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Physical factors affecting the impact strength of polycarbonate

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The effects due to internal stress, physical ageing and thickness have been separated. It is shown that each of these variables can cause a change from tough to brittle fracture. A 6 mm laminate assembled from 2 mm sheet has the toughness associated with the thinner material.

1. Introduction

When polycarbonate sheet is stored at temperatures up to 80 K below its glass transition temperature (physical ageing) it becomes more brittle. So far, however, there has not been an agreed explanation for this effect and, indeed, three basic hypotheses have been advanced:

(a) Embrittlement is due to the relaxation during ageing of internal stresses which have a toughening effect [1–3].

(b) Embrittlement is uniquely associated with an increase in the yield stress, σ_y. With sharp notched test-pieces the effect should be quantitatively represented by the equation [4]

$$K_c = K_{c_1} + \frac{K_{c_2}^2(K_{c_2} - K_{c_1})}{\pi \sigma_y^2 H} \qquad (1)$$

where K_c is the measured fracture toughness, K_{c_1}, K_{c_2} are the plane strain and plane stress components respectively, where $K_{c_2} > K_{c_1}$ [5, 6] and H is the thickness. The effect of thickness, H, in changing the balance between the plane stress and plane strain condition is of course very general for all types of test-pieces.

(c) Embrittlement is due to an increase in strain softening after yield [7] and/or a change in the ratio of yield stress to crazing stress [8, 9]. It has also been argued by one of the present authors that these two effects are related [10].

Additionally, in connection with [1], Saffell and Windle [11] have reported that changes in internal stresses are not an adequate criterion for defining variations in toughness.

It is extremely difficult to separate proposals (b) and (c) above, as both form part of the simultaneously occurring changes in the material during physical ageing. In both cases the changes in mechanical properties are associated with the development of a separately measurable endothermic annealing peak, which may be used as an independent verification of the presence of physical ageing in the material.

In this paper we seek to separate the effects due to (a) from (b) and (c) and to demonstrate that Equation 1 can be used to predict the effect of ageing with sharp notched materials. We have also found that the thickness effect included in Equation 1 can be exploited to improve the impact properties of laminates.

2. Experimental procedures

Samples were prepared from Makrolon polycarbonate sheet and then stress relieved by heating to 152° C for 4 h. They were then treated in one of the following ways:

(a) The material was quenched in ice water. It may also be noted that similar results were obtained when the sample was water quenched at room temperature.

(b) The material was removed from the oven and allowed to cool to room temperature in still air.

(c) The material was cooled slowly at 5 K min^{-1}.

(d) The material was treated as in (a) then aged for 20 min at 130° C.

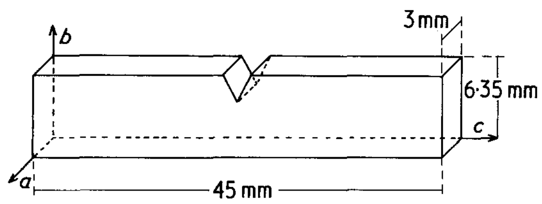

Figure 1 The test-piece used showing axes of viewing in photographs.

Materials treated as in (a) or (b) showed no endothermic peak at the glass transition temperature, T_g, in the differential scanning calorimeter (DSC) trace. Materials from (c) and (d) showed a small peak.

In the experiments with laminates, sheets of untreated Makrolon were stuck together to provide a 3 or 6 mm thick composite. Both the adhesives used were obtained from Bostick Ltd and were selected to have a lower Youngs modulus than the polycarbonate.

2.1. Impact tests

These were carried out with a Monsanto (Hounsfield) impact tester according to manufacturers directions [12]. The samples, as shown in Fig. 1, were notched with the stated notch tip radius to a depth of 1.7 mm.

3. Results and discussion

3.1. Quenched and air-cooled samples

The sheets treated as in (a) and (b) above were both free of DSC peaks and had low yield stresses, i.e. they were both quenched materials from the point of view of physical ageing. However, they differed markedly in the internal stresses present, as shown in Fig. 2. The ice-quenched material showed very marked bi-refringence patterns both through the thickness and in the plane of the material. These were totally absent in the air-cooled specimen. The ice-quenched material, as in (a), was notched both before and after quenching and the results compared with material treated as in

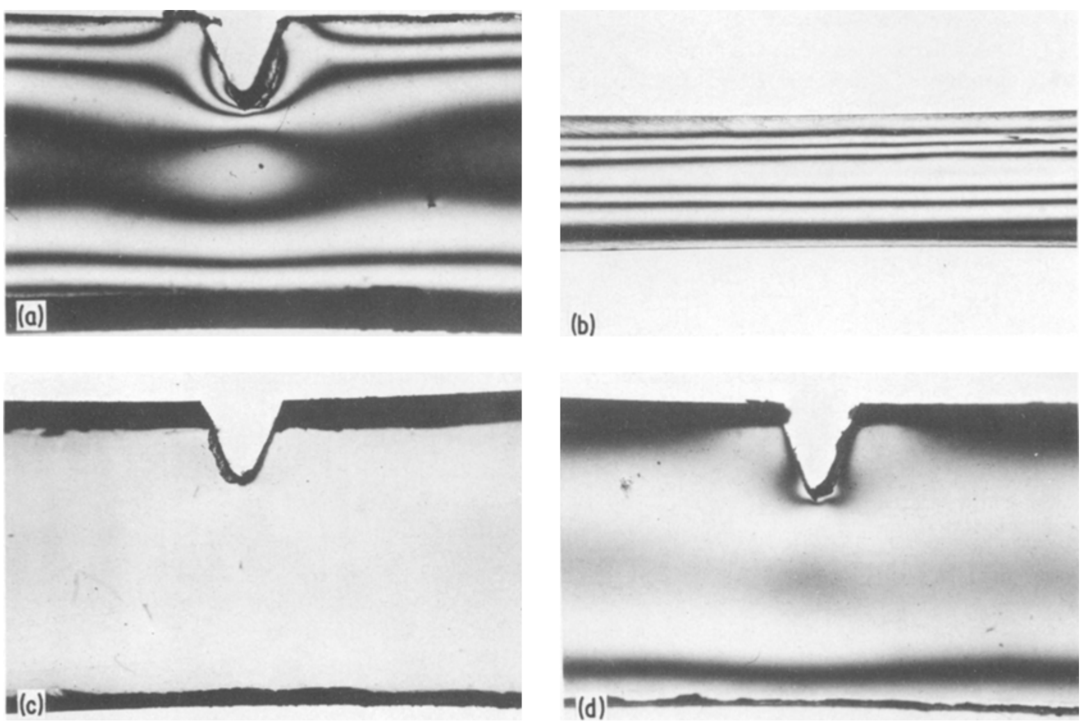

Figure 2 Bi-refringence patterns in polycarbonate sheets subjected to different thermal treatments: (a) Ice-quenched (from 152° C) test-piece viewed along *a*-axis; (b) ice-quenched test-piece viewed along *b*-axis; (c) test-piece cooled in still air (no bi-refringence patterns were seen along the *b*-axis; Method (c) samples gave similar photographs); (d) ice-quenched test-piece aged at 130° C for 20 min (viewed along *a*-axis). Photographs taken using monochromatic (Na) circular polarized light.

TABLE I The effect of internal stress on the impact strength of polycarbonate (see Fig. 1)

Sample	Ageing peak	Yield stress ($MN\ m^{-2}$)	Impact strength ($KJ\ m^{-2}$)	
			Notched before	Notched after
(a) Ice-quenched	None	60.0 ± 0.3	74 ± 5	78 ± 4
(b) Cooled at room temperature	None	61.0 ± 0.7	17 ± 2	17 ± 1
(c) Cooled slowly	Small peak	66.4 ± 0.5	12 ± 1	12 ± 1
(d) Aged 130° C for 20 min	Small peak	66.5 ± 0.6	5 brittle 18 ± 1 9 tough 62 ± 4	

(b) using a 0.25 mm notch radius. Table I shows that the material behaved as predicted in [1–3]. The test-pieces with the internal stresses showed a higher impact strength and, interestingly, it did not matter whether notching was effected before or after quenching. If the ice-water quenched material was then annealed for 20 min at 130° C as in (c), not all the bi-refringence was removed as reported by Sattel and Windle [11] (Fig. 2) and the sample showed transitional behaviour including both tough and brittle fracture as previously observed by Pitman *et al.* [13].

In Fig. 3 it can be seen that all the tough fractures showed a surface topography characteristic of a plastic fracture process [14, 15] as has been previously observed with tough fractures in polycarbonate [16, 17]. This is a process which occurs in a wide variety of polymers.

In these impact tests the material cooled in the room showed a brittle fracture (Table I and Fig. 3b) with initiation from a craze. However, slower cooling caused the measured impact strength to fall further and the yield stress to rise and the site of initiation to occur closer to the notch surface (Figs. 3b, c). There was also a reduction in the area of the shear lips at the edge of the specimen.

3.2. The annealing of stress-free samples

Material treated by method (b) (cooled directly in air), was free of internal stress, had a low yield stress and no DSC endothermic peak. From the

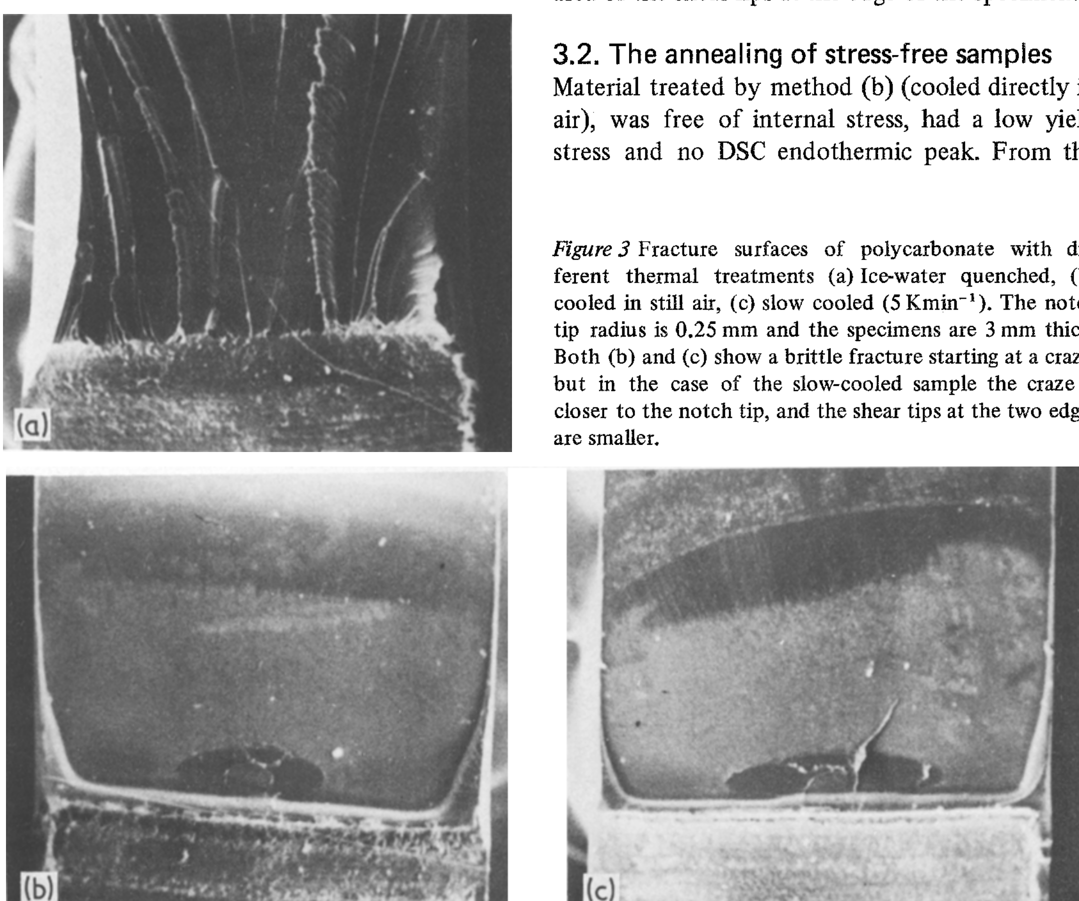

Figure 3 Fracture surfaces of polycarbonate with different thermal treatments (a) Ice-water quenched, (b) cooled in still air, (c) slow cooled (5 $K min^{-1}$). The notch tip radius is 0.25 mm and the specimens are 3 mm thick. Both (b) and (c) show a brittle fracture starting at a craze, but in the case of the slow-cooled sample the craze is closer to the notch tip, and the shear tips at the two edges are smaller.

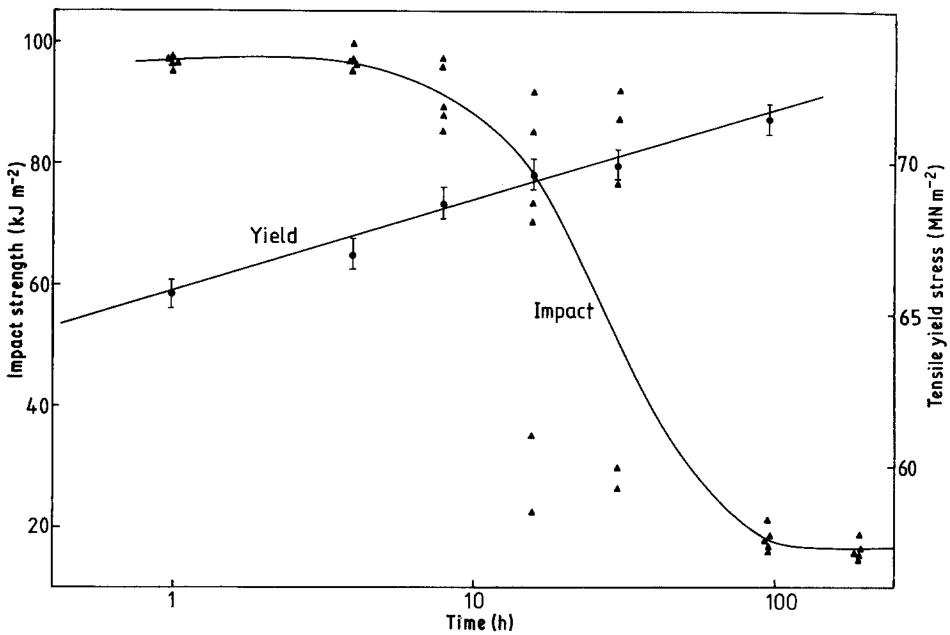

Figure 4 The effect of ageing on test-pieces for samples treated as in (b). A change from ductile to brittle fracture occurs as ageing at 130° C proceeds. The change in basic material properties is shown by the increase in yield stress. As usual this is accompanied by a DSC peak (not shown in the fig.). Fractures with energy above 60 kJ m^{-2} were by plastic fracture (Fig. 3a) and the others by brittle fracture (Fig. 3b, c).

point of view of previous work by Haward [7] and that of other workers it could be described as a quenched material, which should be further embrittled by the normal physical ageing process. For this purpose the notch tip radius was changed to 0.5 mm so as to obtain a tough fracture, and then the samples were annealed at 130° C. This again led to embrittlement accompanied by an increase in yield stress, as shown in Fig. 4. This, together with the previous work, shows that the embrittlement of polycarbonate can occur both by

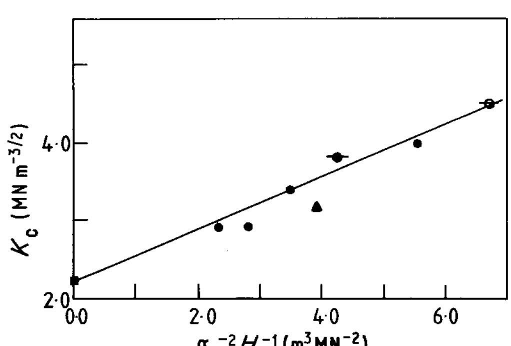

Figure 5 The effect of yield stress, σ_y, and sample thickness, H, on the apparent fracture toughness of polycarbonate (after Newman [6] and Parrin [18]). ⊖ Aged 3 mm sheet, ● quenched 5 mm sheet, various temperatures, -●- aged 5 mm sheet, ▲ quenched 7 mm sheet.

TABLE IIA Charpy impact tests on laminated and solid samples of Makrolon Sheet

Thickness (mm)	Impact strength (KJ m^{-2})
6	9 ± 1
3	17 ± 1

TABLE IIB Laminates prepared with Bostik M502A with activator A

Thickness (mm)	Construction	Impact strength (KJ m^{-2})
6	6 × 1 mm	67 ± 3
6*	3 × 2 mm	67 ± 2
3	2 + 1 mm	72 ± 2

TABLE IIC Laminates prepared with Bostik M890 and activator A

Thickness (mm)	Construction	Impact strength (KJ m^{-2})
6	3 × 2 mm	41 ± 5
6†	3 × 2 mm	56 ± 14

*In most of these experiments all the sheets showed a plastic fracture as in Fig. 6b.

†Heated 72 h at 45° C to complete the cure of the adhesive, then cooled and tested at 23° C as in the other cases. In most cases the centre test-piece showed a brittle fracture as in Fig. 6a.

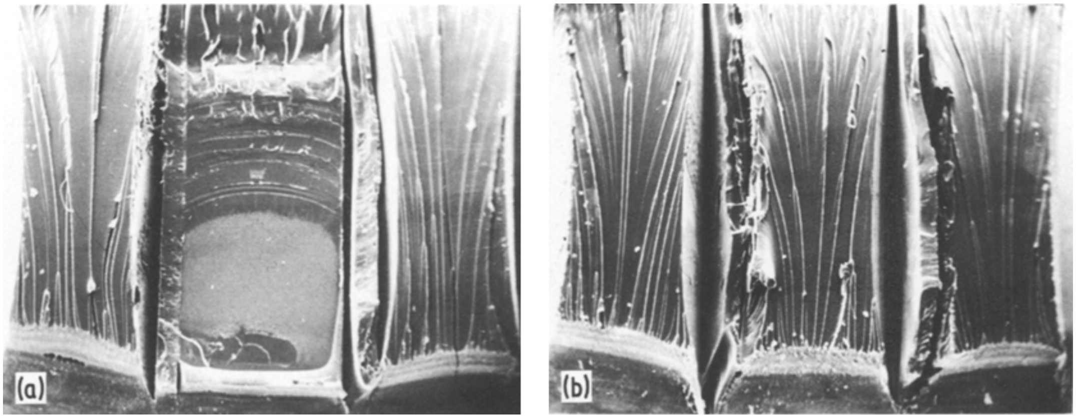

Figure 6 Fracture surfaces for 6 mm laminates. (a) A 3 mm × 2 mm laminate showing each of the outer layers, giving a tough fracture and the inner layer initiating from a craze (Adhesive M890). (b) In many cases the same type of test-piece showed three plastic fractures (adhesive M502A). This is accompanied by failure of the adhesive bond on each of the central sheets.

the relaxation of internal stresses and quite independently through the change of material properties associated with physical ageing.

3.3. The thickness effect

Recently Parvin [18] has reported brittle fracture measurements with aged polycarbonate which may be directly compared with previous work [6] using Equation 1. In Fig. 5 fracture toughness (K_c apparent) is plotted against $(\sigma_y^2 H)^{-1}$. A linear plot is obtained for both aged and quenched materials. This indicates that K_{c_1} does not vary with ageing and that, under brittle conditions, the changes in K_c may be directly related to σ_y. This relationship also underlines the well-established fact that thickness limits the scope for energy absorption in plane stress yielding. Consideration of this point raises the interesting question of what would happen in the case of a laminate made up of thinner sheets joined together by a lower Youngs modulus adhesive. The solid unlaminated sheet, with a 0.25 mm notch, showed a tough fracture at 2 mm thickness but at 6 mm under the same test conditions, fracture was initiated from a craze, as in Figs 3b and c.

All the 6 mm laminates tested as above showed a much higher impact strength than the solid sheet (Table II). With the 3 x 2 mm laminates and adhesive M502A all the separate sheets in the test-piece showed tough fracture see Fig. 6b, but with the other adhesive (M890) there was apparently a greater tendency to the transmission of hydrostatic tension leading to brittle fractures in the centre sheet of the laminate (see Fig. 6a). In the case of the 6 mm x 1 mm, and 2 mm x 1 mm laminates, all the sheets showed plastic fracture.

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