EFFECTS OF APPLIED STRAIN ON RATES OF AGEING
Project overview

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SYNOPSIS

Several procedures were used during Phase 1 for applying strains to Coflon and Tefzel samples during fluid ageing exposures at elevated temperatures and pressures. With a limited number of exposures in chemically-hostile Fluid F, application of strain increased modulus, but no effect was found with crack growth testing. For other fluids, an initially-unexpected apparent modulus loss was observed for Coflon whenever strain was applied during ageing or deplasticization. A possible rationale for this behaviour is given. One specific fluid/strain combination, with methanol, was identified as being an example of environmental stress cracking, and being physico-chemical in nature.

The potential for accelerating chemical deterioration when stress or strain is applied to a polymer is the stored energy thus created, which depends on both of these factors. Difficulty in assessing effects of the strain/chemical combination arose from the general chemical resistance of these polymers (especially Tefzel) and reductions in tensile stored energy due to stress relaxation and deplasticization. This behaviour is less likely in flexible pipe service. Here, compressive stresses arising hydrostatically from the fluid pressure are maintained more-or-less at a constant level, with tensile forces from pipe weight, bend configuration, and dynamic motions being superimposed on these. The stored energy associated with compression is not easily released because of its stabilizing effect. However, when tensile strains are introduced the stored energy could now be released, and in the dynamic situation crack formation and growth is a possibility, perhaps leading to fatigue failures.

It is therefore concluded that Coflon, which during Phase 1 has exhibited some changes due to chemical reactions, should be examined for the combined chemical/strain effect in long-term tests during Phase 2, but not employing the current modes of straining. Although each mode used applied tensile forces to a greater or lesser extent, none of them maintained stored energy at a high level throughout exposure and up to final testing. A method for applying constant stresses (which should maintain high storage energy levels) under severe conditions of temperature and pressure has been designed to a preliminary stage, for development and application early in Phase 2. This would represent some features of the service situation more realistically, and would produce more severe conditions than previously employed.
1 INTRODUCTION

One of the stated intents of this project has been to make some assessment of effects of strain on rates of ageing of project thermoplastics exposed to project fluids. To this end, certain straining jigs which apply in various modes - tensile, four-point bending and crack growth using compact tension samples - were designed and made for holding samples during fluid exposures. During testing, features of the thermoplastics have been observed which have tended to confuse apparent strain effects on the polymers' aged performance, but recent assessments of the topic and its data have led to considerable progress being made in identifying test procedures necessary for strain and related effects on chemical deterioration to manifest themselves. It is the intent of this report to provide a summary of what has been determined on strain and related effects thus far, and provide recommendations for clarifying them in Phase 2 by means of further test procedures which will increase and focus the severity of the conditions applying.

The choice of flexible pipe rather than umbilicals service for assessing service strain conditions reflects the major interest of project members. However, Tefzel data are still provided.

2 BACKGROUND

There are numerous instances cited in the literature where polymers have been exposed to hostile fluids and applied strains at the same time, and resulting degradation has been more rapid than the same exposures with no strain. The so-called geosynthetic polymers employed in civil engineering for foundation purposes provide a good illustration. Horrocks\textsuperscript{1,2} has published many papers in this area showing, for example, how the durabilities of polyethylene, polypropylene and polyamides are reduced in air when strains are applied or residual stresses exist. With these polymers, their susceptibility to chemical attack has meant that, at very low strain rates, a change in the failure mode from ductile to brittle can occur. This particular feature has been discussed in CAPP/M.14, and is not the main theme of the present report; rather, it is whether the additional application of strain to a polymer when exposed to fluid hastens failure onset for project polymers, irrespective of its mode. It is also worth noting that Horrocks consistently refers to effects of stress rather than strain. Clearly, these are related but, with time, effects of stress relaxation and/or creep alter the details of the relationship. The common feature arising from both at any time is the stored energy in the polymer associated with these processes, which provides the potential for failure.

An extreme manifestation of the combination of the type of effects in question is known as Environmental Stress Cracking (ESC). Certain polymers gain their strength not by the presence of crystals, as with PVDF, ETFE, etc, nor by the crosslinking of amorphous polymer (e.g. natural rubber and other elastomers), but by gelation - the production of thermoreversible amorphous gels which form during cooling after processing because of a myriad of interactions between local molecular chains (e.g. polymethylmethacrylate PMMA, or polyvinyl chloride PVC). This last class is particularly prone to ESC, as described by Wright\textsuperscript{3} who, in giving a verbal presentation of the work covered by this reference, showed how a drop of appropriate liquid placed on the outer surface of a strip of PMMA bent by end-constrained flexure caused it to fracture into two parts after 10 minutes or so at room temperature. Liquids containing hydrogen-bonding components of the solubility parameter $\delta$ in the range 2.5 to 4.5 (cal/cm$^3$)$^{1/2}$ were the most likely to bring ESC about for PMMA, although all fluids
do so to a degree. Whatever the reason for this range, it seems that the combination of applied strain and a physico-chemical effect can accelerate failure. This is the most common form of ESC, but with gaseous fluids genuine chemical attack can also cause it, e.g. ozone-cracking of elastomers under strain.

3 IMPLICATIONS OF CHEMICAL/STRAIN INTERACTIONS IN THE FLEXIBLE PIPE PRESSURE SHEATH

The main strain features for the pressure sheath of a flexible pipe during service are

(i) the expansion of the pressure sheath against the constraining outer zeta layer induced by fluid pressure
(ii) static bending up to a minimum bend radius, plus possible dynamic motions (for risers at least)
(iii) end fitting restraints
(iv) weight effects for risers

Feature (i)
At equilibrium (i.e. after any adjustments in pipe length and diameter have settled down) any strains will arise because of essentially isotropically-applied compressive stresses. Secondary features will include the tendency of the sheath to creep ("extrude") into the small helical gap which exists between individual windings of the zeta layer. For this extruded helical polymer ridge in a static situation, stress relaxation at the tip will occur. If stress concentrations arise during initial application of pressure, or when pressure is changed, stress redistribution may apply locally.

Feature (ii)
The largest tensile strains will occur at the bent outer surface of the sheath when the pipe is unpressurized. When internal fluid pressure is applied, the compressive component (Feature (i)) will act to reduce these tensile strains, and so will stress relaxation. Any additional dynamic movement of the pipe will act to change the tensile strains, increasing them if the bend radius is reduced and vice versa.

Feature (iii)
This will be localised at the points chosen by design to bring about clamping during the swaging operation. Stress redistribution and dimensional changes due to deplasticization could be important factors here, but use of suitable geometrical features should minimise their effect.

Feature (iv)
Risers will be subjected to some tensile strains due to the weight of the pipe (and its contents).

The essentially-hydrostatically compressed polymer in the situation described as Feature (i) will possess a high stored energy, but with little potential for its rapid release because of the hydrostatic constraining effects from applied and reaction compressive forces. Even if a crack
existed in the compressed polymer sheath, under these conditions constraints would act to close it. In addition, the increased proximity of other morphological features (e.g. crystalline regions) in the polymer due to compression would produce interactions contributing to the slow rate of stored energy release. As a contrast, retained tensile forces from any bending and pipe weight, and the tensile motions associated with dynamic situations (Features (ii) and (iv)) could lead to a high potential for stored energy release. In the extreme, these could lead to fatigue failure if (for whatever reason) cracks form and grow due to the cyclic motions.

With the possible exception of end-fittings, the construction of a flexible pipe is such that it is highly improbable that failure will occur by bursting during a single event; if failure were to occur, a fatigue mechanism is more likely. The crack-initiation stage might be influenced by a loss of mechanical property levels under circumstances of high stored energy release rate. This property loss could be chemically induced. In a dynamic situation, if for instance the extruded helical ridge of polymer in the zeta layer winding gap became brittle, the tensile forces introduced in outer surface regions could allow rapid release of sufficient stored energy to shear-off the ridge in places; this would form circumferential cracks which would not initially be deep but whose rate of growth would depend on details of the dynamic motion. The strain applied could also increase chemical rates. A similar overall argument might apply to certain features in end-fittings, particularly at the region where the pipe meets the metal fitting with consequential localized large changes in strain.

These possibilities mean that the comments in section 2 concerning the hastening effect of the strain/chemical-reaction combination could be relevant to the flexible pipe situation. This point was recognised at the start of Phase 1, but only with the work performed in this phase have certain salient points come to light. For accelerated testing, appropriate stresses containing tensile components should be maintained throughout, preferably up to and including final evaluation testing. The procedures adopted and the data obtained in Phase 1, described in the following section, have led to initial discussion (section 5) of an improved procedure for following chemical/strain effects in conditions more appropriate to flexible pipe service.

4 APPLICATION OF STRAINS IN PROJECT WORK

4.1 Bending by end-constrained flexure

CAPP/M.6 Rev A described how the exposure of Coflon to 100% methanol (Fluid A) at 140°C and vapour pressure (conditions more severe than those likely to be met in service) resulted in its complete degradation to solution, and then to powder on cooling. The same result occurred for strained and unstrained samples; however, the strained (by end-constrained flexure - see Figure 1(a)) samples degraded ca50% more quickly than the unstrained, via a cracking mechanism (Figure 1(b)). The overall mechanism proposed was a physico-chemical one, the hot methanol dissolving amorphous PVDF as a first step. With strain, the onset of cracking right through the sample exposed more sections to the methanol for easy access and onset of dissolving. It can now be seen that the cracking process was an example of ESC; methanol displays a significant level of hydrogen-bonding component. The fact that PVDF (in this context) is semi-amorphous rather than fully amorphous (cf
PMMA etc in section 2) probably explains why the high temperature is required. It should be noted that this phenomenon was not observed at 5000psi, at least during the test times employed. Hydrostatic compaction at 5000psi presumably inhibited any swelling associated with the dissolving stage of this phenomenon observed at vapour pressure, to reduce the rate of dissolution significantly.

An advantage of end-constrained flexure for bringing about such failures is demonstrated by this work. As a colleague points out, this bending mode, brought about using no jig but by means of the sample strip ends, maintains stress in mid-sample regions even if some stress relaxation occurs (see later).

4.2 Tensile mode

Strains in the tensile mode were applied to samples whilst ageing in test fluids at various stages during the project. The jigs to do this are illustrated in Figure 2. Tables 1 and 2 show all of the data obtained for Coflon and Tefzel respectively, collated mainly from other CAPP reports, but also including a few previously-unreported results.

Project fluids used for exposures discussed herein are:

- Fluid A: 100% methanol
- Fluid B: 97/3 CH4/CO2 + saturated water vapour (SWV)
- Fluid C: 97/3 CH4/CO2
- Fluid F: 94/5/1 CH4/CO2/H2S + SWV + 1% ethylene diamine (in the water below producing the SWV)
- Fluid I: 35/35/20/10 Heptane/cyclohexane/toluene/1-propanol

4.2.1 Coflon
In Table 1, the first comparison to be made is between the unaged unstrained control, and deplasticized samples - one set of samples unstrained and the second being strained to 7.5% during the deplasticization process (conducted under nitrogen in an oven at 140°C). Clearly the actual event of deplasticization has the major effect on modulus. An increase of 85% in modulus occurred for the unstrained samples, and an increase of 60% for the strained ones. Rather than increase the modulus change, application of strain has apparently reduced it. An explanation is considered for these differences after discussing the aged data. A mention of other tensile-related factors is also made later.

Strains were applied to Coflon samples aged in Fluids A, C, F and I. The reasons identified for the modulus changes in unstrained samples have already been collated in CAPP/M.10 Rev A, with details in CAPP/M.3, /M.7 and/or /M.12 Rev A, i.e. for the gases, Fluid C has softened Coflon after 2 weeks at 140°C because of extra plasticization by gas; for the liquids, Fluid I reduces modulus slightly due to a little swelling, and A causes more softening and swelling, having a solubility parameter nearer to that of PVDF (Coflon) than does Fluid I. Whichever of these reasons applies, for all of the tests referred to in Table 1 except Fluid F exposures, the application of strain reduced the modulus, and further strain reduced it even more. The observation of strain-induced reduction agrees with that for deplasticization (previous paragraph), even though in that case a general increase in modulus had occurred. cont on p.6
### TABLE 1  Effects of strain/ageing* combinations on mean Coflon tensile data

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Applied strain during ageing</th>
<th>Ageing temp/time</th>
<th>Modulus (1%)</th>
<th>Yield stress</th>
<th>Yield strain</th>
<th>Ultimate strain</th>
<th>Permanent set*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>0 (°C/weeks) 785 (MPa)</td>
<td>36 (MPa)</td>
<td>22 (%)</td>
<td>63 (MPa)</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂-deplasticized</td>
<td>0 (°C/weeks) 1450 (MPa)</td>
<td>47 (MPa)</td>
<td>9 (%)</td>
<td>29 (MPa)</td>
<td>-5 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂-deplasticized</td>
<td>140/2 (°C/weeks) 1256 (MPa)</td>
<td>54 (MPa)</td>
<td>26 (MPa)</td>
<td>0 (MPa)</td>
<td>1.8 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 0 (°C/weeks) 483 (MPa)</td>
<td>30 (MPa)</td>
<td>1256 (MPa)</td>
<td>54 (MPa)</td>
<td>26 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 20 (°C/weeks) 588 (MPa)</td>
<td>35 (MPa)</td>
<td>711 (MPa)</td>
<td>38 (MPa)</td>
<td>72 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 20 (°C/weeks) 522 (MPa)</td>
<td>41 (MPa)</td>
<td>711 (MPa)</td>
<td>38 (MPa)</td>
<td>69 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 140/2 (°C/weeks) 551 (MPa)</td>
<td>37 (MPa)</td>
<td>711 (MPa)</td>
<td>38 (MPa)</td>
<td>69 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F 140/2 (°C/weeks) 675 (MPa)</td>
<td>37 (MPa)</td>
<td>711 (MPa)</td>
<td>38 (MPa)</td>
<td>69 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I 140/10 (°C/weeks) 658 (MPa)</td>
<td>38 (MPa)</td>
<td>711 (MPa)</td>
<td>38 (MPa)</td>
<td>69 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Strained in tensile mode, aged at 5kpsi (except N₂-deplasticizations, at ambient pressure)
+ Length increase (despite general mass loss from deplasticization)
NM = Not measured
NB Tensile strengths are not shown as these are taken as the maximum stresses reached, and for Coflon they coincide with yield stresses.

### TABLE 2  Effects of strain/ageing* combinations on mean Tefzel tensile data

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Applied strain during ageing</th>
<th>Ageing temp/time</th>
<th>Modulus</th>
<th>Yield stress</th>
<th>Yield strain</th>
<th>Tensile strength</th>
<th>Ultimate strain</th>
<th>Permanent set*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>0 (°C/weeks) 920 (MPa)</td>
<td>25 (MPa)</td>
<td>39 (MPa)</td>
<td>375 (MPa)</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 0 (°C/weeks) 715 (MPa)</td>
<td>25 (MPa)</td>
<td>44 (MPa)</td>
<td>35 (MPa)</td>
<td>351 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 140/2 (°C/weeks) 700 (MPa)</td>
<td>24 (MPa)</td>
<td>40 (MPa)</td>
<td>38 (MPa)</td>
<td>384 (MPa)</td>
<td>(-3.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 7.5 (°C/weeks) 670 (MPa)</td>
<td>26 (MPa)</td>
<td>42 (MPa)</td>
<td>36 (MPa)</td>
<td>327 (MPa)</td>
<td>2.6 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 20 (°C/weeks) 670 (MPa)</td>
<td>26 (MPa)</td>
<td>38 (MPa)</td>
<td>36 (MPa)</td>
<td>314 (MPa)</td>
<td>6.1 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 0 (°C/weeks) 681 (MPa)</td>
<td>24 (MPa)</td>
<td>34 (MPa)</td>
<td>NM (MPa)</td>
<td>NM (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 7.5 (°C/weeks) 695 (MPa)</td>
<td>24 (MPa)</td>
<td>27 (MPa)</td>
<td>NM (MPa)</td>
<td>NM (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 20 (°C/weeks) 682 (MPa)</td>
<td>26 (MPa)</td>
<td>34 (MPa)</td>
<td>NM (MPa)</td>
<td>NM (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I 0 (°C/weeks) 551 (MPa)</td>
<td>19 (MPa)</td>
<td>25 (MPa)</td>
<td>30 (MPa)</td>
<td>333 (MPa)</td>
<td>0 (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I 140/10 (°C/weeks) 583 (MPa)</td>
<td>19 (MPa)</td>
<td>21 (MPa)</td>
<td>36 (MPa)</td>
<td>433 (MPa)</td>
<td>NM (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Strained in tensile mode, aged at 5kpsi
+ Length increase (no mass loss)
NM = Not measured
NB From the bimodal shape of the curves obtained, tensile strength ("maximum stress") values do not coincide with yield stress for Tefzel.
Two possible reasons for this strain effect are:

(a) the effective shifting of the stress/strain plot zero to a point a little along the original curve due to the production of permanent set (see Table 1, right-hand column), which would lessen 1% modulus values because of the curve’s gradually-reducing gradient from the onset.

(b) cavitation at crystalline/amorphous interfaces caused by the initial application of strain when applying the straining rigs before the exposures - leading to reduced density and/or increased capacity for fluid absorption.

Regarding a morphological explanation for (a), crystalline regions or portions, or even molecules, would be moved during the original application of force with respect to their relative positions with surrounding crystallites, molecules etc. Further molecular adjustments would lead to stress relaxation, to reduce the restoring force. When the straining jig is removed, the reduced restoring force is not sufficient to move all of them back to their original locations - probably finally causing some local internal “negative” residually stressed regions. Both (a) and (b) are concerned with physical, not chemical, origins, as would be expected for those fluids which are not chemically aggressive.

In contrast, Fluid F is somewhat chemically aggressive to Coflon (CAPP/M.10 Rev A and /M.12 Rev A). The data in Table 1 refer to Coflon Batch #4; by interpolating between the 2 week/120°C and 6 week/120°C unstrained moduli, a value of 870MPa would be expected for a 4 week exposure. The strained value at 4 weeks/120°C (again with Batch #4) was 863MPa, an increase of 12% (or even more if the physical effects discussed above are superimposed). This suggests an effect attributable to a strain/chemical combination. The point was not pursued further because of complications arising for Fluid F ageing due to one atypical Coflon batch, “Batch #2”, which exhibited significantly more stiffening than other batches, as well as to deplasticization and stress relaxation. The other chemically-hostile project fluid (G) was not employed because the surface cracks observed in unstrained samples after ageing in G would alter the stress/strain plots, and associated data magnitudes, to give spurious values for modulus, etc. Further implications with regard to the possibility of stress/chemical interactions are discussed in section 5.

Regarding tensile properties other than modulus, yield stress may increase with applied strain, but in a haphazard way, and no trends were observed for the other properties. One implication from the ultimate strain values for Fluid F supports the comments above that applying strain during exposures enhanced chemical change somewhat.

4.2.2 Tefzel

The Tefzel moduli in Table 2 exhibit an apparent (but small) reduction with increasing strain after Fluid A exposures (with some permanent set), but with Fluids C and I no such trend is shown. Inspection of the original stress/strain Tefzel plots (not included herein) shows that in general the low-strain linear stage is longer than for Coflon, perhaps explaining how the effective shift of the zero brought about by testing after the application of strain (as discussed above) would not reduce the measured 1% modulus here to the same degree as for Coflon. Inspection also indicated that the linear stage was perhaps shortest for Fluid A exposures, suggesting why there may be a small observed trend of modulus reduction with increasing strain in this case. No trends relating other tensile properties and strain were observed.
As discussed in Tefzel correlation report CAPP/M.13 Rev A, no evidence was found in Phase 1 of any chemical deterioration of Tefzel: hence the minimal effect of strain observed to date is not surprising. Further discussion is given in section 5.

4.3 Other straining modes

The compact tension straining jigs were employed for several Coflon samples to widen the crack gap by 1mm (thought to provide a strain around the crack tip of ca 8%) and 2mm during 7 day/140°C exposures to Fluid C at 5kpsi (CAPP/M.3). Static fracture toughness measurements were made. The 1mm strain lowered fracture resistance considerably from that of the unstrained value, but the 2mm strain only caused a marginal decrease from this control: crack blunting at the higher strain was thought to be a factor here for the second stage.

Dynamic crack growth fatigue tests were used for two other examinations. Coflon samples were subjected to 7% strains by 4-point bending during 4 week/140°C exposures at 5kpsi in Fluid B (CAPP/M.5). After removal from the pressure vessel, compact tension samples were cut out of the larger, strained, 4-point bending ones. The crack growth rate at lower J values when strained was 5 times faster than the unstrained equivalent, even with the non-chemical nature of Fluid B. Further dynamic testing was conducted on samples strained during exposures to the chemically-hostile Fluid F: in this case, lmm strains were applied to compact tension samples, which were compared with unaged controls subjected to the same exposures. The crack growth resistance (value of J giving a crack growth rate of 10nm/cycle) was 2.2 kJ/m² for both strained and control unstrained samples (CAPP/M.12 Rev A). This equivalence applied to the full crack growth rate versus J plots (Figure 32 in that report). Hence from the limited number of data available after chemical ageing, no evidence of any chemical/strain interaction was observed in dynamic testing.

The severe chemical attack of Fluid G on Coflon caused surface crack formation. Hence no crack growth testing was performed on these samples because, if it had been, a proportion of the energy applied would have been used in growing these surface cracks: it would not be clear how much of the applied energy was used for growing the main crack in the contact tension sample. With strained samples, a further complication might have been growth of these random surface cracks during exposures due to the strain application: although this could have demonstrated a combined chemical/strain effect, it would not have been a measurable effect.

The reasons for the paucity of strained samples for dynamic testing arise from the lack of samples aged in Fluid G as just discussed, and because the degree of strain applied to exposed samples generally was difficult to quantify at the end of the exposures, due to stress relaxation and (for Coflon) deplasticization. This was graphically illustrated when a number of Coflon samples, after being strained in the 4-point bend jig for various exposures, could subsequently be removed from the jig with the fingers, without loosening the clamping bars at all. On these occasions, relaxation and deplasticization focused locally around the bars, with a prominent permanent set to the profile of the jig being taken up. These methods of straining did not retain stored energy well enough to examine whether any combined strain/chemical effect should occur.
5 DISCUSSION

As described under Background in section 2, other studies in other applications with certain polymers have led to observations of effects of increased property deterioration rates when chemical ageing and strain are applied together. The combination of chemical reaction and high stored energy associated with the tensile mode must be available for any accelerated chemical/strain polymer degradation to occur. High stored energy may increase chemical reaction rates somewhat and, if present in tensile "quick-release" form, also provide the means of bringing about crack growth once any chemical change has caused appropriate properties to deteriorate sufficiently. In highly-reinforced flexible pipes, tensile strains arise from bent configurations, pipe weight and dynamic motions.

In the work for CAPP Phase 1, with one exception, the strain-induced deteriorations observed for Coflon and Tefzel have been of a physical or physico-chemical nature. However, because of

(i) the significant but not absolute chemical resistance of Coflon,
(ii) the reduction of stored energy with increasing time in the straining jigs used,

it may be the case that use of higher severity long-term tests during which stored energy is not significantly reduced will cause some deterioration of Coflon. It cannot be stated with certainty that chemical deterioration of Coflon induced by stored energy release will not arise in flexible pipe service in the long term. For risers, tensile stresses are present constantly from weight considerations, and more tensile stresses arise from the pipe's configuration as a bend; although the latter stresses are subject to stress relaxation, this will be opposed somewhat in dynamic applications. The pipe situation here is strictly neither one of constant stress nor constant strain but somewhere in-between, and probably nearer to constant stress when dynamic tensile motions are involved.

For laboratory long-term testing, it is necessary to choose methods which maintain a high degree of stored energy in the tensile mode whilst exposing polymer to a chemically-aggressive fluid at high pressure. This is easier to achieve for a constant stress test regime than for tests allowing some stress relaxation. Furthermore, a reasonable accelerated simulation of some features of the dynamic pipe situation is then implied for such methods. Although the tensile straining jigs used in Phase 1 led to some stiffening in Fluid F, the initial storage energy level diminished. Even the use of end-constrained flexure, which contains tensile components and is not associated with local high stress concentration regions, is subject to overall stress relaxation. However, the dead-weight tests proposed in CAPP/M.14 for investigating ductile-to-brittle transitions at very low strain rates would satisfy all of these criteria except for the important one of high pressure. A method for equivalent procedures for applying a constant stress at high pressure exposures, using the test fluid's pressure as the means of applying the required initial hydrostatic strain via a sealed plunger, has been designed to a preliminary stage. It is considered that appropriate long-term tests which examine combined chemical/strain effects in the correct manner can be set in operation early in Phase 2.

Associated with the permanent set observed in strained aged testpieces during Phase 1, some residual stresses might exist. However, these would have formed after the exposures, during cooling, as thermal stresses, so would not have accelerated chemical ageing in any way. They may be one reason for modulus reductions noted after ageing (cf section 4.2.1). To examine the possibility of chemical/residual-stress combinations, samples would need to be bent for
some time in a straining rig in the open laboratory, removed from the rig and then aged in appropriate fluid, comparing with an unstrained control.

Regarding Tefzel, its high chemical resistance may mean that, even with high strains for long times, no degradation will occur. However, the same long-term tests can be applied if necessary.

In keeping with participants' wishes expressed at the Steering Committee meeting in San Marcos (December 1996), an amine-containing hydrocarbon fluid with saturated water vapour (rather than methanol-based Fluid G) should accompany Fluid F to make up the two fluids for this (and other) long-term ageing work.

6 CONCLUSION

One example of the stiffening of Coflon tensile samples deriving from combined chemical/strain effects was observed during Phase 1. An examination of associated factors has led to the opinion that they may occur to a greater degree in long-term exposures of Coflon. The factors considered include:

- In flexible pipe service, the basic strain is applied in compression, with additional tensile strains arising from the 'bend' configuration of a riser, the pipe's weight, and dynamic motions. Stress relaxation does not occur generally, but only in specific local regions. Where tensile forces are applied, crack onset could occur if sufficient embrittlement from chemical means should occur. The tensile strain could cause quick release of stored energy, to exacerbate the chemical reaction rate. In dynamic situations, this could lead to crack growth and fatigue problems.

- Both Coflon and Tefzel (especially) possess a considerable chemical resistance (one reason for the minimal deterioration observed) -

- however, Coflon does exhibit some evidence of chemical susceptibility (a degree of stiffening after 4 weeks ageing at 120°C, which was enhanced by applied strain). Tefzel did not provide any such evidence.

- With laboratory testing, stress relaxation and (for Coflon) deplasticization meant that applied (tensile) stored energies dissipated with time (another reason for the minimal deterioration). A more appropriate constant stress test which would maintain high stored energy levels is required for Phase 2 long-term exposure testing.

An initial design for a constant stress test operating at elevated temperatures and pressures, planned for Phase 2 long-term tests, involves the use of the fluid pressure to apply constant stress hydrostatically. (Existing rigs could be employed to examine whether any residual stress effects exist.)

In one specific case, the strain-accelerated deterioration of Coflon found in Phase 1 for methanol at 140°C is considered to be an example of environmental stress cracking, and being physico-chemical in nature.
REFERENCES


4 M Samulak, personal communication.
**Fig. 1(a)**  Coflon sample bent by end-constrained flexure at 140°C and vapour pressure - initial arrangement (x2.5 magnification)

**Fig. 1(b)**  After 6 hours of exposure as above, showing environmental stress cracking (x3.5)

**FIGURE 1**  Coflon sample during a methanol exposure test in a glass-ended cell
FIGURE 2  Standard tensile testpiece and the environmental applied-strain holding fixtures for exposure to high pressure fluids at 3%, 7.5% and 20% tension