a log-log plot. The straight line is drawn with a slope of 1.63 according to the theory of Kitagawa [20].

derived from Argon's theory, the values of b for the epoxy resins are greater than those for PS and PMMA but less than the values for PC and PET. The fully cured resins (12.3 and 14.7 phr) have Burgers vectors which are similar to that for PC. Bowden [4] pointed out that polymers with small side groups or small repeat units tended to have small Burgers vectors whereas those with large side groups or repeat units tended to have larger values of b . The results of this present investigation are consistent with this suggestion.

Kitagawa [20] has recently expanded and generalized Bowden's theory showing that the relationship between μ and τ can be represented by a power law relation of the form

$$\frac{T_0 \tau}{T \tau_0} = \left(\frac{T_0 \mu}{T \mu_0} \right)^n, \quad (12)$$

where τ_0 and μ_0 are the values of shear yield stress and shear modulus as some reference temperature T_0 (conveniently taken as the ambient temperature) and n is a temperature independent exponent. Kitagawa [20] showed that a relation of the form of Equation 12 held over a wide range of temperature for most polymers. He also found that it had a unique value of 1.63 for all amorphous polymers between 0.8 and 0.9 for semicrystalline polymers. Fig. 11 is a log-log plot according to Equation 12 for the values of τ and μ obtained for the resins of different formulation and tested over a wide range of temperatures. The line drawn on the graph has a slope of 1.63 and it can be seen

that all the points fall close to this line. This is a further indication that the yield behaviour of the epoxy resins studied is identical to that found for other glassy polymers and that the presence of cross-links does not fundamentally affect the yield behaviour of the polymer.

5. Conclusions

It has been shown that the plastic deformation of a series of glassy epoxy resins containing different amounts of curing agents can be explained in terms of the yield theories of Argon and Bowden. These two theories view the yield process as being due to the thermal activation of local molecular kinks and small disc-shaped sheared regions, respectively. It has been found that Bowden's theory applies over a wide range of temperature up to T_g . It has also been shown that the form of the temperature variation of yield stress and Young's modulus is identical to that for glassy thermoplastics. On the other hand, the theory of Argon and Bessonov applies only at low temperatures and does not, in general, give good agreement close to T_g . However, it does allow molecular parameters to be generated and the values of the parameters that have been obtained for the epoxy resins are similar to those obtained previously for glassy thermoplastics with similar chemical structures. It is clear, therefore, that the plastic deformation of epoxy resins below T_g is essentially identical to that of amorphous glassy thermoplastics.

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References

1. O. ISHAI, *J. Appl. Polymer Sci.* **11** (1967) 963.
2. P. B. BOWDEN and J. A. JUKES, *J. Mater. Sci.* **7** (1972) 52.
3. P. B. BOWDEN, "The Physics of Glassy Polymers", edited by R. N. Howard (Applied Science Publishers, London, 1973) p. 279.
4. P. B. BOWDEN and S. RAHA, *Phil. Mag.* **29** (1974) 149.
5. A. THIERRY, R. J. OXBOROUGH and P. B. BOWDEN, *ibid* **30** (1974) 527.
6. A. S. ARGON, *ibid* **28** (1973) 839.
7. A. S. ARGON and M. I. BESSONOV, *Polymer. Eng. Sci.* **17** (1977) 174.

8. *Idem*, *Phil. Mag.* **35** (1977) 917.
9. H. EYRING, *J. Chem. Phys.* **4** (1936) 283.
10. R. W. K. HONEYCOMBE, "The Plastic Deformation of Metals" (Edward Arnold, London, 1968).
11. S. YAMINI and R. J. YOUNG, *Polymer* **18** (1977) 1075.
12. R. A. GLEDHILL, A. J. KINLOCH, S. YAMINI and R. J. YOUNG, *Polymer* **19** (1978) 574.
13. S. YAMINI and R. J. YOUNG, *J. Mater. Sci.* **14** (1979) 1609.
14. R. J. YOUNG and P. W. R. BEAUMONT, *Polymer* **17** (1976) 717.
15. S. YAMINI, Ph.D. Thesis, University of London (1979).
16. P. B. BOWDEN and S. RAHA, *Phil. Mag.* **22** (1970) 463.
17. J. B. C. WU and J. C. M. LI, *J. Mater. Sci.* **11** (1976) 434.
18. N. BROWN, *Mater. Sci. Eng.* **8** (1971) 839.
19. R. RAGHAVA, R. M. CADDELL and G. S. Y. YEH, *J. Mater. Sci.* **8** (1973) 225.
20. M. KITAGAWA, *J. Polymer Sci. Polymer Phys. Ed.* **15** (1977) 1601.

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