CAPP

International Research Project on the Effects of Chemical Ageing of Polymers on Performance Properties

DEGRADATION OF COFLON IN
METHANOL AT TEMPERATURES
AROUND 140°C

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SYNOPSIS

An unexpected result of immersing Coflon samples in methanol at 140°C and at vapour pressure during a scheduled exposure exercise to give samples for other tests was that the samples degraded completely to lose all mechanical integrity. Further tests were performed using a cell with glass end plates to permit observation of the phenomenon. At 140°C using samples subjected to bending strain, complete fracture was observed after 6 hours, followed by surface delamination after 24 hours and disintegration after 8 days. Even unstrained samples had deteriorated, although probably not so rapidly. At temperatures below ca135°C, samples remained intact after medium-term methanol exposures. However, in fatigue work reported in CAPP/M.5, even at 130°C crack growth rate of Coflon after methanol exposure is significantly faster than at lower temperatures.

The phenomenon is less pronounced at high pressures. At 140°C and 5000psi only initial signs of deterioration were seen.

A mechanism involving the amorphous phase of the PVDF and interaction with various changes which can occur in the crystalline regions is discussed. It remains to be established whether Arrhenius-type relationships exist for use in life predictions: these may not apply if the degradation occurs above a critical temperature. The effects of strain may be to increase the deterioration rate and lower the temperature of α-γ transitions in the crystalline structure, when boundary segments may be susceptible to solvation by methanol already in the amorphous phase. Various tests and procedures, involving service-related conditions, have been proposed to resolve the questions.

Methanol can also exacerbate chemical attack of Coflon by amine at high temperatures and pressure.

1   INTRODUCTION

An unexpected and significant physico-chemical degradation of Coflon PVDF specimens was observed at the end of 1994 during routine scheduled exposure exercises on strained material. The intent was to age various samples, including some strained in a 4-point bend configuration, in methanol at 140°C and subsequently submit the aged samples to various tests including dynamic fatigue and fracture toughness. However, as will be seen below, the samples deteriorated to such an extent that such testing was not possible: only when conditions were made less severe was it found possible to perform such testing, as reported in CAPP/M.5. The purpose of the current report is to describe the nature of the PVDF deterioration observed during a number of tests performed to examine this phenomenon.

This report also records, as Appendix 1, some SEM/X-ray microanalysis data on Coflon samples exposed to a methanol/amine mixture, and to other amine or H_2S-aged samples. The samples were not forwarded to TRI for analysis due to lack of time.

2   STRAINED AND UNSTRAINED COFLON IN HOT METHANOL

An initial methanol exposure test at 140°C was performed in the absence of high pressure (i.e. at methanol's vapour pressure of *ca*150psi at this temperature) on strained 4-point bend Coflon samples. Initially, a 6-day test incorporating 14% straining of this type led to several transverse cracks right through the sample: these had occurred at the positions of maximum bending strain (see Figure 1, showing the sample after removal). A duplicate test was run for 2 weeks. On opening the pressure vessel after cooling, the consequences of severe degradation of the Coflon could be seen: only a hollow shell of the sample remained in the 4-point bend rig, as shown photographically after removal from the cell in Figure 2(a), and the methanol colour had changed to a brassy yellow. In addition, an apparently gelatinous deposit had formed at the bottom of the cell (see Figure 2(b), after removal). This was yellow when first observed, but became off-white on drying. Some more crystals were also obtained after evaporation of the remaining methanol and recrystallization.

2.1   Tests using a cell with glass end plates

2.1.1   Tests at 140°C and vapour pressure
A cylindrical flanged pressure cell was manufactured suitable for using smooth thick glass end plates which were sealed against the flanges using rubber gaskets. A test was carried out using this cell to repeat the 2-week procedure above with fresh testpieces: again a strained 4-point bend testpiece was used, together with several unstrained samples. In the event, use of an external thermocouple for this first test with this cell resulted in the internal temperature actually being a few degrees below the required 140°C, so that the final deterioration of the Coflon samples was not so great as before. It was also realised during this test (which lasted 14 days) that the 4-point bending rig obscured much of the strained sample, making viewing difficult. However, a number of observations were possible:

1 The methanol expanded rapidly as it heated up, almost completely removing the small air gap which had been left.
2 After 1 day, the methanol had turned to a yellow/orange colour.
3 After 1 day, a dark band, parallel to the sample face, had developed across the centre of the end face of the most visible unstrained sample (see Figure 3(a), showing the sample *in situ*).
4 After 2 days, the air gap had apparently re-appeared. Minuscule bubbles could be seen forming. Apparently a dissolving process was occurring so that the overall solid/liquid volume present was reducing. No evidence of massive dissolving could be seen.
5 During the period 2-14 days, the fluid yellow colour darkened, but no massive sample deterioration occurred.

After the test finish and cell dismantling, inspection of the samples showed that those in the bending rig had fractured significantly at the bending points (Figure 3(b)). Other cracks, some orthogonal to the main fractures, had also been formed. The observation of some strands at the surface (Figure 3(c)) agreed with the suggestion that dissolving had commenced, albeit more slowly than in the initial test. The unstrained samples, although intact, were in some cases a little bent and also showed numerous fine cracks right through their thicknesses, plus surface discolorations (Figures 3(d) and 3(e)). Strain may not be essential to the phenomenon occurring, but may affect the kinetics.

A further repeat test was performed with the glass-ended cell in which the drawbacks met in the previous test were overcome by modifications to the procedure. By use of extra HP fittings, a means of introducing a thermocouple into the cell and into the methanol was constructed, to ensure that test temperature (140°C) was now known to be accurate. To avoid the problem of the 4-point straining rig obscuring vision, bending strain was applied to two bar samples of length a little longer than the inner diameter of the cell, by bending them lengthways by hand before putting them into the cell. Again, some unstrained samples were added. Figure 4(a) shows the arrangement at the start of the test, with one (upper) strained sample located in front of the second (lower) strained sample, with an unstrained sample behind that. Within 6 hours, significant deterioration had occurred (Figures 4(b) and 4(c)). One strained sample had fractured almost completely, and a small crack had formed in the second (shown in Figure 4(c) near an unstrained sample). After 24 hours, the second strained sample had also fractured completely, and samples also exhibited many signs of surface delamination, with the dark central band seen before visible - as shown in Figure 4(d) for the first strained sample (now in two separate pieces). The unstrained samples also now exhibited surface delamination.

Over the next few days, the yellow colour of the test liquid darkened somewhat and became opaque, eventually obscuring further observations. After 8 days the test was terminated. On opening the cell, a fused mass of degraded material, similar to the initial 13-day exposure result, was observed. Both strained and unstrained samples had deteriorated drastically during the exposure.

Some equivalent tests have been performed at 120°C and 130°C, but only of limited duration - 5 days at 120°C and 4 hours at 130°C - in order to obtain samples for fatigue testing. No visual deterioration was observed on these samples, but after the 130°C

exposure a large increase in crack growth rate was measured compared with the rate following exposures at 120°C (CAPP/M.5). Hence a significant deterioration in fatigue resistance occurs as methanol temperature is raised to 130°C.

2.1.2   Test at 140°C and 5000psi

As part of the routine exposure exercises for providing aged samples for fracture, fatigue and mechanical property testing, 4-point bend strained testpieces plus unstrained samples were exposed to methanol at 140°C and 5000psi for 2 weeks. The samples removed afterwards were all intact, but had shrunk (for instance, the strained sample could be pushed out of the 4-point rig using the fingers without the need for unclamping, as permanent set had accompanied the shrinking). Samples were now a translucent brown colour, with a darker brown central region. Some, but not all, samples had bent somewhat in the lengthways direction. A thin deposited film of material resembling the degraded material discussed in section 2.1.1 covered small portions of some testpieces and other surfaces. Apparently a minor amount of degradation had occurred, but not sufficient to prevent subsequent mechanical testing: deterioration was much less than with the unpressurised exposures.

3   DISCUSSION OF DEGRADATION MECHANISMS

It is clear from the observations from these experiments that Coflon PVDF degrades quite quickly in methanol at 140°C and vapour pressure to an extent where it loses its integrity completely. It is known that dissolution occurs at least to some degree, because PVDF was recrystallized out of the solution after these exposure tests. In unaged PVDF, only approximately 50% of the material is crystalline[1], the remainder being amorphous. It is well-established that amorphous polymers will absorb liquids of a similar solubility parameter δ at ambient temperatures: for PVDF, such solvents (such as dimethyl formamide) possess a δ of about $12(cal/cm^3)^{1/2}$, so that δ for PVDF must also be in this region. The methanol δ value is 14.5 units, which is sufficiently close to 12 to allow absorption by amorphous PVDF, especially perhaps at high temperatures - providing the amorphous phase is accessible.

It is likely that, just as for Tefzel (as described in report CAPP/M.4) hot methanol ingress into Coflon occurred during this work through sample edges or any other exposed sections (e.g. cracks) which cross the extrusion direction of the material at right angles. (This mode of ingress is unlikely to occur in service: for Tefzel it occurred at least 10 times more quickly than ingress through the large surfaces of the samples, equivalent to inner pipe surfaces in service. No equivalent data have been obtained yet for Coflon.) Hence, in the present work, one effect of strain is apparently to bring about cracks more rapidly during high temperature exposure, to open up new surfaces and increase accessibility to methanol ingress. Applied strain therefore contributes to the kinetics of the degradation at least. In contrast, the effect of applied hydrostatic pressure, as indicated by the reduced material deterioration in the test at 5000psi, may reduce accessibility by compacting the PVDF (probably the amorphous region in particular), to increase compression modulus accordingly.

However, this picture is simplistic, as analytical data from the residues from tested Coflon samples sent to TRI (reported in CAPP/T.3) all show

- reduced plasticiser levels (as would be expected)
- reduced crystallinity levels (by about a half)

Methanol absorbed in the amorphous regions has presumably loosened outer segments of crystalline regions to bring them into the amorphous phase. Local swollen regions will possess more molecular mobility to increase the entropic drive for solvation of these boundary segments. At some point, the links or interactions between appropriate crystalline regions (possibly groups of spherulites[1]) which normally give the material its mechanical integrity are loosened by this action and by swelling of the amorphous phase. Consequently, in the extreme, flocculent particles separate out and can settle at the bottom of the surrounding container.

The role of exposure temperature is important to this degradation, as shown by the lower degree of deterioration during the test which did not quite reach 140°C. A major point not yet mentioned is the nearness of the test temperature to transition points associated with different crystalline forms of PVDF. Much published work exists on the crystalline structure and morphology of PVDF, and a comprehensive review of these by Lovinger[1] exists. The crystalline form of unplasticised PVDF can be changed from the so-called α-phase to the γ-phase by temperature alone at 155°C-160°C. The transition involves a small but definite move in the packing positions of individual PVDF molecular chains in crystallites. It is reasonable to suppose that such a transition could occur at lower temperatures when methanol molecules (and plasticiser molecules) are present in neighbouring amorphous regions, and that some methanol molecules could disrupt the transition. Additionally, it is known that a few percent of defects occur in the crystalline structure[1], brought about because some molecules pack "the wrong way around": these can affect the potential energy of the PVDF considerably. One suggestion is that the defects provide a likely point of attack by the methanol[2].

It is essential for life prediction purposes and the defining of long-term temperature limits for Coflon pressure sheaths in flexible pipes that the nature of this degradation is more fully understood. Crack growth aspects have been reported in CAPP/M.5, but only on samples aged for short times at temperatures between 120°C and 140°C. Longer-term exposures at lower temperatures are required (including work at high pressures) to indicate whether an Arrhenius-type temperature relationship exists which will allow reasonable predictions to be made or to identify whether a critical temperature exists, possibly associated with a transition. In the second case, the importance of the role of applied strain needs further examination, to assess whether it causes decreases in transition or melting points for thermodynamic reasons[3] as well as increasing the kinetics of the degradation as discussed earlier. An examination should also be made as to whether this type of degradation would occur so readily in pipe sections where methanol can only enter the PVDF through the large surfaces - the most probable service conditions. Methanol exposure experiments at different temperatures with the permeation cell (especially long-term) and the 'capped' pipe-section liquid uptake procedure should resolve whether Coflon pipes at service temperatures could ever become fully saturated with methanol during a reasonable life time.

It is also recommended that Coflon should be similarly exposed to other relevant fluids, for instance methanol/water mixtures and high aromatic oils, to see if this significant degradation process again occurs and, if so, at what conditions.

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4   HOT METHANOL/AMINE ATTACK ON COFLON AT HIGH PRESSURE

The SEM/X-ray microanalysis data in Appendix 1 show that methanol associated with amine at 120°C and 5000psi for 4 weeks can cause surface dehydrofluorination of Coflon, in a similar way to an amine/H_2S mixture. This is a genuine chemical degradation, and the effects on mechanical properties are described in CAPP/M.5 and CAPP/M.7. Comparison with systems that apparently caused only deplasticisation suggested that amine plus benign gas only brings about some dehydrofluorination (losing *ca*7% of fluorine at the surface), but synergism occurs with amine and methanol, losing *ca*40% of fluorine at the surface, with some effect reaching *ca*1mm into the bulk.

5   CONCLUSIONS

- Coflon samples strained in bending mode and immersed in methanol at 140°C and at its vapour pressure for 6 hours have exhibited complete cracking: at the same time the surrounding methanol became yellow.

- After 24 hours, these samples were displaying surface delamination and other deterioration.

- Over the next 7 days the surrounding liquid became opaque and the samples had degraded into a fused mass. This mass included unstrained samples which had exhibited delamination but a little more slowly than the strained samples.

- At *ca*135°C, much less deterioration was observed, but significant cracking had occurred especially on strained samples. At 130°C there was less visual effect, but a large deterioration in fatigue resistance (CAPP/M.5).

- At 140°C and 5000psi, samples remained largely intact after 2 weeks methanol exposure (with and without strain). Only the initial signs of deterioration were observed.

- The mechanism for the low pressure deterioration at 140°C probably involves absorption of methanol by the PVDF's amorphous phase, and the changing of outer layers of crystalline regions to amorphous material, probably accompanied by solvation. The high temperatures required suggest that α to γ crystalline transitions may be involved. Established defects in the crystalline structure may also contribute. The application of strain probably increases the kinetics of degradation, and may be associated with the lowering of crystalline transition or melting points.

- It remains to be established whether Arrhenius-type relationships exist, to be used for life prediction purposes, or whether the exceeding of critical temperatures brings the degradation about catastrophically. Tests recommended to determine this point include crack growth and permeation or 'capped' liquid uptake tests, after exposures ranging from long times at *ca*120°C, and at high pressures, to short times at higher temperatures. The mode of methanol ingress related to service should also be examined

- Methanol can also exacerbate chemical attack of Coflon by amine, causing dehydrofluorination at high temperatures and pressure.

REFERENCES

1. A J Lovinger, 'Polyvinylidene fluoride', Chap.5 in Development in crystalline polymers-1 (ed D C Bassett), Appl Science Publ (London and New Jersey), 1982

2. M Audenaert, personal communication

3. A Stevenson, personal communication

APPENDIX 1

SEM/X-ray microanalysis of various aged Coflon samples

All aged at 120°C and 5000psi for 4 weeks

FLUID/distance in from surface	COMPOSITION %			COMMENTS ON APPEARANCE
	F	C	O	
Unaged	47.5	43.5	8.5	-
H ≡ B plus amine (wet CH_4/CO_2 + 1% amine (gas phase))				Surface colour change to yellow
Surface	46.5	47.5	6.0	
300μm	51.5	42	6.5	
D (dry $CH_4/CO_2/H_2S$)				Little change
Surface	54	39	7	
300μm	54	39	7	
E (wet $CH_4/CO_2/H_2S$ (gas phase))				Little change
Surface	55	38.5	6.5	
300μm	53.5	40	6.5	
G ≡ A plus amine (methanol + 1% amine)				Surface cracks after exposure
Surface	12.5	70	14	Black all the way through
300μm	36	54	9.5	
2mm	51	41	8	
3mm	53	40	7.5	
F (wet $CH_4/CO_2/H_2S$ + 1% amine (gas phase))				Black colour penetrating 1-2mm
Surface	19	59	16.5	
300μm	46	48	5.5	

An *increase* in F content to *ca*54% probably corresponds to loss of dibutyl sebacate plasticiser. Hence any *decreases* in F content after ageing (showing dehydrofluorination) should be compared with 54%, not 47.5% (the unaged value). Thus the dehydrofluorination-linked diffusion effects away from the surface can be seen.
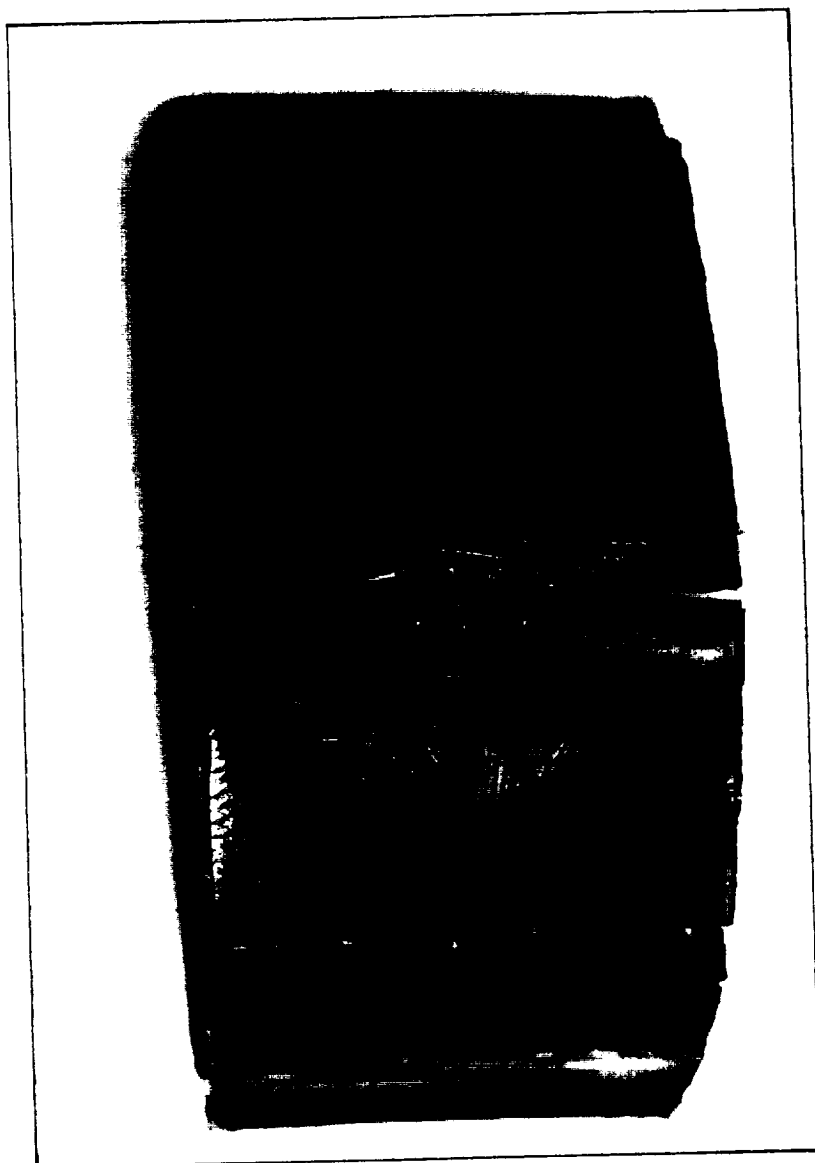
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FIGURE 1   4–point bend Coflon sample (14% strain)
after 6 day exposure to methanol at 140°C
and vapour pressure (x3 magnification)
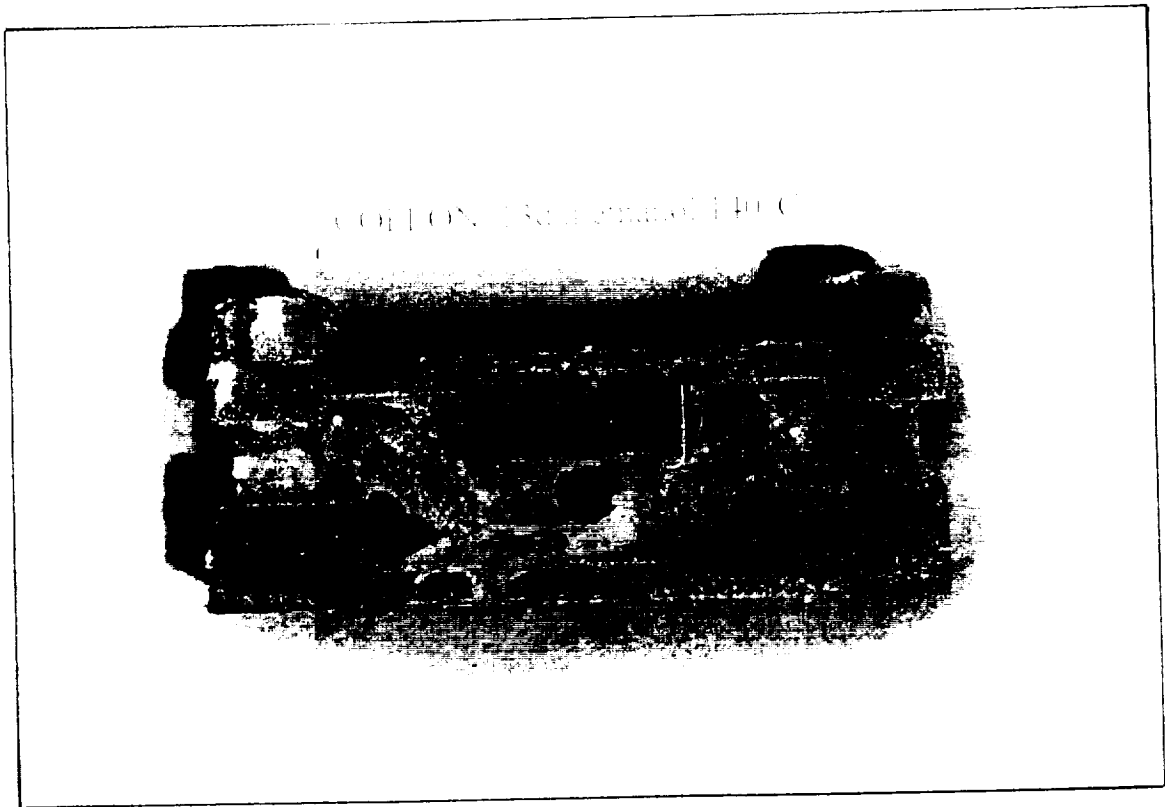
Fig. 2(a)   Hollow shell 4-point bend sample remnant
             (approximately actual size)

Fig. 2(b)   Gelatinous deposit formed at bottom of cell around
             2nd 4-point bend rig (x1.6)

FIGURE 2   Severe degradation of Coflon in methanol after
            13 days at 140°C and vapour pressure

Fig. 3(a)   Unstrained Coflon sample immersed in hot methanol
            at vapour pressure (x4.5 magnification)

FIGURE 3   Coflon samples during the first test in the
           glass-ended cell
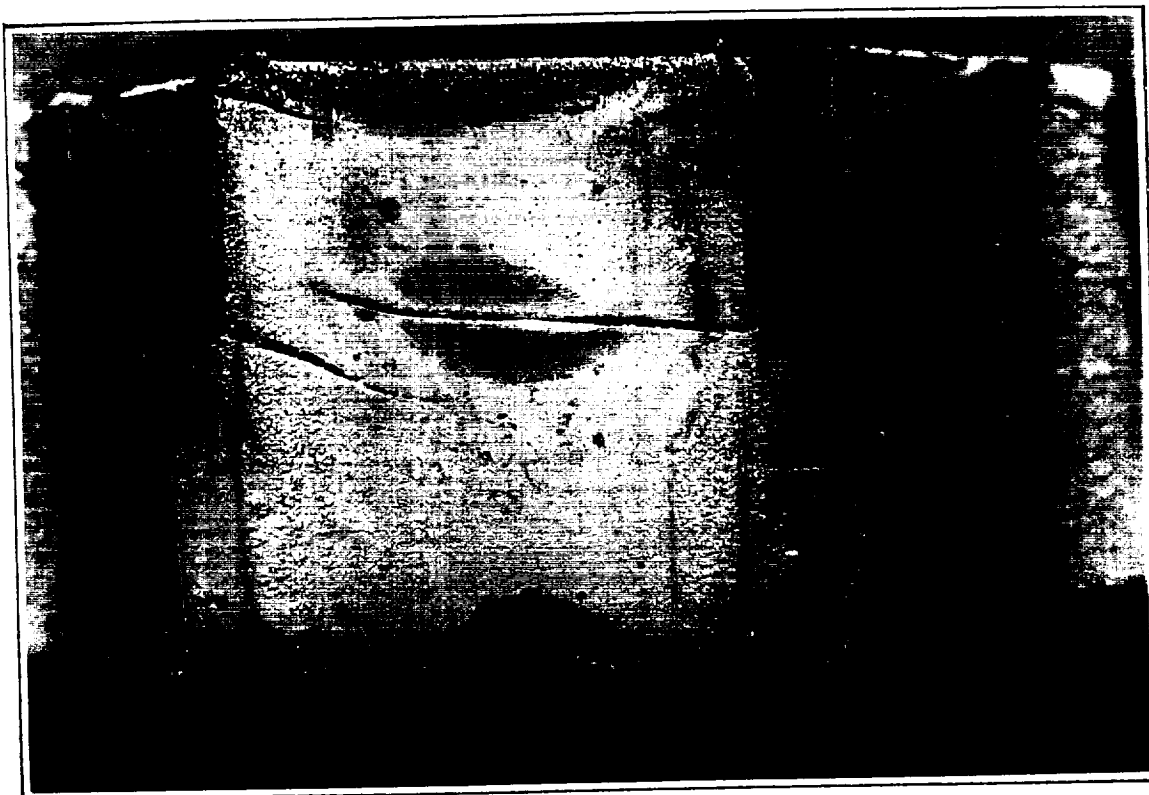
Fig. 3(b)   Fractures in 4-point bend strained sample after exposure to hot methanol at vapour pressure for 14 days (x3)
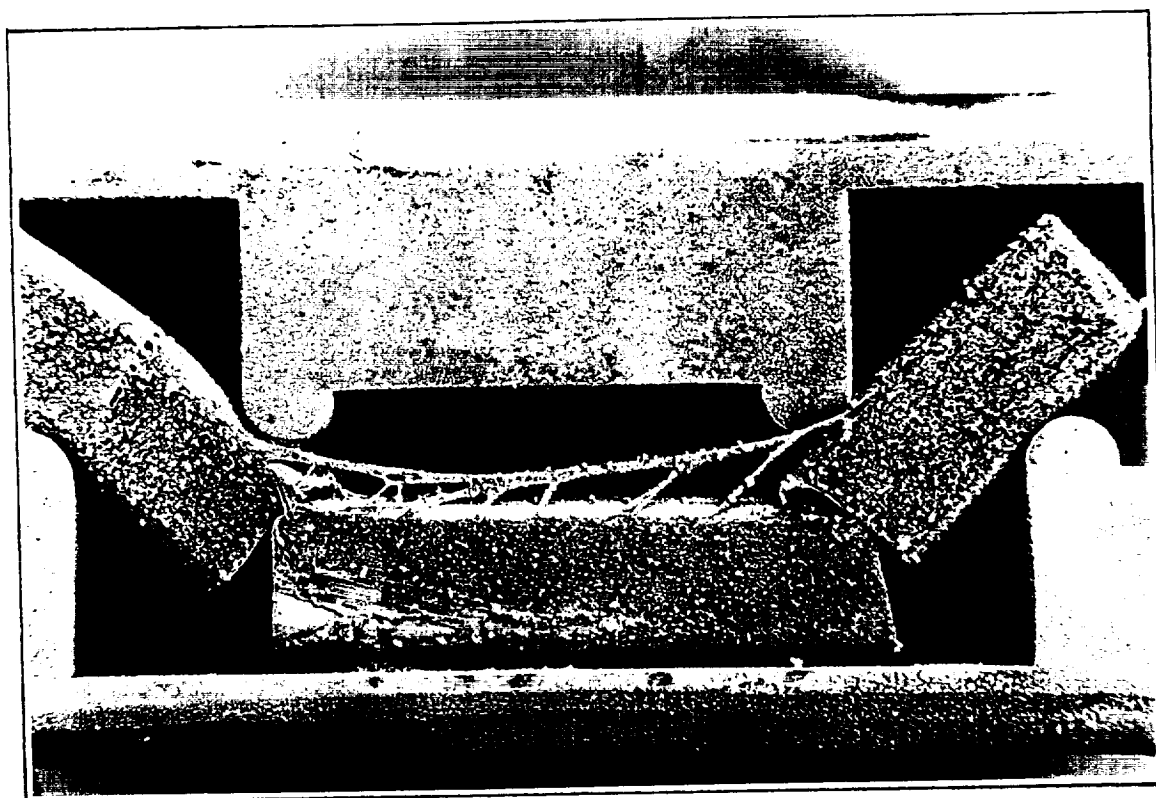
Fig. 3(c)   Deposited filaments of PVDF after the exposure above

FIGURE 3 (cont)   Coflon samples during the first test (at 130-140°C) in the glass-ended cell (x3.5)

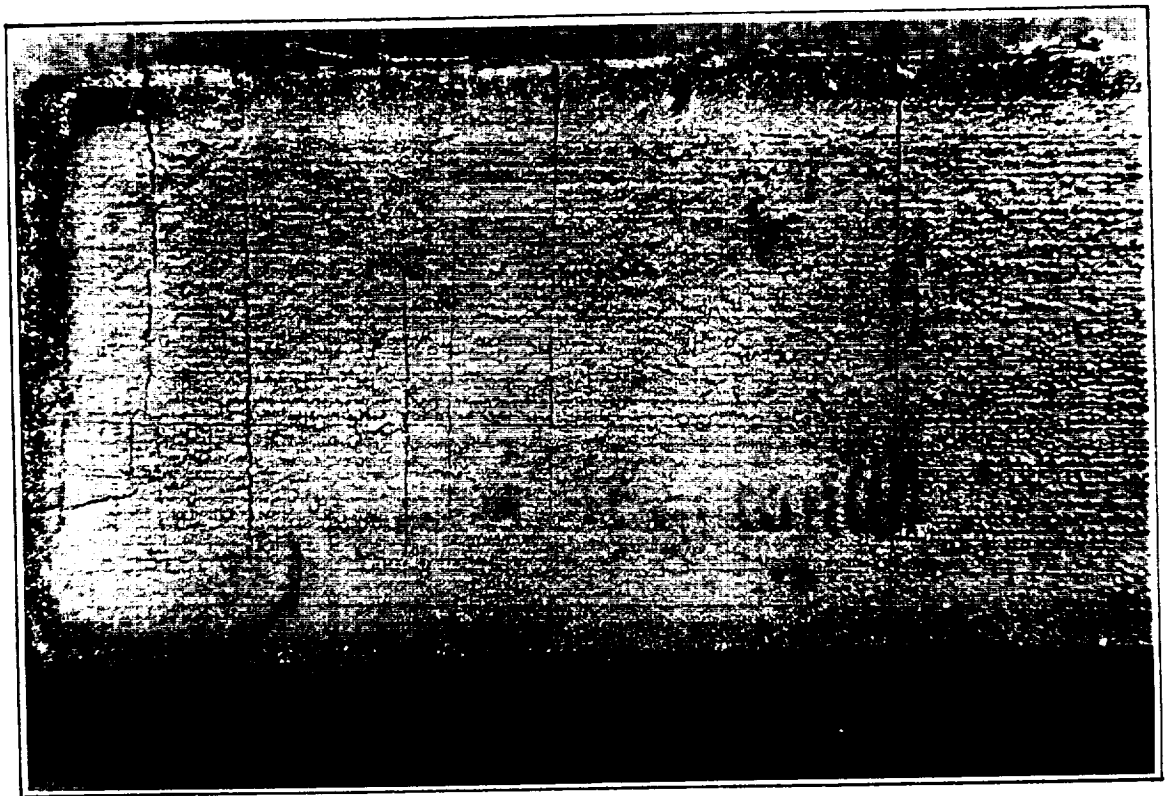Fig. 3(d)   Fine cracks through unstrained sample (x3.5)

Fig. 3(e)   As Figure 3(d) at higher magnification (x14)

FIGURE 3 (cont)   Coflon samples during the first test
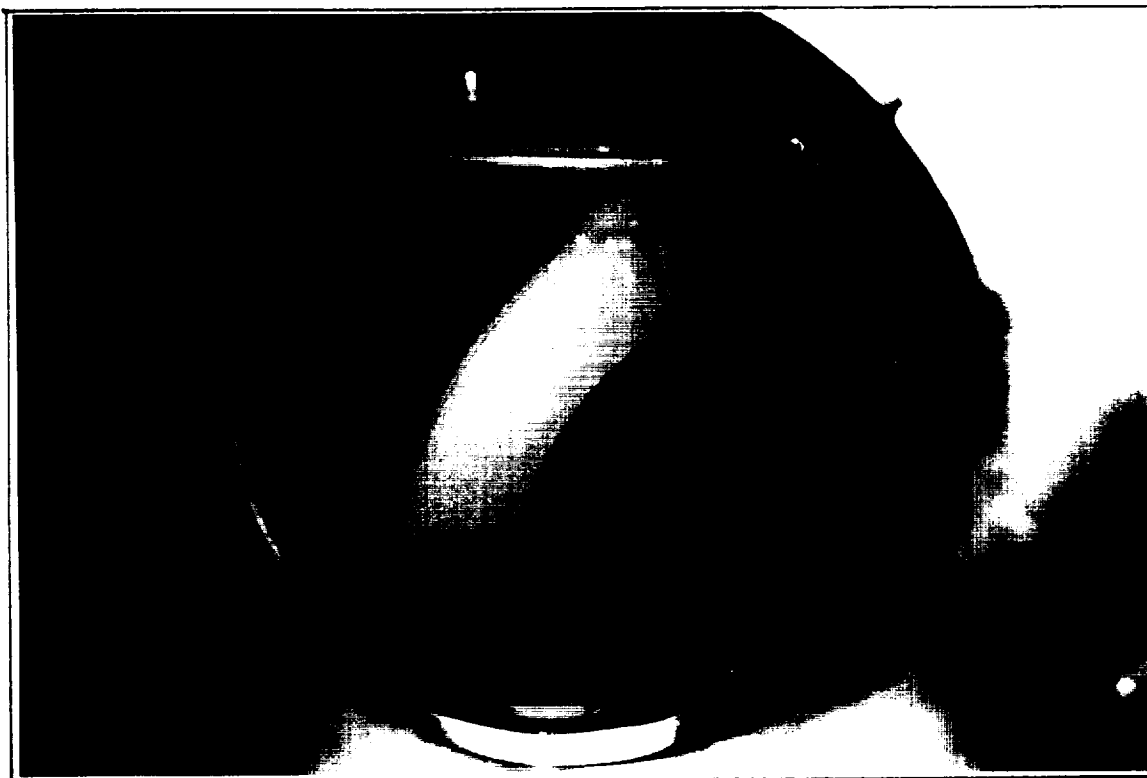in the glass–ended cell

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Fig. 4(a)   Strained (bent) and unstrained Coflon samples in methanol
at 140°C and vapour pressure – initial arrangement
(x2.5 magnification)

Fig. 4(b)   After 6 hours of exposure as above (x3.5)

FIGURE 4   Coflon samples during the second test
in the glass-ended cell
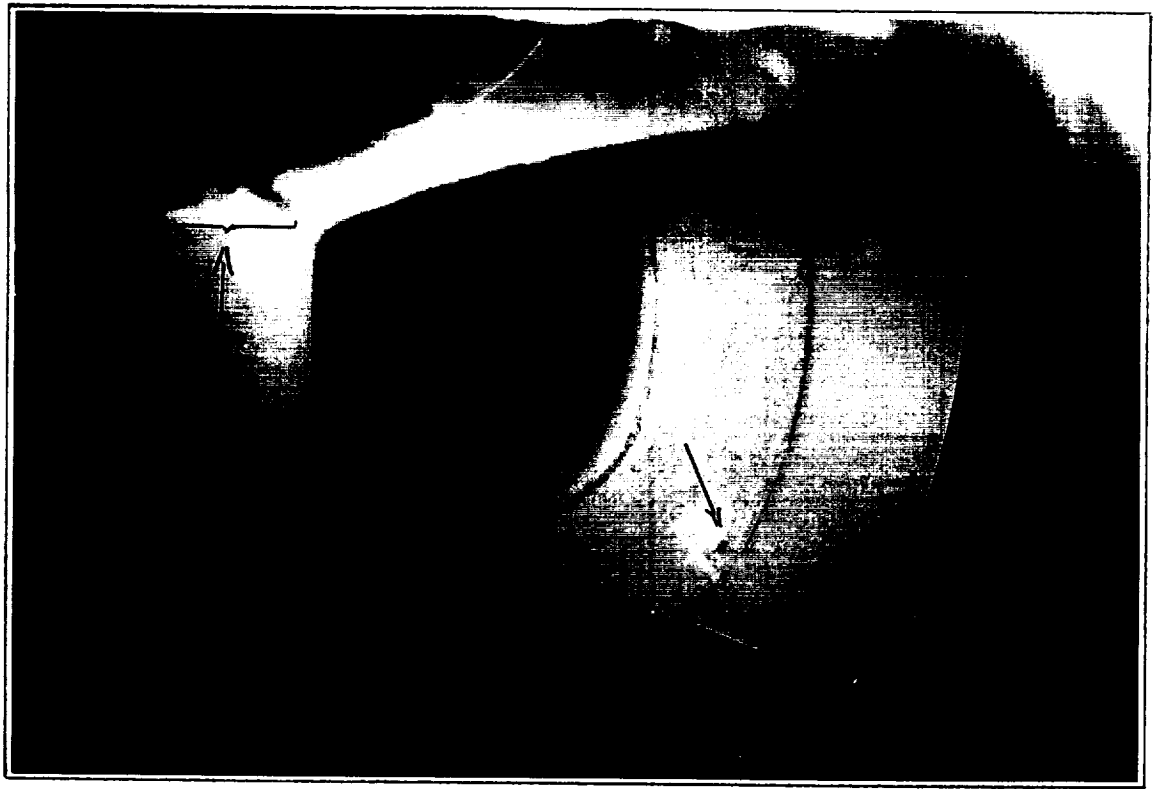
Fig. 4(c)   After 6 hours of exposure - different view
             showing other samples (x4)
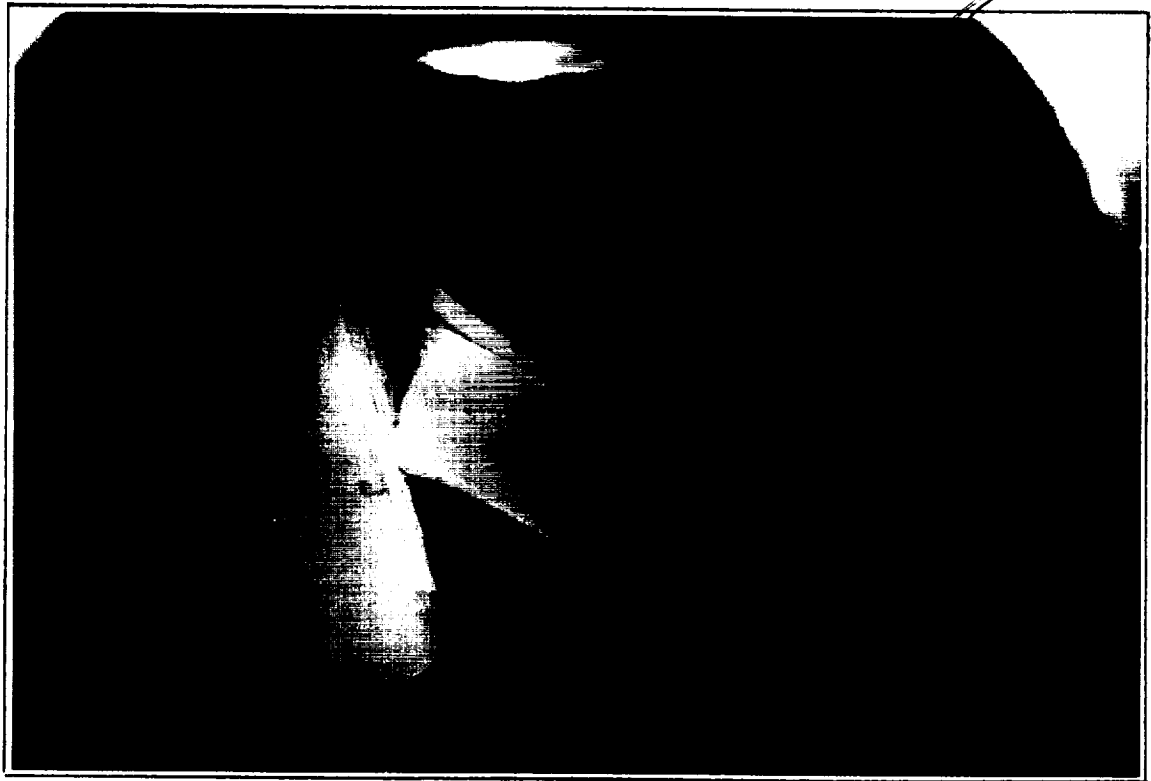

Fig. 4(d)   After 24 hours of exposure (x4)

FIGURE 4 (cont)   Coflon samples during the second test
                   in the glass-ended cell