Mechanisms of plastic deformation in poly(diethylene glycol bis(allyl carbonate))

M. Frounchi, R. P. Chaplin* and R. P. Burford
School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Kensington, NSW 2033, Australia
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The plastic deformation of a highly crosslinked glassy polymer, poly(diethylene glycol bis(allyl carbonate)) (ADC resin) at different temperatures was investigated. It is found that both compressive yield stress σ_y and Young's modulus E decrease as temperature is increased. The relationship between σ_y and E has been analysed using Argon's and Bowden's theories of plastic deformation in glassy polymers. Molecular parameters derived from each theory have been discussed in terms of the chemical structure of the resin.

(Keywords: plastic deformation; glassy polymer; ADC resin)

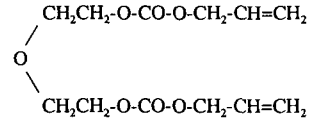
INTRODUCTION

Poly(diethylene glycol bis(allyl carbonate)), also known as poly(allyl diglycol carbonate) or ADC resin, displays limited ductility in tension mode and fails at strains of a few per cent. However, ADC can undergo an appreciable degree of plastic deformation when it is subjected to compression loading.

The plastic deformation of glassy polymers has been analysed by two important theories, based on physical description of plastic flow on a molecular level. These theories have been developed by Bowden and Argon[1-6]. Earlier approaches had been based on modification of viscoelastic models using the Eyring theory of viscous flow[7]. The Bowden and Argon theories differ from each other in approach but are both concerned with the thermal activation of the molecular displacements that take place during plastic flow. The two theories have been tested on a variety of glassy thermoplasic polymers such as polystyrene[2-4], poly(methyl methacrylate) (PMMA)[2-4], poly(ethylene terephthalate)[4] and polycarbonate[4]. In addition, Young and coworkers have recently shown that the theories can also be applied to thermosetting epoxy resin systems[8]. On the whole, both these 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 temperature to near T_g.

There have also been attempts to relate the plastic flow behaviour of glassy thermoplastics to their chemical structure. Argon and Bessonov[6] looked at the effect of introducing long stiff units into the molecules of aromatic polyimides, which were chemical derivatives of resorcinol, hydroquinone, oxydiphenyl and pyromellitic acid. The spacings of natural hinges on molecules, i.e. the lengths of the stiff segments in the polymer chains (from the length of the chemical bonds), ranged from 8.1 to 18 Å. In some instances, the lengths of stiff segments were exactly equal to the lengths of the monomer units. They assumed that the effect of increasing the spacing between the natural hinges on the polymer molecules had the effect of causing the thermally activated yielding to grow in size, and plastic deformation to become less local.

In this present study, we have looked at the plastic flow behaviour of ADC. This material is a highly crosslinked glassy polymer of valuable optical qualities. It is made by the bulk polymerization of diethylene glycol bis(allyl carbonate) of formula:



In a previous study[9] we showed that the major fracture-energy-relieving mechanism in ADC resins is shear yielding. In this study we intend to examine the applicability of the two above-mentioned theories, which although initially developed for glassy thermoplastics should also apply to crosslinked thermosets such as ADC resin systems, and to compare its plastic deformation with well known glassy thermoplastics such as poly(methyl methacrylate).

In a separate publication, attempts to modify the yielding behaviour of ADC by introducing another glassy polymer network with various molecular spacings and crosslink density into the crosslinked network of ADC have been presented[10].

The major focus of our work is to increase the fracture toughness of the brittle ADC resin system by increasing localized yielding without loss in modulus, yield strength or optical qualities, leading to tougher novel resins.

EXPERIMENTAL

ADC monomer was provided by SOLA International, Australia. The monomer was cast-polymerized with 3% anhydrous benzoyl peroxide in glass moulds as detailed

* To whom correspondence should be addressed

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in our previous study[9]. The mould was heated in a temperature cycle ranging from room temperature up to 85°C in a programmable oven. The castings were then annealed at 110°C for 2 h. For compression test pieces the monomer was poured into glass tubes of 5 mm diameter and then polymerized in a similar cycle.

Young's flexure modulus measurements

Young's elastic modulus E was measured in flexural mode. Test pieces cut from cast sheets were 3.3 mm thick, 14 mm wide and 80 mm long. The test span was 60 mm. Testing was carried out in an Instron machine (model 1195) equipped with an Instron temperature chamber (model 3111). The temperature was controlled by electrical heating at elevated temperatures and uses liquid nitrogen as coolant at low temperatures. The Young's modulus was measured from −60 to +80°C. The modulus of each specimen, measured at a crosshead speed of 0.5 mm min^{-1}, was determined using the equation:

$$E = L^3/4bt^3m \quad (1)$$

where m is the slope of the load–displacement curve, L the span, b the width and t the thickness of the specimen.

Compression yield stress measurement

Cylindrical specimens, 10 mm long and 5 mm diameter, were used for the measurement of compression yield stress σ_y. Measurements were determined in uniaxial compression between polished lubricated steel plates at a crosshead speed of 0.5 mm min^{-1}. Measurements were made over a temperature range from −60 to +80°C. The load P was converted into true stress σ_T using the initial cross-sectional area A_0 in the equation:

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

which is derived assuming constant-volume deformation.

Dynamic mechanical analysis and creep test

Glass transition temperatures were determined using a DuPont DMA 983 dynamic mechanical analyser at a heating rate of 20°C min^{-1} in resonant mode from −100 to +200°C. Creep tests used for measuring the molecular weight between crosslinks (M_c) were conducted in creep mode with the DuPont DMA 983. Creep experiments covered the entire range of viscoelastic behaviour from the glassy region at 60°C to the rubbery region at 160°C on specimens measuring approximately $20 \times 11 \times 3.3$ mm^3. Compliance readings were taken at various intervals in time. The master curve was obtained by shifting curves of compliance obtained at various temperatures with respect to a reference temperature, which was chosen to be the glass transition temperature, until they all fit together to form a smooth master curve. The value of M_c was calculated from the equilibrium shear compliance at infinite time $J(t=\infty)$, which is the limiting value of $J(t)$, by means of the theory of rubber elasticity[11], to give M_c with the following equation:

$$M_c = \rho RTJ(\infty) \quad (3)$$

where T is absolute temperature (K) (in this case, 413 K), ρ is the polymer density and R is the gas constant. Shear creep compliance J is related to flexural creep modulus S through the relation $J = 3S$.

RESULTS AND DISCUSSION

Young's flexure modulus measurement

The variation of Young's flexure modulus with temperature is shown in *Figure 1*. It can be seen that the modulus of the ADC resin decreased steadily as the temperature increased. There was a more pronounced decrease as the glass transition temperature of the resin was approached. The T_g of ADC resin based on the loss modulus curve was determined as 100°C.

Compressive yield stress measurement

Though ADC in tension mode fails in a rather brittle manner, it displays quite substantial plastic deformation in compression mode. A typical compression stress–strain curve is shown in *Figure 2*, which also shows the procedure used to obtain the yield stress. The form of yielding remains largely uninfluenced by temperature, having a smooth and gradual transition from elastic to plastic behaviour. The results for compression yield stress as a function of temperature are also shown in *Figure 1*. The behaviour was similar to that of the Young's modulus, but the drop in yield stress with increasing temperature is proportionately more rapid than that of the modulus.

Argon's theory of yielding

Argon's theory of yielding in glassy polymers proposes that yielding occurs by the thermally activated production of local molecular kinks, which is modelled by the

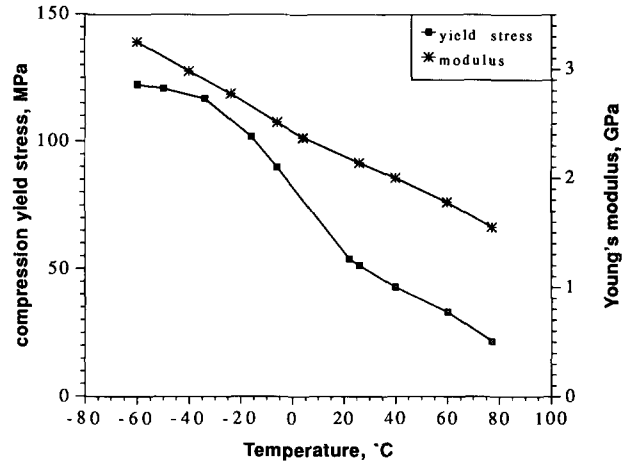


Figure 1 Variation of Young's modulus and compression yield stress as a function of temperature for ADC resin

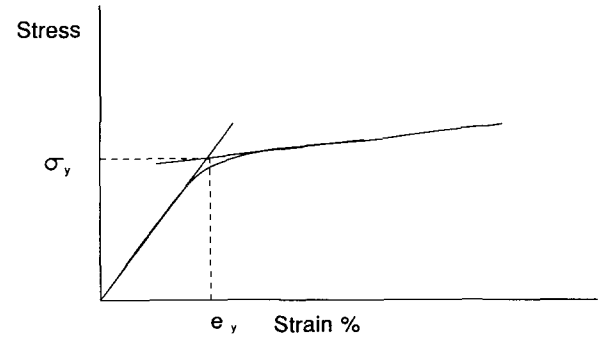


Figure 2 Compressive yield stress measurement from stress–strain curve for ADC resin at 20°C

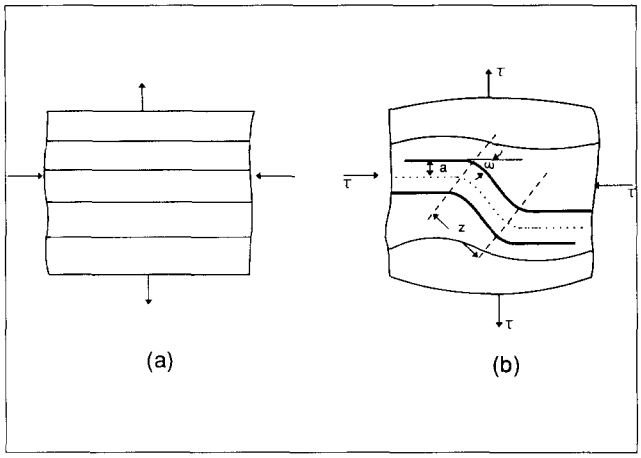


Figure 3 Schematic illustration of the formation of a pair of molecular kinks: (a) fully aligned polymer; (b) formation of a pair of kinks in a polymer molecule as a local contraction. From reference 4

formation of wedge disclinations[4]. The formation of a pair of molecular kinks is illustrated in *Figure 3*. The mathematical analysis is complex but the final equations predicting the relationship between the shear yield stress τ and the shear modulus G are simple. The forms of the equations are given as:

$$(\tau/G)^{5/6} = A - B(T/G) \tag{4}$$

where T is the absolute temperature and A and B are constants, given by:

$$A = \left(\frac{0.077}{1-\nu}\right)^{5/6} \tag{5}$$

$$B = A\left[\frac{16(1-\nu)k}{3\pi\omega^2 a^3}\ln\left(\frac{\dot{\gamma}_0}{\dot{\gamma}}\right)\right] \tag{6}$$

Here ν is Poisson's ratio, k is Boltzmann's constant, ω is the net angle of rotation of the molecular segment between the initial configuration and the activated configuration, and a is the mean molecular radius of the polymer chain. The shear strain rate is given by $\dot{\gamma}$, and $\dot{\gamma}_0$ is a pre-exponential frequency factor usually taken as about $10^{13}\ s^{-1}$. These equations predict that plots of $(\tau/G)^{5/6}$ against T/G should be linear. Also, since for most glassy polymers ν is of the order of 0.35, it is expected that they should all have a common intercept A of the order of 0.169 as the temperature approaches zero. In practice, glassy polymers such as polystyrene, poly(methyl methacrylate) and polycarbonate have been found to have values of $A \simeq 0.17$[6] while aromatic and hetero-aromatic polyimides have $A \simeq 0.14$[6].

In order to test the applicability of this theory to ADC resins, it is necessary to convert the flexural moduli results and compressive yield stress data into the corresponding shear moduli G and shear yield stresses τ_y by using the following relationships[4,5]:

$$G(T) = \frac{E(T)}{2(1+\nu)} \tag{7}$$

$$\tau(T) = \frac{\sigma_y(T)}{\sqrt{3}} \tag{8}$$

The value of Poisson's ratio ν for ADC was taken as 0.35. Strictly speaking, both $E(T)$ and $\sigma_y(T)$ should be measured at the same strain rate; however, it is not envisaged that a significant error will be introduced in the calculations if the same crosshead speed is used as suggested by Young *et al.*[8]. *Figure 4* shows the variation of $(\tau/G)^{5/6}$ with T/G for ADC resin. The full line was drawn as the least-squares best fit of the lower-temperature data. The experimental values deviate from Argon's theory as temperature approaches the T_g of the resin, the experimental points tending to become parallel to the T/G axis. This deviation was also observed by Argon[4] and by Argon and Bessonov[5,6] on thermoplastics, and Young *et al.* on epoxies[8]. These latter authors pointed out that the temperature to which the Argon equation holds is reduced progressively as the crosslink density of the epoxies is increased.

The Argon theory is particularly useful for the description of yield processes in glassy polymers, as it allows molecular parameters to be determined from the values of A and B that are measured experimentally.

Rearranging equations (5) and (6) allows the mean molecular radius a of the polymer chain to be determined:

$$a^3 = \frac{A}{B}\frac{16(1-\nu)k}{3\pi\omega^2}\ln\left(\frac{\dot{\gamma}_0}{\dot{\gamma}}\right) \tag{9}$$

Using a value of $\omega = 2$ and $\dot{\gamma} = 4 \times 10^{-10}\ s^{-1}$ as defined by Argon[4], the value of a was obtained as 4.6 Å. *Table 1* shows the values of A and B together with molecular parameters for ADC together with values determined by other investigators on other glassy polymers for comparison. It can be seen immediately that the values of the parameters for ADC are within the range of those obtained for other glassy polymers.

Another parameter that can be determined for the polymer is the critical value of z, z^*, which is the critical separation at yield of a pair of molecular kinks (wedge disclination) on the polymer molecule. *Figure 5* schematically shows a pair of molecular kinks in a critical configuration. This is given at absolute zero by the equation:

$$\left(\frac{z^*}{a}\right)_{T=0K} = \left(\frac{45}{8(1-\nu)}\right)^{1/6} A^{-1/5} \tag{10}$$

where a is the mean molecular radius of the polymer. The value of z^* is found to be of the order of 9.59 Å for ADC. This value lies between that of the very flexible molecules with a C–C backbone such as poly(methyl methacrylate) and stiffer molecules containing benzene rings in the chain such as poly(ethylene terephthalate) or polycarbonate. The value obtained for a of $a = 4.6$ Å lies

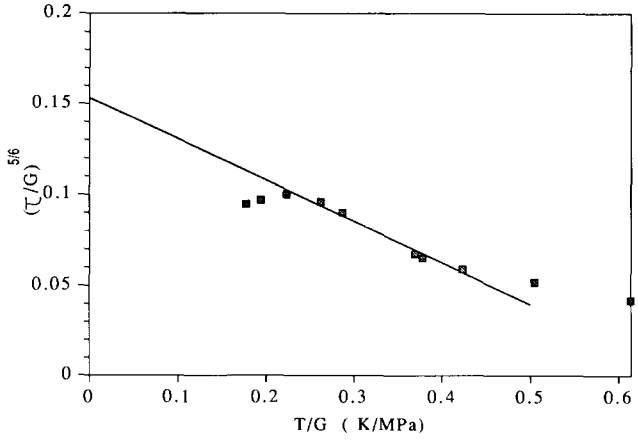


Figure 4 Variation of $(\tau/G)^{5/6}$ with T/G for ADC resin (Argon's theory)

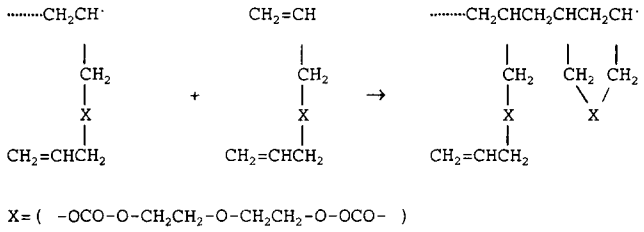
Table 1 Values of the various parameters derived from Argon's and Bowden's theories of plastic deformation in glassy polymers

Polymer[a]	A	B (MPa K^{-1})	a (Å)	z^* (Å)	b (Å)	Ref.
ADC resin	0.153	0.227	4.6	9.59	4.73	This work
	0.176	0.129	5.77	11.6	4.25	2, 6
Polycarbonate	1.171	0.364	4.08	8.22	2.7	2, 6
Poly(methyl methacrylate)	0.125	0.223	4.81	10.3	–	6
Poly(phenylene oxide)						
Epoxy–DGEBA						
9.8 phr TETA	0.158	0.369	3.98	8.25	3.8	8
12.3 phr TETA	0.16	0.289	4.34	8.97	4.2	8
14.7 phr TETA	0.162	0.285	4.38	9.03	4.3	8

[a] DGEBEA, diglycidyl ether of bisphenol A; TETA, triethylene tetramine

with the range for these polymer types. These values are presented in *Table 1*.

Though the molecular structure of ADC monomer has no bulky moieties such as bisphenol A derivative, it is known[12] that cyclization reactions can occur with diallyl monomer in the early stages of polymerization where the crosslinking reaction is negligible. The ring so obtained contains 16 atoms[13] as shown below:



X=(-OCO-O-CH_2CH_2-O-CH_2CH_2-O-OCO-)

The study of the initial stages of the free-radical polymerization of ADC shows that up to about 9.2% conversion the process of polymerization occurs through one double bond resulting in the formation of a linear flexible polymer. The number-average molecular weight is normally 19 000[13]. At later stages crosslinking occurs through the second double bond.

Young *et al.*[8] have claimed that the degree of crosslinking in epoxy resins has very little effect upon the values of a and z^*. This may be because the yield process as conceived by Argon's theory is controlled by the main-chain stiffness.

However, Argon *et al.* have pointed out[6] that the ratio of z^*/l (l is the spacing of natural hinges on the molecular chain) gives the average number of molecular segments between hinges. They showed that, on decreasing the ratio z^*/l through increasing l in polyimides, higher plastic deformation was achieved. From this we may conclude that by introducing crosslinking into a polymer structure the spacings between molecular hinges should be shortened, resulting in less plastic deformation.

Though in ADC homopolymerization the degree of crosslinking cannot be adjusted as such, it is likely that the yielding process in ADC is controlled by the stiffness of the main linear chain segments in the crosslinked network (as those forming in the early stages of polymerization, though crosslinking will substantially reduce the spacings between natural hinges on the molecular network).

The molecular weight between crosslinks in ADC was measured by the creep test method. The creep test spectrum of ADC has been shown in *Figure 6*, which depicts the variation of shear creep modulus (J = shear creep compliance) with time at various temperatures. The shift factors a_T were determined and fitted to the WLF (Williams–Landel–Ferry) equation as shown in *Figure 7*. The creep master curve was created for ADC using the shift factors depicted in *Figure 8*. The value of M_c calculated at $J(\infty)$ was as low as 80. It should be pointed out that the solvent swelling method based on the Flory–Rehner equation[14] was not applicable for ADC,

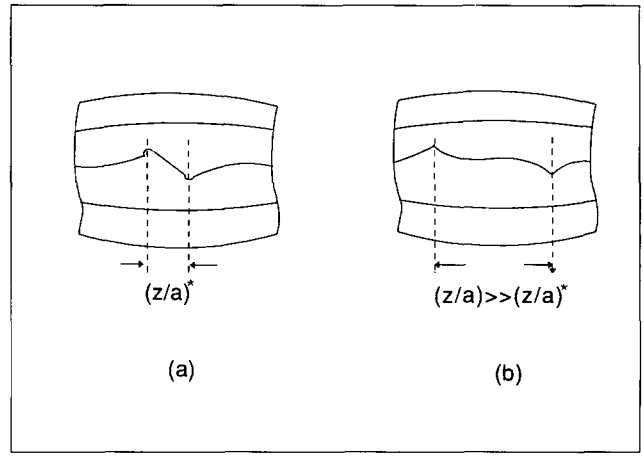


Figure 5 Schematic view of a pair of molecular kinks in a polymer molecule showing: (a) a critical configuration; (b) a configuration for large z/a, suggesting that increasing separation will not produce increasing plastic strain. From reference 4

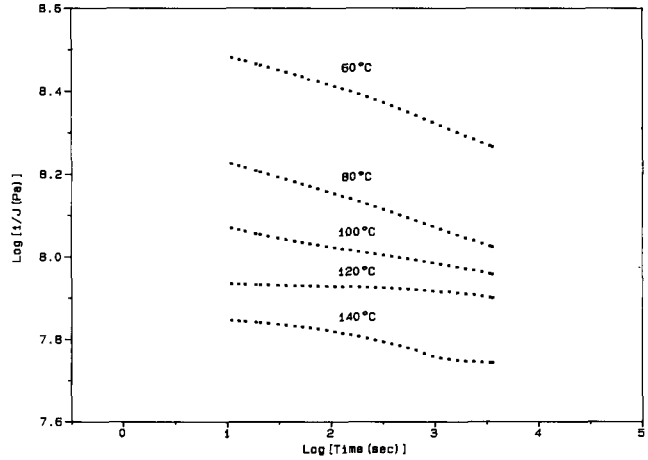


Figure 6 Creep data at a series of temperatures for ADC resin (sample CR39, 2 h at 85°C, 20.89 × 11.56 × 3.36 mm^3)

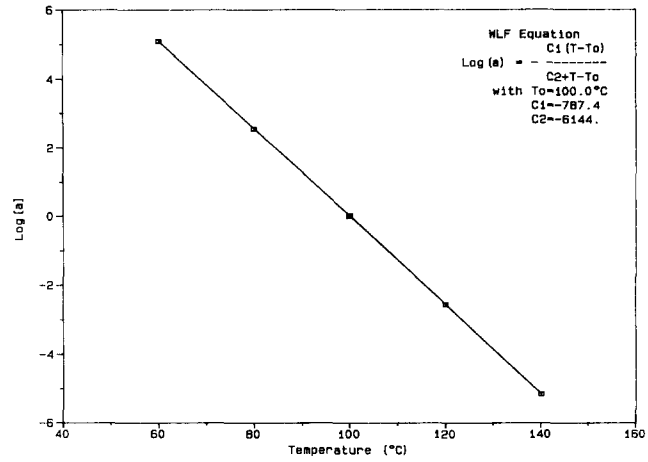


Figure 7 Experimental shift factors a_T and WLF curve for ADC resin (same sample as in *Figure 6*)

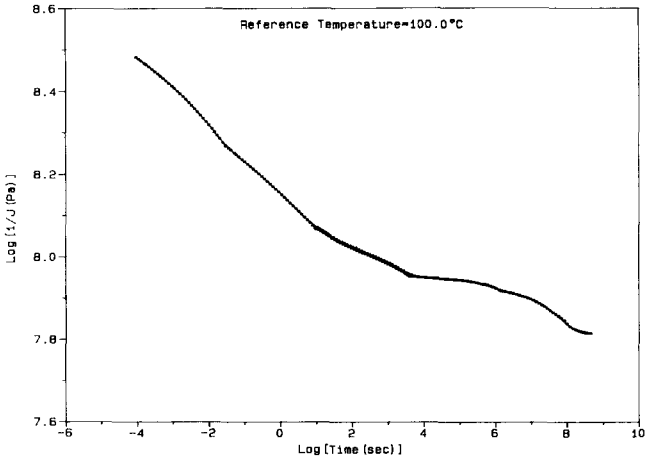


Figure 8 Creep master curve for ADC resin (same sample as in *Figure 6*)

as the amount of swelling in organic solvents is practically zero at any length of time.

Bowden's theory

An alternative model to predict the yield behaviour of glassy polymers was developed independently by Bowden and coworkers[1-3] at about the same time as Argon's theory was developed. This theory suggested that the critical step in the yield process was nucleation of small disc-shaped sheared regions in the polymer by thermal fluctuations under stress. The sheared region of this type is closely analogous to a dislocation loop in a crystal. The elastic strain energy of the sheared region will be close to that of a dislocation loop with Burgers vector equal to the magnitude of the sheared displacement and radius equal to the radius of the sheared region. It is stressed that the dislocation concept is only an analogy and it is not suggested that dislocations are present in glassy polymers. This analogy was introduced because solutions for the energies and stresses in dislocation loops are readily available. In an amorphous polymer the magnitude of the shear displacement (Burgers vector) will be closely related to the distance between the adjacent equilibrium positions of the molecular segments involved in the shear. It cannot be less than this distance or the sheared region would not be stable. It will not be more as the opposing stresses increase rapidly with the magnitude of the shear.

Figure 9 shows an attempt to illustrate some of the displacements that might be involved on a molecular scale in forming such a sheared region. Under an applied shear stress, the energy of a dislocation loop with Burgers vector b, radius R, in a solid with shear modulus G is given by the relation:

$$U=(2\pi R)(Gb^2/4\pi)\ln(2R/r_0)-\pi R^2\tau b \qquad (11)$$

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

$$U_c=(Gb^2R_c/4)[\ln(2R_c/r_0)-1] \qquad (12)$$

at

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

The core radius r_0 can be eliminated by assuming that at absolute zero τ reaches a critical value of $G/\sqrt{3}\pi$ and this leads to a value of r_0 of $b\sqrt{3}/e\simeq b$. Bowden assumed that yielding will occur when U_c reaches an energy of $50kT$ (k is Boltzmann's constant and T is the absolute temperature), which should be available from thermal fluctuations. By using this value of U_c, Bowden's equations can be solved with suitably chosen values of b and experimental values of G to predict the corresponding values of τ at each test temperature. The values of G determined from the modulus data using equation (7) have been used to predict τ values in the temperature range -60 to $+80$°C. These data are represented as a series of lines in *Figure 10*. The measured values of τ are also given in *Figure 10* and appropriate values of b have been chosen to fit the theoretical curve to the experimental points. It is indicated that the experimental points lie between $b=4.2$ and $b=5.3$ Å, and it can be reasonably assumed that the average b value of 4.73 would be most appropriate. The theory appears to hold to near T_g, in contrast to Argon's theory, which does not apply near T_g. *Table 1* compares the value of b determined for ADC with those found for other polymers[1-3]. According to the model, the magnitude of b is related to

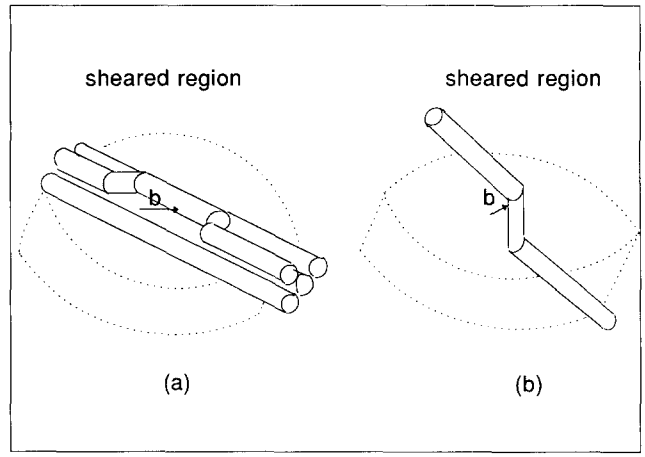


Figure 9 Schematic illustration of the disc-sheared region, with Burgers vector b, in an amorphous polymer. The molecular shear displacement represented by the Burgers vector is related to a number of parameters including (a) the width of the molecular chain and (b) the displacement needed to kink a single chain; also to the spacing of any side groups and the length of links making up the chain. From reference 2

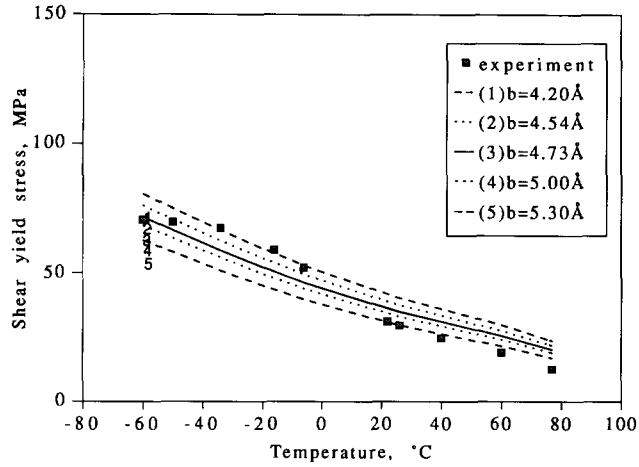


Figure 10 Variation of shear yield stress τ with temperature for ADC resin (Bowden's theory[2]). Plot shows the comparison with theory for various values of Burger's vector b

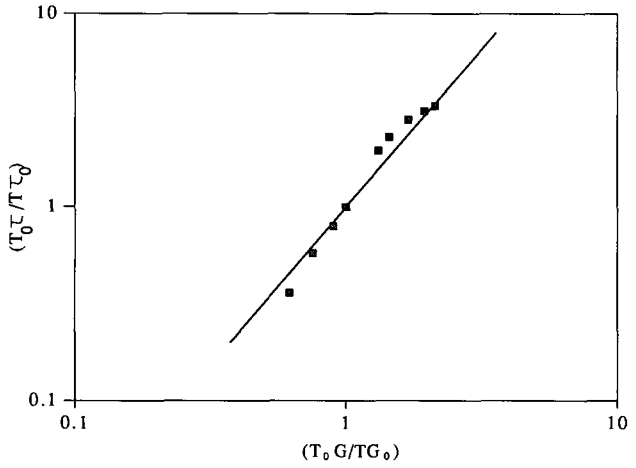


Figure 11 Plot of the relationship between G and τ according to the theory of Kitagawa[15] for ADC resin

the geometry and dimensions of the molecules making up the polymer. Therefore, polymers with large side groups or large repeat units such as polycarbonate have larger Burgers vectors than polymers with smaller side groups or smaller repeat units[2]. It can be seen that, as with the parameters derived from Argon's theory, the value of b for ADC is greater than those for polystyrene and poly(methyl methacrylate) but within the range of those obtained for polycarbonate and epoxies. The results of Young *et al.* for epoxy resins in *Table 1* also indicate that Burgers vector b increases with increasing crosslink density[8]. This may suggest that crosslinking in ADC results in a relatively larger value of b.

Bowden's theory has been generalized by Kitagawa[15], showing that the relationship between G and τ can be represented by a power-law relation of the form:

$$\left(\frac{T_0}{T}\right)\left(\frac{\tau}{\tau_0}\right)=\left(\frac{T_0}{T}\frac{G}{G_0}\right)^n \qquad (13)$$

where τ_0 and G_0 are the values of shear yield stress and shear modulus at some reference temperature T_0 (conveniently taken as room temperature) and n is a temperature-dependent exponent. It was shown that this relationship holds for most polymers. It was found that the value of n is 1.63 for all amorphous polymers and about 0.8–0.9 for semicrystalline polymers. Young *et al.*[8] have also found similar values of $n=1.63$ for epoxies of different crosslink density. *Figure 11* is a log–log plot according to Kitagawa's equation for the values of τ and μ obtained for ADC in 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 further suggests that the yield behaviour of ADC is identical to that found for other glassy polymers and that the presence of crosslinks does not significantly influence the yielding mechanism of the polymer.

CONCLUSIONS

Plastic deformation in ADC has been studied. The experimental results were interpreted by Argon's and Bowden's theories. The molecular parameters determined were related to the molecular structure of the resin. It has been shown that the molecular parameters of ADC derived through these theories, such as the mean molecular radius and the shear displacement of polymer chains, remain within the range of those for glassy thermoplastic polymers. This study suggests that the plastic deformation of ADC, which is a thermoset resin, is identical to that of amorphous glassy thermoplastics, though it is more local due to crosslinking through the second double bond in later stages of polymerization, which shortens the spacing between molecular hinges in the polymer structure. It is expected that, by creating longer segments between crosslinks of the tight cross-linking network of ADC, one can encourage more extensive plastic deformation, which is the subject of ongoing study by the authors.

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