JOURNAL OF MATERIALS SCIENCE 10 (1975) 1582-1590

The effect of thermal pretreatment on the mechanical properties of polycarbonate

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The effect of annealing on the mechanical and thermal properties of polycarbonate resin has been investigated. The previously observed increases in yield strength and decreases in impact strength have been confirmed and it has been shown further that annealed polymer shows a larger strain softening effect after yield than untreated material. This is reflected in an increased negative slope in the stress–strain curve. After yielding the endothermic D.S.C. peak due to annealing is largely eliminated. The extra mechanical energy required to deform the annealed polymer is similar in magnitude to the thermal energy associated with the D.S.C. peak. The reduction in impact strength during annealing is ascribed to greater plastic instability and to the consequent reduction in volume of the zone of plastic yielding in the impact test. This conclusion is confirmed by the examination of annealed and untreated impact test pieces in polarized light.

1. Introduction

Recently, there has been increasing interest in the effect of different types of thermal treatment on the properties of amorphous polymers. For example, it has been shown that the annealing of such polymers just below their glass transition temperatures (T_g) has a quite significant effect on the properties subsequently measured at much lower temperatures. Different observations have been made with a number of amorphous plastics but notable effects have been observed in the case of polycarbonate resin poly(2, 2-propane *bis* (4-phenyl carbonate)) where after long periods of annealing the development of a nodular structure can be observed in the electron microscope [1]. Annealing also brings about a small increase in density together with an endothermic peak at T_g as measured on a differential scanning calorimeter [2-4]. At the same time Golden *et al.* [5] showed there is an increase in the engineering yield stress as normally measured on a stress-strain curve, together with a decline in tensile impact strength. More recently, it has been shown by Allen *et al.* that annealing polycarbonate resin for 3 h at 120°C leads to a drastic fall in the notched Charpy impact strength [6] and that this is *not* accompanied by any substantial changes in the low temperature relaxation peak. Exactly similar results were reported by Wyzgoski and Yeh [7]. The object of this paper is to provide further evidence of the effects of annealing on the properties of polycarbonate resin and to suggest reasons for the changes in impact strength.

For this purpose we carried out a variety of physical measurements, using samples of polycarbonate in several forms, including film, sheet and moulded materials. We also studied a pure polycarbonate resin synthesized in our own laboratory so that we could be sure of its exact composition. However, most of the differences observed between the different grades of polymer were relatively minor in the context of the present research and all the annealed materials showed an endothermic peak at T_g as described by Ali and Sheldon [2, 3]. Differences in peak height, probably due to molecular weight differences, will be discussed elsewhere [8].

2. Experimental methods

2.1. Materials used

Measurements were carried out on several different types of polycarbonate resin including one sample synthesized ourselves. This indicates the limits of variation due to unknown factors in the composition of many commercial products. The four materials used are given below:

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(A) *Compression-moulded sheets*

These were prepared from Bayer polycarbonate grade 5705 having a limiting viscosity number $[\eta]$ of 115 (l Kg^{-1}) and a viscosity average molecular weight $\bar{M}_V$ of 78 000 [9]. The polymer was dried under vacuum at 120°C for 5 h and compression-moulded at 280°C.

(B) *Cast films of bisphenol-A polycarbonate*

Polymer was synthesized by solution polycondensation [10] and had an $\bar{M}_V$ of 80 000 ($[\eta] = 117$). The 20% solution was cast from methylene chloride and evaporated for 12 h at room temperature followed by vacuum treatment for 5 h at 35°C and 10 h at 80°C. This polymer was not sufficiently stable for compression moulding.

(C) *Commercial polycarbonate film*

Bayer Makrofol E (0.7 mm thick) was used. It had a limiting viscosity number of 38.5 and an $\bar{M}_V$ of 20 800.

(D) *Commercial polycarbonate sheet*

Impact tests were carried out on 3 mm Makrolon smooth polycarbonate sheet. It had an $\bar{M}_V$ of 38 000 ($[\eta] = 62$).

2.2. Differential scanning calorimetry

Measurements were carried out with a Perkin-Elmer D.S.C.2 at a heating rate of 10°C min^{-1}. None of the samples used in this work showed a crystalline peak in the D.S.C. curve between 220 and 260°C.

2.3. Tensile tests

An Instron model TTM-BM was used at 23°C and 50% relative humidity. The test-piece was BS 2782 (1970) 301K and the cross-head speed 5 mm min^{-1}.

2.4. Impact tests

The polycarbonate sheet (D) was cut into lengths 3 mm × 6.35 mm × 45 mm and notched to a depth of 2.5 mm. Charpy impact tests were carried out on a Hounsfield Impact Tester according to the manufacturers' directions [11]. In the main series of experiments showing the effect of annealing time and temperature all the test-pieces were initially randomized and eight to fifteen samples used for each condition. Separate samples were prepared under the same conditions for the staircase experiments.

2.5. Thermal fracture

Short dumb-bell-shaped constrictions were cut into long strips of polycarbonate film (C) as previously described [12]. Some 20 to 25 specimens were then extended in the Instron at the specified cross-head speed and the proportion which showed stable necking recorded.

The technique shows the effect of stored elastic energy on deformation immediately after yield resulting in a change over from stable drawing to a type of brittle fracture. (See below.)

3. Experimental results

3.1. Tensile tests

Conventional stress–strain curves are shown in Fig. 1a and b for commercial polycarbonate (A) and synthetic polycarbonate (B), both as prepared and after annealing at 120°C for 48 h. It will be seen that in each case the yield stress increases during annealing (again as previously reported [5]). From the two sets of curves it will also be seen that the increase in yield stress is greater for the synthetic polymer (B) than for the commercial grade (A) a difference which corresponds with differences in D.S.C. peak height. Indeed with these two polymers it appears that the value of the D.S.C. peak height is closely related to the increase in yield stress, so that the results for the two polymers (which

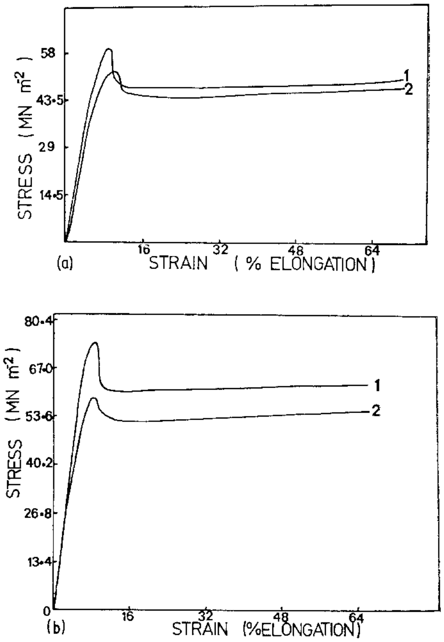

Figure 1 Conventional stress–strain curves for annealed and untreated polycarbonates. (a) Commercial polycarbonate A; (b) synthetic polycarbonate B. Curve (1) annealed 120°C, 48 h. Curve (2) not treated. Strain-rate 2.8 × 10^{-8} sec^{-1}.

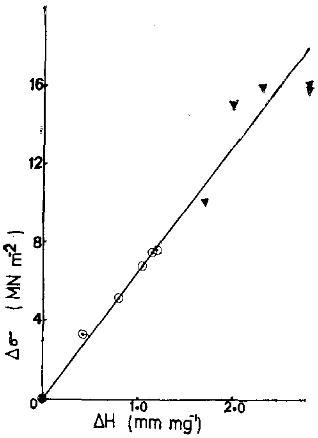

Figure 2 The relation between D.S.C. peak height and the increase in yield strength during annealing. Results for commercial polycarbonate (A) and synthetic polycarbonate (B) having similar molecular weights. Annealing temperature 120°C. Peak height measured as in [3].

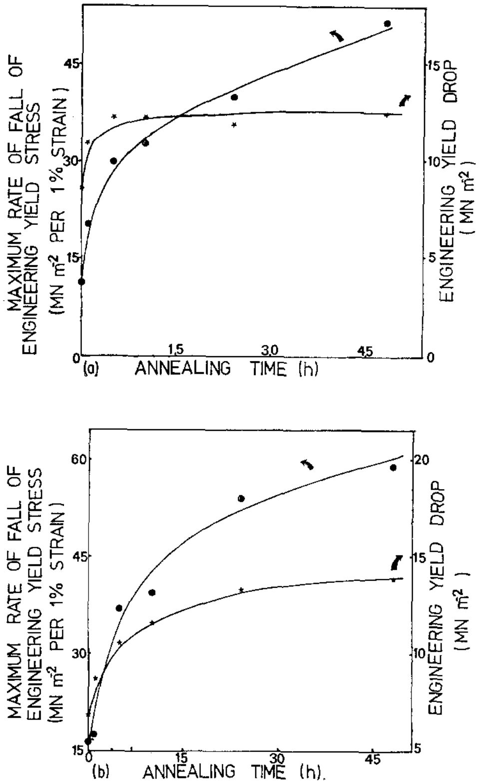

Figure 3 The effect of annealing on the "yield drop" and on the maximum negative slope of the engineering stress–strain curve after yield. (a) Commercial polycarbonate A; (b) synthetic polycarbonate B. Strain-rate = 2.8 × 10^{-3} sec^{-1}.

have very similar values of $\bar{M}_v$), may be fitted to a single line (Fig. 2). Other experiments have shown, however, that the same line would not include other samples of polycarbonate such as, for example, Makrofol E film (C), having a very different molecular weight.

In all cases, however, the increase in yield stress is accompanied by a change in the shape of the stress–strain curve. After annealing the "yield-drop" [13] increases, i.e. the drawing stress does not increase as much as the yield stress.

These differences in strain softening and in the engineering yield stress may be expected to have a significant effect on the post-yield behaviour of the polymer. For example Bowden and Raha [14] showed that the annealing of polymethylmethacrylate leads to an increase in the negative slope of the stress–strain curve after yield. Curves showing our tensile measurements in the form suggested by Bowden and Raha are shown in Fig. 3a and b.

These differences in the negative slope of the stress–strain curve could, in principle, be associated either with changes in strain softening (i.e. changes in true stress) or in the draw ratio during necking. To separate these effects we made two experiments. In the first we photographed a series of bench marks before and after passing through the neck so as to measure the draw ratio in a tensile test. Using annealed polycarbonate film C (see below) we found a draw ratio of 1.75 (average of three experiments 1.68 to 1.80) compared with 1.76 (1.75 to 1.79) for the untreated material. It was concluded that changes in engineering yield drop were not due to geometrical effects. The second experiment is described below.

3.2. Plane-strain compression

A method of carrying out plane-strain compression tests on plastics has been described by Williams [15]. His procedure enables measurements of yield stress to be made without the geometrical complications of the tensile test, and so to determine more precisely the effect of annealing on the strain softening of a polycarbonate. As the test requires a comparatively thick sample of material we used the 3 mm commercial sheet (D) and the results obtained are presented in Fig. 4. They show that the yield stress increases after annealing in the same way as in the tensile test. Annealing also

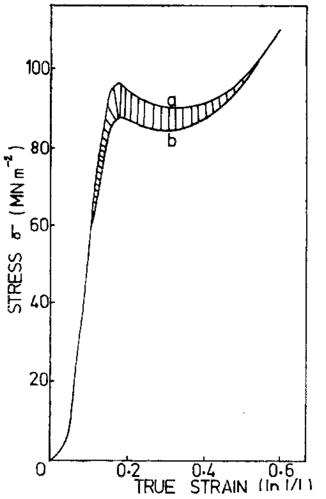

Figure 4 Plane-strain compression experiments with polycarbonate sheet. (a) Annealed 130°C for 16 h; (b) untreated.

increases the yield drop from 3.6 MN m^{-2} (i.e 4.1%) for the untreated polymer to 5.5. MN m^{-2} (i.e. 5.7%) for the annealed polymer (average of five experiments in each case).

An interesting feature of these curves is observed at high strains where the curves for the annealed and the original material become identical. At this point it is, therefore, relevant to examine the strained annealed polymer by D.S.C. to see whether the thermal peak has been eliminated by the mechanical treatment. The results for strained and unstrained annealed polymer are given in Fig. 5. Clearly the D.S.C. peak has been removed by the mechanical treatment. Also the shaded portion of Fig. 5 represents the energy difference between the annealed polymer in its original form and after deformation to the point where the mechanical curves meet and may be compared with the differences in mechanical work for the annealed and untreated material, i.e. with the shaded portion of Fig. 4. The results obtained were each based on the average of five separate experiments.

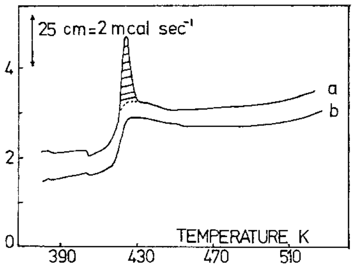

Figure 5 Differential scanning calorimeter curves for annealed polycarbonate sheet. (a) Annealed 16 h, 130°C before testing; (b) after straining beyond the intersection point of the two curves in Fig. 4. The continuous curve has been displaced to separate it from curve (a).

These differences are summarized in Table I for the annealing conditions used in Figs. 4 and 5.

Clearly all these energy differences agree within experimental error.

TABLE I

Type of comparison	Average energy difference (cal g^{-1})	Range of results (cal g^{-1})
Mechanical energy difference in plane strain compression (Shaded area Fig. 4)	0.54	0.47–0.59
D.S.C. difference between deformed and undeformed annealed polymer	0.53	0.47–0.59
D.S.C. difference between annealed and untreated polymer devised as in Fig. 5	0.54	0.49–0.60

3.3. The effect on impact strength

Impact measurements showed that at all temperatures of annealing there is a reduction in impact strength with annealing time (Fig. 6). At

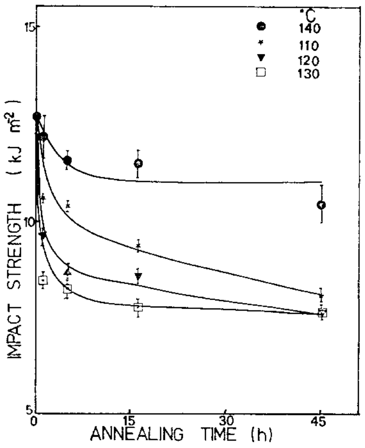

Figure 6 The Charpy impact strength of polycarbonate sheet (D) annealed at different temperatures.

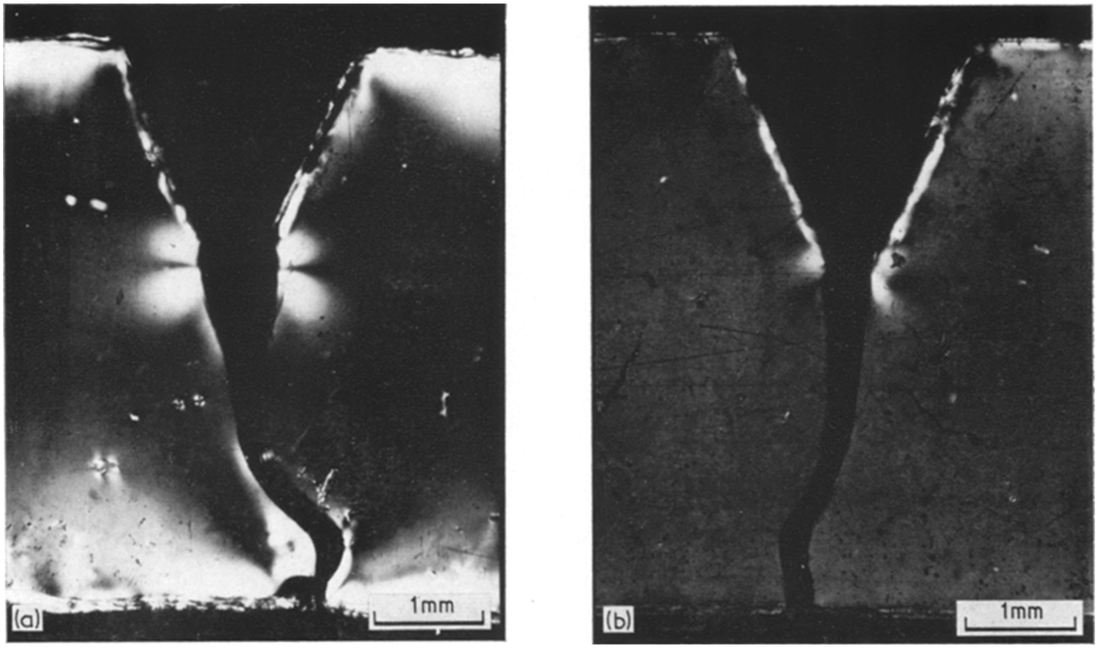

Figure 7 Magnified photographs taken in polarised light of broken Izod test-pieces. (a) Untreated polycarbonate; (b) annealed 130°C, 16 h.

140°C, however, the magnitude of the effect is reduced probably due to a rather close proximity to T_g (146°C as determined by D.S.C. at 10°C min^{-1}). These results confirm previous work [5, 6].

3.4. Plastic deformation during impact

A clear indication of the extent of permanent plastic deformation during impact may be obtained from broken test-pieces. A magnified photograph of these, taken in polarized light is shown in Fig. 7. Here a reduction in the amount of plastic strain at the notch and at the point of impact is clearly observed in the annealed test-piece, as compared with the original material.*

A series of similar annealed and untreated test-pieces were then prepared and broken in a series of incremental impact tests of the staircase type. In this way an average height of fall for the pendulum (*D* [11]) at fracture of 19 cm was measured for the annealed polymer and 26.2 cm for the original material. These tests also provided a series of test-pieces which had not quite broken, having received a blow 5% below that which had broken the previous sample. These test-pieces showed striking differences when viewed in polarized light as shown in Fig. 8. Quite clearly the volume of strained material is much less for the annealed polymer than for the untreated material and this applies to both types of test.

3.5. Thermal fracture

In an earlier paper [12] it was shown that poly(vinylchloride) sheet was susceptible to a type of brittleness not previously described. The phenomenon depends on the occurrence of a high yield stress and a significant engineering yield drop in tension. Therefore, in view of the increased yield drop associated with annealing, experiments were carried out on the thermal fracture of annealed specimens of polycarbonate film (C).

The film sample C was separately shown to behave on annealing (16 hrs. at 130°C) in a similar way to samples A and B with an increase in engineering yield stress (σ_y) from 57.0 to 66.0 MN m^{-2} and an increased yield drop from 7.2

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*These experiments have recently been repeated on a sample of polycarbonate sheet, supplied by Dr R. P. Kambour of G.E.C. Research and Development Centre, Schenectady N.Y. 12301, USA, which have received no previous heat-treatment. Two groups of test-pieces were taken at right angles to each other and half of each group annealed. The results obtained were essentially the same as those described above.

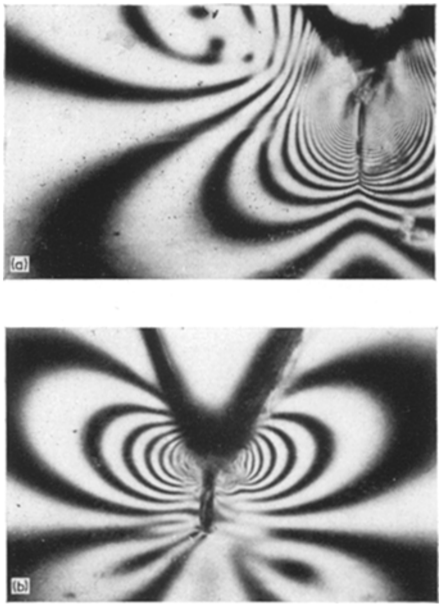

Figure 8 Photomicrographs of Izod test-pieces after impact just below the breaking energy. (a) Untreated; (b) annealed 130°C, 16 h. Taken in circularly polarized light with monochromatic filter. Polycarbonate sheet D. It is argued in the text that the differences in the size of the zones of plastically deformed material shown in Figs. 7 and 8 are responsible for the measured differences in impact strength.

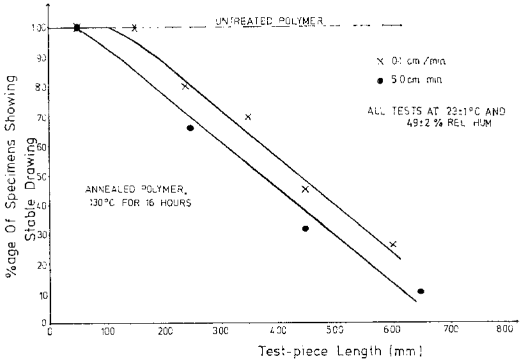

Figure 9 The thermal fracture of polycarbonate. The effect of test-piece length on the percent of samples showing stable drawing for untreated and annealed polycarbonate film C [12]. Cross-head speeds as indicated on the figure. Samples not showing stable drawing show thermally induced "brittle" fracture.

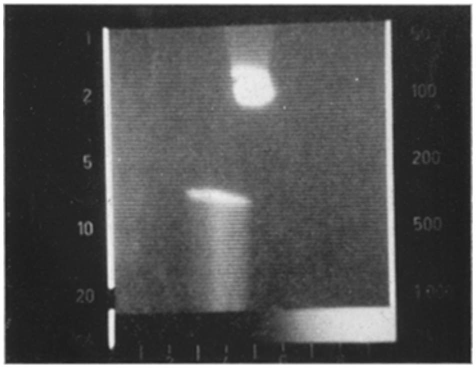

Figure 10 Thermovision picture of polycarbonate test-piece broken in thermal fracture experiment. The white parts of the test-piece have been heated up during deformation and fracture. The bottom part of the test-piece is apparently widened by vibration after fracture.

to 13.2 MN m^{-2} (strain-rate $\sim$ 1 h^{-1}). At the same time the 1% secant modulus fell from 2.20 ± 0.02 to 2.00 ± 0.02 GN m^{-2}. This last result, which was obtained for an average of 17 and 20 measurements respectively on a total of three separately annealed films, was unexpected [7]. These results show that the stored elastic energy at yield ($\frac{1}{2}\sigma_Y^2/E$) increases substantially from 7.4 $\times$ 10^5 to 10.9 $\times$ 10^5 J m^{-3} after the annealing process. This together with the larger yield drop may be expected to promote thermal fracture.

In a thermal fracture experiment a dumb-bell constriction is cut in a long strip of plastic whose total length can be varied. When the strip is extended in a tensile testing machine, either stable cold-drawing may be observed, or what appears as a type of brittle fracture. Results showing the effect of increasing the sample length (and, therefore, the amount of available elastic energy) in reducing the fraction of test-pieces showing stable cold-drawing, are shown in Fig. 9. Since failure occurs essentially by adiabatic heating in the neck, a thermovision photograph taken immediately after "brittle" fracture may be used to show the "hot" ends of the broken test-piece (Fig. 10).

The temperature rise in the neck during thermal fracture can be calculated in two ways [12], one of which may conveniently be applied in the present case. According to this method the temperature increase, ΔT, is then

$$\Delta T = (T_s - 23) \{1 - \exp[\sigma_Y \epsilon_D / CJ\rho(T_s - 23)]\}$$

where T_s is the softening temperature ($\sigma_Y = 0$) and T_g = 160°C, σ_Y the yield stress = 66 MN m^{-2} and ϵ_D the draw strain = 0.75. C, the specific heat = 0.30 cal g^{-1} ([10], p. 147) and the density ρ = 1.20 g cm^{-3}. This equation may be expected to give low results, because the effect of a high strain-rate in raising σ_Y and T_S is not included. The calculated temperature rise is 29°C (24°C if $\sigma_D = 53$ MN m^{-2} is used instead of σ_Y), compared with a surface temperature rise of 41°C estimated by thermovision. However, this measurement may be also lowered by heat losses and test-piece transparency. Agreement between the two results may, nevertheless, be regarded as reasonable.

4. Discussion

4.1. The effect of annealing on tensile properties

The experimental work in this and previous papers has shown that the annealing of several different grades of polycarbonate leads to a similar series of changes, which include the development of D.S.C. peaks and an increase in yield strength, observable both in tension and in plane-strain. It has also been shown that in the tensile test the changes during annealing are not geometrical in origin so that actual strain softening of the annealed polymer must occur.

Such strain softening could logically be associated with a breakdown of the structure introduced by the annealing process as suggested by Wyzgoski and Yeh [7]. This fits in very well with our own observation that the D.S.C. peak developed during the annealing process is eliminated after yielding. The argument is further supported by the similarity in magnitude of the increase in mechanical work caused by annealing and the thermal energy associated with the D.S.C. peak (Figs. 4 and 5).

Generally speaking, it seems unlikely that these quantities are exactly the same, since, in the mechanical test, the material is deformed in bulk so changing the test-piece in other ways besides breaking down the microstructure. However, the work of Stolting and Muller [16] shows that the entropic factor associated with the ordering of polymer chains after a deformation process will not show up as a thermal effect in a free relaxation experiment (as when the polymer is heated above T_g or dissolved in a suitable solvent). Thus only internal energy changes, due to such factors as an alteration in the proportion of trans or gauche configurations, are measured when deformed and undeformed polymer are studied, in the D.S.C., and these may be small.

The further observation that the strain-hardening process is not much affected by annealing accords with the concept that this process is controlled by overall chain configuration, and associated entropy changes, similar to those associated with rubber elasticity [17]. This suggests that annealing leads only to the formation of localized structures and that the larger scale aspects of the configuration of the polymer chain in the glassy state remain unaffected, i.e. they are much the same as in theta solvent [18-20] as originally proposed by Flory [21].

4.2. The relation between annealing effects, plastic instability and impact strength

We have shown that annealing increases the amount of strain softening which occurs during plastic deformation. This is a phenomenon closely associated with plastic instability as understood by engineers [22].

Briefly, plastic instability is associated with a condition in which, once plastic deformation is initiated at a given point in a material it tends to continue at that point and not to spread uniformly throughout the material. The most well-known example of this effect is that of necking in tension, where the initial yield drop leads to the localization of plastic strain at a single point in the test piece. Where orientation (on strain) hardening sets in the neck becomes stable and more material can be drawn into the yielded zone so that the neck spreads outwards through the whole specimen. However, if necking takes place quickly, and if orientation hardening is not well developed (as in thermal fracture) then the drawing stress will drop along an adiabatic curve and fracture becomes inevitable before yielding can extend through the polymer as a whole. In this case the volume of plastically strained material at fracture will be very small. Both these phenomena have previously been described in principle by Vincent [23, 24].

Now in the case of an impact test it is the energy required to break the test-piece which is measured and this energy is the integrated sum of the quantity (stress) × (strain) × (volume of of material) taken over the whole test-piece for the duration of the test. In the case of small Hookean elastic deformations, the strains are generally distributed over the whole test-piece in a manner generally capable of calculation by conventional elasticity theory. With plastic deformations, this is most certainly not the case. On the other hand, the absorption of large amounts of energy by tough homogeneous plastics depends on the occurrence of large plastic deformation. However, as we have seen, in strain softening materials these may be confined to small volumes of material within the test-piece as during thermal fracture or necking. A key factor in determining impact strength is, therefore, the volume of plastically strained material. Any factor which strongly affects this volume will substantially affect impact strength.

Previous work demonstrating the effect of strain softening in limiting the volume of material in which plastic strain takes place is not confined to tensile experiments. For example Bowden and Raha [14, 25] showed that the annealing of polymethylmethacrylate led to the formation of thin shear bands as opposed to more diffuse bands in untreated material. They correlated this difference with the negative slope of the stress–strain curve (as in Fig. 3). Similar results have been reported for very small shear bands by Brady and Yeh [26, 27].

The case of plastic deformation in shear has been mathematically treated by Argon [28] who showed that with increasing time the additional strain occurring in the matrix after shear banding has commenced is proportional to the quantity

$$\frac{1}{\left[\theta - \frac{m}{\tau}\left(\frac{d\tau}{d\gamma}\right)_p\right]}$$

where θ is an adiabatic heating term, τ the shear stress and $(d\tau/d\gamma)_p$ a strain-hardening term which becomes negative in the case of strain softening. $m = (d\ln\dot{\gamma}/d\ln\tau)_T$ is a phenomenological stress exponent term. Argon concludes in line with Bowden that the larger the negative strain-hardening rate the stronger the tendency for banded inhomogeneous deformation to develop. In a similar sense, Haward and co-workers have argued that the formation of crazes is due to the localization of tensile strain due to the combined effect of true and geometrical strain softening in plastics having a high yield stress [29, 30].

Following the above arguments it would be reasonable to expect that the increased strain softening observed in annealed polycarbonate would also lead to the greater localization of plastic strain. This localization effect leads to a reduction in the volume of plastically strained material which occurs near the notch whether by bulk or voided yielding perpendicular to the principal tension, or by angled shear bands, and so to the reduction in energy absorbed both at the notch and in other parts of the specimen. Thus, after annealing the volume of the plastic zone is reduced, as shown in Figs. 7 and 8, and the measured impact strength falls.

The changes in the yielded zones of polycarbonate after annealing may be compared with recent observations on rigid PVC when PVC is quenched it does not strain soften and a test-piece extends uniformly without necking. After annealing or long storage the normal peak in the tensile stress–strain curve returns and necking takes place. In photoelastic studies of the shape of plastic zones using notched samples of quenched and stored PVC, Mills [31] has shown that the width of the plastic zone increases after quenching. This corresponds with the elimination of the "yield drop" and so agrees with our observations on impact test-pieces as shown in Figs. 7 and 8.

Acknowledgements

The authors wish to acknowledge the advice of Dr I. W. Parsons on the preparation of polycarbonate resins. Mr G. Adam and Mr A. Cross wish to thank the Iraqi Ministry of Higher Education and the Dunlop Co Ltd, respectively, for financial support. We are also indebted to Professor J. Llewellyn, Mr J. Moore and Mr. N. J. Mills for assistance in photomicrography.

Note added in proof

Since this paper was submitted we have seen the work of Plati and Williams (*Polym. Eng. and Sci.* **15** (1975) 470) and of N. J. Mills (private communication). These workers demonstrate that under plane strain conditions (sharp notches, thick test pieces) untreated polycarbonates can be relatively brittle. Under these conditions Mills did not observe substantial effects due to annealing. We therefore extended our own impact measurements to include three different available thicknesses of Makrolon polycarbonate sheet. The results are shown below.

Specimen thickness (mm)	Impact strength (kJ m^{-2})	
	As-received	Annealed, 130°C, 48 h
2	72 ± 2	10.4 ± 0.6
3	11.7 ± 0.4	7.6 ± 0.3
6	8.8 ± 0.3	7.1 ± 0.3

Besides showing higher impact strength the two thinner untreated test-pieces showed much greater plastic deformation. We conclude that the arguments presented in this paper apply mainly to plane stress conditions. The effect of annealing (if any) on impact strength with plane strain fracture has not yet been demonstrated. Of course polycarbonate has achieved widespread use as a tough plastic so that it is reasonable to assume that plane stress conditions must relate to a wide range of conditions for conventional use.

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Received 31 December 1974 and accepted 3 March 1975.