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Thermal Contraction Effects in Epoxy Resin Composites at Low Temperatures

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ABSTRACT

Because of their electrical and thermal insulation characteristics, high strength fibreglass/epoxy composites are widely used in the construction of bubble chamber and other cryogenic equipment. Thermal contraction effects on cooling to operating temperature present problems which need to be taken into account at the design stage.
This paper gives results of thermal contraction tests carried out on fibreglass/epoxy composites including the somewhat anomalous results obtained with rings and tubes. Also considered are some of the problems associated with the use of these materials at temperatures in the region of 20K.

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INTRODUCTION

Composites based on epoxide resins and particulate filler or woven glass fabrics are widely used in the manufacture of nuclear physics research apparatus, such as bubble chambers and as superconducting magnets support structures. Frequently, the apparatus is operated at temperatures in the region of 20K and where epoxy resins are used in conjunction with other materials, any differences in their thermal contractions have to be minimised in order that the strains introduced during cooling do not result in failure or distortion.

Where high strength is important, glass fabric composites are commonly used and since many components are circular in cross section, they are conveniently manufactured by winding on glass fabric when dry for subsequent vacuum impregnation (ref. 1) or by wet lay up techniques (ref. 2). However, the thermal contraction of glass fabric laminates is greater through the thickness than it is along the laminate fibres and this anisotropic behaviour must be taken into account when designing such components.

A selection of laminated tubes and rings is investigated in the test programme described in this report, together with a range of flat laminates having various glass contents, in order to quantify this anisotropic behaviour and its effect on the properties of tubular laminates at very low temperatures.

It is well known that the incorporation of fillers into epoxide resins modifies their thermal contraction behaviour and reduces their sensitivity to thermal shock (ref. 3). In order to examine in greater detail the effect of different fillers on the thermal contraction of epoxide resin and because filled resin systems do not generally show the anisotropic effects inherent in laminated structures, the test programme also includes thermal contraction tests on a series of filled resin systems.

EXPERIMENTAL

In order to limit the number of tests, a common resin system was employed for preparing the laminated specimens:-

Ciba Geigy	MY 740	100 pbw	
Ciba Geigy	HY 219	50 pbw	
Ciba Geigy	DY 219	2 pbw	cured at room temperature.

For the filled specimens, the base resin system was one which has been shown (ref. 3) to possess good thermal shock resistance:-

Ciba Geigy	MY 740	100 pbw	
Texaco	D 230	40 pbw	cured at room temperature for 16 hours followed by a post cure at 60°C.

SPECIMEN PREPARATION

1) Glass Fabric Reinforced Rings

These were prepared around circular mandrels by both wet lay up using woven tapes, and dry lay up of glass fabric followed by vacuum impregnation. Glass contents achieved by these techniques were approximately 60% by weight or 40% by volume.

2) Flat Laminates

The laminates were laid up by hand using 0.15 mm thick plain weave glass fabric. After the appropriate number of plies had been wetted, the laminate was pressed between stops and cured. Glass content was determined from the number of plies in the given thickness and in some cases this was confirmed by the determination of weight loss on ignition.

3) Filled Resins

Specimens in the form of rods approximately 100 mm by 15 mm diameter were prepared by pouring the vacuum degassed mix into glass tubes previously coated with a release agent. The fillers examined are listed in Table 1 together with some of their physical properties. The concentrations were limited to those producing a resin mix of pourable consistency, and excluded putties and other compounds which would require moulding under pressure. In some cases, a certain amount of settling of the filler occured, giving a slight variation of filler content along the length of the specimen, but this was thought not to significantly change the overall contraction of the specimen.

DETERMINATION OF CONTRACTION ON COOLING

A commercial Thermomechanical analyser (TMA) was used to determine the thermal contraction of the laminate specimens through the thickness and longitudinally.
The TMA could not readily be adapted to measure the dimensional changes of the rings and the larger, cast, filled resin specimens. These were measured using a dial gauge on the specimen after cooling to 77K. The specimen was set in an apparatus with the ball ended foot of a dial gauge located in a small depression machined into the end of the specimen, the other end of the specimen being similarly located against a stop. After zeroing the dial gauge the specimen was removed and immersed in liquid nitrogen. When cold, the specimen was removed from the nitrogen and rapidly returned to the apparatus in order to measure its change in length, this technique however, does not give readings at intermediate temperatures during warming as does the TMA.

A purpose built apparatus, shown diagramatically in figure 1 exists at the Rutherford Laboratory for measuring the thermal shrinkage of materials down to the temperature of liquid helium (4.2K). The apparatus is designed to accommodate specimens up to 100 mm in length and 25 mm diameter and dimensional changes are recorded relative to a copper reference.

RESULTS

Integrated contractions from room temperature to liquid nitrogen temperature (77K) of the glass fabric laminates are shown as a function of glass content in figure 2.

The results obtained with the tubular laminated specimens are presented in Table 2 and are shown graphically in figure 3.

Integrated contractions from room temperature to liquid nitrogen temperature (77K) are shown for the filled resin specimens in Table 3, and to allow comparison of the effectiveness of different fillers in reducing the thermal contraction of epoxy resin, the filler contents are expressed as volume percentages and are shown in this manner in figure 4.

Figure 5 shows the thermal contraction versus temperature for a glass fabric laminate through the thickness and figure 6 shows the dimensional changes for the pure unfilled resin system as a function of temperature.

DISCUSSION OF RESULTS

It is readily apparent that some fillers are more effective than others in reducing the thermal contraction of the resin. This is probably associated with the particle size and shape; fibrous (glass) or acicular (woolastonite) particles being more effective than granular materials, with a contribution from the thermal contraction of the filler itself. The practicalities of using various fillers to match specific thermal contraction requirements must also be considered. Whilst chopped glass fibres were the most effective in reducing the thermal contraction integrals they also had the greatest effect on viscosity. At relatively low loadings of chopped glass fibres the mix becomes highly viscous and difficult to pour. With zirconium silicate, high particle loadings are possible thereby enabling resin mixes to be formulated with thermal contraction integrals matching common metals yet retaining a pourable consistency. Maximum filler loadings to give pourable mixes are given in Table 1.

It is usual for particulate fillers to detract from the strength of the base resin at room temperature while bringing about a substantial increase in modulus. Glass fibre, even when used as chopped fibre, does not result in a composite of reduced strength and the effect on compressive strength of various glass fibre loadings is shown in figure 7 and Table 4.

Polytetrafluorethylene has a higher thermal contraction than the base epoxy resin and whilst its incorporation increases thermal contraction it nevertheless reduces the tendency of the resin to crack when thermally stressed at low temperatures. PTFE is known to retain some ductility at very low temperatures and it probably acts in a manner analagous to the toughening of polystyrene by the incorporation of rubber particles.

The anisotropic behaviour of glass fabric laminates is well illustrated in figure 2. It is unfortunate that at the normally achieved glass content of 60% by weight (40% by volume approximately), the difference in thermal contraction between the lengthwise and thickness directions is a maximum. On cooling a tubular laminated specimen this anisotropic behaviour induces a compressive strain in the outer layers, a tensile strain in the inner layers and an overall tensile strain through the thickness of the laminate, the magnitude of these strains varying with specimen geometry and the temperature range through which the specimen has been cooled. At some point the strains may be large enough to result in the formation of interlaminar cracks.

Over the temperature range 300 - 77K the maximum thickness/diameter ratio that may be accommodated without cracking is approximately 0.15. Some thick laminated rings cured at elevated temperatures have been known to crack on cooling to room temperature. Shown in figure 3 are dimensional changes associated with cooling glass fabric/epoxy composite rings to 77K. Apart from the internally induced stresses discussed, it should be noted that the contraction on the inside diameter of the tube may be significantly lower than most metals and this could result in an increased tendency for interlaminar cracking or debonding if adhesives are used to fasten composite rings around metal cores. On the outside diameter the dimensional changes may be greater than with metals such as stainless steel, again increasing the risk of delamination and debonding. In order to minimise these possibilities, the thickness to diameter ratio of the tubular composite should be as low as possible.

REFERENCES

1. D Evans, J U D Langridge and J T Morgan. International Cryogenic Materials Conference, July 1978.

2. D Evans, J U D Langridge and J T Morgan. Manufacture of an epoxy/glass composite piston, paper to be read at I.C.M.C., Madison, U.S.A. August 1979.

3. D Evans, J T Morgan and G B Stapelton. Rutherford Laboratory Report R251.

TABLE 1

PHYSICAL CHARACTERISTICS OF VARIOUS FILLER PARTICLES

FILLER	PARTICLE SHAPE	AV PARTICLE SIZE μm	S.G.	BULK DENSITY	MAX. CONCENTRATION FOR MIX OF POURABLE CONSISTENCY, VOL %
PTFE	amorphous	5	2.2	0.49	52
Zirconium Silicate	granular	50	4.6	1.65	59
Talc	acicular & lamellar	8	2.8	0.61	42
Aluminium Oxide	granular	<40	3.75	0.74	46
Woolastonite	acicular	3	2.9	0.73	46
Silica	granular	40	2.65	1.02	55
Glass	acicular	90 x 12	2.6	0.97	41
Glass	acicular	150 x 12	2.6	0.80	31

TABLE 2

THERMAL CONTRACTION OF G.R.P. TUBULAR SPECIMENS

DIAMETERS (mm)		WALL THICKNESS / MEAN DIAMETER	CONTRACTION ($\times 10^{-3}$) $\int_{77K}^{298K} \alpha \, dT$	
OD	ID		OD	ID
108	100	0.039	2.82	2.38
327	300	0.043	2.7	2.2
95	84	0.062	3.0	2.38
120	100	0.091	2.95	1.9
95	75	0.118	3.4	-
108	84	0.125	3.3	1.8
140	100	0.167	3.4*	2.35*
150	100	0.20	3.7*	2.42*

*specimen showed interlaminar cracking after test, consequently the results may be erroneous.

TABLE 3

THERMAL CONTRACTION OF FILLED EPOXY RESINS
(INTEGRATED VALUES 298K - 77K)

WT% / FILLER	25.5	41.0	58.0	67.5	73.5	83.5	85.5
PTFE	0.010	0.011	0.012	0.013	-	-	-
Zirconium Silicate	-	-	0.0062	-	0.0039	0.0028	0.0026
Talc	0.0079	0.0065	0.0033	0.0022	-	-	-
Aluminium Oxide	-	0.0069	0.0054	0.0047	0.0043	-	-
Woolastonite	0.0077	0.0062	0.0044	0.0042	-	-	-
Silica	0.0075	0.0067	0.0056	0.0046	0.0045	-	-

WT% / FILLER	16.6	28.6	36.5	44.4	50.0	61.5
Glass 90 x 12µm	0.0080	0.0064	0.0056	0.0051	0.0044	0.0036
Glass 150 x 12µm	0.0069	0.0057	0.0052	0.0043	0.0042	-

Fig. 1

THERMAL CONTRACTION APPARATUS.
(Diagrammatic).

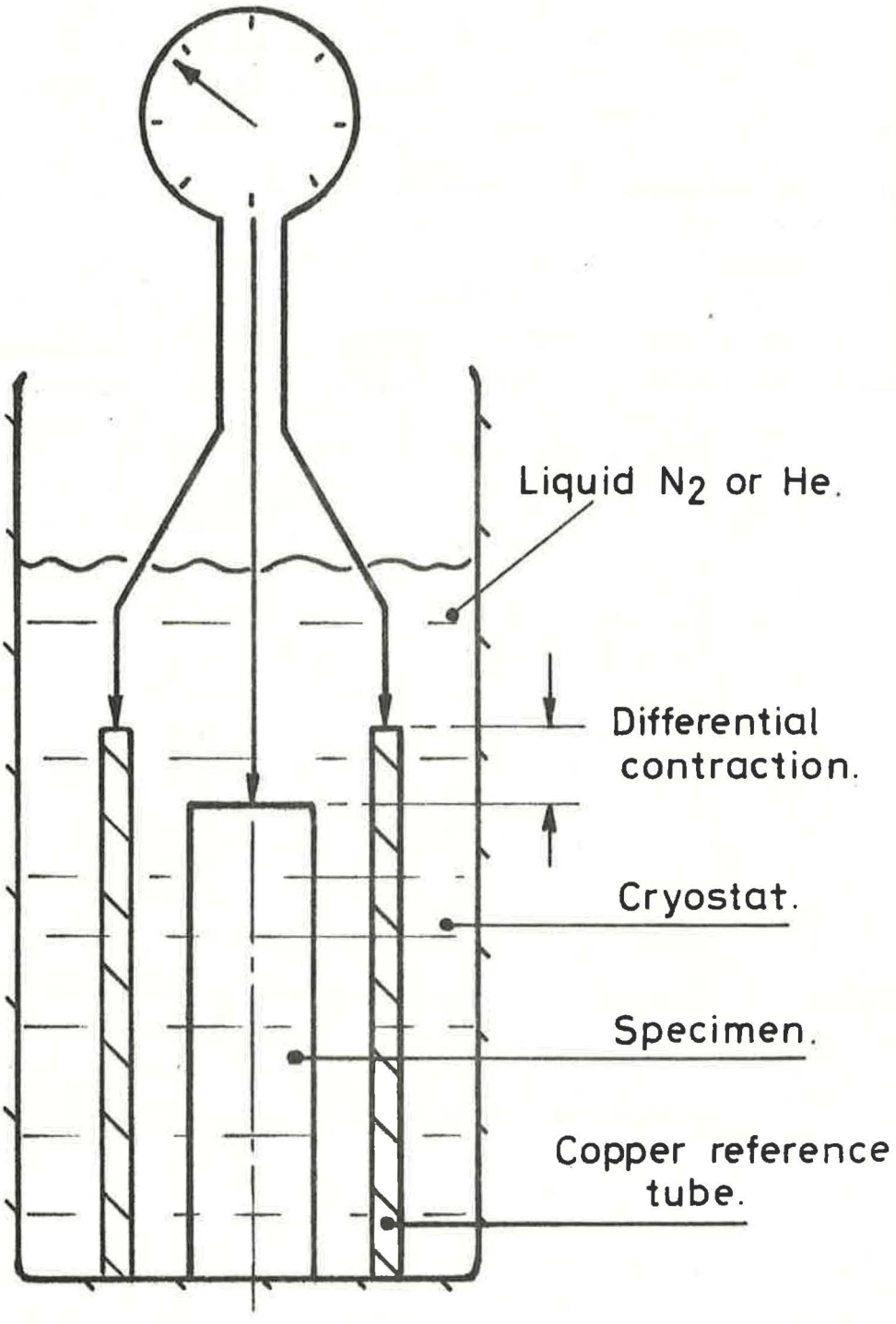


Fig. 2

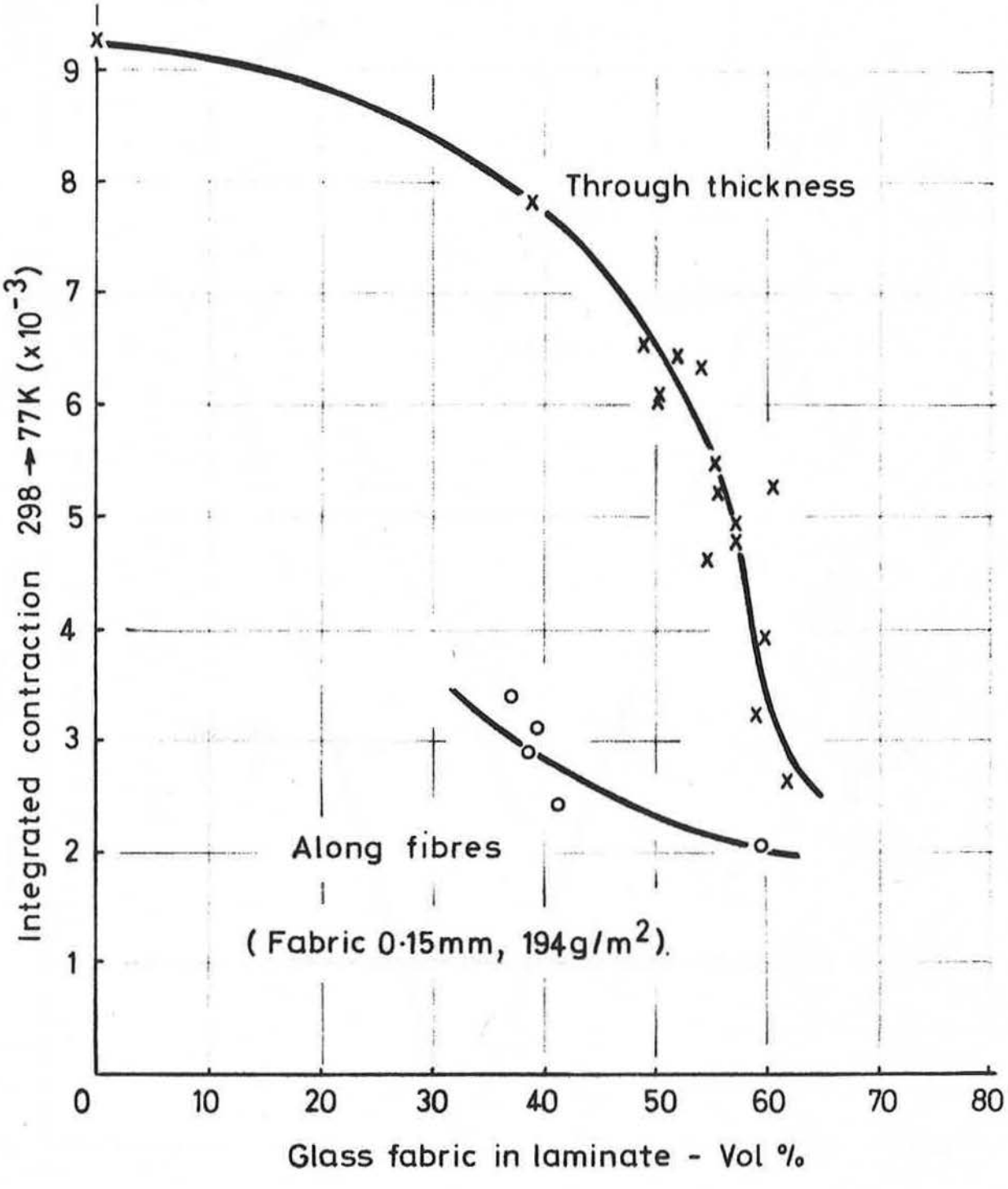

Integrated contraction 298 → 77K (x10⁻³)
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
Through thickness
Along fibres
(Fabric 0·15mm, 194g/m²).
Glass fabric in laminate - Vol %

Fig. 3

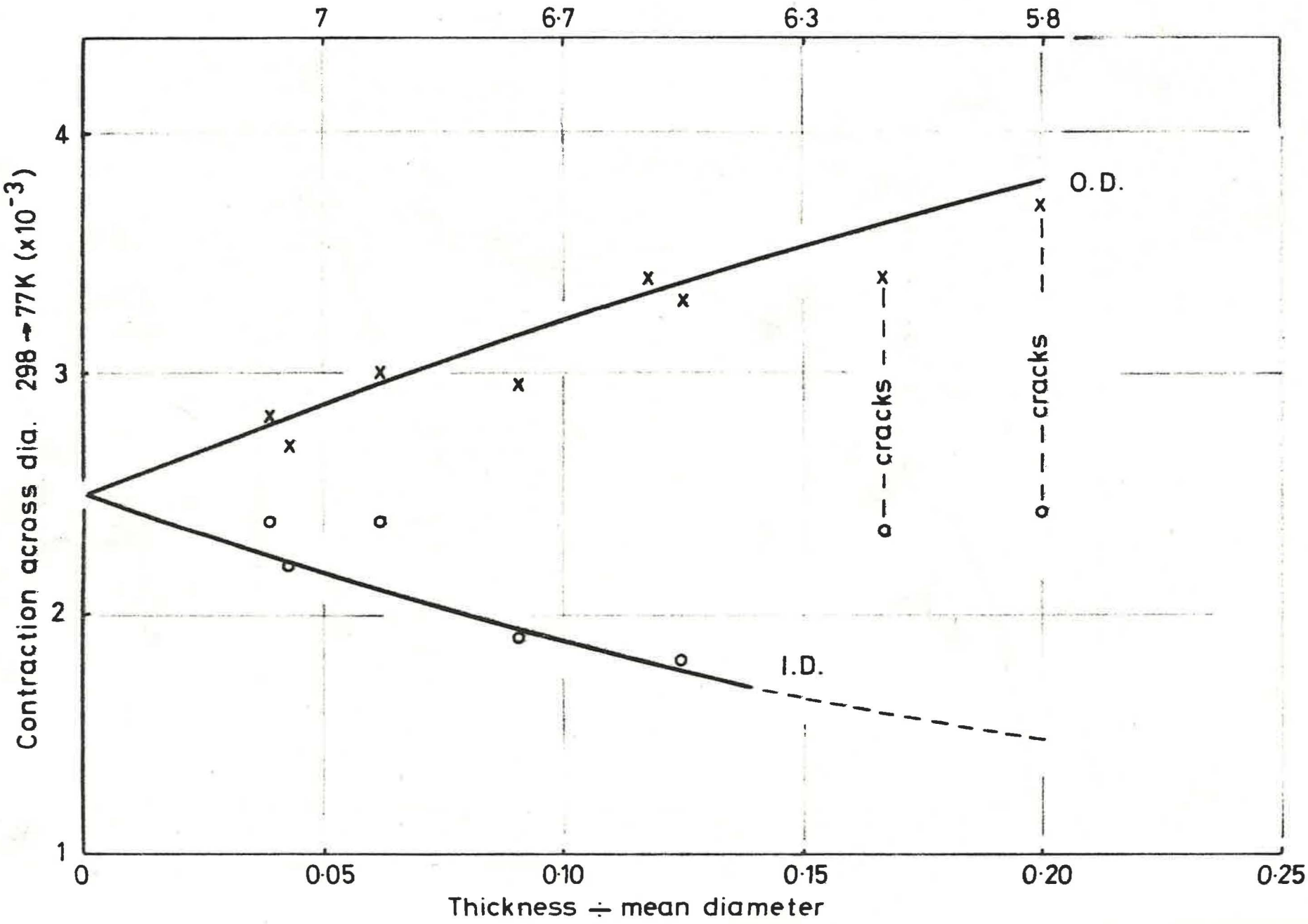

Contraction thro' thickness (x10⁻³) from drawn lines.
7
6·7
6·3
5·8
4
3
2
1
Contraction across dia. 298→77K (x10⁻³)
O.D.
I.D.
cracks
cracks
0
0·05
0·10
0·15
0·20
0·25
Thickness ÷ mean diameter

Fig. 4

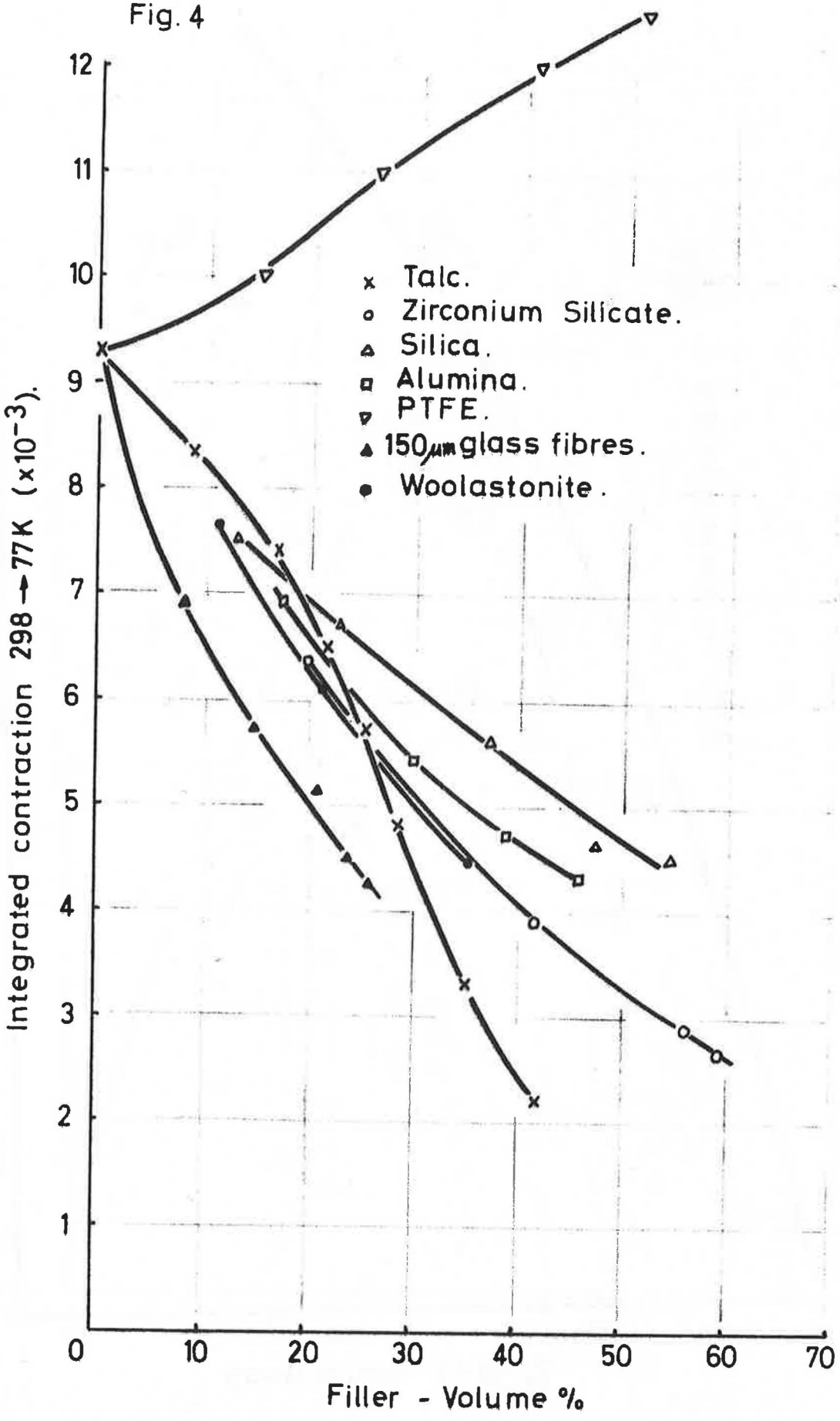

Integrated contraction 298→77K (x10⁻³).
Filler - Volume %
Talc.
Zirconium Silicate.
Silica.
Alumina.
PTFE.
150μm glass fibres.
Woolastonite.
0
10
20
30
40
50
60
70
1
2
3
4
5
6
7
8
9
10
11
12

Fig. 5

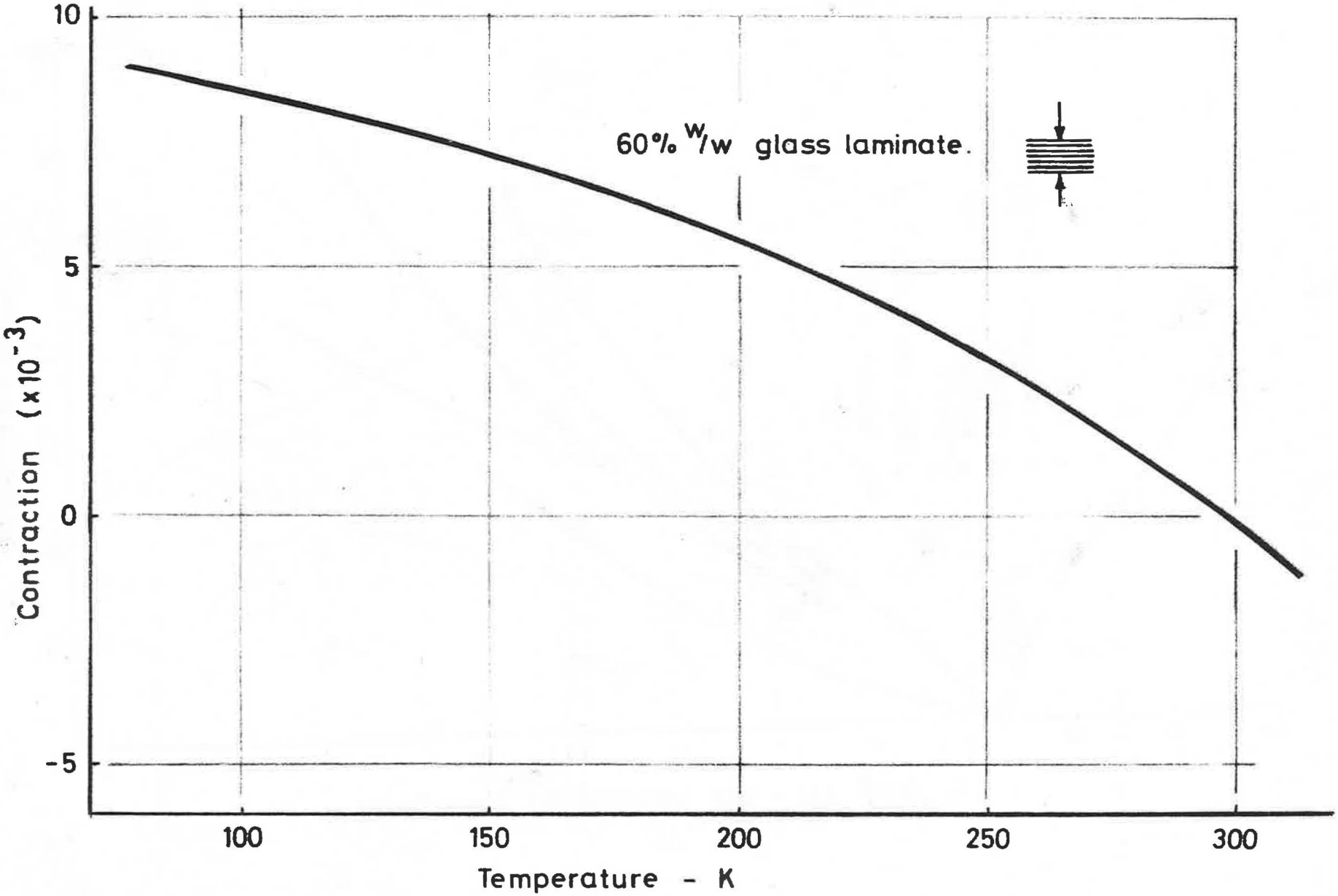

10
5
0
-5
Contraction (x10⁻³)
60% w/w glass laminate.
100
150
200
250
300
Temperature - K

Fig. 6

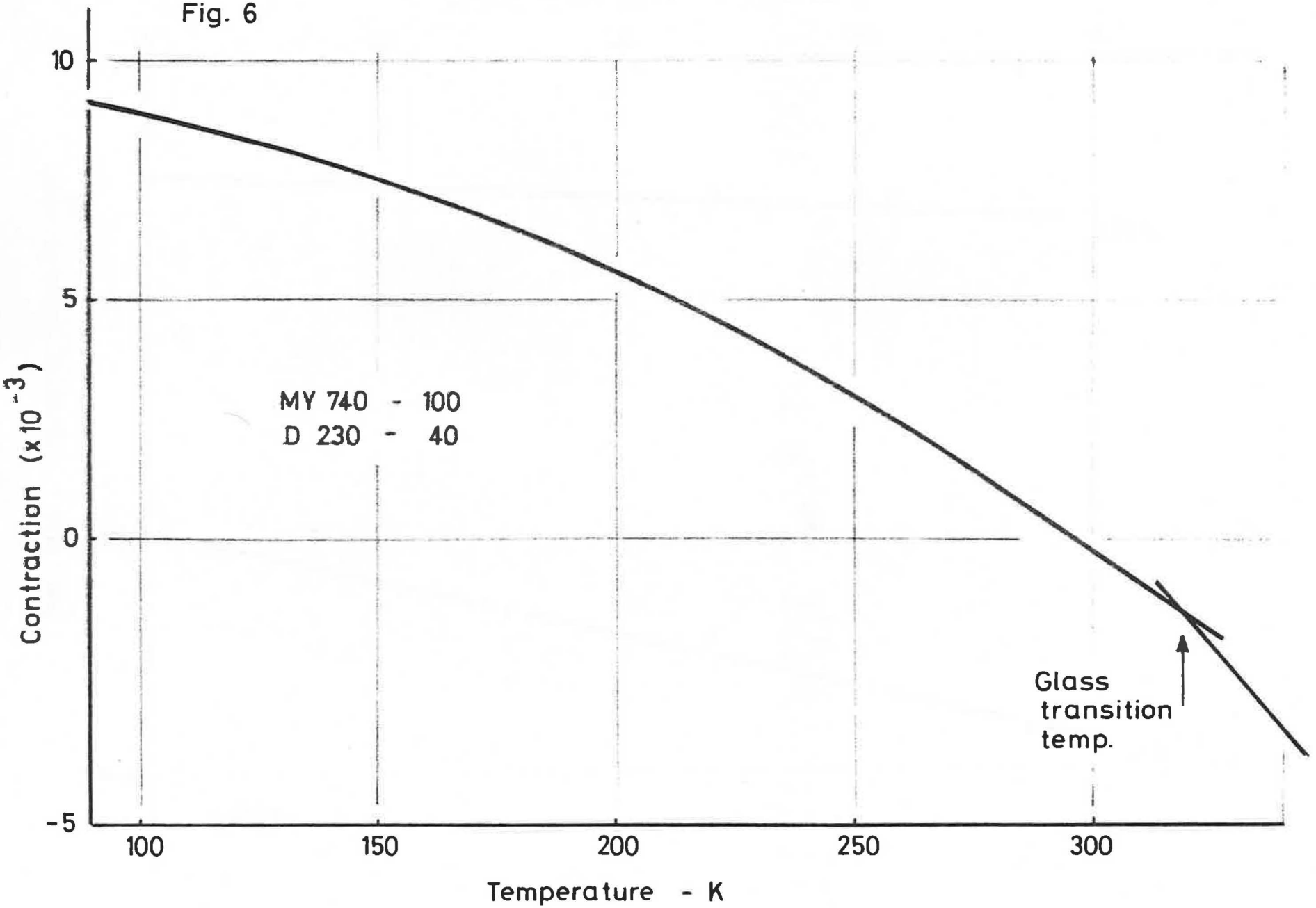
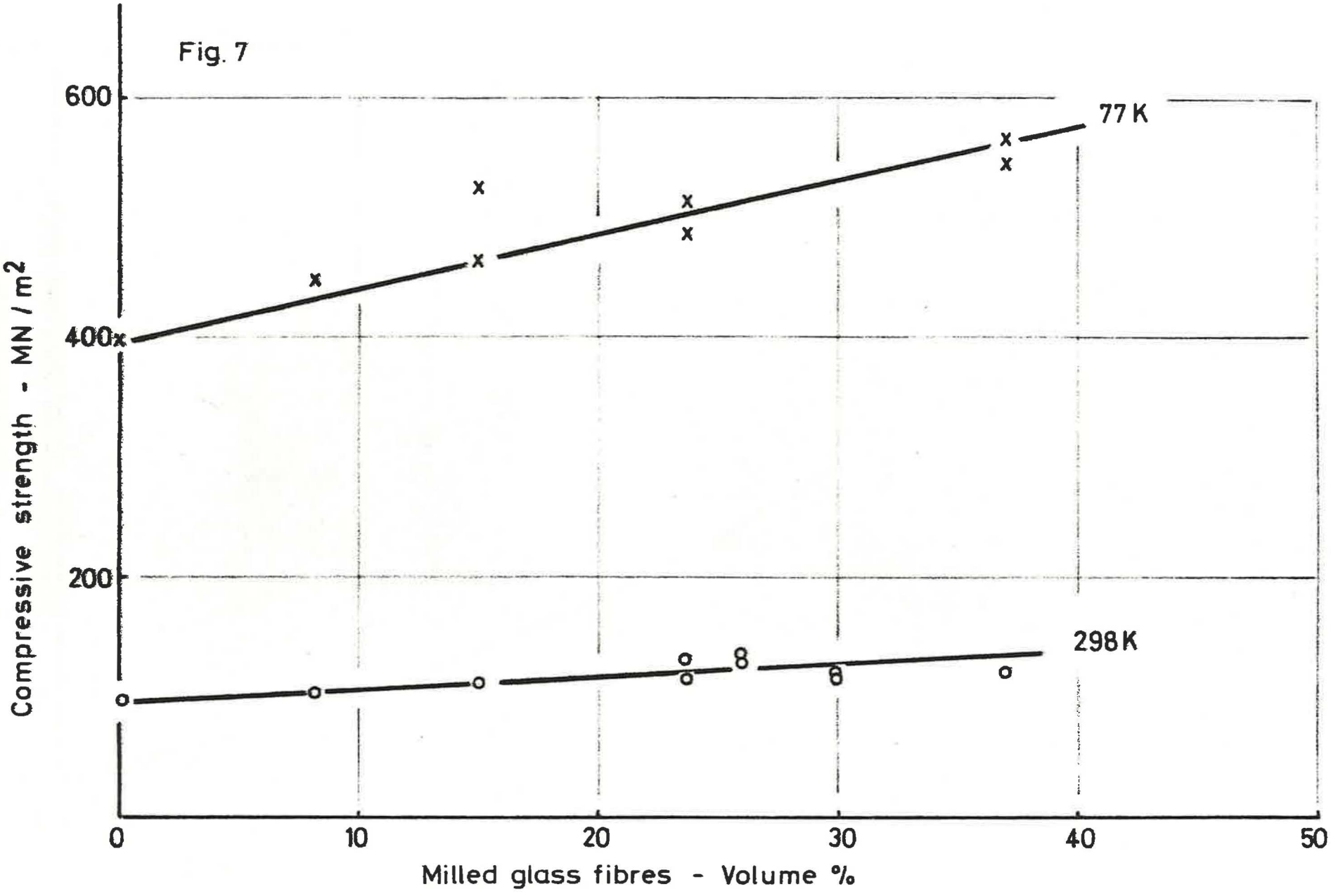

10
5
0
-5
Contraction (x10^{-3})
MY 740 - 100
D 230 - 40
Glass transition temp.
100
150
200
250
300
Temperature - K

Fig. 7


600
400
200
77 K
298 K
Compressive strength - MN / m²
0
10
20
30
40
50
Milled glass fibres - Volume %