

The mechanical properties of elastomers in high-pressure CO₂

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Elastomer seals are widely used to contain high-pressure gases and can suffer from decompression damage when the contained gas is depressurized. The generally accepted mechanism for the damage is that there is a considerable degree of dissolution of the gas into the elastomer which cannot diffuse out quickly enough when the contained pressure is reduced; hence bubbles and fissures occur in the bulk of the elastomer. Attempts to model this behaviour typically assume the elastomer material properties are measured in the absence of the dissolved gas. In this study, a standard dumb-bell test piece tensometer has been developed which allows the elastomer material properties to be measured while saturated with CO₂ and N₂ (two gases with markedly different solubilities) at pressures of up to 4 MPa. The equipment was shown to be capable of providing accurate measurements under these conditions and various fluorocarbon, nitrile and silicone elastomers were tested. These tests showed that the high-pressure CO₂ induced a slight reduction in initial modulus compared to tests in air, accompanied by a more significant loss in both strength and ultimate extension. The reduction was greater than 50% in some cases. Electron micrographs of the samples showed that the fracture surfaces were of a smoother nature for the samples tested in CO₂, suggesting a mechanism of disruption of interchain forces. The implications of these results for models of decompression damage are noted. © 1999 Kluwer Academic Publishers

1. Introduction

Elastomer seals are often used to contain high-pressure gases. An operational problem for such seals, particularly where the gas has a relatively high boiling point, is decompression damage. The industries for which this has particular relevance are the oil/natural gas industry (methane and sour gas) and parts of the nuclear power generating industry (high-pressure CO₂ coolant). In order to ensure seal integrity in both these applications, it is important that the mechanism associated with decompression damage is properly understood. At present, theoretically based methods are not sufficiently developed to underwrite the integrity. Therefore, where specific assurances are required, plant simulation tests are typically carried out.

The generally accepted mechanism for decompression damage is that during exposure to certain high-pressure gases, there is a considerable degree of solution of the gas into the elastomer. If the external pressure is then reduced for some reason, a state of supersaturation will occur. This can result in the nucleation and growth of internal gas bubbles in the elastomer which

can then develop into surface blisters or larger tears and in extreme cases can cause seal failure. This explanation of the phenomenon is supported by the fact that low-solubility gases, such as nitrogen or helium, rarely cause a problem. The effect is aggravated if the diffusion rate of the gas through the elastomer is slow compared to the decompression rate. Silicone elastomers, for instance, are very permeable to gas and tend to suffer far less from decompression damage than other elastomers.

There have been many studies of the mechanisms and degree of decompression damage seen with elastomers. Of the controlling factors, the solubility and diffusion behaviour have received considerable attention [1–13], with the general conclusions that high solubilities and low diffusion rates (seen with low chain mobility) increase the severity of decompression damage. Decompression damage is most commonly seen as a single-cycle phenomenon, although it is possible that a fatigue process can occur. It is also likely that there is a critical decompression rate, below which no damage will occur, although evidence to support this view is not conclusive [2, 3].

After solubility and diffusion rate, which are difficult to influence for given applications, the most important material parameter would seem to be the stiffness of the elastomer. This follows work by Gent [4] who found that the internal pressure required to expand precursor voids was equal to $5E/6$, where E is the tensile modulus. Later work [5, 6] however, showed that for very small precursor voids, the tearing energy was also important. The importance of material stiffness has been highlighted by work on highly cross-linked and filled elastomers, where decompression damage resistance was found to increase with the stiffness [7]. Stiffening due to strain crystallization has also been found to be beneficial. The operational value of controlling the stiffness of an elastomer is limited as the successful operation of a seal requires a material that is flexible enough to conform to surface irregularities on the sealing faces.

There have been several attempts at modelling decompression damage, following on from work on cavitation [4, 5, 9, 11]. These include numerical simulations of the diffusion behaviour and the stresses produced during decompression [12, 13]. The one major problem with such predictive models is that the material properties of interest (stiffness, strength, tearing energy) are typically assumed to be those measured in the absence of the high-pressure gas. It is highly probable that these properties will be quite different in high-pressure gas, a view borne out by the results of extensive work on the related area of swelling by organic liquids [14–21]. It has generally been found that, for a number of possible reasons, swelling leads to a loss in both modulus and strength. The only work known to the authors to be published on the mechanical properties of elastomers in high-pressure gases has reported that the acoustic modulus of a silicone rubber increased in high pressure nitrogen due to a reduction in free volume caused by the external pressure [22]. In CO_2 , it was found that at higher pressures, the modulus decreased due to swelling effects [23].

Until the mechanical properties of elastomers in high-pressure gases are known, the use of predictive models of decompression damage will be highly questionable. The main purpose of this work is to address this point by directly measuring the mechanical properties of a range of elastomers when saturated in high-pressure CO_2 as well as studies in high-pressure nitrogen, a non-swelling gas intended as a control. This involved the development and construction of specialized test equipment. It is hoped that with a more detailed knowledge of the behaviour of elastomers under these conditions, the understanding of, and ability to predict decompression damage will improve.

2. Experimental procedure

2.1. Test rig design

In order to overcome the problems of testing in high-pressure gases, a specially designed tensometer pressure vessel was constructed. This is shown diagrammatically in Fig. 1. The pressure vessel was constructed with an upper section (approximately 60 cm high) that could be bolted on to the base section. Separation of the

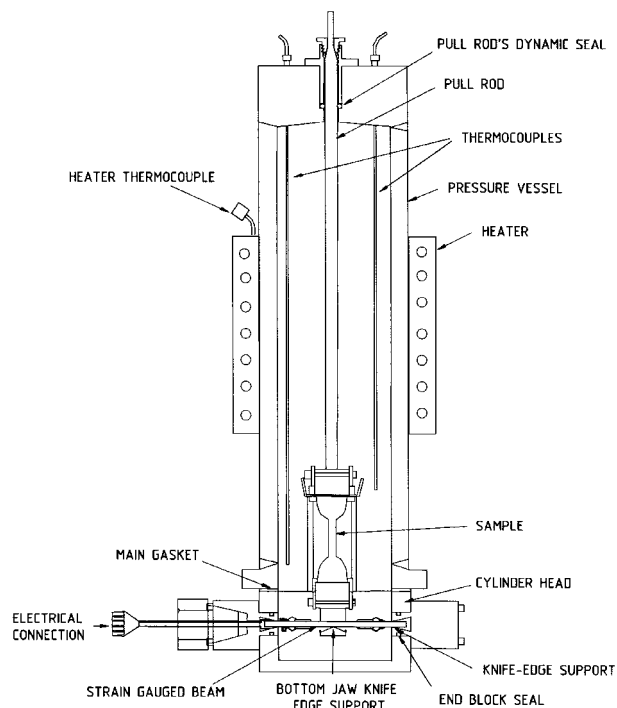


Figure 1 A schematic diagram of the tensometer used for testing in high-pressure gases.

vessel at this joint allowed for the insertion and removal of samples.

A major feature of the tensometer was an internal load cell, comprising a strain-gauged beam at the base of the pressure vessel. The arrangement with the load cell inside the vessel eliminated concerns over force errors arising from the drag of the dynamic seals on the pull rod or the correction required for the gas pressure-induced loading of the pull rod. The load cell was calibrated in ambient air against a traceable standard and was found to be both accurate and linear to within 1% over the range of interest. The accuracy of the load cell when testing in high-pressure gases was checked by measuring the force/displacement characteristics of a calibrated spring in ambient air and with the tensometer pressurized with 4 MPa nitrogen and CO_2 . No significant differences were seen. The effect of long-term exposure of the load cell to high-pressure CO_2 was also investigated and shown to be negligible.

The tests were carried out in a modified proprietary tensile testing machine. The output of the load cell was fed into the control and measurement circuitry and the action of the pull rod was provided by attachment to the machine crosshead. Another important feature of the tensometer pressure vessel was that it could be removed from the tensile testing machine in order to allow for the relatively long saturation periods required before testing. The tensometer pressure vessel was also surrounded by a band heater to allow for elevated temperature tests. These results will be reported in a future publication.

2.2. Test procedure

Standard dumb-bell samples (BS903) were punched from sheets of the materials to be tested. For each

test the sample was placed in the specially designed cam grips of the tensometer and the pull rod was held in place at the top by a retaining nut. The vessel was then pressurized with the test gas and allowed to equilibrate for 24 h. Separate tests conducted in a pressure vessel allowing sample monitoring via a window and video camera showed that equilibrium swelling occurred well within 24 h for all the elastomer types tested in 4 MPa CO₂. The pressure was controlled and monitored throughout the soak time and the test itself using regulators and pressure gauges. Temperature was monitored using the thermocouples shown in the schematic diagram in Fig. 1.

At the end of the soak time, the tensometer was clamped to the base of the tensile testing machine and the pull rod was attached to the crosshead. A very small pre-load was applied to take up any slack in the sample. The sample was then extended at a constant rate of 500 mm min⁻¹. The extension was measured from the crosshead displacement. This measure was found to be sufficiently accurate from tests conducted where the extension of the gauge length could be monitored. In addition, calibration marks were put on the sample by the grips to ensure that if slippage occurred, the test result could be discounted. The load against extension behaviour was recorded and converted into engineering stress against strain.

2.3. Materials

A total of six formulations were tested. These were based on three elastomer types with a limited range of hardness formulation variants for two of the elastomers. The materials used were:

- (i) F60-Fluorocarbon rubber of Shore hardness 60 (unfilled);
- (ii) F80-Fluorocarbon rubber of Shore hardness 80;
- (iii) F90-Fluorocarbon rubber of Shore hardness 90;
- (iv) N60-Nitrile rubber of Shore hardness 60 (unfilled);
- (v) N80-Nitrile rubber of Shore hardness 80;
- (vi) S65-Silicone rubber of Shore hardness 65.

The F60, F90, N60 and S65 were tested in ambient air and in 4 MPa nitrogen. The F80, N80 and S65 were tested in ambient air and in 4 MPa CO₂. For each combination, three tests were performed. All testing was performed at about 23 °C.

3. Results and discussion

3.1. Tests in nitrogen

Individual tensile test results in air and in 4 MPa nitrogen are shown in Figs 2–5 for F60, F90, N60 and S65, respectively. It can be seen that there is very little difference in the observed modulus between the samples tested in air and those tested in high-pressure nitrogen. Although there is some degree of scatter in the values of ultimate tensile strength (UTS), there is not a large difference between the two environments. Indeed, average values of tensile strength, shown in Fig. 6, show that for

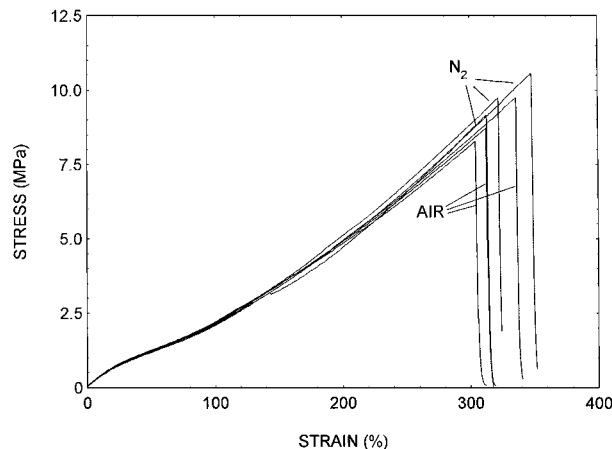


Figure 2 Stress/strain curves for samples of F60 tested in air and in 4 MPa nitrogen.

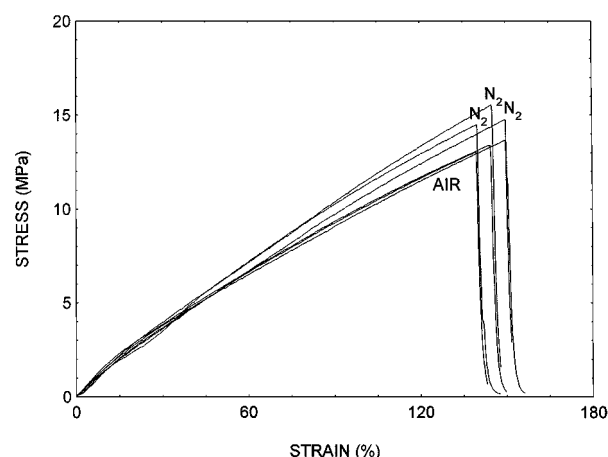


Figure 3 Stress/strain curves for samples of F90 tested in air and in 4 MPa nitrogen.

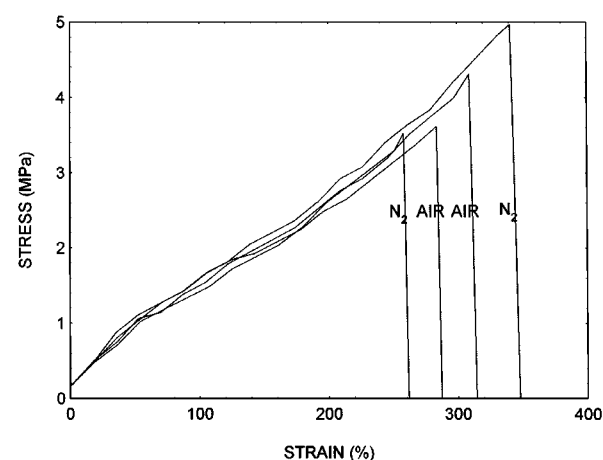


Figure 4 Stress/strain curves for samples of N60 tested in air and in 4 MPa nitrogen.

the fluorocarbon rubbers, the strength is slightly higher in nitrogen. Examination of the fracture surfaces of all materials did not show a marked change in morphology between samples tested in air and high-pressure nitrogen. The slight increase in tensile strength for the fluorocarbon rubbers in high-pressure nitrogen may be due to an increase in T_g , causing greater hysteresis,

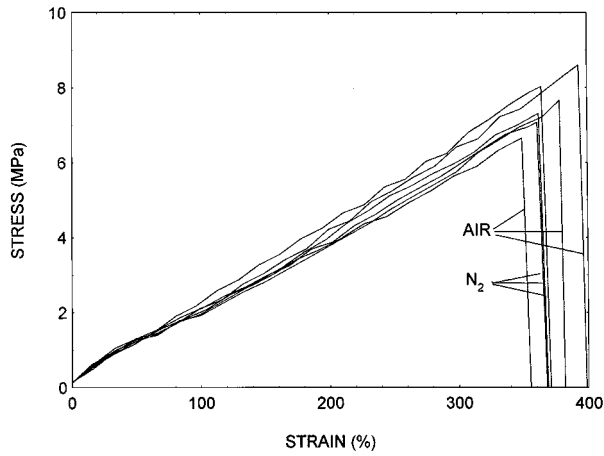


Figure 5 Stress/strain curves for samples of S65 tested in air and in 4 MPa nitrogen.

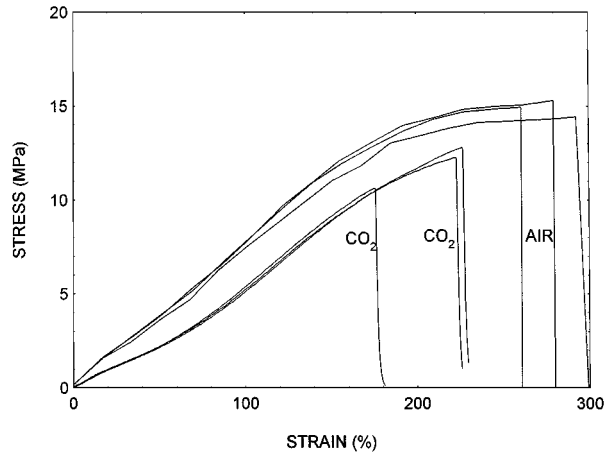


Figure 8 Stress/strain curves for samples of N80 tested in air and in 4 MPa CO₂.

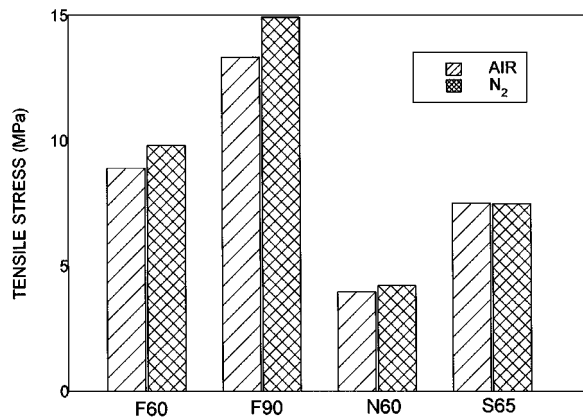


Figure 6 The average UTS for samples tested in air and in 4 MPa nitrogen.

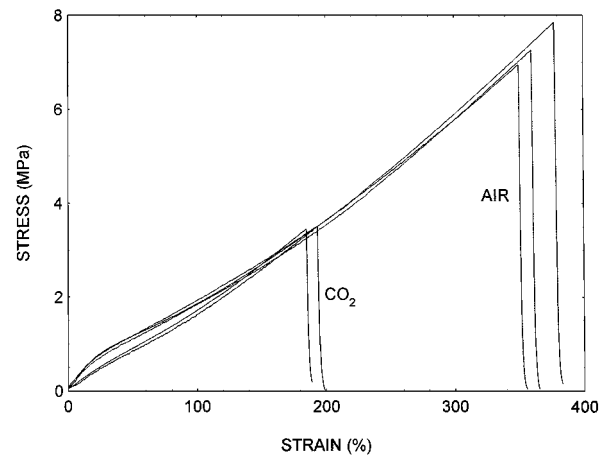


Figure 9 Stress/strain curves for samples of S65 tested in air and in 4 MPa CO₂.

although there may also be some compression of surface flaws.

3.2. Testing in CO₂

The tensile test results in 4 MPa CO₂ show significant differences to the results in air. These are plotted individually in Figs 7–9 for F80, N80 and S65. The average values of UTS for all the materials are shown in Fig. 10.

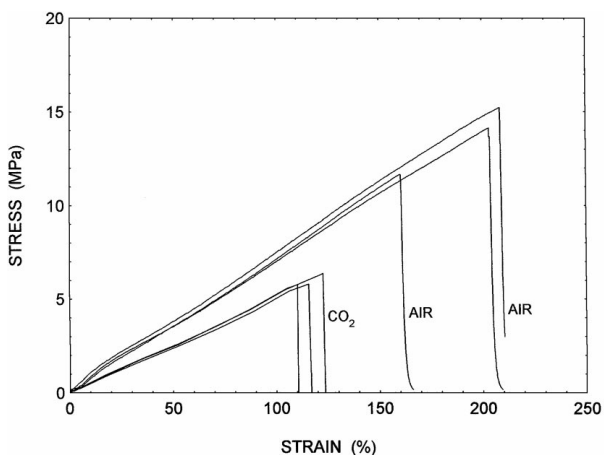


Figure 7 Stress/strain curves for samples of F80 tested in air and in 4 MPa CO₂.

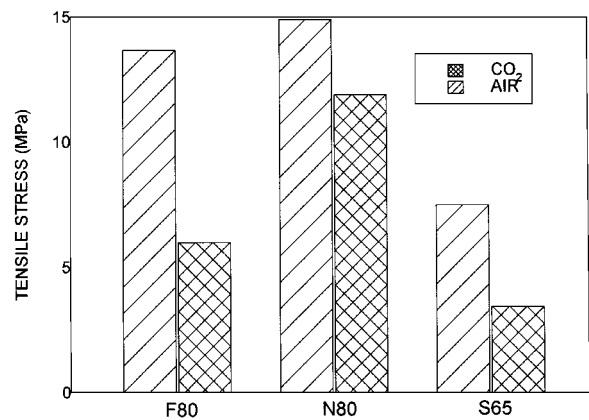
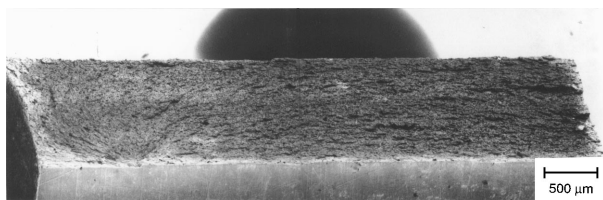
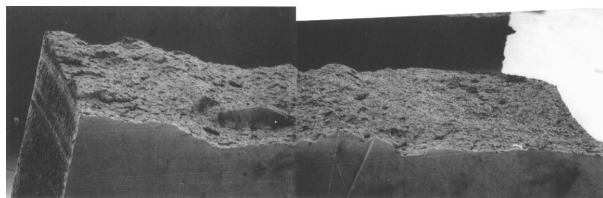


Figure 10 The average UTS for samples tested in air and in 4 MPa CO₂.

In all cases, the samples tested in CO₂ had a lower initial modulus, a significantly lower strength and a lower elongation at break. These effects are most noticeable for the F80, and least so for the N80. The S65, although exhibiting the least difference in modulus, has a UTS 50% lower in CO₂ than in air. The fracture surfaces in ambient air and in 4 MPa CO₂ are shown in Figs 11 and 12. Examination of these shows consistently smoother fracture surfaces in CO₂ than the equivalent tests in air.

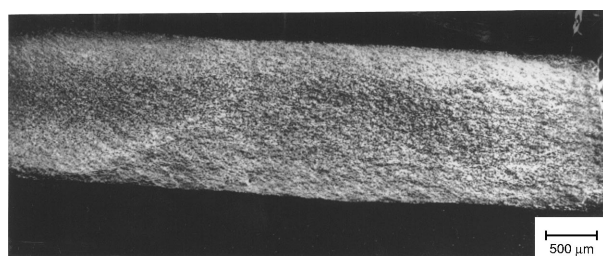


(a)

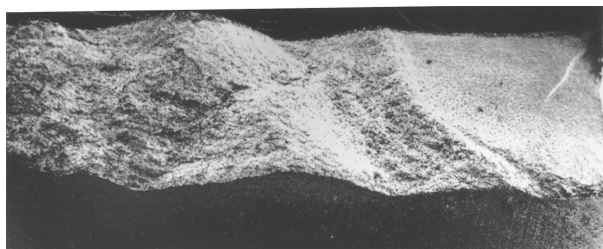


(b)

Figure 11 Fracture surfaces of F80 tested in (a) 4 MPa CO₂ and (b) ambient air.



(a)



(b)

Figure 12 Fracture surfaces of N80 tested in (a) 4 MPa CO₂ and (b) ambient air.

Apart from the change in fracture surface morphology, there is another indicator as to the reasons for the substantially different behaviour in high-pressure CO₂. For the samples tested in air, the stress/strain curves rise most steeply over the first 20% strain. This effect is thought to be due to the interaction between the rubber and the filler particles involving load sharing between the shortest chains. This effect is completely absent for the samples tested in high-pressure CO₂.

The smooth morphology of the fracture surfaces and the absence of the initial steep rise of the stress/strain curve point to a mechanism of plasticization by the high-pressure CO₂. By analogy with the effects that occur in elastomers swollen by liquid organic solvents [14–21], the plasticization by high-pressure CO₂ could lead to the disruption of filler–polymer bonds, as well as the polymer–polymer entanglements. This, in turn, will result in reduced load sharing, leading to a lower strength, lower modulus without the initial steep section of the curve, lower elongation at break and a smoother fracture surface.

3.3. Effects of findings on the depressurization resistance of elastomers

It is clear that the strength, stiffness and elongation to break of a range of elastomers are all significantly reduced by the presence of high-pressure CO₂. This is of great importance to the understanding and particularly the theoretical modelling of decompression damage, and it is possible that substantial revision of current ideas are needed. To develop the full understanding of the properties of elastomers in high-pressure CO₂, it will be necessary to investigate tear strengths as well as the effects of pressure and temperature; aspects that will be covered in future papers.

4. Conclusions

1. Elastomer seal materials (fluorocarbon, nitrile and silicone) are substantially weakened when saturated with high pressure (4 MPa) CO₂. The modulus also falls slightly.

2. Fluorocarbons are very slightly strengthened in high pressure (4 MPa) nitrogen; nitriles and silicones are unaffected.

It is concluded that high-pressure CO₂ has a plasticization effect on the elastomers and has important implications to the understanding of depressurization damage.

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