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Effects of some injection moulding variables on the properties of injection-moulded rigid PVC

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EFFECTS OF SOME INJECTION MOULDING
VARIABLES ON THE PROPERTIES OF
INJECTION MOULDED RIGID PVC

BY

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Submitted in partial fulfilment of the
requirements for the award of Ph.D. of
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SUMMARY

The present work forms part of a larger programme concerned with the interaction between the processing, structure and properties of rigid PVC compounds.

This work aimed at investigating the influence of some of the injection moulding variables namely, injection time, mould temperature and melt temperature on the following properties of injection moulded rigid PVC:-

- (i) Degree of orientation
- (ii) Formation of oriented skin
- (iii) Overall internal stress level (residual stress)
- (iv) Changes in density
- (v) Tensile strength

Degree of orientation was measured by heat shrinkage measurements and percentage shrinkage was computed. Degree of orientation decreased with shorter injection time and higher mould and melt temperature.

Thin sectioned microtomes were cut through the plaques to investigate the influence of the variables on the skin. This skin appeared as a highly oriented region when examined microscopically between two crossed polars. Skin thickness decreased with shorter injection time and higher mould and melt temperature.

In the light of the obtained results it was possible to furnish an intimate correlation between skin thickness and degree of orientation at varying processing conditions under investigation (degree of orientation increased with skin thickness).

Density was measured by a flotation method. Measurements carried out on the bulk specimens (skin and core) revealed that density increased with higher mould temperature and shorter injection time. Skin and core densities were also measured. Core density was higher than the skin which was attributable to higher relaxation of the core region due to its insulation by the skin from the relatively cold mould surface.

The density/melt temperature relationship was somewhat anomalous in that it falls with increasing melt temperature. This anomaly was ascribed to the formation of a thicker skin at lower melt temperature which insulated the core thus allowing greater packing in the core material, which resulted in raising the bulk density.

Residual (internal) stresses were measured by a stress relaxation method. Using this technique it was possible to investigate the influence of the processing variables on the magnitude of the residual stress. It decreased with shorter injection time and higher mould and melt temperature.

Tensile yield stress was measured by standard testing method.

However the obtained results indicated that there was no significant variation in the tensile yield values. It is believed that the failure of this test to distinguish between moulding conditions is ascribed to the composite structure of the rigid PVC mouldings of which the skin and core possessed different crystalline natures and structures and that bulk properties are dominated and governed by the core rather than skin.

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CHAPTER 1

INTRODUCTION

1.1. Poly (vinyl chloride)

1.1.1 Vinyl Chloride Polymers:-

Vinyl chloride polymers, containing the repeating unit - CH_2CHCl - include, in addition to the homopolymer copolymers with such monomers as vinyl acetate, propylene, or vinylidene chloride. The polymers are used in both flexible and rigid form as mouldings, foams, fibers, and films and sheeting. They are also used as plastisols, or vinyl dispersions, for coating and moulded articles. The homopolymers and also polymers with minor amounts of a comonomer are collectively referred to as PVC or PVC-type polymers in the literature.

1.1.2 Historical Background:- (1)

The first mention of poly (vinyl chloride) was in 1872 by Baumann when he described the formation of the white powder by the action of sunlight on vinyl chloride contained in a sealed tube. He had no idea of the composition of the new product but his examination showed that it was unaffected by a wide range of solvents. The formation of a compound with the formula $\text{C}_2\text{H}_3\text{Cl}$ had been reported earlier in 1835 by Regnault, but apart from these two references, there was no further interest in vinyl chloride for forty years.

Renewed interest was brought about by the overcapacity which had arisen in Europe in the production of Calcium Carbide. The potential of acetylene as an illuminant had been greatly overestimated and this had led to the construction of many new carbide plants.

This resulted in a substantial price drop in the early part of the twentieth century; in 1905 the price of calcium carbide was £28 per ton, but in 1909 it had dropped to £9. The position was particularly acute in Germany and it was here that an extensive research programme was set under way to investigate possible chemical uses of acetylene. In 1912, Klatte of Griesheim-Elektron filed a patent claiming the manufacture of vinyl chloride monomer by the reaction between acetylene and hydrogen chloride in the presence of a mercuric chloride catalyst. The formation of the polymer by the action of ultraviolet radiation was confirmed and in 1914 the use of organic peroxides as accelerators for the polymerisation was known.

At the same time work on vinyl halides was being carried out in Russia by Ostromislensky. The polymer was being used as an intermediate in an attempt to produce synthetic rubber by dehydrochlorination, using alcoholic and aqueous potash. There were some interesting observations on the solubility of various forms of poly (vinyl chloride) due undoubtedly to differences in molecular weight. Ostromislensky did not continue this work until he emigrated to the United States some years later. The significance of Klatte's work was not realised and there was no followup after the initial patents, which were allowed to lapse in 1926.

In 1928 the publication of number of patents revealed that several industrial groups were working in the field, and three independent companies had discovered that the processing of vinyl chloride polymers could be realised by copolymerising vinyl chloride with vinyl acetate to improve handling characteristics.

The real breakthrough was made by Semon of B.F. Goodrich who showed that PVC could be processed and converted into a rubbery product by mixing and heating it with a high boiling solvent such as tritolyle phosphate.

Industrial development ran parallel in Germany and the United States during the 1930's. Production in Europe got under way in Germany in 1931 and about the same time Imperial Chemical Industries in England started their investigations into methods of polymerisation and manufacture of vinyl chloride. In the United States production was started in the late 1930's by both Union Carbide and B.F. Goodrich. In conjunction with General Electric, B.F. Goodrich developed plasticised PVC as an insulator for wire and cable. The outbreak of World War II put a high pressure on this type of new insulating material which aged well, and had good chemical and flame resistance. During those years most of the production was put on allocation for military purposes. Both the copolymer and PVC were also used for military rainwear and waterproofing materials. It was only after the war that the development of new products for the consumer market grew and the industry really expanded.

In the United Kingdom, Imperial Chemical Industries had followed up their development with the construction of an 85 ton/year pilot plant which started operations at the end of 1940. In 1942 this was followed by the first production plant with a capacity of 450 ton/year. During the war a number of compounding plants were constructed to use both home-produced resin and material which was imported from the United States under the Lendlease agreement.

In Europe all the first PVC plants had used the emulsion technique for the polymerisation of monomer following the general practise of synthetic rubber manufacture. In Germany this practise was followed throughout World War II. The suspension polymerisation process was followed from the start by the early American plants, but it was not adopted in the United Kingdom until about 1943, when the need for PVC with good electrical properties became critical.

1.1.3 Applications

PVC compounds may reasonably be considered as the most versatile of plastic materials; its uses range from building applications to toys and other daily used goods.

PVC compounds particularly unplasticised grades are extensively used in chemical plants e.g. hydrocarbons handling. It is necessary when considering PVC compounds for applications in which contact with other chemicals will occur to check that all of the compounding ingredients will be resistant to these other chemicals and also that leaching out of the additives will not occur. Also the ingredients of the PVC compound must not affect the nature and properties of the chemicals.

Unplasticised PVC, which when carefully compounded and processed has excellent resistance to weathering, has a great potential importance to the building industry. It is now becoming used increasingly in place of traditional materials for many uses. e.g. window frames and translucent roof sheeting.

Unplasticised PVC bottles have better clarity, oil resistance and barrier properties than those made from polyethylene and

compared with glass are of course less brittle and lighter and have greater design flexibility. They have largely taken over the bathroom toiletry packaging market and have made extensive penetration into the market for fruit juice and low cost wine.

Plasticised PVC has been used for electrical insulation for many years. Although of only limited value in high frequency work it is of great value as an insulator, for direct current and low frequency alternating current carriers. It has almost completely replaced rubber insulated wire for domestic flex and is widely used industrially.

At one time of the largest applications for plasticised PVC was in the mine belting. Although still important in terms of the actual tonnage of material consumption this market has not grown as have other PVC outlets in recent years. Two of the most important applications for vinyl chloride - vinyl acetate copolymers, are gramophone records and flooring compositions.

In car manufacturing industries PVC leathercloth is widely used for upholstery and trim. Compared with leather PVC material has greater abrasion resistance and flexing resistance and can be more easily washed. Other uses include the flexible rear windows of sports cars, car covers and tool bags. PVC adhesives, generally containing a polymerisable plasticiser, are also finding useful outlets in car manufacture.

Plasticised PVC sheet backed by a variety of materials such as plywood, chipboard, asbestos, concrete and aluminium is of value for wall cladding for both interior and exterior application. In house and other furnishings PVC compounds find many outlets. PVC leathercloth is now generally accepted in kitchen upholstery whilst printed sheet is used in utilitarian kitchen and bathroom curtaining.

There are a number of examples of PVC used in personal apparel. Ladies handbags are frequently produced from PVC leathercloth. All PVC shoes are of value in beachwear and increasingly for standard footwear. PVC is proving to be an excellent abrasion resistant shoe-soling material. The sole may be applied by direct injection moulding, paste injection moulding or adhesive techniques.

From the above examples it can be seen that the range of usage of poly(vinylchloride) is wide indeed. Success in any one of these applications is however vitally dependent on careful attention to compound formulation, processing conditions and product design.

1.2 Injection Moulding

Injection moulding is one of the major methods by which thermoplastics are fabricated. It provides economical rapid production of high-quality precision parts from a wide selection of plastic materials.

1.2.1a History and Development: (2)

Development began first in the late 19th century utilizing a modified form of existing diecasting machines for the manufacture of lengths of rod and tube, the earliest recorded moulder being situated in Holloway, (London). The material used was a mixture of cellulose nitrate and camphor. The process had the disadvantage of the risk of fire and explosion, due to the nature of the material, and its development was, therefore, retarded. However, a single-action hydraulic injection machine was designed by Hyatt in the U.S.A in 1870. This process was adapted for covering metal and wooden parts. The cellulose nitrate/camphor mix was extruded in the plastic state, round a core contained in a mould cavity, and the covered component allowed to cool in the cavity instead of in the open.

The advance of injection moulding was almost entirely dictated by the availability of suitable materials for moulding, and there was no early alternative of cellulose nitrate.

Hence further advances were held up until some twenty five years later, when cellulose acetate became available. This material was first used as an aircraft dope and subsequently as a textile. Its use as a moulding material was slow in developing, however, because injection moulding was not established and compression moulding of cellulose acetate, with its necessary heating and cooling, was a slow process.

Cellulose acetate was first used to make a solid part by an injection moulding process in the early 1920's, and it is from those beginnings that injection moulding, as we know it today, really began. Progress initially was slow, as this was a pioneering stage, but by the early 1930's, in addition to development in Great Britain, horizontal machines for injection moulding were available in Germany and injection moulding was starting to reduce the very much greater lead held by compression moulding. Heating cylinder design was first recognised in a patent issued to Adam Gaston in 1932.

The addition of polymethyl methacrylate and polystyrene to the range of injection moulding materials gave further impetus to the trade. In particular, machines now had to be capable of working to closer tolerances, because of the increasing speed of operation, the larger mouldings being attempted, and the smaller plasticity ranges of the new materials.

Injection moulding became established as an engineering process, a role it fulfilled with distinction during the Second

World war. The addition of polyethylene and later nylon to the list of injection materials emphasised the growing ^{need} for technical knowledge.

1.2.1.b. Morphology and Particulate Structure of PVC During Processing:-

Processing of PVC involves the progressive break down of the particulate structure of the resin under the influence of shear and/or heat.

On close electron microscopy examination of a microtomed section of suspension polymerised PVC, Berens and Folt (40) found the resin had an open aggregate of roughly round particles 0.5 - 1.5 μm in size. They called these primary particles and stated that they were the melt flow units. Vidyaikina et al (41) investigated the effect of shear and temperature on PVC resin by electron microscopy. They concluded that the original macroglobular structure of PVC resin is first broken down during processing to reveal what they called "microglobular" structure (0.1 μm in size). On further processing, these microglobules disappear leaving stretched "cap-like" formations.

Hattori et al (42) using the technique of PMMA embedding and ultrathin sections, examined the structure of PVC powders and mouldings by electron microscopy. They showed PVC resin particles to be made up of 0.5 - 1.5 μm particles bounded together in a three-dimensional sponge like lattice. During processing, the original resin particles break down to 0.5 - 1.5 μm particles and as the processing conditions become more severe, fibrils 300 \AA thick appear. These fibrils are practically indestructible.

Hattori presented a structural arrangement of PVC shown in Fig. (1.1.a.).

Shinagawa (43) in his own study of microstructure of PVC and its mouldings used suspension, emulsion and mass polymerised PVC of various degree of polymerisation and some modified PVC. He identified (1 - 2 μm in size) particles which he called secondary particles and their substructures of 200 - 500 \AA he called primary particles. His illustration of PVC microstructure is shown in Fig. (1.1.b.). During polymerisation one molecular chain grows, curling itself into a particle of 20 - 30 \AA in diameter. These particles cluster together to form the primary particles 200 - 300 \AA in diameter. They in turn build up the secondary particles (1 - 2 μm) diameter. Shinagawa estimates about 100 million primary particles are contained in a secondary particle. Finally the secondary particles agglomerate into the resin particle (100 μm) in diameter.

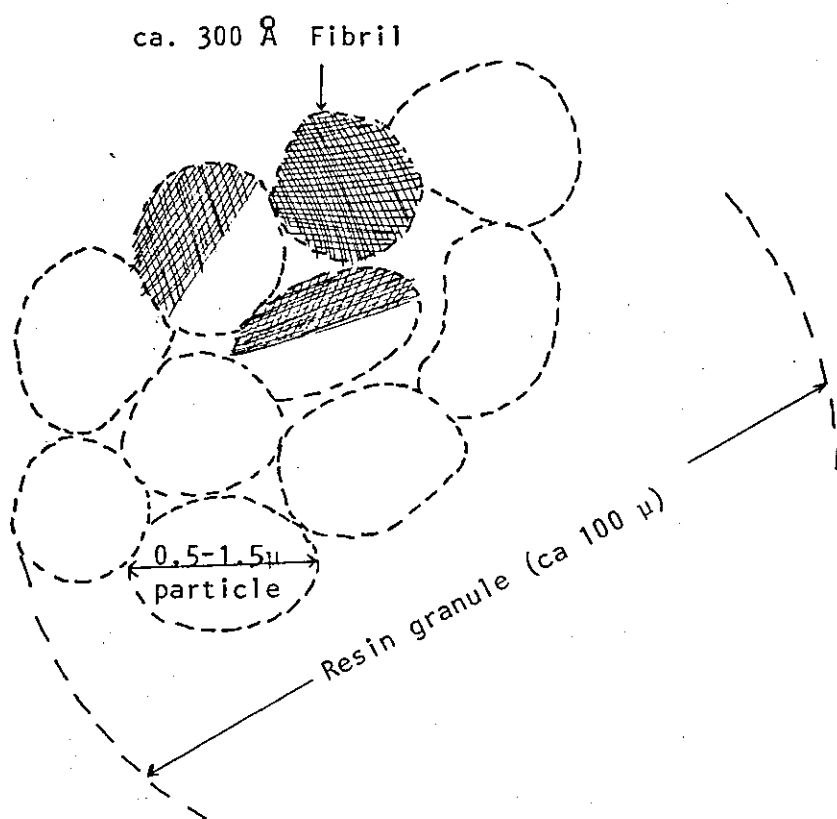


Fig. 1.1.a. Schematic illustration of PVC Structure⁽⁴²⁾

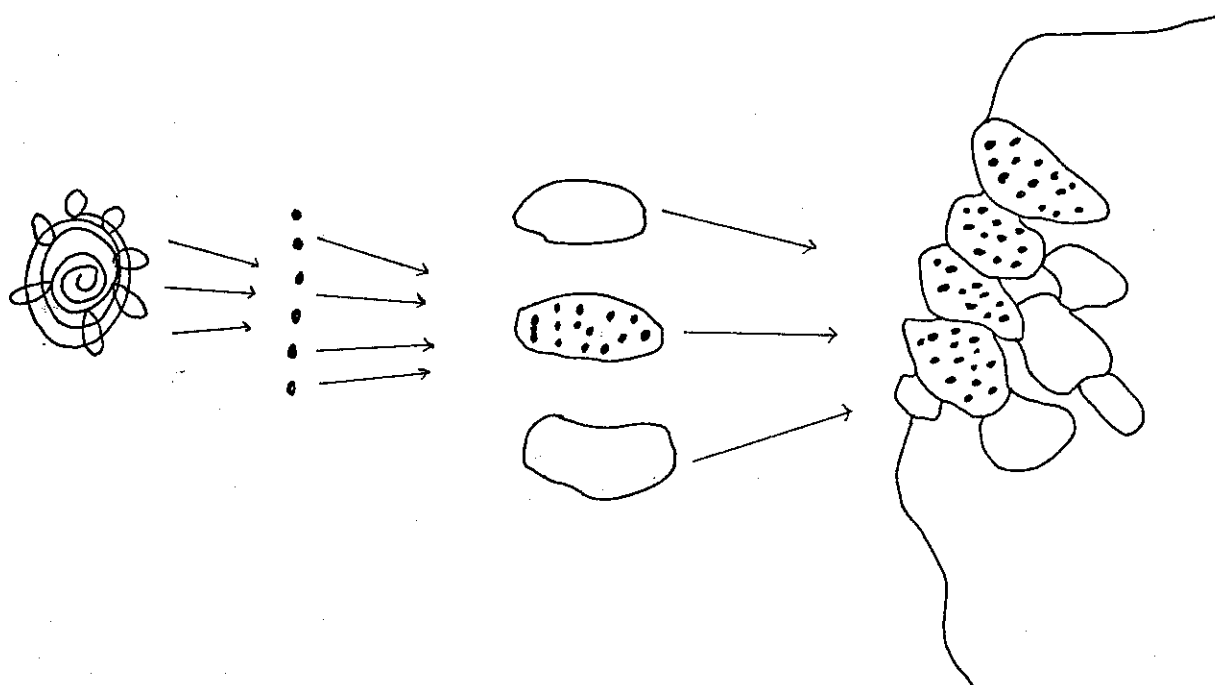


Fig. 1.1.b. Microstructure of PVC⁽⁴³⁾

1.2.2 The Basis of Injection Moulding:⁽²⁾

The underlying principles upon which injection moulding is founded are those appertaining to the theory of hydraulics. Among these is Pascal's Law which can be given as:

"The pressure exerted upon a stationary fluid contained in an enclosed system is immediately transmitted without loss in every direction. The normal force acting across any given area will, therefore, be the same as that across any equal area anywhere in the system."

This assumes that the fluid is incompressible. From this we can arrive at a hydrostatic balance as shown in Fig. (1.1).

Assuming (A) is a ram exerting a load of 5 tons over an area of 5 in^2 , the pressure build up in the cylinder will, therefore, be 1 ton/in^2 . Using the statement made above, 1 ton/in^2 will, therefore, be developed throughout the system. The force applied against the ram (B), assuming the area to be 10 in^2 , will therefore be 10 tons.

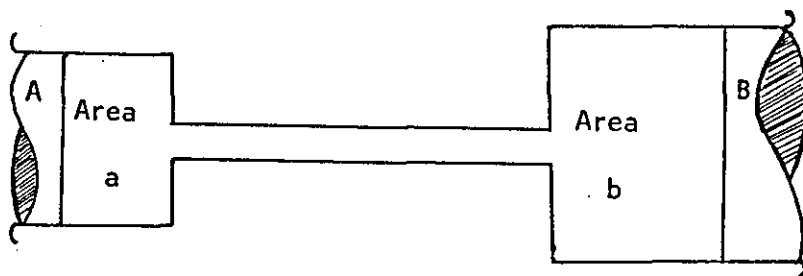


FIG. (1.1)

HYDROSTATIC BALANCE

If injection moulding was concerned with *Pascalian Fluids*, therefore, the pressure developed in the cavity would be the same as that exerted by the ram in the injection cylinder. The melt is not an incompressible fluid, and the pressure loss due to compressibility of the material, in its granular, semi-plastic and melt forms, considerably reduces the pressure build up in the cavity. Also we have to consider the friction in the boundary layers, which also increases pressure loss.

It should be remembered that the restrictive effects of cylinder construction, nozzle tips, sprues, runners and gates will also increase the pressure loss.

The first attempt to apply theory to practise, was the subject of a patent granted to A. Eichengrun in 1921. The machine described consisted basically of a chamber in which a ram was able to move up and down. The cavity formed the bottom of the chamber and was covered by a plate through which ran ports connecting the upper part of the chamber with the cavity below. Moulding material was put in the upper part of the chamber and, after heating, pressure was applied to the ram, forcing material through the ports into the cavity.

The system was then cooled, the moulding formed in the cavity removed and the system recharged. A diagram indicating this principle is shown in Fig. (1.2).

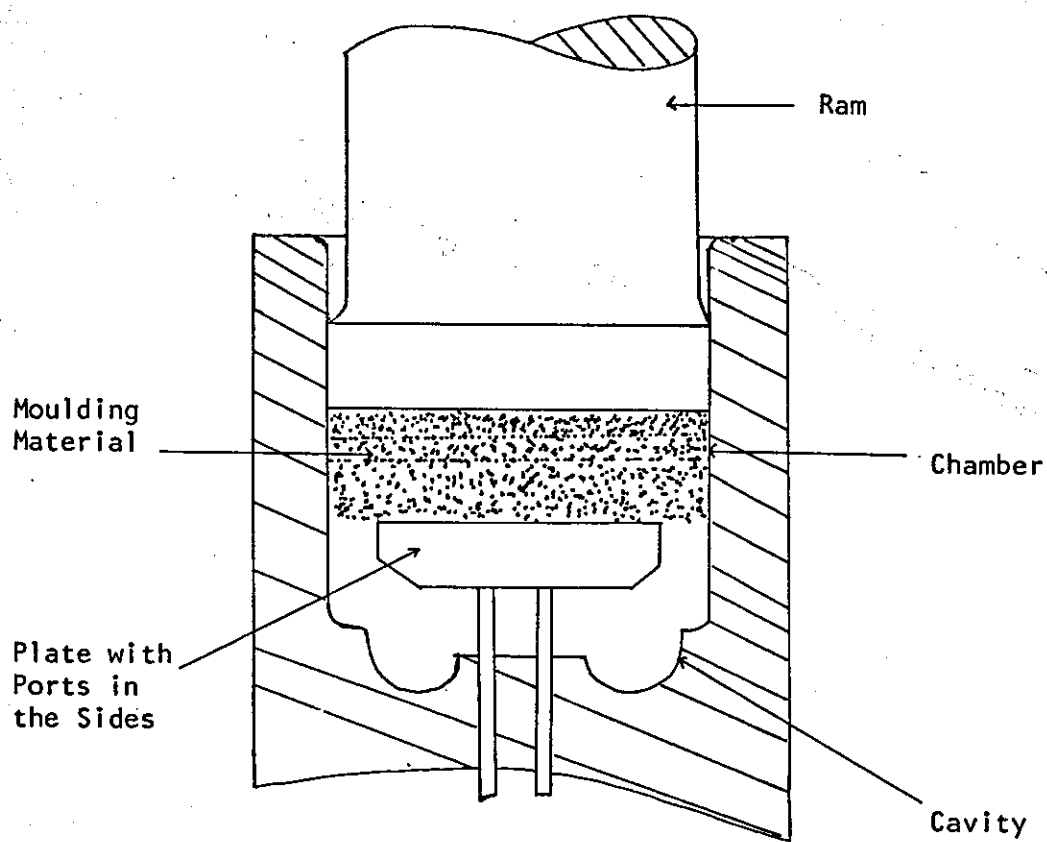


FIG. (1.2)

EICHENGRUN'S PATENT

1.2.2.1. Reciprocating Screw Injection Moulding ⁽³⁾

Rigid, unplasticised PVC compounds, have a relatively low coefficient of heat transfer. In a plunger machine the heater bands are the only source of plasticising heat, the melt must be achieved by transferring heat from the cylinder walls through the plastic into the innermost particles of the material in the cylinder. Since rigid, unplasticised PVC does not transfer heat readily, the material adjacent to the cylinder walls will become overheated, sometimes to the extent of decomposing, before the inner portion of material becomes a satisfactory melt. It therefore becomes virtually impossible to obtain a uniform melt temperature as the PVC passes through the cylinder. For this reason plunger machines are not considered adequate for processing rigid, unplasticised PVC.

Reciprocating - screw machines on the other hand have made possible the injection moulding of PVC compounds especially rigid, unplasticised PVC. When heat is generated into rigid, unplasticised PVC through the shearing forces induced by the rotation of the screw, this material can be plasticised to a controlled, uniform melt temperature.

A reciprocating-screw machine comprises a barrel or a cylinder, and a screw which rotates to melt and mix the material and then moves forward to force the melt into the mould cavity. In the

reciprocating screw machine the material is fed from the hopper, plasticised in the screw and forced past a one-way valve at the injection end of the screw. The material accumulates in front of the screw, forcing back the screw, the screw drive and motor. When the screw reaches a position, determined by the amount of feed required, a limit switch is activated stopping the screw rotation. This happens while the previous shot cools in the mould. After that shot has been ejected and the mould closed, hydraulic injection cylinders bring the screw assembly forward and use the screw as an injection ram.

Generally, a screw is specified as either a general-purpose screw or a PVC screw with a smear tip. All general-purpose screws have in common some type of valve near the screw tip that prevents the backflow of material through the screw flights during injection. All PVC screws on the other hand were designed in earlier days to be used for moulding pipe fitting compounds of high viscosity and low thermal stability. The extremely high viscosity of these early-days PVC compounds precluded the need for a backflow check valve. Further, a backflow check valve offered a possible hangup point for material that could not be flushed away in time before it decomposed.

With the advent of general purpose PVC compounds, which have a lower melt viscosity and much greater thermal stability, it became possible to process these compounds with a general-purpose screw equipped with a backflow check valve.

1.2.2.2. Advantages of Screw Plasticising:-

In a screw the melting of plastic is caused by the shearing action on the polymer between the barrel and root of the screw. As the polymer molecules slide over each other they convert the mechanical energy of the screw drive into heat energy. The heat is applied directly to the material. This process and the mixing action of the screw contribute to its major advantages as a plasticising method. These advantages are:

1. High shear rates are obtained which lower the viscosity of the melt and makes the material flow more easily.
2. Good mixing is developed resulting in homogeneous melts.
3. Flow of the melt is non-laminar and residence time in the cylinder is much less than in a plunger machine.
4. The action of the screw reduces chances of material hold-up and subsequent degradation.
5. Reciprocating-screw machine can be used with heat - sensitive materials, such as PVC.
6. The screw is easier to clean and purge than a plunger.

1.2.3 Advantages of Injection Moulding:- ⁽³⁾

1. Parts can be produced at high production rates.
2. Large volume production is possible.
3. Relatively low labour cost per unit is obtainable.
4. Process is highly susceptible to automation.
5. Parts require little or no finishing.
6. Many different surfaces, colours, and finishes are available.
7. For many shapes this process is the most economical way to fabricate.
8. Process permits the manufacture of very small parts which are almost impossible to fabricate in quantities by other methods.
9. The scrap loss from runners, gates and rejects can be reground and reused leading to minimal total waste.
10. Same item can be moulded in different materials, without changing the machine or mould in some cases.
11. Close dimensional tolerances can be maintained.
12. Parts can be moulded in a combination of plastic and such fillers as glass, asbestos, talc, and carbon.
13. The inherent properties of the material give many advantages such as high strength-weight ratios, corrosion resistance, strength, and clarity.

1.3 Mould Filling Studies:-

Investigations into mould filling process in injection moulding were made by many researchers (4-14). The process is divided into three major stages: filling, packing and cooling. The three stages are best described by the schematic pressure-time curve, shown in Fig. (1.3).

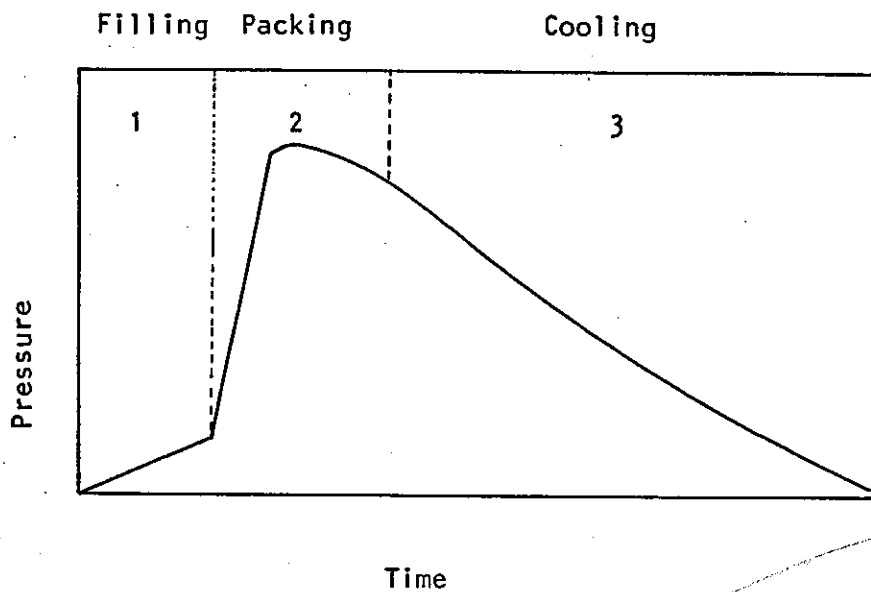


FIG. (1.3)

MOULD FILLING PROCESS

1.3.1. Filling Stage:-

Filling is represented by the unsteady flow of a hot non-Newtonian compressible melt into an empty cold cavity, which is held at a temperature below that of the polymer. Simultaneous heat transfer and unsteady flow occur in the cavity.

After the melt front reaches the outer boundaries of the cavity, more polymer continues to flow in under high packing pressure. The flow of polymer into the mould leads to an increase of pressure corresponding to an increase of the polymer density in the cavity. After filling and packing are complete, cooling continues due to the temperature gradient between the polymer and the cold wall.

A number of theoretical and experimental studies of the filling stages have been reported in the literature, in connection with mould cavities of various shapes. The flow of molten polyethylene and polystyrene in a long cold cavity had been observed by Ballman, Shushman and Toor (4). Their cavity consisted of parallel plates. Empirical correlation for the progression of the melt front and pressure, were achieved and explained by assuming isothermal conditions.

Grinbalt (5) studied the flow of polystyrene in a rectangular cavity. He divided the melt into two zones, a solidified stationary skin and an isothermal flowing core. The heat conduction equation was used to derive the thickness of the stationary layer. Based on experimental data, empirical equations were developed for the total length of flow and velocity of the melt as a function of time.

Other researchers studied the filling stage of injection moulding in cavities of more practical shapes, which allowed the melt to spread radially from the gate to the outer boundaries of the cavity.

The flow pattern of polystyrene in a disc-shaped cavity was photographed by Spencer and Gilmore (6) and Spencer and Beyer (7). A complete description of the shape of the melt front was given, as the melt emerged from the gate at one point of the circumference until it filled the cavity.

Experimental and empirical results on the filling of a rectangular thin mould were reported by Buer (8). He assumed isothermal and incompressible flow, and attempted to describe the progression of the melt front in terms of spherical waves propagating from the injection point. He was able to derive an empirical expression for the flow front velocity as a function of the injection screw velocity.

Barrie (9-10) measured and analyzed the melt pressure distribution in a circular, central-gated dish cavity, in an attempt to correlate the pressure profile obtained experimentally with machine variables. By using an empirical approach, he was able to relate the pressure measurements from transducers located at different radii, to mould clamping requirements and dimensions of the moulding.

Berger and Gogos (11) treated the mould cavity and the channel leading to as one single flow system. Assuming constant density and thermal properties of the melt, they simulated the filling of a centre-gated circular mould under constant pressure, at the injection end. No experimental results, however, were obtained to support the validity of the model.

Kenig and Kamal (12) studied the filling stage of a semi-circular cavity with a parallel feed from the central gate. They observed spreading radial flow in this simple-shaped cavity and developed a theoretical model for the filling stage, based on solving the equations of phase change coupled with practical boundary conditions in the mould.

1.3.2 Packing and Cooling Stages:-

A few attempts have been reported in the literature concerning the analysis of the packing and cooling stages. Spencer and Gilmore (6) used an equation of state and an empirical formula for the filling time to relate temperature, pressure and cycle time in the mould. Their main contribution was focused on the thermodynamics of the process, in particular with regard to relating maximum mould pressure and gate sealing pressure to shrinkage.

Theoretical treatment of the cooling stage had been attempted by Gloor (13) who solved the heat conduction equations with phase change for various crystalline polymers. Constant material properties over the relevant temperature range were assumed, as well as atmospheric pressure condition during cooling.

In their recent work, Kenig and Kamal (14,12) proposed an integrated model for the packing and cooling of thermoplastic in a semi-circular cavity. Both the dynamics and thermodynamics of the packing stage were included in the model. Temperature and pressure were calculated over the cooling stage by employing the heat conduction equations with change of phase together with an equation of state. The material properties were considered dependent on temperature throughout the whole treatment.

As the polymer melt flows from the heating zone through the gate into the cold mould cavity, the velocity of the inner core will be higher than that of the outer layers due to (a) the drag between melt and the walls of the cavity and (b) higher viscosity of the outer layers arising from the cooling effect of the walls, thus the molecules are oriented during the viscous flow owing to the shear forces exerted on the melt during the filling of the mould cavity. Part of this orientation is retained in the moulded object as it cools, i.e. freezing the oriented melt. As a result of this frozen state the properties of the material are said to be "anisotropic" e.g. different mechanical strength in different directions of the test specimen.

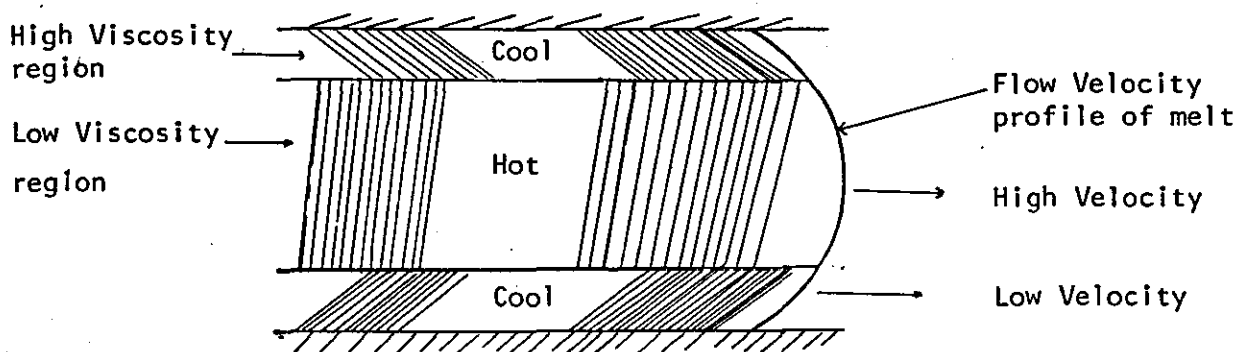


FIG. (1.4)

Polymer chains laying across regions of different flow velocity being stretched and oriented.

1.5 Determination of Orientation:-

The most important methods for measuring the orientation are X-ray structural analyses, the measurement of orientation double refraction and shrinkage measurement.

X-ray measurement of state of orientation requires expensive apparatus and recording and evaluating X-ray diagrams is not simple and time consuming.

Orientation double refraction can be measured only on colourless optically active materials such as polystyrene, polymethylmethacrylate and polycarbonates.

Shrinkage can be measured on all thermoplastic moulding compounds. Shrinkage that occurs on heating oriented small specimens is a measure of orientation.

In the past, there have been a number of studies made on the molecular orientation in injection moulding (16-18).

The investigations by Menges and Wubken (19) of flow phenomena during mould filling and the influence of processing conditions on molecular orientation in injection moulding explained the state of orientation in injection moulding.

Investigations of the flow phenomena occurring during the filling phase had been made at mouldings of simple geometry. The mould had an acrylic window. The filling of the mould was recorded by a high speed camera. Contrasting particles flowing with the melt illuminated the flow directions and velocities

at different locations.

As shown in Fig. (1.5) the shape of the flow front in the "source" flow is comparable to concentric circles having the gate as their centre. In this area of the moulding the melt is tangentially stretched and oriented and simultaneously sheared by velocity differences. Far from the gate there is a nearly straight flow front.

As indicated in Fig. (1.6) which shows the vertical cross section of Fig. (1.5), the flow phenomena of the main flow behind the flow front must be considered apart from that occurring next to the front. Behind the flow front there is no motion in the already frozen surface layers. The highest velocity gradients i.e. the biggest velocity differences are below the frozen surface layer - Fig. (1.7).

The melt is very intensively sheared and oriented. In this area directly below the surface a relative orientation maximum will be found in the moulding.

The velocity vectors of the main flow are parallel to the y-axis. The velocity maximum is much greater than the velocity of the flow front. Therefore, the melt particles behind the front rapidly catch up with the front and flow immediately at the front transverse to the main flow direction (in x- and z-direction), by this, the already more intensively cooled high-viscous flow front will be expanded like a skin perpendicular to flow direction and will instantly be frozen^{on} touching the cavity wall.

Since there is no velocity component transverse to ^{the} y - axis behind the flow front, this section (the inner of the moulding) is mainly oriented in flow direction (y-axis).

After the mould is filled there are also stock transport processes during the compression and pressure holding phase. Mostly, additional material is pushed into the mould to compensate volume shrinkage during the cooling process. Sometimes also discharge processes as a result of sudden pressure drops occur. These melt motions causes additional orientation, especially near the gate.

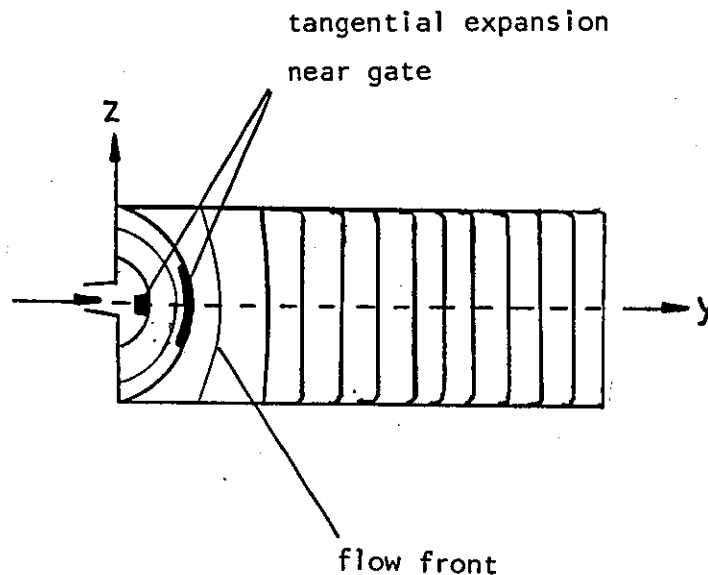


FIG. (1.5)

Formation of the flow front
in a plate - shaped moulding.

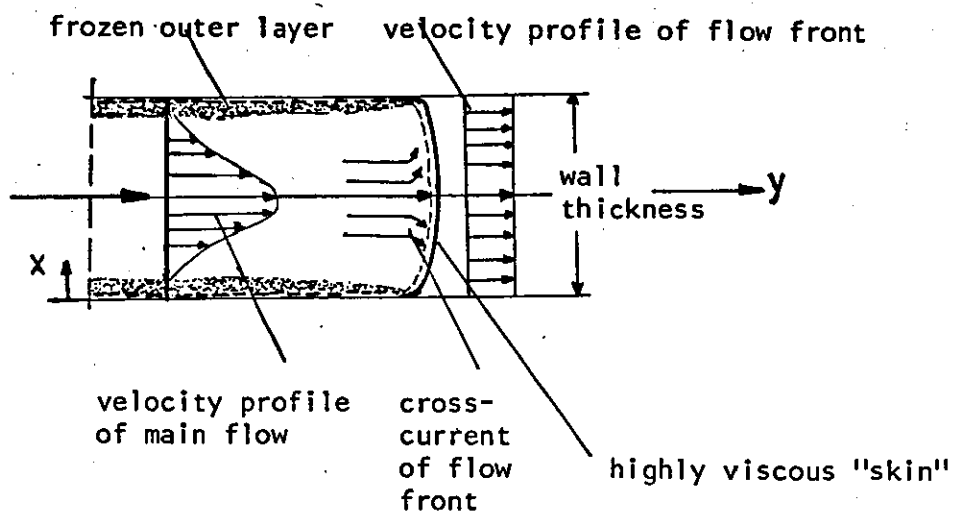


FIG. (1.6)

Flow conditions inside the cavity.

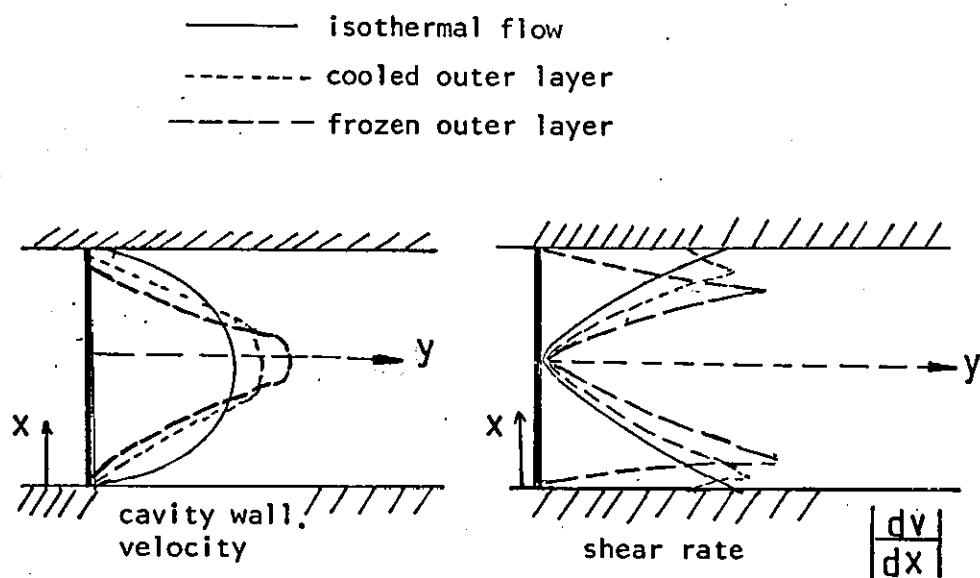


FIG. (1.7)

Profiles of velocity and shear rate during
mould filling.

Menges et al (19) investigated the influence of processing conditions (injection rate, melt temperature, mould temperature and distance from the gate) on molecular orientation in injection moulding using polystyrene. To determine the direction and the degree of molecular orientation microtome cuts were taken from various sections of rectangular mouldings parallel to the surface. The dimensions of the mouldings were (90 mm x 115 mm x 2.5 mm) and (160 mm x 60 mm x 3 mm). The microtome samples were heated above the softening temperature (Polystyrene, 5 minutes and 120⁰C) and the shrinkage which resulted was used to rate the degree of orientation. Their results were graphically demonstrated.

V_f = Velocity of the flow front

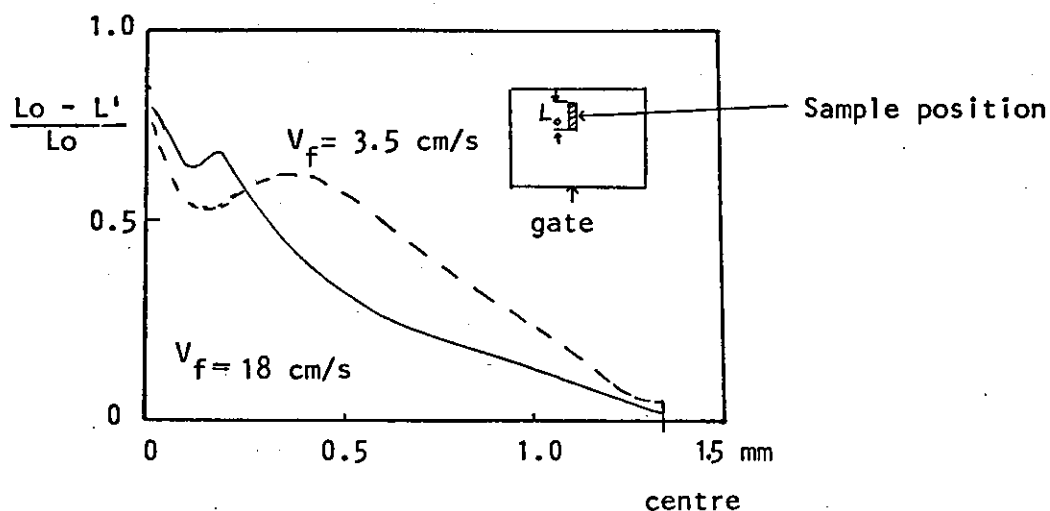


FIG. (1.8)

Longitudinal shrinkage at different injection rates.

Fig (1.8) shows the longitudinal shrinkage in flow direction at a high and low injection rate. The maximum will be found always at the surface, since the oriented state is frozen immediately and no possibility of relax exists. A little below that surface there is relative maximum, which result from the shear rate maximum Fig. (1.7). In the centre of the moulding the degree of orientation is nearly zero, because there is practically no shearing, and melt may nearly totally relax.

The increase of orientation at the surface at increasing injection speed can easily be understood. With increasing injection speed the shear rate increases, too, and thus the oriented molecules will directly be frozen at the wall. In contrary to that, relaxation predominates in the centre. During rapid injection only little heat is withdrawn from the melt and because of internal friction heat may be generated so that the stock temperature increases compared to low injection rates, and relaxation will be improved.

Fig (1.9) shows the longitudinal shrinkage and Fig. (1.10) the transverse orientation at different stock temperatures. The degree of orientation decreases with rising melt temperature within the whole range, because relaxation increases. Rising cavity wall temperature caused a similar effect on reducing orientation, but increased stock temperature was more effective than a comparable increase of the wall temperature.

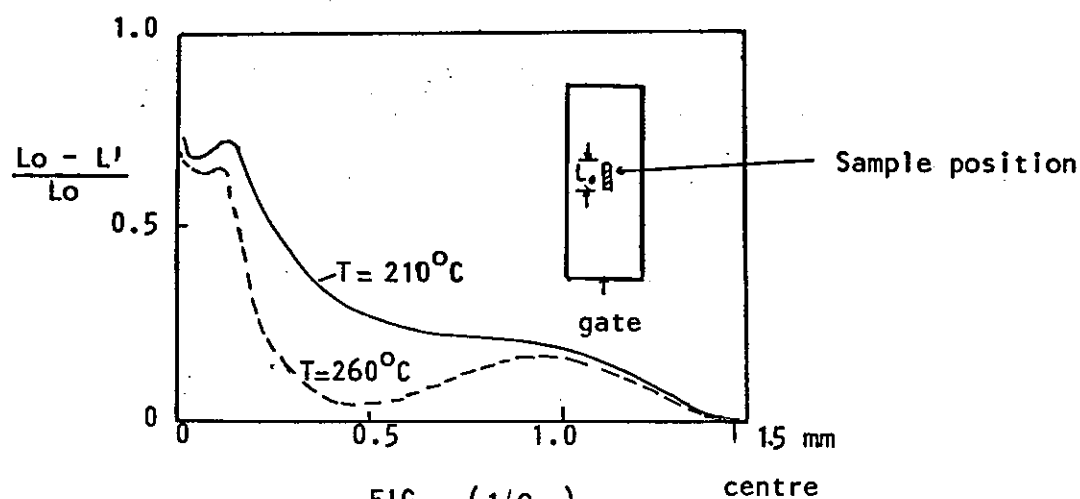


FIG. (1.9)

Longitudinal shrinkage at different stock temperatures.

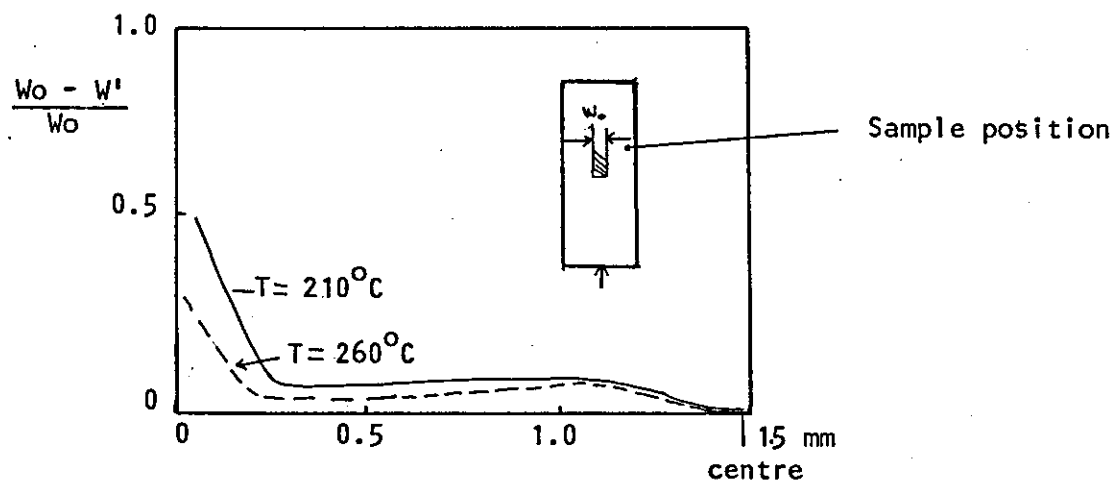


FIG. (1.10)

Transverse shrinkage at different stock temperatures.

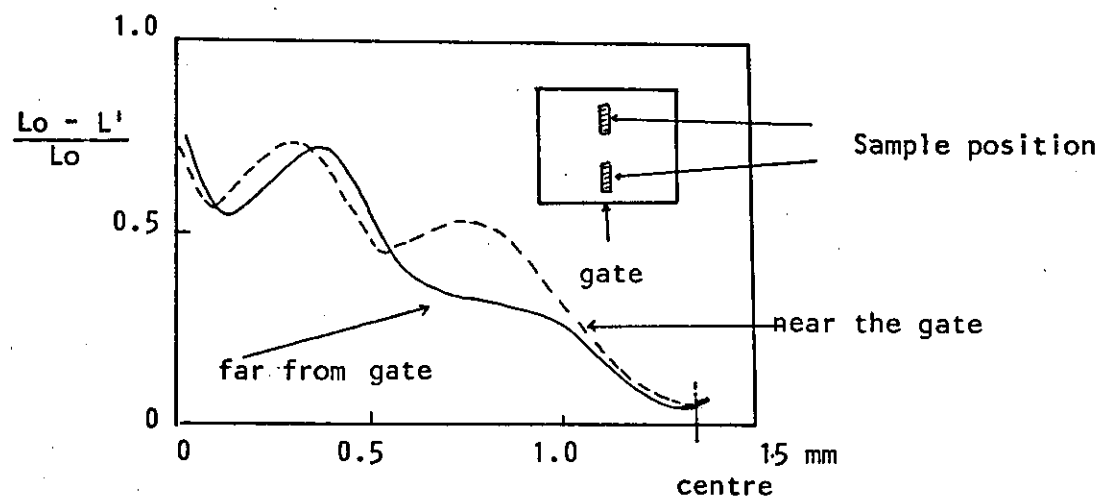


FIG. (1.11)

Longitudinal shrinkage near and far the gate.

The second relative maximum of longitudinal shrinkage near the centre at high stock temperature Fig (1.11) is caused by melt movements during the pressure holding phase. The maximum is more distinctive with rising melt temperature.

Their conclusions were that, (a) the main direction of orientation in plane-shaped mouldings is the flow direction, (b) orientation is found to be highest at the surface, (c) the centre of the mouldings showed no or only very small orientation and (d) a ^{second} distinct maximum of longitudinal orientation located near the gate which is due to melt movements during the pressure holding phase.

1.6 Internal Stresses in Injection Moulding:-

Internal stresses are the result of a temperature gradient which forms through the cross-section of the moulding during the cooling phase in the mould. When a hot melt flows from the heating zone through the gate into a cold mould cavity the melt surfaces adjacent to the relatively cold wall will cool more rapidly than the inner parts (core), thus forming a solid skin. Owing to the low thermal conductivity of the plastics melt, the core within the moulding remains viscous and solidifies much later during the cycle, in doing so its contraction (shrinkage) is opposed by the skin zones already solidified, this will result in compressive stresses in the surface layers balanced by tensile stresses in the interior of the specimen (20-21).

1.7 Measurement of Internal Stresses:-

Internal stresses in fabricated plastics material could be determined qualitatively by stress cracking in liquid media, this method provides a relatively easy technique for such determination. When thermoplastics are brought into contact with certain liquids e.g. n-heptane, their surfaces are traversed with fine cracks. The cracks are propagated at right angles to the stress and their density increases with the amount of stress and the duration of contact with the liquid. (22).

A quantitative method for determining internal stresses in plastics has been reported (23). The milling method consists of removing a uniform layer or successive layers of material from the surface of a test specimen. Where in a free specimen the internal stresses are self equilibrating. Removing a part of the stress distribution, as in removing a layer of material, leaves an unbalanced distribution of internal stress so that external restraints are required to prevent deformation. When restraints are released, the specimen so deforms as to restore internal equilibrium, the measured deformation is equivalent to the internal stress in the removed layer.

A modified milling method had been adopted by D. Burkle and his co-workers (24) to investigate the distribution of internal stresses in nylon 12 and other plastics material, and the influence of processing conditions on the internal stress. The method consisted of using a U-shaped moulding gated at the far end of one of the straight legs.

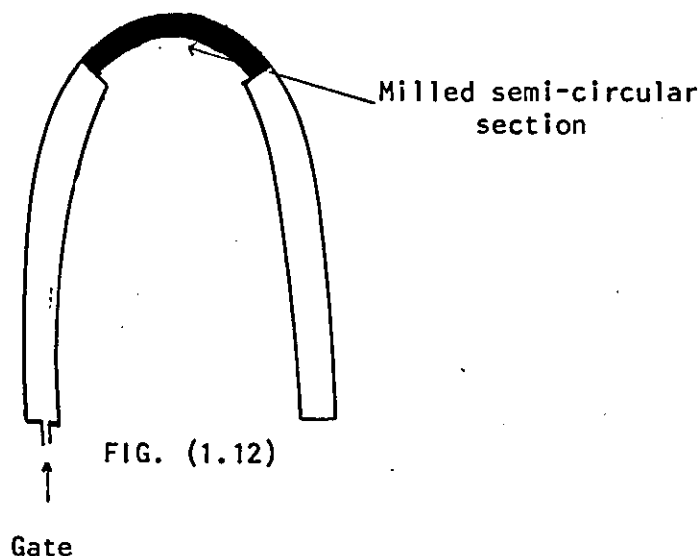


FIG. (1.12)

When the semi-circular section had been milled off, great deformation occurred on such U-shaped mouldings. This deformation resulted from the elimination of internal stresses originally existing in the removed layer. The change of the angle between the two legs of the U-shaped component permitted the calculation of the mean internal stress in the removed layer.

Burkle et al (22) investigated the influence of processing conditions and annealing treatment on the internal stresses. Their investigations revealed that internal (compressive) stresses existed in the layers near the skin zone and they decreased with increasing (i) mould temperature (ii) injection temperature (melt temperature) and (iii) decreasing injection time. As a result of annealing for 2 hours in oil at 140°C, followed by gradual cooling in the oil bath over 15 hours the internal stresses decreased to about 30% of the original level.

However, both, the milling method and the modified one, require very lengthy calculation work, moreover, they suffer from the drawback of layers removal, as the heat build-up during milling of the test specimen may initiate relaxation process and most of the stress will diminish accordingly.

Recently Kubat and Rigdahl (25) had attempted a method for the assessment of internal stresses in plastics by a stress relaxation method in which they were able to assess the overall internal stress level (σ_i).

They carried out their investigations on Injection moulded low density polyethylene. The internal stress parameter (σ_i) revealed a negative value i.e. indicated the presence of compressive stresses. They also investigated the influence of annealing on the internal stress level (overall internal stress). The sample was annealed at 70°C for five days and slowly cooled which resulted in lowering the internal stress value. They further supported their work by introducing compressive thermal stresses in low density polyethylene, which consisted slight compression of the samples at 80°C then rapid cooling in water. The compressed samples revealed negative value of (σ_i) (overall internal stress level) which confirmed the presence of compressive stresses.

1.8 Aims and Objectives of Present Work:-

The aims and objectives of this work are first to investigate the influence of some injection moulding variables ((i) injection time, (ii) melt temperature and (iii) mould temperature).

On the following properties of rigid PVC.

- (i) Degree of orientation
- (ii) Formation of oriented skin
- (iii) Overall internal stress level
- (iv) Changes in density
- (v) Tensile strength

and secondly, to establish interrelationships between aspects related to injection moulding variables previously mentioned and the consequent effects on properties. (i - v)

CHAPTER II

EXPERIMENTAL AND MATERIALS

2.1 Formulation of Poly (vinylchloride):-⁽¹⁾

In its natural form poly (vinyl chloride) is a colourless rigid material with limited heat stability and with a tendency to adhere to metallic surfaces when heated. PVC is readily susceptible to decomposition under the influence of heat, light and oxidants. For these reasons it is necessary to compound the polymer with other ingredients to make useful plastics materials.

A PVC compound may contain the following ingredients:

1. Polymer
2. Stabilisers
3. Plasticisers
4. Extenders
5. Lubricants
6. Fillers
7. Pigments

Other miscellaneous materials also used occasionally include fire retardants, optical bleaches and blowing agents.

Rigid PVC compounds normally consist of the resin, the stabilisers, a modifier and a lubricant. (or processing aid)

2.1.1 Stabilisers:-⁽¹⁾

Since the resin is unstable at the elevated temperatures required to process PVC compounds, heat stabilisers are added in order to avoid the evolution of hydrogen chloride and prevent discolouration. Materials that are effective in this capacity are generally capable of chemically reacting with the hydrogen chloride as it is formed and thus preventing the autocatalytic effect of the decomposition products from becoming apparent. A stabiliser is consumed during the whole time the ingredients in a formulation are being converted into a fully fused or (gelled) compound, and an adequate amount must still be left to allow the final processing to be carried out in safety, e.g. extrusion and moulding of profiles where burn marks and discolourations are prevented.

Stabilisers may be divided into five main groups:

1. basic lead compounds.
2. metallic salts of phenols, and of aromatic and aliphatic acids.
3. additives such as antioxidants, chelating agents, ultraviolet-radiation absorbers, and epoxides oils.
4. amines.
5. organotin compounds.

The largest class of stabilisers is based on compounds of lead, such as white lead, basic lead carbonate, and basic lead sulfates, in addition, dibasic lead phosphite, dibasic lead phthalate, dibasic and monobasic lead stearates and basic lead silicate. White lead was used extensively for stabilisation of plasticised extrusion compounds for cable covering, but if ^(replaced by tribasic lead sulfate) the cable is required to work at elevated temperatures the basic lead phthalate is frequently used because of its antioxidant properties. The major limitations to the use of lead stabilisers in flexible compounds are the opacity, which makes it impossible to produce a transparent material, and the toxic properties, which prevent their inclusion in materials intended for use in contact with food.

The long chain aliphatic acid salts of cadmium and barium find extensive use as stabilisers, particularly in blends of two. Cadmium soaps give excellent heat stability for a fairly short time, after which the compound darkens rapidly; barium soaps are less effective but longer lasting. Mixture of the two makes them particularly suitable for flexible compounds where clarity or translucency and freedom from staining are required. Besides the aliphatic acid salts, barium phenoxide is sometimes included, as well as zinc soaps in amounts ranging from one eighth to one third of the amount of the barium-cadmium stabiliser.

A single salt of this class is hardly ever used as a stabiliser. This class of stabiliser cannot be used for compounds intended for food packaging because of the toxic properties of both the barium and cadmium salts. This type of stabilisers which is rich in cadmium and phosphites, is also very effective as a light stabiliser.

Other types of material have found use as stabilisers, either alone or mixed with other stabilising compounds in package systems. Epoxy resins are frequently used with other types because they are not sufficiently effective when used alone. Epoxidised oils and esters are also frequently used as auxiliary stabilisers. Mixtures of calcium and zinc carboxylates form the basis of a number of stabilisers which find use for rigid compounds for bottles, inspite of their inferior stabilising properties, because their residual odour and toxic properties are lower. Amino crotonic esters are also used for PVC bottles because of their low toxicity, but they tend to leave a residual odour that is not acceptable for many foodstuffs.

Organotin stabilisers are generally used where effective stabilising action, together with high clarity, is required. The compounds used are generally to be found within the following classes of compounds: di-n-alkyltinmercaptides, di-n-alkyltin dilaurates, and dibutyltin dimaleate.

The high clarity obtained with this class of stabiliser is due to the fact that the organotin compounds react with hydrogen chloride produced during processing to form dialkyltin dichlorides, which are highly soluble in both plasticised and rigid vinyl compounds. The organotin stabilisers and the tin mercaptides are generally used in the production of food-packaging material. The tin mercaptides are unsuitable for food contact because of their disagreeable odour. The dibutyltin stabilisers are used for applications where good outdoor performance is required e.g., clear rigid sheeting.

2.1.2 Lubricants:- (1)

Lubricants in rigid PVC have a decisive influence both on the behaviour during processing and on the properties of the finished product. The primary requirements of a lubricant are to improve the flow properties of the fused compound and to help flow through equipment by lubrication of the interface between the PVC and the metal surfaces.

Lubricants are generally divided into two classes, internal and external. An internal lubricant should be easily compatible with PVC so that it can reduce the melt viscosity of the compound, improve its flow characteristics, and thereby reduce the frictional heat developed by shear forces. An external lubricant must act as a lubricating layer on the surface of the PVC where it comes into contact with the metal surfaces of the processing equipment. It should therefore have only limited compatibility with the PVC, particularly at processing temperature, so that it exudes readily to the surface where it should form a continuous film.

Among commonly used external lubricants are synthetic waxes; fatty esters, ethers, and alcohols; low molecular weight polyethylenes; and lead stearate. Internal lubricants include long-chain fatty acids, calcium stearate, alkylated fatty acids, and long-chain alkylamines.

2.1.3 Impact Modifiers:-⁽¹⁾

Modifiers are required principally in rigid compounds, where their main functions are to facilitate processing in modern techniques involving fast rates and high temperatures e.g., calendering, extrusion and injection moulding, and to improve the impact strength of the product. Modifiers include various acrylic co-polymers, chlorinated polyethylene, ethylene/vinyl acetate co-polymers, and butadiene co-polymers.

2.1.4 Processing Aids:-⁽¹⁾

These products improve speed of fluxing and enhance flow behaviour during compounding of the ingredients. They reduce melt fracture and improve physical properties and surface finish (surface smoothness and gloss) of the finished products, e.g. of processing aids, styrene-acrylonitrile co-polymers and chlorinated polyethylenes.

2.1.5. Interaction of Additives:

The end-use properties of formulated rigid PVC compounds is dependent on the amount and number of additives used and the interactions between them which occur during processing into the finished products.

An example is demonstrated by studies carried out by Detweiler and Purvis (44) on the interaction of lubricants with other common PVC formulation ingredients revealed that impact modifiers alter the performance of some lubricants, upsetting the expected balance of properties. With an impact modifier lubricants of the long carbon chain, such as paraffin wax, and calcium stearate appear to lose much of their 'external' functionality. In other words they have much less effect on clarity and fusion time than without a modifier. Another interaction noted was that acidic lubricants can cause poorer heat stability when used with an impact modifier, whereas without a modifier these lubricants have little effect on stability. A lubricant system that is optimised without impact modifier may exhibit quite different properties when a modifier is used. Interaction effects not only occur in lubricant systems but are extended throughout the PVC formulation.

2.2 Processing:-

2.2.1 Formulation of PVC :-

The formulation of the PVC resin was carried out in the following proportions: (pph)

	<u>INGREDIENTS</u>	<u>PPH</u>
1.	Mass PVC resin (Breon M80/50)	100
2.	Acrylic Processing Aid (Paraloid K120 n)	4.00
3.	Organotin Stabiliser (Stanclere T135)	3.00
4.	Internal Lubricant (Calcium Stearate B.P.)	0.50
5.	External Lubricant (Wax O.P)	0.75

2.2.2 Blending of Batches:-

Batches were mixed in a high speed power blender (T.K. Fielder). The blender converts horsepower into mechanical energy. The high shear action of the mixing blades is responsible for uniform dispersion and thorough mixing. The mixer can prepare batches, with relatively short cycles (10-15 minutes) and achieve excellent dispersion. The PVC resin was heated to a point where residual moisture is driven off ($50-60^{\circ}\text{C}$) and the resin becomes absorptive; at this point the liquid compounding ingredients are added (the organotin stabiliser in this case). The solid additives (Processing aid, calcium stearate and wax) were premixed. The blend was cooled to approximately ($25-30^{\circ}\text{C}$) and stored for injection moulding. The mixing and cooling process is automated and each cycle consumes 13-15 minutes.

2.2.3 Blending Conditions:-

- | | |
|---------------------------------|--|
| 1. Total Batch Weight, | 2,165 kgs |
| 2. Rotor Speed, | 3,500 R.P.M. |
| 3. Mixer Jacket Temperature, | 75°C |
| 4. Stabiliser Addition, | 50°C mixture temperature |
| 5. Powder Discharge Temperature | 120°C |
| 6. Cooler Rotor Speed, | 1000 R.P.M. |
| 7. Cooling Temperature, | $25 - 30^{\circ}\text{C}$ |
| 8. Total Blending Cycle, | 13 - 15 minutes |

2.2.4

Injection Moulding Conditions:-

I.	1. Barrel Zones Temperature:	A	B	C	D
	Zone 1 °C	140	150	165	170
	Zone 2 °C	150	160	175	180
	Zone 3 °C	160	170	185	190
	Nozzle °C	170	180	195	200
	Melt Temperature °C	165	171	181	191
2.	Injection Pressure (Hydraulic)	1000 psi (6.897 MN/m ²)			
	Peak Nozzle Pressure	8000 Psi (55.176 MN/m ²)			
3.	Hold-on time	10 sec			
4.	Cooling time	25 sec			
5.	Mould Temperature	40 °C			
6.	Screw Speed.	100 R.P.M .			

With condition (B) above, 2 - 6 constant the following injection times were attempted:

II.	<u>Injection Time</u>	<u>Sec.</u>
	1	6.00
	2	4.00
	3	3.00
	4	1.50
	5	0.90
	6	0.60

III. Barrel Zones Temperature °C

Zone 1 150

Zone 2 160

Zone 3 170

Nozzle 180

Melt temp. 171

Mould Temperature 50°C

Injection pressure — 1000 psi (6.897 MN/m²)

Hold-on-time 10 sec

Cooling time 25 sec

Injection time 6.00 sec

IV. Mould Temperature (70°C)

all other parameters as above (III.)

2.2.5 Injection Moulding:-

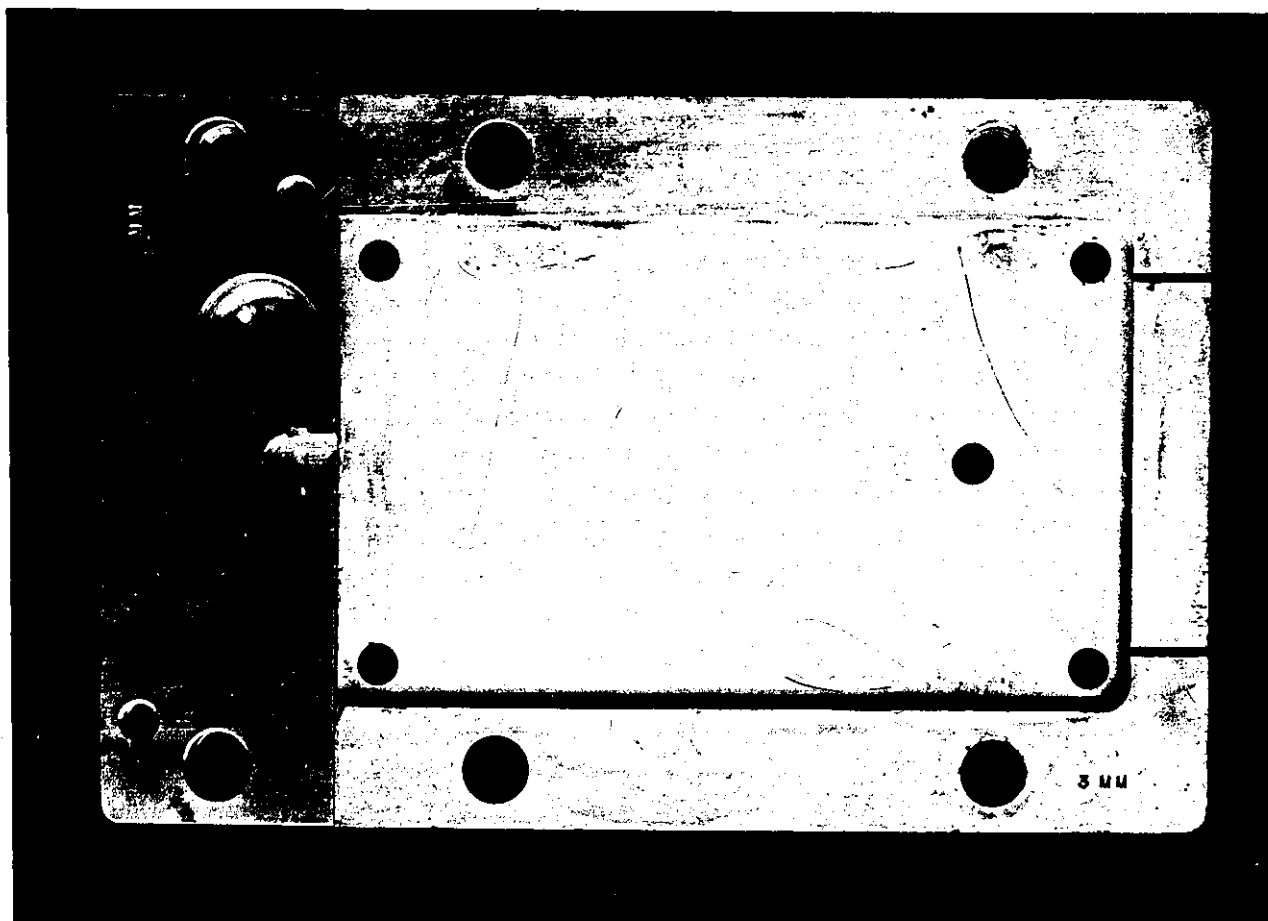
Injection moulding was carried out in a reciprocating screw injection moulder manufactured by "Bipel" which has the advantage to deliver a homogeneous melt into the mould cavity with the minimum possibility of stagnation. The machine is equipped with a mould heater to maintain the mould at a desired temperature.

Technical Data:

Hopper capacity :	9.20 kg
Screw diameter :	66.68 m m (2 $\frac{5}{8}$ inches)
Maximum cylinder heating consumption	2.40 Kw
Maximum thrust on screw :	7785 kg
Stroke of screw :	63.5 m m
Screw speed :	variable up to 220 R.P.M.
Maximum clamping pressure :	(310 kgf/cm ² = 30.392 MN/m ²)

2.2.6 Mould Cavity:-

A rectangular mould cavity was used, with dimensions (126.90 mm x 76.09 mm x 3.00 mm), Fig (2.1).



MOULD CAVITY

FIG. (2.1)

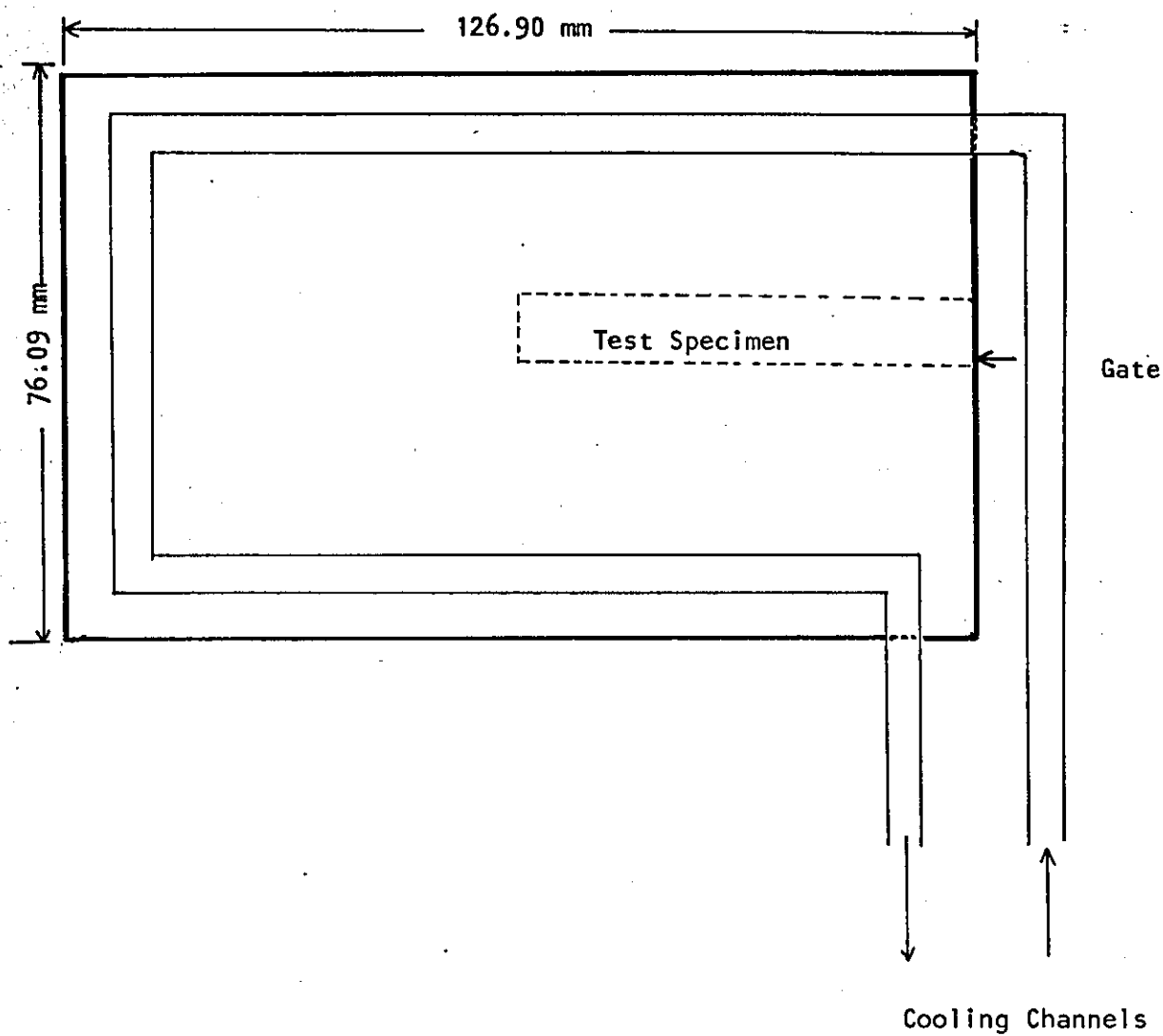


FIG. (2.2)

CAVITY LAYOUT

2.3

Instrumentation:-

Considerable instrumentation had been incorporated on the Bipel injection moulder, it provided monitoring of cycles. Although there was a controller available for sequencing if required but was not in use. These comprised:

1. Melt pressure transducer "Dynisco 460" with the range (0-20,000 psi) fitted in the injection nozzle, Fig (2.3 and 2.4). The output signals were recorded on a "Chessell 301 recorder".
2. Melt thermocouple fitted in the injection nozzle, the signals were recorded on a second channel in the same recorder above.
3. A simple digital timer to monitor the injection speed operated by two microswitchs activated by the carriage movement Fig.(2.5)

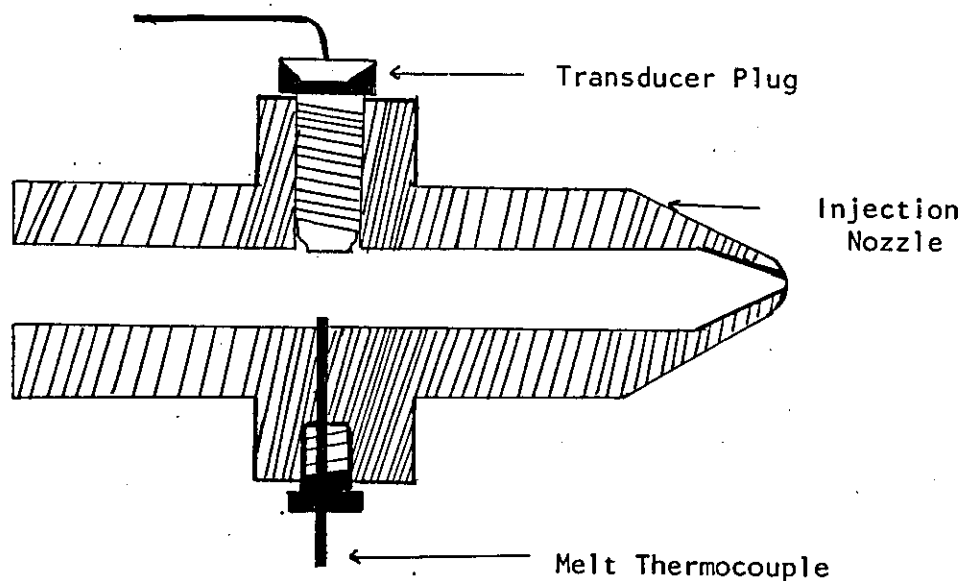
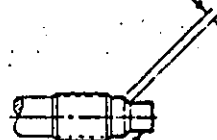


FIG. (2.3)

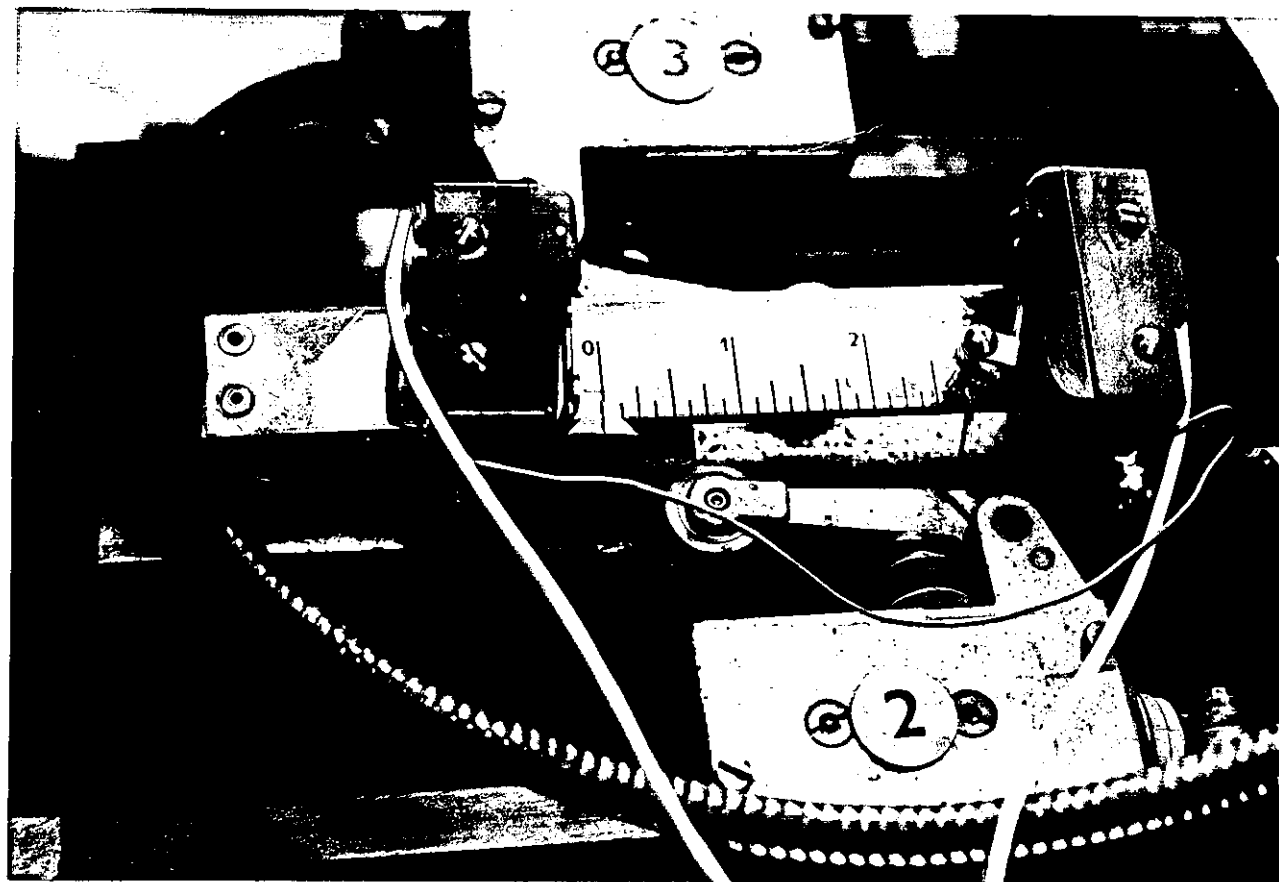
Technical drawing of a bolt and nut assembly. The bolt is labeled $\frac{5}{8}$ HEX and 45° CHAM TYP. The nut is labeled $\frac{1}{2}$ - 20UNF-2A. Dimensions include $\frac{1}{2}$ DIA, .405 DIA, .309 DIA, .307 DIA, .416 DIA, .414 DIA, 1, $\frac{5}{8}$, 2.20, 2.23, 4.25, 4.35, and PT NO. 180942-13.

ONLY AREA WHERE METAL TO
METAL CONTACT MAY TAKE PLACE-



PAINT ALL SURFACE AREAS
SHOWN IN DARK OUTLINE
WITH DYKEM STEEL BLUE.

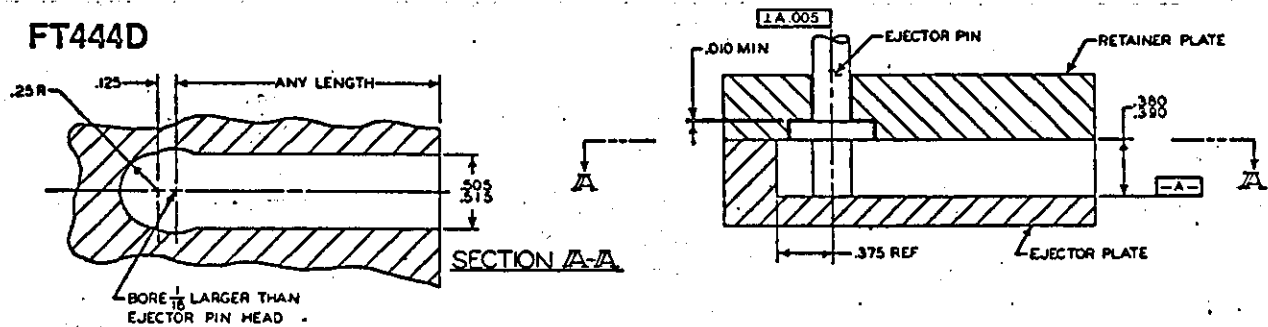
FIG. (2.4)



MICRO SWITCHES

FIG. (2.5)

4. A cavity sensor transducer "Dynisco FT 444 D" mounted behind an active ejector pin in the ejector plate Fig.(2.6) (installation drawing). The pressure in the melt in the mould cavity is exerted on the face of the ejector pin creating a force (or load). The transducer measures this force and produces an electrical signal proportional to the amount of force generated. The transducer is supplied with an excitation power supply / amplifier unit "Dynisco Cavity Pressure Controller CPC".
5. A thermocouple in the mould cavity through a close-fit drill, thus accurate control of mould temperature was possible by adjustment controls on the mould heater unit.



INSTALLATION DRAWING

FIG. (2.6)

2.4 Materials:-

(26)

2.4.1 Mass PVC Resin Breon M80/50:-

The Breon M series is a range of PVC homopolymer resins manufactured by the mass (or bulk) polymerisation process.

Mass PVC resins are polymerised in vinyl chloride monomer alone and this method of manufacture yield materials characterised by excellent processing properties; thus resulting in end products of consistent high quality, particularly for unplasticised applications.

Breon M80/50 is a low molecular weight resin for unplasticised applications where easy processing properties, high clarity and freedom from fisheyes are required. This resin is particularly suitable for blow-moulding, injection moulding and calendered sheet and film applications.

The bulk density of the resin is 0.60 - 0.64 g /ml
(BS 2782 part 5, method 501 A)

2.4.2 Acrylic Processing Aid Paraloid (K 120N):- ⁽²⁷⁾

Paraloid acrylic processing aid offers several important performance features:

faster, more controlled fusion and homogenisation of PVC compounds, improved melt elasticity, reduction of melt fracture and other surface defects and eliminate plate-out.

Paraloid K 120N is fine, white, free flowing powder. Its bulk density is (0.46 g/ml) and specific gravity is (1.18). Insoluble in water, soluble in aromatic or ketone solvents.

2.4.3 Organotin Stabiliser Stanclere T 135:- ⁽²⁸⁾

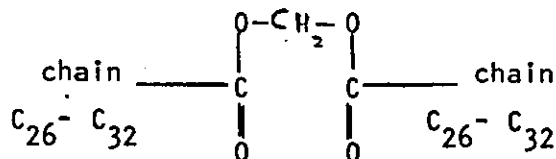
Stanclere T 135 is one of the general purpose liquid Butyl Thiotin stabiliser, giving good heat stability in most type of PVC polymer. It finds wide applications in rigid sheet, film and bottles, and may also be used in flexible applications and plastisols.

The density of stanclere T 135 at 20°C is (1.115 g/ml) refractive index n_D^{20} is (1.508) and viscosity at 20°C is 0.5 p.

2.4.4 Wax 0.P (Hoechst) (29) :-

Wax 0.P is a product with a wide range of uses. It is highly effective as a lubricant in suspension polymerised and mass polymerised PVC. Finished PVC articles containing Wax 0.P have comparatively good transparency. It does not tend to produce excessive lubrication effects.

It is partly saponified ester wax from montanic acids with liquefying point 100 - 105 °C, density at 20°C 1.01 - 1.03 g./ml. The chemical constitution is

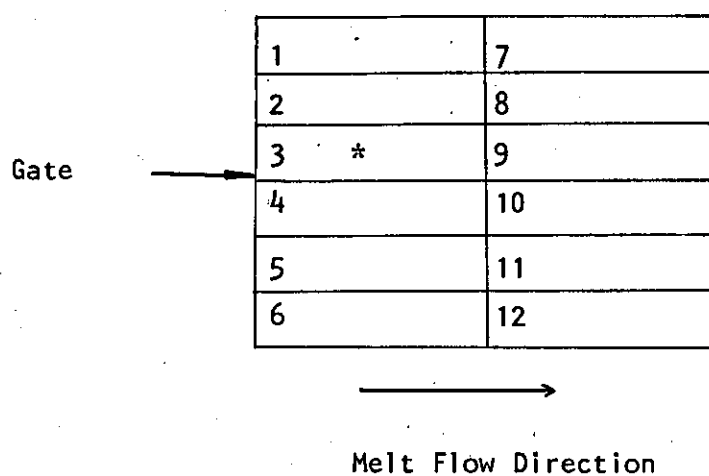


Wax 0.P partly saponified ester

2.5 Testing:-

2.5.1 Heat Shrinkage Measurements:-

Heat shrinkage specimens were cut along flow direction, Fig. (2.7), their ends properly polished and their lengths accurately measured. The numbering on the plaques is a convention used in previous research work.



* test specimen

FIG. (2.7)

Specimens were left to shrink in an oven at 130°C for (3) three hours, cooled and their lengths measured.

% Shrinkage (along flow) was determined as,

$$\frac{L_o - L^i}{L_o} \times 100$$

where L_o - original length (mm)

L^i - final length (mm)

Determination of shrinkage transverse to flow was attempted but the results were not significant.

2.5.2 Determination of Internal Stress Level:-

The method is based on recording a number of stress relaxation curves with different initial stresses (σ_0) (deformation stresses). When the maximum slope (F) of the curves (Fig.2.11) as determined from stress-log (time) diagram. (Fig.2.10), is plotted against the initial stress (σ_0) (Fig.2.12), a straight line is obtained. The intercept of this line with the stress axis is taken as a measure of the internal stress level (σ_i) i.e. $\sigma_0 = \sigma_i$ at $F = 0$.

Symbols:-

σ_0 initial stress (deformation stress), at the moment the straining is stopped.

$\sigma_{01} - \sigma_{06}$ initial stresses applied to six different specimens.

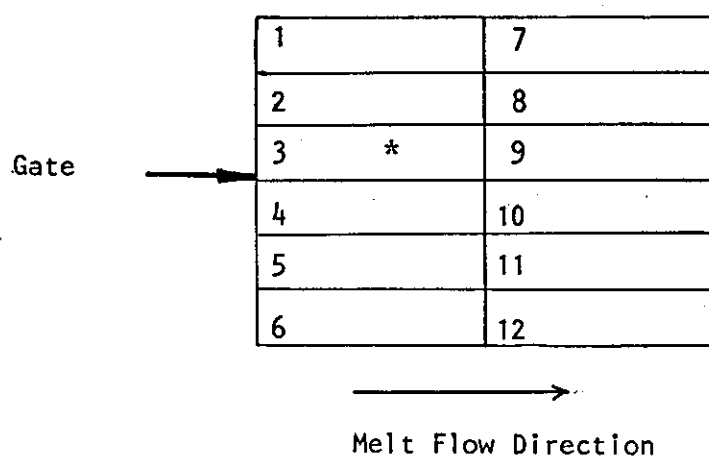
t time, measured from the moment the straining is stopped.

F maximum slope of stress-log (time) plot.

σ_i internal stress parameter, the extrapolated value of the σ_0 intercept at $F=0$ of the $F-(\sigma_0)$ relationship.

2.5.3 Test Specimens:-

Specimens were cut along flow direction from injection moulded rigid PVC plaques as shown, Fig. (2.8)



* test specimen

FIG. (2.8)

Each specimen was milled on a high speed diamond rotor to the shape of a tensile bar in accordance with (Type V - ASTM D 638). Air cooling was applied to take away generated heat build up on milled specimen edges, all machine marks were eliminated with a soft emery cloth and cross sectional area was accurately measured. A new specimen was used for each relaxation curve.

(30)

ASTM D638 TYPE V

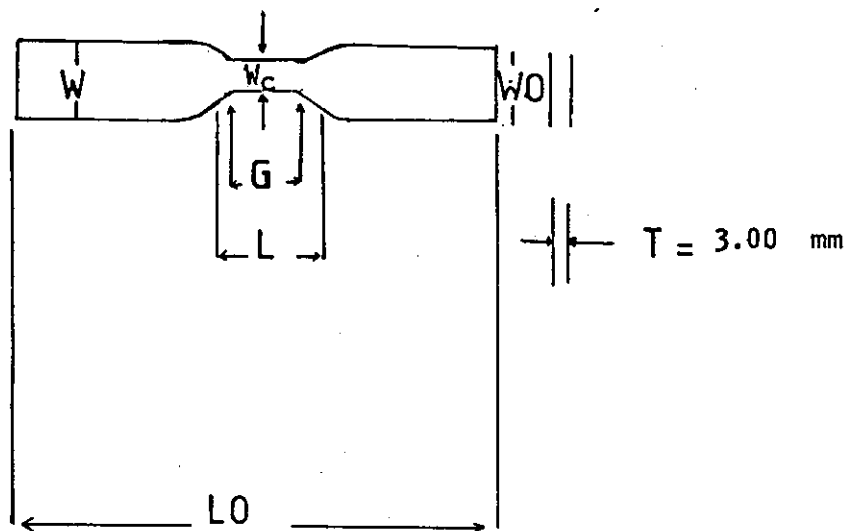


FIG. (2.9)

W_c	- width of narrow section	- 3.18 mm
L	- length of narrow section	- 9.53 mm
W_0	- width over-all	- 9.53 mm
G	- gage length	- 7.62 mm
L_0	- length over-all	- 63.50 mm
T	- thickness	- 3.00 mm

2.5.4 Testing Conditions:-

The test was performed on an Instron Universal testing machine. Both grips and specimens were confined in a well controlled - temperature chamber. The chamber was allowed to attain the test temperature for at least one hour before any specimen was tested as fluctuation of temperature is not favoured. Temperature was set at $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Specimens were conditioned to the test temperature for 5 minutes. Moving cross head speed was 5 mm/min according to (ASTM D 638).

2.5.5 Graphical Representation and Calculation:-

The measurement of the internal stress level in a specimen required a number of relaxation curves (five or six at least). Each curve was obtained by applying an initial stress (σ_0) to the specimen (deformation stress), keeping the deformation constant and recording the stress decay (stress vs. time) Fig. (2.10), the data then was transformed into stress-log (time) diagram (Fig.2.11), from which the maximum slope (F) was calculated using a linear regression formulae where a series of points on the graph may be approximated to the straight line ($y = mx + c$), where (m) is the slope (F in this case) and (c) the intercept. The formulae are:-

$$m = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2}$$

n - number of data points

and

x_i - (σ) stresses values

$$c = \frac{\sum y_i \sum x_i^2 - \sum x_i \sum x_i y_i}{n \sum x_i^2 - (\sum x_i)^2}$$

y_i - log (time) values

The maximum slope values for each relaxation curve determined from σ -log (t) plot, were plotted against the initial stresses ($\sigma_{o_1} - \sigma_{o_6}$). At $F=0$, the intercept of the line with the stress axis is the measure of the (σ_i) internal stress level i.e. at ($\sigma_o = \sigma_i$), (Fig. 2.12).

FIG. (2.10)

Stress Relaxation Curves

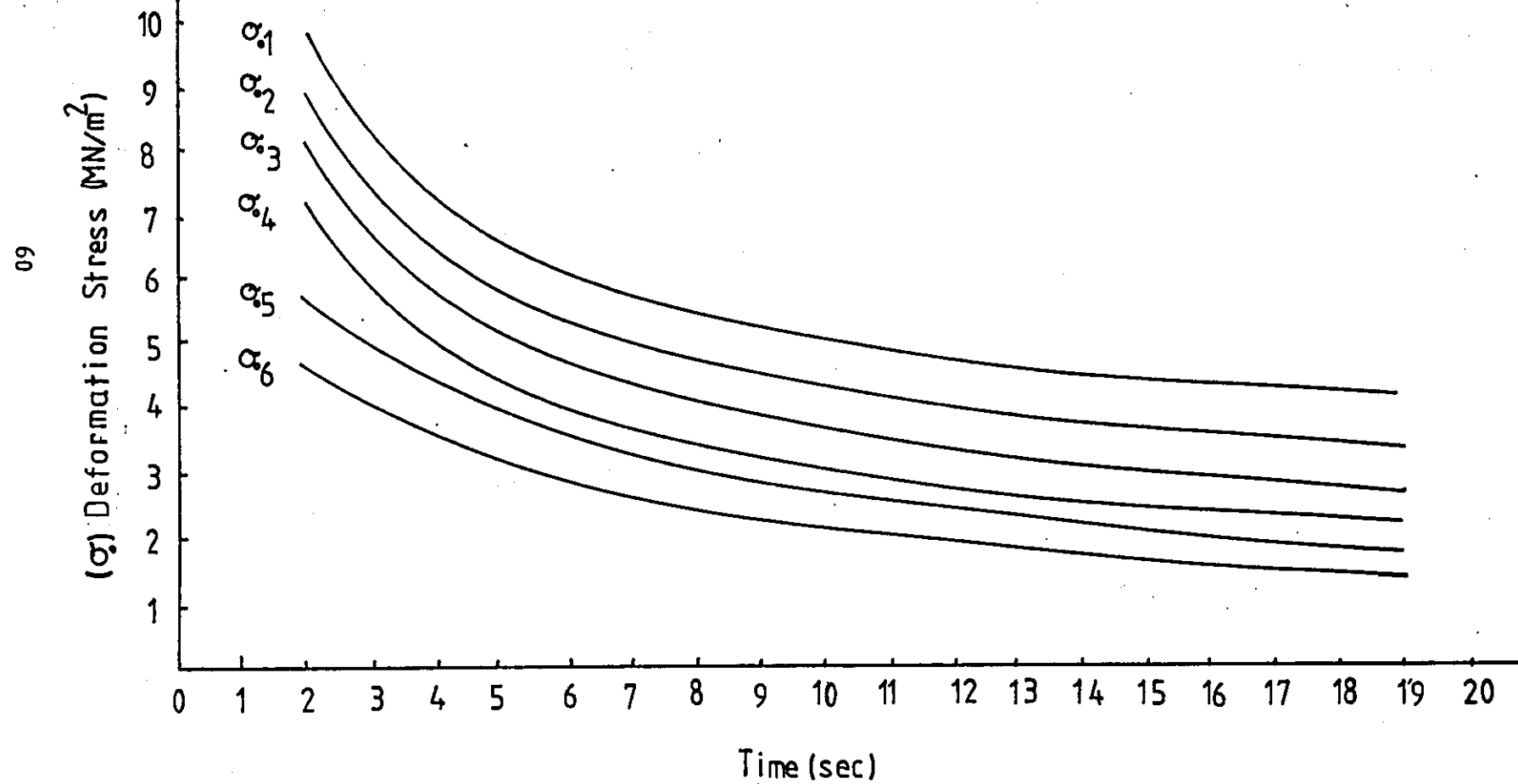
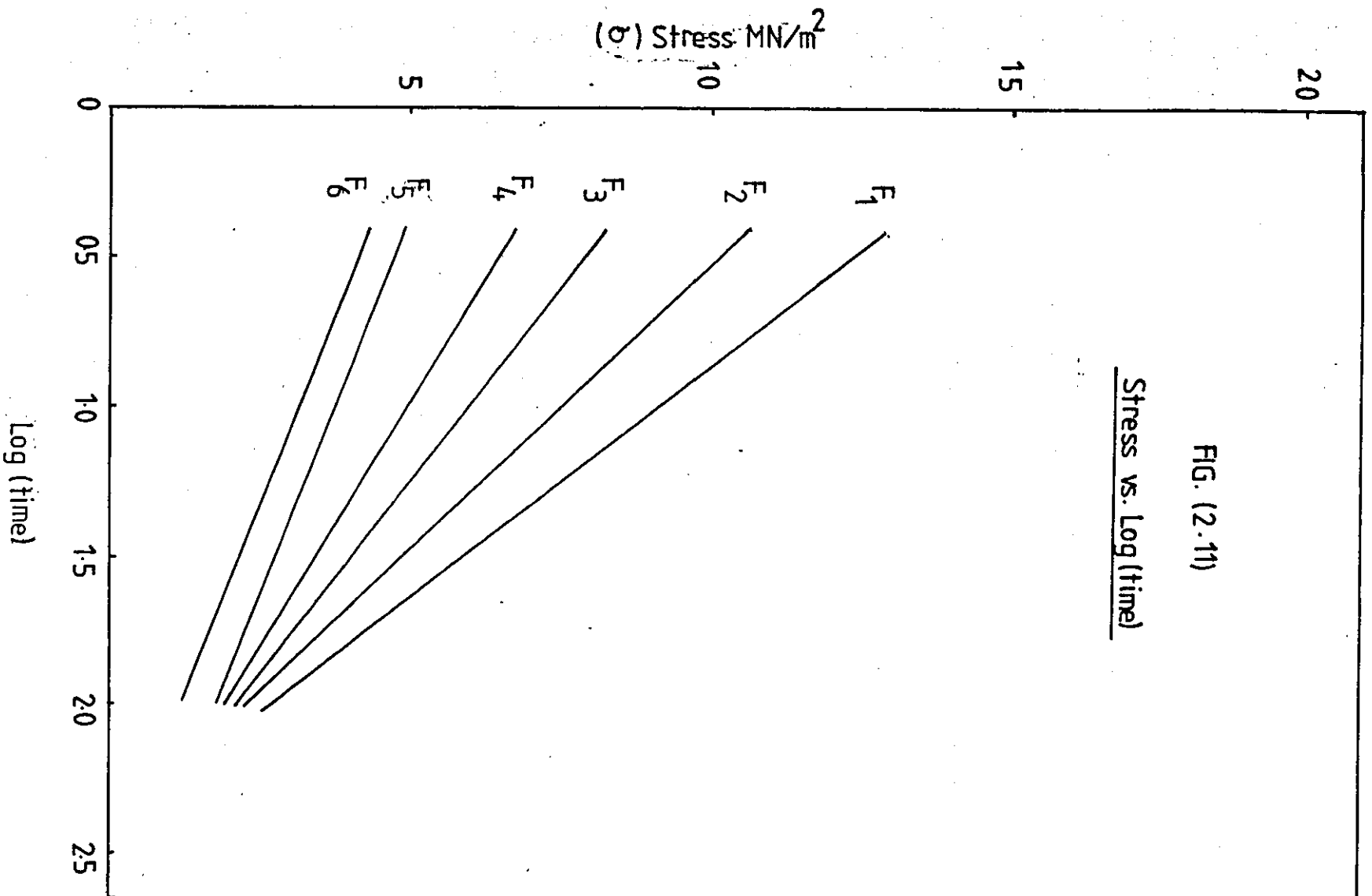
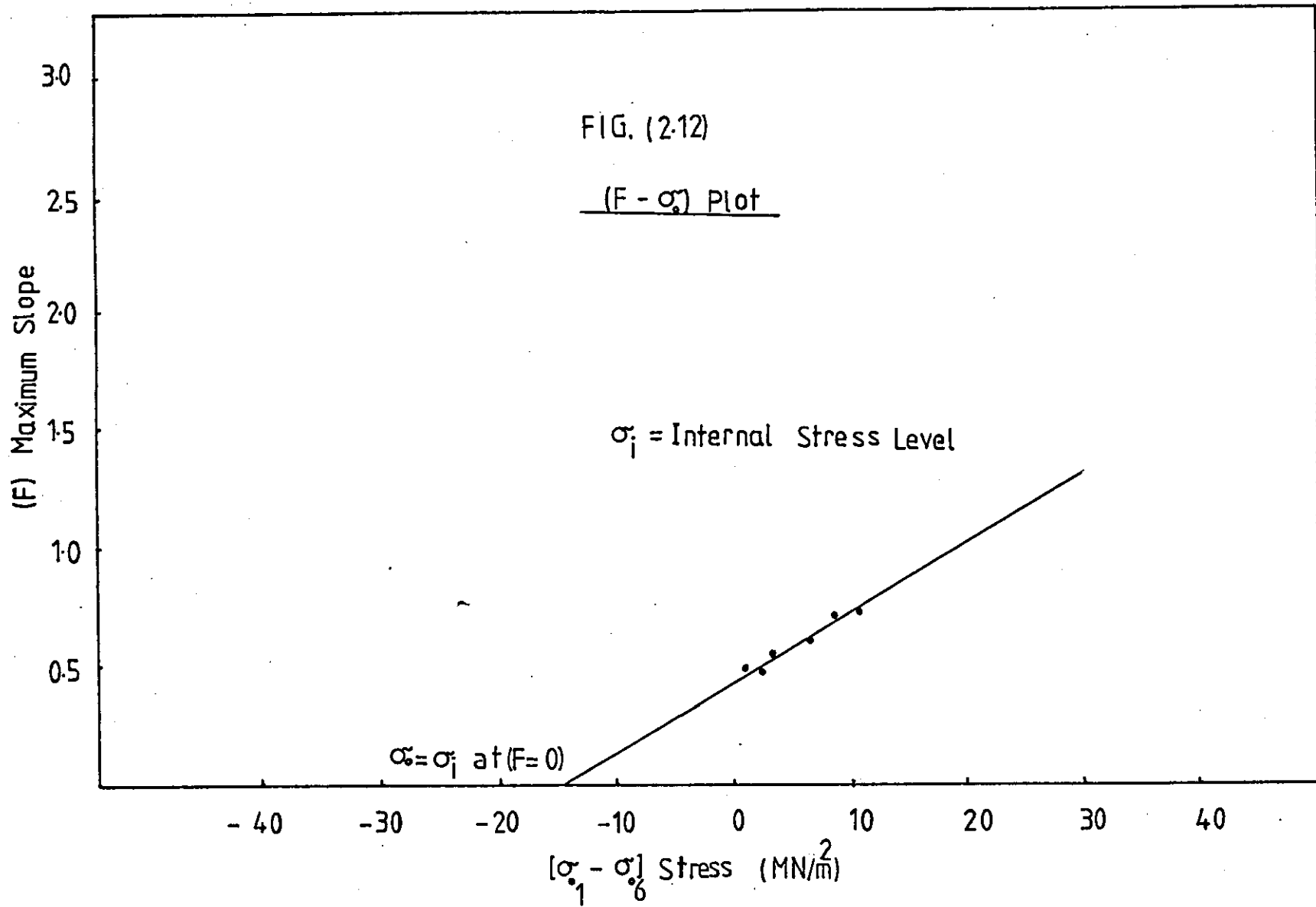


FIG. (2.11)
Stress vs. Log (time)





2.5.6 Measurement of Tensile Stress:-

The test was performed on an Instron Universal testing machine. Tensile stress specimens were cut and prepared in accordance with (ASTM D 628 Type V), previously described. (30)

Test Specimens:-

Test specimens were cut and prepared from location 3.

Fig. (2.8).

2.5.7. Testing Conditions:-

Instron cross-head speed	5 mm/min
Testing temperature	$25^{\circ}\text{C} \pm 2^{\circ}\text{C}$
Number of specimens per test	6

$$\text{Tensile strength} = \frac{\text{maximum load} - \text{kgf}}{\text{initial cross-sectional area}}$$

2.5.8 Density Measurements:-

Density measurements were performed on a Density Gradient Column in accordance with (B.S. 2782, Flotation Method). (31)
A calibration graph was obtained by the use of floats of known density, thus density of specimens was determined from their equilibrium position in the column. Test specimens were cut and prepared from location (3) near the gate.

2.5.9 Measurement of Oriented-Skin Thickness:-

Preparation of Specimens:-

In order to measure thickness of oriented skin, microtomes (20 μ) were sectioned across the plaque thickness and transverse to melt flow direction as shown in Fig. (2.13)

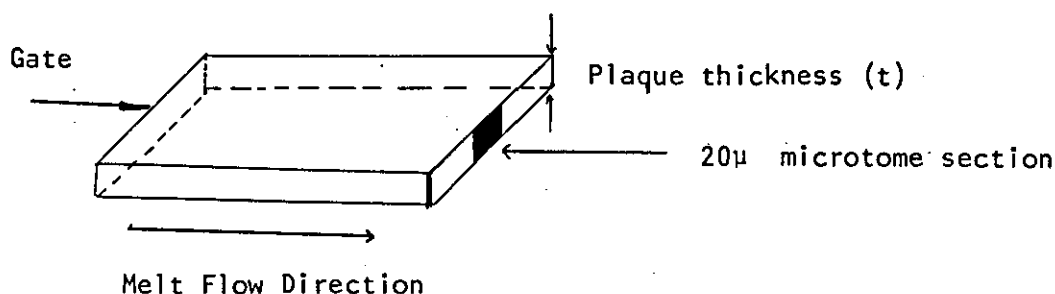


FIG. (2.13)

Each microtomed specimen was mounted on a slide with clove oil and covered with transparent cover slip.

The oriented skin was revealed by a cross polarised light microscop - (Nikon), and photographic plates were prepared and printed later.

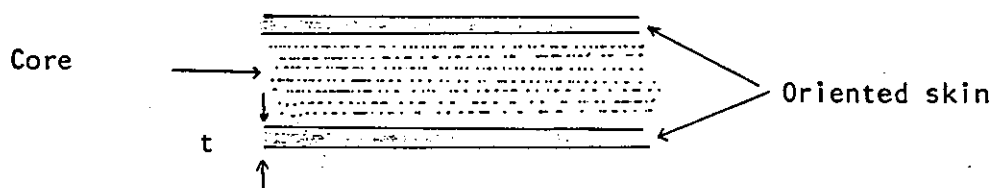


FIG. (2.14)

"Section cut through the test plaque showing highly oriented skin"

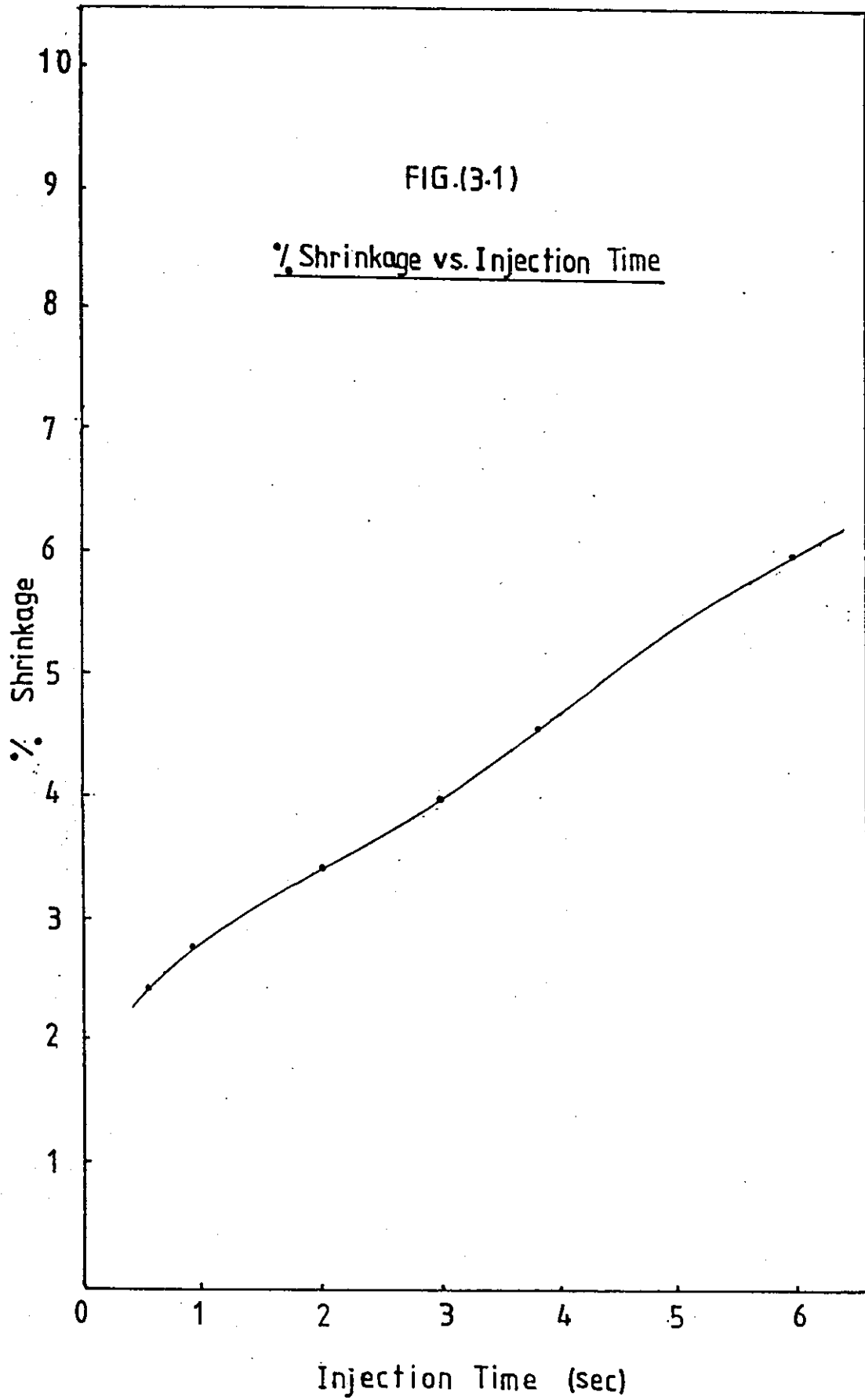
$$\text{Skin Thickness} = \frac{\text{width (t) on Photographic Prints}}{\text{Magnification (100)}}$$

RESULTS

CHAPTER III

FIG.(3-1)

% Shrinkage vs. Injection Time



3.1

% SHRINKAGE VS INJECTION TIME

Specimens were cut along melt flow direction from position (3) near the gate as shown in Fig. (2.7)

Six specimens were tested to obtain each point shown on the curve.

% Shrinkage was calculated as

$$\frac{L_o - L'}{L_o} \times 100$$

L_o = original length

L' = final length

Moulding Conditions:Variable:

Injection time 6.00, 4.00, 3.00, 1.50, 0.90 and 0.6 sec

Constants:

Mould temperature 40°C

Melt temperature 171°C

Injection pressure 1000 psi (6.897 MN/m²)

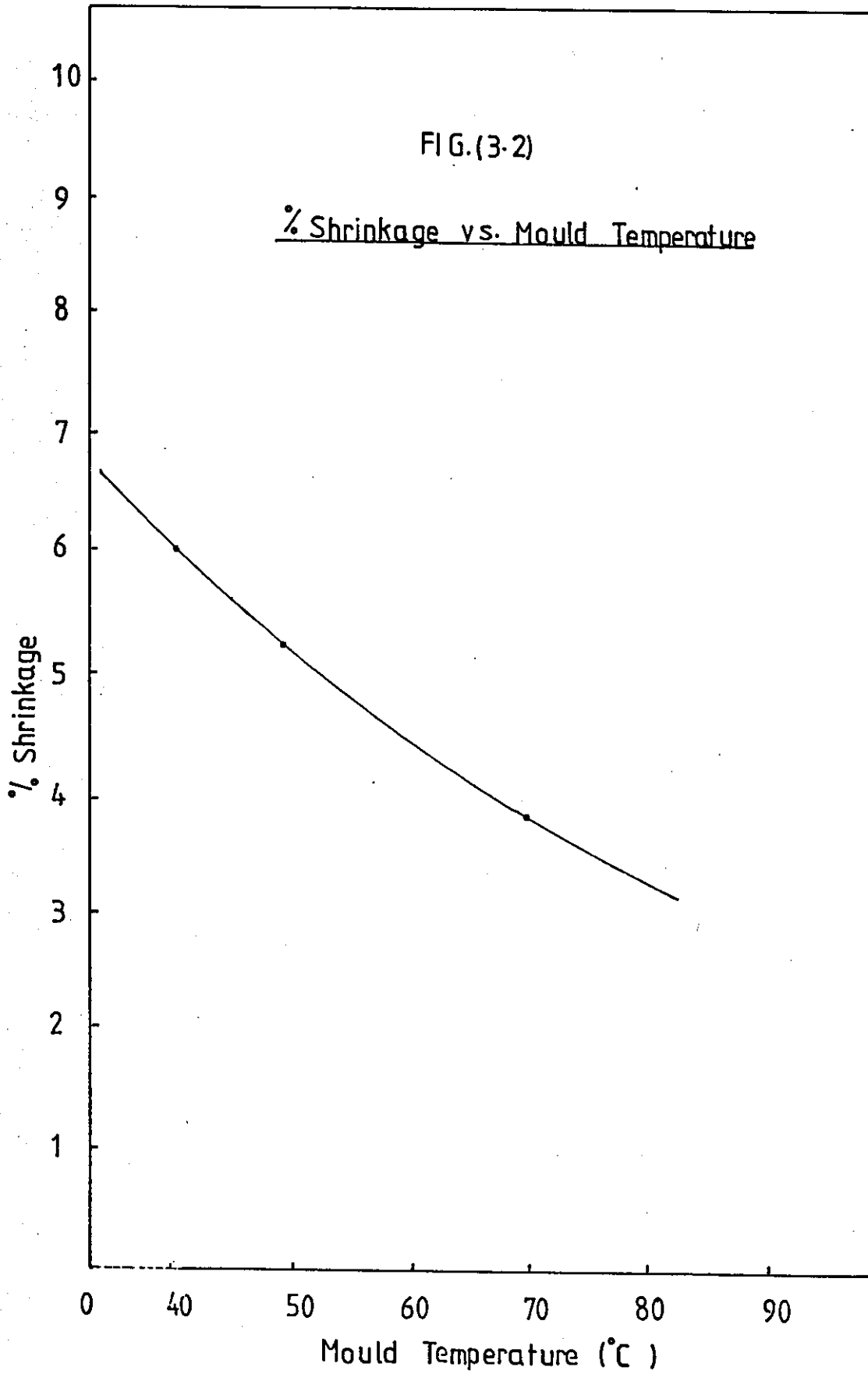
Hold on time 10 sec

Cooling time 25 sec

Cavity thickness 3 mm

FIG.(3-2)

% Shrinkage vs. Mould Temperature



3.2

% SHRINKAGE VS MOULD TEMPERATURE

Specimens were cut from same location as in Fig.(2.7) .

$$\% \text{ Shrinkage} = \frac{L_0 - L'}{L_0} \times 100$$

Moulding Conditions:Variable:

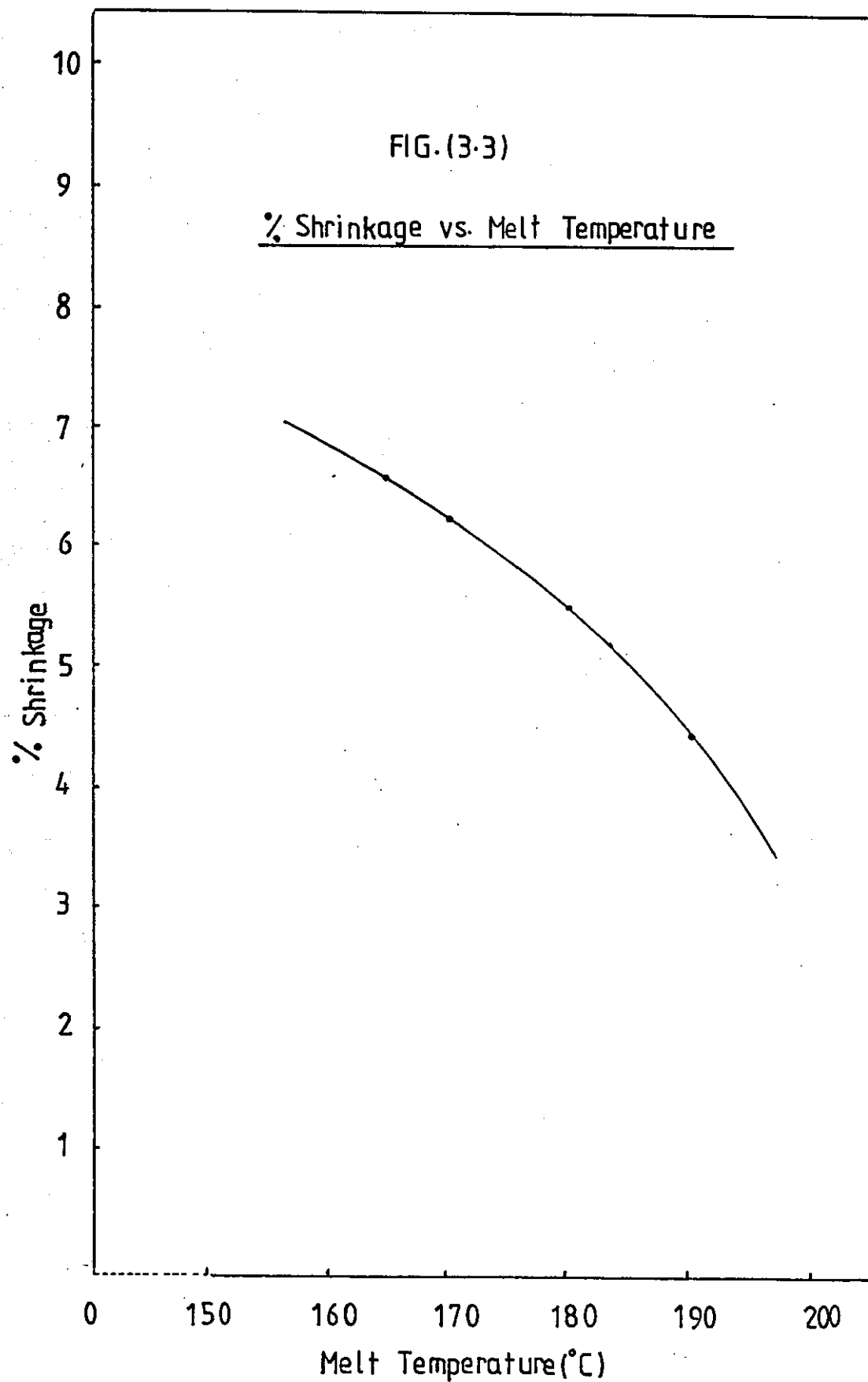
Mould temperature 40, 50 and 70°C

Constants:

Melt temperature	171°C
Injection time	6.00 sec
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm

FIG.(3.3)

% Shrinkage vs. Melt Temperature



3.3

% SHRINKAGE VS MELT TEMPERATURE

Specimens were cut from same location as in Fig. (2.7)

$$\% \text{ Shrinkage} = \frac{L_o - L'}{L_o} \times 100$$

Moulding Conditions:Variable:

Melt temperature 165, 171, 181 and 191°C.

Constants:

Mould temperature 40°C

Injection time 6.00 sec

Injection pressure 1000 psi (6.897 MN/m²)

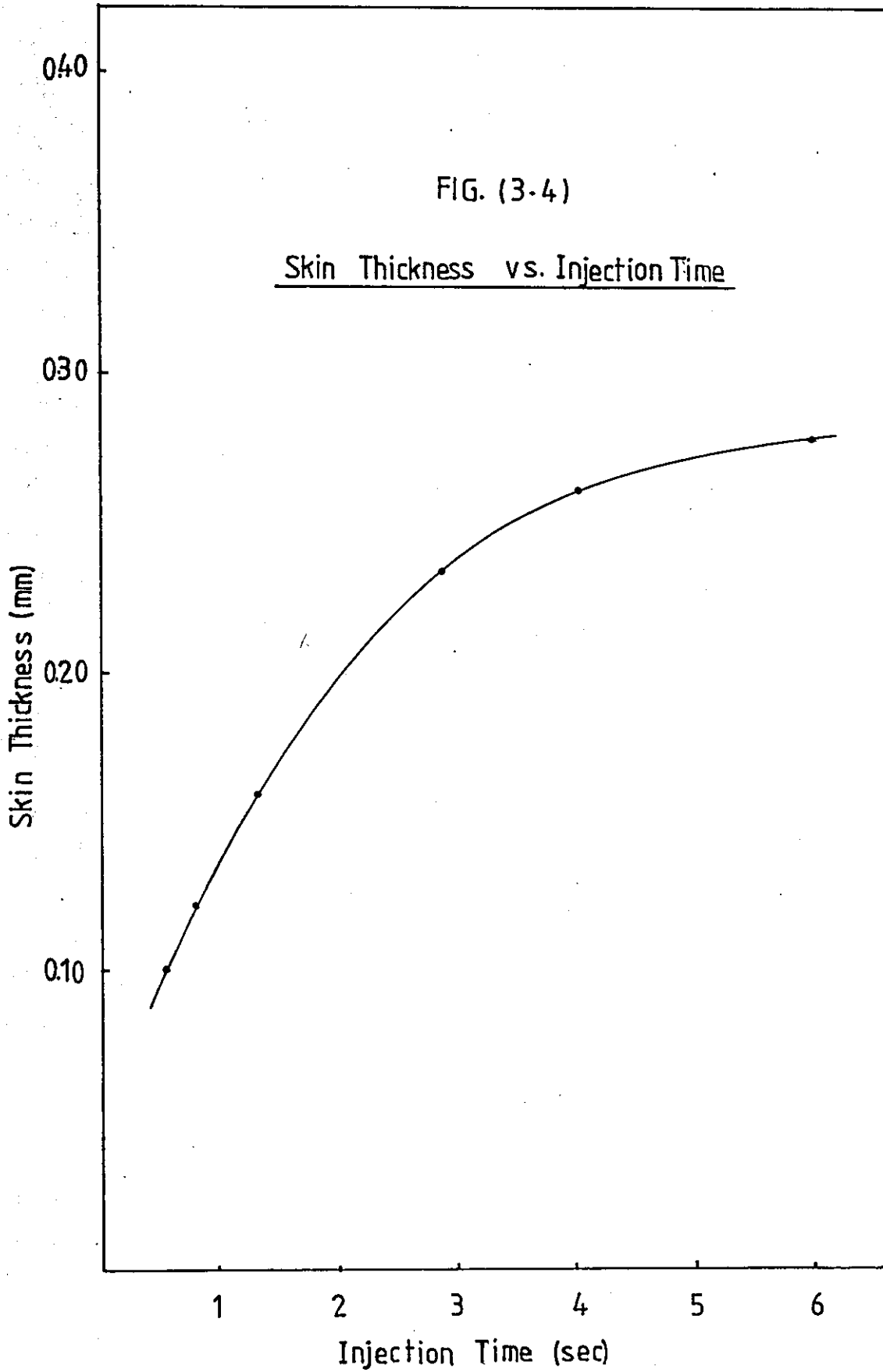
Hold on time 10 sec

Cooling time 25 sec

Cavity thickness 3 mm

FIG. (3-4)

Skin Thickness vs. Injection Time



Microtomes 20 μ thickness were sectioned from location
(3) near the gate as shown in Fig. (2.13)

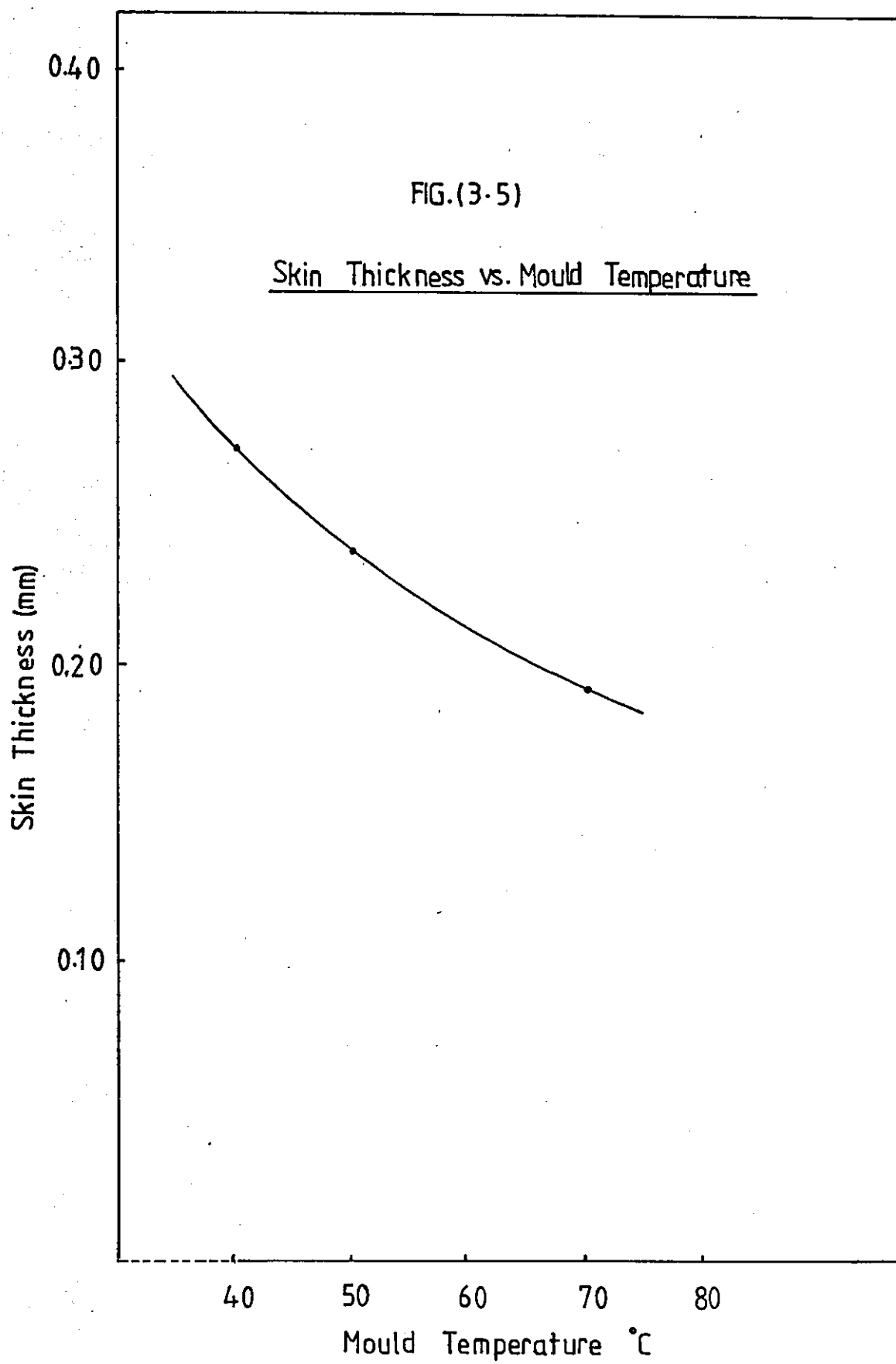
Moulding Conditions:

Variable:

Injection time 6.00, 4.00, 3.00, 1.50, 0.90 and 0.60 sec.

Constants:

Melt temperature	171°C
Mould temperature	40°C
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm



Microtomes were prepared as in Fig. (2.13).

Moulding Conditions:

Variable:

Mould temperature 40, 50 and 70°C.

Constants:

Melt temperature 171°C

Injection time 6.00 sec

Injection pressure 1000 psi (6.897 MN/m²)

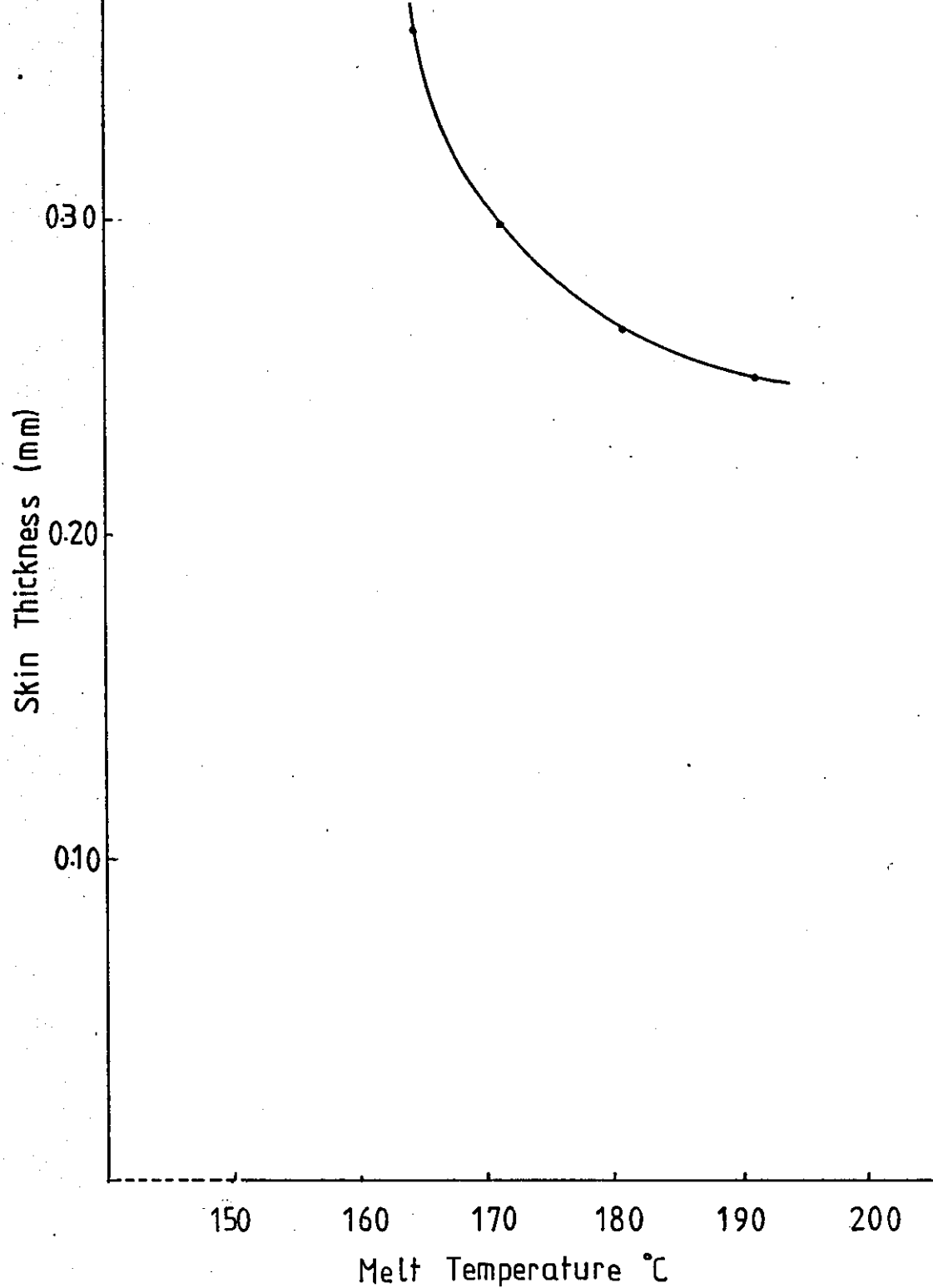
Hold on time 10 sec

Cooling time 25 sec

Cavity thickness 3 mm

FIG.(3·6)

Skin Thickness vs. Melt Temperature



Microtomes were prepared as in Fig. (2.13).

Moulding Conditions:

Variable:-

Melt temperature 165, 171, 181 and 191 °C

Constants:

Mould temperature 40°C

Injection time 6.00 sec

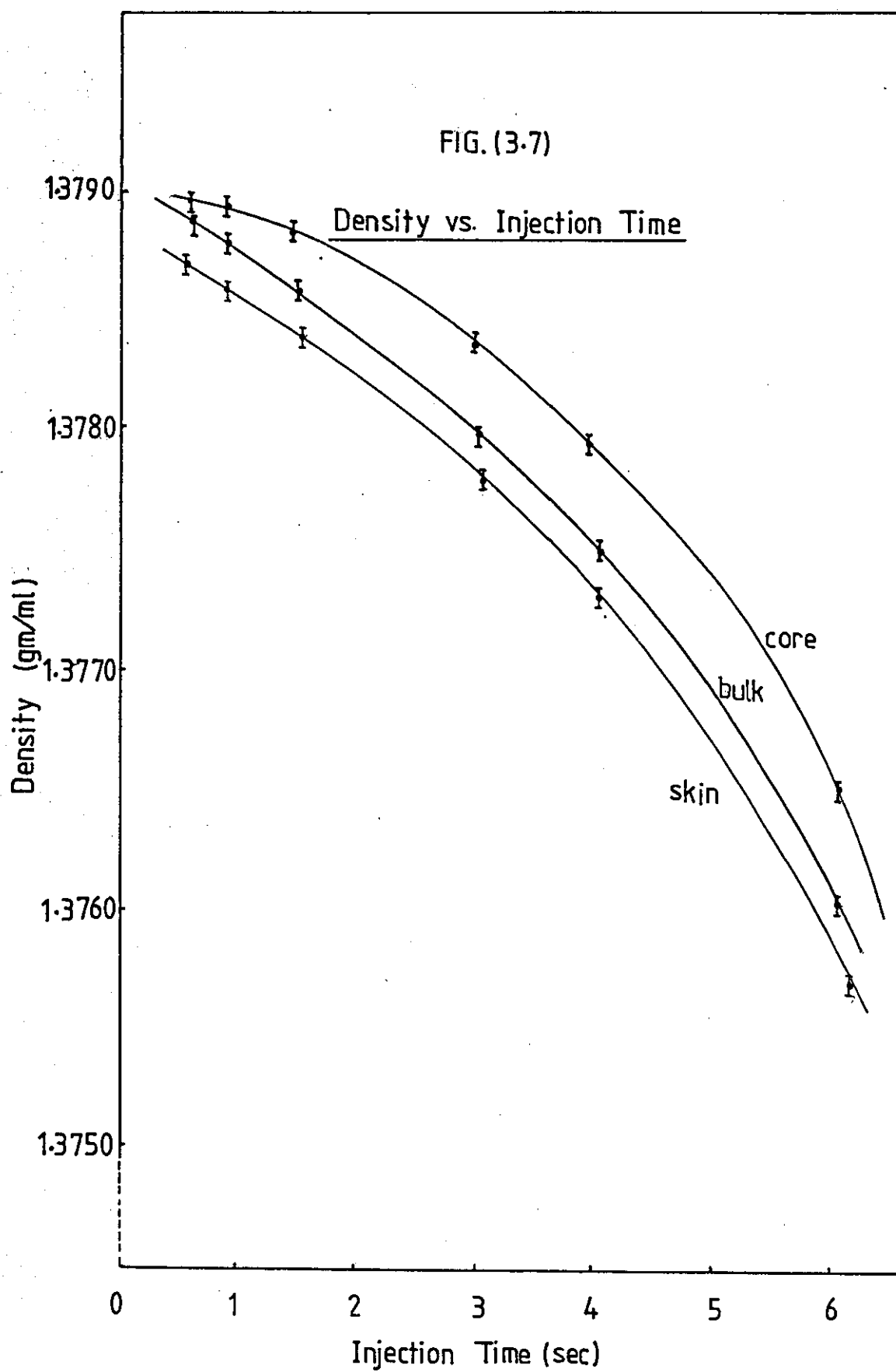
Injection pressure 1000 psi (6.987 MN/m²)

Hold on time 10 sec

Cooling time 25 sec

Cavity thickness 3 mm

FIG. (3.7)



Density was measured by flotation method previously described (2.5.8.).

Specimens were prepared from location (3) near the gate, central curve depicts variation of bulk density (skin and core) with injection time. The upper one depicts variation of core density with injection time and the lower depicts variation of skin density with injection time.

The core was obtained by milling off few layers from the test piece from both surfaces. The skin was obtained by the same procedure by milling off from either surfaces of the test piece.

Moulding Conditions:-

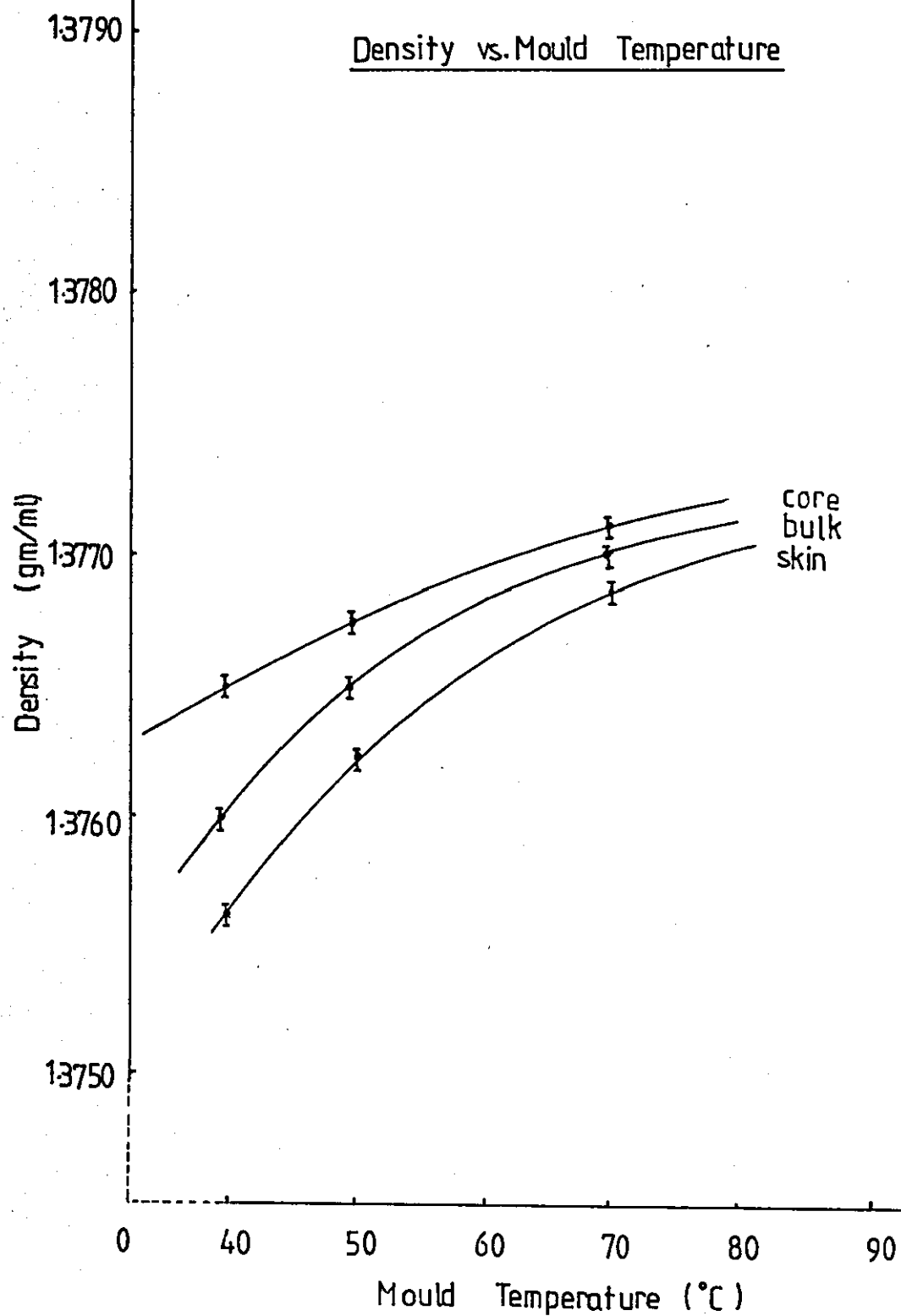
Variable:

Injection time 6.00, 4.00, 3.00, 1.50, 0.90 and 0.60 sec.

Constants:

Melt temperature	171°C
Mould temperature	40°C
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm

FIG. (3·8)



Density was measured as in Fig. (3.7).

Moulding Condition:

Variable:

Mould temperature 40, 50 and 70°C

Constants:

Melt temperature 171°C

Injection time 6.00 sec

Injection pressure 1000 psi (6.897 MN/m²)

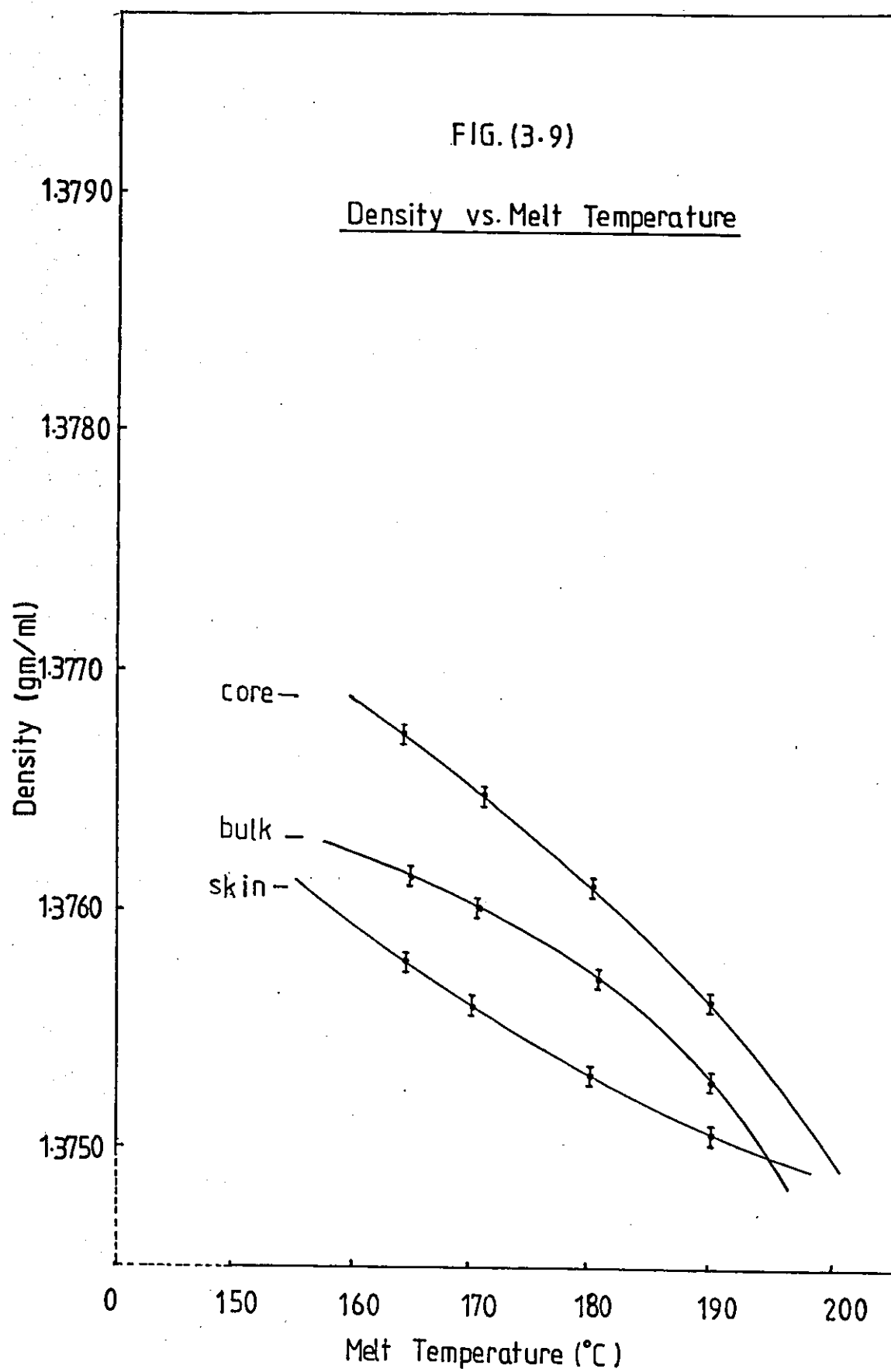
Hold on time 10 sec

Cooling time 25 sec

Cavity thickness 3 mm

FIG. (3.9)

Density vs. Melt Temperature



Density was measured as in Fig (3.7) .

Moulding Conditions:

Variable:

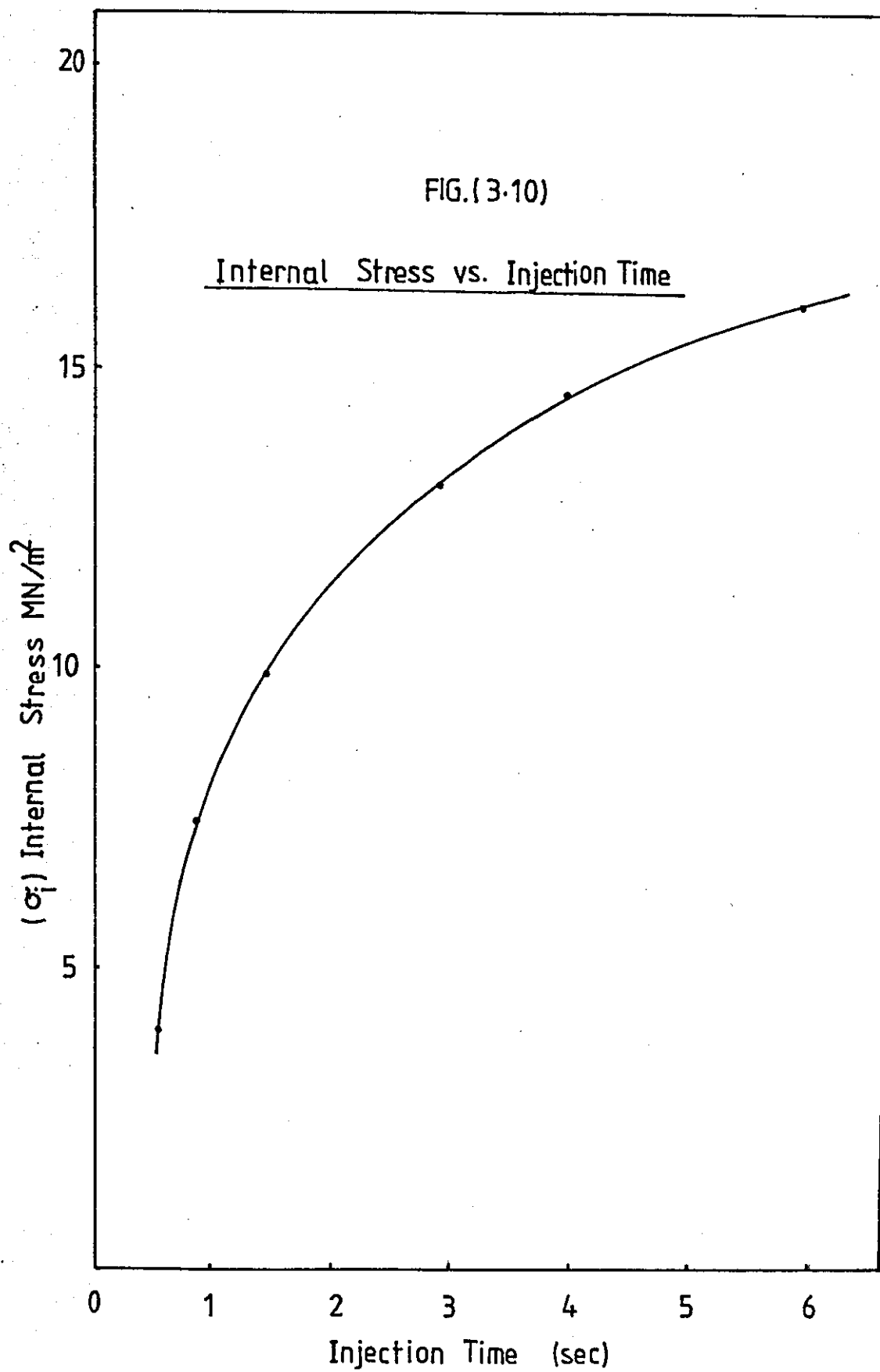
Melt temperature 165, 171, 181, 191 °C.

Constants:-

Mould temperature	40°C
Injection time	6.00 sec
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm

FIG.(3.10)

Internal Stress vs. Injection Time



3.10 INTERNAL STRESS VS INJECTION TIME

Internal stresses were measured by the stress relaxation method previously described (2.5.5). Specimens were prepared from location No. (3) near the gate. Fig. (2.8)

Moulding Conditions:

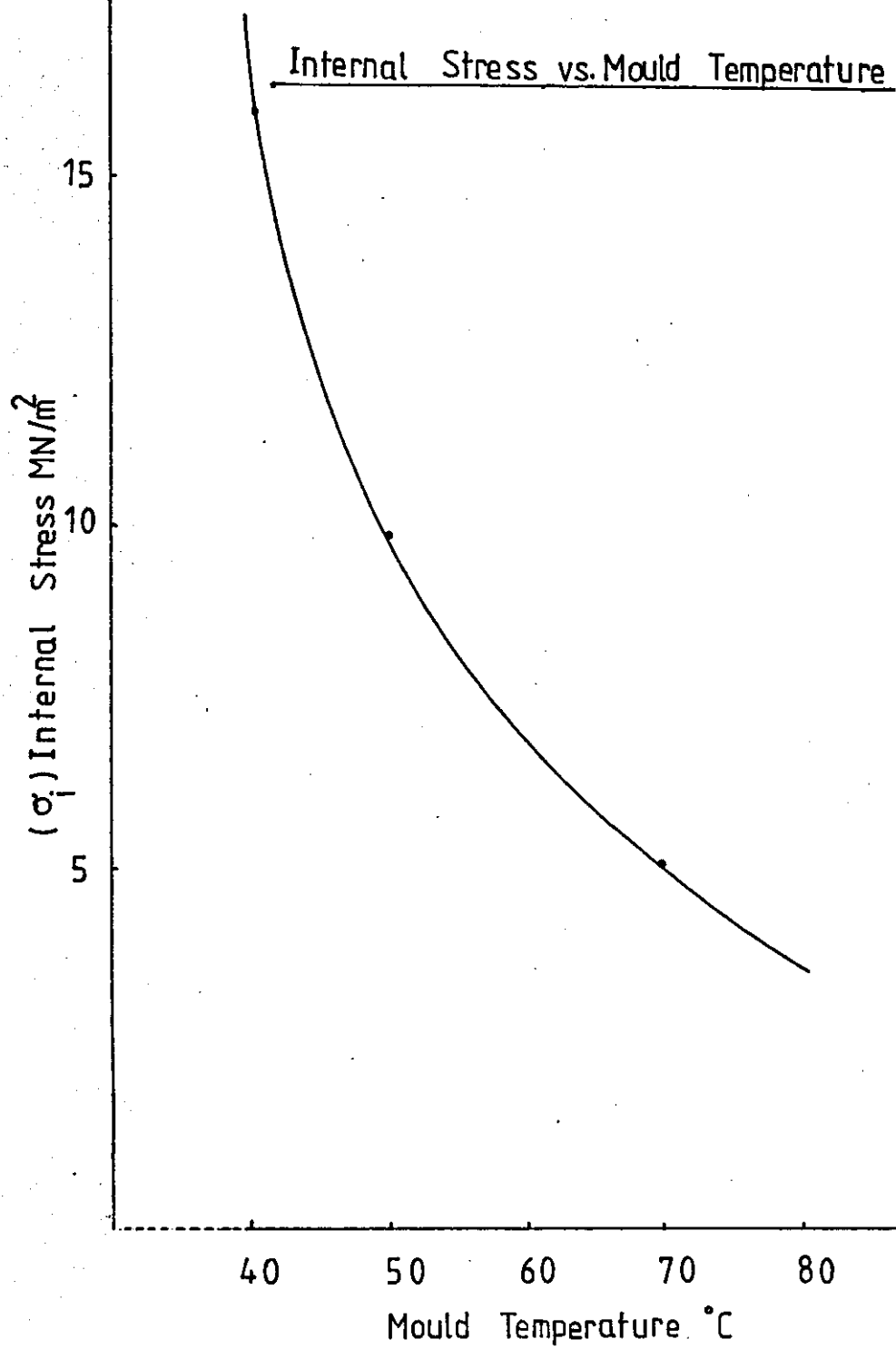
Variable:

Injection time 6.00, 4.00, 3.00, 1.50, 0.90 and 0.60 sec.

Constants:

Mould temperature	40°C
Melt temperature	171°C
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm

FIG. (3-11)



3.11.

INTERNAL STRESS VS MOULD TEMPERATURE

Internal stresses were measured by the stress relaxation method. Specimens were prepared from location (3), Fig. (2.8).

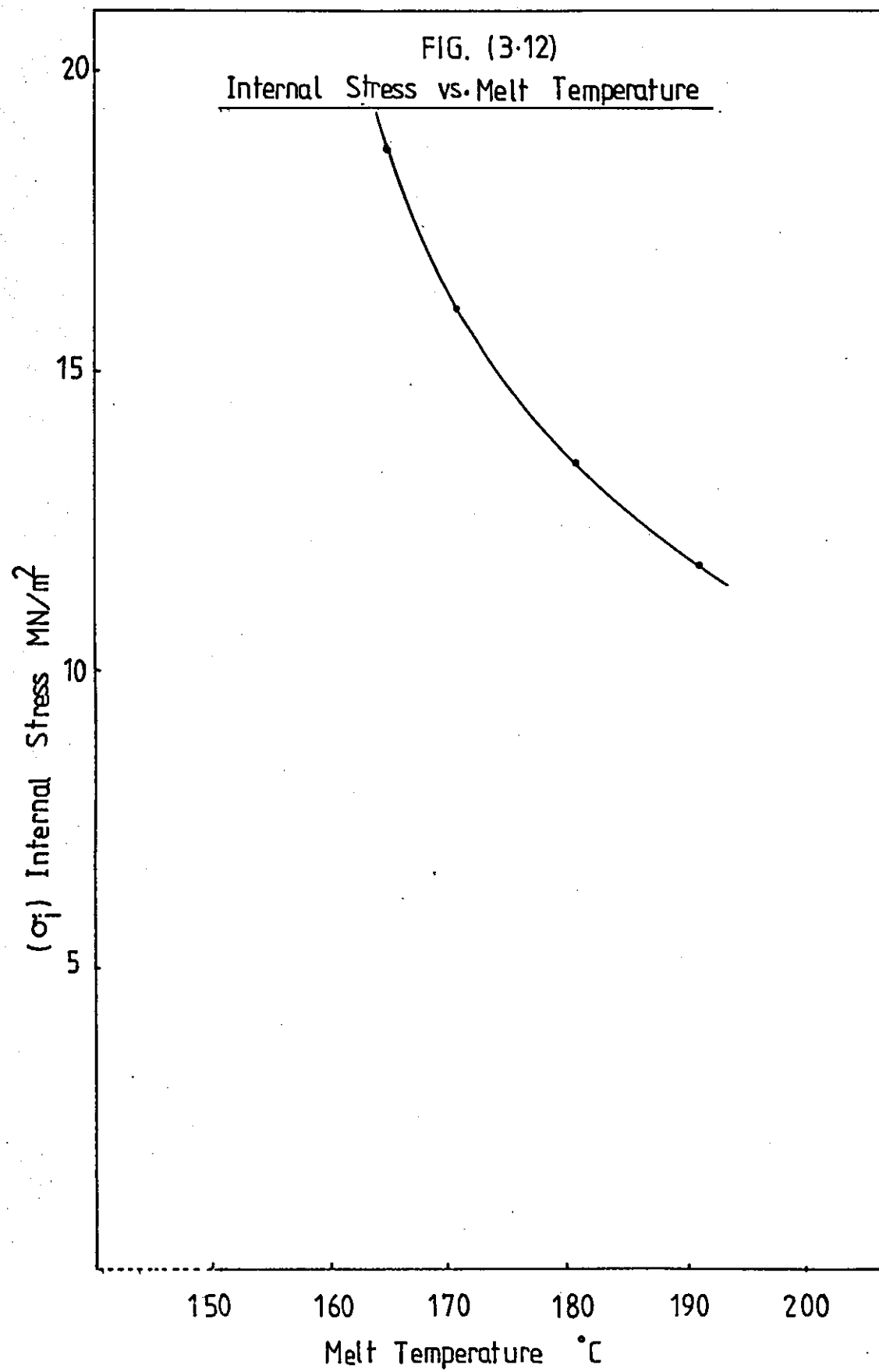
Moulding Conditions:

Variable:

Mould temperature 40, 50, and 70°C.

Constants:

Melt temperature	171°C
Injection time	6.00 sec
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm



Internal stress were measured by the stress relaxation method. Specimens were prepared from location. No. (3), Fig. (2.8) .

Moulding Conditions:

Variable:

Melt temperature 165, 171, 181 and 191°C.

Constants:

Mould temperature	40°C
Injection time	6.00 sec
Injection pressure	1000 psi (6.897 MN/m ²)
Hold on time	10 sec
Cooling time	25 sec
Cavity thickness	3 mm

DISCUSSION OF RESULTS:4.1 Effects of injection moulding variables on the degree of orientation and formation of oriented skin.

It is observed in Fig. (3.1) (% shrinkage vs. injection time) that degree of orientation (as measured by % shrinkage), decreases with decreasing injection time. The decrease in degree of orientation is explained in terms of cooling effects of the hot melt inside the cavity, where during rapid injection, only a little heat is withdrawn from the melt and because of the internal friction as the melt layers slides on top of each other, melt temperature inside the cavity is at least maintained and probably increases, consequently relaxation of the polymer chains will occur.

In Fig. (3.2) (% shrinkage vs. mould temperature) it is observed that degree of orientation decreases with increasing mould temperature. This decrease is attributed to the slower rate of melt cooling inside the cavity due to smaller $\Delta T = T_{\text{melt}} - T_{\text{mould}}$, and allowing greater chance for the polymer chains to relax while melt solidification takes place inside the mould cavity. Whereas at lower mould temperature the melt in the cavity cools and solidifies at a faster rate thus relaxation of polymer chains is partially hindered.

Increase of melt temperature would result in increasing melt relaxation further as observed in Fig. (3.3) (% shrinkage vs. melt temperature), thus decreasing degree of orientation due to thinner skin formation as will be discussed later.

Influence of processing conditions namely, injection time, mould temperature and melt temperature on the degree of orientation in injection moulding has been dealt with by several workers. Menges and Wubken (19) investigated the state of orientation in injection moulded polystyrene, their heat treatment of thin sectioned microtomes revealed that maximum orientation was at the surface layer (skin) and diminished towards the centre of the moulding. Because the temperature of the mould is far below that of the plastic melt, the outer molecular layer solidifies when contacting the mould and the temperature gradient between the mould wall and the inside of the plastic melt stream is the cause of a high shear speed gradient and of orientation effects at the mould wall. (32).

Knappe and Woebcken (32) had drawn attention to the state of orientation of injection moulded articles, Knappe et al carried out similar work on polystyrene and their results also indicated that maximum orientation occurred at the surface layer (skin). The degree of orientation in injection moulded polystyrene varied similarly to previous observations carried out in this work.

In interpreting the influence of injection moulding variables (injection time, mould temperature and melt temperature) on the degree of orientation, the concept of formation of "oriented skin" should be accounted for. In the literature the flow phenomena occurring during the filling phase of the mould had been fully investigated and explained by Menges and Wubken (19). The mechanism of formation of oriented skin in injection moulding had been demonstrated in Figs. (1.6, 1.7.).

Structural investigations carried out in the past (33 - 38) on injection moulded specimens from semi-crystalline polymers such as polypropylene (34,35) and polyacetal (35, 36) also revealed that mouldings possessed a highly oriented skin, a non-oriented core and one or more additional layers separating the skin from the core. However, the work carried out in this research was not aimed at investigating the structural changes and morphology of the injection moulded PVC. Investigations in this respect were confined to correlate processing variables and the formation of the oriented skin and the way it contributed to influence the degree of orientation.

The influence of the processing variables (injection time, mould temperature and melt temperature) on the thickness of oriented skin are demonstrated by Figs. (3.4, 3.5 and 3.6) respectively.

In Fig. (3.4.) (skin thickness vs. injection time) it appears that skin thickness decreased sharply with shorter injection time. It is believed that the high shear within the melt layers beneath the skin resulted in an increase in the melt temperature and a remelting of part of the skin formed initially in the filling phase of the mould cavity.

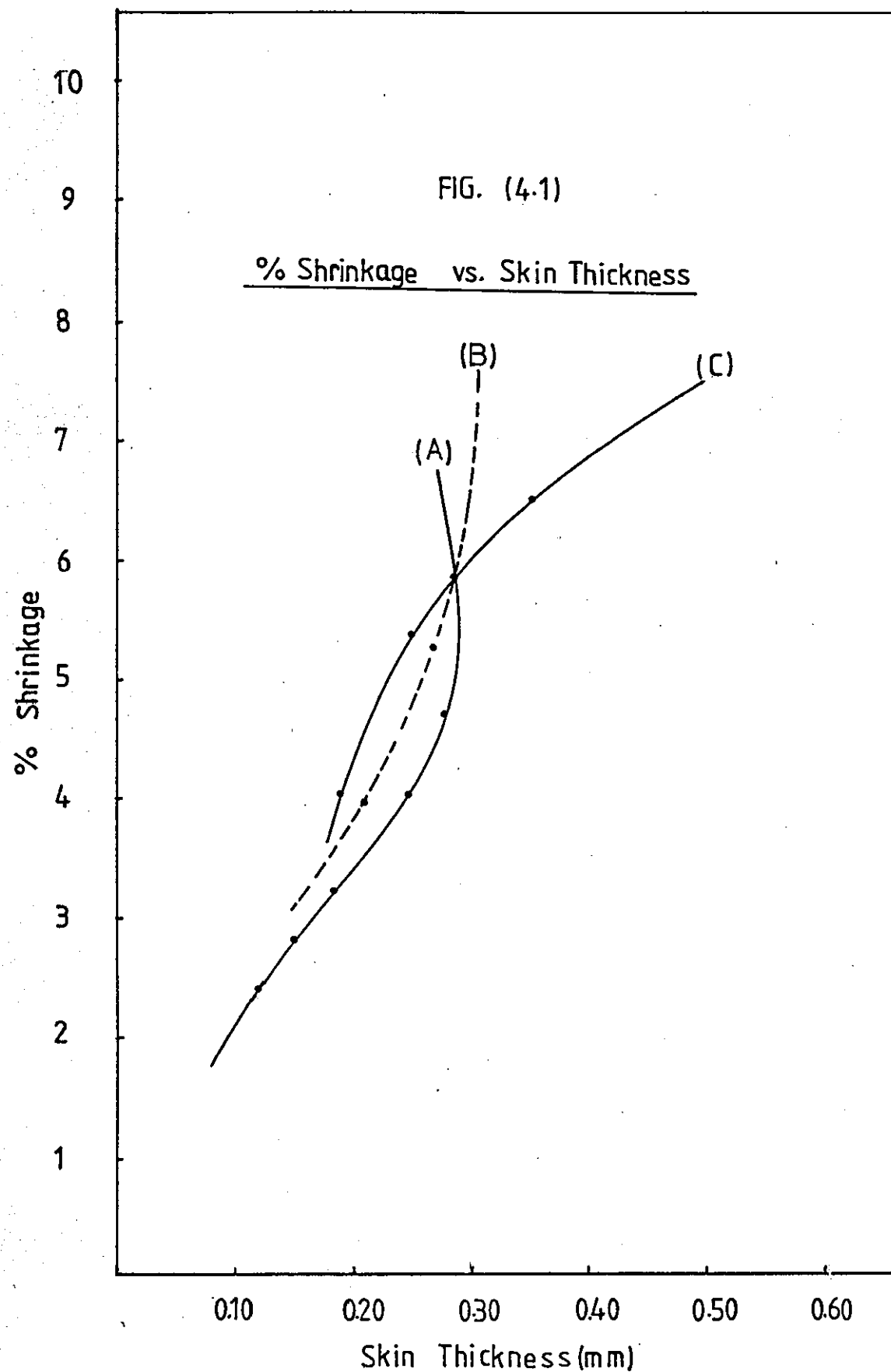
In Fig. (3.5) (skin thickness vs. mould temperature) it is observed that skin thickness also decreases with increasing mould temperature, because, cooler mould walls freezes a thicker layer of the polymer melt as it comes into contact with and hinders or slows down any possible relaxation taking place, hence the skin formation is facilitated. Increase of mould temperature will slow down the freezing of skin and thus enhance relaxation of the melt and results in less skin formation.

In Fig. (3.6) (skin thickness vs. melt temperature), the drop in skin thickness with melt temperature is steeper than Fig(3.5) The increase in melt temperature produced a hotter melt in the mould cavity hence slowing down skin formation due to the slower freezing as the melt fills in the cavity towards the end of the cycle.

The observed relations between processing variables previously mentioned and degree of orientation on one hand and skin thickness on the other, suggest that degree of orientation is affected and interrelated to the thickness of oriented skin.

This interrelationship is demonstrated by Fig. (4.1.) (% shrinkage vs. skin thickness) where curves (A), (B), and (C) interpret the variation of shrinkage with skin thickness at varying injection time, mould temperature and melt temperature respectively.

Similar work in this respect was attempted by Gilbert M. et al (38) but was only confined to variation of skin thickness and % shrinkage as a function of mould temperature . It confirmed their interdependency and suggested that orientation in the mouldings was largely confined to the skin.



When a polymer is melted, the molecules are kept apart to the extent that there no longer is an ordered structure. Large molecular segments vibrate and rotate to give a disordered structure. When the plastic is cooled a point is reached where the forces of attraction are strong enough to prevent free movement and lock part of the polymer into an ordered or latticed position.

Crystal growth requires time and high mobility of the chains so that the molecular segments can get close together therefore the slower the cooling (in this work short injection time or high mould temperature) particularly as the polymer passes through its melting temperature, the higher the degree of crystallinity (3).

In Fig. (3.7) (density vs. injection time) it is observed that density of the bulk (skin and core) is lowest at the slowest injection time (6.00 sec) and highest at the shortest (0.60 sec).

The increase in density with reduced injection time is ascribed to the rate of cooling of the melt inside the cavity. As the polymer melt begins to cool the molecular chains approaches each other closely and begins to form into crystallites (3).

If cooling is slow as the case with shorter injection time where little heat is dissipated from the melt, the number of chains that have time to organise themselves into the crystal forms is large, therefore the degree of crystallinity rises giving more compact structure and leading to increased density.

It is possible to express changes in density in terms of volumetric mould shrinkage, where crystalline structure has the molecules closer together than the amorphous structure, the decrease in volume is indicative of the onset and amount of crystallisation. Such observations had been reported for polypropylene volumetric mould shrinkage (3).

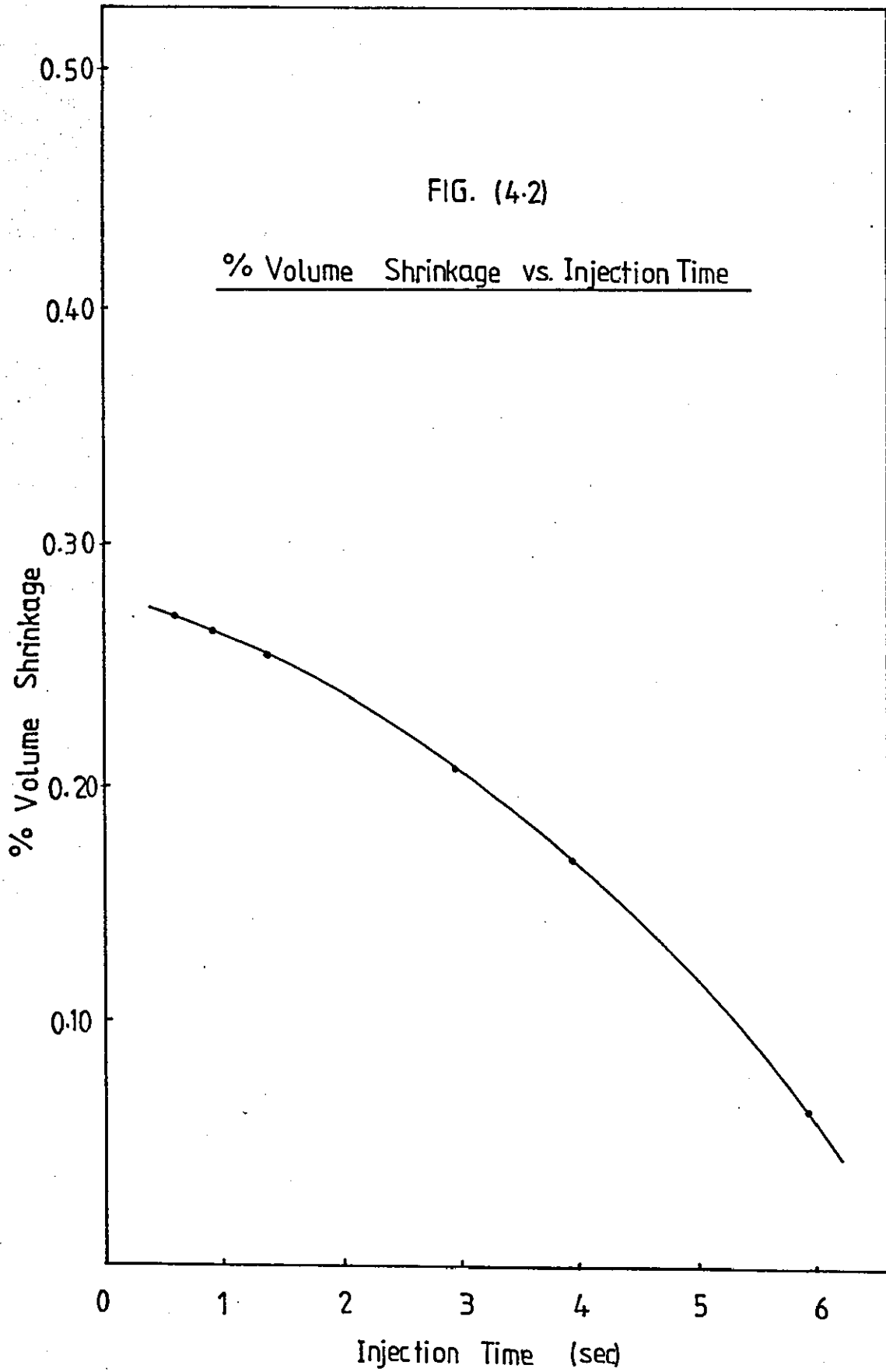
A relation between volumetric mould shrinkage and injection time was established Fig. (4.2) (% V vs. injection time) it is observed that % V is highest at shortest injection time (i.e. mould shrinkage is greater), which is attributed to better chain compaction and higher crystalline order.

The increase in density with increasing mould temperature is another case related to the slower rate of cooling of the polymer melt Fig. (3.8) (density vs. mould temperature).

At low mould temperature the cooling rate is relatively fast and crystallisation is somewhat retarded as melt solidification will minimise the opportunity for the polymer chains to organise into the crystal form.

FIG. (4.2)

% Volume Shrinkage vs. Injection Time



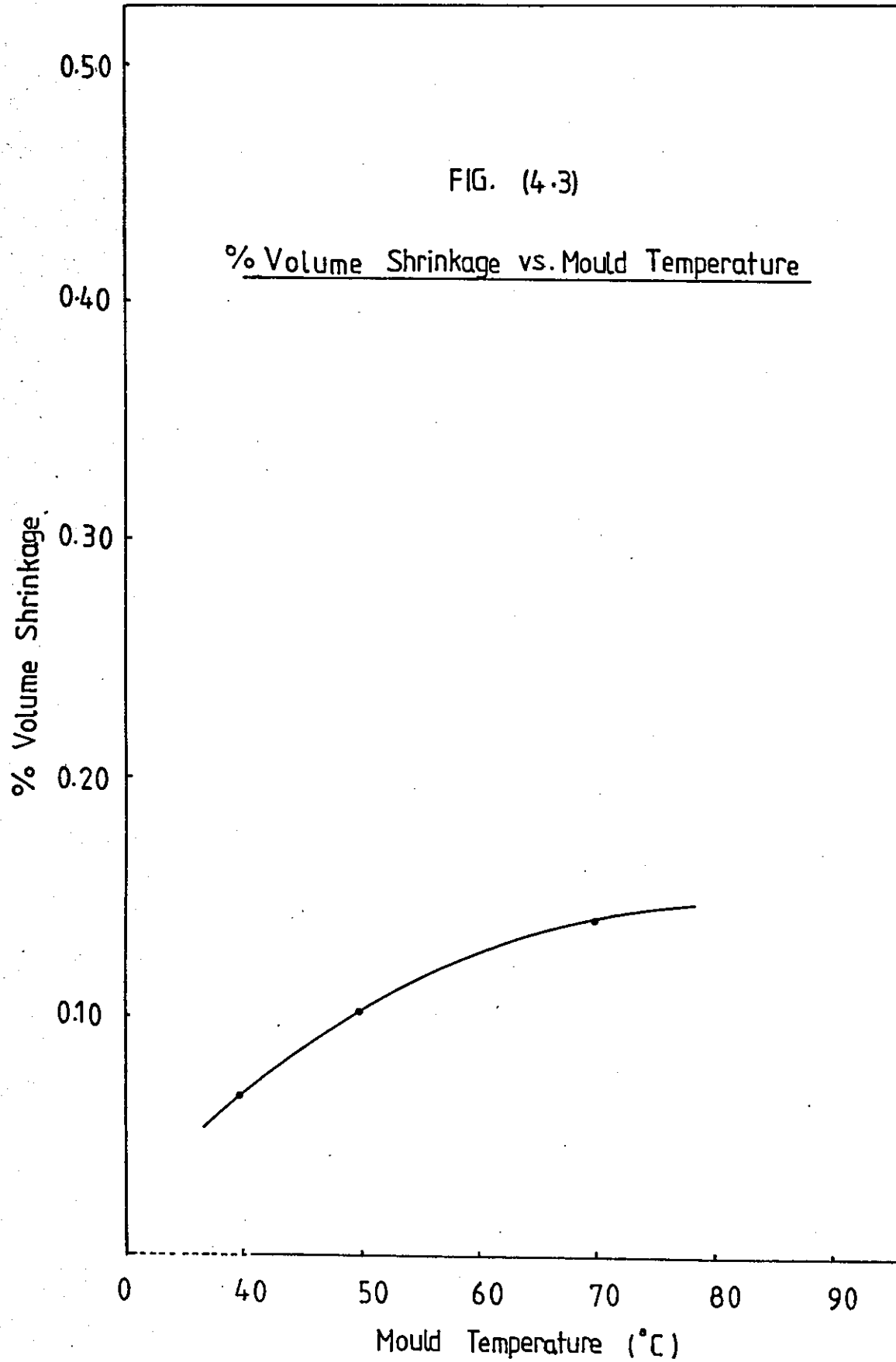
At higher mould temperature there is more molecular and segmental motion of the chains. This condition increases the probability of bringing the molecules close enough together to be frozen into a crystalline state (3,15). A similar relationship was established between volumetric mould shrinkage and mould temperature Fig. (4.3) $\rho_{136}(\% V \text{ vs. mould temperature})$. It is observed that $\% V$ increases with mould temperature, which is attributed to improved melt chain compaction and favoured crystallisation. The latter observations are in agreement with density measurements by the flotation method.

In contrast to the response of density changes to injection time and mould temperature, density varied with melt temperature rather anomalously. It is observed in Fig. (3.9) (density vs. melt temperature) that density decreased with increasing melt temperature. The high shear forces on the melt at higher melt viscosity (low melt temperature) might have been the cause of initiating further crystallisation within the polymer lattices which resulted in higher density. A second effect which might have contributed to increased density at lower melt temperature is that of thicker skin formation at lower melt temperatures Fig. (4.4) (Bulk and core density vs. skin thickness). At low melt temperature skin thickness exhibited the highest value which decreased with raising melt temperature.

The skin in this case acted as a shell which insulated the core material from the cold mould surface, thus maintained

FIG. (4.3)

% Volume Shrinkage vs. Mould Temperature

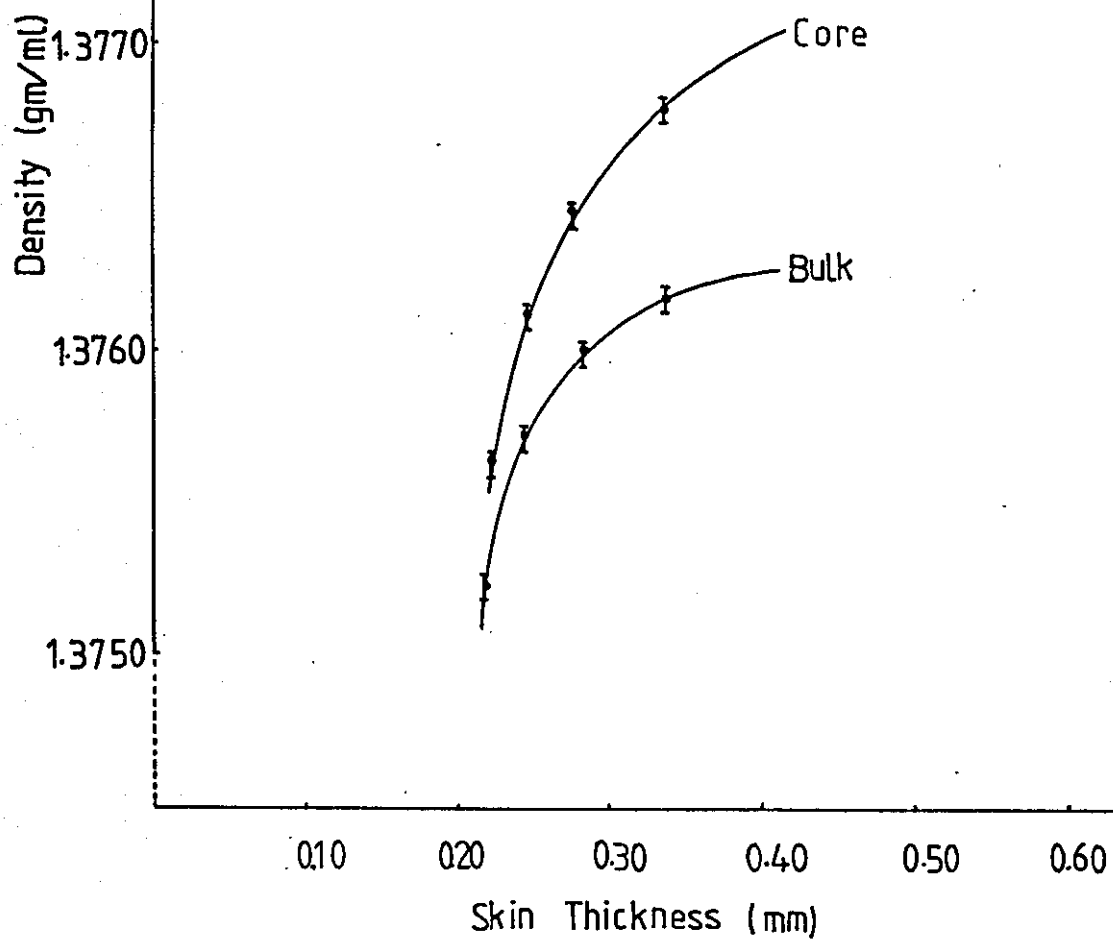


a slower rate of cooling and allowed sufficient time for the core material to attain a higher degree of crystallinity (higher density) which inevitably increased the bulk density.

As the variation in density with melt temperature is controlled by the factors previously mentioned (high shear forces and thicker skin formation) therefore it was not possible to apply the concept of volumetric mould shrinkage to the latter condition as it would not interpret the anomalous response of density relative to melt temperature (in this case decrease of density with increasing melt temperature).

FIG. (4.4)

Density vs. Skin Thickness As
A function Of Melt Temperature



4.3 Effects of injection moulding variables on the internal stress level (σ_i)

In order to account for the effects of processing variables namely, injection time, mould temperature and melt temperature on the internal stress level (σ_i) it was essential to establish an intimate relationship between the actual causes of these residual stresses and the processing variables within the scope of the current investigations. The magnitude of internal stress in injection moulded objects seems to be the result of complicated interplay of a number of factors among which injection time, mould temperature and melt temperature appear to occupy an important role.

Stress associated with non-uniform crystallisation is very large in processed crystalline and semi-crystalline polymers e.g. (injection moulded polystyrene, polypropylene and PVC). As the test piece is rapidly cooled, the rate of solidification (crystallisation) will be inhibited more in the rapidly cooled outer zones (skin) than in the interior (core) of the test piece which will be relatively crystalline and have a higher density. The greater contraction in the interior of the test piece causes compressive stress in the outer zones (21,24,25).

The first result to be noted is that (σ_i) level decreased with reducing injection time Fig.(3:10). The crystallisation takes place when the temperature in different parts of the mould passes a

critical value T_g (glass transition temperature) which is attained at different times. With long injection time i.e. slower cavity filling, crystallisation is slow, in contrary to that, short injection time i.e. faster cavity filling, crystallisation can take place simultaneously and minimises temperature gradients.

(σ_i) level decreased with increasing mould and melt temperature Figs(3.11,3.12). This decrease is caused by slowing down the process of cooling i.e. having homogeneous crystallisation of the melt thus minimising temperature gradients within the moulding as it cools and crystallises so as to induce an annealing effect on the stretched polymer chains molecules under stress, (pressure exerted on the mould and melt).

The different rates of crystallisation for the skin and core of the mouldings were revealed by the density measurements which confirmed higher density in the core than the skin. Such observations were reported by Knappe for investigations carried out on polystyrene (21).

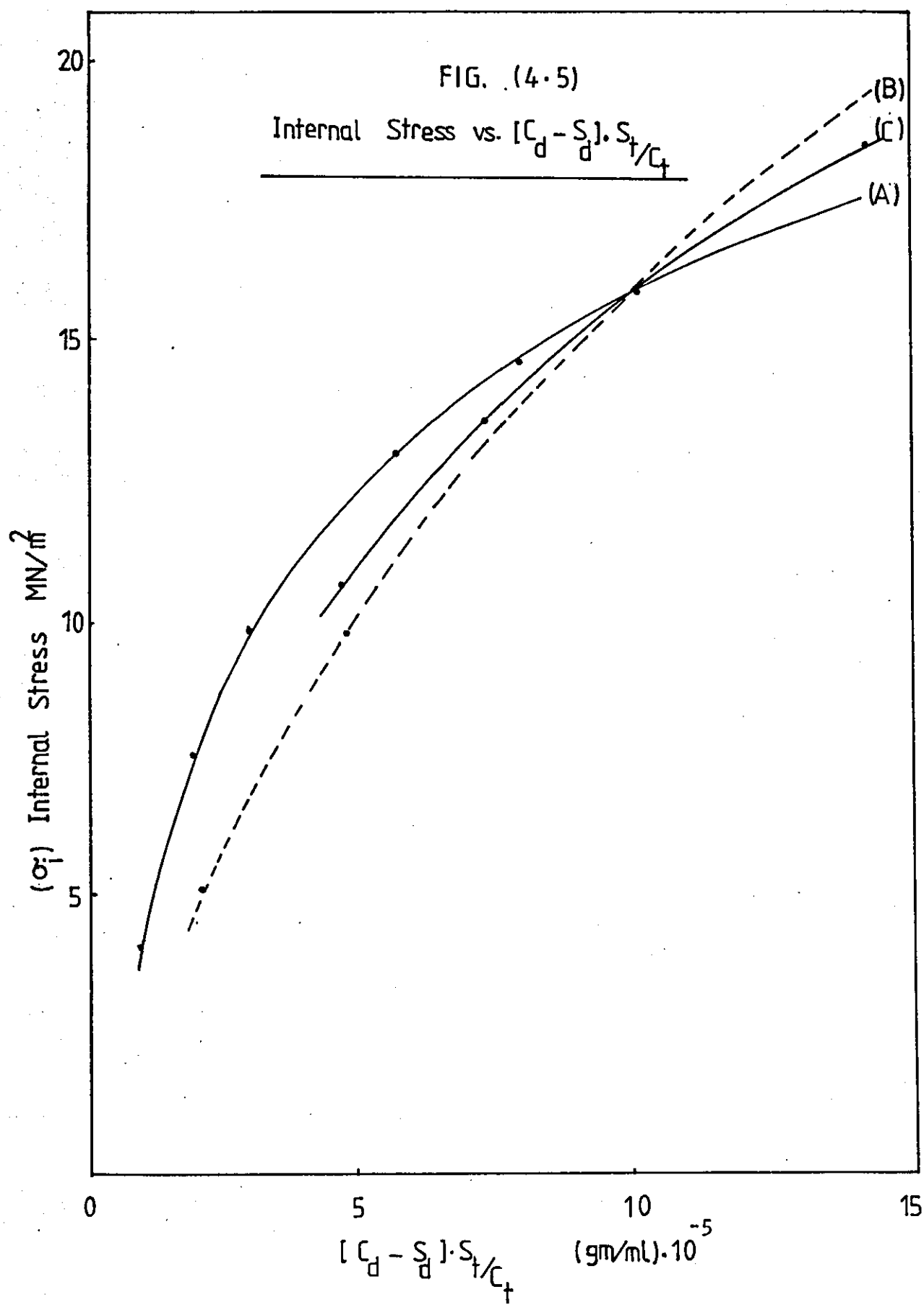
It was possible to substantiate the current investigations by establishment of a relationship between (σ_i) and previous observations regarding density differences. Fig. (4.5.) $(\sigma_i \text{ vs. } (C_d - S_d) \times S_{th}/C_{th})$ shows the relationship between the (σ_i) and density differences between the core and the skin multiplied by the ratio of skin thickness to that of the

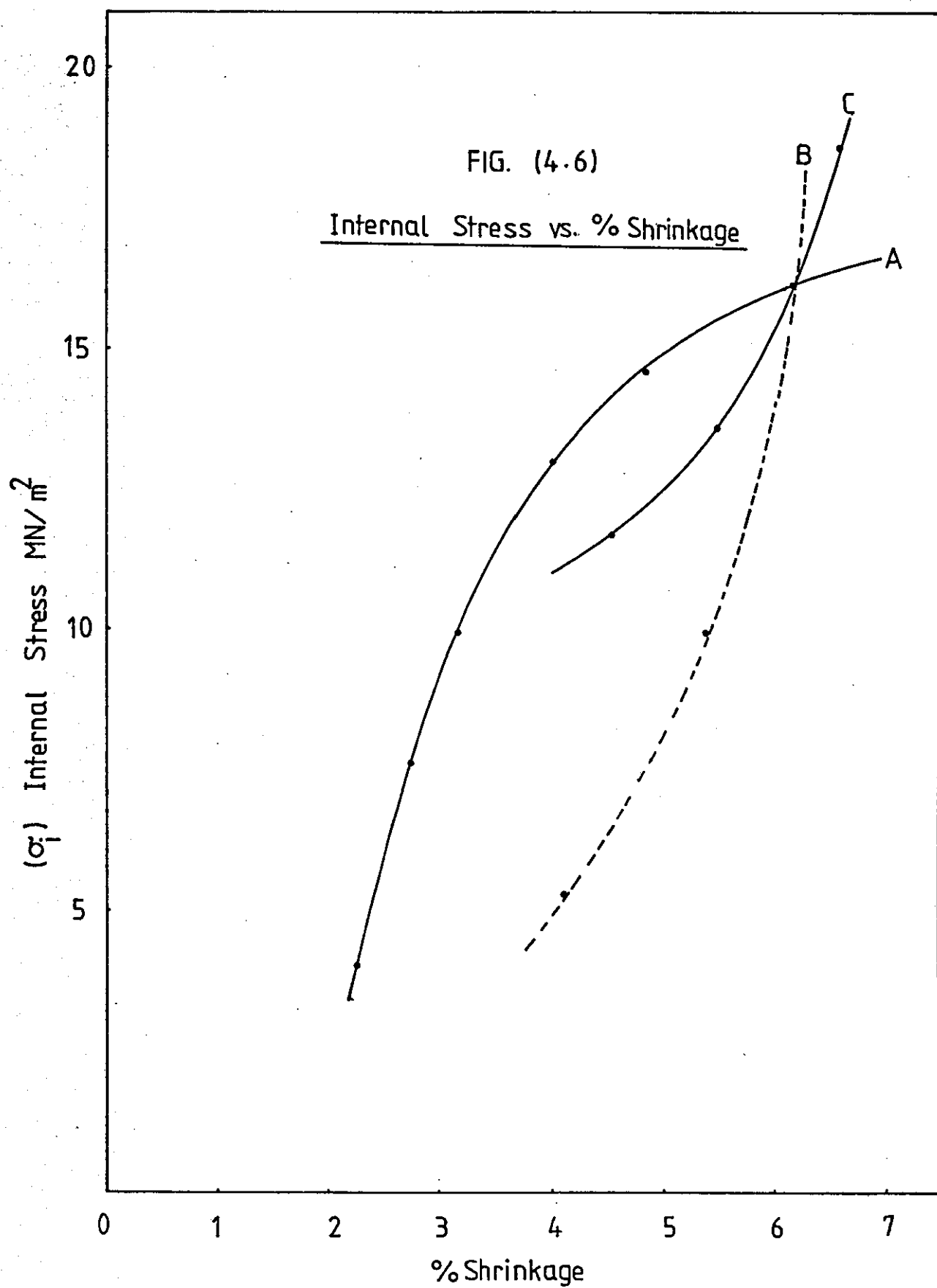
core so that to account for the whole volume of the specimen.

It is observed that (σ_i) increases as the term $(C_d - S_d) \times S_{th}/C_{th}$ increases at varying injection time, mould temperature and melt temperature, curves (A), (B), and (C) respectively.

On the molecular level there seems to be a relationship between (σ_i) and the molecular orientation. Such observations were reported by Gleng W. and Peterlin A. (39). Their I. R. studies on stretched high density polyethylene (HDPE) had shown that shrinkage on annealing is caused by relaxation of the tie molecules and a linear relationship between σ_i and % shrinkage (degree of orientation) was established.

A similar attempt was made in respect with the current investigations although I. R. studies were beyond the scope of this work, it was possible to establish a relationship between (σ_i) and the degree of orientation (% shrinkage). Fig. (4.6) $(\sigma_i$ vs. % shrinkage, i.e. degree of orientation) demonstrates the variation of (σ_i) with % shrinkage at varying injection time, mould temperature and melt temperature curves (A), (B), and (C) respectively. Although a simple proportionality does not exist, it may suggest an analogous mechanism of (σ_i) - % shrinkage relationship to that observed by (Gleng W. et al).





4.4 Effects of injection moulding variables on tensile yield stress

Tables below demonstrate the tensile yield values at different injection time, mould temperature and melt temperature.

I.	<u>Injection Time (sec)</u>	<u>Tensile Yield Stress MN/m²</u>
	6.00	56.018
	4.00	56.025
	3.00	56.0492
	1.50	56.216
	0.90	56.135
	0.60	55.992

II.	<u>Mould Temperature °C</u>	<u>σ_y MN/m²</u>
	40	55.875
	50	56.102
	70	56.225

III.	<u>Melt Temperature °C</u>	<u>σ_y MN/m²</u>
	165	55.969
	171	56.276
	181	56.072
	191	56.357

The above results indicated that there is no significant variation in the tensile yield stress. Taking into account that the injection moulded rigid PVC specimens were a composite of a skin and a core of which the crystalline natures and structures are different. It seemed that simple tensile test failed to distinguish between moulding conditions and the bulk properties were dominated and governed by the core rather than the skin.

CHAPTER V

Conclusions and recommendations for further work

5.1 Conclusions:-

Experimental work has reaffirmed the dependence of some properties associated with the injection moulding of unplasticised PVC (molecular orientation, formation of oriented skin, changes in density and overall internal stress level) on processing variables (injection time, mould temperature and melt temperature).

The following practical conclusions can be drawn:-

1. Degree of orientation, as measured by % shrinkage increased with increasing injection time (lower injection rate) and decreased with increasing both mould and melt temperature.
2. Thickness of the oriented skin increased with increasing injection time and decreased with increasing mould and melt temperature.
3. Degree of orientation and skin thickness appeared to be interrelated, as orientation increased with skin thickness at decreasing injection time and increasing mould and melt temperature.
4. Bulk density (skin and core), skin density and core density decreased with increasing injection time and increased with increasing mould and melt temperature.

In all cases core density was higher than that of the skin.

5. Overall internal stress level (σ_i) was associated with differences between core density and skin density, it increased as the term $(C_d - S_d) \times S_{th}/C_{th}$ increased (i.e. as density differences became greater).
6. Overall internal stress level (σ_i) decreased with reducing injection time and increasing mould and melt temperature.
7. Overall internal stress level and degree of orientation seem to be interrelated as (σ_i) decreased with decreasing degree of orientation (i.e. lower % shrinkage).
8. Tensile yield stress appeared to be dominated by the core morphology rather than by presence of skin.

5.2. Recommendations for further work:-

The field of PVC research work is extremely wide and there seems to be a vast area in the processing/characterisation field that may be investigated. In particular it is suggested that further work be undertaken in the following areas:-

1. The influence of mould geometry (cavity thickness and gate design) on the degree of orientation and residual stresses.
2. Investigate structural changes and morphology of the injection moulded rigid PVC and their effects on mechanical and physical properties.
 - a. investigate the structure of the skin of the moulding (e.g. by optical methods) and its influence on the degree of orientation.
 - b. the structure of the core and its influence on the mechanical strength.
3. Investigate and analyse the residual stresses in injection moulded PVC on the molecular level and correlate observations to anisotropy in different layers of the specimen.

4. In this work the observed relationships have been explained almost exclusively in terms of crystallinity effects, however, it would be worthwhile considering these and other relationships on the basis of free volume within the mouldings as an alternative to crystallinity changes (45).

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APPENDIX

Tables (1 - 3) demonstrate the variation of
% shrinkage with processing variables.

TABLE 1

% shrinkage as a function of injection time

<u>Injection Time (sec)</u>	<u>% Shrinkage</u>
6.00	6.107
4.00	4.750
3.00	4.029
1.50	3.211
0.90	2.904
0.60	2.389

TABLE 2

% shrinkage as a function of mould temperature

<u>Mould Temperature °C</u>	<u>% Shrinkage</u>
40	6.107
50	5.400
70	4.105

TABLE 3

% shrinkage as a function of melt temperature

<u>Melt Temperature °C</u>	<u>% Shrinkage</u>
165	6.600
171	6.107
181	5.495
191	4.550

Tables (4 - 6) demonstrate the variation of skin thickness with the processing variables.

TABLE 4

Skin thickness as a function of injection time

<u>Injection Time (sec)</u>	<u>Skin Thickness (mm)</u>
6.00	0.275
4.00	0.260
3.00	0.235
1.50	0.155
0.90	0.120
0.60	0.100

TABLE 5

Skin thickness as a function of mould temperature

<u>Mould Temperature (°C)</u>	<u>Skin Thickness (mm)</u>
40	0.275
50	0.240
70	0.195

TABLE 6

Skin thickness as a function of melt temperature

<u>Melt Temperature ($^{\circ}\text{C}$)</u>	<u>Skin Thickness (mm)</u>
165	0.340
171	0.275
181	0.245
191	0.235

Tables (7 - 9) demonstrate the variation of bulk density, core density and skin density with the processing variables.

TABLE 7

Density as a function of injection time

<u>Injection Time</u> (sec)	<u>Bulk Density</u> (g/ml)	<u>Core Density</u> (g/ml)	<u>Skin Density</u> (g/ml)
6.00	1.3760	1.3765	1.3756
4.00	1.3775	1.3780	1.3772
3.00	1.3780	1.3783	1.3777
1.50	1.3786	1.3788	1.3783
0.90	1.3788	1.3790	1.3786
0.60	1.3789	1.3790	1.3787

TABLE 8

Density as a function of mould temperature

<u>Mould Temperature</u> (°C)	<u>Bulk Density</u> (g/ml)	<u>Core Density</u> (g/ml)	<u>Skin Density</u> (g/ml)
40	1.3760	1.3765	1.3756
50	1.3765	1.3767	1.3763
70	1.3770	1.3771	1.3768

TABLE 9

Density as a function of melt temperature

<u>Melt Temperature</u> (°C)	<u>Bulk Density</u> (g/ml)	<u>Core Density</u> (g/ml)	<u>Skin Density</u> (g/ml)
165	1.3761	1.3768	1.3758
171	1.37600	1.3765	1.3756
181	1.3768	1.3761	1.3753
191	1.3752	1.3756	1.3751

Tables (10 - 12) demonstrate the variation of internal compressive stress with the processing variables.

TABLE 10

Compressive stress as a function of injection time

<u>Injection Time (sec)</u>	<u>(σ_i) Internal Stress (MN/m²)</u>
6.00	- 16.096
4.00	- 14.785
3.00	- 12.900
1.50	- 9.900
0.90	- 7.668
0.60	- 4.177

(negative sign indicates compressive stresses)

TABLE 11

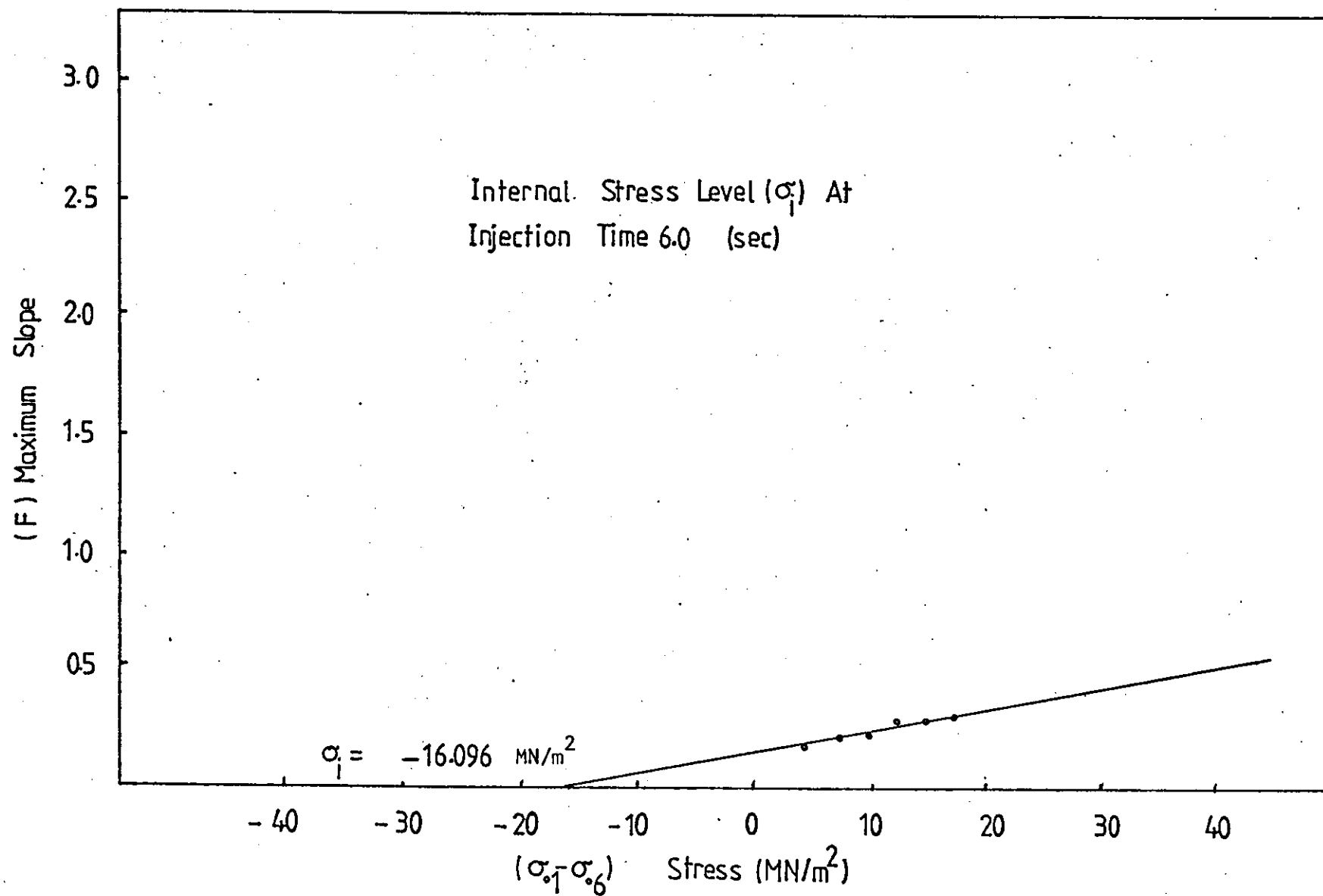
Compressive stress as a function of mould temperature

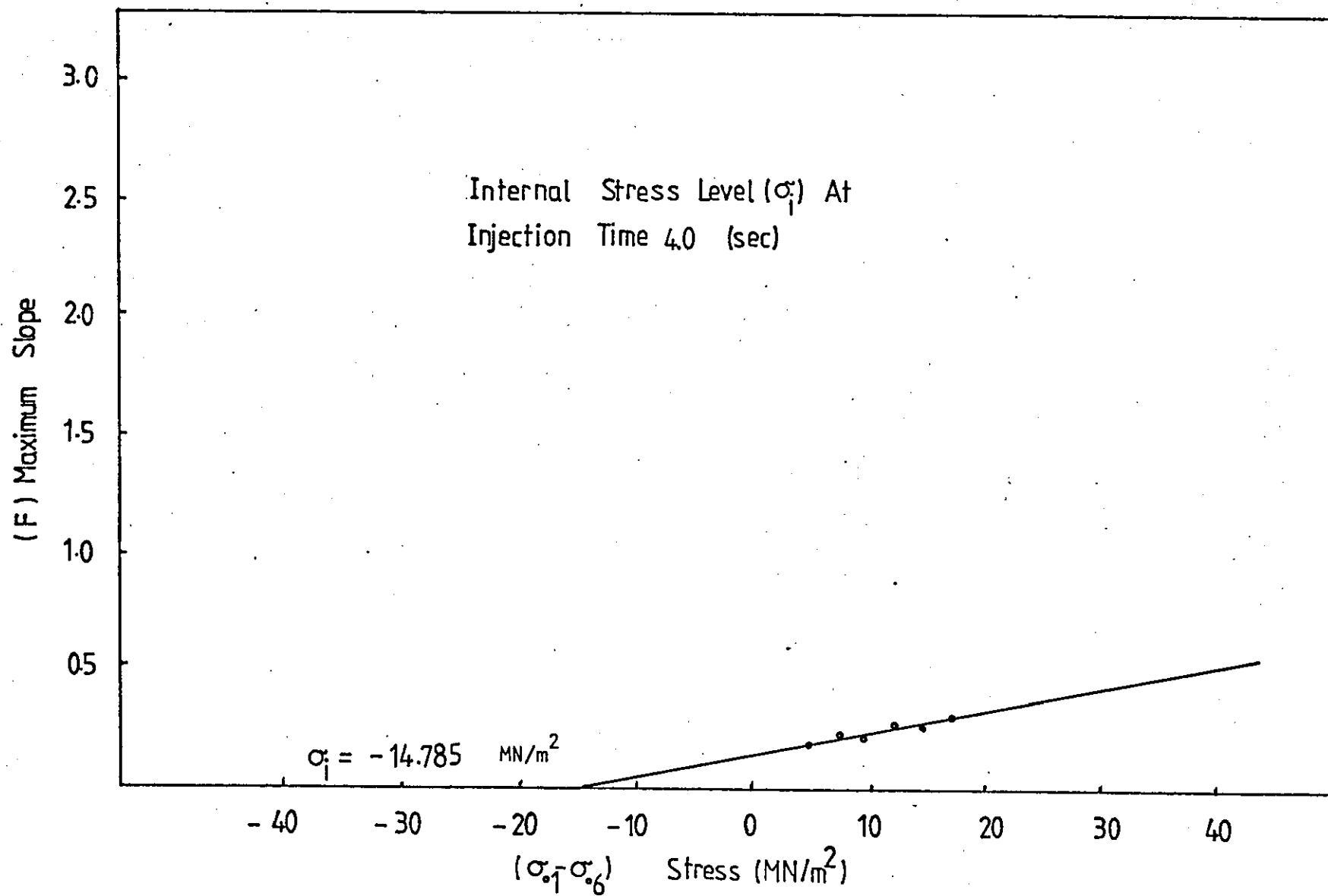
<u>Mould Temperature (°C)</u>	<u>(σ_i) Internal Stress (MN/m²)</u>
40	- 16.096
50	- 9.989
70	- 5.232

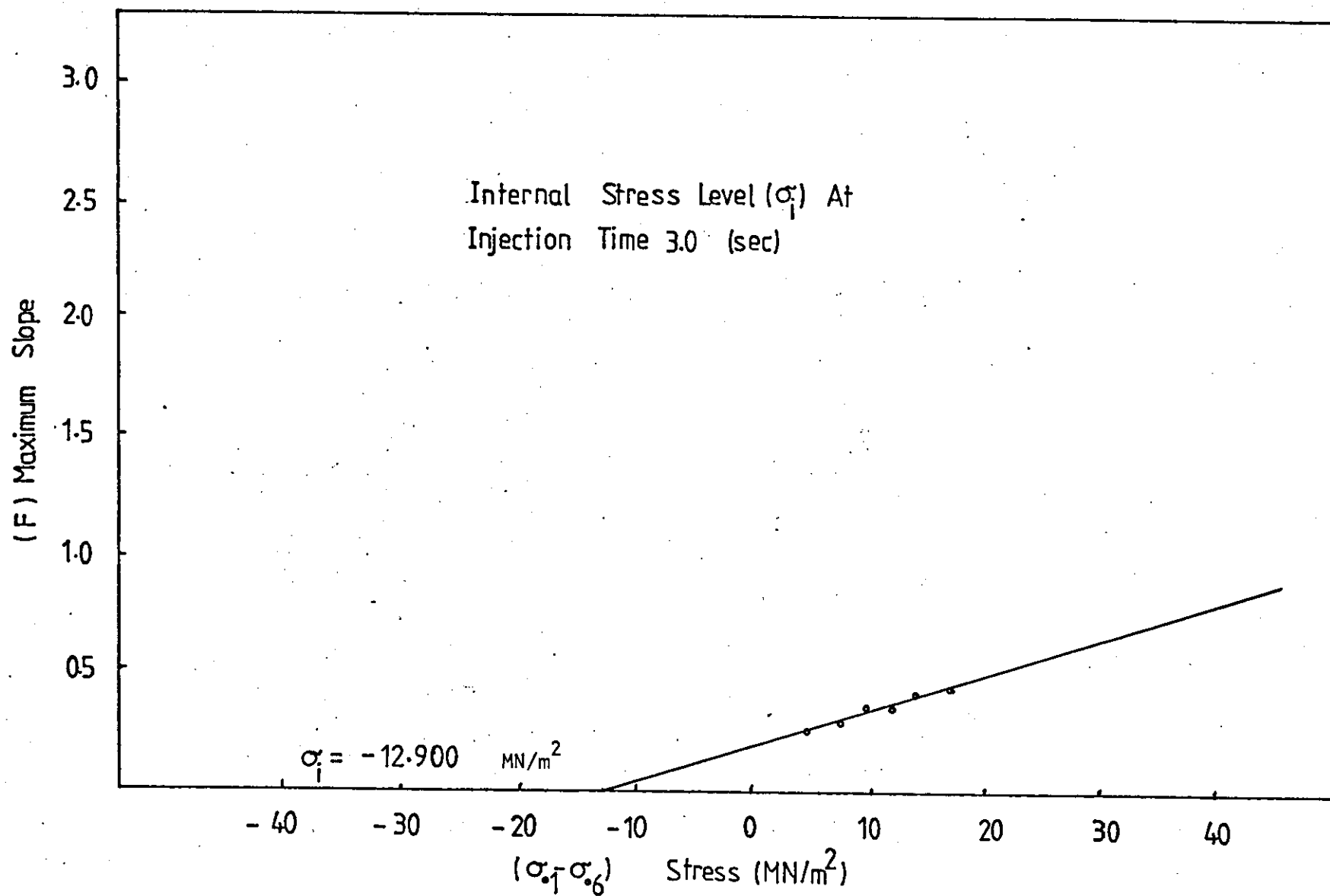
TABLE 12

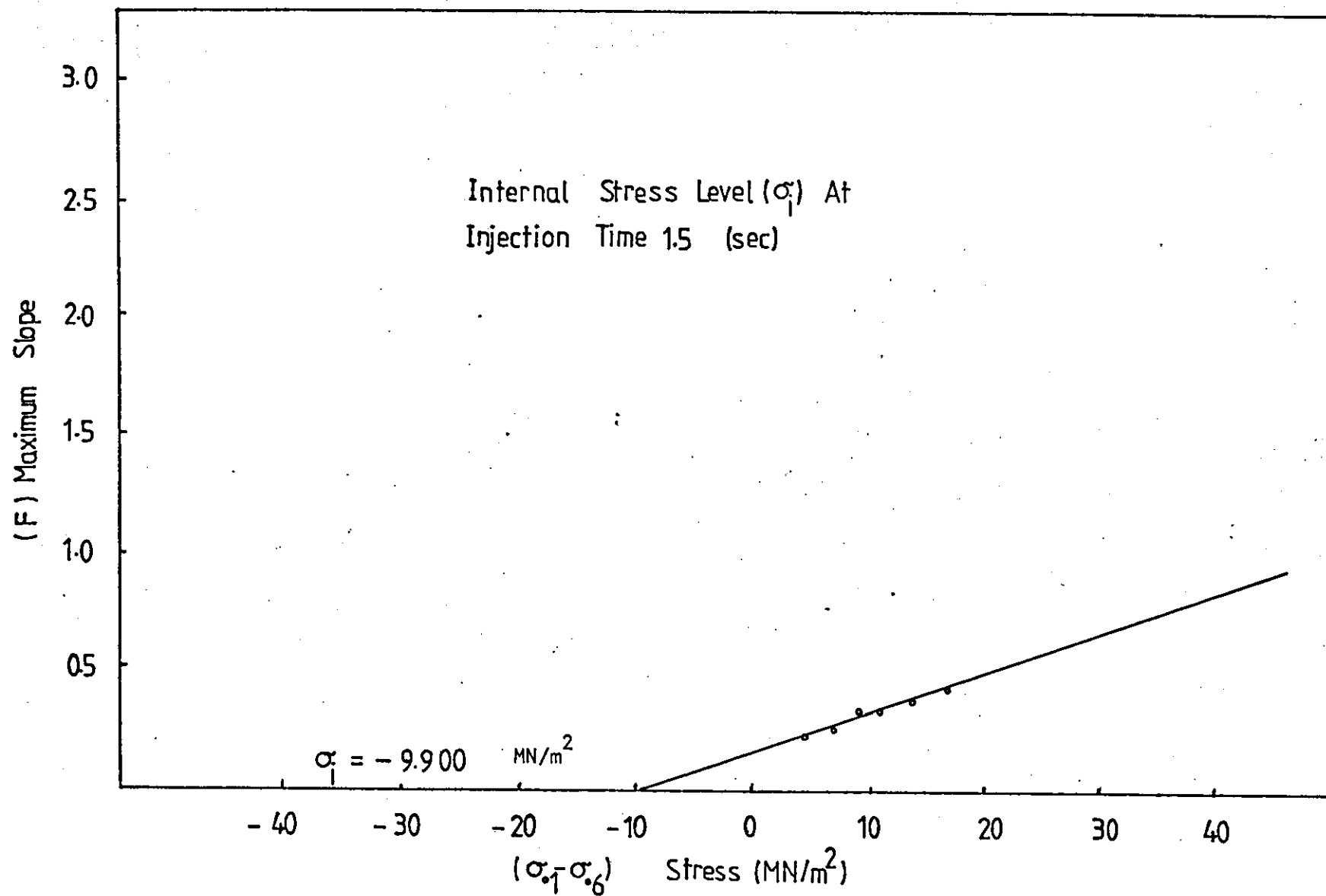
Compressive stress as a function of melt temperature

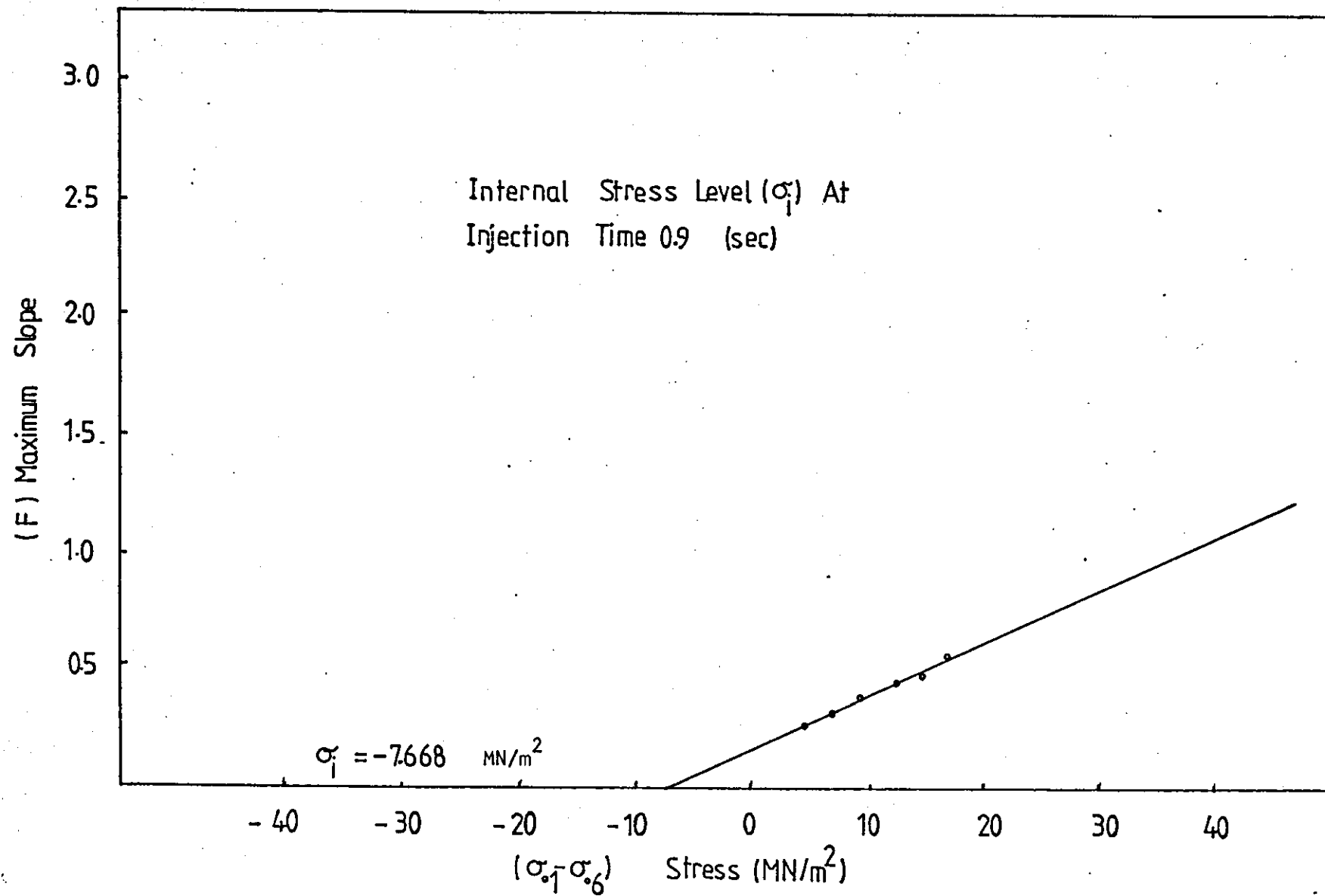
<u>Melt Temperature ($^{\circ}\text{C}$)</u>	<u>(σ_i) Internal Stress (MN/m^2)</u>
165	- 18.609
171	- 16.096
181	- 13.535
191	- 10.737

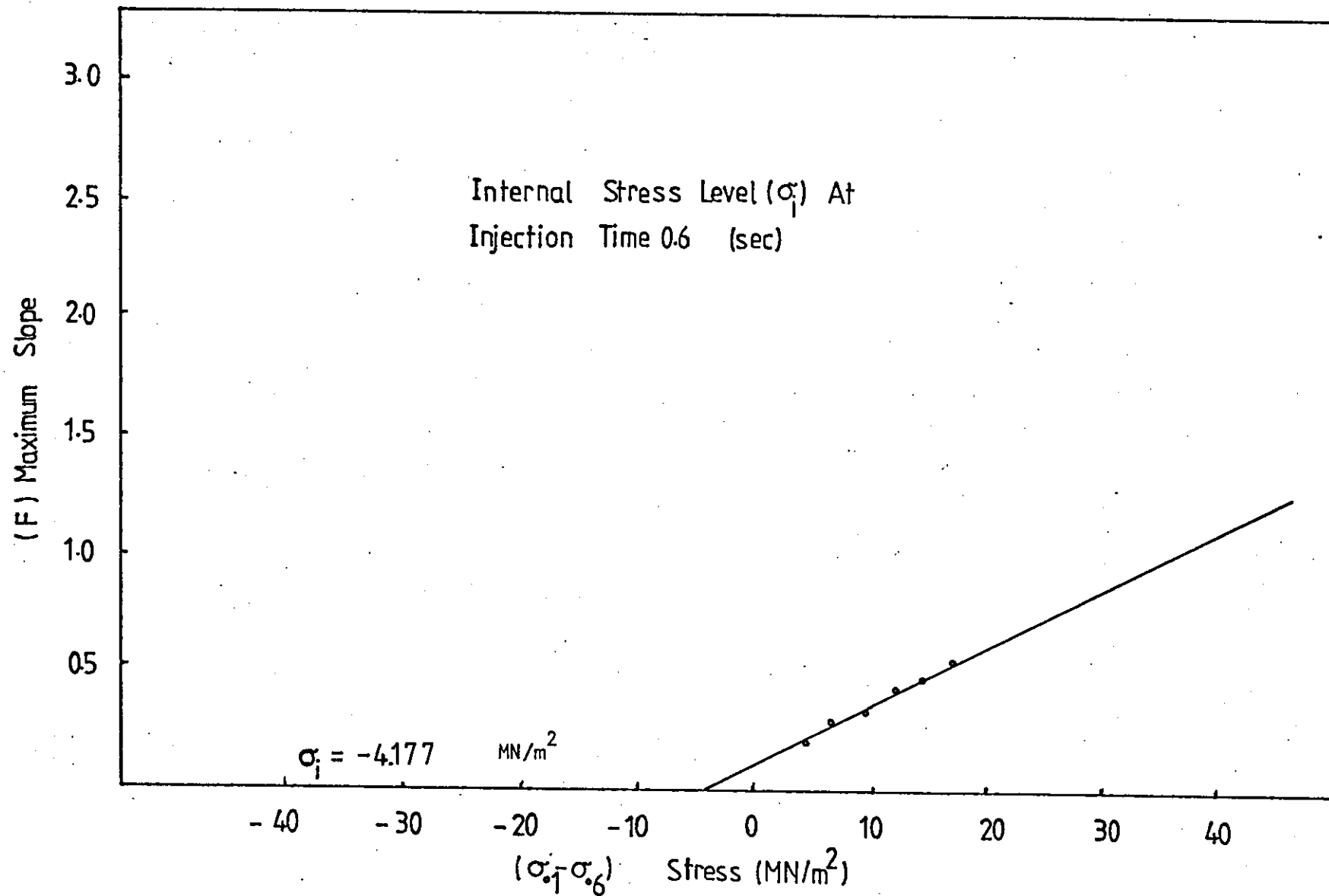


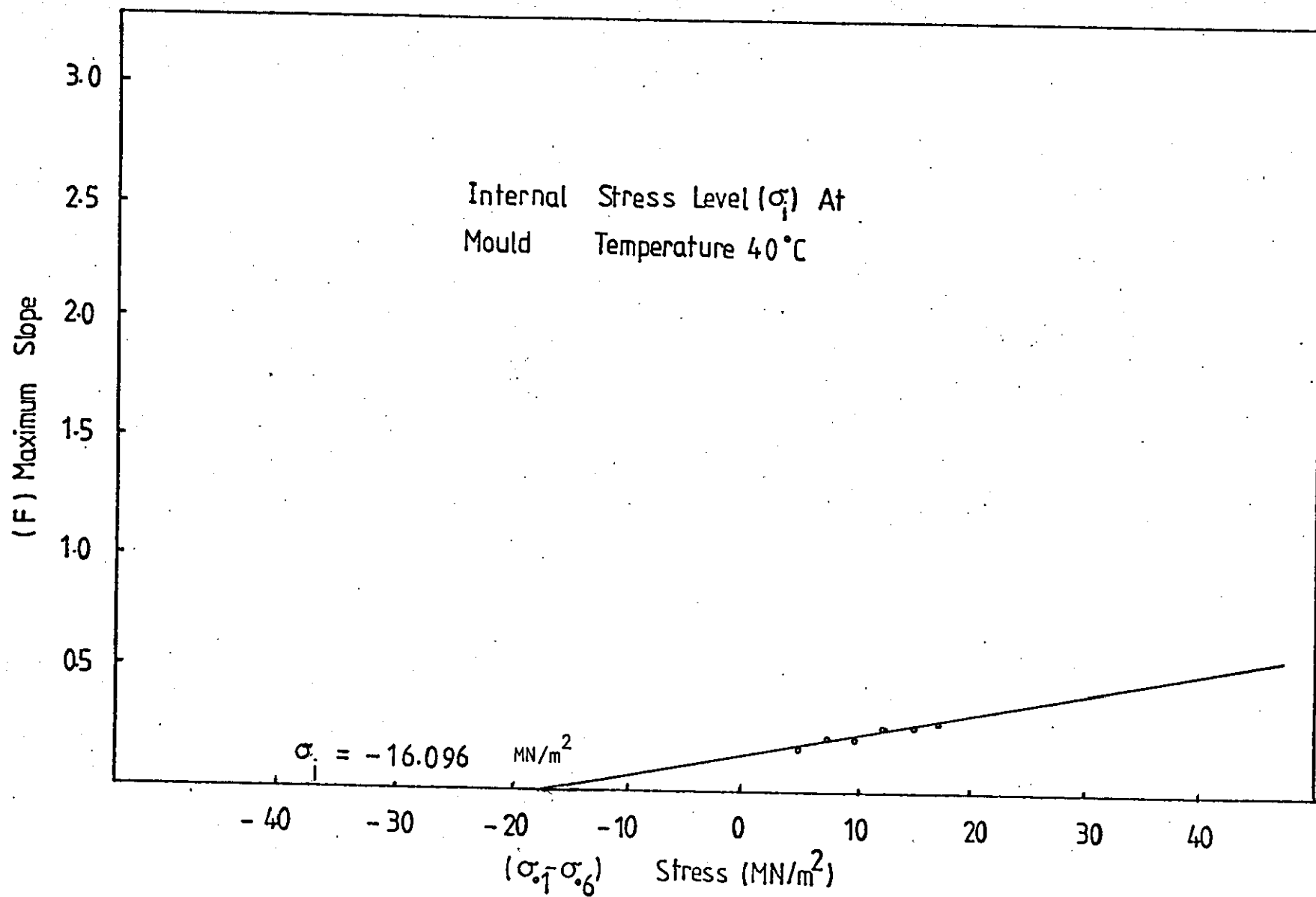


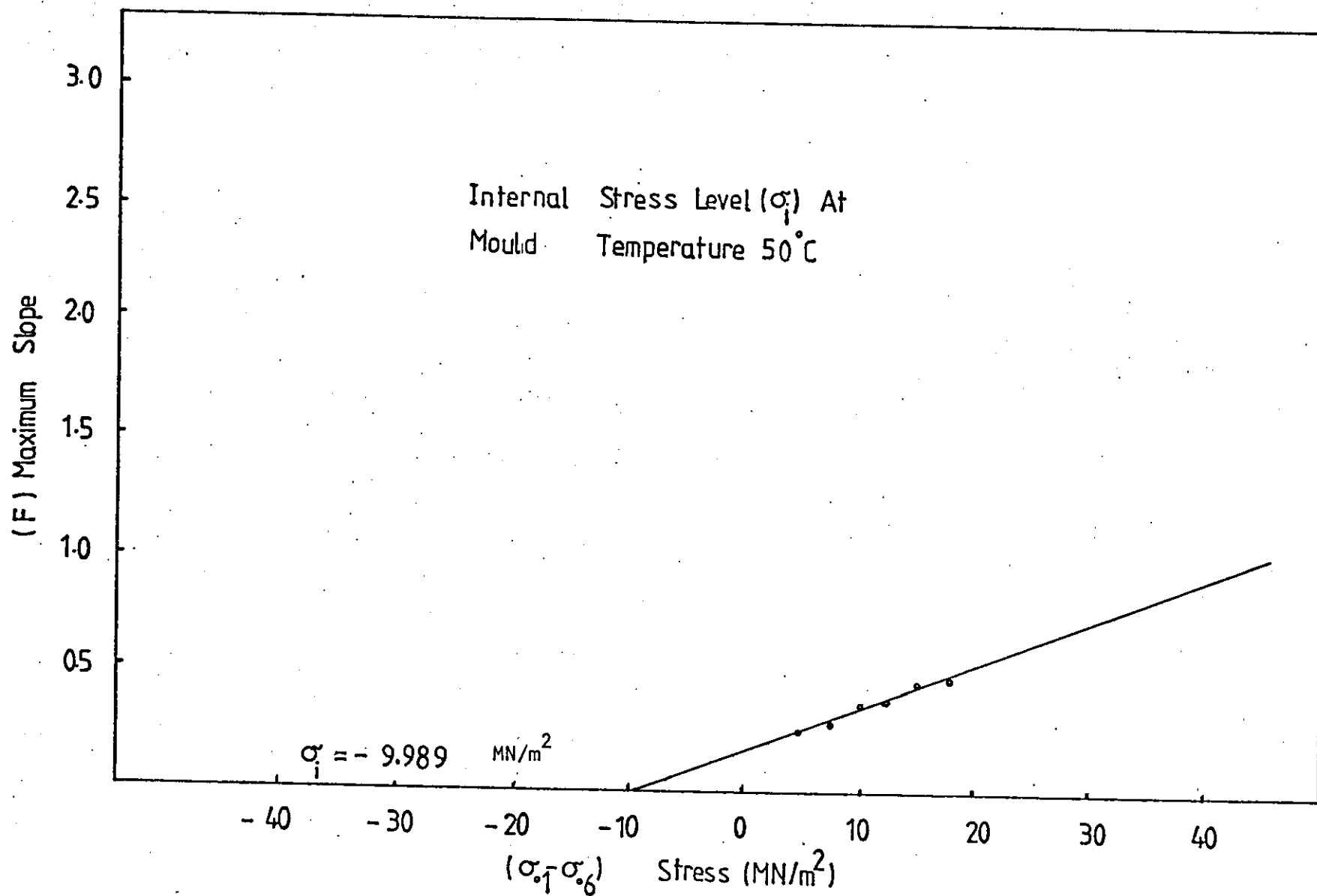


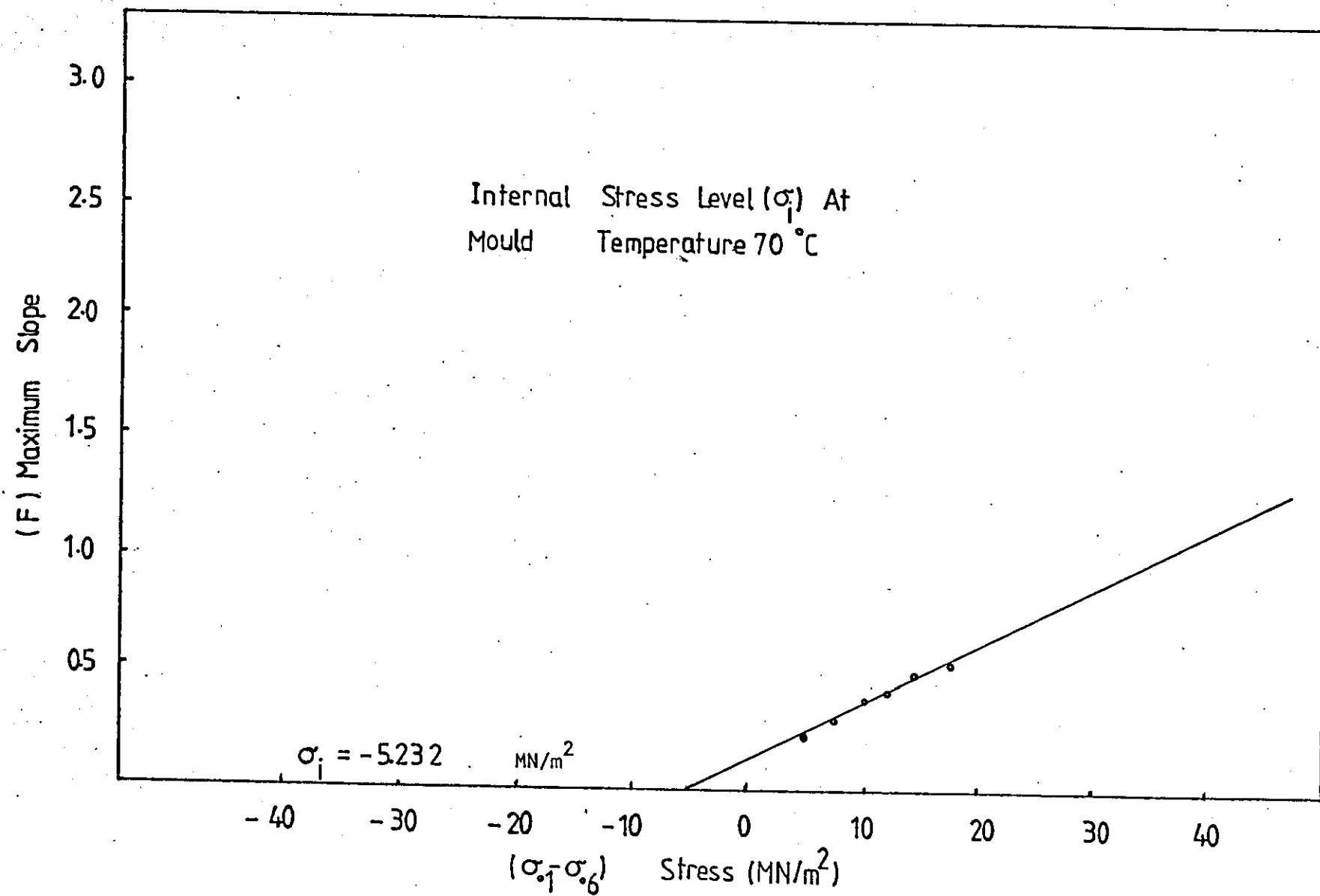


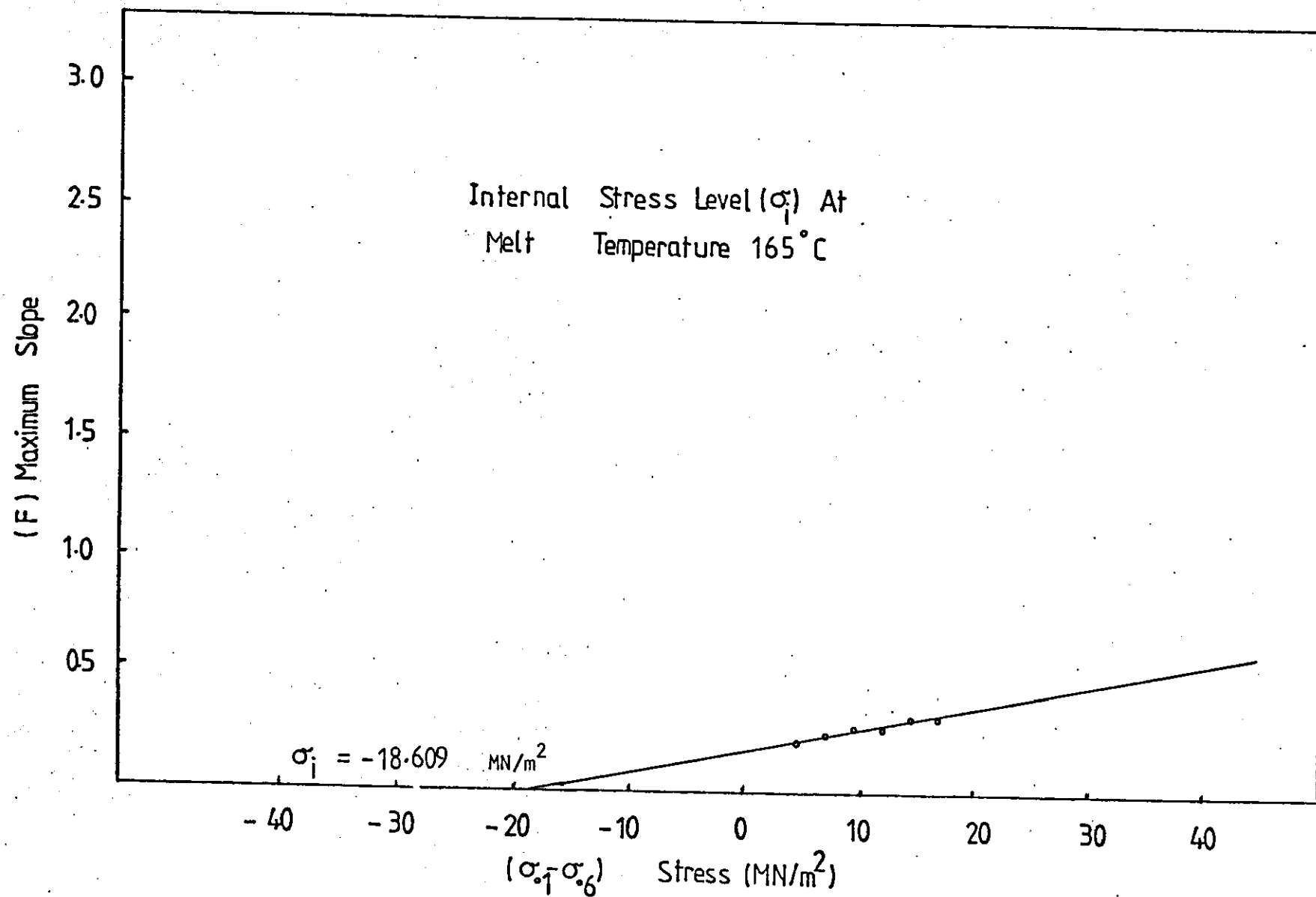


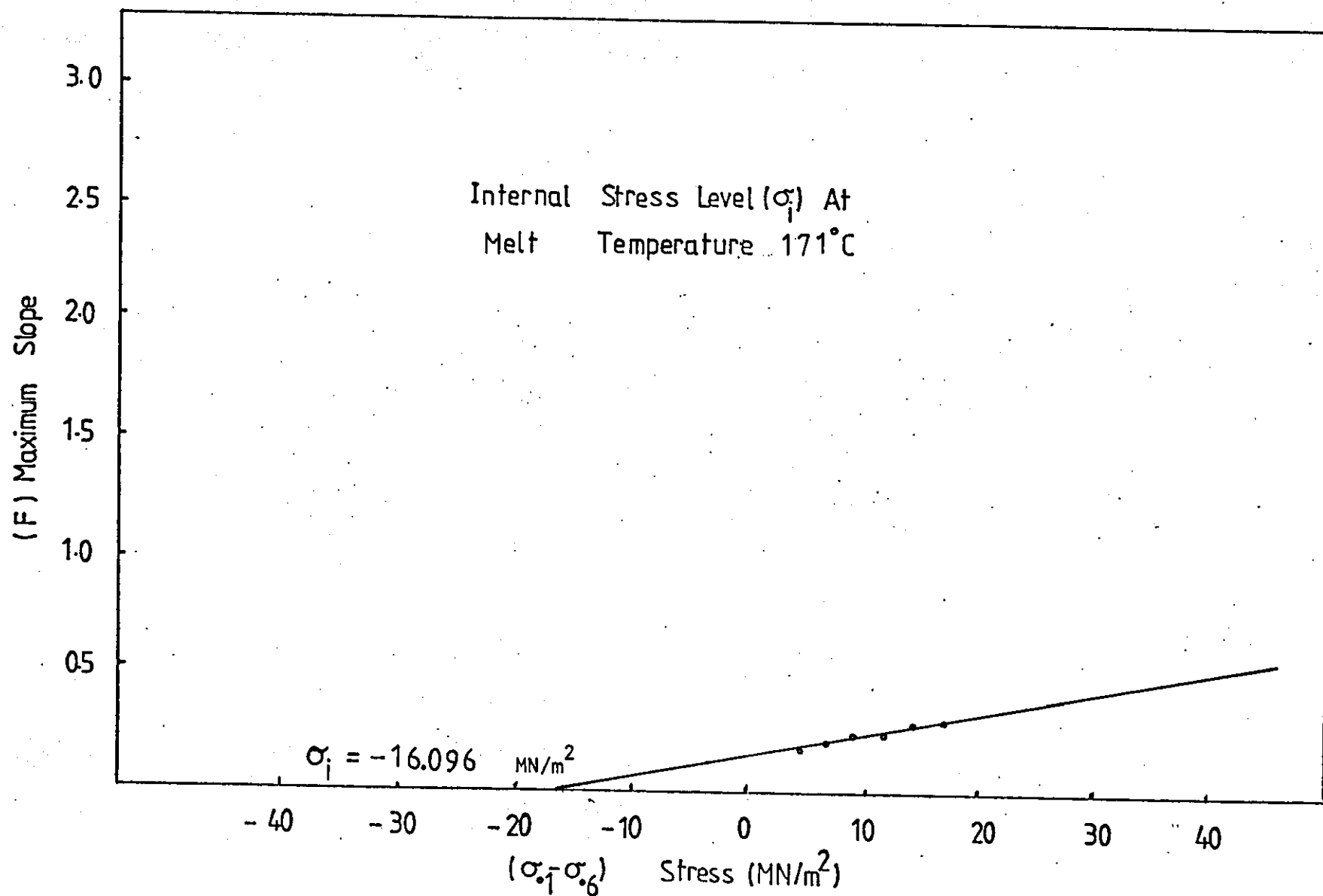


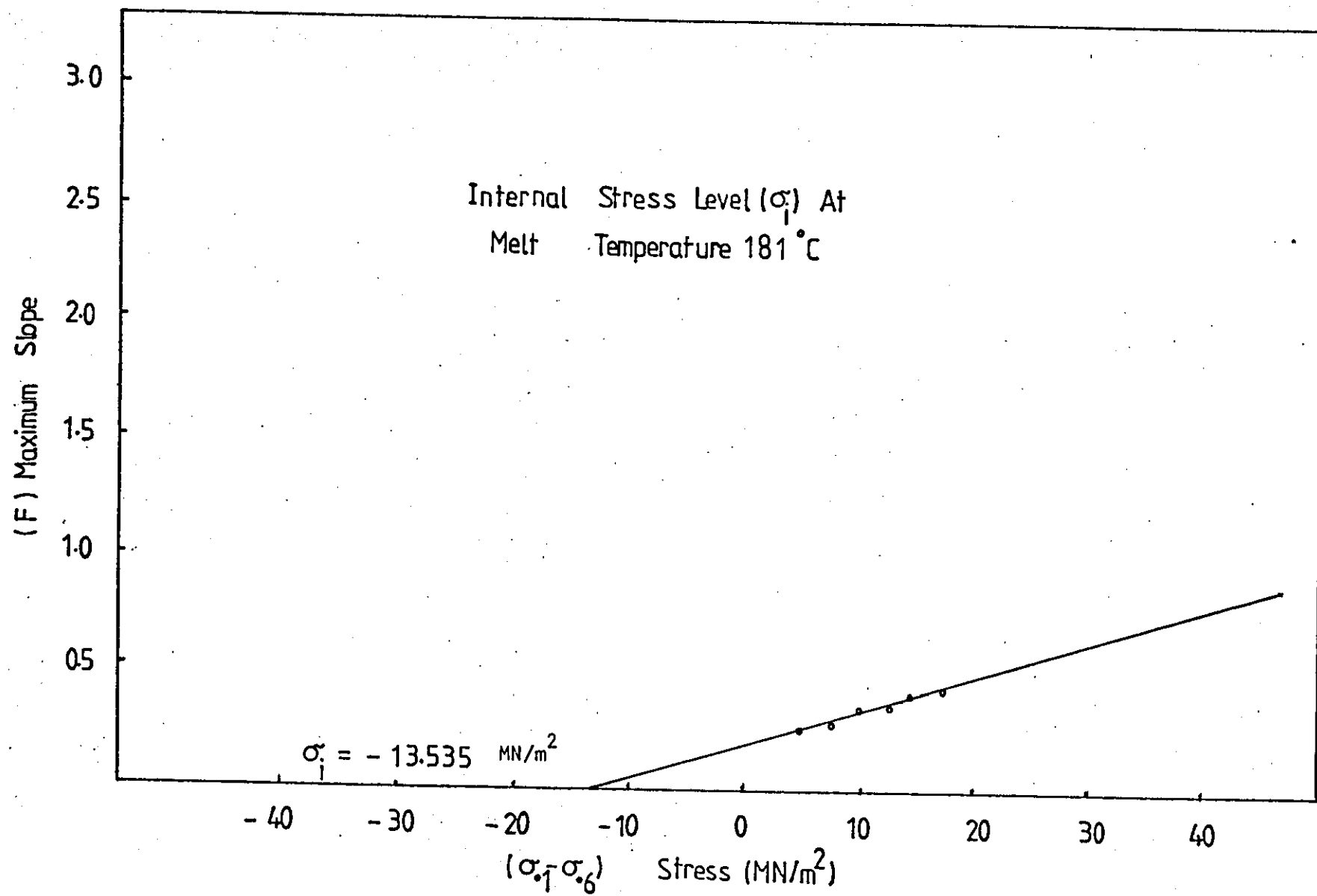












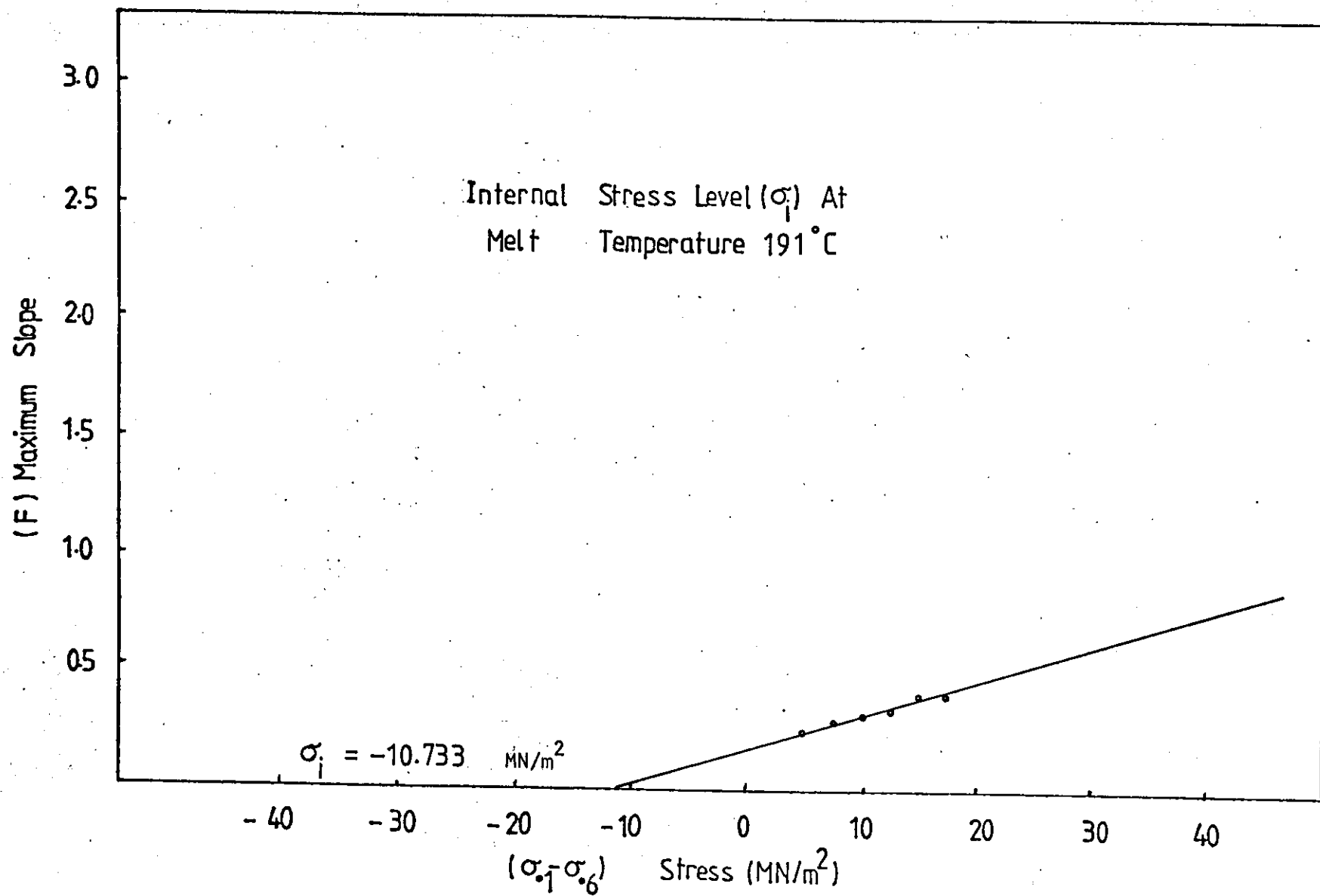


Table (13 - 14) demonstrate the variation of % volumetric mould shrinkage with injection time and mould temperature.

$$\% V = \frac{V_{\text{cavity}} - V_{\text{mould}}}{V_{\text{cavity}}} \times 100$$

TABLE 13

Volumetric mould shrinkage as a function of injection time

<u>Injection Time (sec)</u>	<u>% Volume Shrinkage</u>
6.00	0.0656
4.00	0.1745
3.00	0.2107
1.50	0.2541
0.90	0.2686
0.60	0.2758

TABLE 14

Volumetric mould shrinkage as a function of mould temperature

<u>Mould Temperature. (°C)</u>	<u>% Volume Shrinkage</u>
40	0.656
50	0.1019
70	0.1382

