JOURNAL OF MATERIALS SCIENCE 6 (1971) 110-114

Shear Strength of Polymers under Hydrostatic Pressure: Surface Coatings Prevent Premature Fracture

J. S. HARRIS, I. M. WARD
Physics Department, University of Leeds, Leeds, UK
J. S. C. PARRY
Department of Mechanical Engineering, University of Bristol, Bristol

The effect of surface rubber coatings on the stress-strain behaviour in shear of polymethylmethacrylate (PMMA), polyethylene terephthalate (PET) and polyethylene has been examined. Uncoated PMMA fractures without yielding at high pressure, while it is ductile at lower pressures. The high pressure fracture is thought to be due to pressure fluid penetrating into surface cracks allowing them to grow in spite of the applied hydrostatic pressure. Coating in rubber prevents such penetration and PMMA remains ductile up to 7 kbar. PET and polyethylene are normally ductile at all pressures, and coating in rubber has no effect on their behaviour. Failure here is due to internal flaws.

1. Introduction

In a recent publication [1] we described the effect of hydrostatic pressure on the stress-strain behaviour in shear of polymethylmethacrylate (PMMA), polyethylene terephthalate (PET), and polyethylene. In polymethylmethacrylate the shear yield stress at first rose with increasing hydrostatic pressure and there was a corresponding increase in the strain at yield.

At higher hydrostatic pressures there was a change in behaviour and the polymer failed at the maximum load in a brittle manner. This failure showed all the signs of tensile fracture, occurring on planes whose normals lie very close to the direction of maximum tensile stress.

These fractures occurred under conditions where there is no tensile component of stress in the bulk of the material (due to the superimposed hydrostatic pressure). It was therefore proposed that the fracture was being initiated at flaws in the surface of the specimen where fluid entered the crack, equalised the hydrostatic component of stress and allowed the crack to spread.

It has been established by many workers [2-8] that the fracture behaviour of many materials under applied hydrostatic pressures can be very much affected by whether the hydraulic fluid is in direct contact with the surface of the material. We have therefore undertaken a further series of experiments to test the behaviour of hollow specimens of these polymers coated with a thin layer of solidified rubber solution.

2. Experimental Procedure

As the apparatus and specimen geometry have already been described in a previous publication [1], only the more important details will be described here.

The specimens consisted of hollow cylinders, 62.5 mm long, with square ends (18 mm square) to prevent slipping in the grips. The centre region of the cylinders was turned down to 8.9 mm outside diameter, and hollowed out to 7.16 mm internal diameter. This region was 10.92 mm long which, applying the correction for the intermediate region gave an effective gauge length of 12.7 mm. The specimens were mounted vertically, the lower grip being connected to a drive shaft, and the upper grip to a hollow cylindrical steel torsion bar. The torsion bar and specimen were both totally immersed in a pressure fluid inside a pressure bomb. Two mirrors were attached to steel stalks connected to the two ends of the bar respectively, and the relative movement of the mirrors used through a calibration curve, to measure the shear stress in the bar and hence the shear stress in the specimen. An electric motor connected by a chain drive to the drive shaft produced a constant rotation of 3° min^{-1} of the lower end of the specimen. This gave shear strain rates $\sim 10^{-4}$ sec^{-1} in the specimen.

The application of the rubber coatings was achieved by dipping the specimens into a Dunlop rubber/petroleum solution. The specimens were individually dipped into the viscous solution long enough for the solution to "wet" the entire surface of the material. They were then removed from the solution and the excess fluid allowed to drain off, and the specimens allowed to dry in air at room temperature, over a period of 13 to 16 h. This treatment produced a fairly even thickness of coating over the specimens, the thickness being $\sim$ 0.038 mm. Many of the specimens coated in this way were then given a second coating by repeating the treatment, giving a total coating thickness of $\sim$ 0.076 mm, enabling us to examine the effect of coating thickness.

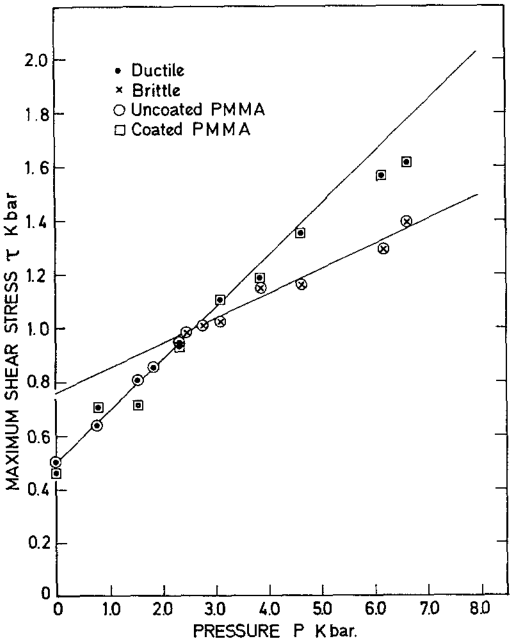

Figure 1 Maximum shear stress τ as a function of hydrostatic pressure P for polymethylmethacrylate.

3. Results

3.1. Yield Behaviour

The results are shown in fig. 1, where the maximum shear stress is plotted as a function of pressure. Also shown, for comparison, are the results for uncoated PMMA. The first important factor that emerged from these results was that in the coated material, there was no change in behaviour as the pressure was increased, as was observed in uncoated material. That is, the material yielded at all pressures, prior to failure. The second, and in many ways equally important point was that the yield behaviour appeared to be unaffected by the rubber coating.

This second point is important because it suggests that the rubber coating is bearing little or none of the applied load, and that its sole function is to provide a protective barrier between the polymer and the fluid.

It has been reported [9] that many rubbers show a rapid increase in modulus at high pressures due to the pressure raising the glass transition temperature. The pressures reported for this transition are $\sim$ 5 kbar. Fig. 1 indicates that at pressures in the region of 5 kbar and above, the observed maximum shear stress does not deviate appreciably from a linear dependence. If the modulus of the rubber did increase to such an extent that the coating was bearing an appreciable portion of the applied load, we would expect the observed yield stresses to be too high. The rise in modulus referred to above was often sufficient to give a modulus greater than 10^{10} dynes cm^{-2} which is the same order of magnitude as that of PMMA. The thickness of the rubber $\sim$ 0.152 mm (rubber was on the inside of the specimens as well as on the outside surface), while the specimen wall thickness was 0.86 mm; the fraction of the total thickness of each cylinder, of the rubber coating was thus $\sim 15\%$. We would expect, if a modulus rise of this sort were taking place, that it would be detectable. This suggests, therefore, that at pressures up to 7 kbar, this type of coating can be used without fear of interfering with the true stress-strain characteristics of the material, that is, it is acting purely as a protective coating.

All of the uncoated specimens fractured soon after yielding (within 5 to 10% strain after yield), the mode of fracture being similar to those specimens which did not yield. This was not the case for the coated specimens, however, most of which tended to buckle soon after yielding. The shapes of the stress-strain curves up to yield in specimens which buckled were the same as for those which did not buckle. The curves after yield were different depending on whether the specimens buckled or not. These results indicate that buckling only takes place after yielding and that the yield stresses measured are true yield stresses and not "buckling" stresses.

In our previous publication [1] we reported that similar experiments done on crystalline polyethylene and polyethylene terephthalate gave different results. Here both materials failed in a ductile manner at all pressures and again buckled after yielding. Whereas the failure of PMMA was thought to be due primarily to surface flaws, it was suggested that internal flaws were responsible in the case of PET and polyethylene. If this were the case, coating such specimens in rubber would not be expected to affect the mechanical properties. Fig. 2 shows that this is indeed the case. This figure also provides further evidence for concluding that the rubber coating is bearing little or none of the applied load.

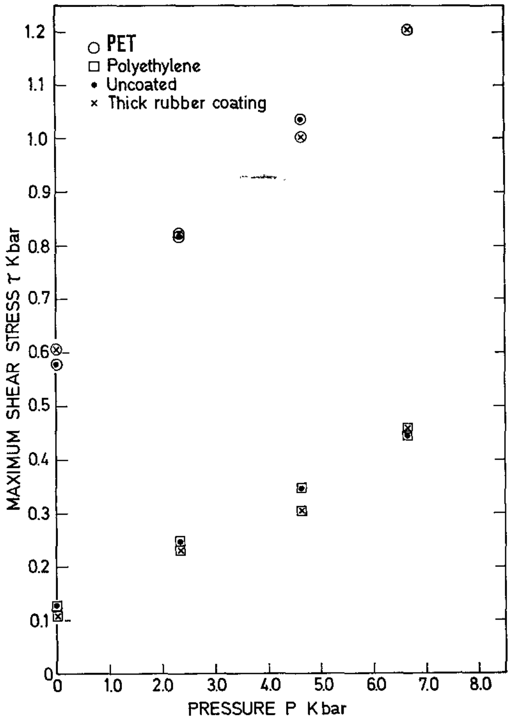

Figure 2 Maximum shear stress τ as a function of hydrostatic pressure P for PET and polyethylene.

3.2. Fracture Behaviour

As shown in fig. 1, above a certain pressure, the uncoated material does not yield, but instead fractures at the maximum stress in a brittle manner. The fracture plane indicates that the fracture is a tensile rather than a shear fracture, since the plane lies at an angle close to 45° to the torsion axis, which makes it normal to the direction of the maximum tensile component of stress (and thus the zero shear component of stress). In all tests, except those at atmospheric pressure, the net state of stress in the bulk of the material is compressive due to the superimposed hydrostatic pressure. That is to say, the maximum tensile component of stress in the bulk of the material produced by the applied shear stress, is less than the hydrostatic component of stress. This being the case, one might ask how a tensile-type fracture can occur. Though the bulk of the material is under compression, there may be a net tensile component of stress at the tip of a crack originating at the surface. This occurs if the hydraulic fluid penetrates the crack and hence gives rise to a hydrostatic component of stress acting on the surface of the crack, which balances the hydrostatic component in the bulk of the material. Thus we have a situation where the bulk of the material is under compression, yet there is a net tensile component of stress at the crack tip. (Under these conditions, the applied hydrostatic stresses no longer have the effect of closing up *surface* cracks, however *internal* cracks *will* be prevented from growing.) In our previous publication [1] we showed how the modulus and surface energy of PMMA rise with increasing pressure. The net effect of hydrostatic pressure is thus to reduce the segmental mobility of the molecular chains producing a rise in modulus and surface energy. It is these factors which cause the rise in fracture stress with increasing pressure, rather than "crack closing" effects due to the applied hydrostatic stresses. When such specimens are coated with rubber, fluid is no longer allowed to penetrate such cracks and the applied pressure closes them up, preventing fracture from occurring at all pressures up to 7 kbar. We have seen in the previous section, that instead of fracturing at the maximum stress, such specimens yield and then buckle.

Examination of the fracture surfaces and the fracture planes indicated that the mode of fracture was the same in uncoated PMMA at all pressures. Even those specimens which yielded first fractured on planes indicating a tensile rather than a shear fracture. Fig. 3 shows a typical stress-strain curve at low pressure and one must ask the question why, since the failure stress σ_f is less than the yield stress σ_y the material does not fracture before yielding, since the topographical features of the fracture are the same as for those specimens at higher pressures when this did indeed happen.

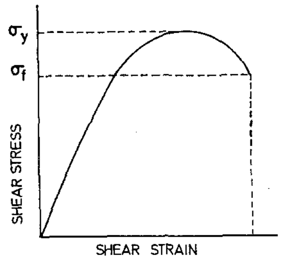

Figure 3 Schematic diagram showing a typical shear stress-shear strain curve for polymethylmethacrylate at low pressures.

Fig. 4 illustrates the situation. If yield had not occurred, we would expect fracture to occur at pressure P at stress σ_f', found by extrapolating the brittle fracture stress line back. In practice, the material does yield and fractures at a lower stress σ_f. The fracture is the same, however, as if fracture had occurred at stress σ_f'.

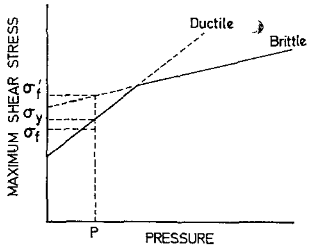

Figure 4 Schematic diagram showing maximum shear stress as a function of pressure for polymethylmethacrylate.

Professor F. C. Frank has suggested the following explanation. Prior to yield, the distribution of stress is homogeneous throughout the gauge length of the specimen. As the stress increases, flaws in the surface act as centres of stress concentration, and the material yields at some point. This yielding is only local, and results in an extremely inhomogeneous distribution of stress. The material does not neck as it would in a tensile test, but shears instead. By the very process of shearing, high stress concentrations are set up at the edges of the yield zone. As the material yields, the shearing increases, and the macroscopic shear stress on the specimen drops, as is observed. Locally, however, as the shear becomes more pronounced, the stress concentration rises until it eventually reaches the value σ_f' and a crack starts to grow. The crack starts at the edge of the yield zone where the stress concentration is highest. Although the macroscopically observed fracture stress is lower than the yield stress ($\sigma_f < \sigma_y$) the true fracture stress which is only local, is the expected value of σ'_f. For this reason the fracture is the same at all pressures, whether the material yields or not.

Observations of the fracture surface under crossed polarisers indicate that the crack starts in a region of birefringent material. Initially the material is isotropic, and it is only when it yields that any orientation takes place, and this orientation is, of course, in the yield zone. The results indicate, therefore, that the crack starts in the yield zone. Similar observations made on other parts of the specimens show them to be isotropic except near the tip of the crack. It therefore seems that this model is compatible in all respects with the experimental observations.

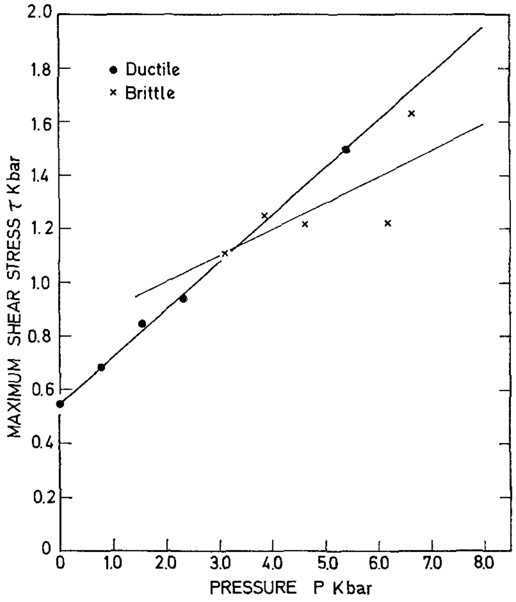

Figure 5 Maximum shear stress τ as a function of hydrostatic pressure P for polymethylmethacrylate with a thin rubber coating.

4. Effect of Rubber Thickness

All the results above refer to experiments performed on specimens with rubber thickness of 0.076 mm on each surface (two dippings in the rubber solution). Some tests were done on specimens with a rubber thickness of 0.038 mm; the results are shown in fig. 5. Here we can see that the material is still failing in a brittle manner at high pressures, though the transition from ductile to brittle behaviour has shifted to a slightly higher pressure than for uncoated specimens. This suggests that with such a thickness, either the fluid is forcing its way through the rubber layer, or it is forcing the rubber itself into some of the flaws. Either way, there appears to be a minimum thickness required if brittle failure is to be prevented at high pressures. Similarly there is an upper limit since too thick a coating might result in the rubber bearing appreciable portions of the applied load.

5. Effect of Rubber Coating on the Materials

It was feared that the petroleum solvent in the rubber solution might have a plasticising effect on the polymers. The results in figs. 1 and 2 indicate that this is not happening to any appreciable extent, since the yield stresses in coated and uncoated specimens agree well with one another. In addition, a couple of specimens were coated in rubber and left for 4 to 5 days, the rubber stripped off and the specimens then tested. The results were in excellent agreement with similar results on uncoated material.

6. Summary

We can summarise the processes involved in the failure of PMMA under hydrostatic pressure, as follows. During the machining of the specimens, surface flaws and cracks are inevitably introduced. On surrounding the specimens with the hydraulic pressure fluid, some of the fluid penetrates these cracks. As the pressure is increased, material properties such as modulus, yield stress and surface energy increase due to reduced molecular chain mobility among other factors. Stress conditions at the crack tip are not altered, however, and the growth of cracks is dependent solely on the material properties.

At low pressures the yield stress is lower than the fracture stress, however it increases with increasing pressure at a faster rate than the fracture stress. At some intermediate pressure, the yield stress becomes greater than the fracture stress and we observe the transition from ductile to brittle behaviour. By coating specimens in rubber, fluid penetration is prevented and the applied hydrostatic pressure tends to close cracks. Crack propagation is now also restricted by the effect of pressure closing cracks. The result is that the fracture stress in such specimens rises at a faster rate than in uncoated material, and PMMA remains ductile up to 7 kbar.

In the case of crystalline PET and polyethylene, failure is due to internal cracks and flaws, which are prevented from growing by the applied pressure, whether the specimens are coated in rubber or not. The result is that they are ductile at all pressures, and no change in behaviour is observed if the material is coated.

Acknowledgement

The authors would like to thank Mr J. D. B. Watts for his help in obtaining the experimental results. One of us (J.S.H.) is grateful to the Science Research Council for financial support during the course of this work.

References

1. S. RABINOWITZ, I. M. WARD, and J. S. C. PARRY, *J. Mater. Sci.* **5** (1970) 29.
2. E. F. CHANDLER, *NEL Report No.* 255 (November 1966).
3. TH. VON KARMAN, *Z. Ver. dtsch. Ing.* **55** (1911) 1749.
4. R. BOKER, Dissertation, Tech. Hochschule zu Aachen, "The Mechanics of Plastic Deformation in Crystalline Bodies".
5. P. W. BRIDGMAN, *J. Appl. Phys.* **18** (1947) 246; "Studies in Large Plastic Flow and Fracture with special emphasis on the effects of hydrostatic pressure" (McGraw-Hill: London and New York, 1952).
6. B. CROSSLAND and W. H. DEARDEN, *Proc. IME* **172** (1958) 805.
7. H. LL. D. PUGH and D. GREEN, *NERL Plasticity Report No.* 128 (East Kilbride, Glasgow: National Engineering Laboratory 1956).
8. B. D. GROZIN, "Mechanical Properties of Hardened Steel" (in Russian, Moscow, 1951).
9. M. S. PATERSON, *J. Appl. Phys.* **35** (1964) 176.

Received 28 September and accepted 20 November 1970.