JOURNAL OF MATERIALS SCIENCE 8 (1973) 1449–1452

The impact strength of polycarbonate

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Measurements of the Charpy notched impact strength of polydiancarbonate indicate that the polymer can exist in one of two modifications A and B. There is a temperature (below room temperature) above which the A form is unusually tough; the B modification is comparatively brittle at all temperatures. The A form can be converted to the B form by an annealing process which proceeds rapidly above 80°C. We have not been able to determine the precise morphological difference between the A and B forms but most of the data can be explained by making a hypothesis about the yield behaviour of the A form.

1. Introduction

Polydiancarbonate is noted for its unusually high impact strength. The properties of the polymer have been described by Schnell [1] and Peilstocker [2, 3]. LeGrand [4] was the first to note that an annealing process can cause embrittlement in the polymer. In this paper we report a more detailed study of the embrittlement.

2. Experimental

The polymer used in these experiments was GE Lexan 101. After drying for 12 h at 120°C the polymer was injection moulded into 11 cm diameter discs with barrel temperatures in the region of 320 to 330°C with the mould maintained at 90°C. These discs were subsequently cut up into Charpy impact specimens of dimensions 5 cm × 0.15 cm × 0.36 cm. The centrally located notch tip was 0.58 cm from the struck face.

The "as-moulded" specimens are referred to as polycarbonate A. Specimens of polycarbonate A were converted into a brittle form B by annealing for 3 h at 120°C.

In the experiments on wet polycarbonate the samples were notched after wetting. The impact testing was performed on a Hounsfield impact testing machine [5].

Dynamic mechanical measurements were carried out on a torsion pendulum operating near to 1 Hz, and covering a range of about − 150 to + 150°C. The instrument is similar to that described by Nielsen [6]. Radial distribution functions were obtained from X-ray studies of the polymer carried out using a method to be described in another publication [7].

3. Results

An examination of notched impact strength versus temperature was made for both polycarbonates A and B. The samples were held in a temperature chamber close to the impact tester and removed immediately prior to the test. Thus behaviour of "as-moulded" polycarbonate was compared with an "annealed" polycarbonate.

The results of the impact strength measurements are shown in Fig. 1. Polycarbonate A

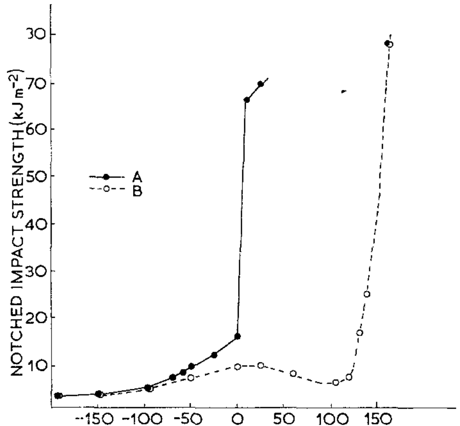

Figure 1 Impact strength versus temperature for polycarbonate.

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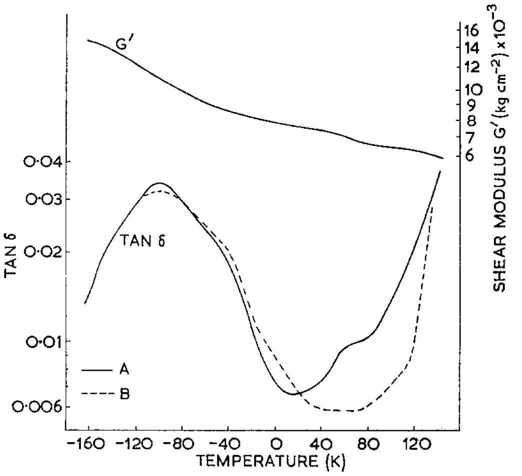

Figure 2 Shear modulus and tan δ.

undergoes a sharp change in its impact strength in the region of 5° C giving rise to a region of high toughness above this temperature. The B material, however, shows a small broad peak in the impact strength around 5° C and remains comparatively brittle until T_g ($\approx$ 150° C) is approached.

In Fig. 2, the results of measurements on the shear modulus and loss curve are shown. There is a small change in the loss curve, just below the α transition. These results agree closely with the observations of Golden *et al* [8] on the Bayer polycarbonate Makrolon S. Very similar impact strength/temperature diagrams are found for wet material containing about 0.4% by weight of water.

Samples of the A polymer broken in the region above the transition point show evidence of cold flow; there is considerable necking of the sample near the break line. In Figs. 3 and 4 the NIS is examined as a function of specimen geometry, the notch radius and sample thickness being varied.

By making up a quantity of samples and holding groups at different temperatures for different times it was established that there is a "critical annealing temperature" in the region of 80° C: by this it is meant that samples may be held at 77° C for at least 3 h without any noticeable effect on their impact strength whilst a period of 15 min at 85° C is sufficient to convert the A form almost entirely to the B form, as judged by the reduction in NIS. The observations which lead to this conclusion are summarized in Table I.

TABLE I

Annealing temperature (°C)	Annealing time (min)	Initial NIS (kJ m⁻¹)	Approx. final NIS
65	120	70	70
	180	70	70
72	60	70	70
	120	70	70
	180	70	70
77	120	70	70
	180	70	70
81	15	70	20
	120	70	20
	180	70	20
90	120	70	20
	180	70	20
105	180	70	10
111	180	70	10
114	180	70	10

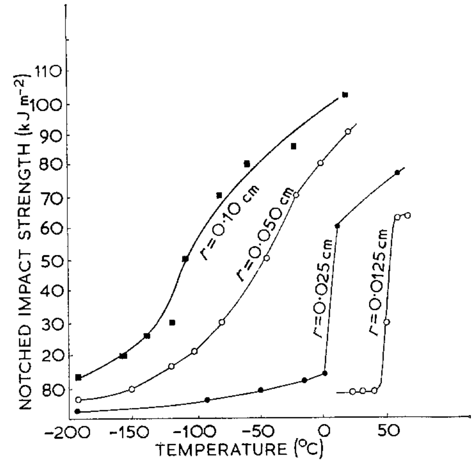

Figure 3 Impact strength versus temperature varying the notch radius.

4. Discussion

It is clear from the results presented in the previous section that the polycarbonate can exist in two different forms A and B. The difference between the forms must lie in some physical, rather than chemical, modification.

It is known [4, 8] that polycarbonate B is ~ 0.2% more dense than polycarbonate A. This densification though small, suggests that some crystallization may be taking place. However, this hypothesis is hardly borne out by other considerations: firstly there is evidence which shows that crystallization is extremely slow below about 175° C [9, 10] certainly not fast enough to produce any appreciable degree of crystallinity;

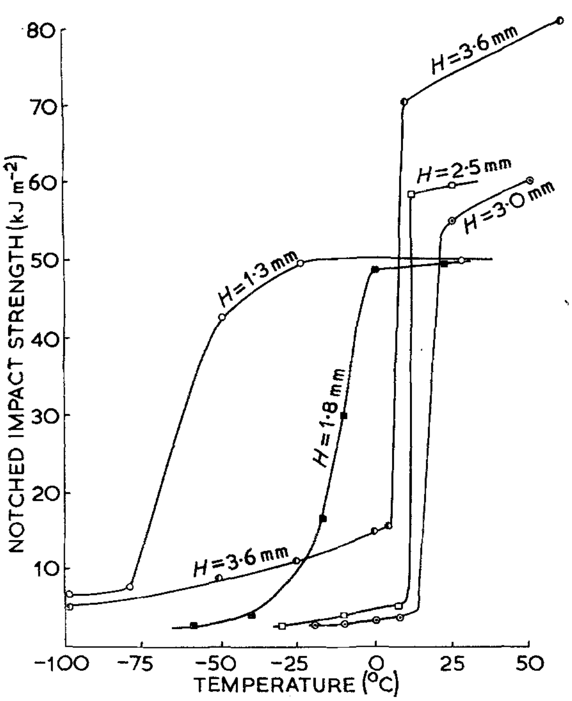

Figure 4 Impact strength versus temperature varying the thickness.

secondly the detailed X-ray analysis by Wignall and Longman [7] fails to reveal any evidence of ordering. The observed difference in toughness is, therefore, very unlikely to be due to the presence of small crystals.

The measurements of Golden *et al* [8] on the mechanical properties of polycarbonate are of interest. They measured, *inter alia*, the tensile yield strength of the polymer as a function of annealing time and annealing temperature. They found that the yield strength was strongly dependent upon the annealing time for temperatures above about 90° C.

Yannas and Lunn [11] observed a relaxation process in drawn polycarbonate film. They used films of polymer drawn to a ratio of 1.8. They observed the orientational characteristics of the film by an infra-red dichroic method. They noted that the dichroic ratio was independent of time at 72° C, but at 83° C the ratio was significantly time dependent and, therefore, deduced that a relaxation process was occurring at this temperature.

Frank *et al* [12] conducted experiments with films of polycarbonate in which the surface was examined with an electron microscope after an ion etching process. They compared the appearance of film quenched from 160° C with quenched film that had been subsequently annealed for 72 h at 110° C. They noted differences in the appearance of these two types of film, and found that subsequent heating and requenching of the annealed films reconstituted the original quenched appearance.

Taking the polycarbonate A through the range 75 to 105° C does not give rise to any sharp change in either the optical absorption or the specific heat [13].

It seems clear then that annealing the polymer above about 80° C causes some internal rearrangement in the material which is reflected in the yielding properties of the polymer. The precise nature of the change has not been identified so far.

In the past it has been suggested that the toughness of a polymer is somehow connected with the presence of low temperature peaks in the low frequency mechanical spectrum. This hypothesis was apparently first advanced by Bobalek and Evans [14], and has been reviewed from time to time. (See for example Heijboer [15].) The idea seems to be strongly contradicted in the case of polycarbonate. Large differences in mechanical behaviour especially with respect to NIS, can occur for samples A and B which only have minor differences in their mechanical loss curves (see Figs. 1 and 2).

5. Mechanical considerations

Whatever the precise nature of the differences in molecular organization between the A and B polycarbonate, the A form is able to yield at rates of the order of 10^2 sec^{-1} and this ability to yield falls with decreasing temperature.

Suppose that for a given strain rate one plots a notional craze stress versus temperature, and a notional yield stress curve against temperature for the A form. Then any cross-over of the two stress lines such as are shown in Fig. 5a will result in behaviour similar to that shown in Fig. 1 If the effect of the annealing process is to shift one or both of the stress lines so that the cross-over point lies above about 150° C as in Fig. 5b, then most of the features of Fig. 1 can be understood.

This model can be extended to cover some of the features of Figs. 3 and 4. If one imagines a hypothetical tensile experiment could be performed at different rates over a small localized region in the bulk of the sample, then if the

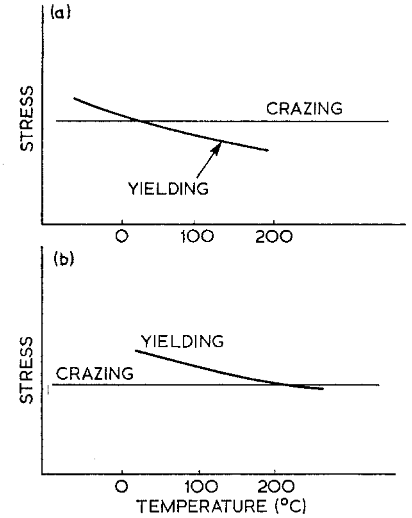

Figure 5 Possible relationship between yield stress and craze stress.

material were initially in the tough regime it is possible that there could be a rate of testing for which the maximum rate of yielding was slower than the applied stress rate. Then brittle failure would be expected to occur. So if strain-to-failure were plotted against rate of testing then behaviour consistent with Fig. 6 would be expected.

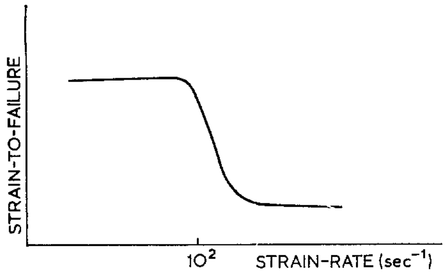

Figure 6 Probable effect of strain-rate on failure.

Consider now the rapid four point bending procedure that constitutes the Charpy impact test. Changing the radius of the notch tip has the effect of changing the gauge length and, therefore, the rate of straining. In the Charpy test then, the rate at which the polymer near the notch tip is tested is roughly proportional to the radius of the notch. Thus as the notch radius is increased the temperature at which the brittle-tough transition should take place should move back to lower temperatures. Furthermore, since the fracture energy must be roughly related to the deformed volume one should find that the larger the notch radius the larger the deformed volume. Hence the behaviour recorded in Figs. 3 and 4 is to be expected.

6. Conclusion

Polydiancarbonate may be prepared in two different forms which have substantially different bulk properties. The A modification may be converted to the B modification by an annealing process which proceeds rapidly above about 80°C. The precise conformational differences between the A and B form are not understood, but the A form seems able to be deformed at rather greater rates than the B form.

Acknowledgements

We are indebted to Imperial Chemical Industries Ltd for permission to publish this paper. We are also grateful to Professor D. Hull for several very helpful discussions.

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Received 19 March and accepted 8 April 1973.