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MECHANICAL AND PHYSICAL PROPERTIES OF BOTH UNAGED AND AGED COFLON AND TEFZEL

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SYNOPSIS

The examination of effects of pure methanol, Fluid A, at vapour pressure on Coflon has been completed and shows that none of the gross degradation mechanisms (previously-observed at 140C) occur at 120C or below, even after considerable exposure times. However some deterioration does occur.

Effects of Fluid F on Coflon have been considerable. Complex chemical reactions seem to occur with Coflon in which the plasticizer could play a crucial role in determining subsequent reactions and hence mechanical behaviour. One Coflon batch performed more badly than the others. Tefzel is not significantly affected chemically by Fluid F. Arrhenius plots from both tensile and fatigue data (Coflon) and tensile data (Tefzel) have been generated and activation energies determined.

Methanol with 1% amine, Fluid G, has caused extreme degradation to Coflon, which increases significantly with longer exposure times at 120C. From a study at four temperatures, good Arrhenius time-temperature degradation plots were generated from tensile property changes in Coflon. These plots have been used to predict degradation rates at other exposure temperatures. Tefzel was not significantly affected by Fluid G.

The strong effect which ethylene diamine has on Coflon was illustrated further by its reaction with the polymer (turning it black) in a simple water mixture, Fluid J, at 100C.

A high aromatic oil mixture, Fluid I, significantly affected aged Tefzel, reducing its tensile properties by up to 50%. Longer exposures, however, did not reduce its properties by any further significant amount; the effect was not chemical. This fluid did not affect Coflon in a major way.

It has been further established that unaged Coflon suffers considerable stress relaxation in both compression and tension modes. Near-linear force decay has been found with logarithmic time for testing durations up to two days. The time for a 50% loss from originally-applied stress can be as low as 19 hours, and could therefore raise questions regarding local effects, for instance, associated with possible sealing difficulties at flexible pipe end-fittings. However, much of the relaxation is at short times: the logarithmic influence of time means that over 90 years are required for generally-applied stresses to decay to zero. Extreme Fluid F, G and I exposures did not affect the stress relaxation rates of Coflon. Tefzel's stress relaxation rate did increase by one fifth after Fluid I exposures.

1 INTRODUCTION

This report deals with all recent mechanical testing performed on variously aged samples of Coflon and Tefzel, to complete the work for Phase 1. Earlier results were reported in CAPP/M.7. Fluids A, F, G and I (see below for formulations) have all been used for ageing in the last 12 month period, with particular attention concentrated on the effects of Fluid F as a result of discussions at the December 1995 steering committee meeting in Austin. Dramatic mechanical and physical changes occurred to Coflon in our initial studies after 4 weeks at 120C in this sour gas mixture and so a detailed matrix was drawn up to investigate the effects of time and temperature of exposure. Subsequent tensile tests and compact tension (CT) fatigue tests were performed. Fatigue testing has been limited during this period to Coflon only; however, Tefzel CT samples have been exposed to the same conditions as the Coflon allowing the possibility for fatigue tests to be performed at a later date.

Fluid A exposures during the last 6 months have been long-term at 65C, 100C and 120C only. These exposures have been a continuation of earlier work and will complete the investigation of this fluid.

Other chemical ageings have involved Fluid G at 120C to confirm and investigate the hostile nature of this fluid on Coflon. Again, this fluid will not be used in Phase 2. Finally, long-term exposures in Fluid I, a high aromatic oil mixture, were carried out to investigate the effects on the polymers of aromaticity in a simulated service fluid.

Selected Test Fluid Formulations

Fluid A	100% Methanol
Fluid F	94/5/1% Methane/CO_2/H_2S/saturated water vapour over water containing 1% ethylene diamine
Fluid G	99/1% Methanol/ethylene diamine
Fluid I	35/35/20/10% Heptane/cyclohexane/toluene/1-propanol
Fluid J	Water with 1% ethylene diamine

The full list of fluids and details of every exposure in Phase 1 are given in Appendix 1. Ageings have normally been conducted at 5000psi, with a few exposures at vapour pressure (e.g. for Fluid A): Appendix 1 gives details in every case.

2 TEST PROCEDURES

Tensile testing was performed on ASTM D638 type IV dumbbells machined from 6mm extruded Coflon and stamped from 3mm sheet Tefzel. Testing at 23C and at a rate of 50mm/minute was carried out on a Zwick universal test machine (screw driven). From the resulting force-deflection data, Young's Modulus (measured at 1% strain), yield stress and strain, and ultimate strain and tensile strength were calculated. Fluid F aged samples were always tested within 3 days of completion of ageing, whereas the liquid phase exposure samples A, G and I were kept in their respective fluids at room temperature and subsequently tested 'wet'. This procedure was adhered to in order to prevent drying of the testpieces which could effect scatter in the measured results.

All CT fatigue testing was performed at 70C on the MTS servo-hydraulic test machine. Repeat-testing of several aged samples, the results of which were presented at the Dec.'95 meeting, were performed on the MTS which provides results relatively rapidly. These could be added to the limited number of data points measured originally on another (multi-station) fatigue machine. The results of the repeat tests are given in this report. Test frequency was limited to 5Hz to prevent any temperature build up. A detailed procedure of this test is included in the fatigue resistance report CAPP/M.5.

Stress Relaxation tests were performed in several modes on unaged samples of Coflon only, to gain more knowledge on the longer term response of the polymer to applied displacement. Compression relaxation rates up to one hour were documented previously in report CAPP/M.8 - however, it was deemed important that longer times be explored. Fifty hour tests have now been performed on both tensile and CT testpieces. The tensile dumbbells were deflected to 7% axial strain, whereupon force-time data were continuously logged. For the CT test an opening displacement of 1mm was applied to the sample, chosen as the value used for straining CT samples during ageing (in the steel strain rigs). Again force-time data were recorded and used for (a) relaxation rate calculation and (b) total force reduction during the time period.

3 TENSILE RESULTS OF FLUID F EXPOSURES (GAS PHASE)

The tensile test results for Coflon samples exposed only in the gas phase of Fluid F are shown in Table 1. Over this period, 4 separate batches of polymer samples were used (batches #2, 3, 4 and 5). For comparison purposes, all unaged properties from each batch have been included in the table, along with an identification of which control batch specific aged samples originated from. The original 3mm sheet Tefzel has been used throughout this work and a recent check was performed on unaged samples which showed only a slight reduction of its modulus (910 MPa compared to 950 MPa).

Because the thicknesses of Tefzel and Coflon samples are very different, results should *not* be compared directly between the two polymers. When tensile-testing thermoplastics, thickness changes affect stress/strain curves considerably.

In the tables, 'Tensile Strength' means the highest stress recorded. This usually means the yield stress for Coflon, but not for Tefzel. (To check why this should be so, please examine suitable figures - see sections 3.1.1 and 3.2.1.)

3.1 Coflon Results

TABLE 1 Coflon tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control (#2)	761	-	15.8	35.6	89.8	35.7
Control (#3)	670	-	17.1	37.0	99.9	37.1
Control (#4)	750	-	14.7	35.5	114	35.5
Control (#5)	790	-	15.6	35.7	90.1	35.7
85C 8w (#5)	759	-4	19.7	39.9	55.3	40
85C 17w (#5)	769	-2.7	17.3	36.4	67	36.5
85C 26w (#5)	794	+0.5	15.8	39.2	68.3	39.3
100C 4w (#3)	608.7	-9.2	19	38.0	80.2	38.0
100C 12w (#3)	626.7	-6.5	21.9	38.2	91.3	38.3
100C 25w (#3)	685.2	+2.2	44.8	37.6	70.5	37.6
120C 1w (#4)	718.3	-4.2	17.4	35.9	60.6	36.2
120C 2w (#3)	711.3	+6.1	17.4	37.9	71.9	38.1
120C 2w* (#4)	818.3	+9.2	19.9	37.6	79.7	39.5
120C 3w (#4)	748.3	-0.2	32	36.7	74.1	37.3
120C 4w (#2)	895.6	+17.6	12.4	37.8	15.9	37.9
120C 6w (#4)	824.3	+10	38.3	38.0	69.2	38.1
140C 3d (#3)	621.1	-7.4	20.2	36.5	82.6	36.7
140C 5d (#3)	562.0	-16.2	21.5	35.6	91.4	35.9
140C 8d (#3)	556.1	-17.1	25.0	35.0	94.2	35.3
140C 2w (#4)	901.7	+20.3	15.9	37.8	59.6	37.9
140C 4w (#4)	845	+12.7	40	37.4	66.6	38.4

* deplasticized by 7.7% prior to ageing

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3.1.1 Discussion of Coflon Results

It is clear from the table that Fluid F ageing affects tensile characteristics significantly, and exceptionally so for the Batch #2 samples. Stress-strain curves for the various times at 85, 100, 120 and 140C are shown in Figures 1-4, at the back of the report. (NOTE each curve is for a specific testpiece in the group of three tested for each ageing condition, and so the mean values quoted in the table may not tie in exactly with values from the curve plotted). Photographs of selected aged samples from this work, but not including Batch #2 samples which were described in CAPP/M.7, are shown in Figure 5. From these photographs it is clear that no recent samples have turned black, unlike the original (Batch #2) Fluid F exposure (120C 4 weeks, CAPP/M.7). Coflon (translucent when unaged) has only suffered mild discoloration after ageing at any other condition. The 100C and 120C samples show gradual darkening with increased exposure times; however, at 140C all samples appear light brown.

On inspection of the stress-strain curves it is clear that, with the Batch #2 exception, the polymer remains ductile at the testing conditions. This is shown by the significant plastic deformation incurred after yielding and before final fracture. The only near-brittle condition shown is the original 120C 4 week exposure performed in 1995 in which the black brittle casing had formed. Concern was initially raised about the recent testing series when this degradation did not occur again, especially in the 6 week 120C and 4 week 140C exposures. An explanation is now offered.

Deplasticization studies on the latest batches of Coflon yielded less mass loss, at a slower rate, than Batch #2 deplasticization results. Regarding PVDF's chemical structure, although the amine-induced formation of conjugated double bonds, and hence the black outer layer colour (detailed in the correlation report CAPP/M.10 Rev A), does not directly involve the plasticizer, it is now considered a possibility that plasticizer (an ester) will be chemically competitive with the PVDF in reacting with a component of Fluid F. Some TRI analytical evidence on plasticizer extract suggests that the component most likely to be competed for is H_2S. With Batch #2, plasticizer was removed easily, so that H_2S crosslinking reactions on PVDF conjugated double bonds formed by a previous reaction could continue unhindered. The earlier amine-induced conjugation-forming reactions will thus be enhanced by removal of a product, continuing until a black colour is produced. Later Coflon batches had a slower rate of deplasticization (possibly for crystallinity level reasons). If H_2S is removed by remaining plasticizer, it will not attack the PVDF so much: the drive for conjugation (by removal of a product) will then be much reduced. Black-colouration is thus diminished.

Measured modulus values from the tensile tests highlight the complexity of the ageing process for Coflon. For all three temperatures it might be thought that an initial fall in stiffness occurs due to further plasticization of the polymer by the methane gas. However, equilibrium of methane uptake, by diffusion, is reached within hours at 140C; therefore the continual drop in modulus must be due to ageing - it turns out to be crystallization level (CAPP/M.10 Rev A). On reaching a minimum value the modulus then increases. This stiffening is probably due to both slow loss of processing plasticizer and a crystallinity upturn. This down-up modulus trend is only disrupted by the 2 and 4 week 120C ageings where the moduli increases are already above the 3 week data.

The other discrepancy found - where the 4 week 140C modulus is lower than the 2 week 140C value - may be significant or may arise from variations occurring for the reasons above.

These conflicting effects of exposure along with the inconsistency in repeatability of the severe ageing mechanism make Arrhenius plots from the obtained data tentative. To understand better the pure chemical effects on the PVDF structure, full removal of the plasticizer would be beneficial. On the other hand, the real life pipe application involves plasticizer being present and so our ageing conditions have been more realistic. Moreover, the main inconsistency has involved one batch only, so that some comparison across temperatures might be acceptable. Reasonable Arrhenius plots have been obtained by first plotting property versus time curves as well as possible and using these when taking the log reciprocal of the time it takes for the modulus (i) to fall to a minimum and (ii) then to increase back by 10% against reciprocal of the ageing temperature. These are shown in Figure 6a and yield an activation energy of 12k.cal/mol for reaching the minima and 19.5k.cal/mol for the 10% increase.

Some other non-H_2S chemistry occurring slowly might also be involved for Fluid F attack of Coflon. Mechanistic aspects are discussed in detail in CAPP/M.10 Rev A.

Finally, in an attempt to repeat the original severe, blackening, degradation and support validation of the plasticizer reaction theory, some diagnostic tests were performed on the latest batch of Coflon. Unaged samples were deplasticized to 7.5% and 10% mass loss and then aged at 120C for 2 weeks in Fluid F. Increasing darkening of the samples was observed with respect to increased pre-exposure deplasticization. This result is shown in Figures 7 & 8. These samples, although not yet brittle, have clearly undergone the degradation process detailed previously, with increased attack on the 10% deplasticized sample.

3.2 Tefzel Results

TABLE 2 Tefzel tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control	910	-	20	24.3	426	42.3
85C 8w	927	+1.8	18.2	26.7	402	42
85C 26w	884	-2.9	19.1	25.5	414	42.2
100C 4w	862.9	-5.2	20	25.6	>250	>30
100C 12w	897.3	-1.4	20	24.6	>250	>30
120C 1w	798.4	-12.3	20.4	22.9	434	41.7
120C 3w	775	-14.8	19.6	22	413.7	39.2
120C 4w	810.9	-10.9	19.9	26.0	369	39.3
120C 6w	865.1	-4.9	20.7	24.5	359	35.2
140C 3d	789.6	-13.2	23.5	23.4	244	>30
140C 5d	737.4	-19	25	23.1	>250	>30
140C 8d	714.5	-21.5	24.3	23.4	>250	>27
140C 2w	891.7	-2	19.6	23.4	390	38.9
140C 4w	900	-1.1	21.3	23.9	382	38.11

3.2.1 Discussion of Tefzel Results

From Table 2 the results show that the general behaviour of Tefzel has remained basically unaffected by the various Fluid F ageings. Both yield stress and strain along with ultimate strains are close to the unaged values. A slight, 10% maximum, reduction in tensile strength was observed after 4 weeks at 140C.

In more detail, a similar effect on modulus values as seen for Coflon has occurred with the Tefzel. Mechanisms have been discussed in CAPP/M.13 Rev A. An initial drop, again probably caused by methane ingress coupled with crystallinity loss, takes place reducing the modulus by as much as 20%. After a minimum, the polymer re-stiffens due to another ageing process involving Fluid F. Loss of low molecular species is thought to be the cause. However, since the material is largely unaffected both mechanically and physically - no samples suffered any discoloration at all - longer exposure periods would be required to investigate the possibilities of further modulus increases, and perhaps embrittlements. Of course, these changes may well not occur, from the stability exhibited by this polymer to date.

Examples of stress-strain curves are shown in Figure 9.

4 TENSILE RESULTS OF FLUID G EXPOSURES

4.1 Coflon Results and Discussion

TABLE 3 Coflon tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control (#2)	761	-	15.8	35.6	89.8	35.7
Control (#4)	750	-	14.7	35.5	114	35.5
Control (#5)	790	-	15.6	35.7	90.1	35.7
65C 2w (#5)	695	-12.1	17	36.1	40.9	36.1
65C 8w (#5)	952	+20.5	14.7	39.5	16.9	39.9
65C 26w (#5)	630	-20.3	8.4	25	9.3	25.1
85C 8w (#5)	913	+15.6	13.4	38.1	14.4	38.5
85C 10w (#5)	920	+16.4	11.8	36.3	12.6	36.6
85C 12w (#5)	575	-27.2	13.6	30	14.6	30.3
100C 6w (#5)	788	-0.3	11.9	32.2	13.1	32.4
100C 8w (#5)	455	-42.4	11.3	27.6	11.6	27.6
100C 12w(#5)	419	-46.9	7.9	19.5	8.4	19.5
120C 2w (#4)	698	-6.9	15.1	31	16.8	31.1
120C 4w (#2)	452.1	-40.6	14.3	26.1	14.8	26.3
120C 6w (#4)	330	-56	10.9	16.8	11.2	16.8

The above data coupled with the stress-strain curves in Figures 10-13 clearly show the severe degradation, chemically-induced, caused by Fluid G. Modulus, break, strain and strength values all decrease with increased exposure time at all temperatures, although the lower two temperatures did indicate an initial rise in measured values prior to this decrease. Physical damage can also be seen from photographs in Figures 14-21, affecting surfaces and bulk regions also.

After the first exposure, for all temperatures, by cutting open some samples, they were found to be already black right through, with some surface cracking visible on certain of them. However, after testing, samples only displayed black colour on a thin 'casing' layer, see macrographs in Figures 15,17,19,21. The thickness of this black layer increased towards the centre as exposure times increased. It became apparent that the extent of black casing layer illustrated material which had suffered fast brittle fracture. The central remaining sample portions has failed in ductile mode, the ensuing "stress-whitening" largely masking the underlying black (so that colours were generally light brown).

Many longer exposures produced samples that were severely cracked prior to tensile testing, the longest-aged samples producing a fine powdered debris near the break region when disturbed. The presence of the cracks strictly diminished the original sample cross-sectional area, influencing modulus and strength values: however, any such effect has not been considered in calculating data for Table 3.

These results show consistent degradation effects caused by differing exposure times and temperatures. Arrhenius plots were generated from these data to see whether they could be used as a tool for predicting 'service life' at other temperatures. The basis for the Arrhenius plots was taken as:

i) The time to a drop in tensile strength of 25%
ii) The time to a drop in Young's modulus of 25%

The graphs covering the 4 exposure temperatures for these two bases are shown in Figure 22. The first observation from these graphs is that a good linear relationship has been established between the plotted data. Confidence can therefore be expected when reading-off different degradation rates at other exposure temperatures. For example, using the calculated x-y relationship (displayed on each plot), at an exposure temperature of 50C a 25% drop in material strength would be estimated as follows:

$$y = -4667 * (1/273+50) +10.5$$
$$y = -3.94$$

so Time Required = 1/[inverse ln (-3.94)]
=51.4 weeks

A similar time of 57.2 weeks would be needed for a corresponding 25% drop in modulus.

Activation energies of *ca*10kcal/mole were obtained from these plots. These probably reflect physical fracture (as a *consequence* of chemically-induced embrittlement) as well as crystallinity loss. Chemical degradation effects occur in the amorphous region, and are probably quantified in Ea terms in crack growth tests rather than tensile tests: however, the surface cracking precluded such testing. Once again, some mechanism discussion occurs in CAPP/M.10 Rev A.

At the higher temperature of 140C, the expected times for a 25% drop in strength and modulus would be 2.2 and 1.9 weeks respectively.

Although Fluid G is not considered to be a very realistic service fluid in flexible risers (see minutes of the San Marcos steering meeting), it has provided consistent degradation (of Coflon). This has again enabled the construction of time/temperature property relationships which was a prime objective of the project to date, and is the first time that the concept is linked with genuine degradation.

4.2 Tefzel Results and Discussion

TABLE 4 Tefzel tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control	910	-	20	24.3	426	42.3
65C 2w	897	-1.4	19.8	26.1	457	45.2
65C 26w	783	-14	20.2	23.6	416	37.7
85C 8w	873	-4.1	20.9	26.9	410	41.4
85C 10w	828	-9.1	21.6	26.2	385	39.8
85C 12w	773	-15	25.3	26.4	398	41.3
100C 6w	803	-11.8	25.2	25.9	391	40.7
100C 8w	797	-12.5	23.2	25.7	414	39.0
100C 12w	863	-5.1	22.3	26.9	372	38.8
120C 2w	804	-11.6	21.2	23.4	399	39.2
120C 4w	805	-11.5	24.2	24.6	448	41.2
120C 6w	755	-17	30.5	23.7	466	40.7

No visible physical degradation occurred to Tefzel after any of the Fluid G exposures. Although Tefzel is structurally an isomer of PVDF, the amine-led attack did not occur in Tefzel too. The explanation is that electronegativity differences are the key to this reaction process, which leads to only the Coflon samples forming conjugated double bonds, and hence going black (CAPP/M.13 Rev A).

Yield and ultimate stress and strain values show no significant deterioration following exposures. Young's modulus has been reduced on average by 10-15% of the unaged value for the longest exposures at each temperature. The only anomaly to any downward trend is the modulus from the 100C 12 week ageing, which has actually increased, after an initial fall of 12.5% after 8 weeks. From this extended exposure programme, it is clear, as initially reported, that Tefzel is not significantly affected by Fluid G

5 TENSILE RESULTS OF FLUID I EXPOSURES

5.1 Coflon Results and Discussion

TABLE 5 Coflon tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control (#3)	670	-	17.1	37.0	99.9	37.1
Control (#4)	750	-	14.7	35.5	114	35.5
140C 2w (#3)	668	-0.4	17.3	38	75	38.1
140C 10w (#4)	675	-9.9	17	36.6	52.7	37
140C 10w* (#4)	710	-5.3	16.7	35.8	64	36.1
140C 30w (#4)	717	-4.4	16.3	41.1	52.3	41.1
140C 30w* (#4)	652	-13.1	20.2	36.1	68.5	36.2

* denotes exposure at vapour pressure only (all other exposures were at 5000psi)

After 2 weeks at 140C and 5kpsi in this simulated high aromatic oil, the mechanical behaviour of Coflon was unaffected. No physical changes were observed as this material remained translucent with no measured mass change. After a further 8 weeks at 140C 5kpsi, the modulus had fallen by 10% and a slight yellow-brown hue was evident in the samples, see Figure 23. The ultimate strain had then reduced to around 50%. After 30 weeks ageing, however, the modulus drop was only 4.4% suggesting a re-stiffening of the material. This is an effect consistently observed throughout Fluid F exposures. The observation that the modulus was still reduced by some 10% after 10 weeks suggests that a complicated interaction between polymer, plasticizer and ageing fluid is probably occurring. No ‘true’ chemical change is indicated.

Less of a modulus drop was seen after 10 weeks when exposed at vapour pressure only. However, after 30 weeks - at vapour pressure - the value had dropped by 13%. This further drop in stiffness is opposite to what happened at 5000 psi, suggesting a possible hydrostatic influence of the applied fluid pressure in the former case. Exposed samples were darker in colour after vapour pressure ageing.

In general, this service-representative oil mixture had no significant effect on Coflon - the material's strength does in fact increase after the longest exposures - supporting the polymer's validation as an oil line flexible riser material. The differences in modulus behaviour at low pressure is, however, interesting and should be investigated further if deemed relevant.

5.2 Tefzel Results and Discussion

TABLE 6 Tefzel tensile-tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control	910	-	20	24.3	426	42.3
140C 2w	444.5	-51.2	25	17.5	256	28
140C 10w	550.8	-39.5	25.4	18.9	333	30.3
140C 10w*	516.7	-43.2	26	18.4	351	29.4
140C 30w	517.5	-43.1	25	20.3	341	29.7
140C 30w*	493.7	-45.8	25.8	19.9	350	30.4

* denotes exposure at vapour pressure only (all other exposures were at 5000psi)

After a considerable loss in modulus after 2 weeks at 140C 5ksi (-51%), the modulus rises to 550 MPa after a further 8 weeks at 5 kpsi. After 30 weeks, however, the stiffness does reduce again, by 43% of its original unaged value. After the large initial reductions in both modulus and strength, it appears that no further significant changes have occurred after longer exposures. This would suggest that physical swelling of the polymer is the likely reason for the early - 2 week - weakening. These results infer that the solubility parameter of Tefzel is lower than that of Coflon (11.3(cal/cm^3)^{½}) as it apparently absorbs Fluid I (8.5(cal/cm^3)^{½}). There is no known chemically-inactive solvent for Tefzel, so exact quantification of this parameter is not easy. Again, at vapour pressure the modulus after both 10 and 30 week ageings are lower than the high pressure equivalents. Stress-strain curves for this group are shown in Figure 24.

6 TENSILE RESULTS AND DISCUSSION OF FLUID A & FLUID J EXPOSURES

The relative inertness of Tefzel to methanol is described when considering absorption measurements in CAPP/M.2 and /M.4. Again, a solubility parameter (δ) argument holds, as δ for methanol is 14.5 $(cal/cm^3)^{1/2}$ - Coflon's value is nearer to this than is Tefzel's. Hence mechanical test data were obtained (at moderate temperatures) for Coflon only, which can behave at the other extreme, deteriorating badly, at above 130C - see CAPP/M.6 Rev A.

6.1 Fluid A aged Coflon

All exposures were only performed at vapour pressure (15 to 150 psi).

TABLE 7 Coflon tensile - tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Change in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Tensile Strength (MPa)
Control	803	-	15.8	35.3	58.3	35.5
65C 28w	572	-28.8	19.4	37.7	74.6	37.9
65C 48w	587	-26.9	16.6	38.5	118	38.6
100C 11w	508.8	-36.7	24.2	33.5	65.6	33.5
100C 18w	479.2	-40.4	24	34.5	59.3	34.9
100C 31w	476	-40.8	22.5	33.4	78.1	33.6
120C 3w	460	-42.7	28.8	32.5	82.1	32.1
120C 11w	423.8	-47.3	30.1	32.8	84.1	32.8
120C 18w	421.9	-47.5	30.8	32	74.8	32.1
120C 31w	403	-49.8	26.1	29.4	69.2	30

The 65C, 100C and 120C ageing data are shown above. From photographs in Figure 25, there is a marked change in appearance after the 31 week exposures at the two higher temperatures - a 120C sample has actually turned black. These visual differences are accompanied by consecutively higher reductions in Young's modulus; using the 28 week and 31 week data above it can be seen that the % change increases approximately linearly with temperature from -29% to -50%. (There were insufficient data at suitable times to construct Arrhenius plots). However, at 100C and 120C these modulus values are not a lot lower than the previous, 18 week, measurements. At 65C the subsequent, 48 week, exposure has led to a slight increase in modulus. This would suggest that slight deplasticisation of the PVDF is taking place. In general, modulus values decrease to a stable plateau, but the level of the plateau decreases with increasing temperature.

Although this effect has led to large modulus reductions, it is interesting to note that the tensile strength of the Coflon is not affected in such a dramatic way. No significant strength loss was seen due to any 65C or 100C ageing, with the highest reduction at 120C being only 15%. Stress-strain curves for the above data are shown in Figure 26.

All samples in the three Fluid A vapour pressure cells have now been used up. These exposures were primarily to see whether the gross degradation seen in the 130-140C temperature range (CAPP/M.6 Rev A) occurred at the lower temperatures. From the above results and testpiece integrity it is safe to say that the Coflon has resisted the gross degradation; however, the formation of a black surface does suggest that another degradation process is occurring after long exposures at 120C, and the rapidly-occurring modulus reductions (even if eventually stable) need heeding.

6.2 Fluid J aged Coflon

A single exposure was performed on samples of unaged Coflon in Fluid J in order to isolate the crucial effect of the ethylene diamine on the polymer. For simplicity the fluid (1% amine in distilled water) was refluxed at 100C in glassware so that the Coflon's appearance could be constantly monitored for any colour changes. Within ten days the material's surface had clearly turned black. After longer times, the boiling liquid had turned white, thought to be due to formation of an emulsion of extracted plasticizer in the water. This indicates how, in an environment which would encourage ionic reactions and at high concentrations of amine, the chemical reactions leading up to non-sulphur crosslinking (as described on page 6 in correlation report CAPP/M.10 Rev A) take place readily.

The 5 week fluid J aged tensile test data is shown in Table 8. The only significant change has been to the ultimate strain which has reduced by over three quarters - a dramatic effect. Embrittlement is being approached. Stress/strain curves for this condition are shown in Figure 27.

TABLE 8 Coflon tensile - tested at 23C

Ageing condition (control batch)	Modulus (MPa)	% Drop in Modulus	Yield Strain (%)	Yield Stress (MPa)	Ult.Strain (%)	Ult. Strength (MPa)
Control	790	-	15.6	35.7	90.1	35.7
100C 5 weeks	789	-0.2	14.7	39.1	20.2	39.2

7 DYNAMIC FATIGUE RESULTS

7.1 Tefzel Results

Due to the time involved in performing the CT fatigue tests and, for a long time, the unavailability of 6mm thick Tefzel, it was originally decided that priority should be given to the Coflon samples. Recently, for completeness, unaged 6mm Tefzel along with some Fluid F and Fluid I aged samples have now been tested. These limited results were presented at the San Marcos meeting and can be seen in Figure 28.

From the unaged data it is clear that a large amount of scatter is present, compared to the better behaved Coflon. This has been due to the difficulty in measuring crack extension within the Tefzel compact tension testpiece. The crack actually grows at different rates at the side and centre of the geometry. Being more translucent than Coflon, backlighting the Tefzel samples during testing revealed the total crack extension at any particular time. When measuring crack growth, it was found that the distance measured at the side of the crack (i.e. near the sample surfaces) advanced only slowly while the actual crack tip, at the middle of the testpiece, continued extending at a normal rate. After 5-10kcycles the side-measured crack had stopped growing completely, due to a blunting effect within the Tefzel. Therefore to obtain a true crack resistance curve, similar to those obtained for the non-blunting Coflon, it was decided to measure the total centre testpiece growth. Due to the greater inaccuracies in the measurement technique, using backlighting and careful judgement of the crack tip position, it was therefore inevitable that greater scatter became introduced into the plotted J vs. dc/dn data.

The actual crack growth resistance of 6mm (nominal) Tefzel is very similar to that of Coflon. The most extreme Fluid F exposed samples, 4weeks at 140C, were tested, and from the plotted data in Figure 28 no change has occurred to the material's fatigue performance. The 30 week Fluid I aged samples were also tested, since this was the one fluid that showed significant deterioration of Tefzel tensile properties. Once again, given the large amount of inherent scatter, no significant change in fatigue resistance has occurred due to the fluid exposure. (Data from a strained sample also lay within the scatter.) As this test may concentrate failure on amorphous regions, which are much more prone to chemical attack than the crystalline regions, these data illustrate once again the chemical inertness of Tefzel.

7.2 Effects of Pipe Extrusion Direction of Coflon

To see whether crack growth resistance in unaged Coflon was affected by extrusion direction, compact tension testpieces were cut from 6mm wall thickness pipe sections so that samples were with the machined notch both parallel and perpendicular to the pipe length. Fatigue tests were performed on each type of testpiece at 70C. From the results in Figure 29, no significant difference was detected in crack resistance in the different directions (0 deg is with the crack growth parallel to extrusion direction whereas 90 deg signifies growth perpendicular to extrusion direction. Square symbols are for extruded bar data, as used for all ageing work). This result is interesting since the higher strain static compact tension tests have previously shown the material to be tougher in the direction perpendicular to extrusion (CAPP/M.5). This suggests that at small deflections fatigue crack growth is not affected by extrusion direction, but it is for higher deflection tests in which plastic flow is also more dominant.

7.3 Effects of Fluid F on Coflon

During the past 6 months CT fatigue tests were performed at higher J values to speed up test duration. Any points at values below 2kJ/m^2 were gained from the multi-station test machine in 1995 and were the basis of the data presented at the last meeting and in the subsequent correlation report. For this reason certain values given below, from repeat tests on the MTS, will be different from earlier quoted numbers. The data in the correlation report will be similarly modified if necessary when the final revision is issued. J at 10nm/cycle has been empirically defined as crack growth resistance, chosen at a convenient position just away from the high scatter region at low crack growth rate.

TABLE 9 Coflon after Fluid F ageing at 5kpsi

Ageing Conditions	dc/dn at J=2	J at 10nm/c$^+$
Unaged	0.5	3.2
Deplasticized	0.5-1.0	4.1
85C		
8 weeks	-	4.2
100C		
1 month	-	2.6
3 months	3	2.4
6 months	-	3.4
120C		
1 week	2	2.2
1 week*	2	2.2
2 weeks	100	1.8
4 weeks	-	2.4
6 weeks	2	2.2
140C		
3 days	100	1.5
5 days	100	2
8 days	100	1.8
4 weeks	-	3.4

* denotes CT sample strained 1mm during exposure, ~8% at the crack tip

\+ crack growth resistance

The dc/dn vs J curves for the above data can be seen in Figures 30-33. For all 4 temperatures it can be seen that the material becomes less resistant to crack growth after initial short exposures. The curve shifts to the left yielding lower crack growth resistance (J for growth rate of 10nm/c). This behaviour is similar to the initial modulus drop recorded from the tensile tests, and is probably linked directly. At later times, the curve moves back to the right, indicating an increase in crack growth resistance. However, the timings of these opposite effects have varied somewhat for the different temperatures, as detailed below.

At 85C there was only time to test the first exposed condition. The result shows a surprising amount of toughness for this 2 month exposure, the line having already shifted onto the deplasticized curve.

At 100C, after the initial decrease in resistance, the longest (6 month) exposure has caused the curve to shift back to the right and has toughened the Coflon to a value close to that of the deplasticized control.

At 120C, the Coflon weakens after 1 week and further still after 2 weeks. However, after the 6 week exposure the material has re-toughened but not back to its original unaged values.

At 140C, the 3 to 8 day exposures have all caused a similar degree of weakening in fatigue. Again after the largest available exposure, 4 weeks, the Coflon has re-toughened. Unlike the 6 week 120C exposure, however, this 140C ageing period has toughened the material beyond its control value.

From this fatigue data Arrhenius plots have been generated using the following criteria from the 100C, 120C and 140C ageing data. The log reciprocal of time required to reach the minimum fracture resistance value (J integral) at dc/dn=10nm/c has been plotted against the reciprocal of the ageing temperature. A second plot has also been generated in which the exposure time required to increase this J value by 25 % has been used to form the reciprocal time values. These two plots superimpose, as shown in Figure 34, and yield activation energies of 23kcal/mol. each. This is at a chemical level, and accords with the concept that this test is influenced mainly by the amorphous region - the region most affected by chemical attack.

7.4 Effects of Fluid G on Coflon

Due to extreme degradation caused by the 4 and 6 week 120C exposures, fatigue testing of these cracked samples was not possible. The 2 week ageing which only produced slight crazing on the material surface was tested at 70C and a considerable worsening in crack growth resistance was measured. This result is shown in Figure 35.

8 STRESS RELAXATION TESTS

Stress relaxation was investigated in some detail earlier in the project and the results were included in a specific report, CAPP/M.8 The test method used involved compression loading of various samples of thermoplastic to a fixed displacement with a special indentor. Time-force measurements were recorded for durations up to 2 hours at the maximum. Stress relaxation rates were then calculated. The following sections below look at longer term stress relaxation tests on different geometries with this and other, more standard, tests, to see whether the decay rate continues to be linear with log time at extended times. Effects of chemical ageing on the stress relaxation rates of both Coflon and Tefzel, from the indentor test, are then discussed.

8.1 Longer Term Tests on Unaged Coflon

Longer term tests were performed on unaged Coflon at 23C on both tensile testpieces and compact tension samples. These two testpieces were considered of greater relevance than the previously-used compression test samples, since strained tensile and CT samples have previously been put into fluid ageing cells. Therefore stress relaxation data for these geometries would give information on likely stress fall-off during exposures.

TABLE 10 Stress Relaxation Data from Long Term Tests

Testpiece Geometry	Peak Deformation	Relaxation Rate (% per decade)	Time to 50% Peak Force (hours)
Compression Indentor	20% of thickness	13.3*	No Data
Tensile Dumbbell	8% axial strain	10.6	19
Compact Tension	1mm deflection	12.5-14.6	48

* Short-term test, from CAPP/M.8

The relaxation curves can be seen in Figures 36 and 37. From the true relaxation curves, which have their selected origins at 5 minutes from the start of sample deflection (to avoid errors associated with applying the initial stress), it is clear that the relaxation rate remains fairly linear with respect to log time, and can be quoted as % per decade (based on minutes). From the CT test it appears that the rate increases slightly from 12.5 to about 14.6 % per decade. The tensile result was 10.6% per decade. These relaxation rates are very similar to the rates measured from the indentor compression test performed previously. This suggests that mode of deformation of the polymer and extent of applied strain do not significantly affect stress relaxation rates.

As a result of these tests it has become apparent that the time required for a 50% drop from the originally-applied force is short indeed, 19 and 28 hours for tensile and CT testpieces respectively. These short times help to explain the apparent insignificance of applied strain to CT samples undergoing fluid ageings. No crack growth was monitored during sample inspections nor changes in fatigue resistance found from strained-during-ageing CT samples of Coflon. Due to the fast decay of stress, relatively little strain energy is present during subsequent ageing to produce any crack extension. To decay a further 50% from the 5-minute point (at which time about one quarter of the originally-applied force has already been lost - see figures) would take 4 decades (*ca*1 week). Also, the plots indicate that generally-applied stress will not deteriorate to zero for many years (see section 8.2). Locally creep and shrinkage may exacerbate the problem near to a particular fixing: complete loss of grip by the jaws of the strain test rigs has been noted after ageing on several occasions.

8.2 Effects of Chemical Ageing on Stress Relaxation Properties

Room temperature compression indentor tests to 20% sample thickness (see CAPP/M.8 for detailed procedure) were performed on selective aged samples of both Coflon and Tefzel (all nominally 6mm thick). The results are shown below.

As previously reported, deplasticizing unaged Coflon has no effect on the stress relaxation rate of the polymer. Extreme Fluid F exposures at both 120C and 140C also have no significant effects on relaxation properties. Despite severe chemical attack, Fluid G aged samples of Coflon only see a slight increase in relaxation rate after the longest exposure of 6 months. Perhaps surprisingly, the longest, high pressure, Fluid I exposure reduces the rate of stress relaxation by one fifth. No change was measured after the 5 week water + 1% amine (J) exposure.

Although the relaxation rates are high, with over 40% of the maximum applied force being lost after only 50 minutes, the remaining force on the material would, however, take a long time to decay away completely. Since the relaxation rates were calculated using the force at 5 minutes (for steady state reasons - see CAPP/M.8) then at a relaxation rate of 13% per decade, the time required for this 5 minute force of 1053N (unaged condition) to decay to zero would take at least another 7 decades of time (minutes). This would be well over 90 years, given a linear/log relaxation rate over all decades. This highlights the fact that although a high force decay is seen in just minutes, the applied force will actually take a very long time to decay away completely (not the case mis-reported earlier in CAPP/M.8). It does, however, suggest careful consideration is required as to the allowable local stress fall-off in service, at end fittings for instance. Clearly 'working' stresses need to be high enough for successful sealing for a considerable period of time.

TABLE 11 Results for Coflon

Condition	Stress Relax. Rate (% per dec)	F max (N)	F at 5min (N)	% loss to 5 mins	F at 50min (N)	% loss to 5 mins
Unaged	13.1	1567	1053	32.8	905	42.2
deplasticd.(-9%)	12.7	2541	1706	32.9	1488	41.5
F 120C 4w	12.9	2264	1515	33.1	1313	42.0
F 140C 4w	12.3	2478	1644	33.6	1433	42.2
G 65C 2w	13.5	2369	1536	35.2	1324	44.1
G 65C 8w	13.3	2482	1620	34.7	1398	43.7
G 65C 26w	14.2	2421	1547	36.1	1323	45.4
I 140C 30w	10.7	2242	1541	31.3	1375	38.7
J 100C 5w	12.9	2288	1500	34.4	1301	43.1

NOTE : all exposures at 5kpsi except Fluid G 65C data - vapour pressure only
The Fluid F 120C 4w exposure was the early one which yielded a black sample.

Turning now to Tefzel, from the limited testing performed it would appear that the stress relaxation rate is affected by the 30week 140C Fluid I exposure, with an increase in rate of one fifth. A slight increase in relaxation rate, to 10.3% per. decade, was also measured after the most extreme Fluid F exposure. This does not represent a very significant change as a whole.

TABLE 12 Results for Tefzel

Condition	Stress Relax. Rate (% per dec)	F max (N)	F at 5min (N)	% loss to 5 mins	F at 50min (N)	% loss to 5 mins
Unaged	9.4	1217	818	32.8	742	39.1
F 140C 4w	10.3	1356	843	37.8	754	44.4
I 140C 30w	11.6	898	543	39.5	480	46.5

9 CONCLUSIONS

- Long-term methanol exposures of Coflon at 65C-120C and vapour pressure have not caused the type of gross degradation previously found at 130-140C. However, the 120C samples did turn black, suggesting another possibly influential ageing reaction, and significant modulus losses apparently down to a stable level were observed.

- Complex reactions between Fluid F and Coflon cause initial weakening of the polymer followed by re-stiffening due to continual deplasticization. Reaction between the Fluid F components and the plasticizer could also be occurring which lessens the amount of subsequent cross-linking and formation of black brittle layer. This has been partly supported by blackening of pre-deplasticized samples after subsequent 2-week exposures at 120C.

- Fatigue resistance of Coflon again drops to a minimum level before re-toughening occurs after longer exposure times in Fluid F.

- The severe embrittlement of Coflon in Fluid F obtained in 1995 after 4 weeks at 120C was not repeated during the latest 85, 100, 120 or 140C exposures. It seems that one batch of Coflon has been associated with this phenomenon.

- Tefzel also displayed an initial modulus fall followed by a re-stiffening after Fluid F ageings. With Fluid G a slow steady modulus loss was observed.

- After Fluid F exposures, good Arrhenius plots were obtained from both tensile and fatigue data for Coflon and tensile only for Tefzel. Activation energies obtained were summations of several interdependent processes all occurring during the exposures.

- Severe progressive degradation of Coflon occurred in Fluid G at 65, 85, 100 and 120C. From the measured property changes, good Arrhenius plots were generated to relate exposure time and temperature to real material degradation.

- Tefzel appeared basically unaffected by Fluid G, with only small modulus reductions incurred.

- A solution of 1% ethylene diamine in water caused a blackening of Coflon after several days at 100C.

- The high aromatic oil mixture, Fluid I, was well resisted by Coflon suffering only small tensile property changes. Tefzel did suffer large reductions in strength and modulus after early Fluid I ageings. Longer exposure times did not cause continual property loss of any significant amount, suggesting that the large initial effects were the result of physical swelling rather than chemical degradation.

- Stress relaxation tests up to 2-day durations on both tensile and CT testpieces of unaged Coflon, tested at 23C, showed fairly good linearity of relaxation with log time. Relaxation rates between 10% and 14% per decade were measured, similar to values from earlier indentor compression tests. A significant loss of applied stress occurs in a short time. However, due to the logarithmic time component involved, general applied stresses should not decay to zero for 90 years or so.

- Fluid ageings had no significant effect on relaxation rates of Coflon; however, Fluid I did increase Tefzel's rate by one fifth.

APPENDIX 1

Table of all CAPP Fluid Exposures (Ex) and subsequent performed Tests (T) for Phase One

EXPOSURE DETAILS (fluids key on reverse of this sheet)	SAMPLES EXPOSED COFLON TTP	COFLON CT	COFLON PM	TEFZEL TTP	TEFZEL CT	TEFZEL PM
Fluid A at 5000 psi						
140C 8 days	T	T		T		
14 days	T	T	Ex	T		T
Fluid A at Vapour Pressure						
65C 28 weeks	T	T				
100C 11 weeks	T					
18 weeks	T	T				
31 weeks	T					
120C 18 hours	T	T				
5 days	T	T				
3 weeks	T					
11 weeks	T	T				
18 weeks	T	T				
31 weeks	T					
130C 4 hours	T	T				
140C 4 hours	T	Ex				
18 hours	T	Ex				
2 weeks	T	Ex				
Fluid B at 5000 psi						
120C 4 weeks	T	Ex		T		
12 weeks	T	T		T		
140C 2 weeks	T	T	T	T		T
4 weeks	T	T		T		
90C 12 weeks	T			T		
Fluid C at 5000 psi						
140C 2 weeks	T			T		
Fluid D at 5000 psi						
120C 4 weeks	T			T		T
Fluid E at 5000 psi						
120C 4 weeks	T		T	T		T
Fluid F at 5000 psi						
85C 2 months	T	T		T		Ex
4 months	Ex	Ex		Ex	Ex	Ex
6 months	Ex	Ex		Ex	Ex	Ex
100C 4 weeks	T	T		T	Ex	
12 weeks	T	T	T	T		T
25 weeks	T	T	T			
120C 1 week	T	T		T	Ex	
2 weeks	T	T	T	T	Ex	T
3 weeks	T	Ex		T	Ex	
4 weeks	T	T	T	T	Ex	T
6 weeks	T	T	T	T	Ex	T
140C 3 days	T	T		T	Ex	
5 days	T	T		T		
8 days	T	T	T	T		T
2 weeks	T	Ex		T	Ex	
4 weeks	T	T	T	T	T	T
Fluid G at 5000 psi (except * temperatures)						
65C* 2 weeks	T					
8 weeks	T			T		
26 weeks	T			T		
85C 8 weeks	T			T		
10 weeks	T			T		
12 weeks	T			T		
100C 6 weeks	T			T		
8 weeks	T			T		
12 weeks	T			T		
120C 2 weeks	T	T		T		
4 weeks	T	Ex	T	T		T
6 weeks	T	Ex		T		T
Fluid H at 5000 psi						
120C 4 weeks	T		T	T		T
Fluid I at 5000 psi						
140C 2 weeks	T			T		
10 weeks	T	T		T	Ex	
30 weeks	T	T		T	T	
Fluid I at Vapour Pressure						
140C 10 weeks	T	Ex		T	Ex	
30 weeks	T	Ex	T	T	Ex	T
Fluid J at Vapour Pressure						
100C 5 weeks	T					

TTP - Tensile Testpiece CT - Compact Tension Testpiece PM - Permeation Disk

* At vapour pressure

(continued)

APPENDIX 1 (cont)

FLUID A	100% Methanol
FLUID B	97/3 Methane/CO_2 + saturated water vapour (SWV)
FLUID C	97/3 Methane/CO_2
FLUID D	94/5/1 Methane/CO_2/H_2S
FLUID E	94/5/1 Methane/CO_2/H_2S + SWV
FLUID F	Fluid E + 1% ethylenediamine (in the water below producing the SWV)
FLUID G	Fluid A + 1% ethylenediamine
FLUID H	Fluid B + 1% ethylenediamine (in the water below producing the SWV)
FLUID I	35/35/20/10 Heptane + cyclohexane + toluene + 1-propanol
FLUID J	Water + 1% ethylenediamine

FIGURE 1 Coflon in Fluid F at 85C - all batch #5

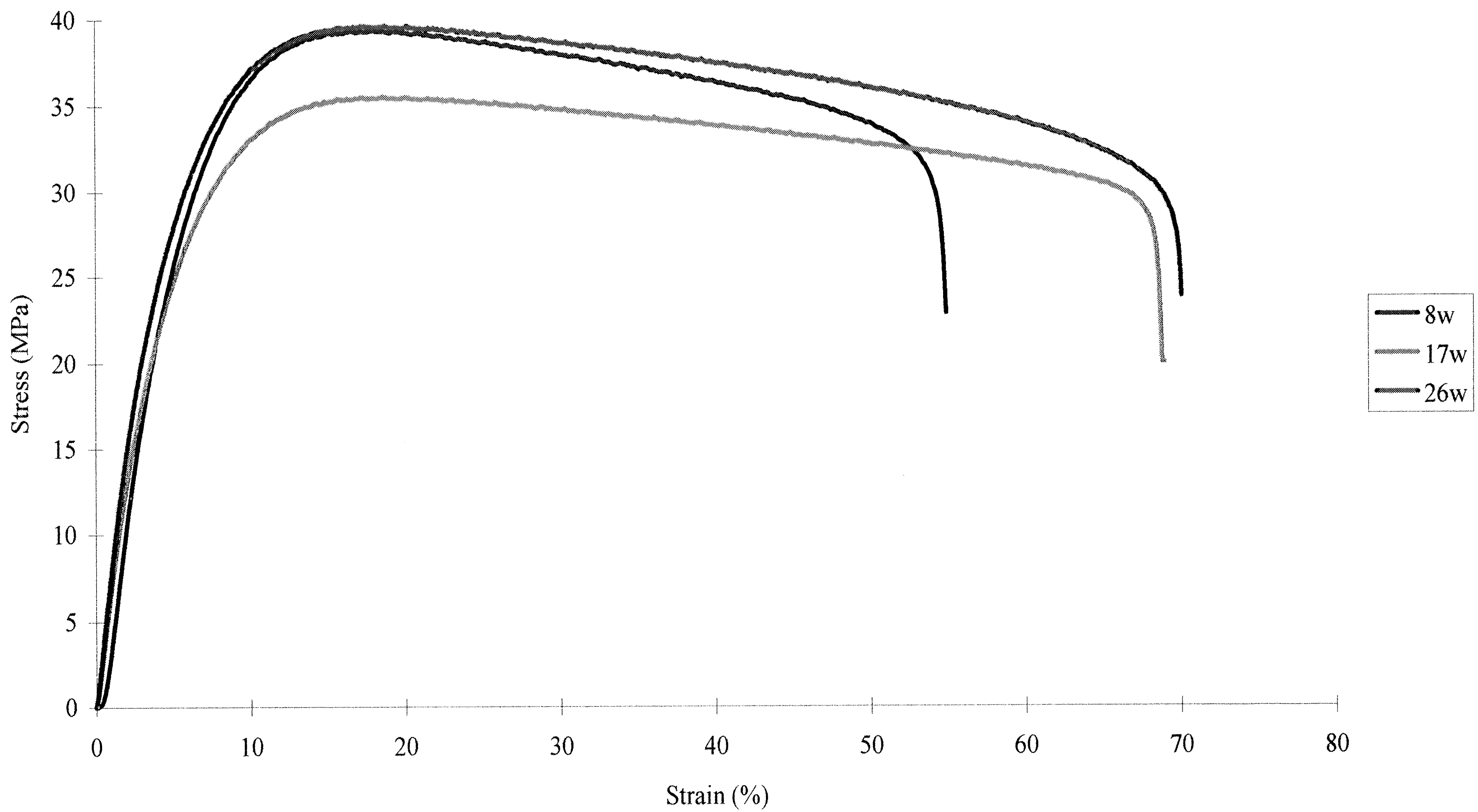


FIGURE 2 Coflon in Fluid F at 100C - all batch #3

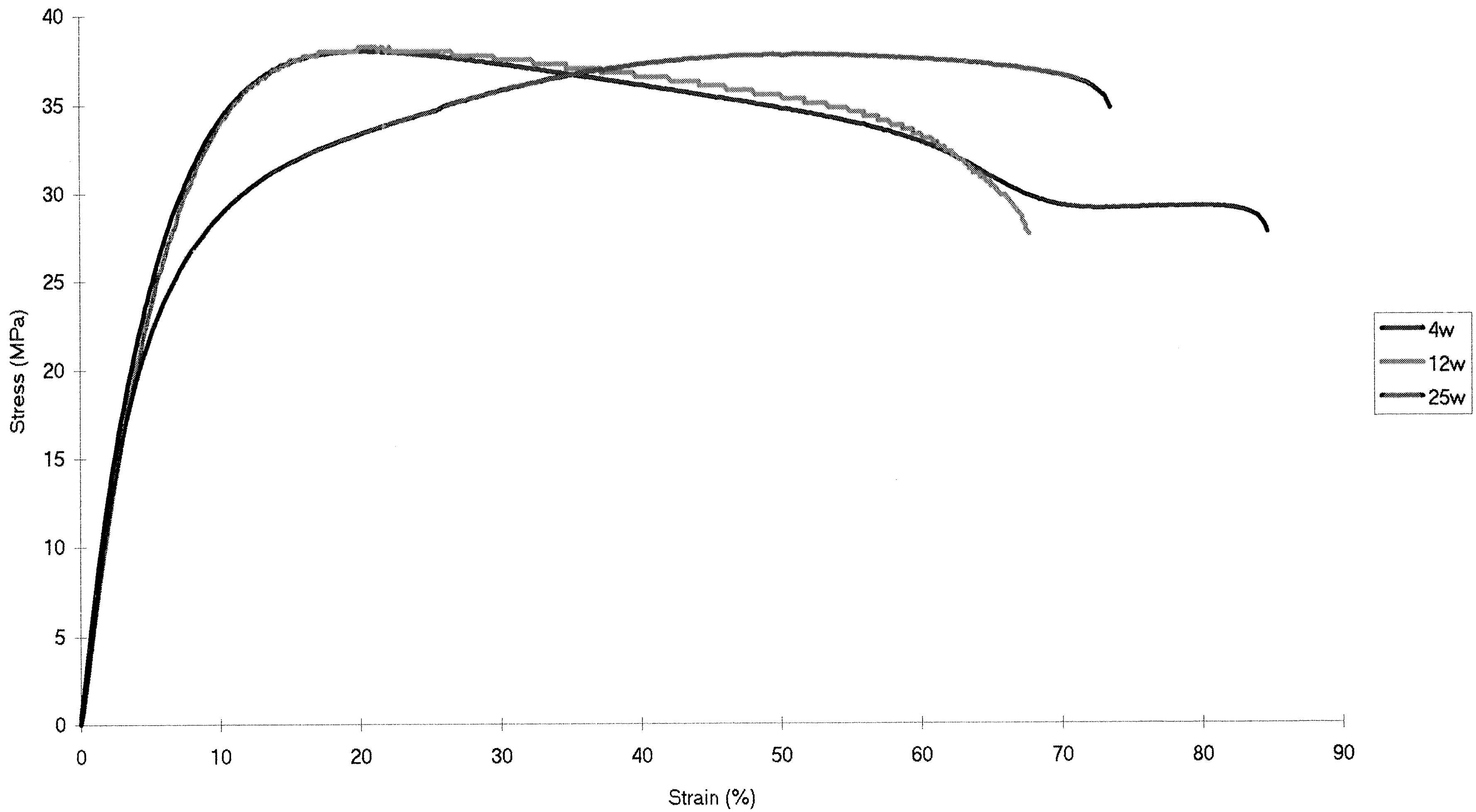


FIGURE 3 Coflon in Fluid F at 120C - all batch #4 unless indicated

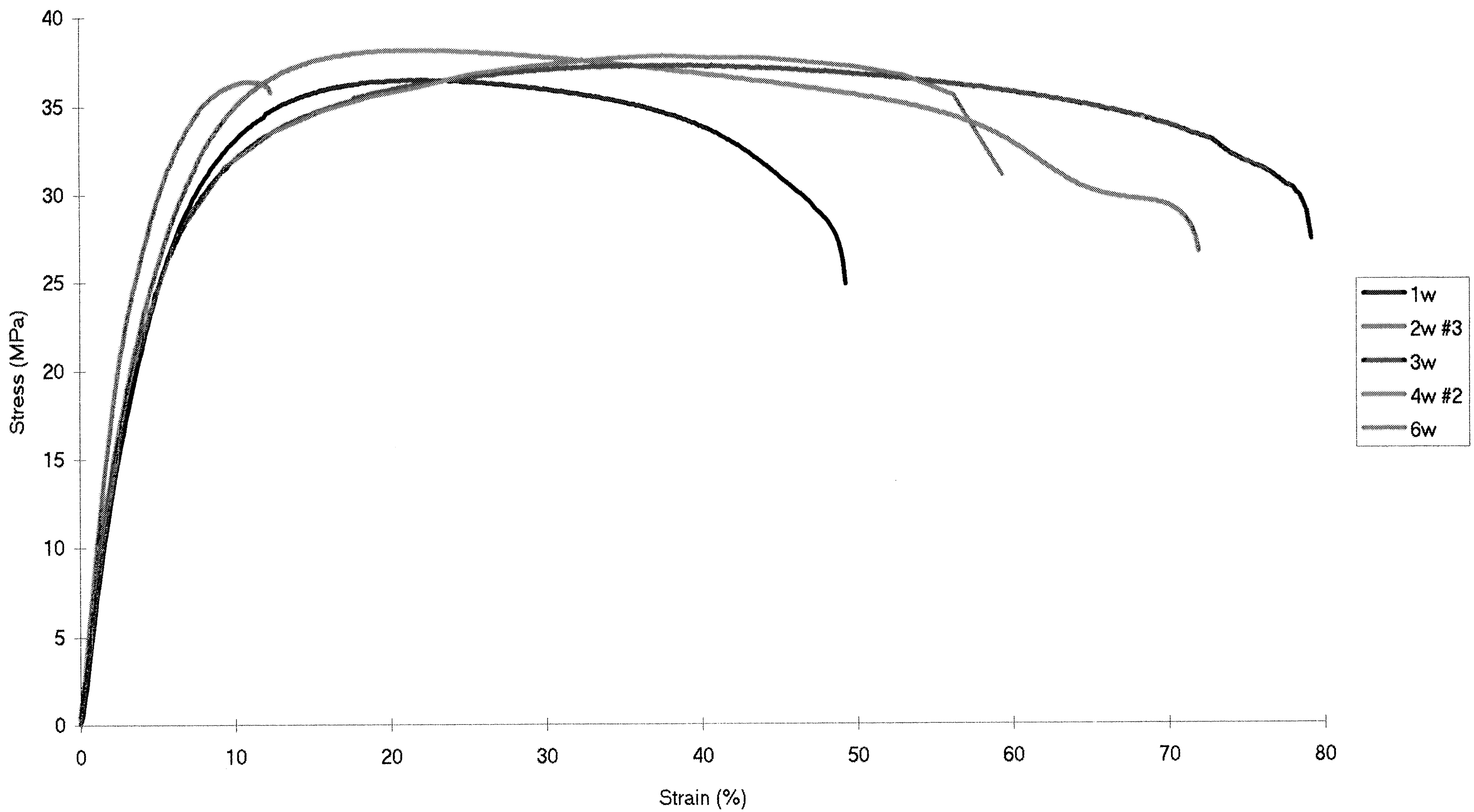
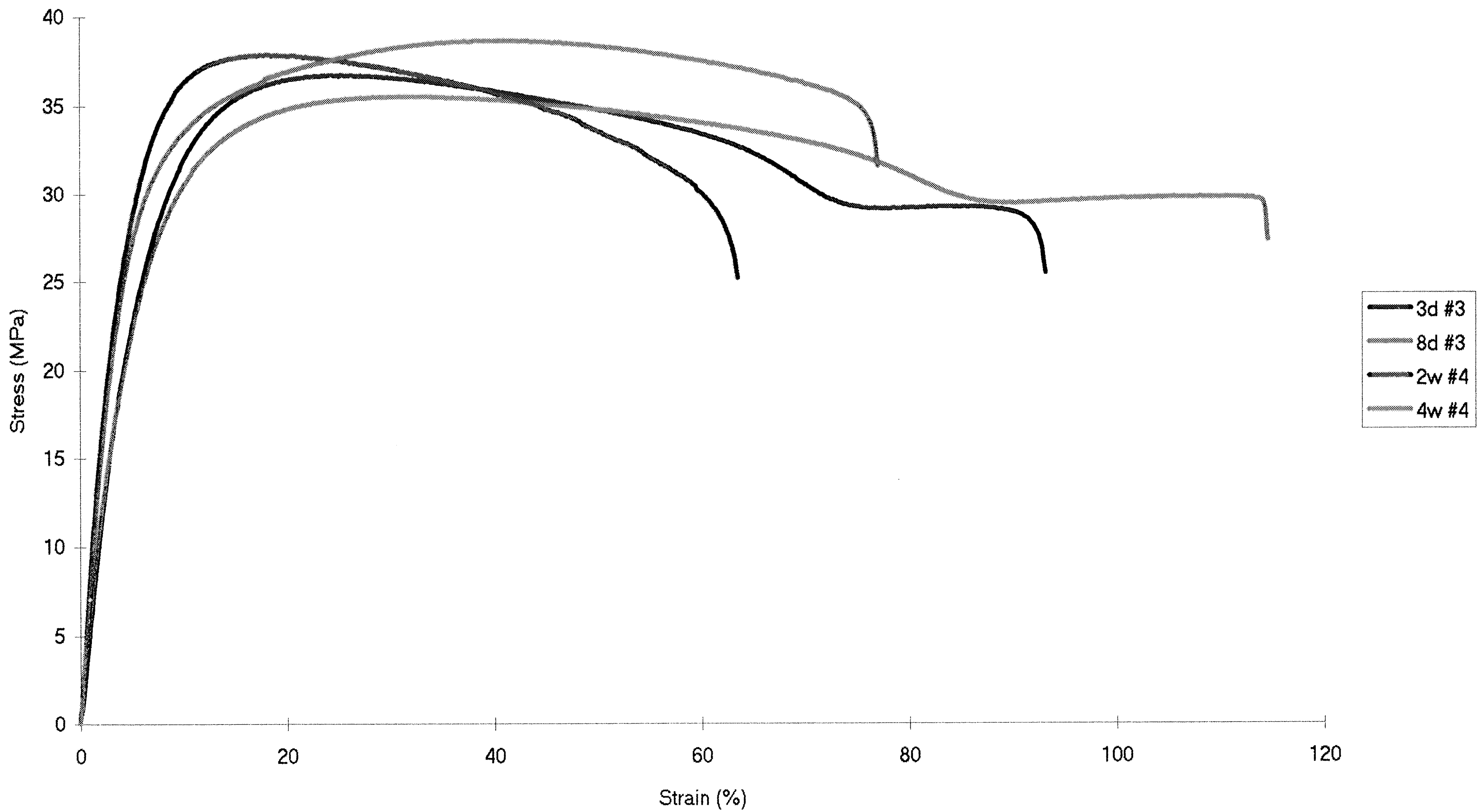


FIGURE 4 Coflon in Fluid F at 140C - batches as indicated #



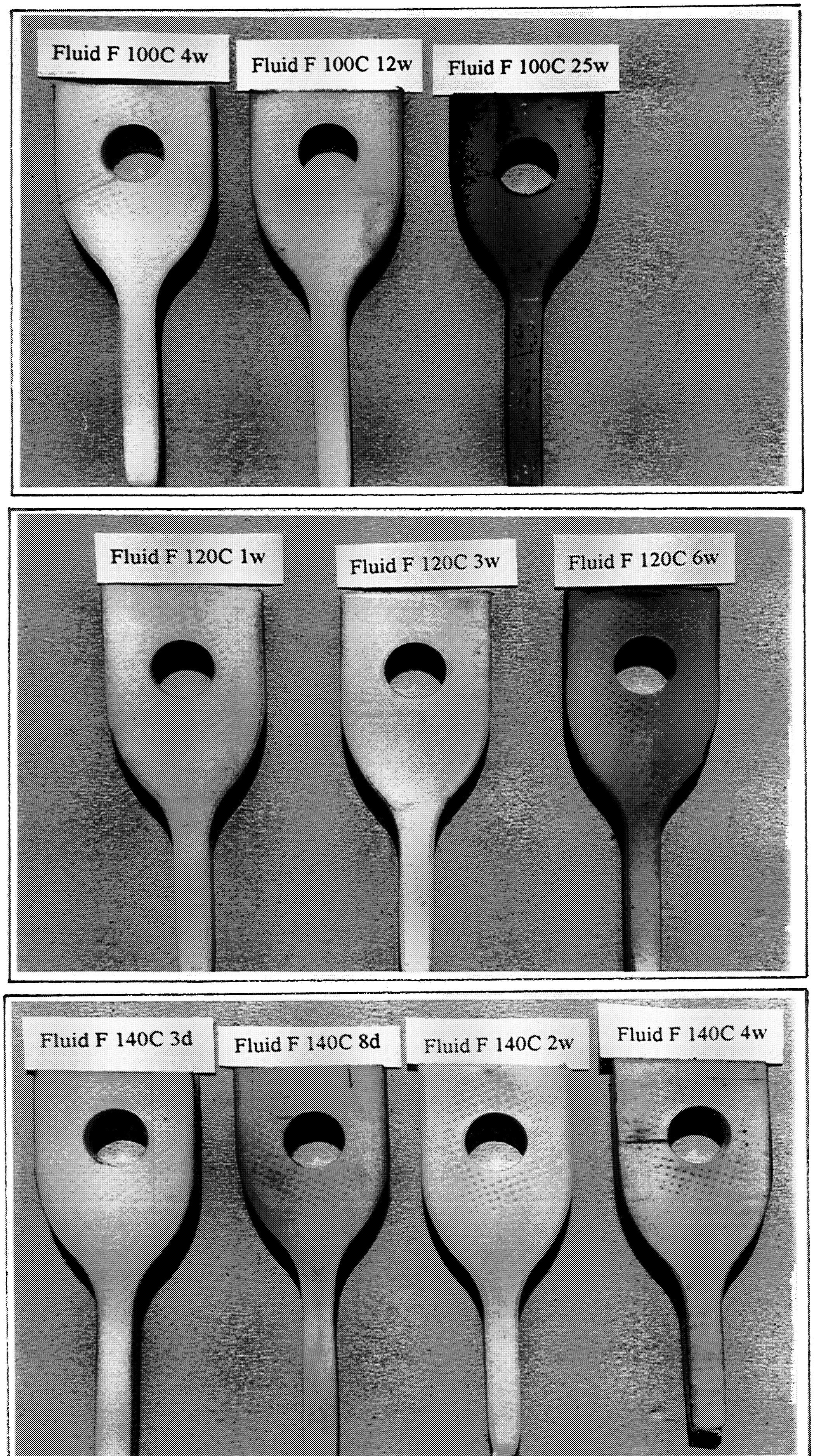


FIGURE 5 **Coflon samples after varying Fluid F exposures**

FIGURE 6a Arrhenius Plots from Young's Modulus of fluid F aged Coflon

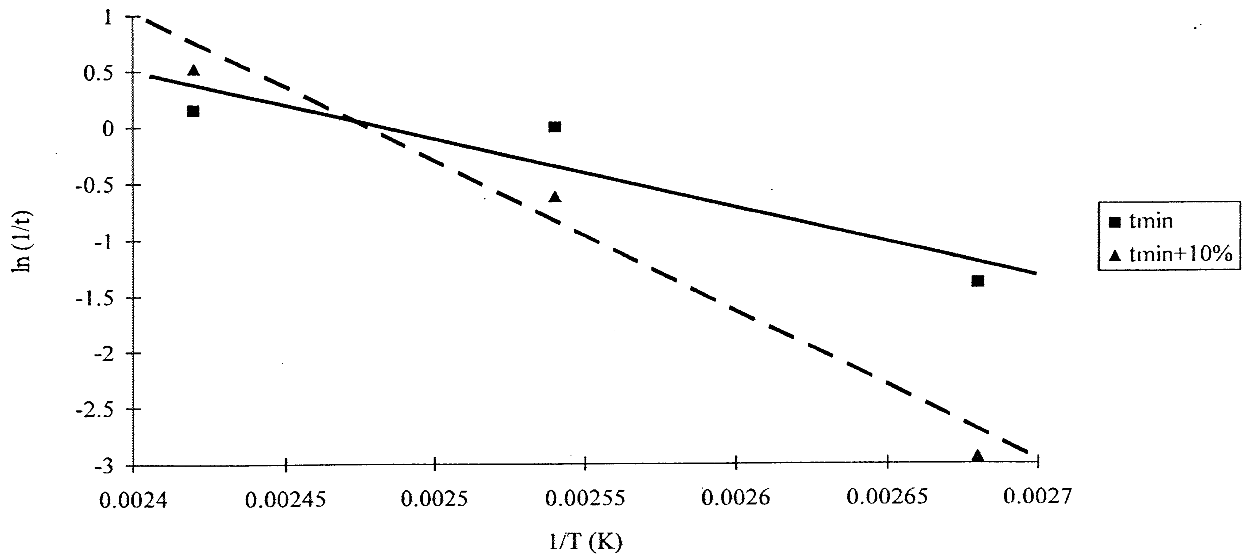
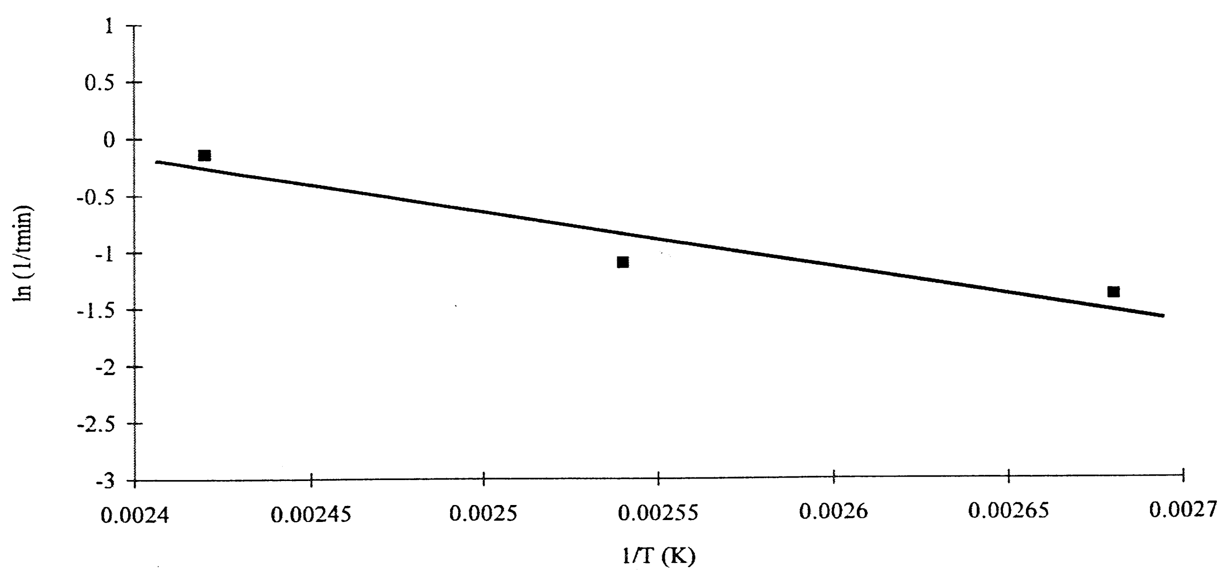


FIGURE 6b Arrhenius Plot from Young's Modulus of fluid F aged Tefzel



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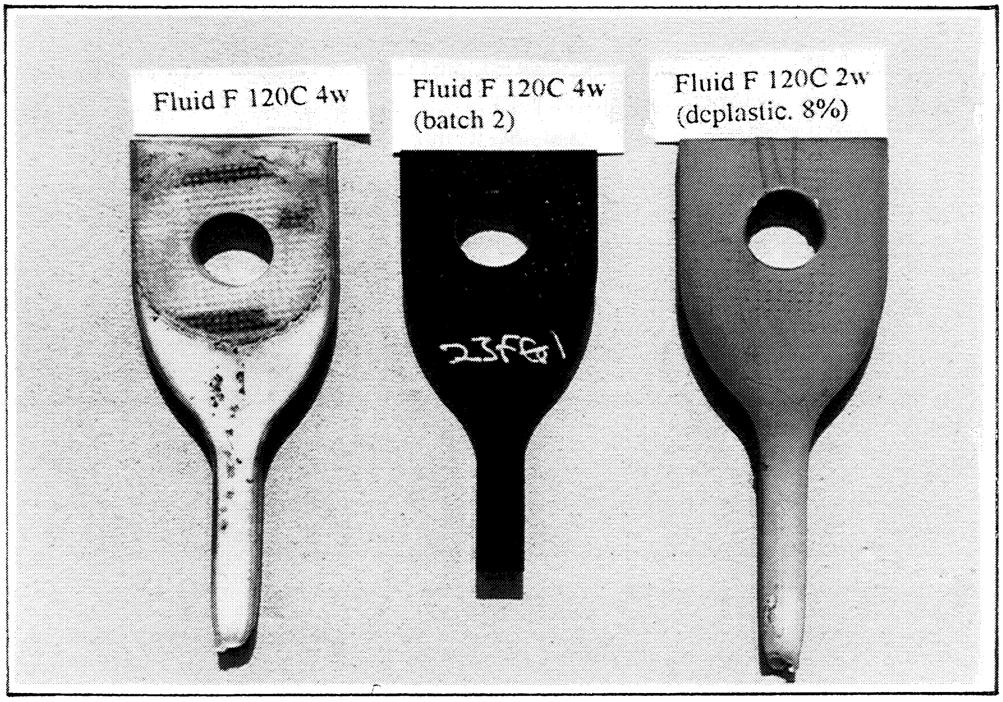


FIGURE 7 **Comparison between batches showing lack of severe degradation in batch #4 samples. Signs of discolouration appear in pre-aged deplasticized sample.**

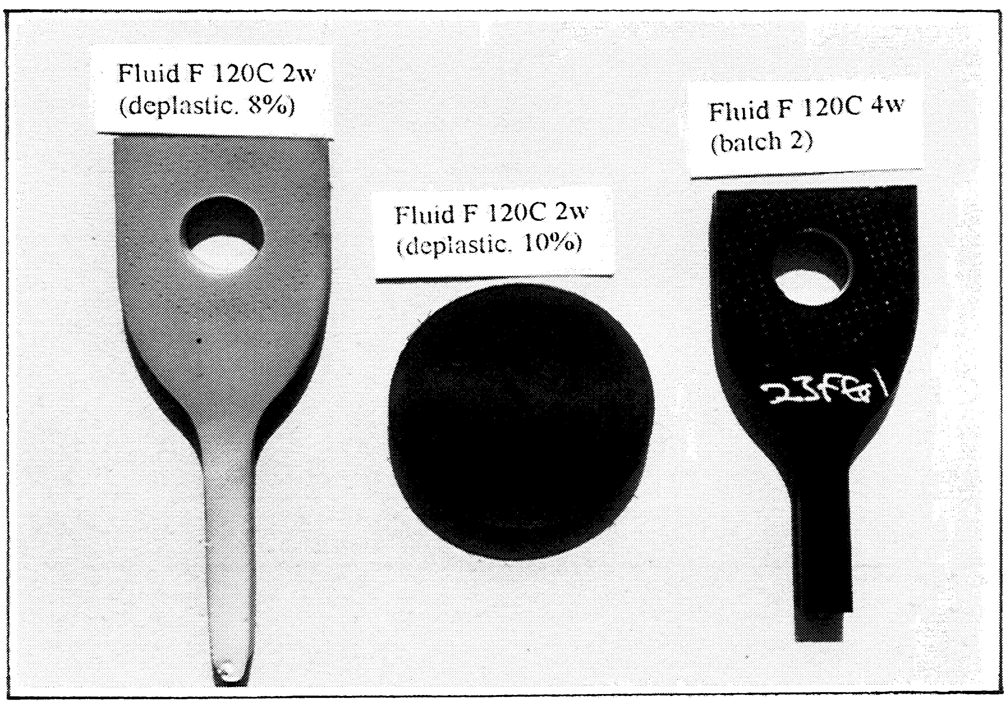


FIGURE 8 **Further evidence of increased Fluid F attack on a further deplasticized Coflon sample (batch # 4).**

MERL

FIGURE 9 Typical Stress-Strain curves for Tefzel after Fluid F Ageings

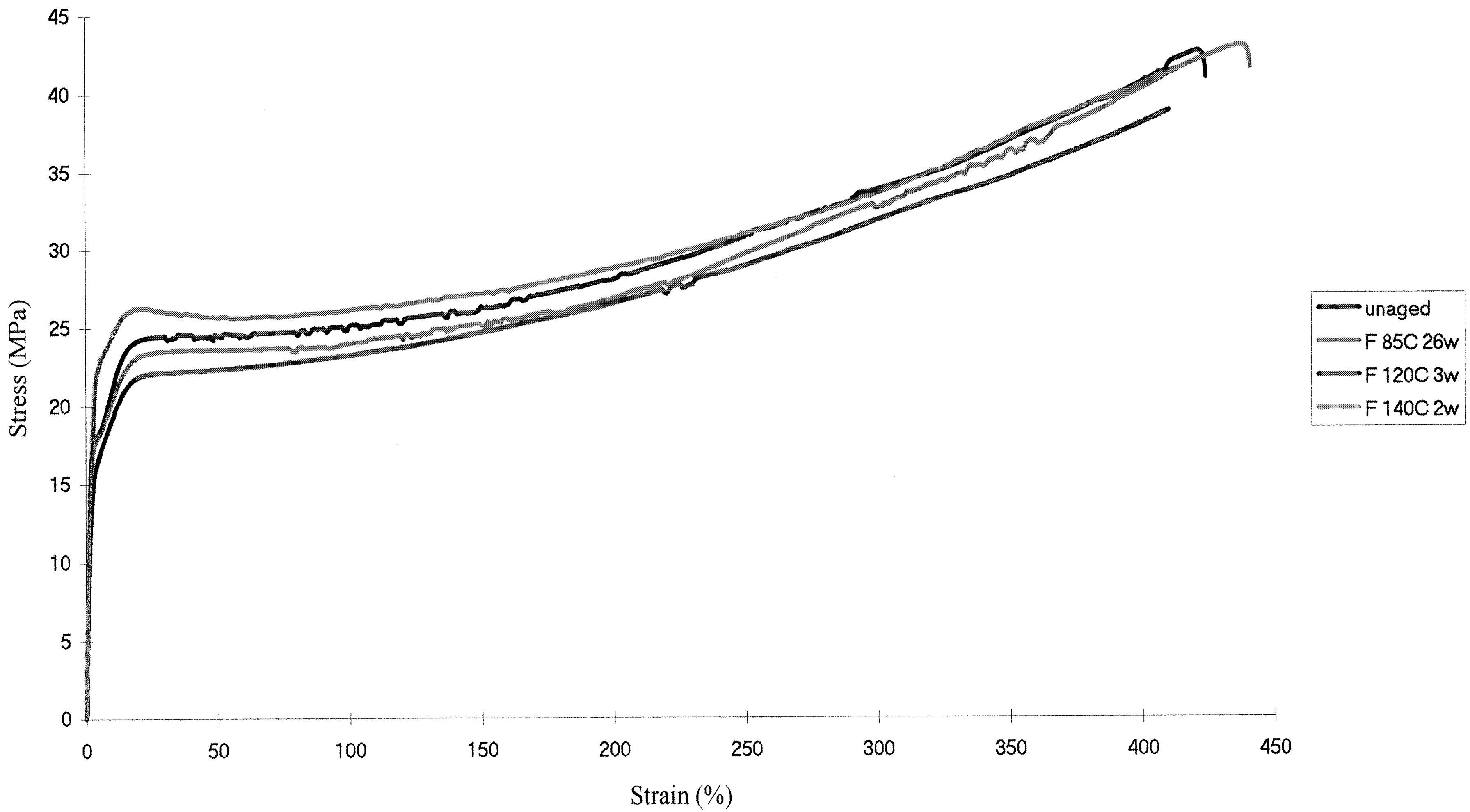


FIGURE 10 Coflon in Fluid G at 65C vapour pressure

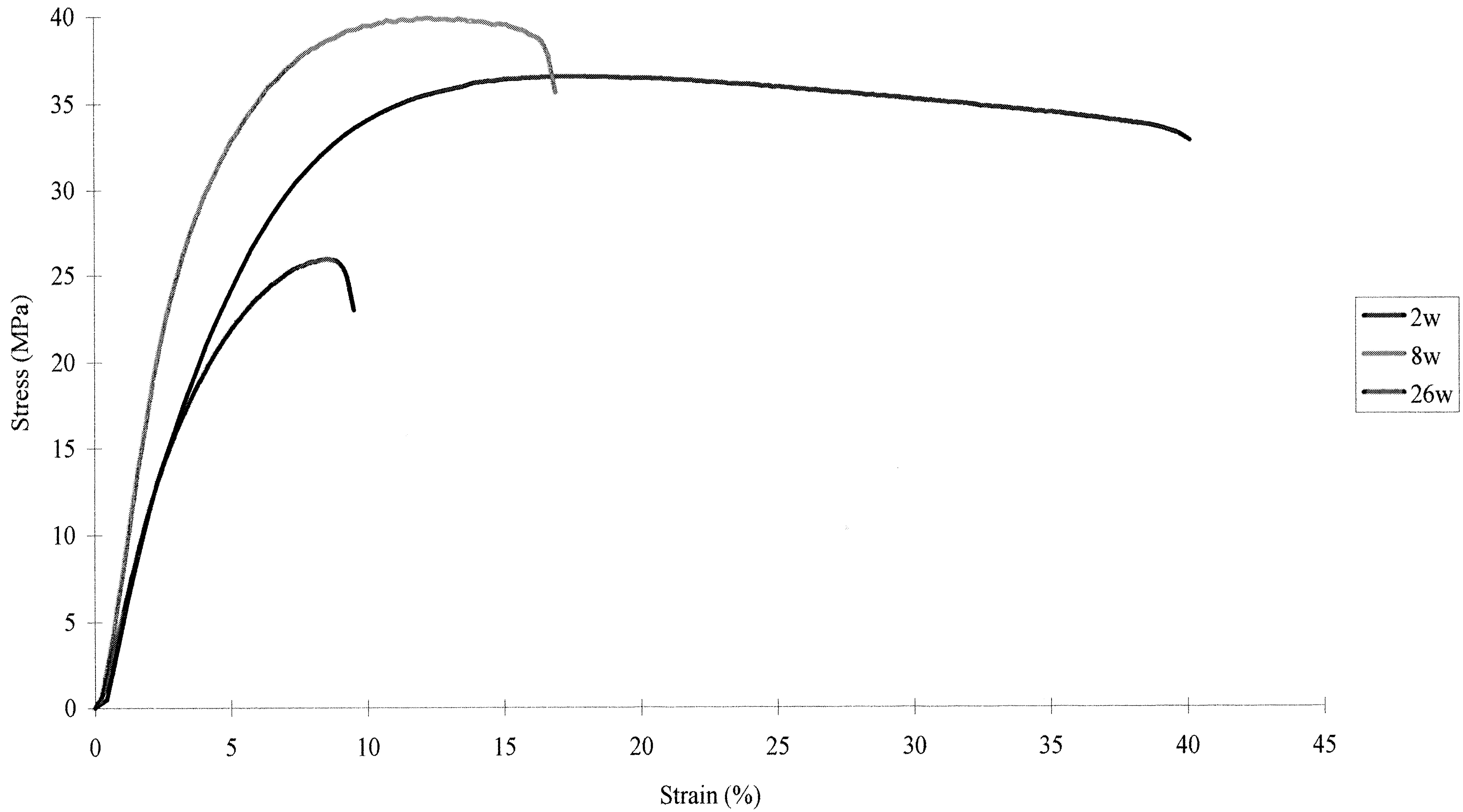


FIGURE 11 Coflon in Fluid G at 85C and 5kpsi

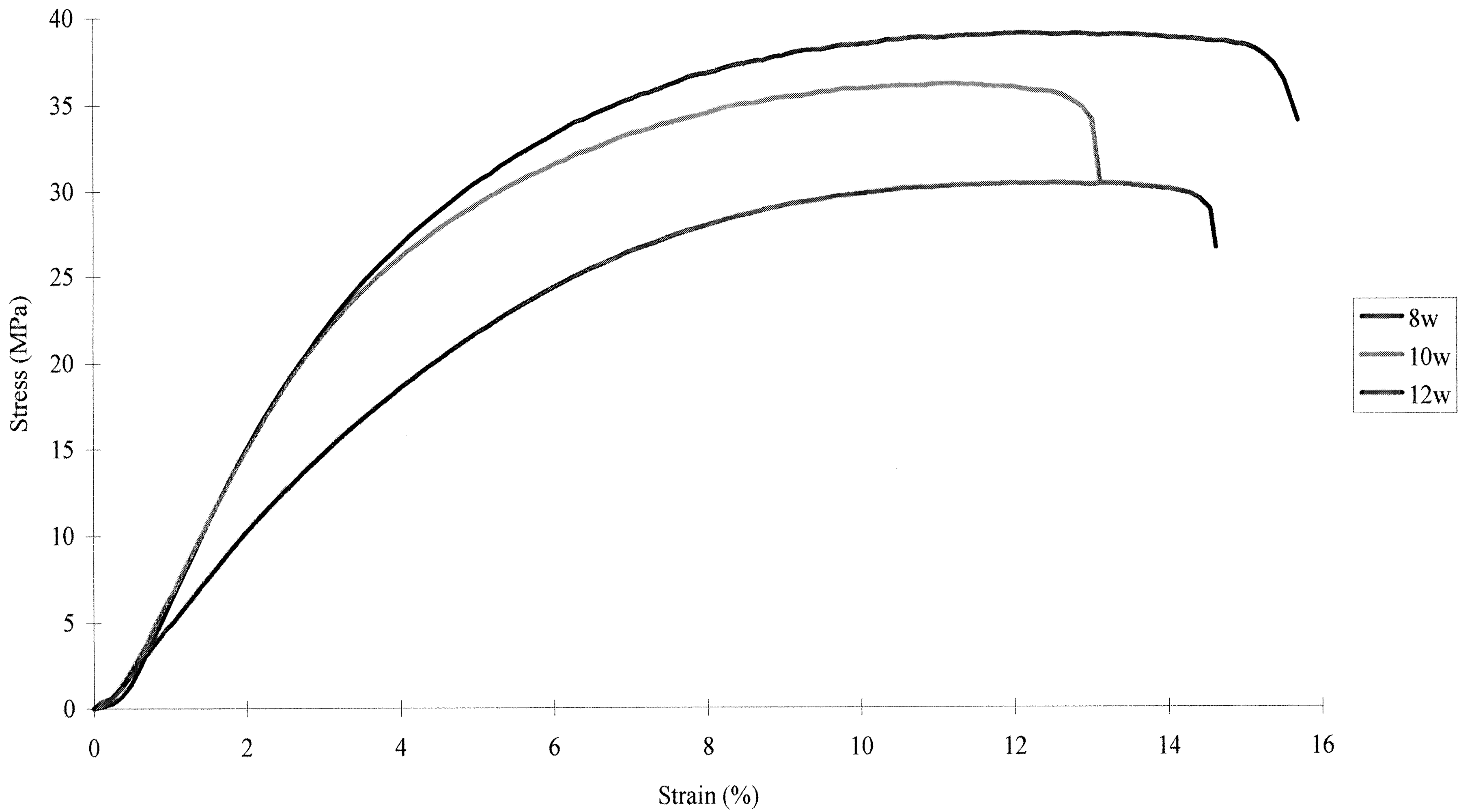


FIGURE 12 Coflon in Fluid G at 100C and 5kpsi

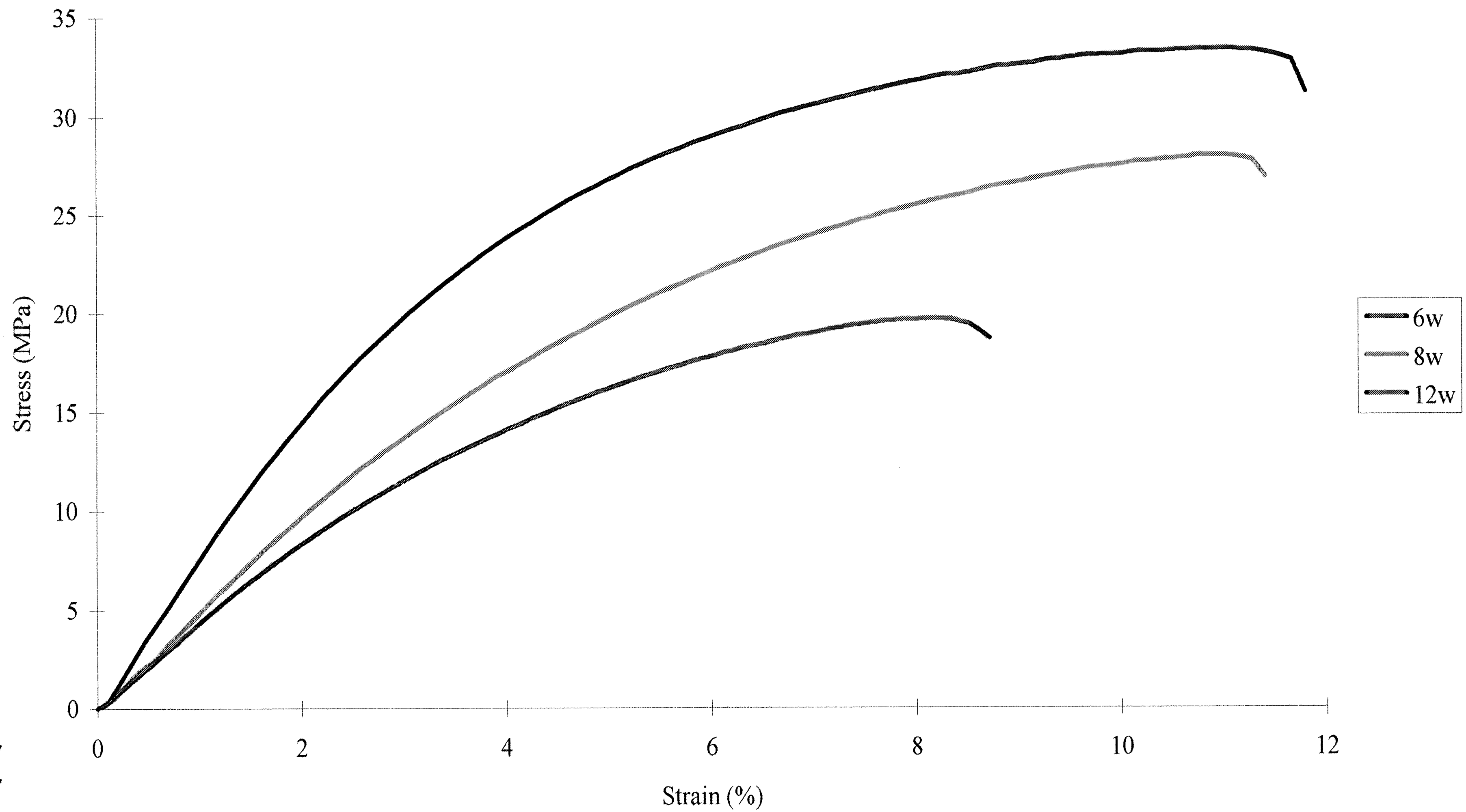
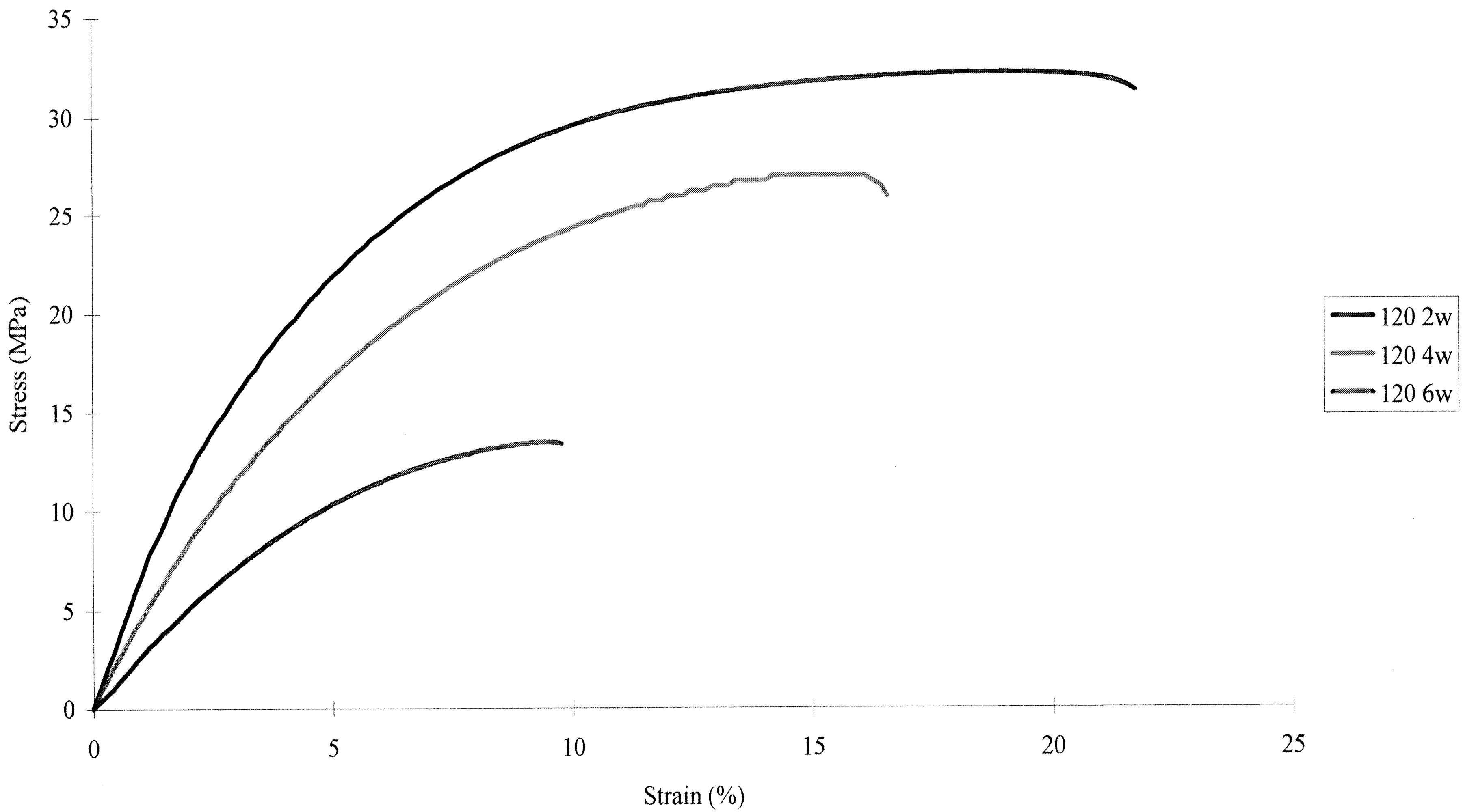
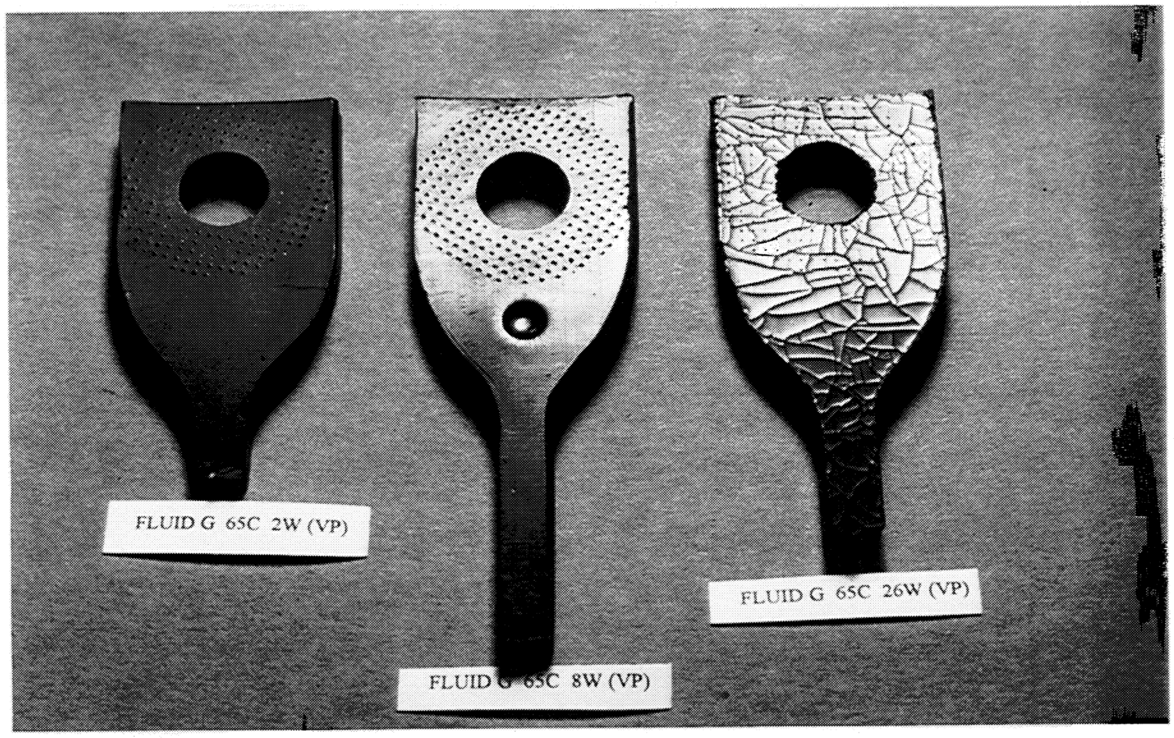


FIGURE 13 Coflon in Fluid G at 120C and 5kpsi





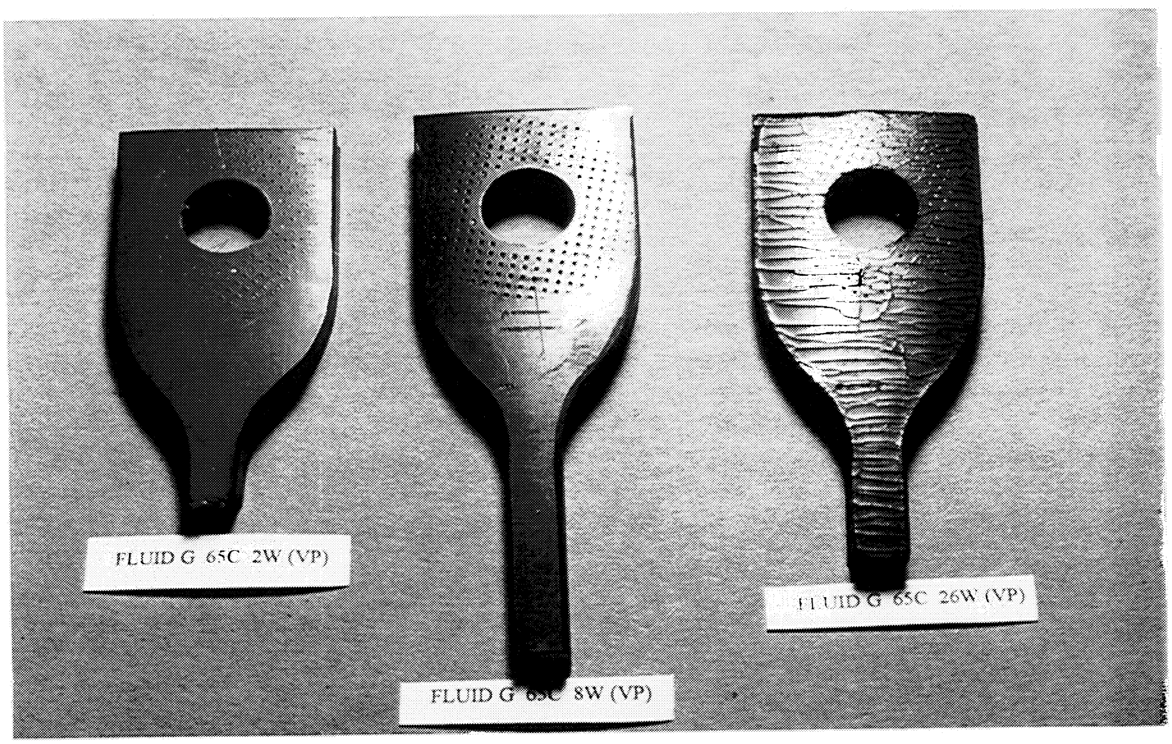


FIGURE 14 Effects of fluid G at 65C (reflux) on Coflon

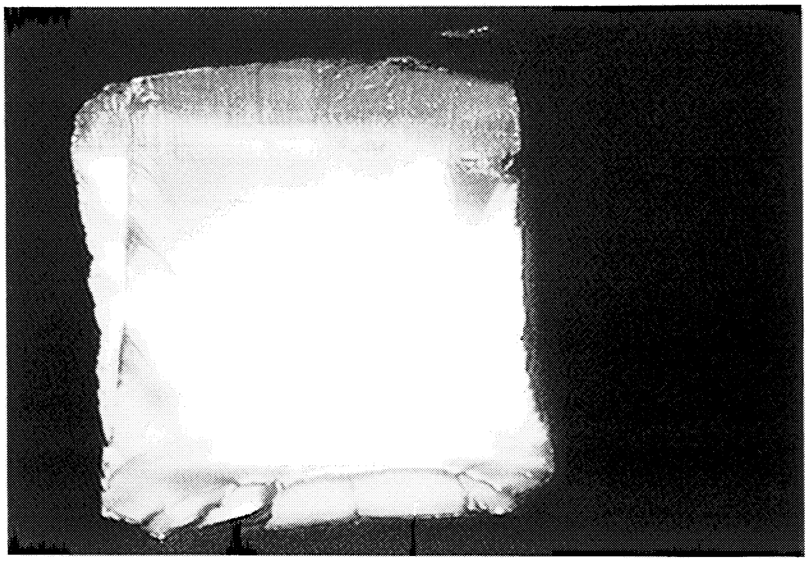


Figure 15a 2 week ageing

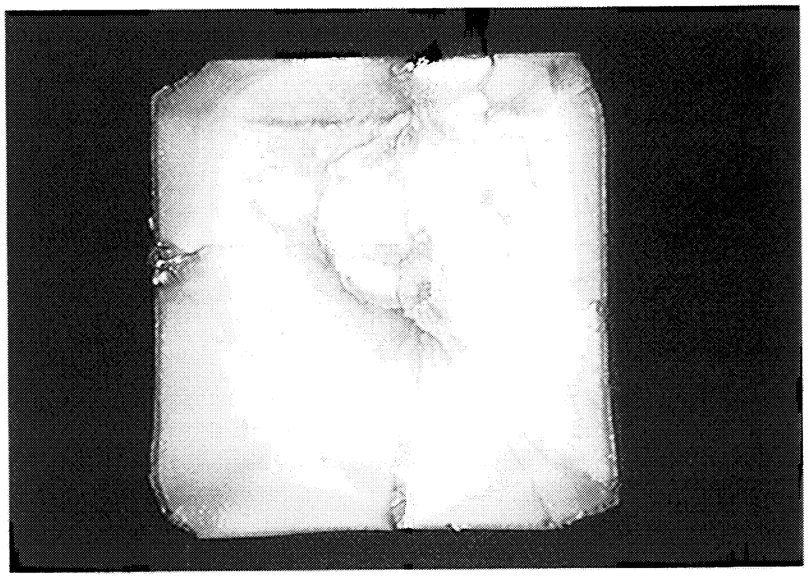


Figure 15b 8 week ageing

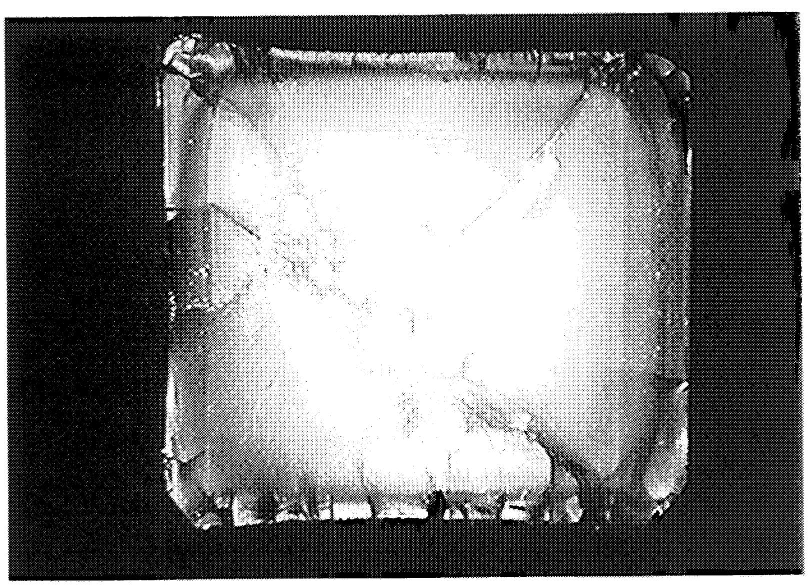


Figure 15c 26 week ageing

FIGURE 15 Fracture surfaces of Coflon after 65C fluid G exposures

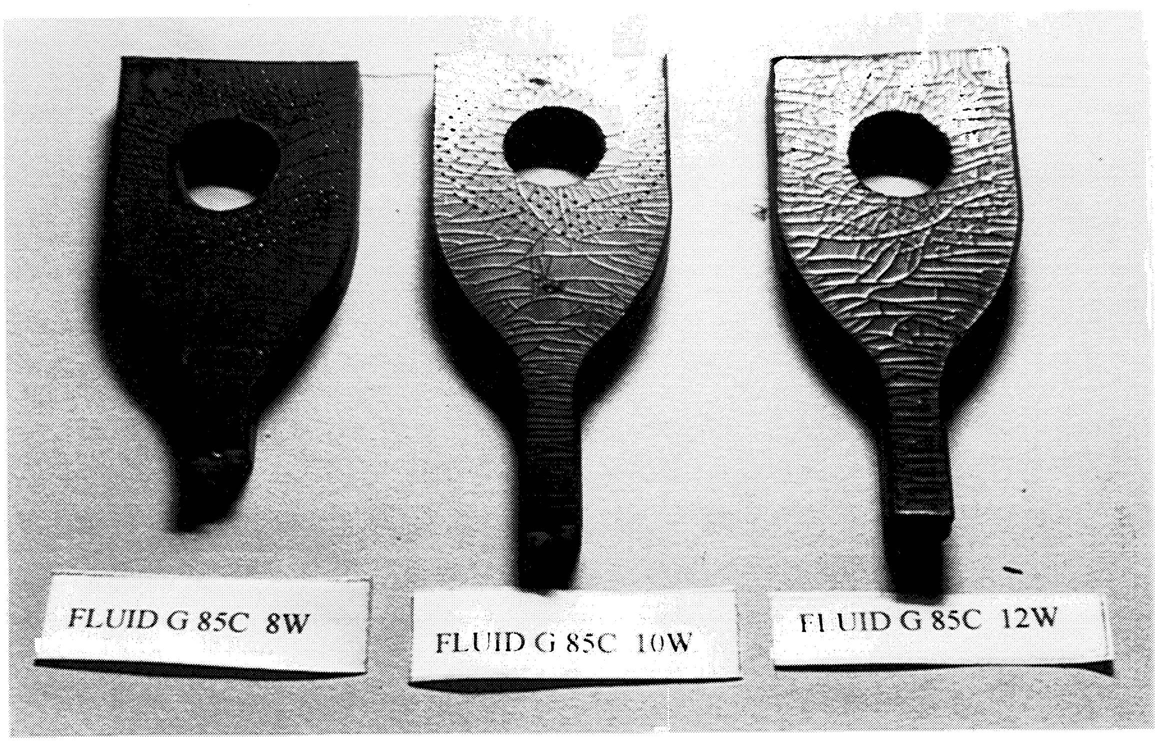


FIGURE 16 Effects of fluid G at 85C and 5kpsi on Coflon

MERL

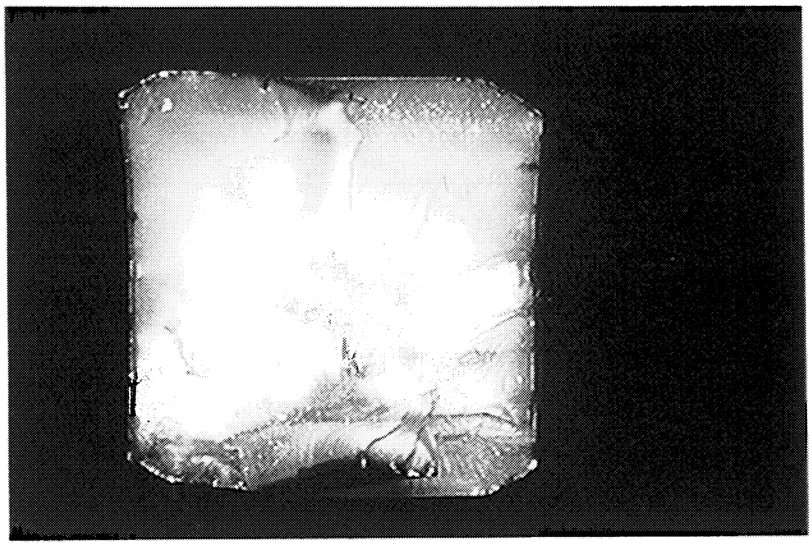


Figure 17a 8 week ageing

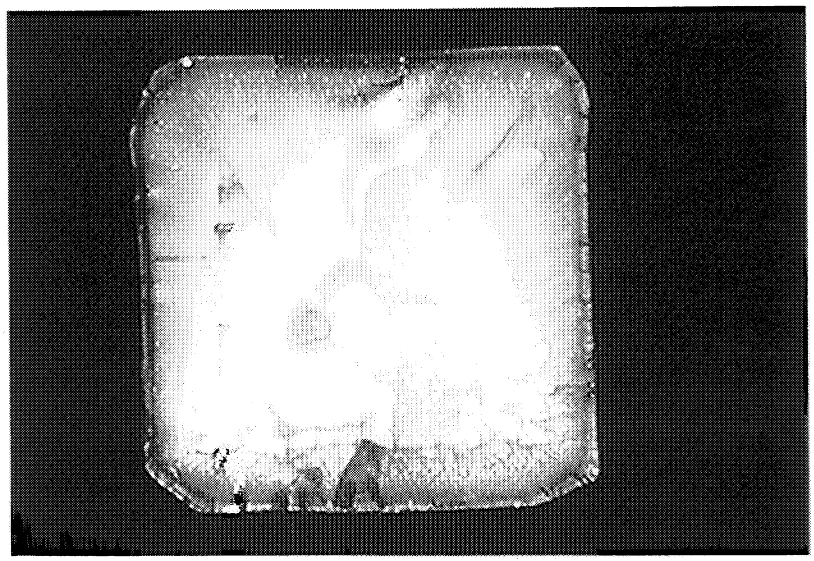


Figure 17b 10 week ageing

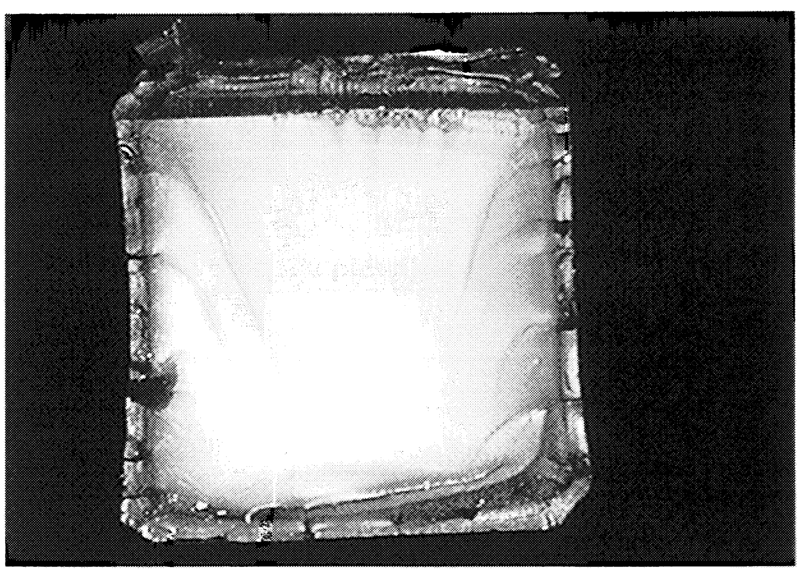
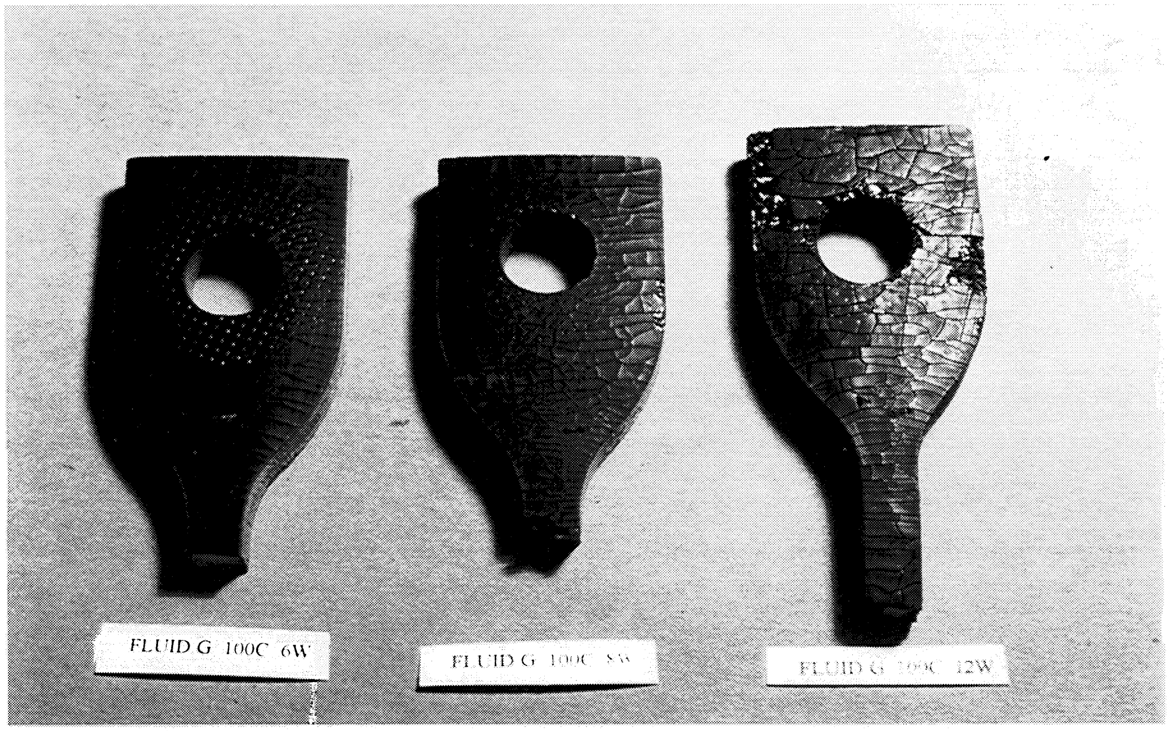


Figure 17c 12 week ageing

FIGURE 17 Fracture surfaces of Coflon after 85C fluid G exposures



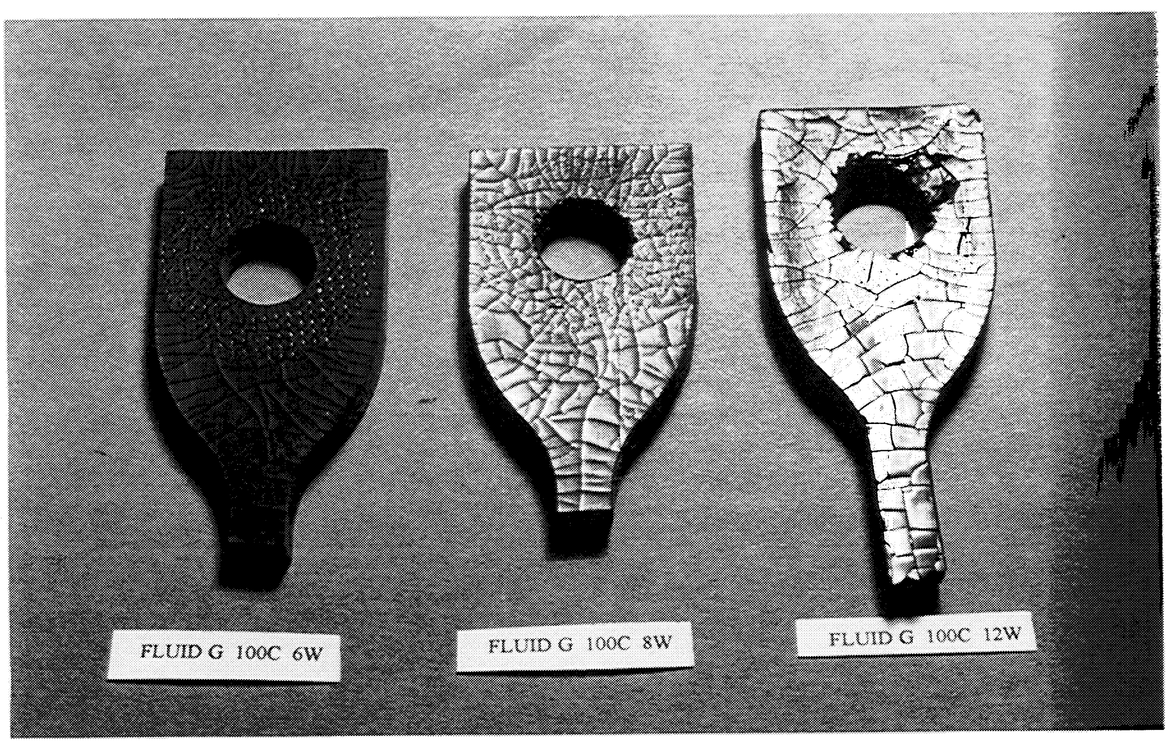


FIGURE 18 Effects of fluid G at 100C and 5kpsi on Coflon

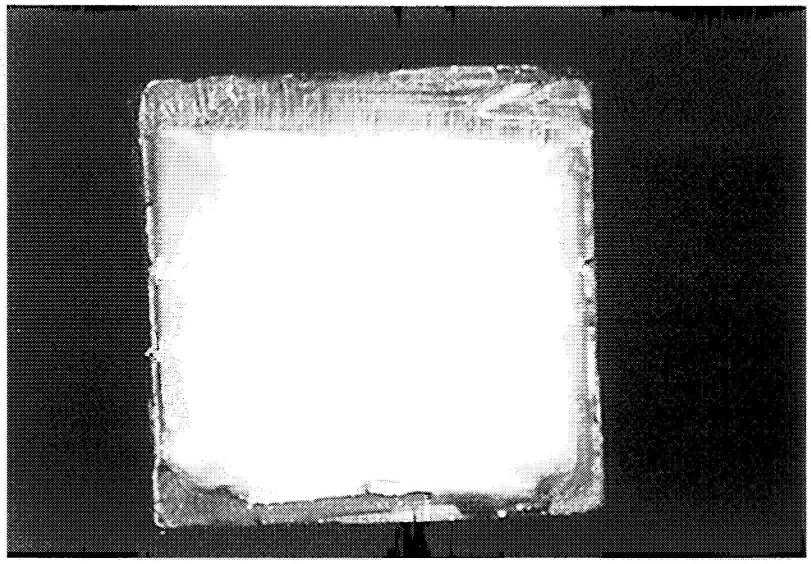


Figure 19a 6 week ageing

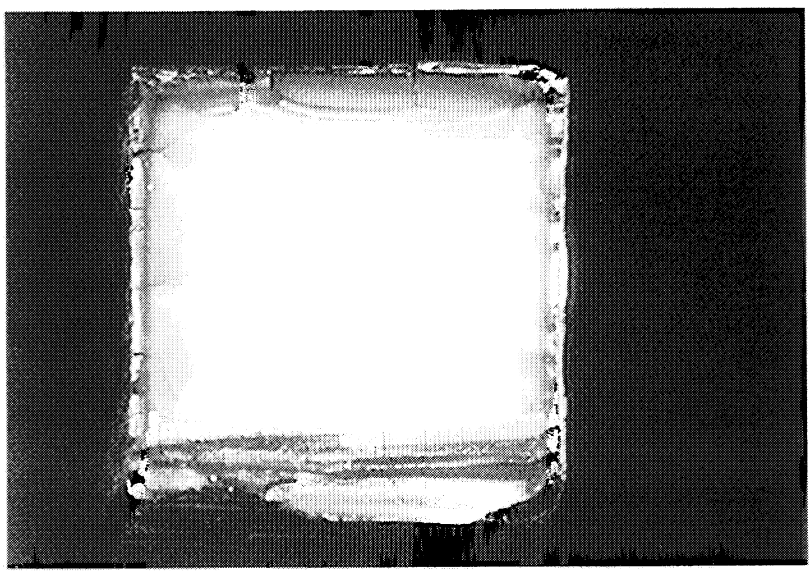


Figure 19b 8 week ageing

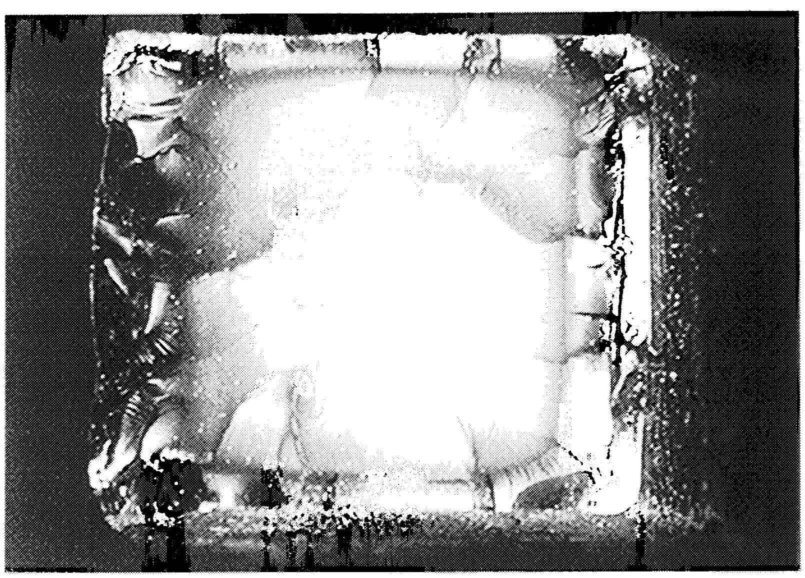
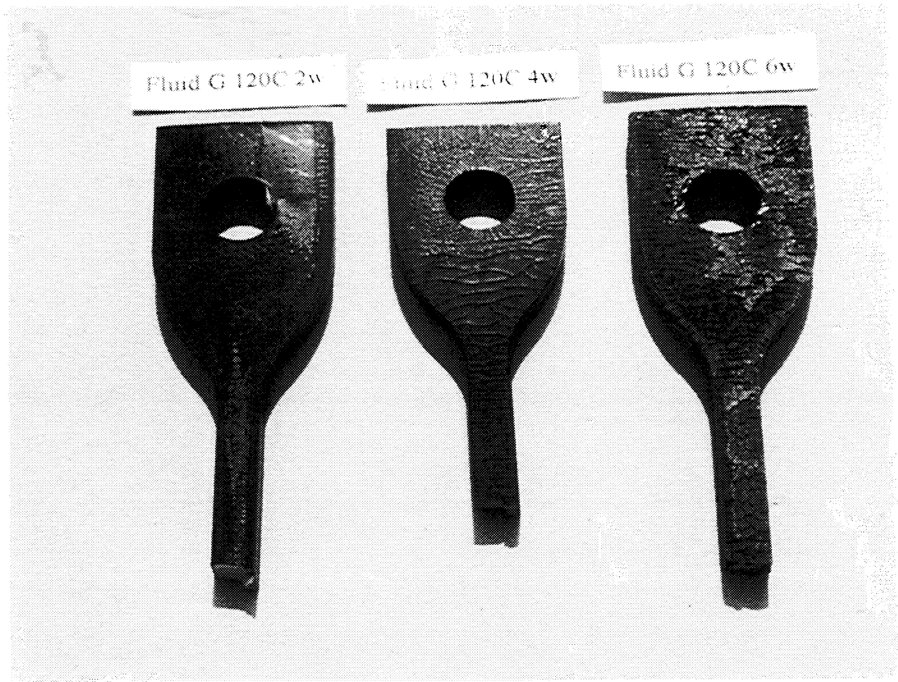


Figure 19c 12 week ageing

FIGURE 19 Fracture surfaces of Coflon after 100C fluid G exposures



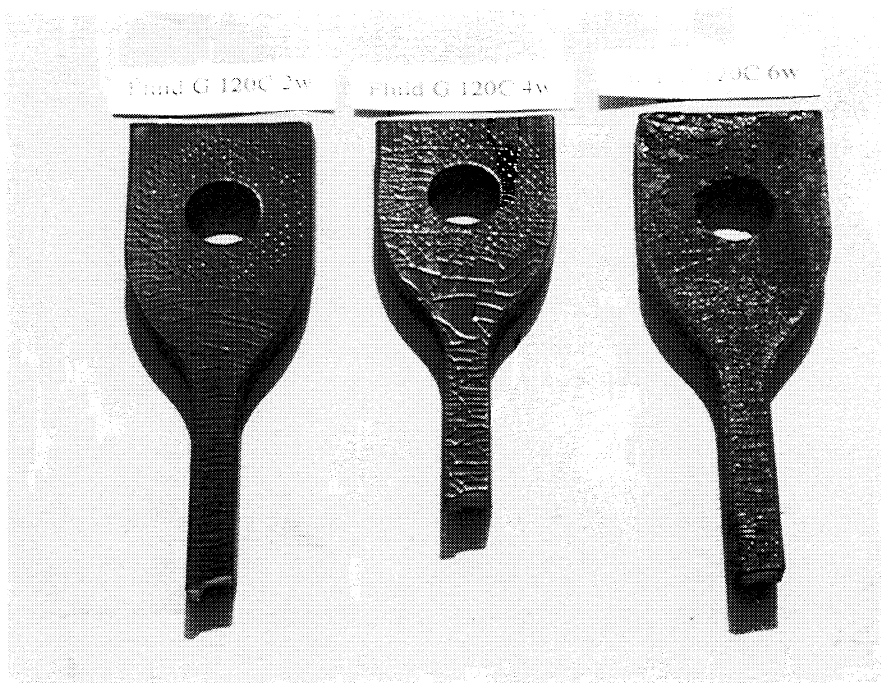


FIGURE 20 Effects of fluid G at 120C and 5kpsi on Coflon

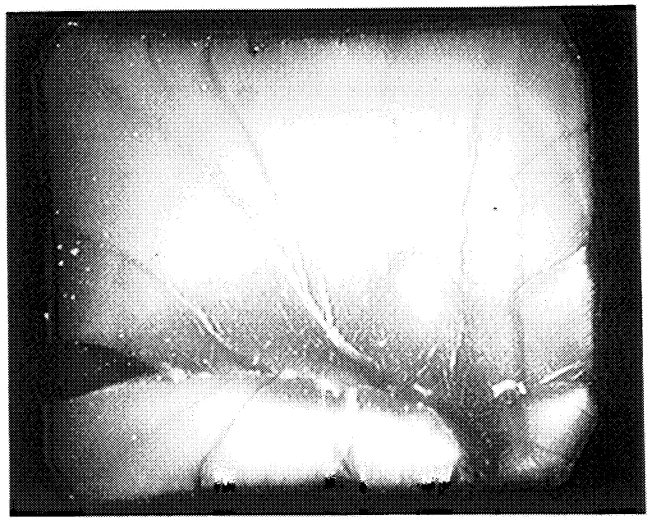


Figure 21a 2 week ageing

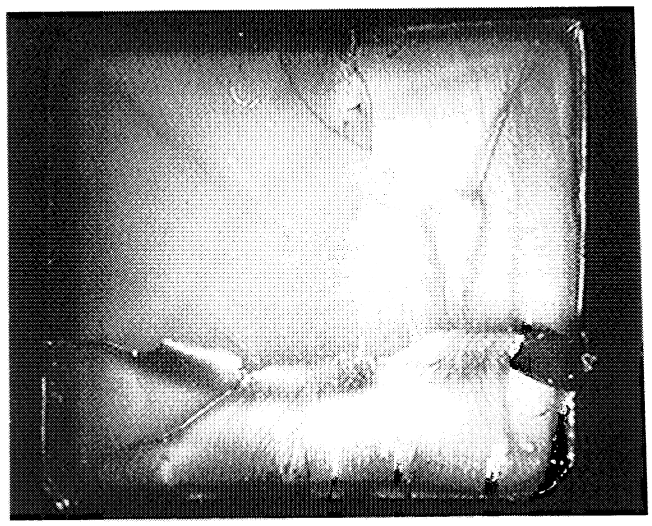


Figure 21b 4 week ageing

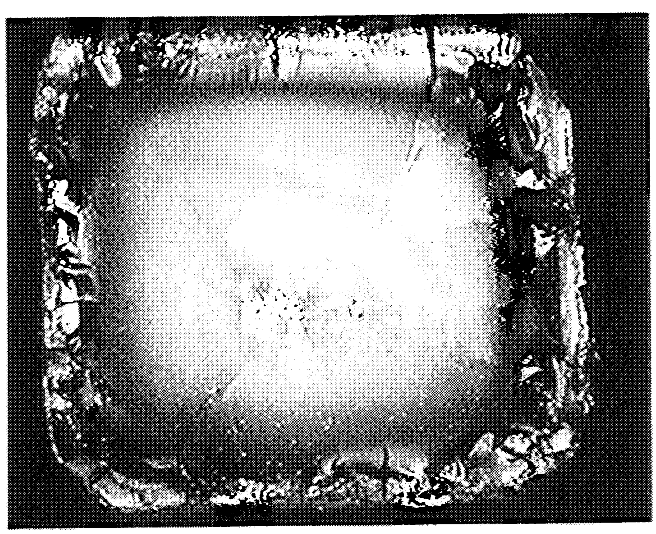


Figure 21c 6 week ageing

FIGURE 21 Fracture surfaces of Coflon after 120C fluid G exposures

FIGURE 22a Arrhenius Plot for Strength drop (25%) of Fluid G aged Coflon

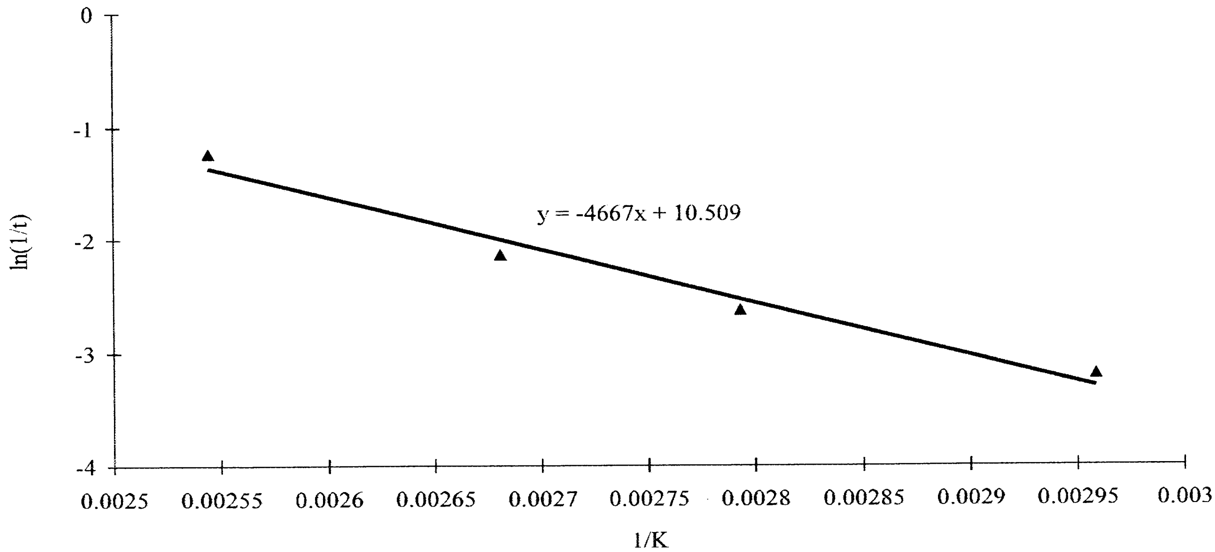
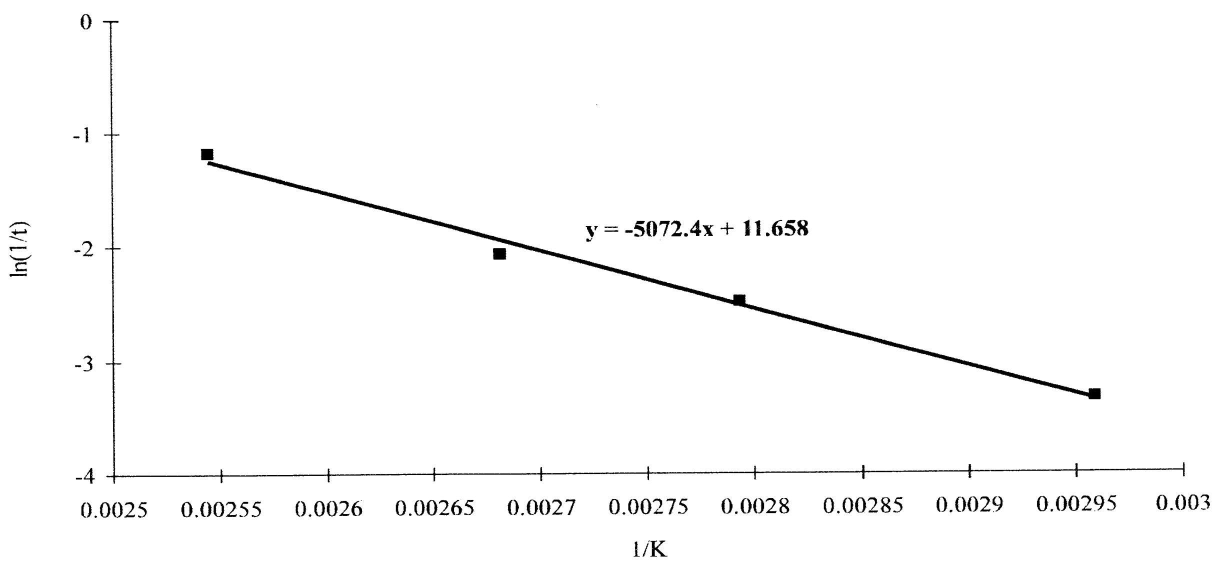


FIGURE 22b Arrhenius Plot for Modulus drop (25%) of Fluid G aged Coflon



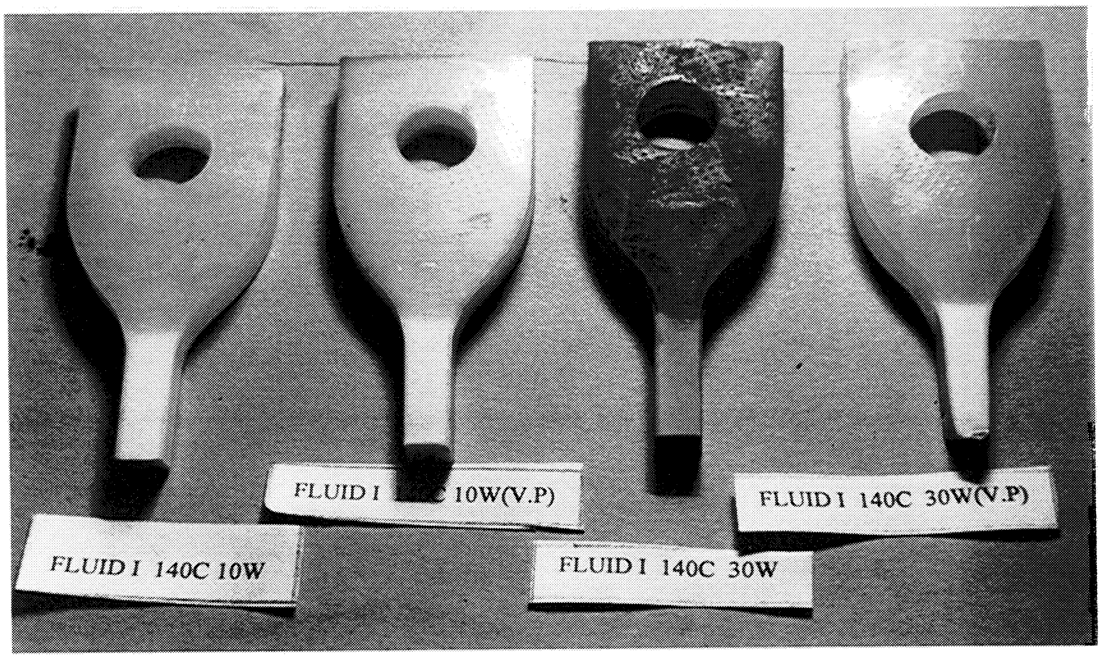


FIGURE 23 Effects of Fluid I ageing on Coflon

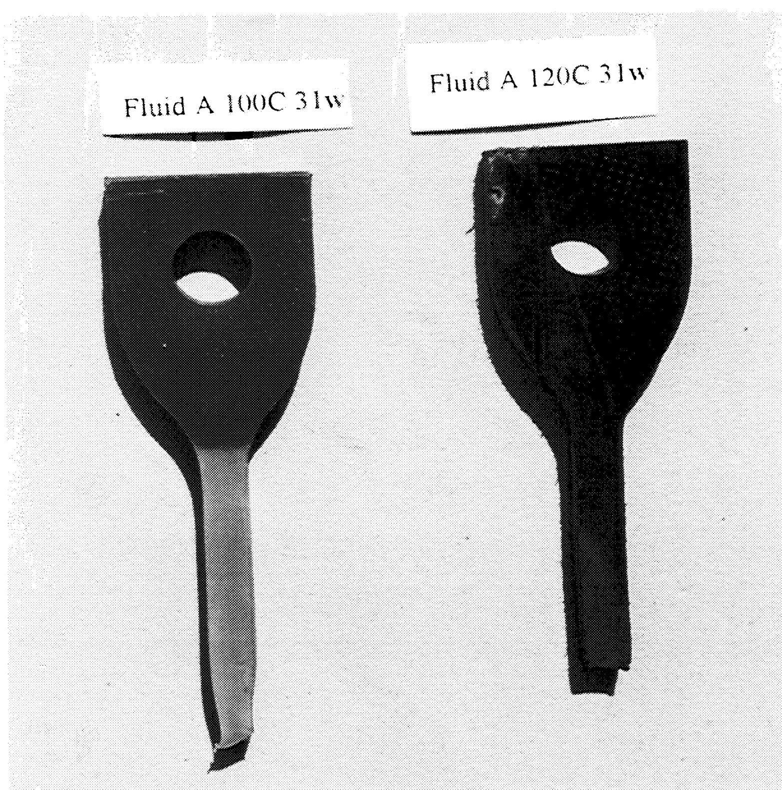


FIGURE 25 Coflon after fluid A vapour pressure exposures

FIGURE 24 Tefzel in Fluid I at 140C and 5kpsi

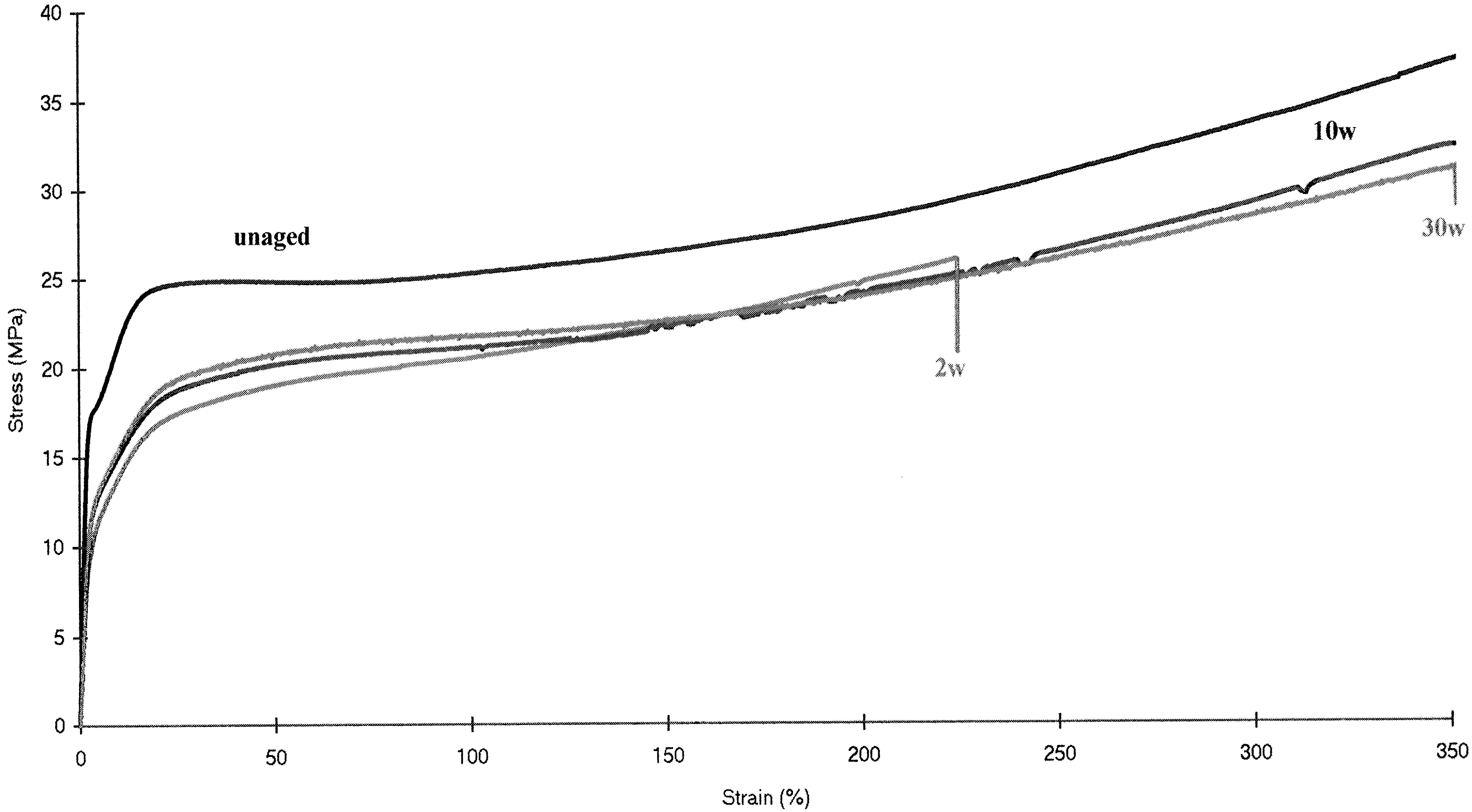


FIGURE 26 Coflon after Fluid A exposures at vapour pressure

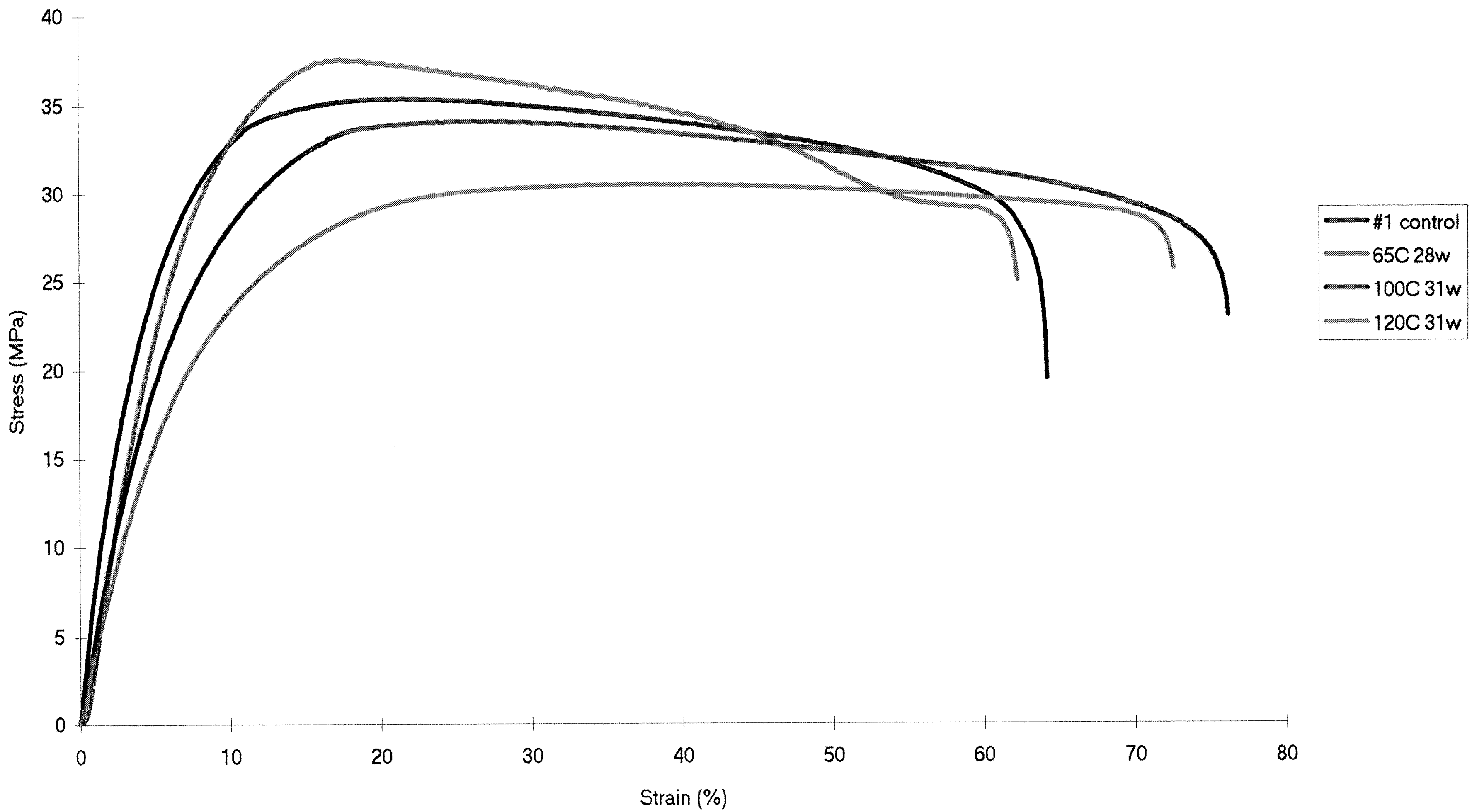


FIGURE 27 Coflon after 5 weeks in Fluid J at 100C - vapour pressure

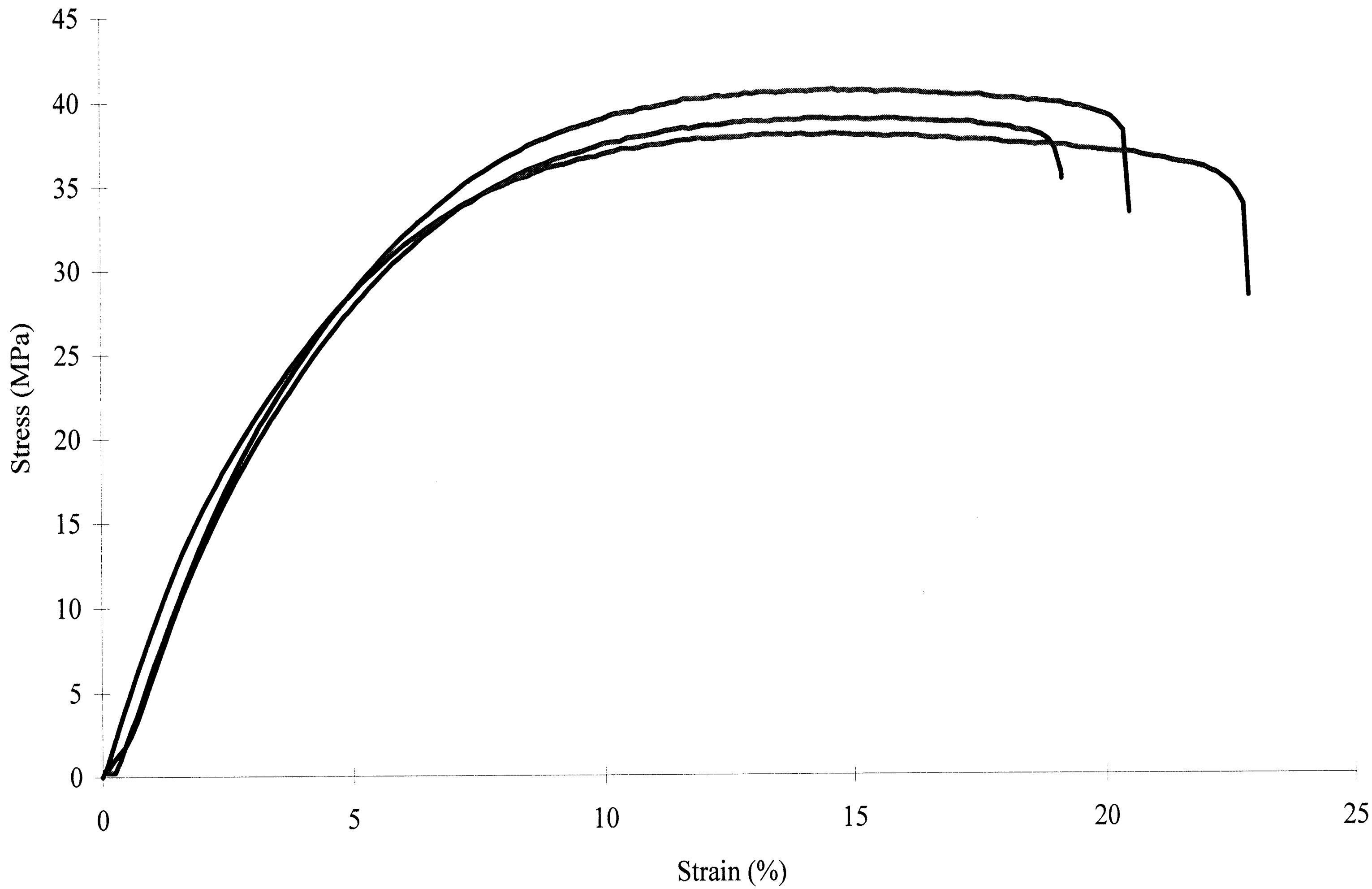


FIGURE 28 70C Fatigue testing of unaged and fluids F and I aged Tefzel

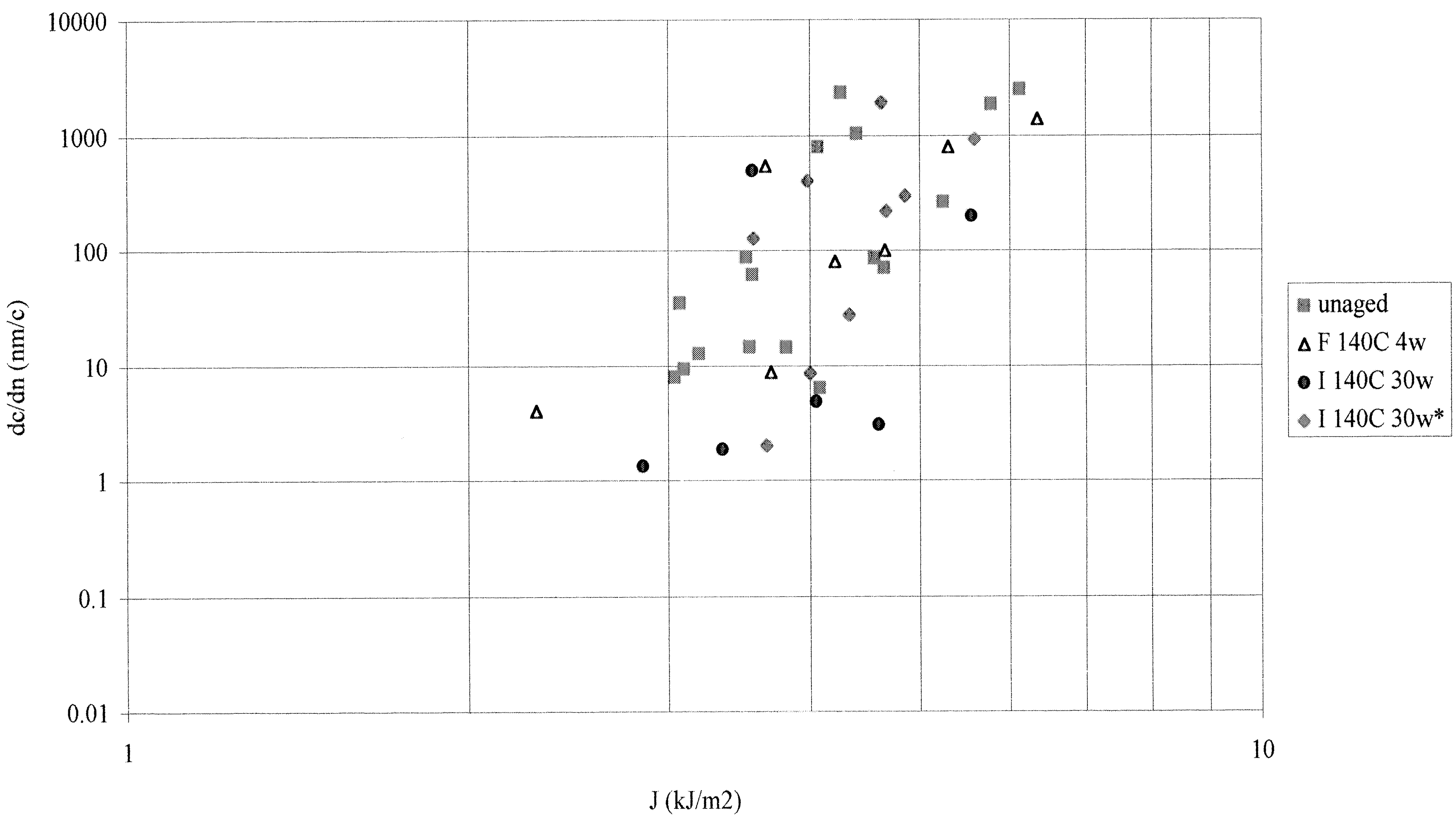


FIGURE 29 Effects of Pipe extrusion direction on Fatigue curve at 70C of Coflon

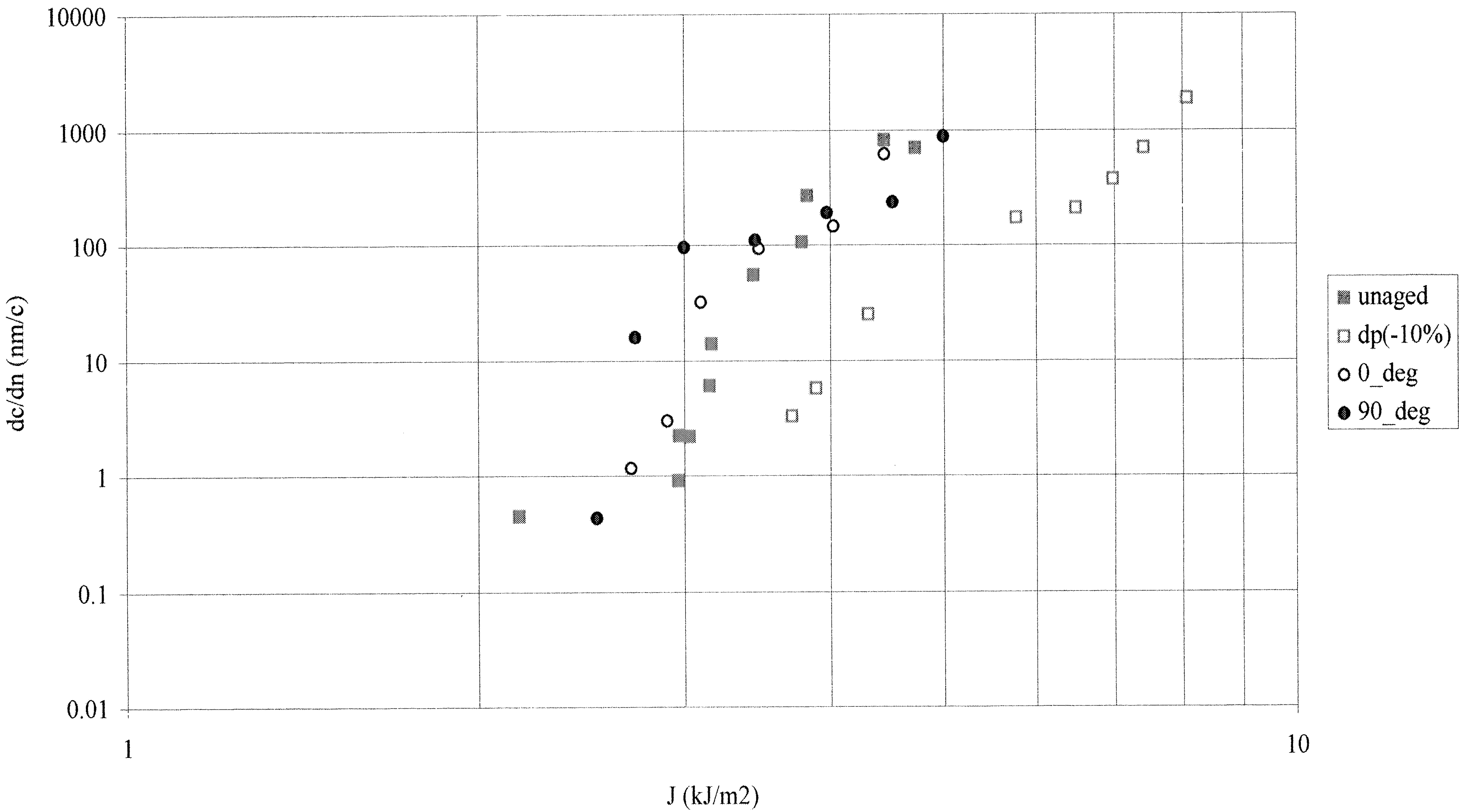


FIGURE 30 Effects of Fluid F at 85C on Coflon Fatigue Resistance

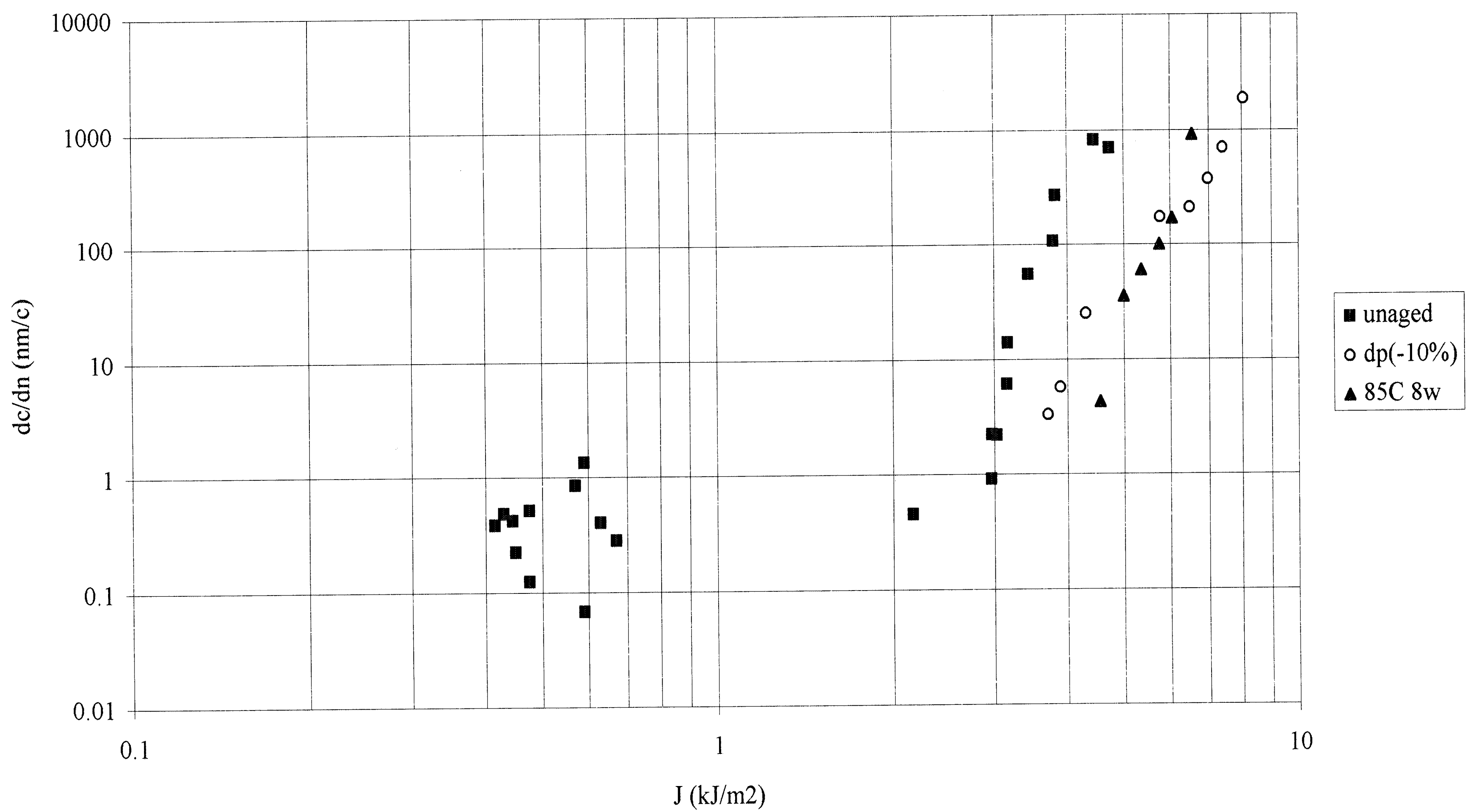


FIGURE 31 Effects of Fluid F at 100C on Coflon Fatigue Resistance

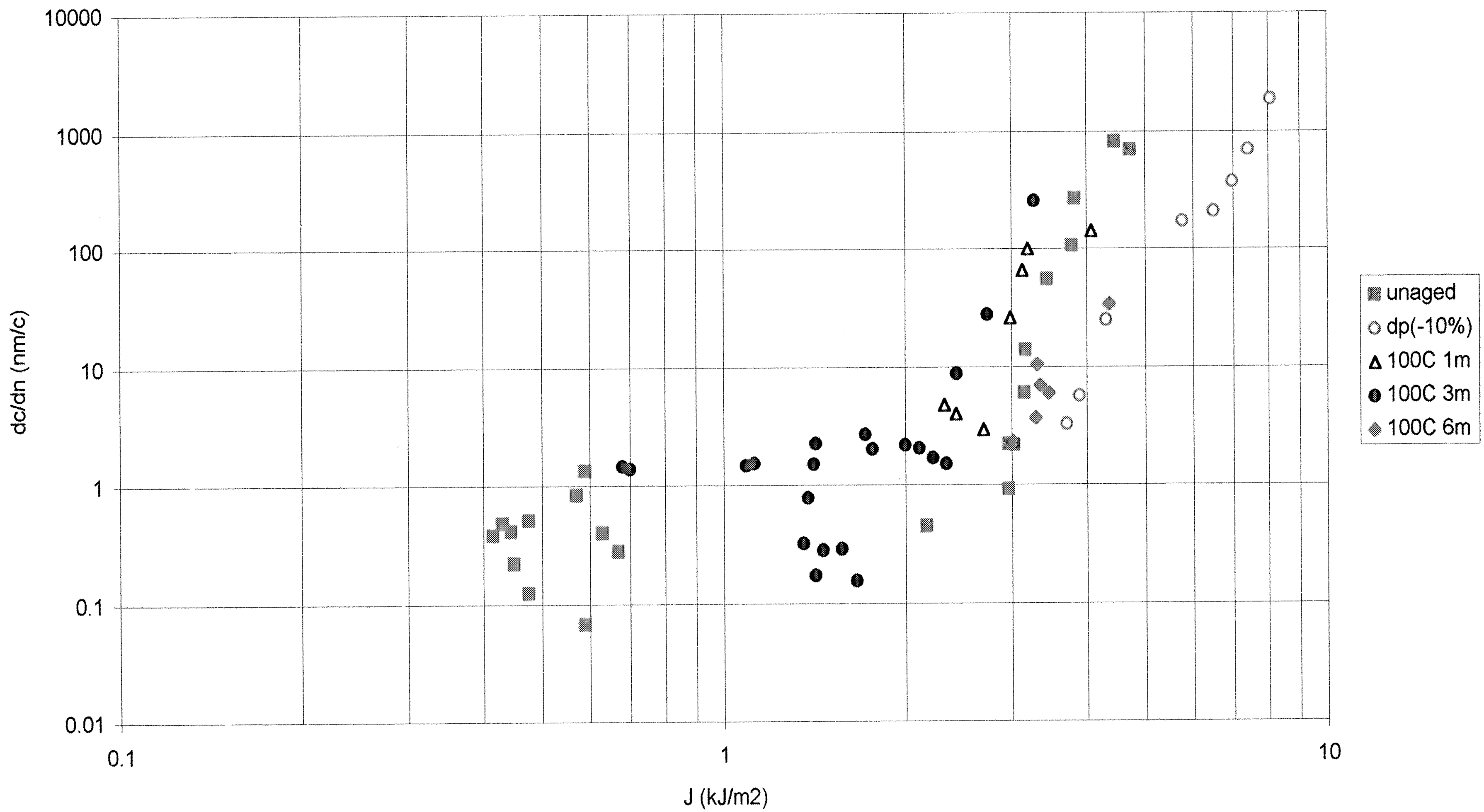


FIGURE 32 Effects of Fluid F at 120C on Coflon Fatigue Resistance
* strained during ageing

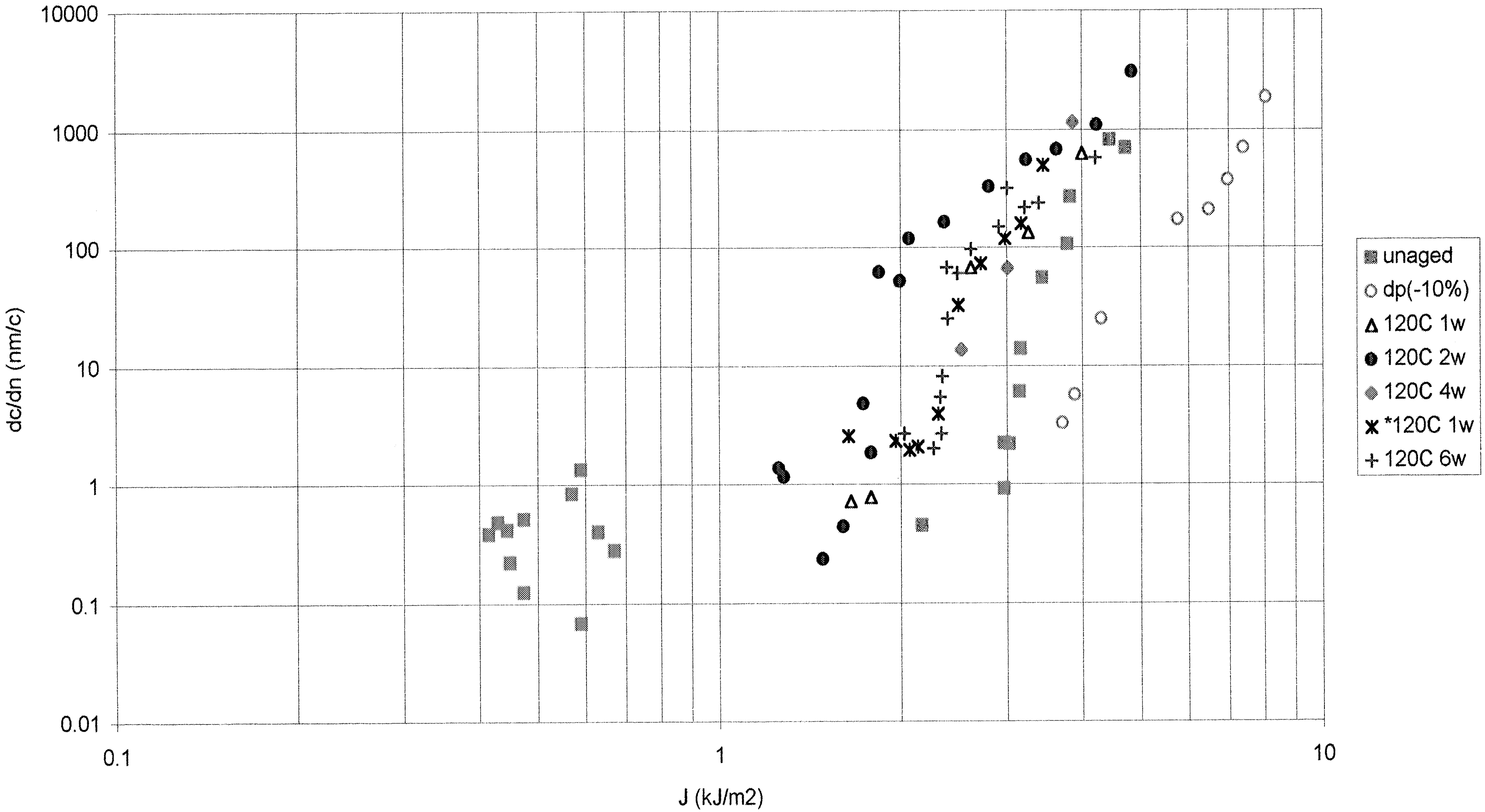


FIGURE 33 Effects of Fluid F at 140C on Coflon Fatigue Resistance

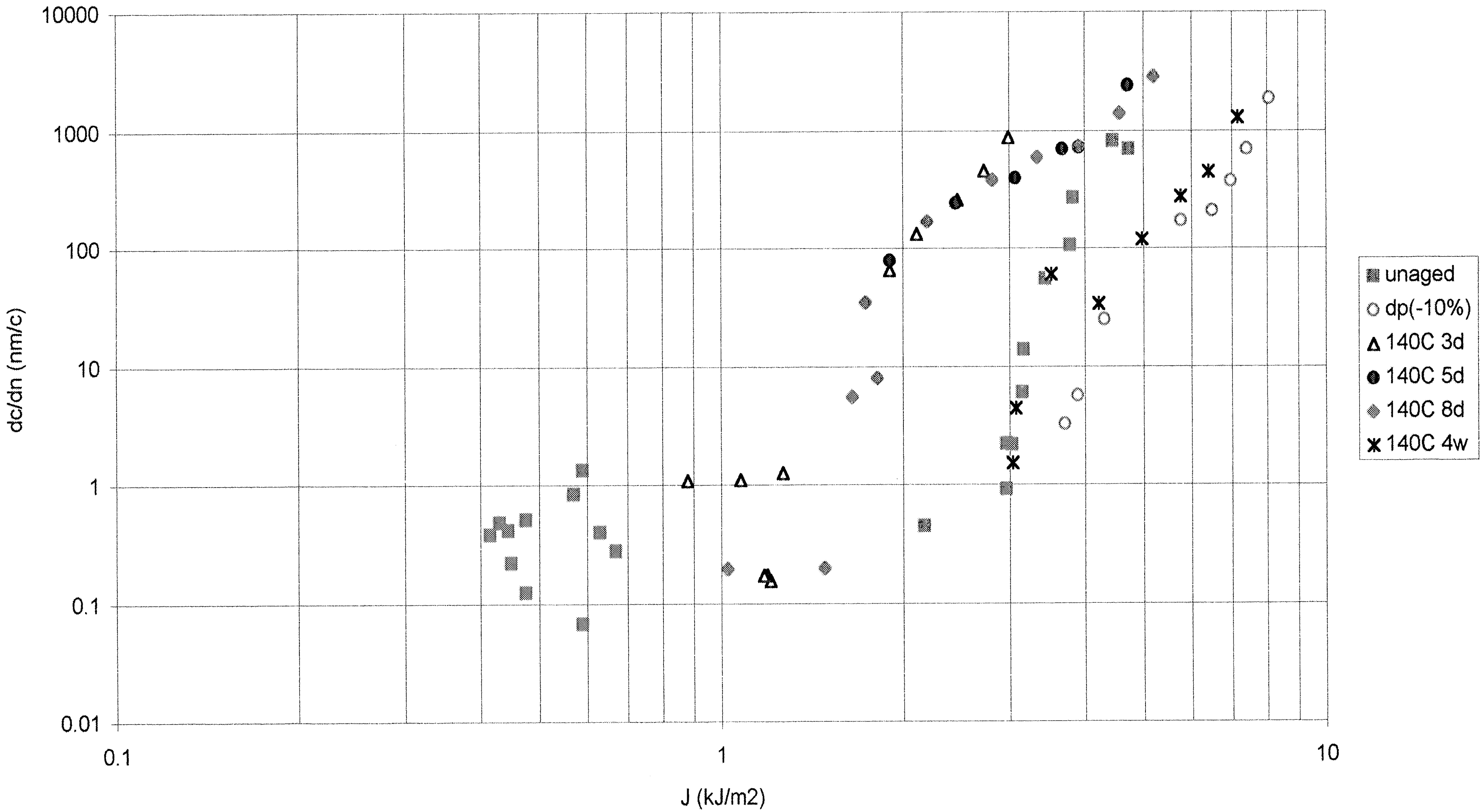


FIGURE 34 Arrhenius plots of fatigue resistance changes in Coflon after fluid F exposures

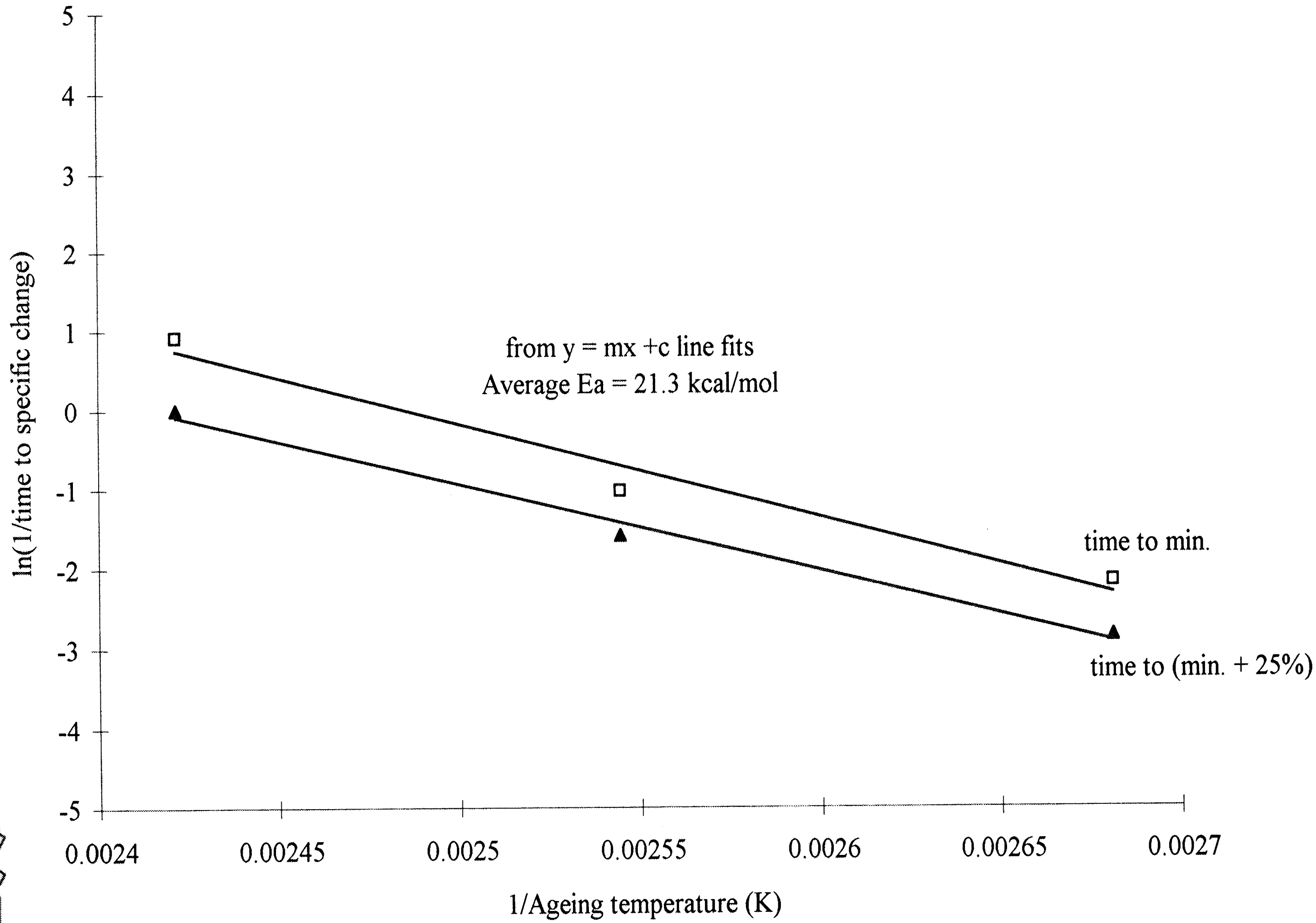


FIGURE 36 Stress Relaxation of unaged Coflon tensile testpiece at 23C

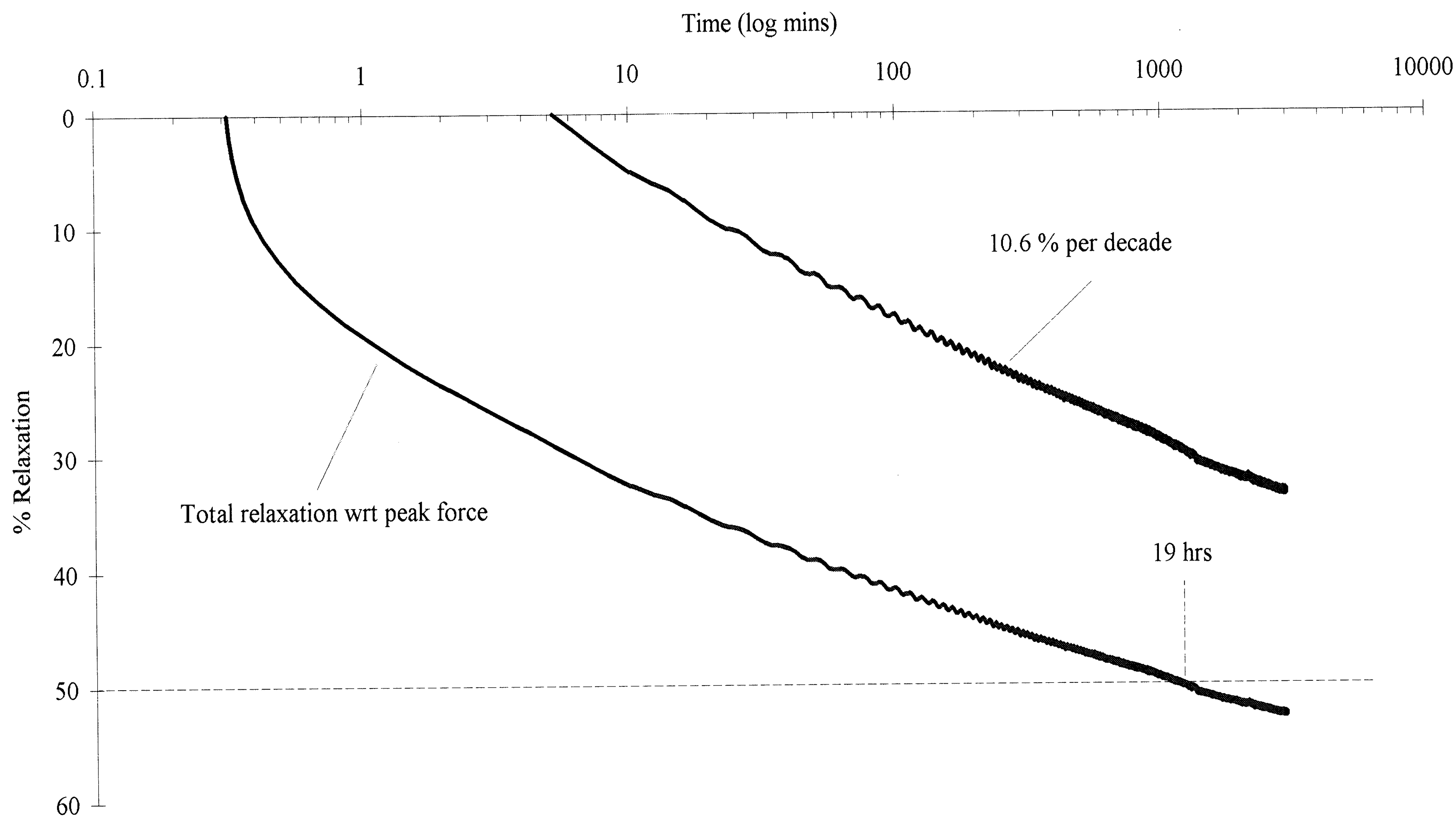


FIGURE 37 Stress Relaxation of unaged Coflon CT sample at 23C