THE MECHANICAL AND BALLISTIC PROPERTIES OF POLYCARBONATE APPOSITE TO RIOT SHIELD APPLICATIONS

M R Edwards and H Waterfall

Department of Materials and Applied Science, Cranfield University, Shrivenham Campus, Swindon SN6 8LA, United Kingdom

Polycarbonate is commonly used as the material of riot shields. Firings of 8.3 g steel ball bearings at velocities of 23-98 ms⁻¹ produced damage in the form of dents.

Subsequent tensile testing showed a small drop in yield strength and ductility for impact velocities greater than 58 ms⁻¹. This drop in yield strength and ductility was more marked for specimens that had been soaked in acetone for 10 minutes after ballistic impact. Soaking in n-heptane produced no similar effect to that seen with acetone. Measurements were taken of the velocities of projectiles likely to be thrown by rioters. These showed that the measured velocities were lower than those velocities that caused macroscopic damage to polycarbonate when hit by a ball bearing. Thus susceptibility to brittle failure is likely to be associated with shields that have been hit by sharp objects and exposed to solvents after impact. Mechanical stressing of polycarbonate at the point of impact by the ball bearing had no effect on the subsequent mechanical properties. This is in contrast to the embrittlement seen in polycarbonate when internal strains are present produced on fast cooling from the melt.

Keywords: polycarbonate, ballistic impact, mechanical properties, solvents, riot shields

Introduction

Polycarbonate is the material of choice when a transparent polymer with good impact resistance is required. An example of its use is in the riot shields used by police forces. At room temperature and quasi-static, typically 10^{-5} - 10^{-1} s⁻¹, strain rates there is necking in tensile specimens and tensile ductilities are 80-140%. Other transparent polymers, such as polymethylmethacrylate, do not show any plastic deformation. Dean et al showed that the number of fragments created in polycarbonate when a detonator containing 0.75 g PETN explosive was fitted into a 7.5 mm diameter hole in a 10 mm diameter rod was 25. This compared to a figure of 157 for polyvinylchloride, another polymer with a glass transition temperature of above room temperature. Polymers with glass transition temperatures below room temperature produce smaller numbers of fragments in similar experiments, an example being high density polyethylene which produced 24 fragments. Thus, over a range of strain rates from quasistatic to explosive-driven, polycarbonate behaves as a tough ductile polymer, in spite of its glass transition temperature of 145-150°C². Brittle behaviour is only seen below the secondary glass transition temperature (T_{gg}) . This latter has been reported³ to be a temperature of -100°C at a frequency of 1 Hz.

Lewis⁴ has reported cases of brittle failure in polycarbonate battery cases used in coal mines. This brittle behaviour, more commonly seen when the molecular weight of the polymer is low, was associated with frozen in strain created during cooling, especially when the mould temperature is low. This strain freezes the polymer chain into non-equilibrium morphologies and can only be relieved by crack formation, a process which can be aided by solvents. The in-chain movements of the carbonate group are no longer possible and the material is brittle at room temperature.

Factors influencing the impact behaviour of polycarbonate include temperature, strain rate and notch radius. In a notched flexural strength test there is a sharp transition to brittle behaviour at temperatures of around 10°C⁵. In compression split Hopkinson bar experiments on polycarbonate Lee and Kim⁶ showed that the strength of polycarbonate increased from 150 to 400 MPa over a strain range of 4000-8500 s⁻¹. For comparison tensile strengths of polycarbonate measured at quasi-static strain rates are approximately 65 MPa. Cho et al⁷ concluded that the energy absorbed in the fracture of a blunt notched bar was proportional to the square of the notch root radius. Thus, assuming no environmental interaction with the polycarbonate, the likely circumstances where brittle behaviour will occur would include events at high strain rate, the presence of sharp notches and lower than ambient temperatures. The effect of testpiece geometry on the impact behaviour of polycarbonate aged at 130°C was observed by Brady⁸. She showed that the Izod notched impact strength was reduced from 890 Jm⁻¹ to 64 Jm⁻¹ after 5 days ageing. The absorbed energy by a falling weight (velocity 3 ms⁻¹, mass 14.4 kg, no notch present) only fell from 53 J to 48 J after ageing for 30 days at 130°C, confirming the adverse effect of the notch that was present in the Izod tests. Brittle behaviour was seen at -20°C for notched samples, rather than the -100°C seen for unnotched tensile tests. It is interesting to see in an early investigation by Wright et af on the ballistic properties of polycarbonate that no mention was made about a ductile-brittle transition. Cracking was mentioned for thick plates hit by both spherical and cylindrical projectiles. The impact velocities used ranged from 200 to 450 ms⁻¹.

Over long periods of time polycarbonate will sometimes weather and discolour. This weathering under the influence of cooling and lubricating fluids and vapours was recognised by Wurz and Modden¹⁰ as having the effect of reducing the ballistic properties of the polycarbonate windows used in machine tools. Hydrolysis effects were measured by Gardner and Martin¹¹ on polycarbonate over a range of relative humidities at temperatures of 63-93°C. They showed that brittle behaviour was associated with a drop in average molecular weight and that a drop in ductility was seen before any drop in tensile strength is seen. A more general review relating crazing strains to solubility for alkanes and alkane mixtures was carried out by Jacques and Wyzgorski¹². A reduction from 0.8% to 0.4% in the critical strain to produce crazing in polycarbonate was seen¹³when the percentage of aromatic compounds in petrol was raised from 10% to 30%.

Al-Saidi et al¹⁴ carried out experiments on the effects of solvents on stressed samples of polycarbonate. They showed that the critical strain to produce environmental stress cracking in 72 h exposure varied from 0.29% for ethylene glycol monomethyl ether to 1.74% for methanol with a strain of 1.21% for a specimen immersed in isopropyl alcohol. The higher the applied strain the shorter the time required for evidence of environmental stress cracking, a strain of 1.85% in isopropyl alcohol producing such evidence within a period of 10-100 s. Hansen¹⁵ explained stress cracking in terms of absorption of the liquid into the surface layers of the polymer. Thus, if a hole or dent is produced mechanically, such as by impact, absorption may be facilitated. From this it can be surmised that surfaces damaged by scratching or impact may show signs of stress cracking at shorter times than for the case of smooth surfaces.

In riots missiles of varying types are thrown and it is useful to know the typical mass and velocity of such projectiles. Most data on thrown objects come from measurements in sports science, such as the balls bowled by cricket fast bowlers or hurled by baseball pitchers. Data from these events, where the thrower is a professional athlete who is restricted by the laws of the appropriate game, cannot be relied on in the derivation of the velocity of projectiles thrown in a riot.

The aim of the present work is to examine the effect of projectile impact velocity on the tensile properties of polycarbonate sheet. In addition the effects of prior soaking in organic solvents on the tensile properties after projectile impact will be studied. Finally the behaviour of polycarbonate when a pellet is fired at a mechanically stressed sample will be examined.

Experimental

Materials used

Transparent polycarbonate sheet, 4 mm thick, for ballistic trials was supplied by DIY Plastics UK Ltd, Faringdon. The molecular weight (weight average M_w) of the sheets was measured by light scattering to be 29200 with a polydispersity index (M_w/M_n) of 1.2. In all cases photoelastic examination showed that there were no damaging internal strains of the type noted previously by Lewis⁴.

Ballistic testing

Fifteen male subjects under the age of 35 were invited to throw the missiles as hard as they could against a target which was placed 5 m from the throwing point. The

6

velocity was measured by videoing the throws at 1000 frames per second against a background of distance markers. The time taken for the missile to travel a distance of 1 m close to the target was measured. Each subject threw each missile once.

The missiles used described in Table 1. The bricks used were standard house bricks. The ball bearings were fired from an air cannon, 14 mm bore, with a sabot to ensure minimum leakage of air past the ball bearing.

Tensile testing

Ballistic impacts were carried out by firing a ball bearing whose dimensions are in Table 1 at point blank range into tensile specimens cut from 4 mm thickness sheet. Velocities varied from 23.2 to 96.2 ms $^{-1}$. The gauge section was 98 mm long and 20 mm wide. In each specimen there were three dents. All tensile tests were carried out at a crosshead speed of 10 mm min $^{-1}$, corresponding to a strain rate of 1.70 x 10^{-3} s $^{-1}$. Measurements were made of the yield strength, defined as the stress at which necking commences.

The effects of solvents, all GPR grade, were determined using the following solvents: acetone (Sigma-Aldrich Company Ltd), 99% heptane (Sigma-Aldrich Company Ltd). Samples that had been ballistically impacted were placed in stainless steel trays and covered with the solvent for a period of 10 minutes. Specimens were dried before tensile testing.

Determination of residual tensile stress effects

Specimens were loaded to loads of up to 4 kN in a Houndsfield tensile test machine. The crosshead was then stopped and a pellet (Fig.1) of mass 0.887 g and energy 32 J fired from an air rifle at the gauge length at point blank range. From the energy of the rifle and the mass of the pellet the impact velocity was estimated to be around 270 ms⁻¹. The specimen was then tensile tested at a crosshead speed of 10 mm min⁻¹, corresponding to a strain rate of 1.70 x 10⁻³ s⁻¹. The strength of the specimen was defined as the stress measured when the specimen had extended by 50 mm. This extension was chosen to represent a strain where the stress-strain curve was essentially horizontal due to the extension of the neck formed by plastic deformation Elongation was measured using a 98 mm gauge length.

Results

Ballistic testing

The results of the throwing experiments are shown in Fig.2. The mean velocity of the golf balls was 24.2 ± 5.3 ms⁻¹, whilst for the house bricks it was 11.7 ± 2.5 ms⁻¹.

Effect of ballistic damage on tensile properties

Results of tensile testing are shown in Fig.3 for yield strength and in Fig.4 for tensile elongation. Tensile strengths were reduced for impact velocities above 40 ms⁻¹ (impact energy 6.7 J), even when no immersion in solvent had taken place after ballistic impact. When the specimen was immersed in n-heptane after impact the yield strength was similar to that of the specimens that had not been immersed in solvent. When the specimen was immersed in acetone there was a reduction in strength even

without any effect of ballistic impact. This was more marked for velocities above 58 ms⁻¹ (impact energy 14 J). However, ductility was reduced after soaking in acetone at all velocities, reaching a value of less than 25% at an impact velocity of 23 ms⁻¹ (impact energy 2.2 J).

For samples that had not been impacted fracture tended to start from a corner of the cross-section, as shown for an untreated sample in Fig. 5(a). When the impact velocity was up to 41 ms⁻¹, there was evidence of damage in and around the dent created by the impact, although damage emanating from the corner was still seen. This is shown in Fig. 5(b) for an untreated sample impacted at 41 ms⁻¹. However, when the impact velocity is 58 ms⁻¹ or higher, fracture starts exclusively from around the dent, as shown for acetone treated samples in Fig.5(c)-(e).

Effect of ballistic firings on pre-stressed tensile specimens

Results are shown in Table 2. Even with stresses of 50% of the yield stress applied before firing there was no appreciable effect on the strength and ductility of the specimens. In all cases there was necking of the specimens with failure occurring remote from the dent created by the pellet. This was in contrast with the results with ball bearings shown in Fig.5 where failure at high impact velocities was associated with the damage created by the impact.

Discussion of Results

The need for the material of a riot shield is that it should show impact toughness when hit by a missile as well as being transparent without any discoloration due to weathering. Damage in ballistic penetration is a function of the kinetic energy of the projectile and the area impacted by the projectile. Thus the damage created by a sharp object, such as a knife, may be greater than that of a bullet, even though the bullet may be travelling at a much higher velocity. The results of Table 1 show that the kinetic energy of the ball bearing and the golf ball are similar, whilst the energy of the house brick is much larger. This would suggest that the house brick could be very damaging, provided that the impact on the shield is made by a corner or edge of the brick rather than a flat face. At velocities typical of the golf ball (24 ms⁻¹) the smaller diameter ball bearing failed to produce a visible dent in the polycarbonate. Thus the greatest danger to the person behind the riot shield when faced with a barrage of thrown objects come from the shield being hit by irregular shaped objects impacting on a corner rather than for more regular objects hitting the shield on a flat or spherical face.

In use there will be occasions when the material of the shield is placed under tensile strain, an example being when several shields are linked together to provide a protective barrier behind which the police or military personnel place themselves. Clearly the situation described by Lewis⁴, where strains set up during cooling in manufacture render the material brittle, is unacceptable. The aim of the experiment, whose results are in Table 2, is to determine whether stress, applied purely mechanically rather than through cooling, was likely to produce brittle behaviour. The worst case would have been if the tensile specimen had broken in a brittle manner immediately on impact of the pellet. Next would have been the case where the tensile

the site of the impact, such as occurred with the ball bearing at velocities of greater than 58 ms⁻¹, and where ductile failure occurred remote from the impact site are examples of successively less damaging occurrences. The results of the ballistic tests shown in Table 2 indicate that the dent created by the pellet was less damaging than the dent created by the heavier slower-moving ball bearing on an unstressed sample, as seen in Figs. 3-5. Thus it is suggested that, for applied stresses of up to 33 MPa, there is not a risk of brittle behaviour resulting from purely mechanical applied stresses. Indeed the tensile behaviour of the polycarbonate appears not to have been affected by the firing of the high velocity lightweight pellet.

Comparing the yield strengths of specimens that had been immersed in solvents after ballistic impact (Fig.3), it can be seen that immersion in acetone produced a drop in strength at impact velocities greater than 60 ms⁻¹. The decrease in ductility (Fig.4) when soaked in acetone after impact occurs at lower velocities and even when not impacted at all. This confirms the work of Gardner and Martin¹¹ whose work on humidity effects at temperatures of 63-93°C had indicated ductility reductions before any effects on strength were seen. The association of the final failure in the tensile test with the dent created by the impact can be seen in Fig.5, this being most marked at the highest impact velocities. The greater effect of the short immersion time would appear to be related to the ease of incorporation of the solvent into the polycarbonate at the site of the impact, where the surface has been damaged. This effect is similar to that seen by Wurz and Modden¹⁰ in the case of polycarbonate windows incorporated into machine tools and points out the hazard involved in the use of polycarbonate riot shields that have been scratched and damaged in prior exposure. The shallowness of

the dents created by the ball bearing would suggest that the effect was not similar to the effect of the presence of a notch, as seen by Brady⁸ in her comparison between Izod notched tests and drop weight impact testing on plain sheet specimens. This had shown that ageing effects were substantially greater when Izod notched bar impact strengths were considered, rather than results from dents created by a dropping weight. This lack of major effects of ageing when dented by a dropping weight was also noted by Halliwell and Gardner¹⁶. They found that the impact energy absorbed by polycarbonate was not affected by abrasion. This was in contrast to polyvinylchloride (PVC) samples that showed decreased energy absorbed and brittle fracture when abraded.

Conclusions

- a) The velocities of projectiles thrown by rioters are lower than that producing macroscopic damage when ball bearings are fired from an air gun.
- b) There is a loss in strength and ductility seen when tensile tests are carried out after specimens have been hit at velocities greater than 50 ms⁻¹. This effect is more marked when the specimen has been soaked in a ketone after impact.
- c) The degradation of impact properties is associated with damage created at the point of projectile impact. This damage will be a function of the mass and shape of the impacting projectile as well as its kinetic energy.
- d) When a ball bearing is fired at a specimen that is being mechanically stressed, there is no effect on the mechanical properties of the polycarbonate. This is in contrast to the behaviour of polycarbonate which has internal strains set up through fast cooling.

Acknowledgements

The authors would like to thank their Cranfield colleagues Adrian Mustey (tensile testing), as well as Phil Gill (molecular weight determination), Celia Watson and Dave Miller (ballistic testing). They would also wish to thank Eran Bauer (Civil Defence Supplies Ltd) for a series of stimulating discussions about the applications of polycarbonate in riot shields. Helpful discussions with Peter Lewis (Open University) are gratefully acknowledged.

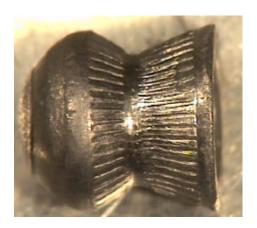
References

- 1. R Dean, M R Edwards, A Lister and J F Lockett: Proc. 21st Int Symposium on Ballistics, (ed. N Burman, J Anderson and G Katselis), **2**, 691-697; 2004, DSTO Australia.
- 2. L L Clements: in "Engineering Plastics", Engineered Materials Handbook, **2**, pp.48-67; 1988, Metals Park, ASM International.
- 3. L E Nielsen and R F Landel: "Mechanical Properties of Polymers and Composites", 2nd ed, pp 202-212; 1994, New York, Marcel Dekker, New York.
- 4. P R Lewis, K A Reynolds and C R Gagg: "Forensic Materials Engineering: Case Studies", pp 229-231, 2004, Boca Raton, CRC Press, Boca Raton.
- 5. D Freitag, U Grigo, P R Müller and W Nouvertné: in "Encyclopaedia of Polymer Science", 2nd ed, (ed H F Mark, N M Bikeles, C G Overberger and G Menges); **11**, pp 648-718; 1988, New York, John Wiley.
- 6. O S Lee and G H Kim: J Materials Science Letters, 2000, 19, 1805-1808.
- 7. K Cho, J H Yang, B I Kang and C E Park: *J Applied Polymer Science*, 2003, **89**, 3115-3123.
- 8. J M Brady: *Polymer*, 1992, **33**(14), 2981-2988.

- 9. S C Wright, N A Fleck and W J Stronge: *International J Impact Engineering*, 1993, **13**(1), 1-20.
- 10. T Wurz and H Modden: Werkstatt und Betrieb, 2002, 135(11), 47-49.
- 11. R J Gardner and J R Martin: J. Applied Polymer Science, 1979, 24, 1269-1280.
- 12. C H M Jacques and M G Wysgorski: *J. Applied Polymer Science*, 1979, **23**, 1153-1166.
- 13. M G Wysgorski and C H M Jacques: *Polymer Engineering and Science*, 1977, **17**, 854-860.
- 14. L F Al-Saidi, K Mortensen and K Almdal: *Polymer Degradation and Stability*, 2003, **82**, 451-461.
- 15. C M Hansen: Polymer Degradation and Stability, 2002, 77, 43-53.
- 16. S M Halliwell and D Gardiner: Proc 10th Int Conf on Deformation, Yield and Fracture of Polymers, pp 242-245: 1997, Institute of Materials, London.

LIST OF CAPTIONS

- Fig.1 Pellet fired from air rifle (left) and in cross-section (right). Overall length of pellet 6.13 mm
- Fig.2 Frequencies of velocities of golf ball and house brick produced by throwing
- Fig.3 Yield strength as a function of impact velocity (10 minutes soak after firing)
- Fig.4 Tensile elongation as a function of impact velocity (10 minutes soak after firing)
- Fig.5 (a) Failure across the cross-section of an untreated polycarbonate tensile test sample. The dimensions of the sample are 7 mm by 3 mm. (b) Untreated sample impacted with a steel ball bearing at a velocity of 41.6 ms⁻¹ and then tensile tested. The maximum crack length is 2 mm. (c) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 58.0 ms⁻¹. The diameter of the dent is 6 mm. (d) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 77.6 ms⁻¹. The original diameter of the dent was 8 mm. (e) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 96.2 ms⁻¹. The original diameter of the dent was 10 mm.



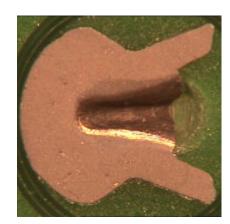


Fig.1 Pellet fired from air rifle (left) and in cross-section (right). Overall length of pellet 6.13 mm

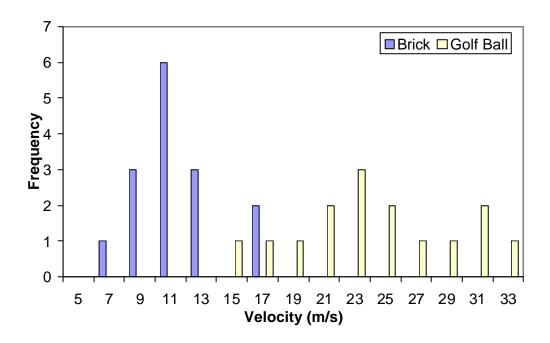


Fig. 2 Frequencies of velocities of golf ball and house brick produced by throwing

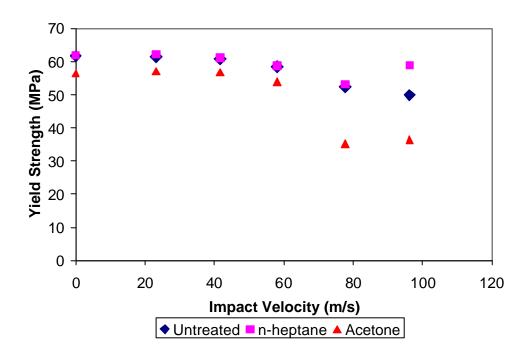


Fig.3 Yield strength as a function of impact velocity (10 minutes soak after firing)

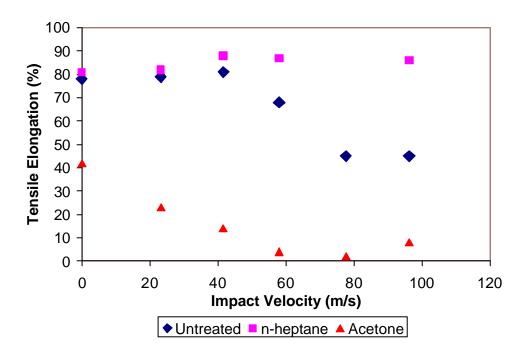


Fig.4 Tensile elongation as a function of impact velocity (10 minutes soak after firing)



(a)



(b)



(c)



(d)



(e)

Fig. 5 (a) Failure across the cross-section of an untreated polycarbonate tensile test sample. The dimensions of the sample are 7 mm by 3 mm. (b) Untreated sample

impacted with a steel ball bearing at a velocity of 41.6 ms⁻¹ and then tensile tested. The maximum crack length is 2 mm. (c) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 58.0 ms⁻¹. The diameter of the dent is 6 mm. (d) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 77.6 ms⁻¹. The original diameter of the dent was 8 mm. (e) Failure of a sample treated with acetone and impacted with a steel ball bearing at a velocity of 96.2 ms⁻¹. The original diameter of the dent was 10 mm.

Table 1 Missiles used in experiments

Measurement	Brick	Golf Ball	Ball Bearing
Mass (kg)	2.45	0.0452	0.083
Dimensions (mm)	217 x 101 x 66	42 (diameter)	12 (diameter)
Mean Velocity (ms ⁻¹)	11.7	24.2	23.2 – 96.2
Kinetic Energy (J)	168	13.2	2.2 - 38.4

Table 2 Tensile tests on pre-stressed samples

Stress at firing	Stress at 50 mm	Elongation	
(MPa)	extension (MPa)	(%)	
0	49.4	91	
15	49.0	58	
20	48.5	77	
33	49.0	75	
unfired	48.7±0.7 (N=3)	72±2 (N=3)	