INFLUENCE OF MELT SPINNING CONDITIONS ON SOME PHYSICAL PROPERTIES OF A POLYESTER FIBRE

THESIS

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S U M M A R Y

The main aim of this work was to investigate the effect of variable conditions of melt spinning and drawing on some of the physical properties of a polyester fibre. Not only the chemical composition but also spinning and drawing conditions are responsible for the ultimate physical properties of a fibre forming polymer. Thus, it was thought essential to investigate the influence of spinning and drawing conditions on some physical properties of polyethylene terephthalate filament. This material was chosen merely as a representative of the family of thermoplastic fibre forming polymers capable of being melt spun.

A melt spinning apparatus, supplied by I.C.I. Ltd., has been used. The polymer was spun at three rates of extrusion and three different winding speeds at a temperature of 285°C, using a constant diameter spinneret.

Spun filaments of polyethylene terephthalate were drawn on a continuous drawing apparatus at three different draw ratios viz: 2:1, 3.5:1, and 5:1, keeping the hot pin and hot plate at temperatures of 90 and 95°C respectively.

/To study

To study the effect of hot plate temperature on physical properties filament was drawn at 5:1 draw ratio at hot plate temperatures of 95, 115 and 130°C.

Density, tensile properties, birefringence and modulus of rigidity were measured by standard techniques.

From the results it appears that the melt spun filaments have relatively poor physical properties, which can be improved by a separate drawing process carried out above the glass transition temperature and below the softening point of the polymer. Although drawing has a great influence on physical properties, rate of extrusion and winding speed also play an important role in determining the final fibre properties of polyethylene terephthalate filaments.

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CHAPTER I

INTRODUCTION

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1 - INTRODUCTION

The conditions under which a fibre-forming polymer is spun and drawn are responsible, together with its chemical composition, for its ultimate physical properties. Thus it was considered essential to determine, for thermoplastic fibre-forming polymers, the effect of spinning and drawing conditions on the physical properties of a man-made fibre. In order to do this a series of fibres were spun at different rates of extrusion, winding speeds, draw ratios and drawing temperatures. The physical properties of the fibres produced under these different conditions have been determined.

Polyethylene terephthalate, supplied by I.C.I. Ltd., has been used in these investigations as the representative of the family of thermoplastic fibre-forming polymers. The investigations on this polymer should throw light on the general relationships between spinning conditions and fibre properties applicable to all thermoplastic polymers.

Polyethylene terephthalate is a synthetic, linear polyester which was prepared and developed as a fibre by

/Whinfield

Whinfield and Dickson[1] of the Calico Printers Association in 1941. It is a direct development of the work carried out by Carothers[2] on polyesters in 1928-32. Its commercial development was seriously delayed by the Second World War. In 1955, however, I.C.I. Ltd., started operating a large plant for the production of polyethylene terephthalate. Since then many types of linear polyesters have been prepared and examined.[3-7] A considerable amount of research has also been carried out with the object of improving the actual methods of manufacturing the polymer.[8,9] A review of the development of Terylene has been given by Whinfield.[10]

Since industry has taken over this thermoplastic fibre-forming polymer for the production of Terylene, comparatively little work has been published to show the techniques used to improve its properties. To achieve the best out of synthetic fibre, it is important to improve its over-all physical properties (e.g. tensile properties, modulus of rigidity, etc.) in order to increase its uses in the textile industry.

1.1 Spinning Methods:

There are three major processes by which bulk polymers may be converted into fibres.

1.11 Wet Spinning:

A polymer solution is forced through tiny spinneret holes into a coagulating bath where it forms continuous filament which is then washed and dried.

1.12 Dry Spinning:

A solution of polymer in a volatile solvent is forced through a spinneret into a stream of warm air. The solvent evaporates and the liquid stream solidifies into a continuous filament which is then drawn off.

1.13 Melt Spinning:

A molten polymer is forced through spinneret holes into cool air which solidifies it into a continuous filament.

Melt spinning has advantages over dry and wet spinning. Solvents are not required and hence neither solvent nor a spinning bath recovery process is necessary. Further, melt spinning is not complicated by the necessity for reagents to be

/given

given time to react, or for the volatile solvent to be removed from the filament. Speeds of extrusion are higher than those for dry and wet spinning.

1.2 Melt Spinning Processes:

For a melt spun fibre the term "spinning" embraces the acts of melting, filtering, extrusion, quenching and winding up.[11] Carothers[2] was the first to indicate that a continuous filament could be extruded from synthetic linear condensation superpolymers.

The actual spinning process used in this thesis is not identical with the industrial process described below, but, in fact, simulates it in a laboratory apparatus. Commercially, dried polymer chips are fed from a storage hopper and melted in an oxygen free atmosphere against a heated plate or grid, or, alternatively, in a screw-extruder.[12] The molten polymer flows at a constant rate, usually controlled by a gear wheel type metering pump, and is filtered before being extruded through a spinneret into air at room temperature.

It has been found that the temperature of the melt depends on the rate at which the polymer is pumped, the required melt temperature and the available heating surface area.[13] Apparently a polymer can melt and be extruded before being fully

/heated

heated to the required temperature. In order to ensure reproducible filaments, therefore, the polymer must be held at a constant temperature for a constant time.[14] The load of melt should be kept constant and small so that it does not stay for a long time in the spinning head. During this interval many different changes can occur, e.g. redistribution of molecular weight, a change in average molecular weight or thermal decomposition may set in leading possibly to the formation of gas bubbles which interfere with extrusion.[13]

When a molten polymer emerges from a spinneret in a thin fluid stream it begins to cool, partly by radiation and partly by conduction to the surrounding atmosphere.[13] Solidification takes place about two feet below the spinneret. The filament is finally collected on a bobbin which is driven at a constant speed.

In the case of polyethylene terephthalate the filaments are quenched rapidly to below the glass-rubber transition temperature of 80°C., and the spun filament is almost completely amorphous. Most of the stretching which occurs during the drawing-down

/between

between the spinneret and wind-up bobbin takes place while the filament is still molten and it is thought that there is sufficient time for the polymer molecules to relax before the fibre cools.[15] In the solid state polyethylene terephthalate can be amorphous or possess various degrees of crystallinity, depending upon its thermal and mechanical history.

There are many patents on spinning techniques which describe spinning apparati,[16, 17] extruders,[18,19] spinning packs[20,21,22] and rod spinning machines.[23,24] These patents give information about the manufacture of fine denier synthetic filaments;[25,26] improved methods of heating the polymer,[27,28] cooling of the extruded filaments[29] and control of the rate of cooling of the extrudate to produce exceptionally uniform filaments[30,31] of improved physical properties at high speeds. For example, Thompson and Marshall[32] have described a spinning process whereby improved properties of polyethylene terephthalate are obtained without using a separate drawing step.[12] This is achieved by increasing the tension on the extruded filaments and passing them through hot

/liquid

liquid (water), above the second order transition temperature of the polymer, so that a degree of molecular orientation is obtained.

1.21 Mechanism of Flow Behaviour

During melt spinning the molten polymer is forced through a capillary. A relationship has been established for Newtonian flow through a tube of length l and radius r, known as Poiseuille's Law.[14]

$$M = \frac{P\pi r^4 \rho}{8 l \eta}$$

where M, P, ρ and η are the rate of flow, applied stress, polymer density and viscosity respectively.

At very low rates of shear, high polymers show Newtonian flow behaviour. On increasing the shearing stress, the rate of shear also increases but much faster than would be expected for a Newtonian fluid. This type of behaviour can be described in terms of a flow parameter[33] 'n' where

$$\dot{\gamma} = K\tau^n$$

$\dot{\gamma}$ is the rate of shear, τ is shear stress and K is constant.

/Over

Over a wide range of shear stress, n is found to be constant for a particular polymer and the value of n (i.e. the extent to which it exceeds unity) may be regarded as a measure of the non-Newtonian behaviour of the polymer. Thus, in practice, the flow rate increases more rapidly than anticipated from Poiseuille's Law. This "non-Newtonian" nature of the flow may arise for two reasons.[15] Firstly, viscosity is dependent on the rate of shear which can be high in narrow capillaries; and secondly, the melt may be visco-elastic. It seems from the evidence that the deviation from Poiseuille's Law is due to visco-elastic effects.

When a polymer flows through a capillary some orientation of the molecular chains occurs, and a characteristic swelling of the polymer stream develops immediately below the capillary exit. This swelling occurs at even low shear rates and increases with shear rate towards a limiting value.[34] It is independent of capillary length at low shear

/rates.

rates. At higher shear rates, however, an increase in capillary length causes a decrease in post-extrusion swelling. On the disappearance of the shear stress at the capillary exit the molecules are able to relax with the result that there is an elastic recovery.[15] It has been reported that birefringence is not observed in the extruded filament below the swelling region. This indicates that the polymer has relaxed back to its isotropic form. Hence, although molecular orientation is induced during the extrusion of a polymer it is lost after extrusion.[15]

There are two explanations for post-extrusion swelling.[34] Firstly, it has been suggested that it is due to the randomisation of polymer molecules oriented during flow through the capillary, i.e. as described above. Secondly, post-extrusion swelling may be a consequence of the transition from a 'near parabolic' velocity distribution across the filament at the capillary exit to a constant velocity distribution some way down the extruded

/filament.

filament. This, however, would not account for the large amount of post-extrusion swelling observed at high shear rates.

The limiting speed of the extrusion is governed by the fact that at high shear rates the flow becomes unstable, resulting in a phenomenon often described as 'melt-fracture'. This appears as a periodic irregularity in the extrudate. Even at the highest shear rates obtainable in the apparatus described in this thesis melt-fracture was not encountered.

1.22 Hot Drawing during the Spinning Operation.

2 Hot Drawing during the Spinning Operation. filament is elongated. It has been suggested that the inertia of the material and the drag of the surrounding air apparently supply sufficient tension, in the form of drag on the molten filaments emerging from the capillary, to induce some orientation of the polymer molecules in the solidification ranges.[15] In this range the filaments elongate. By increasing the winding speed, and hence the tension, a high degree of orientation may apparently be achieved and fibres with useful

/textile

textile properties are produced. It is usual, nevertheless, to make filaments of low degrees of orientation and to draw them in a separate operation.

1.3 Drawing Processes.

Melt spinning and hot drawing are two distinct physical processes.[35] During the spinning process, most of the extension takes place in the filament at the high temperature end of the thread line, i.e. where the polymer is molten. Generally, at this high temperature the material has a relatively low viscosity. Thus very little stress is set up and the resultant filament has poor orientation. During the drawing process, the material is stretched while passing through a heated zone such that the maximum temperature attained by the filament is limited to a value just above the glass-rubber transition temperature. The rate of straining, resulting from the applied stretch ratio, has been found to give sufficient stress to cause reinforcement and orientation in the partially crystalline filament.[35]

Farrow and Ward[36] have reported that the principal cause of reinforcement in polyethylene terephthalate is the presence of entanglements, since chemical cross-links do not occur. In the case of polyethylene terephthalate it was previously thought that the reinforcement occurring in the drawing process arises from stress-induced crystallisation.[35, 37] Although

/the

the crystallisation process may increase the reinforcement, it has been experimentally confirmed[36] that the latter is not essentially due to stress-induced crystallisation.

Spun filaments of polyethylene terephthalate have been reported to be amorphous, weak and highly extensible, with a random configuration of polymer chain units.[11] To convert these into useful textile fibres, with desirable properties of high strength and flexibility, it is essential to stretch them. This stretching or drawing[38] seems to be a straight-forward process of extension accompanied by attenuation.

Man-made fibres[11] obtain their strength largely from the presence of oriented polymer chain units locked in position by crystallinity, but these crystallisation or orientation processes occur with difficulty in polyethylene terephthalate below glass-rubber transition temperatures. Below this temperature the amorphous region is locked in a glass like structure and is unable to yield to applied stresses. Thus the tension required to draw spun filaments of polyethylene terephthalate is likely to break them, or produce some voids in the

/filaments.

filaments. Certain molecular segments possess sufficient thermal energy to revolve above the glass-rubber transition temperature. Thus under an applied stress, the long chain polymer molecules will be able to move over each other, become oriented, and hence crystallise.

In practice, a continuous filament of polyethylene terephthalate is drawn between feed and draw rolls. During drawing the filament is heated on the feed or draw roll,[39] or is passes through a heating zone situated between these rolls. The heating zone may comprise an inert liquid, inert gas, non-rotatable pin[40] or a stationary hot plate.

During, or prior to, drawing, the filament may be passed through a wetting agent[41] at an elevated temperature. A high speed drawing process giving improved fibre physical properties is reported in some British patents.[42,43]

It is advantageous to use both a hot pin and a hot plate for the drawing operation.[44,45] During conventional drawing operations the continuous filament is stretched in two stages. Primary stretching occurs at the surface of the non-rotatable pin where the draw point is located, and secondary

/stretching

stretching on the surface of a hot stationary plate.[46] This secondary draw may require a higher temperature to permit the necessary internal rearrangement of the molecular structure of the filaments, and so the plate is maintained at a slightly higher temperature than that of the pin. In partially crystalline polymers, most of the crystallisation takes place at this secondary drawing step, and so, in order to stabilise this crystallisation, the hot plate temperature should be as high as possible. In most commercial processes about 80-90% of draw occurs at the hot pin and the rest occurs at the hot plate.

During the drawing of polyester filament round the hot pin, two requirements have to be fulfilled.[47] Firstly, localisation of the draw zone and secondly, uniform heat transfer to the filament. A uniform heat transfer can be achieved by using a hot pin of large diameter, but the draw zone is not localised in the smallest possible area, with the result that filaments of non-uniform properties may be obtained. If a pin of small diameter is used the draw zone can be localised within desirably small limits, but heat transfer to the filament is inadequate, particularly at high speeds of drawing.

/Risley[47]

Risley[47] has described an improved drawing process to overcome the above difficulties.

1.31 Continuous Isothermal Drawing

A polymer can be extended either uniformly or by a necking process, according to the experimental conditions.

A continuous two roller drawing machine, operating at a single temperature and using material that extends uniformly has been described by Marshall and Thompson.[48] They have observed that all the extension occurs on the feed roll where the tension is rising, and most of the extension occurs in a very short length which is visible as a draw area on the feed roll. While discussing drawing on a flat heater, they have reported that most of the extension takes place on the hot plate, and not, as before, on the feed roll.

Marshall and Thompson[48] have also considered continuous machine drawing in terms of the three factors; load, extension and temperature surface characteristics of the material in order to explain the mechanism of drawing. Drawing is always uniform at all machine ratios.

/They

They have concluded that:-

(i) The sigmoidal shape of the load/extension/temperature surface characteristics curve of many polymers gives rise to a localised drawing zone which may appear as an apparent draw point.

(ii) The position of this draw point can be predicted from the load/extension/temperature properties of the material being drawn, particularly when the yarn tension is less than that required to form a neck.

(iii) This point should remain fixed in the space.

(iv) Small changes in heater temperature and draw ratio can profoundly alter the temperature at which the extension is taking place.

1.32 Necking:

The behaviour referred to as cold drawing was first reported by Carothers and Hill.[2] When filaments of polymers such as nylon, polyethylene terephthalate, etc., are stretched rapidly, at one or more points, shoulders or necks develop where the thin drawn material joins the thicker

/undrawn

undrawn part.[15] The necks then travel along the filament as more material passes from the undrawn to join the drawn portion, the thickness of which remains constant. During the necking process the ratio of undrawn to drawn cross-sectional areas is generally known as the natural draw ratio of the polymer. This depends to some extent on the rate of drawing, the thickness of the specimen and the temperature. When the drawing is carried out slowly, i.e. to avoid necking, it has been reported that the birefringence of all parts of the filament increases steadily and simultaneously,[15] but when drawing is carried out rapidly the filament forms one or more necks.

After a neck develops in the material the drawn portion is subject to a higher stress than the undrawn portion because of the reduction in cross-section area. The stress continues to increase as the cross-section area decreases. Thus a "strain-hardening" process is essential[49,50] otherwise the material will break soon after the neck develops. This strain-hardening

/process

process comes about as a result of the orientation of the molecules.

Drawing seems to convert a specimen with randomly orientated crystalline regions to one in which the crystalline regions are orientated with one axis parallel to the fibre axis. The necking phenomenon was first considered to be confined to crystalline or partially crystalline polymers,[51] but polyethylene terephthalate filament also necks when stretched from an amorphous undrawn state to a crystalline drawn one. Thus necking phenomena and natural draw ratio appear to be connected with crystallinity in drawn filaments, as polymers which are amorphous both before and after drawing do not show such behaviour.

In polymers like nylon, crystallisation occurs when the extruded polymer cools and, during drawing, crystalline and amorphous materials are oriented. A suggestion has been made that drawing at a neck, since the temperature may become quite high, is equivalent to melting crystalline material at reduced

/pressure

pressure at the centre of the neck and reforming.[52]

Bunn and Alcock[51] have proposed molecular slipping as the basic process involved in cold drawing. Tearing the crystallites during drawing is more likely than the breaking of them by shear.

Jäckl[53] has suggested that since high polymers do not draw at a neck above a certain critical temperature (softening temperature), the temperature in the flow zone of the neck should be equal to, or slightly greater than, the softening temperature.

Recently, some workers[48,50,54] have treated the phenomena of necking macroscopically.

Necking can occur under conditions which are

Adiabatic

or

Isothermal

1.321 Adiabatic necking

Much experimental and theoretical work on the necking process has been carried out by Marshall and Thompson.[48,54,55] They have reported, for example, that when a fixed

/length

length of amorphous polyethylene terephthalate filament is stretched at a constant rate a characteristic load/extension curve is obtained. The tension rises until the extension reaches about 2% then suddenly a neck occurs at the maximum in load. The propagation of the neck proceeds at a somewhat lower constant load, until the shoulders of the neck have traversed the whole length of the specimen. Further extension gives rise to a steady increase in tension up to the breaking load. It will be seen from the experimental results that this agrees in general with the results obtained in this work.

Instead of observing a neck moving along a fixed length, when the filament is supplied continuously, the neck may remain fixed in space under steady state conditions. This has been investigated, when a monofilament was stretched between feed and draw rollers.[54] A stationary condition of the neck may be maintained if the ratio of roller speeds, R, equals the natural draw ratio, r. When R is

/greater

greater or less than r the neck will move backwards or forwards between the rollers. The relationship between velocity of the neck and natural draw ratio can be obtained as follows:[54] let A_1, d_1, and V_1 be the cross-section, density and velocity at the feed roll and A_2, d_2, V_2 those at the draw roll. So $V_2/V_1 = R$, the applied machine ratio and $A_1/A_2 = S$, the natural self-maintained draw ratio. The velocity of shoulder is V_x. The rate of change of mass between the rollers is

$$(V_1 d_1 A_1 - V_2 d_2 A_2) = V_x(A_1 d_1 - A_2 d_2)$$

$$\text{Hence } V_x = \frac{V_2\left(\frac{d_1 A_1}{d_2 A_2} - \frac{V_2}{V_1}\right)}{\frac{V_2}{V_1}\left(\frac{d_1 A_1}{d_2 A_2} - 1\right)} = \frac{V_2\left(\frac{d_1}{d_2}S - R\right)}{R\left(\frac{d_1}{d_2}S - 1\right)} =$$

$$= \frac{V_2(r - R)}{R(r - 1)}$$

where the natural draw ratio r is equal to Sd_1/d_2. This equation serves as a means of calculating the natural draw ratio r,[54] since V_x can be measured easily.

Marshall and Thompson[48,54] have experimentally

/shown

shown that the natural draw ratio increases to some extent with draw speed. At a given temperature an advancing neck can be turned into a retreating neck by altering the draw speed. Thus, at the appropriate draw speed a stationary neck can be produced. With polyethylene terephthalate above 60°C multiple necking has been reported and so the natural draw ratio is difficult to find. In the temperature range of 70°-80°C, necking disappears and the natural draw ratio drops to unity at the glass-rubber transition temperature of the polymer. A further increase in temperature causes a decrease in the load required for drawing, and also a decrease in deformation. At very high temperatures the definite yield point disappears, and an inflection appears in the stress/strain curve in its place. The entire sample undergoes homogeneous strain, i.e. an approximately adiabatic process occurring at the shoulder becomes an isothermal one over the entire sample. At this point necking

/disappears

disappears and the specimen stretches uniformly throughout its length. Isothermal behaviour can be obtained at lower temperatures provided drawing is carried out at lower speeds and with very good dispersion of heat.

When the filament diameter decreases, or the initial molecular orientation of the specimen increases, the natural draw ratio decreases at constant speed of drawing.[54] Thus the natural draw ratio obtained is a function of the experimental conditions.

A theory of cold drawing, according to Marshall and Thompson,[49,55] assumes that the work of stretching the polymer largely goes into heating the polymer in the region of the neck. This, in turn, implies, for visco-elastic material, a poor conductivity so that the work done appears as heat rather than potential energy, and heat losses must be small. The maximum amount of heat is generated near the glass transition temperature of the polymer. Thus, when a polymer is stretched, heat will be built up

/in

in small regions where deformation occurs. As the temperature of this small region builds up more heat will be generated and the modulus will decrease. In this way necking will tend to appear in very localised regions.

The effect of temperature on the load/extension curves has been determined by passing the filament over a hot plate in a two roller machine.[54] It is found that the filament rapidly reaches the temperature of the hot plate. A stable range for drawing on a hot plate, with a steady neck between the two rolls, is considered to exist over a range of draw ratios from the natural draw ratio, at room temperature, down to the natural draw ratio at the heater temperature.[48]

The load/extension/temperature curve obtained by Marshall and Thompson,[48] analyses all drawing processes over a hot plate. From this, one can find the draw tension, the temperature at which each part of the extension occurs, and the position of the draw point in the thread line.

On the assumption that no heat escapes, an

/adiabatic

adiabatic load/extension curve[54] may be calculated from the isothermal load/extension curves. If this load/extension curve of a material falls to a lower load at a higher temperature then it is possible for an adiabatic curve to reach a negative slope, and for necking to occur. An alternative process of extension at constant tension in a shoulder, coupled with exchanges of heat along the specimen by conduction appears to be possible at a lower tension than that needed for pure adiabatic extension. For this process the length of the shoulder, the tension at which it operates, and the draw ratio across it can be calculated from the simple adiabatic curve.[54]

Newman[56,57] has reported the same theory of cold drawing as Marshall and Thompson.[48,54] Hookway,[52] while studying the cold drawing of nylon 6.6, has put forward a general molecular mechanism for a drawing process which combines the ideas set out previously by Dunn and Alcock,[51] Jäckl,[53] and Marshall and Thompson.[48,54]

/Nylon

Nylon 6.6 has a sigmoidal type load/extension curve which drops to lower loads at higher temperatures. Hence nylon will form necks at a high enough rate of extension or at large specimen cross sections. The temperature rises to 60-70°C inside the neck.[52]

Vincent[50] suggests that cold drawing occurs whenever $\sigma/R = d\sigma/dR$ at two places, where σ is the true stress and R is the draw ratio. He objects to the adiabatic theory of cold drawing suggested by Marshall and Thompson,[54] and Jäckl.[53] He proposes a theory in which the stress on the polymer lowers the softening point to about the temperature at which drawing occurs, rather than a straining process generating heat which raises the temperature of the material to the softening temperature. This objection was confirmed experimentally by Vincent.[50]

Vincent does not offer a molecular mechanism for the lowering of the modulus and softening temperature when a material is strained, but it is well known that a large

/stress

stress on a visco-elastic polymer will greatly reduce its relaxation times and lower its apparent softening or glass transition temperature.

Recently another experimental technique for studying cold drawing has been developed by Williams and Bender.[58] They applied a constant load to an undrawn fibre and measured the creep extension as a function of time. During this experiment cold drawing was observed by a marked yield region on the logarithmic time scale. The following equations were obtained by them:

$$t_n = \frac{x}{V_1} = \frac{xR}{V_2}$$

$$t_f = \frac{40 + x(R - 1)}{V_2}$$

where t_n is the time required for the neck to form, and x is the distance of the neck from the feed roll. The machine draw ratio is $R = \frac{V_2}{V_1}$ where V_1 and V_2 are feed and draw roll speeds respectively. The distance between the feed and draw rolls is 40" and t_f is the

/transit

transit time occurring during the stretching operation, which depends on the speeds of the two rollers.

A two-roller drawing machine then imposes an extension R-1 in time t_f. This machine essentially operates at constant load so the results are directly comparable with the static creep curves.

Williams and Bender[58] have proved that the natural draw ratio defined by Marshall and Thompson[48,54] is simply related to the extension produced by the yielding process. They have tried to relate the position of the neck between the two rollers, the drawing tension and speed dependance of the rollers.

Recently Roth and Schroth[46] have carried out an extensive experimental programme to explain the phenomenon of cold drawing during continuous stretching of polyester and polyamide filaments.

1.322 Isothermal necking:

It is possible to achieve necking isothermally. The behaviour of isothermal necking has been

/described

described by Lazurkin,[59] Vincent[50] and Peters.[15]

In practice of course draw speeds are generally very high, which naturally develops heat. So even though the load/extension curves are sigmoidal the drawing is far from isothermal, and the temperature increase will indicate that the process is at least partly adiabatic.

1.4 Previous Work on the Relationship between Spinning and Drawing Conditions and Fibre Properties.

Roth and Schroth[60] have carried out an extensive programme to study the effect of the spinning conditions on the pre-orientation for polycondensate filaments. The changes of the structure in the fibre during the formation of filament are discussed, and stretching under various conditions is examined by them. It has been reported that by the action of heat and swelling agents on drawn and undrawn polyester filaments[61] structural changes occur, influencing the density, shrinkage, and stress/strain behaviour.

Roth and Schroth[46] have also investigated the effect of heat developed during drawing, supplied heat and loss of heat during the drawing process on the structure and properties of polyester and polyamide filaments. They have discussed the relationship between the temperature of the hot pin, hot plate, speed and degree of stretching, force of stretching, shrinkage, and tensile properties of drawn fibre. They have reported from their observations that:

(i) the effect of heat on polyethylene terephthalate being greater than that on nylon;

/the

the influence of stretching is greater on polyethylene terephthalate filaments than on nylon

(ii) the stretching tension of the undrawn fibre and the molecular orientation at the same draw ratio decreases with an increase in temperature of the hot pin. Thus, at a higher temperature of the hot pin the draw ratio can be increased without any significant change in molecular orientation.

(iii) the breaking strength of a man-made fibre strongly depends on the rate of stretching, but at high temperatures of hot pin the draw ratio increases resulting in some brittleness in the fibre which, in turn, decreases the breaking strength. By pre-stretching, a fibre of good textile properties with less brittleness can be obtained.

(iv) during the drawing of the fibre, if the effect of heat is constant, the resistance to deformation of the fibre will increase with increase in stretching speed. This, in turn, will increase the stretching work and internal stress, but when the effect of heat increases

/with

with the stretching speed because of the rise of temperature in the neck and small loss of heat, lower stretching tension and shrinkage values are obtained.

(v) if the temperature of the hot plate is less than that of the undrawn fibre, stretching takes place either before or after the hot plate.

(vi) at a high temperature of the hot plate very little stretching occurs at the secondary stage. This small after-stretching has great influence upon the textile properties of the fibre.

(vii) an increase in hot plate temperature will decrease the stretching tension which, in turn, lowers the stress of the material leading to less brittleness of the fibre and thus the breaking strength increases. At very high temperatures most of the stretching takes place on the hot plate.

Ziabicki[62,63] has investigated the phenomena of macromolecular orientation as observed in the melt spinning process for polycapronamides, copolyamides, polyurethanes and polyesters. He concludes, from the study of these polymers, that fibre birefringence

/a comparative

(a comparative measure of mean degree of molecular orientation) practically does not depend on the deformation ratio, and monotonically increases with velocity differences (the difference between the velocity of the polymer near the spinneret and on the spin bobbin) and the reciprocal of the fibre diameter (a measure of cooling rate).

A general theoretical analysis of mechanical effects in fibre spinning processes which is based upon the thermodynamics has been reported by Ziabicki.[64] He has discussed the possibility of the occurrence of a radial velocity gradient and the effect connected with the radial velocity distribution. The tensile force and its constituents, the external take up of force, gravitational force, aerodynamical drag, surface tension and internal constituents have been analysed and discussed. He has mentioned that in the spinning of fibres of very fluid liquids, from the spinneret, the surface tension may come into consideration as a factor tending to split the stream into single drops.

Keller[65] and Sattler[66] have also studied the molecular orientation of the spinning fibre by birefringence and shrinkage measurements.

/Recently,

Recently, Gröbe[67] carried out a survey of the problem connected with fibre formation in melt spinning, and discussed particularly the question of cooling the jet extruded from the melt and the problem connected with the change in shape and ordered states of the filaments. It seems from the results obtained that initially, up to about the distance of 5 cm., the diameter of the fibre increases and then it drops to a constant diameter at about 80-90 cm.

H. de Vries[68] has obtained an empirical relation between the draw ratio and birefringence of man-made fibres.

Hookway,[52] while studying the cold drawing of nylon, has reported that the yield stress of a high polymer sample is closely related to the molecular mobility within the amorphous regions of the filament. The mobility can be altered by varying the moisture content, temperature and density of the undrawn sample. The magnitudes of the factors controlling the weakening and strengthening of the portion of the filament for a given small extension vary with initial birefringence, moisture content and the chemical composition of the undrawn sample. When a poorly

/oriented

oriented filament first yields, i.e. at low draw ratios, at the point of draw there is partial freeing of structure. At high draw ratios, in the later stages of drawing, the structure is consolidated.

Crystallinities in drawn fibres have been measured by many workers[69-73] by methods based on density, infra-red spectra and X-ray diffraction. The results have been compared and no correlation has been found to exist between them. However, Johnson[71] was able to obtain a good correlation between the crystallinity measured by X-ray diffraction and density on a number of polyethylene terephthalate fibres of different draw ratios. Farrow[72] has also found a good correlation with randomly oriented specimens, but not with drawn fibres prepared under laboratory conditions.

Yorugi,[73] while studying the effect of drawing and annealing on the crystallinities of the polymer, found no quantitative correlation between density and X-ray measurements. He suggested that this disagreement may be because of preferred orientation of the molecular chains in non-crystalline regions and imperfection in the crystalline regions.

Thompson and Woods[70] have reported that by increasing the draw ratio of polyethylene

/terephthalate

terephthalate, density rises to a flat maximum or may decrease. They have noticed that birefringence, initial modulus and infra-red absorption ratios, continue to increase. They thought, from their observations, that crystallinity measurements from infra-red spectra are more reliable than those of density measurements. Increase in spinning speed and the heat treatment after drawing may delay the reduction in density. It has been suggested that it is the non-crystalline orientation which changes with draw ratio and heat treatment.[69,70]

The effect of heat on unoriented amorphous polyethylene terephthalate fibres with different degrees of polymerisation and orientation were observed by density, birefringence and X-ray diffraction methods, by Sakajiri.[74]

The effect of heating temperature on molecular orientation in drawn polyethylene terephthalate filament has also been discussed by Shirakashi.[75]

The effect of wet spinning conditions on the structure of viscose rayon filaments have been discussed by Gumberbirch.[76,77]

Molecularly homogeneous fractions of secondary

/cellulose

cellulose acetate were also spun, by Cumberbirch,[78,79] into monofilaments by the wet spinning method. Different degrees of orientation were obtained by stretching filaments to different extents and birefringence and tensile properties were measured. A relationship has been obtained between percentage effective stretch, molecular weight, tenacity, and birefringence properties. It was found that the tenacity of a filament can be computed from its molecular weight distribution, and relations between tenacity and molecular weight for filaments made from fractions.

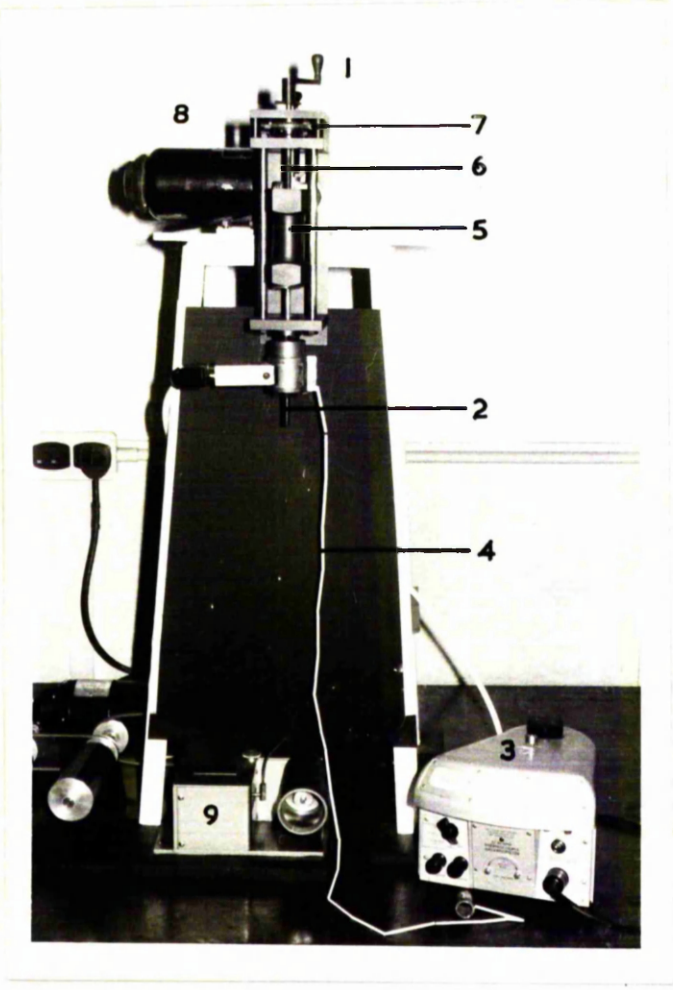
CHAPTER II

EXPERIMENTAL METHODS

CONTENTS

2. EXPERIMENTAL METHODS

The object of this work was to investigate the effect of variable conditions of melt spinning and hot drawing on some of the physical properties of polyester fibres. Polyethylene terephthalate, as supplied by I.C.I. Ltd., was used for the spinning and drawing experiments. This polymer imposes certain restrictions, e.g. one cannot spin below the melting point of the polymer, i.e. 252°C, and also it cannot conveniently be drawn below its glass-rubber transition temperature, i.e. 69°C. Melt spinning should be carried out at a temperature about 30°C higher than that of the melting point of the polymer, and so the spinning temperature was maintained at 285°C. During the drawing of the filament, the temperature of the hot pin was maintained at 90°C (which is above the glass-rubber transition temperature of the polymer) and the temperature of the hot plate[45] was kept at 95°C.



1. Handle
2. Vacuum tube
3. Pye Scalamp Thermocouple Galvanometer
4. Thermocouple
5. Barrel
6. Threaded shaft
7. Gears
8. Variable speed motor
9. Miniature wind-up mechanism

Plate I. Spinning Apparatus

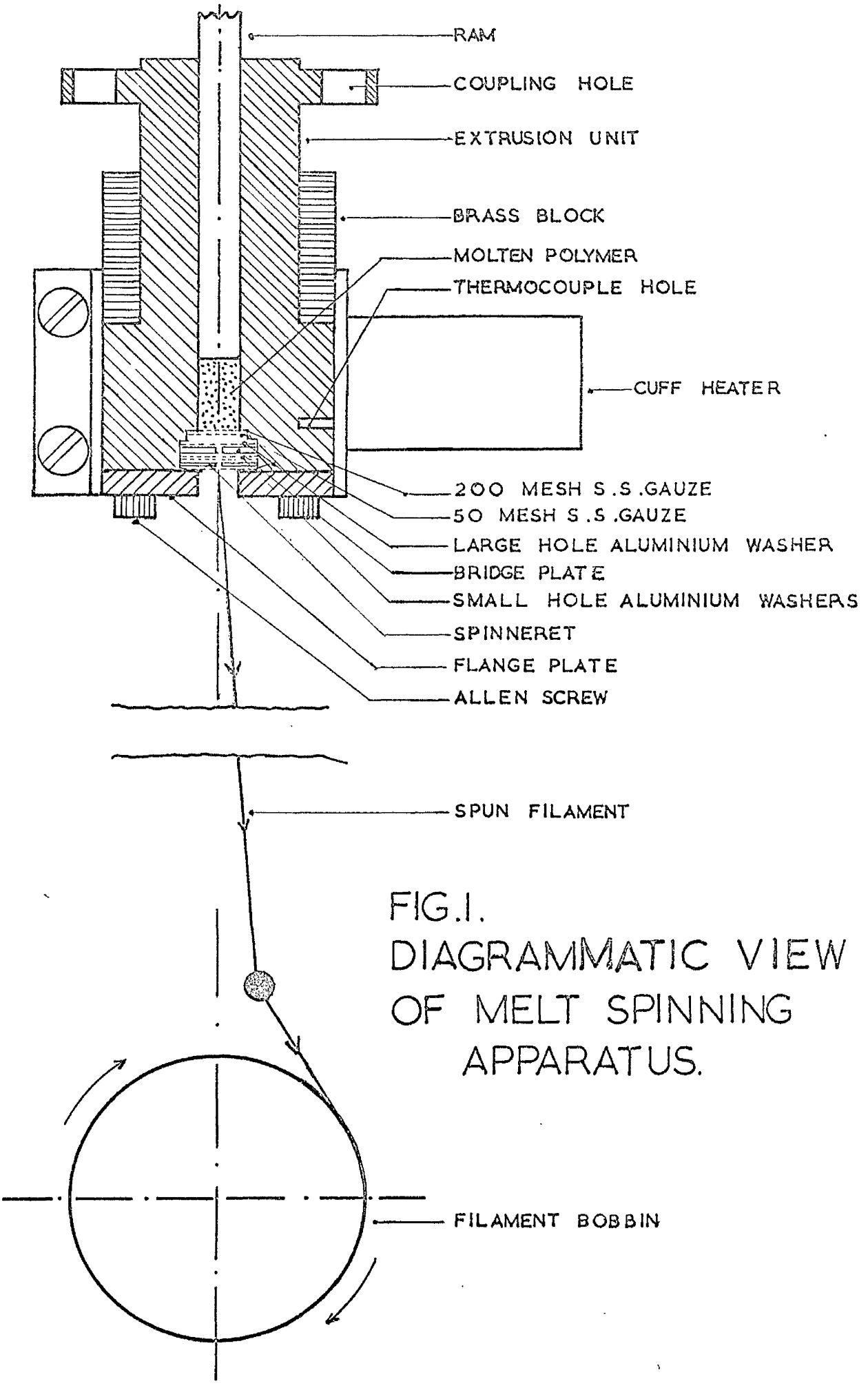


FIG.1.
DIAGRAMMATIC VIEW OF MELT SPINNING APPARATUS.

2.1 Description of the Apparatus

The apparatus used for these investigations can be divided into two major parts:

2.11 Melt Spinning

and

2.12 Hot Drawing

2.11 Melt Spinning Apparatus

This instrument was supplied by I.C.I. Ltd., (see Plate I). The diagrammatic front view of the spinning apparatus is drawn in Figure 1. The preparation of polymer "candle" from polymer chips, and its melt-spinning, can be very easily carried out on this spinning apparatus. The main sections of the melt spinning device are as follows:

2.111 Extrusion unit

2.112 Temperature control unit

2.113 Driving mechanism

2.114 Winding unit

2.111 Extrusion unit

The extrusion unit is a solid block of polished drawn stainless steel, with a through hole of 0.25 in. diameter at the

/centre

centre (see full size sketch in Figure 1). The lower end of this hole is 0.5 in. in diameter, in order to accommodate the necessary filters, bridge plate and spinneret. The 0.094 in. thick metallic bridge plate has a centre hole of 0.06 in. diameter, while the metallic spinneret is only 0.03 in. thick with a centre hole of 0.015 in. diameter. A solid stainless steel ram, 2.5 in. long and 0.25 in. in diameter is used to force the viscous molten polymer through the spinneret at constant speed, the upper end of the ram being attached to the driving mechanism. Vertical movement of the ram can also be obtained by the handle (see Plate I), situated at the top of the apparatus. This manual operation is useful when the preparation of polymer "candle" is carried out. Before spinning it is important to check that the ram moves straight inside the extrusion unit.

During the melt spinning process, it is essential to observe that the ram does not move inside the extrusion unit beyond the specified limit (length of the ram), otherwise

/the

the soft silver steel shear pin, connected to the gear, may break and disturb the driving mechanism.

In the preparation of polymer "candle" from polymer chips, the bridge plate and the spinneret are replaced by a vacuum tube, (see Plate I) which makes an airtight fitting with the bottom end of the extrusion unit when held in position by the flange plate. The flange plate also ensures that there is no leakage of the polymer during extrusion. The extrusion unit is fixed at the appropriate position in the spinning apparatus (see Plate I) by two allen screws. All the screws used were greased with silicone grease in order to avoid sticking to the metal when hot.

2.112 Temperature control unit

Brass blocks and cuff heater are placed on the extrusion unit as shown in Figure 1. The function of the brass blocks is merely to increase the effective heating area. The cuff heater is connected to a Variac with a variable voltage capacity of from 0 to 260 volts; thus

/the

the required temperature of the polymer can be maintained by adjusting the Variac. A Pye Scalamp Thermocouple Galvanometer (see Plate I) provides an accurate and rapid means of determining temperature through the ranges 0-150°C and 0-300°C, using a thermocouple as a temperature sensing device. One of the main features of this galvanometer is the automatic 'cold junction' compensating device. On compensated ranges one can directly measure the true temperature of the hot junction. The galvanometer gives a direct reading in degrees Centigrade when connected to a Copper/Constantan thermocouple (see Plate I) of 30 ohms resistance. This thermocouple is made by hard soldering "Advance" wire (resistance = 6.9 ohms/ft.) with enamelled copper wire (resistance 0.1 ohms/ft.) at one end and then covering these wires with two inch twin bore ceramic insulators. The thermocouple leads are connected to the galvanometer and the thermocouple is placed at the hot junction inside the thermocouple hole

/of

of the extrusion unit. This enables direct measurement of the true temperature of the polymer.

2.113 Driving mechanism

The threaded upper end of the ram is screwed to a barrel of bright drawn steel (see Plate I). This barrel, through a threaded shaft, is further connected to a system of gears which, in turn, is driven by the main driving shaft coupled with a variable speed motor (see Plate I). Thus the speed of the motor can be varied accurately between 60 and 200 r.p.m., giving a ram speed of from 0.75 in./min. to 1.3 in./min. The speed of the motor, and hence the ram, can be accurately measured with a standard tachometer.

2.114 Winding unit

This unit is a miniature wind-up mechanism (see Plate I) consisting of a hollow aluminium reel called a filament bobbin (see Figure 1). A variable speed motor (100-600 r.p.m.) is the main source of power for the axial rotation of this bobbin. The miniature wind-up mechanism has a movable metal guide so that the filament

/emerging

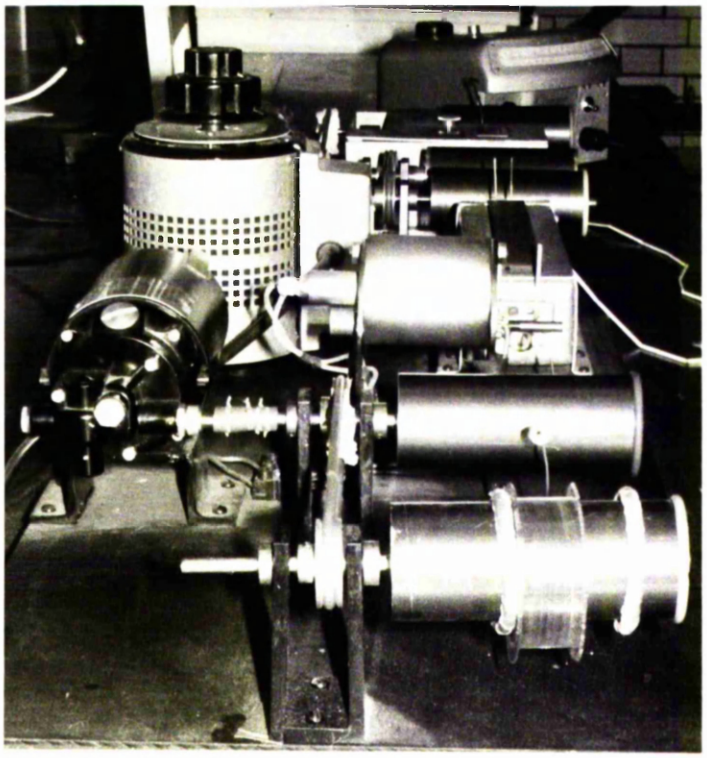


Plate II. Continuous hot drawing apparatus

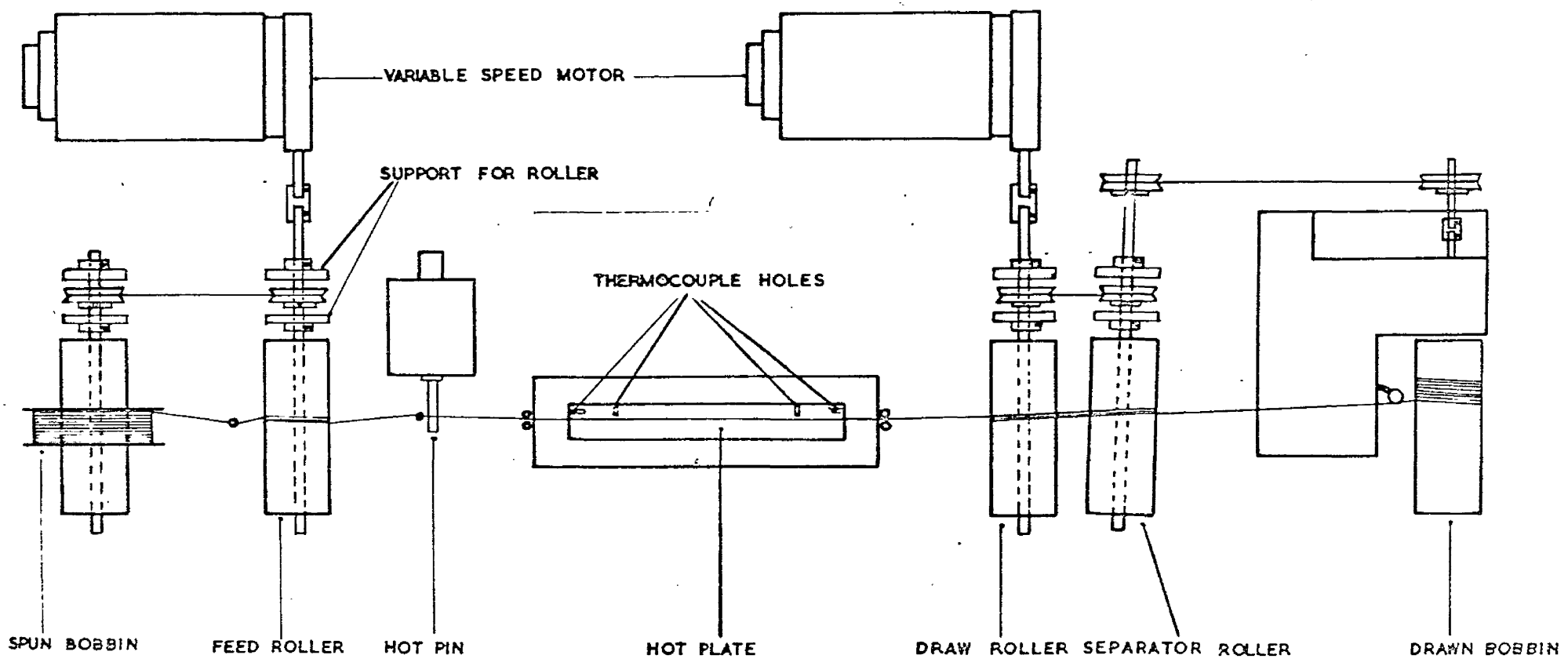


FIG.2. SKETCH OF CONTINUOUS HOT DRAWING APPARATUS

emerging from the spinneret can be evenly wound on the filament bobbin. This bobbin is 4.75 in. long and 1.875 in. in diameter. A shaft passing through this metal roller is connected to the above-mentioned variable speed motor. This enables accurate control of the surface speed of the filament bobbin, between 100 ft./min. and 500 ft./min. The speed of the filament bobbin can be accurately measured by a standard tachometer. The distance between the spinneret and the filament bobbin is maintained at 18 in. so that the spun filament acquires normal room temperature during its passage from the spinneret to the filament bobbin.

2.12 Hot Drawing Apparatus

A general sketch of this apparatus which was designed and constructed in the laboratory (for photograph see Plate II) is given in Figure 2. Hume[44,45] and others[11,46] have worked successfully on a similar unit. The essential features of the apparatus can be described under three main headings:

/2.121

2.121 Feeding unit

2.122 Temperature control unit

2.123 Drawing unit

2.121 Feeding unit

This, essentially, consists of two aluminium rollers, 4.75 in. long with diameters of 1.875 in. These rollers are supported on a wooden bobbin through the centre of which runs a metal shaft, 0.25 in. diameter, connected to a variable speed motor (60-200 r.p.m.) (see Figure 2). The speed of the feed roller (one of the above-mentioned rollers) can be kept constant at any linear speed between 50 ft./min. and 150 ft./min. The spun filament of the polyethylene terephthalate can be transferred to a spun filament bobbin for storage. This bobbin is made of plastic and is 2.5 in. diameter. This unit is further used for the hot drawing of the filament. The distance between the spun filament bobbin and feed roller is kept at 7.25 in. There is a porcelain guide between them.

/2.122

2.122 Temperature control unit

This unit consists of two main parts:

Hot pin and

Hot plate

Hot pin

Hot pin

This is a round stainless steel metal rod of 0.25 in. diameter and 1.25 in. long, situated 5 in. from the feed roller (see Figure 2). This pin is screwed to a heater with a built in thermostat. The heater and thermostat of the hot pin are connected in series with a Variac (see Plate II). The voltage on the Variac should not be increased beyond the capacity of the heater (50 volts). Any desired temperature of the hot pin can be maintained either by altering the Variac or the thermostat. The true temperature at which primary drawing occurs is the temperature at the surface of the hot pin. By proper contact between the thermocouple hot junction and the hot pin, the temperature of the latter can be directly measured on the Pye Scalamp Thermocouple Galvanometer (described in detail in the

/paragraphs

paragraphs on the temperature control unit).
A porcelain guide is fixed in front of the hot pin, but at a lower level, so as to obtain an arc of 120° between the hot pin and the filament.

Hot plate

This is a 1" x 8" rectangular metal plate, slightly convex in shape, with a decrease in thickness from the centre (0.3 in.) towards each end (0.125 in.). The distance of the centre of the plate from the hot pin is 9 in. (see Figure 2). In order to ensure that the filament, during the drawing process, touches the surface of the hot plate two metal guides (see Plate II) are situated at each end of the hot plate. The hot plate is provided with a 50 volt capacity heater and a thermostat.
The source of heat and temperature control for the metal plate is exactly the same as in the hot pin system described earlier.
The whole hot plate unit is firmly supported on a wooden block with an asbestos sheet placed between them. The true temperature at which secondary drawing occurs is that of the surface

/of the

of the hot plate. This temperature can be measured by placing the hot junction of the thermocouple on the surface of the hot plate, and can be directly read on the Pye Scalamp Thermocouple Galvanometer.

By using the hot pin and hot plate thermal drawing of the filament in two stages is possible.

2.123 Drawing unit

This essentially consists of three hollow aluminium rollers, viz. draw roller, separator roller and drawn filament bobbin (see Figure 2). These rollers are of the same dimensions as those described in the feeding unit, and are supported in the same way. The draw roller is driven through a shaft of 0.25 in. diameter by a variable speed motor (100-600 r.p.m.), which in turn drives the separator roller and drawn filament bobbin through a simple device of light aluminium pulleys and P.V.C. belts (see Figure 2). These three rollers rotate at the same surface speed which can be varied from 100 ft./min. to 300 ft./min. The axis of the draw roller

/is situated

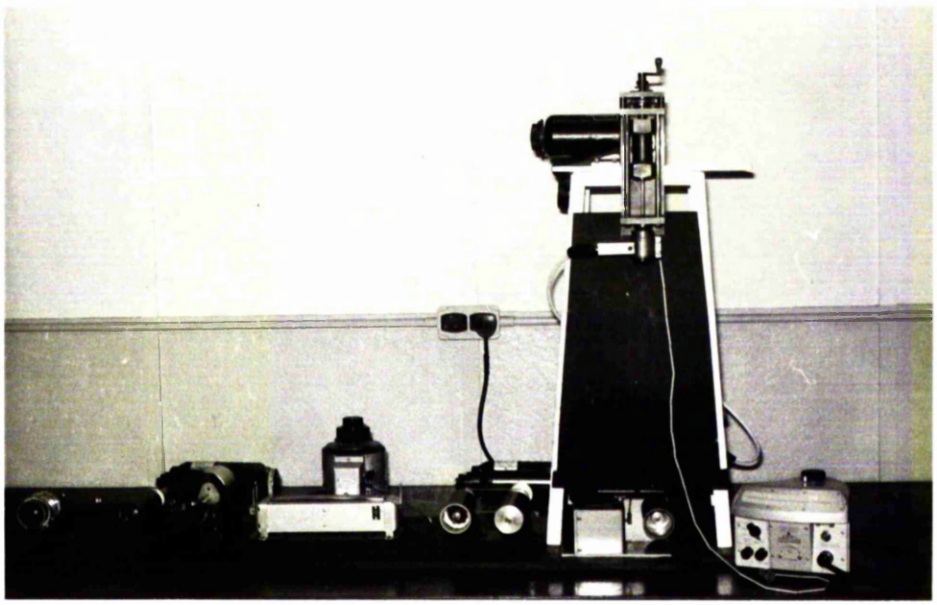


Plate III

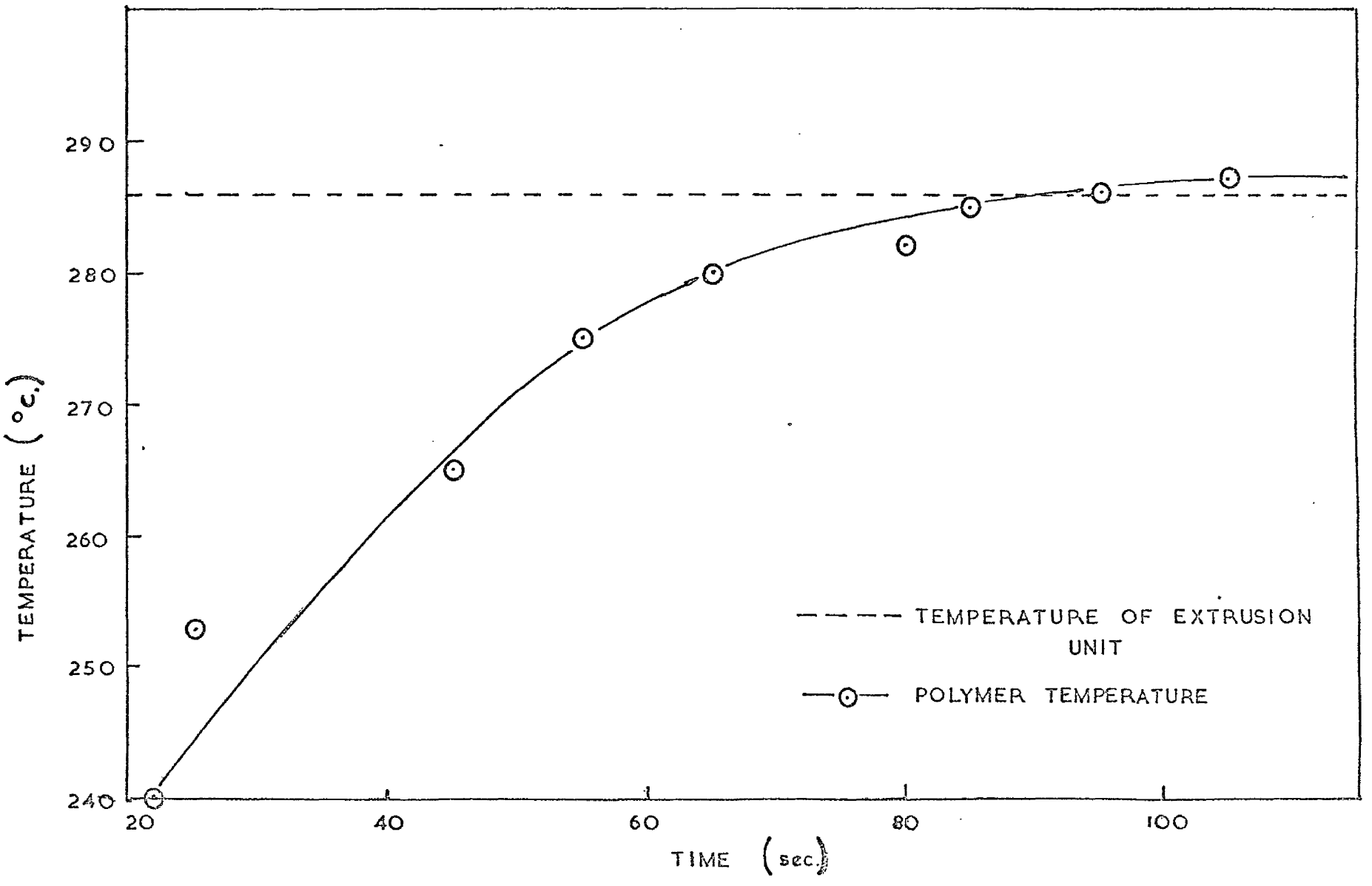
A combined view of spinning and drawing apparatus

roller is situated at 10 in. from the centre of the hot plate and 5.5 in. from the axis of the separator roller. These rollers are slightly inclined to each other in order to avoid entanglements. The distance between the axis of the separator roller and the axis of the drawn filament bobbin is 12 in.

The photograph of the spinning and drawing apparatus together is shown in Plate XXI.

FIGURE 3

INCREASE IN POLYMER TEMPERATURE WITH TIME



2.2 Experimental Procedure

2.21 Calibration of Apparatus

Prior to the actual experiments it was thought necessary to calibrate the spinning and the drawing device in order to determine experimental accuracy.

2.211 Accuracy of polymer melt temperature control

A calibration was carried out to determine the proper temperature conditions to be maintained for accurate melt spinning. The extrusion unit was heated to 286°C (as read on the Pye Scalamp Thermocouple Galvanometer). The polymer "candle" was then inserted from the top end of the extrusion unit, and immediately the hot junction of the thermocouple was pushed through the lower end into the molten polymer. It was noticed that there was a gradual increase in the thermocouple temperature. This gradual increase in polymer temperature, with time in seconds, was recorded from the galvanometer (see Figure 3).

/From

From this graph it appears that in about 110 seconds the temperature of the polymer reaches a steady and constant value which is 1°C higher than that obtained by the thermocouple through the thermocouple hole. Thus, throughout the experimental investigations the true temperature of polymer melt was recorded as the actual temperature, in degrees Centigrade, read on the thermocouple galvanometer, plus one degree Centigrade. This calibration proves that the polymer candle should be heated at the required temperature for at least two minutes, before it is actually spun, to achieve uniform temperature of the melt.

2.212 Variation in the ram speed during melt spinning.

Spinning was carried out at 0.8"/min. and 1"/min. ram speed at 285°C. (see page 57) At different intervals of time, during spinning, samples were collected for the period of 10 seconds and weighed. The results obtained are tabulated in Table I. These results indicate that there is about 5% decrease in

/the

the denier of the filament during spinning, which implies that the speed of the ram slightly decreases as spinning progresses.

There seems to be a logical explanation for this decrease in ram speed during melt spinning. As the spinning progresses friction is developed between the walls of the centre hole of the extrusion unit and the ram passing through this hole. This is because, during spinning, a coating of polymer melt is left between the walls of the centre hole of the extrusion unit and the ram. This frictional force increases as the ram moves downwards inside the extrusion unit because more and more polymer melt sticks in the gap between the ram and the centre hole of the extrusion unit. This continues till the end of the spinning operation hence decreasing the speed of the ram.

2.213 Accuracy of hot plate temperature control

The temperature of the hot plate was measured by placing the thermocouple inside the thermocouple holes on the surface of the hot plate. The temperature measured through the thermocouple

/holes

holes was found to be 2°C higher than that found at the surface of the hot plate. This difference in the surface temperature of the hot plate can be accounted for as loss of heat through radiation and convection. For actual experimental purposes the temperature of the hot plate was directly measured by the thermocouple contact with the surface of the plate.

2.22 Preparation of the Polymer "Candle" for Spinning.

In molten polyethylene terephthalate some degradation may occur; to prevent this the polymer chips were dried in an open oven for two hours at 165°C before being used for the preparation of "candle".

Polyethylene terephthalate can be moulded into the form of a rod in the apparatus described in Figure 1. At the lower end of the extrusion unit filters were inserted in the following order:

(1) 200 mesh stainless steel gauze (filter)

(2) 50 mesh stainless steel gauze (filter)

(3) Two or three large hole aluminium washers.

The vacuum tube (see Plate I) was fitted on

/filters

filters which were then secured by a flange plate. Several large hole aluminium washers were used in order to avoid leakage of polymer at the flange plate. The extrusion unit was then fixed to the main spinning apparatus and the brass blocks and cuff heater were attached as shown in Figure 1. The temperature of the extrusion unit was maintained at 240°C, which is slightly higher than the softening temperature of Terylene. This temperature was achieved by adjusting the voltage of the Variac to 160 volts, and was measured on the Pye Scalamp Thermocouple Galvanometer.

Moisture free polymer chips were inserted into the top of the extrusion unit. The "candle" was formed by the ram pressure on these polymer chips under vacuum at 240°C. The purpose of this vacuum was to prevent air bubbles being moulded into the candle and interfering with spinning. After applying ram pressure for 4 minutes the extrusion unit was cooled quickly by a blast of compressed air. The flange plate and vacuum tube were removed and the "candle" was pushed out by

/hand

hand control of the ram and a small metal rod. A number of such polymer "candles" were prepared before the actual spinning was started. The "candles" had an average weight and dimensions of 1.5 gm., 0.25" diameter and 1.5 in. length. These candles were stored in a moisture free desiccator.

2.23 Melt Spinning

The lower wide opening of the extrusion unit was packed much as described above with various filters, washers, etc. in the following order:

(1) 200 mesh stainless steel gauze (filter)
(2) 50 mesh stainless steel gauze (filter)
(3) Large hole aluminium washer
(4) Bridge plate
(5) Three small hole aluminium washers
(6) Spinneret
(7) Large hole aluminium washer

The extrusion unit was then packed tightly with the flange plate. Several small hole aluminium washers were used in order to avoid a leakage of polymer at the flange plate. The extrusion unit was then fitted on the main spinning apparatus and brass blocks and

/cuff

cuff heater were placed at appropriate positions as shown in Figure 1. The spinning temperature was maintained at 285°C. A polyethylene terephthalate "candle" was then inserted in the extrusion unit. The polymer was kept for two minutes in the molten state before it was extruded. The temperature of the polymer fell by about 2°C during this period. In order to avoid sticking of the filaments when they emerge through the spinneret, silicone oil was sprayed at that end of the extrusion unit.

Spinning was commenced by setting the ram in motion against the polymer at the predetermined rate. As soon as the filament emerged through the spinneret and congealed it was picked up by a rapidly revolving filament bobbin (see Figure 1).

Three different ram speeds, i.e. 0.8"/min., 1"/min. and 1.25"/min. were used during melt spinning. Three different speeds of the filament bobbin were used for each of the above speeds, ranging from 425 ft./min. to 150 ft./min. These corresponding speeds are given in

/Table II

Table II with extrusion speeds in gm./min.

$$\text{Extrusion speed in gm./min.} = \frac{\text{filament bobbin speed in ft.} \times 0.3048 \times \text{denier}}{9{,}000}$$

where 1 ft. = 0.3048 m.

2.24 Hot Drawing

Spun continuous filament of polyethylene terephthalate was first of all transferred to a "spun filament bobbin" which was then attached in position for drawing (see Figure 2). The filament was led from the spun bobbin, through a porcelain guide, on to the feed roller round which it was turned twice (see Figure 2). The purpose of the feed roller is to deliver the filament at a constant rate hence more than one turn was required to prevent slippage. From the feed roller the filament was passed over to the hot pin, through another guide, maintained at 90°C. The filament was then passed through a pair of guide bars over the hot plate maintained at 95°C. After leaving the hot plate through a similar pair of guide bars the filament was wound round separator and draw rollers at least three times (see Figure 2) in order to prevent slippage and also

/to help

to help cool the filament before releasing it from tension. The drawn filament was finally wound on to the winding device called the drawn filament bobbin. A movable guide attached to the winding device assists in obtaining uniform winding of the filament.

The surface speed of the feed roller was kept constant throughout, e.g. 50 ft./min. and the surface speed of the draw roller was varied according to the required draw ratios. In practice three draw ratios were chosen, i.e. 2:1, 3.5:1 and 5:1 on all the samples of melt spun filaments. These draw ratios correspond to the differential speed ratios of the draw roller and the feed roller.

A separate experiment was carried out to find the effect of hot plate temperature on the physical properties of the filament. The temperature of the hot plate was increased from 95°C to 115°C and 130°C, keeping all other factors constant; i.e. filament produced at a rate of extrusion of 0.915 gm./min., winding speed 300 ft./min. was drawn at a

/5:1

5:1 draw ratio at each of these three hot plate temperatures.

Note:

The main difficulty in using a continuous drawing apparatus is that it can be operated only within a limited range of conditions. Out-side this range the filament either breaks or becomes non-uniform.

2.3 Determination of Fibre Properties

2.31 Measurements of Diameter and Denier

Diameters of all the samples, mounted in paraffin, were measured on a standard polarisation microscope. Each sample was measured at three different places along the length of the filament with three readings each time. The mean of these readings was taken as the average diameter of the sample.

Measurements of the deniers of all the samples were carried out on the precision torsional balance of 50 mg. capacity. A test length of 90 cm. was selected for each observation. Five readings were taken for each sample. The mean of these readings was taken as the average denier of that sample.

2.32 Measurement of Tensile Properties

With a specimen length of 2 in., load/extension curves of all the samples were obtained on an Instron tester at a constant rate of extension of 1.66%/sec., the cross head speed was fixed at 2"/min., and chart

/speed

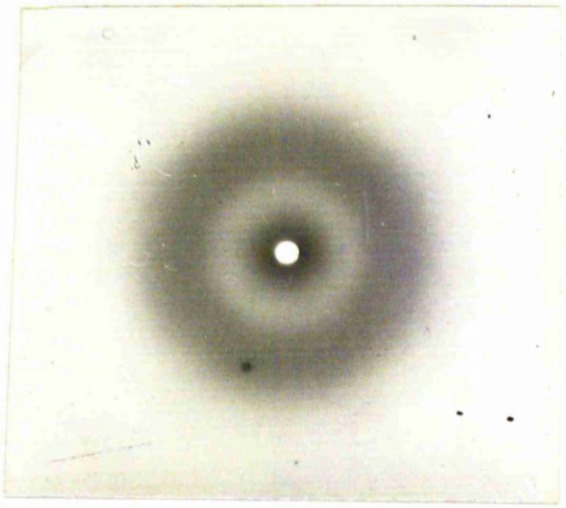


Plate IV

An X-ray photograph of undrawn

polyethylene terephthalate filament

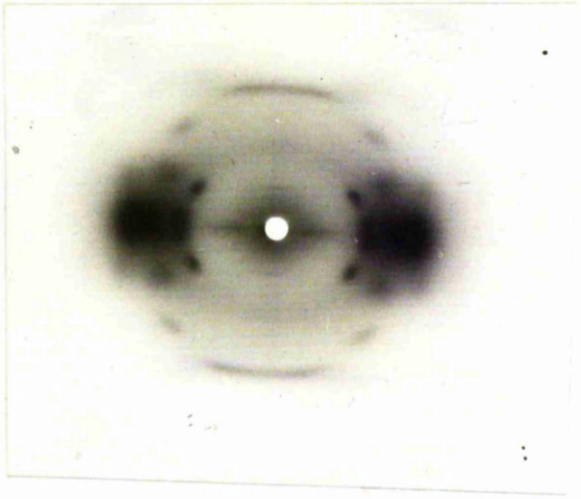


Plate V

An X-ray photograph of drawn

polyethylene terephthalate filament

speed at 2"/min. and 20"/min. (to obtain values of initial modulus and yield stress). These tests were carried out under standard conditions of 20°C ± 2°C and 65% ± 2% R.H. From these load/extension curves values of initial modulus, yield stress, breaking stress and breaking extension were determined on the original cross section of the specimen.

2.33 Measurement of Combined Orientation and Crystallinity.

An X-ray photograph of a filament of polyethylene terephthalate, spun at a rate of extrusion of 0.915 gm./min., and winding speed of 300 ft./min. was taken. Another photograph was taken of the same filament but drawn at 5:1 ratio on hot drawing apparatus. Both these fibre photographs were taken on a standard X-ray equipment and are shown in Plates IV and V.

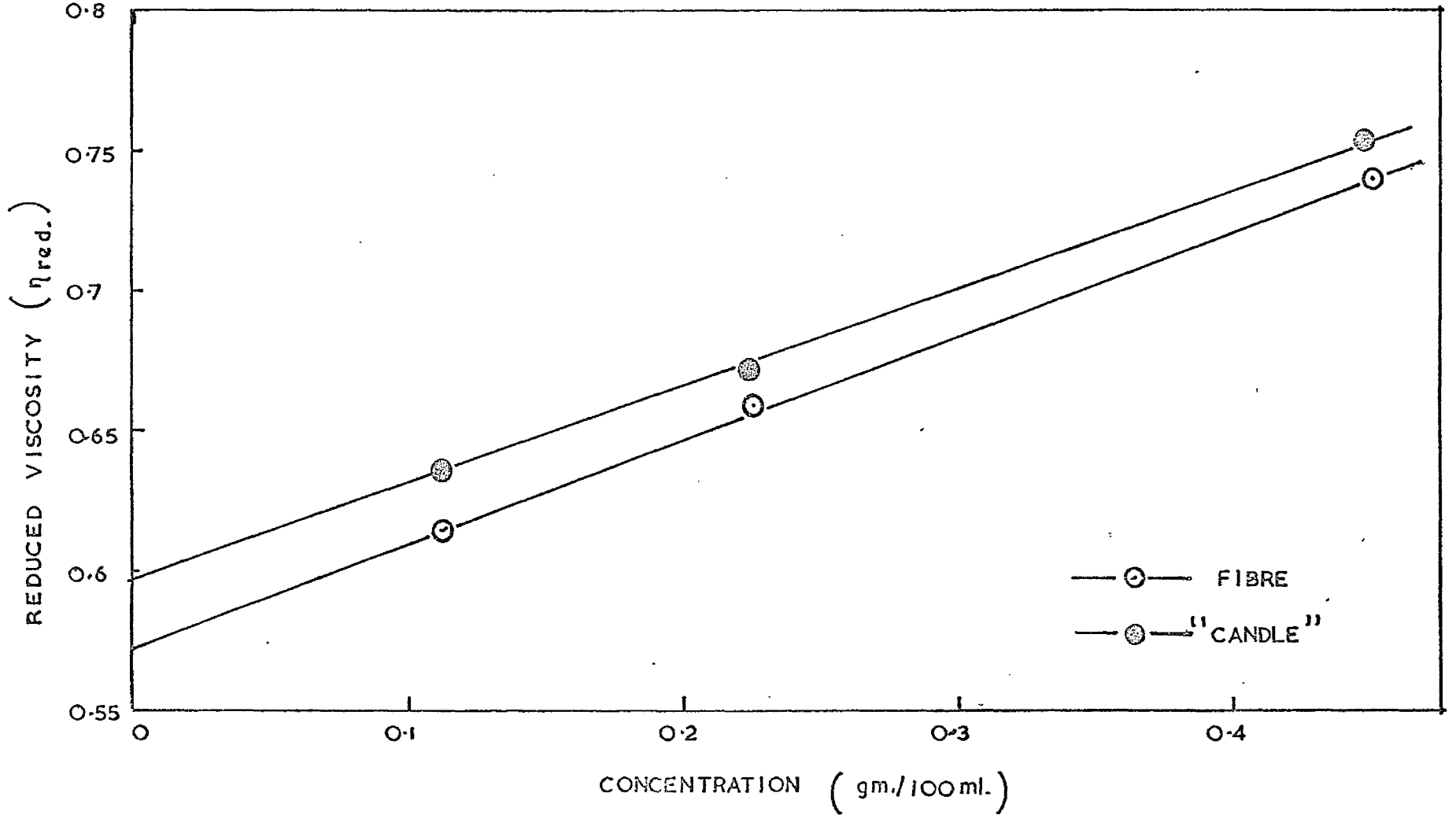
2.34 Measurement of Viscosity-Average Molecular Weight

The viscosity-average molecular weight of polyethylene terephthalate can be obtained by measuring the intrinsic viscosity of the polymer in various solvents.[80,81,82] The intrinsic viscosity of the polyethylene terephthalate fibre and polymer "candle" were determined in

/this

FIGURE 4

DETERMINATION OF INTRINSIC VISCOSITY OF FIBRE AND POLYMER "CANDLE"



this work using a solvent containing a mixture of tetrachloroethane:phenol (50:50) at 20°C.

The actual procedure for the measurement of viscosity was as follows:

About 0.5 gm. dried polyethylene terephthalate was accurately weighed out and dissolved in 100 ml. of solvent. The relative viscosity of the solution was determined in a U-tube viscometer at 20°C, by measuring the time in seconds for the fall of solution from the upper to the lower meniscus. The time of flow for each solution of three different concentrations and for the solvent was determined three times and averaged. The results are tabulated in Table III.

Intrinsic viscosity $[\eta]$ was determined from the following relationship:

$$[\eta] = \text{Limit}_{C} \left(\frac{\eta_{sp}}{C} \right)$$

where η_{sp} is the specific viscosity and C is the concentration of solution. Reduced viscosity $\frac{\eta_{sp}}{C}$ is plotted against concentration C in Figure 4. From this curve, at zero

/concentration

concentration, intrinsic viscosity can be obtained. Knowing the intrinsic viscosity $[\eta]$ of the fibre and the polymer "candle", the viscosity average molecular weight $\overline{M}_v$ was determined from the formula:

$$[\eta] = 1.27 \times 10^{-4} \overline{M}_v^{0.86}$$

2.35 Measurement of Density

Determination of the density of polyethylene terephthalate "candle" by the floatation method:

The density of a small piece of polymer "candle" was measured by this method[83] at 20°C. Polymer "candle" was placed in boiling xylene for 2 minutes to remove entrapped air. The "candle" was then transferred to a 50 ml. capacity centrifuge tube containing a mixture of carbon tetrachloride and xylene of approximate density 1.38 gm./cm.^{3} and centrifuged for 2 minutes at about 2,000 r.p.m. If the candle had either risen to the surface or sunk to the bottom, after this, it would have been concluded that the polymer was either lighter or heavier, respectively, than the liquid. Xylene or carbon tetrachloride was then added and centrifuging repeated until the

/"candle"

"candle" was suspended half way in the tube. At this time the density of the "candle" was the same as that of the immersion mixture, which was then determined by specific gravity bottle method.

Determination of the density of polyethylene terophthalate filament by density gradient tube:

Some workers[83-88] have measured the density of fibres using different types of density gradient tubes, with different techniques. In this work the density of the polyethylene terophthalate filament was measured by a density gradient tube,[85] about 65 cm. long, at 20°C. A density gradient tube was prepared, containing a mixture of carbon tetrachloride (sp. gr. 1.60) and xylene (sp. gr. 0.87), and was calibrated by a series of small glass floats of known density. The density of the liquid from the top to the bottom end of the tube was found to vary from 1.303 to 1.454 gm./cm.^{3} The filament was boiled in xylene for 2 minutes to remove entrapped air and then immediately dropped

/into

into the density gradient tube. It sank until it reached the level corresponding to its own density. After some time, when the filament reached a stable equilibrium, the level was noted with a travelling microscope. The density of the filament was obtained from a graph of density against height of column. Two readings were taken for each sample of filament.

2.36 Measurement of Modulus of Rigidity

The torsional rigidity, i.e. initial resistance to twisting, is defined as the couple needed to obtain unit twist; i.e. unit angular deflection between the ends of a specimen of unit length. It is proportional to the product of modulus of rigidity and square of area of cross-section. The modulus of rigidity or shear modulus is defined as the ratio of shear stress to shear strain, i.e. a measure of inherent resistance of the fibre material to a change of shape.

The modulus of rigidity of polyethylene terephthalate filament was measured[89] by the torsion pendulum method at 20 ± 2°C. and

/65 ± 2% R.H.

65 ± 2% R.H. Six inertia bars were calibrated and used for the measurement of modulus rigidity. The moment of inertia of these bars was measured by three different means.(see Table IV). All the three methods give close agreement. Moments of inertia obtained from comparison with bars of known length and weight were used in the calculation of modulus of rigidity.

One end of the 3 cm. long filament was mounted, with molten brown wax, to the inertia bar and the other end to the stirrup. This was hooked on to a wire frame, kept inside the glass vessel, so that the unit forms a torsion pendulum. Five torsion pendulums were prepared for each sample. The period of oscillation was measured by displacing the inertia bar from its equilibrium position and timing five oscillations, three times for each pendulum. The free length of the filament was measured with a travelling microscope (accuracy 0.02 mm.) and the mass/unit length of the same was determined by measuring the weight of measured length, on a cantilever microbalance.(accuracy 0.00357 mgm.)

(0.00357 mgm.).

Modulus of rigidity (G) was calculated from the equation:[69]

$$G = \frac{8\pi^2 I \ell \rho^2}{T^2 m^2 \varepsilon}$$

where

I = moment of inertia of inertia bar, gm.cm.^{2}

ℓ = free length of mounted filament, cm.

ρ = density of filament, gm./cm.^{3}

T = mean period of oscillations, sec.

m = mass per unit length, gm./cm.

ε = shape factor which equals unity for Terylene.

2.37 Measurement of Birefringence and Orientation Factor

Birefringence is related to the internal (molecular) structure of any compound. When plane polarised light is passed through an anisotropic body, e.g. a fibre, the transmission velocity of the light will be different in one direction from that in the other direction for the same wavelength. Birefringence is a numerical difference between the refractive index along the fibre axis and the refractive index across the fibre axis.

/A fibre

A fibre will be positively birefringent if the refractive index parallel to the fibre axis is greater than the refractive index perpendicular to the fibre axis.

Polyester fibres are known to have practically the highest birefringence of all the synthetic fibres.[90] Measurement of birefringence of polyethylene terephthalate fibre, however, causes several difficulties. The refractive index of Teryleno is about $n_{\parallel} = 1.725$ and $n_{\perp} = 1.537$. Hence the difference of these values (i.e. birefringence) is usually about 0.188. The most commonly used method of measuring birefringence of fibres is the immersion method developed by Bèeke.[90] As the refractive index of Teryleno is very high there are not many suitable immersion liquids. This method is laborious. This makes the method unsatisfactory. Commonly used compensators[90] (the Berek compensator) for measuring retardation and hence birefringence, have limited ranges. The determination of the birefringence of polyethylene terephthalate fibre by visual examination of the polarisation colour becomes impossible since at the higher

/orders

orders the colour becomes less distinctive and very closely spaced. Even the use of retardation plates or a quartz wedge is hampered at the high interference orders, which may be encountered with Terylene.

Owing to these difficulties a modified compensator method was used. The birefringence of filaments were measured by Mercer's method, as described by Quynn and Steele,[91] and Mares,[92] at 20°C. A flat wedge was obtained, by obliquely cutting the end of the filament with a sharp razor blade. The filament specimen was then mounted in paraffin.

A polarisation microscope was set as follows:

The vibration plane of the polariser was oriented into the 90° position and that of the analyser into the 0° position. A quarter wave plate (mica) was inserted into the tube slots, below the analyser, with its vibration direction at extinction, i.e. parallel with the principal planes of the polarising unit. If the field of vision remains dark the microscope setting is correct.

When the fibre was lying with the oblique area

/upwards

upwards, the black interference rings were counted with cross-polaroids, in monochromatic light provided by a sodium vapour lamp. The filament was adjusted in 45° position during measurement, where its centre appears brightest. The number of such interference rings, plus one, gives directly the order of interference. The last fraction of the wavelength lag was measured by using a Sênarmont compensator (by using a quarter wave plate with a rotatable analyser). This was achieved by turning the analyser so as to make both interference rings that are nearest to the fibre centre melt into each other, i.e. the angle θ ($< \pi$ radians) was measured by turning the eye-piece analyser (which can be rotated through 360°), in order to produce the extinction down the centre of the filament. Finally the diameter was measured with great accuracy.

Birefringence was calculated from the equation:

$$n_{\parallel} - n_{\perp} = \frac{(\theta + n\pi)\lambda}{\pi d}$$

where

n = number of interference rings seen on the fibre wedge in monochromatic light

/ $\pi = 180^{\circ}$

$\pi = 180^{\circ}$

λ = wavelength for monochromatic light which is 589.3 mμ.

d = diameter of filament in mμ.

Birefringence was measured twice for each sample of polyethylene terephthalate and averaged. This method is more suitable for fibres with perfectly circular cross-sections.

The birefringence of a fibre is related to how well the polymer molecules are oriented and may be regarded as a measure of the average orientation of all the molecules whether in the crystalline or amorphous regions. The measurement of orientation is complicated in the fibre as it is a non-homogeneous material consisting of crystalline and amorphous phases. Herman[93] has defined the orientation factor (f) as

$$f = \frac{n_{\parallel} - n_{\perp}}{n_{\gamma} - n_{\alpha}} \cdot \frac{d_{cr}}{d}$$

where $n_{\gamma} - n_{\alpha}$ is the birefringence of perfectly oriented specimen and d_{cr} is the density of the crystalline fibre.

Palmer[69] has obtained a value of 0.212 for a

/theoretical

theoretical maximum birefringence ($n_{\gamma} - n_{\alpha}$) of a set of uniaxially oriented crystallites of polyethylene terephthalate using polarisation data published by Daubeny and Bunn.[94] The density[94] of perfectly crystalline polyethylene terephthalate filament has been found to be 1.455 gm./cm.^{3} Thus, if birefringence and density of polyethylene terephthalate filament is known, the orientation factor can be found. Knowing the orientation factor (f), the average angle of orientation (ϕ) can be obtained from the equation:[93]

$f = 1 - 3/2\sin^2\phi$

CHAPTER III

RESULTS AND DISCUSSIONS

CONTENTS

3. RESULTS AND DISCUSSIONS

The influence of melt spinning conditions viz: rate of extrusion, winding speed, draw ratio and hot plate temperature on some of the physical properties of a polyethylene terephthalate fibre have been studied in the course of this research. It is obviously important, before discussing the influence of spinning conditions on properties, to examine the effect of spinning conditions on the molecular weight of the polymer. The results of all these experiments are given and discussed in this chapter.

3.1 Variation of Molecular Weight during Melt Spinning:

Synthetic high polymers are heterogeneous, being composed of long chain molecules of different chain lengths. The molecular weight of any polymer is therefore an average molecular weight and different kinds of average molecular weight can be measured depending upon the experimental method used.

Ideally, the molecular weight should remain constant during spinning and drawing, since it is well known that a fall in molecular weight causes the physical properties to deteriorate. The intrinsic viscosity (η) of a polymer "candle" and of polyethylene terephthalate filament was found, using

/the method

the method described previously, to be 0.60 and 0.57 respectively (see Figure 4). From those results the molecular weight of polymer "candle" and polyethylene terephthalate filament was found to be 18,700 and 17,700 respectively. This represents a slight fall in molecular weight during the spinning and drawing processes, which may be due either to oxidative degradation or chain scission during shearing. This fall in molecular weight is, however, not large enough to have any significant effect on the physical properties of the fibre.

3.2 Influence of Rate of Extrusion on Fibre Properties at Various Draw Ratios

In order to examine the influence of the rate of extrusion on final fibre properties, a series of experiments were carried out in which all the experimental conditions except extrusion rate were kept constant. In each experiment three rates of extrusion (i.e. 0.712, 0.915 and 1.212 gm./min.) were used. Since there was also the possibility of draw ratio influencing these results, the resultant filaments were drawn at draw ratios of 2:1, 3.5:1 and 5:1. These results, coupled with those on the undrawn filament (1:1) enabled the data to be examined from the point of view of influence of the rate of extrusion on properties over the range of draw ratios.

3.21 Influence of Rate of Extrusion on Tensile Properties

As described in Chapter II, the tensile properties measured were: initial modulus, yield stress, breaking stress and breaking extension.

Initial modulus, yield stress and breaking stress were calculated on the original area of cross-section as determined by measuring the mass per unit length and dividing by density.

/Yield

FIGURE 5

INFLUENCE OF RATE OF EXTRUSION ON INITIAL MODULUS AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO

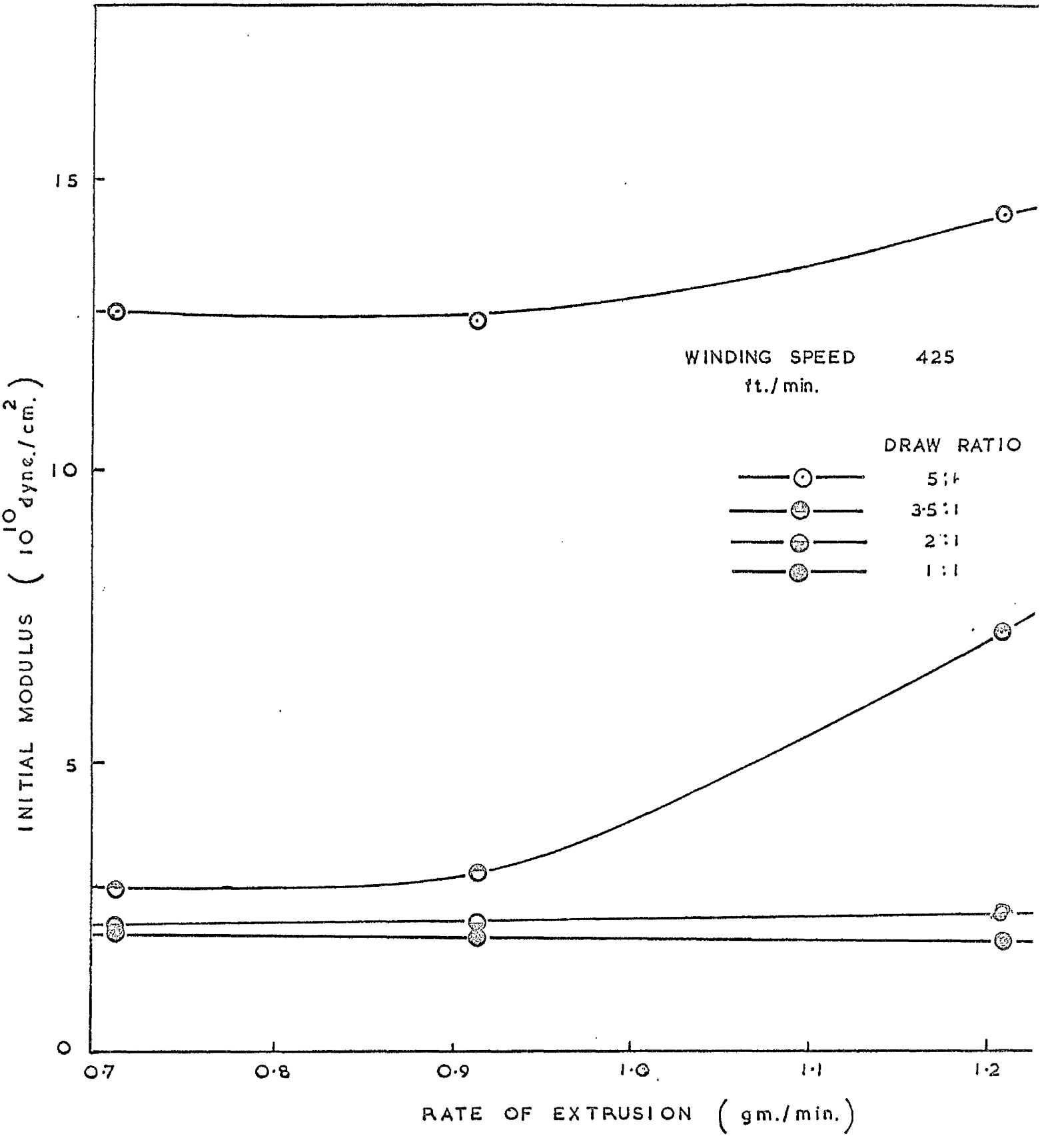


FIGURE 6

INFLUENCE OF RATE OF EXTRUSION ON YIELD STRESS AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO

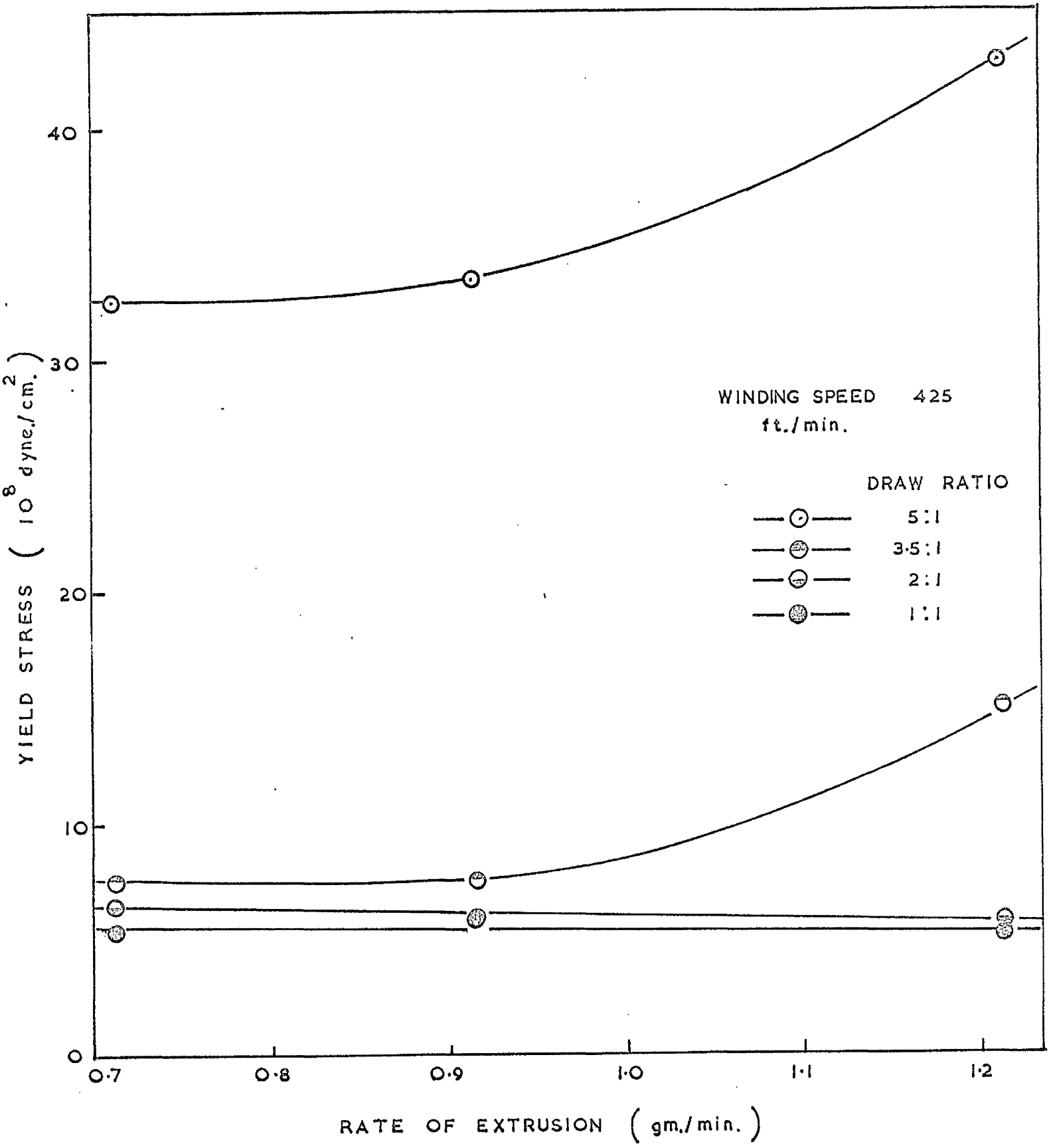
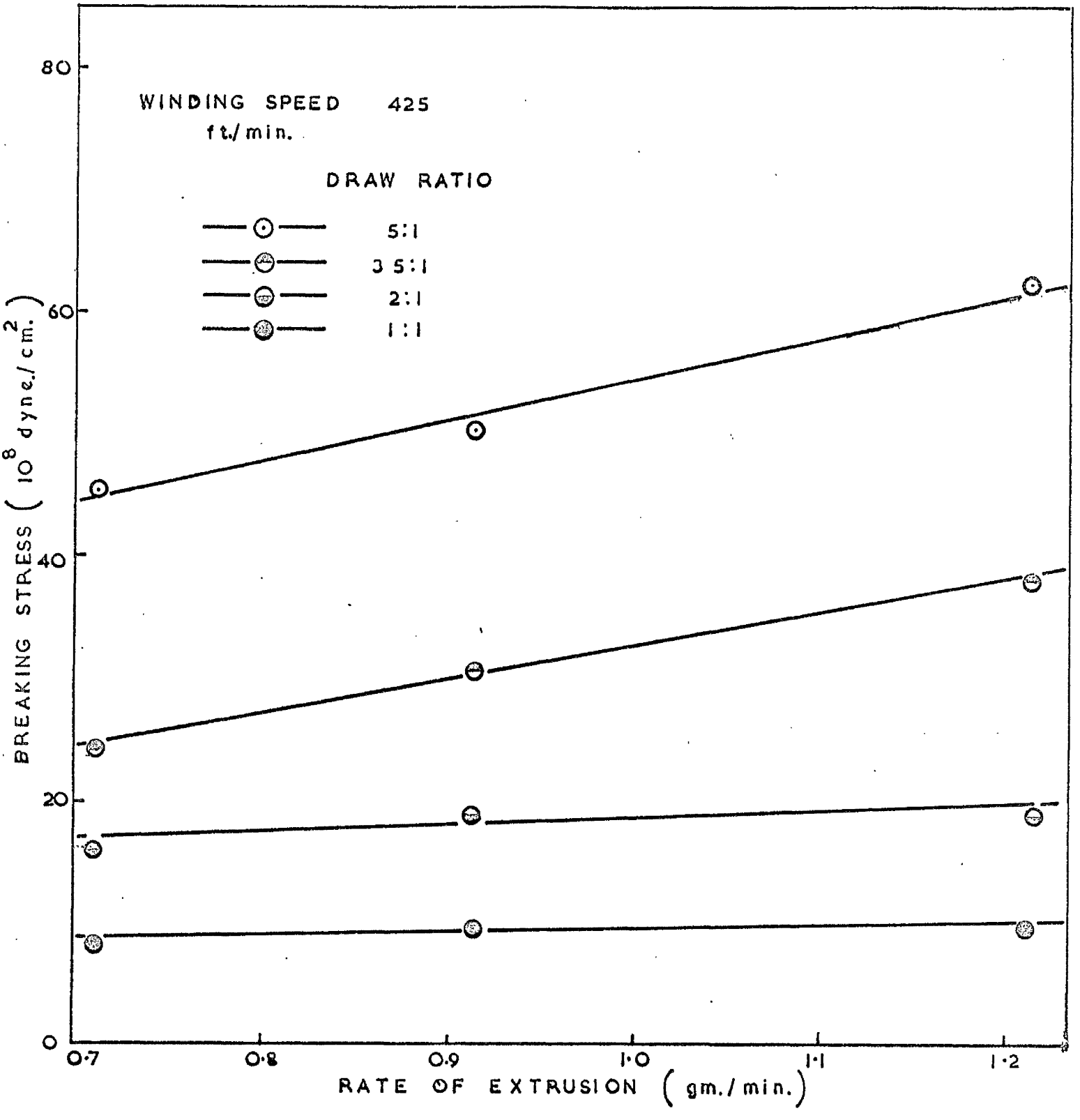


FIGURE 7

INFLUENCE OF RATE OF EXTRUSION ON BREAKING STRESS AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO



Yield point was determined by Coplan's method.[95]

The variation of initial modulus with rate of extrusion is shown in Figure 5 and Table V. Up to speeds of 0.9 gm./min. initial modulus is virtually constant. Above this value, however, it shows an appreciable increase at the higher draw ratio, although remaining virtually constant in the undrawn and 2:1 draw ratio filaments. Figure 5 shows clearly, therefore, that the rate of extrusion has a significant effect on initial modulus only at higher draw ratios.

The variation of yield stress with rate of extrusion is shown in Figure 6 and Table VI. The trends shown are virtually identical with those for initial modulus. This is to be expected, of course, since both the initial modulus and yield stress are quantities indicating resistance to deformation, albeit at slightly different points in the stress/strain curve.

Breaking stress is plotted against rate of extrusion in Figure 7 from Table VII. This

/figure

FIGURE 8

INFLUENCE OF RATE OF EXTRUSION ON BREAKING EXTENSION AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO

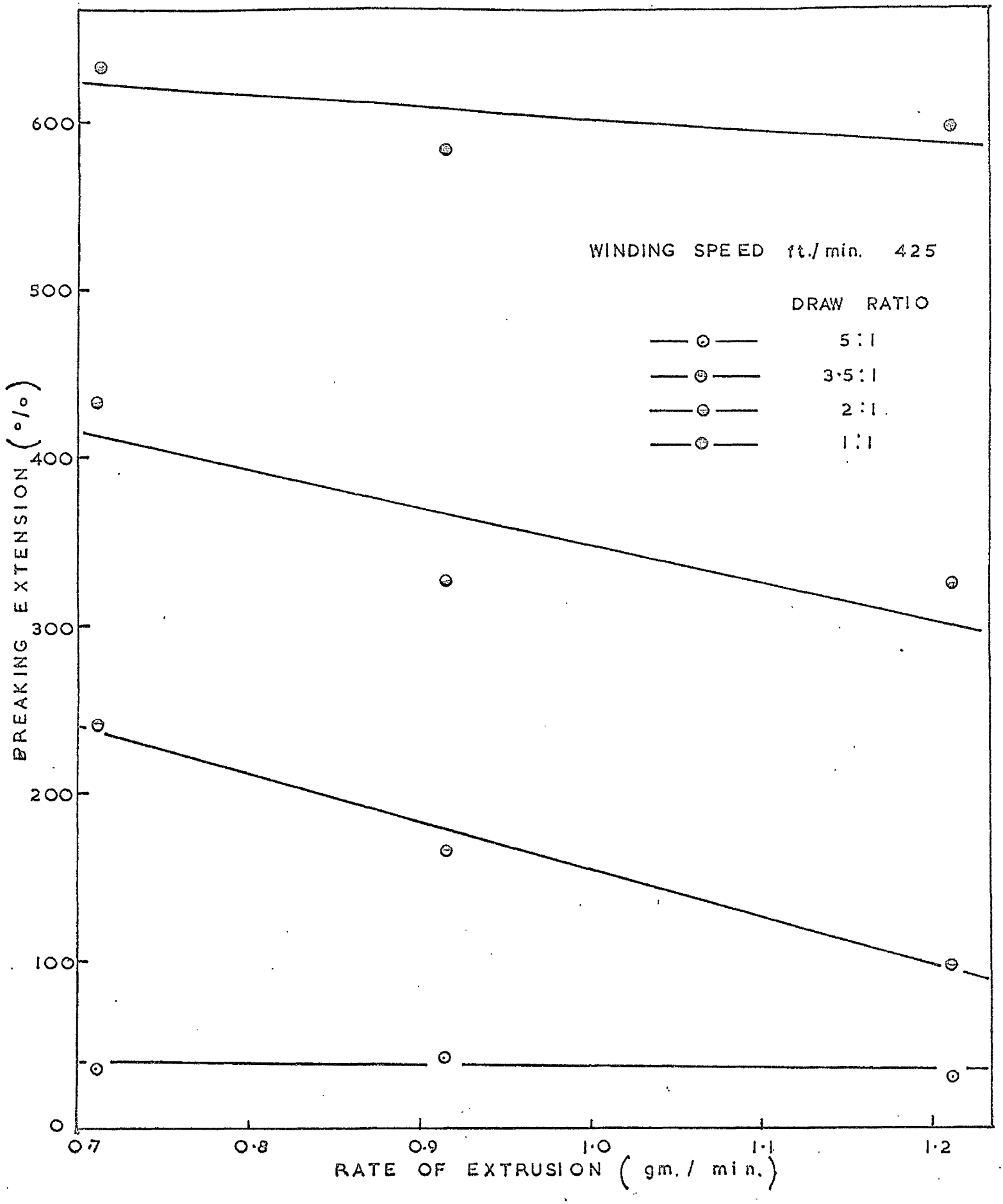


figure shows a slight but interesting variation from the results obtained for initial modulus and yield stress. As has been pointed out these quantities were substantially unaffected below a rate of extrusion of 0.9 gm./min. Breaking stress, however, shows a linear increase with increase in rate of extrusion.

The variation of breaking extension with rate of extrusion is shown in Figure 8 and Table VIII. The breaking extension linearly decreases as the rate of extrusion increases for fibres of all draw ratios except for the 5:1 draw ratio filament where the values of breaking extension almost remain constant. This suggests that at higher draw ratios the rate of extrusion has no significant effect on breaking extension. Considerable experimental error was found at the lower draw ratios but the general trend of the results was quite clear.

3.22 Influence of Rate of Extrusion on Modulus of Rigidity

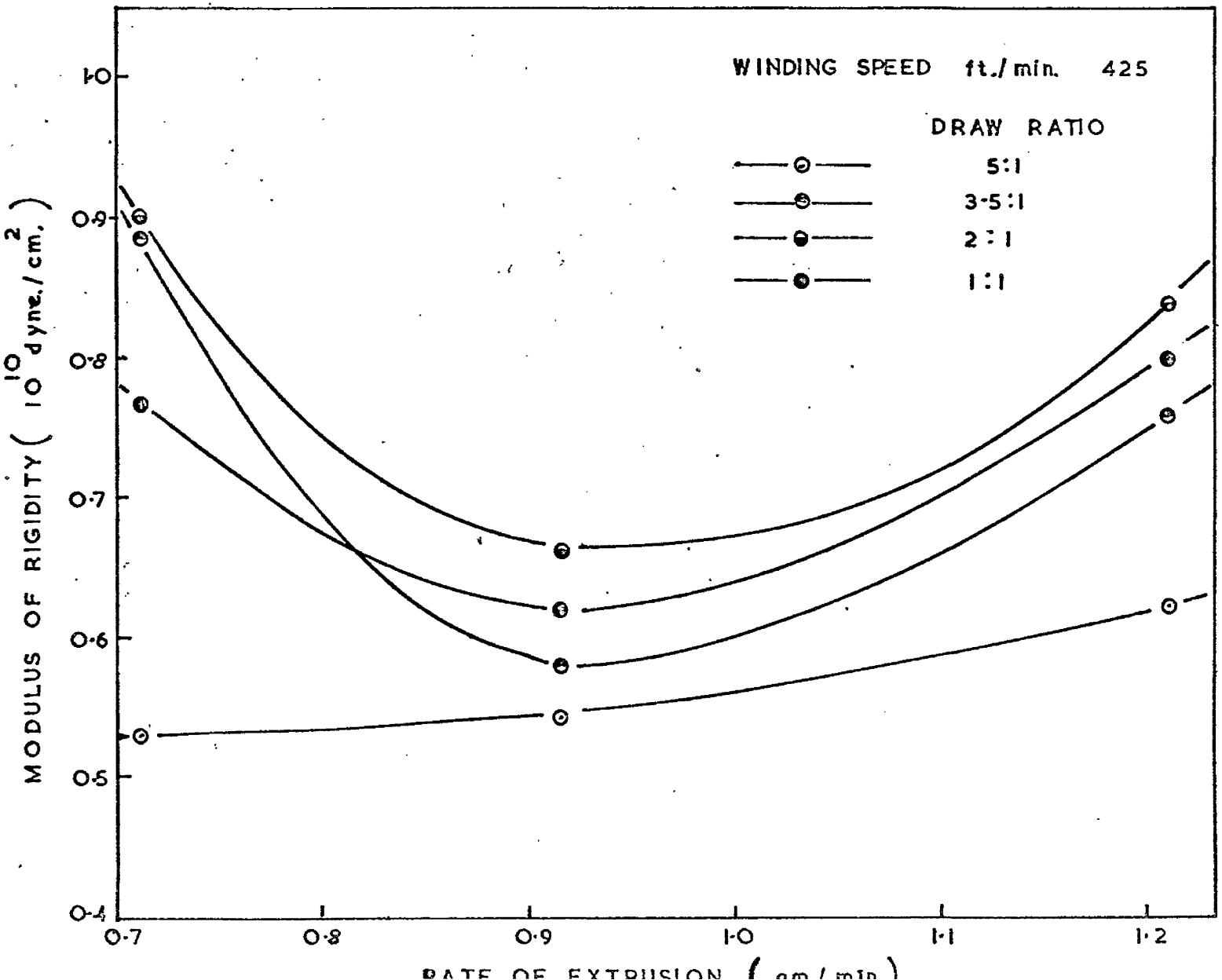
Modulus of rigidity is the ratio of shear stress to shear strain which is a measure of the inherent resistance of the fibre to a change

/of shape.

FIGURE 9

INFLUENCE OF RATE OF EXTRUSION ON MODULUS OF RIGIDITY

AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO



of shape. In torsional rigidity, the forces concerned are at right angles to the fibre axis, i.e. they act between the molecules, and not along their length as they do when oriented fibre is stretched.

The variation of modulus of rigidity with rate of extrusion is shown in Figure 9 and Table IX. As the rate of extrusion increases there is a small linear increase in modulus of rigidity for filament of 5:1 draw ratio. The remaining three curves (viz. undrawn, 2:1 and 3.5:1 draw ratio filaments) are convex to the rate of extrusion axis as the modulus of rigidity first decreases, passing through a minimum value, and then increases as the rate of extrusion increases. The highest values of modulus of rigidity are obtained for filament of 2:1 draw ratio, the curve of which then shifts downwards in order of filaments of 1:1, 3.5:1 and 5:1 draw ratios.

The behaviour of these peculiar curves is very difficult to explain on the molecular level and no proper explanation has been obtained for this phenomenon.

/3.23

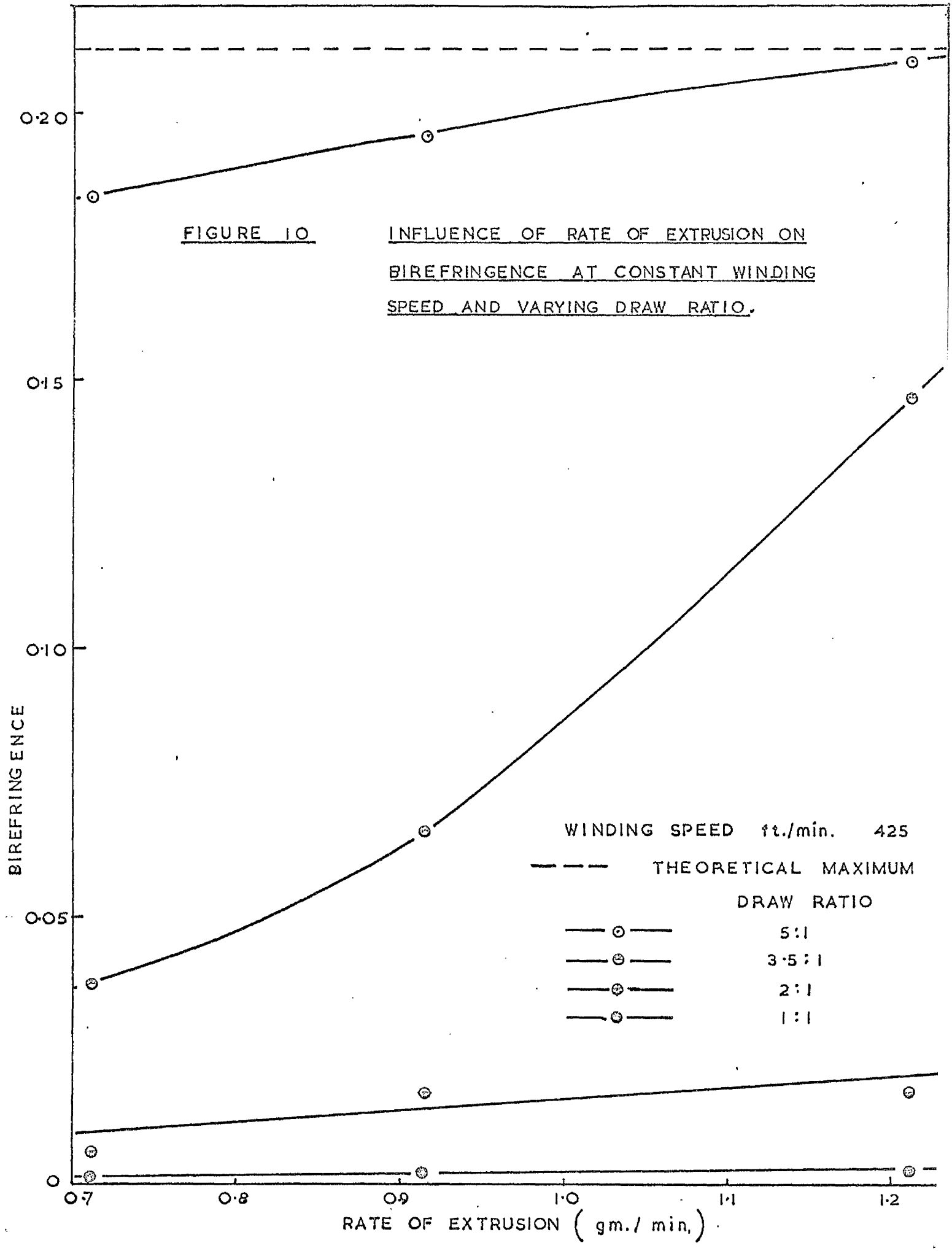


FIGURE 10 INFLUENCE OF RATE OF EXTRUSION ON BIREFRINGENCE AT CONSTANT WINDING SPEED AND VARYING DRAW RATIO.

3.23 Influence of Rate of Extrusion on Birefringence

Birefringence can be regarded as a molecular property, which is determined by the structure and configuration of the molecules and by their mutual orientations. Birefringence is a measure of orientation and not of crystallinity since oriented chain molecules are themselves birefringent but not necessarily crystalline.

The difference in the refractive indices (birefringence) depends on the relation between the direction of polarisation of light and the direction of alignment of the molecular chain. So when the molecules are aligned parallel to the fibre axis, birefringence will be greatest, and it will be zero when they are randomly directed.

The variation of birefringence with rate of extrusion is shown in Figure 10 and Table X. The birefringence of undrawn filament (1:1 draw ratio) is about 0.002, which remains virtually constant as the rate of extrusion increases. This proves that undrawn filament has virtually no orientation and

/molecules

molecules are randomly directed. In fact, molecular orientation is induced during the extrusion of a polymer, but is lost after extrusion when the polymer relaxes back to its isotropic form. Molecular orientation is therefore reintroduced by a separate drawing step. It can be seen from Figure 10 that higher values of birefringence are obtained at higher draw ratios.

Palmer [69] has reported a value of 0.212 as the theoretical maximum birefringence of a set of uniaxially oriented crystallites of polyethylene terephthalate. This is shown by a dotted line in Figure 10.

As the rate of extrusion increases birefringence slightly increases and then remains almost steady for filament of 2:1 draw ratio, while a much greater increase is shown for filament of 3.5:1 draw ratio. The 5:1 draw ratio filament, however, like the 2:1 draw ratio filament, only shows a small increase. This is because this filament has a birefringence close to the theoretical maximum at low rates of extrusion.

/Figure 10

Figure 10 indicates then that the rate of extrusion has less effect on birefringence values at low and high draw ratios, but at intermediate draw ratios the rate of extrusion plays an important role in determining the birefringence properties of the filament.

3.3 Influence of Winding Speed on Fibre Properties at Various Draw Ratios.

In order to examine the influence of winding speed on final fibre properties, a series of experiments were carried out in which all the experimental conditions except winding speed were kept constant. In each experiment three winding speeds, between 150 and 425 ft./min. were used. Since there was also the possibility of draw ratio influencing these results, the resultant filaments were drawn at draw ratios of 2:1, 3.5:1 and 5:1. These results, coupled with those on the undrawn filament (1:1), enabled the data to be examined from the point of view of influence of winding speed on properties over the range of draw ratios.

Owing to the large difference between the rate of extrusion and the rate of winding, a stretch ratio of between 20:1 and 60:1 was imposed on the molten extruded filament. This stretch ratio is much higher than that obtained by hot drawing (5:1) on the continuous hot drawing apparatus. Thus, although maximum stretch was obtained during spinning, the resulting filaments were found weak in all the textile properties.

/3.31

FIGURE 11

INFLUENCE OF WINDING SPEED ON INITIAL MODULUS A

CONSTANT RATE OF EXTRUSION AND VARYING DRAW RAT

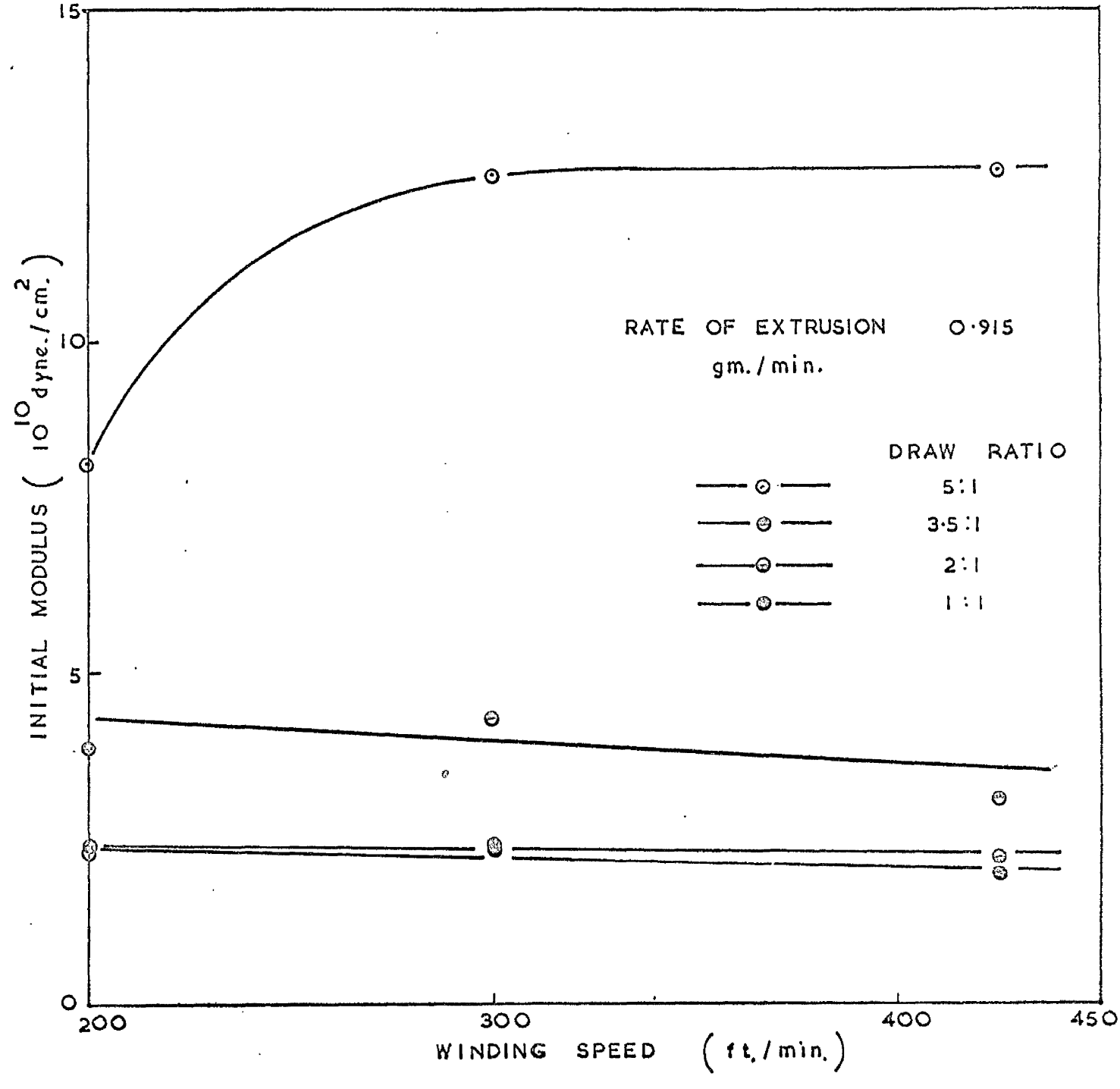


FIGURE 12

INFLUENCE OF WINDING SPEED ON YIELD STRESS AT CONSTANT RATE OF EXTRUSION AND VARYING DRAW RATIO.

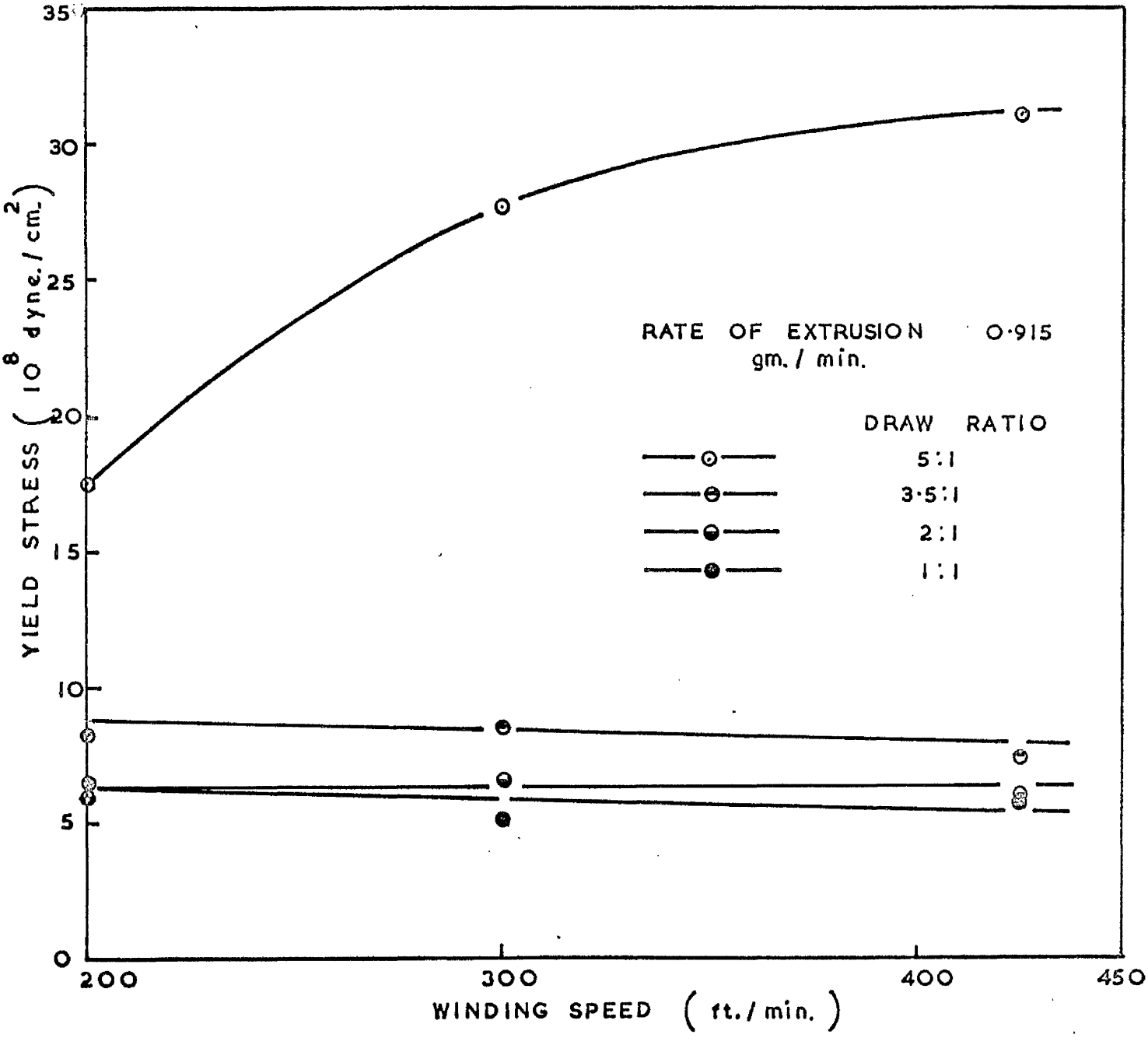
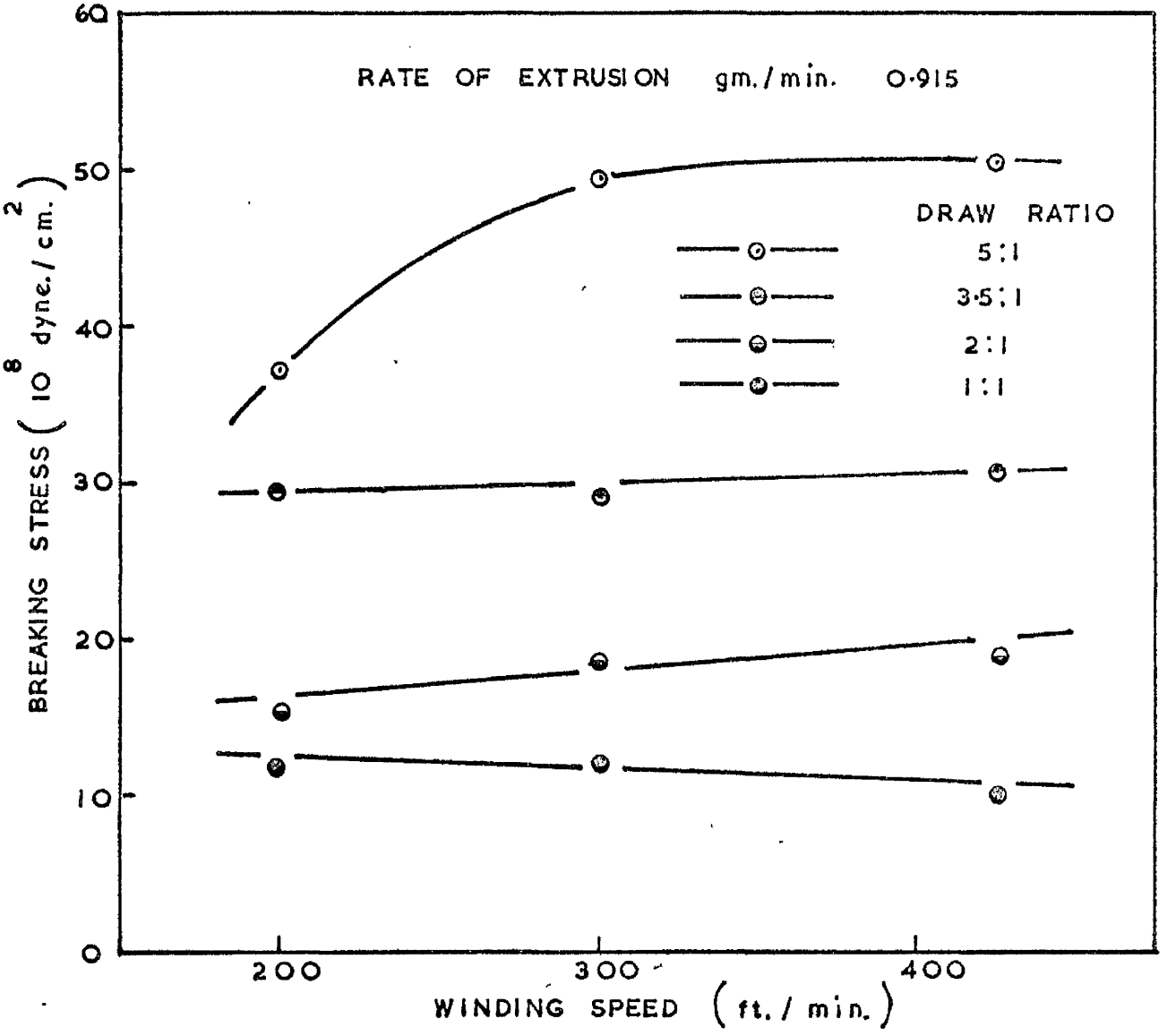


FIGURE 13

INFLUENCE OF WINDING SPEED ON BREAKING STRESS AT CONSTANT RATE OF EXTRUSION AND VARYING DRAW RATIO



3.31 Influence of Winding Speed on Tensile Properties

Initial modulus, yield stress and breaking stress are plotted against winding speed in Figures 11, 12 and 13 from Tables V, VI and VII respectively.

Initial modulus remains constant or possibly may decrease slightly with increase in winding speed for undrawn, 2:1 and 3.5:1 draw ratio filaments (see Figure 11). With increase in winding speed, initial modulus increases until a winding speed of about 300 ft./min. and then remains constant for the 5:1 draw ratio filament.

It appears that winding speed has no significant effect on yield stress, for undrawn, 2:1 and 3.5:1 draw ratio filaments.(see Figure 12). As with initial modulus, however, at a draw ratio of 5:1 there is a large significant increase in yield stress with increase in winding speed.

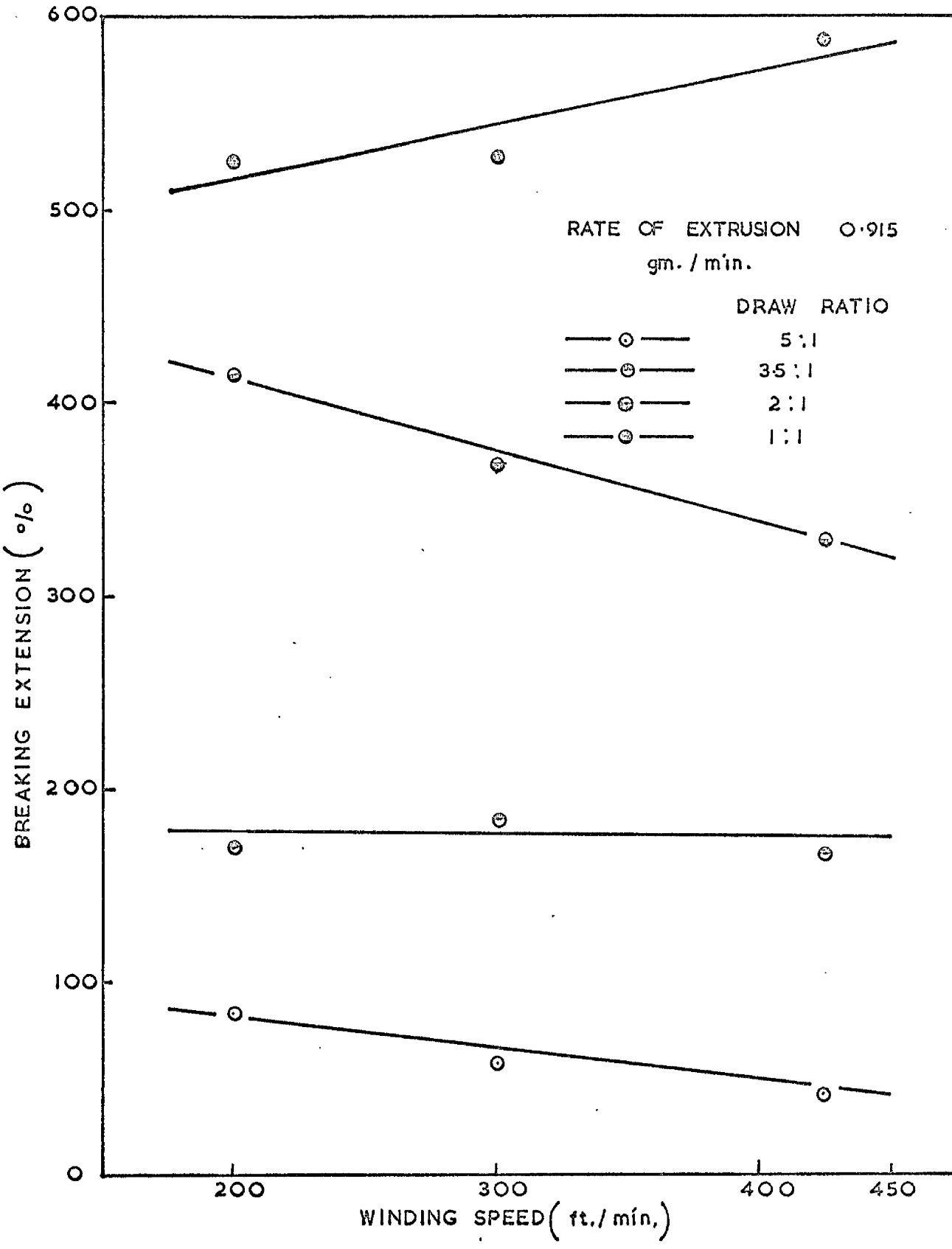
The influence of winding speed on breaking stress is shown in Figure 13. These results are rather similar to those found with initial modulus and yield stress in that at draw ratios

/of 1:1

FIGURE 14

INFLUENCE OF WINDING SPEED ON BREAKING EXTENSION

AT CONSTANT RATE OF EXTRUSION AND VARYING DRAW RATIO



of 1:1, 2:1 and 3.5:1 breaking stress is only very slightly, if at all, influenced by winding speed. At the 5:1 draw ratio, on the other hand, there is a definite increase in breaking stress particularly between winding speeds of 200 and 300 ft./min. There does, moreover, appear to be a levelling out at winding speeds above 300 ft./min.

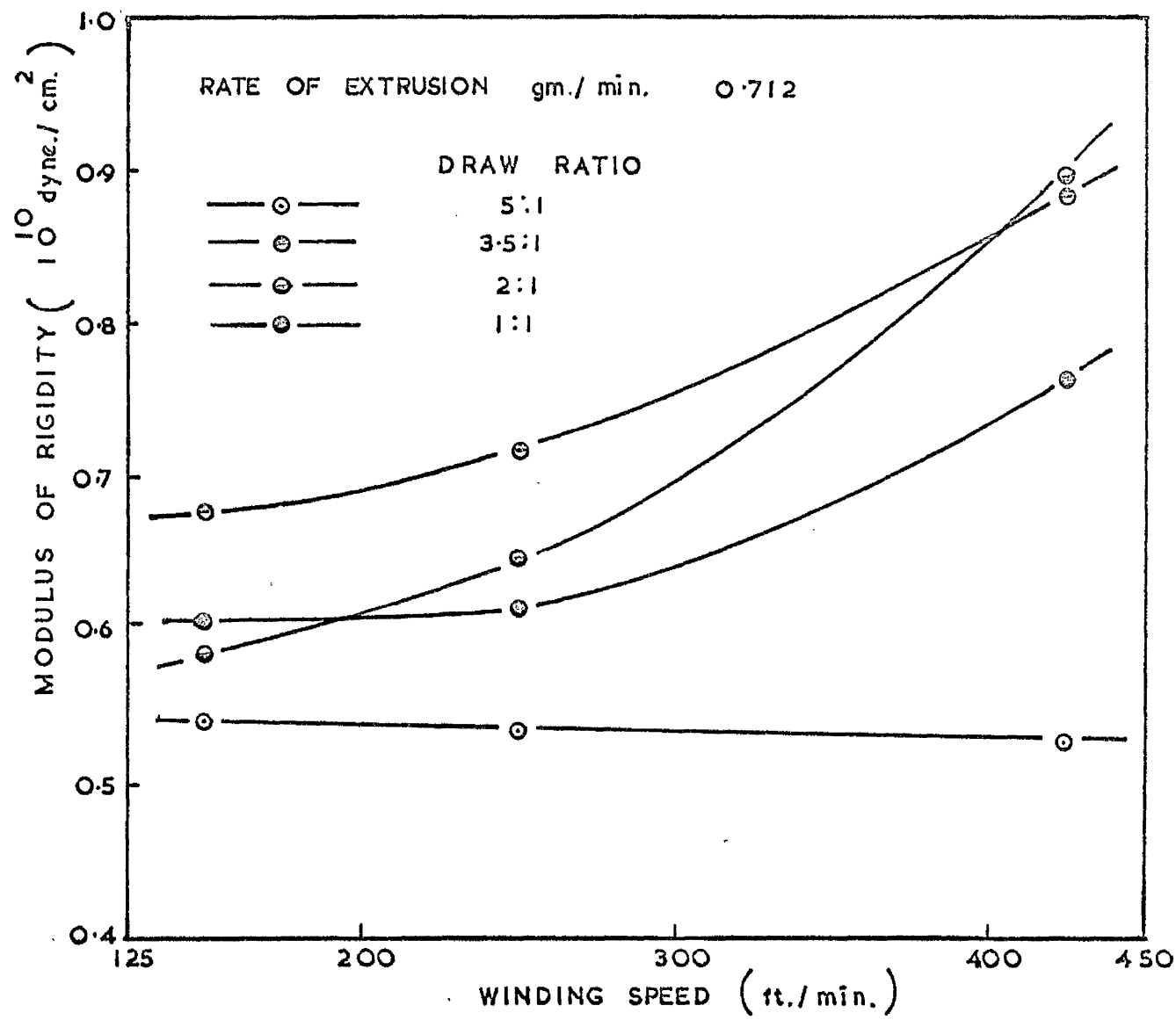
These results suggest that winding speed can influence the initial modulus, yield stress and breaking stress only at higher draw ratios and at the lower winding speeds.

Figure 14 and Table VIII show the variation of breaking extension with winding speed. These results show not very definite or systematic trends. Compared with the influence of draw ratio, the changes in breaking extension with increase in winding speed are small. The fact that the 3.5:1 draw ratio shows no change, the 1:1 a slight increase and the 2:1 and 5:1 slight decreases, would suggest that experimental error is rather greater than any possible changes in breaking extension due to change in the winding speed.

/It is

FIGURE 15

INFLUENCE OF WINDING SPEED ON MODULUS OF RIGIDITY AT CONSTANT RATE OF EXTRUSION AND VARYING DRAW RATIO



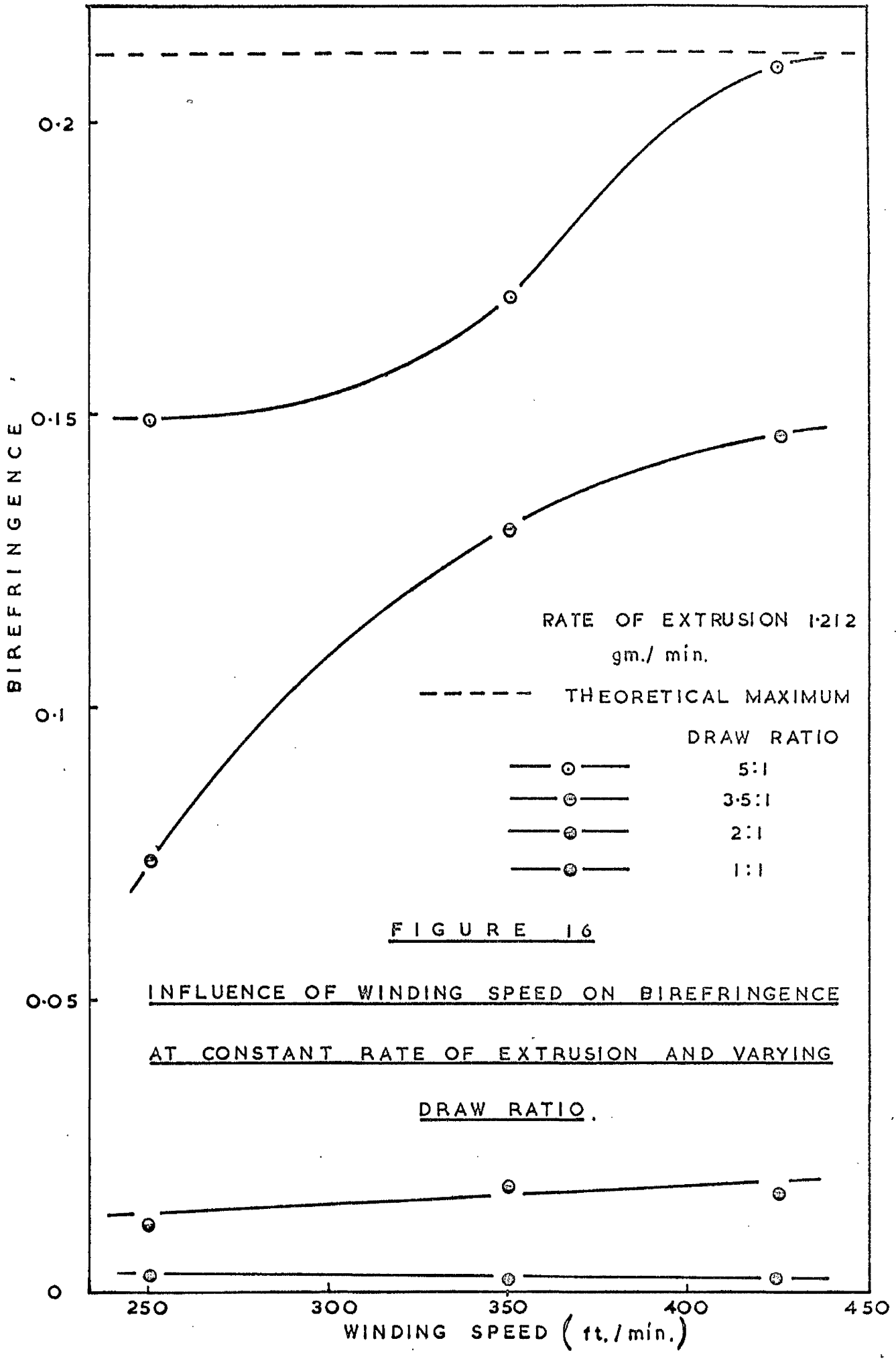


FIGURE 16

INFLUENCE OF WINDING SPEED ON BIREFRINGENCE AT CONSTANT RATE OF EXTRUSION AND VARYING DRAW RATIO.

It is worth noting that in general the trends shown for the variation in tensile properties with winding speed are very similar to those found for the variation of tensile properties with rate of extrusion. Both are, of course, melt flow processes involving simultaneous orientation and relaxation processes.

3.32 Influence of Winding Speed on Modulus of Rigidity

The variation of modulus of rigidity with winding speed is shown in Figure 15 and Table IX. Winding speed appears to have no effect on modulus of rigidity for the filament of 5:1 draw ratio. With increase in winding speed, modulus of rigidity increases for the filaments with draw ratios of 1:1, 2:1 and 3.5:1. These curves are slightly convex to the winding speed axis, but unlike the variation with rate of extrusion (see Figure 9) they do not seem to pass through a minimum with increase in winding speed.

3.33 Influence of Winding Speed on Birefringence

The variation of birefringence with winding speed is shown in Figure 16 and Table X. The birefringence of undrawn filament (1:1 draw

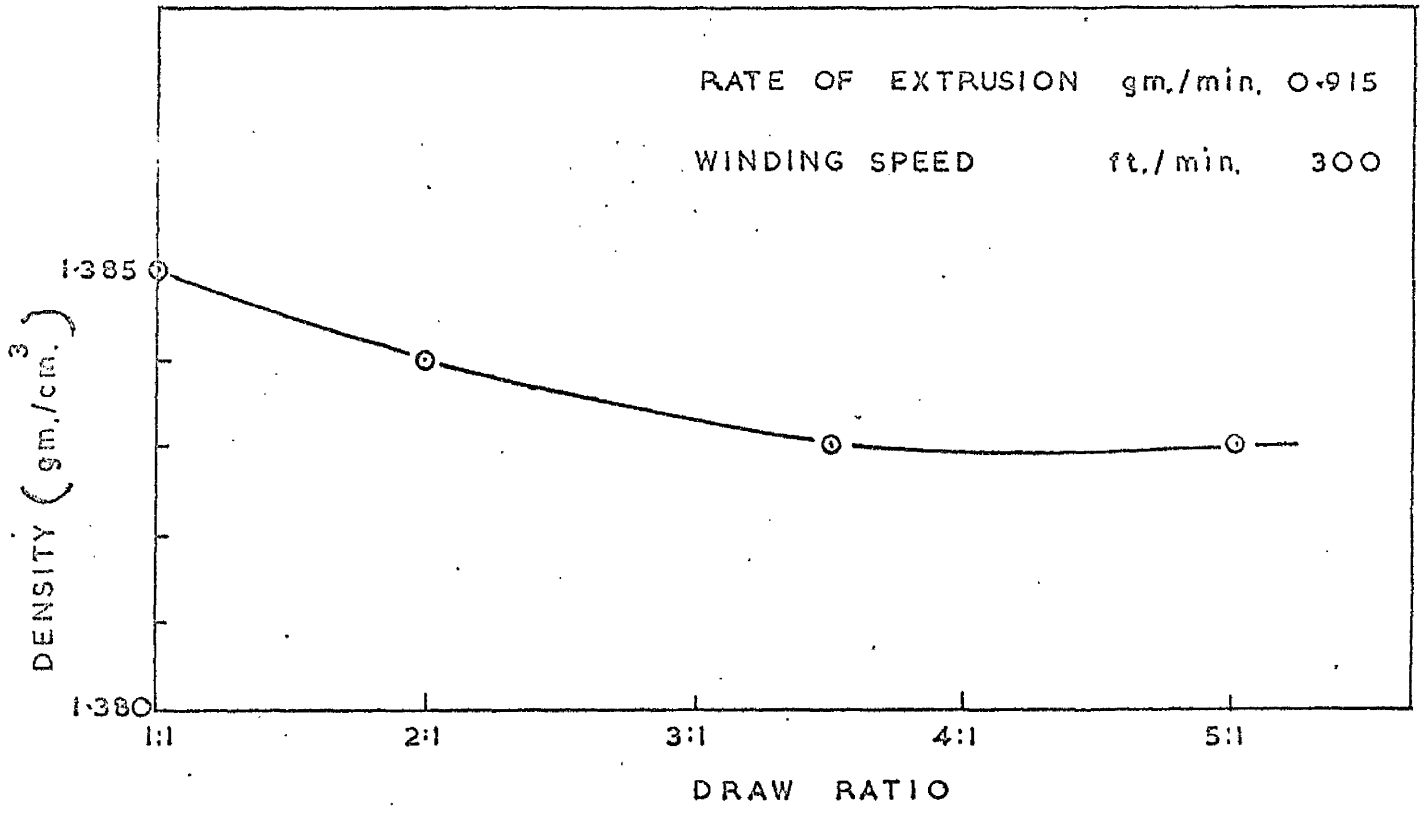
/ratio)

ratio) is about 0.003, which remains virtually constant as the winding speed increases. This confirms the view expressed on Page 4 that undrawn filament has virtually no molecular orientation and the molecules are randomly directed. With increase in winding speed, values of birefringence slightly increase for 2:1 draw ratio filament, but for 3.5:1 draw ratio filament it increases at a much faster rate. This curve appears to be slightly concave to the winding speed axis. For 5:1 draw ratio filament a sigmoidal type of curve is obtained, if it is assumed that 0.212 represents the true maximum birefringence for polyethylene terephthalate.

Figure 16 shows clearly that the winding speed has very little effect on birefringence values at lower draw ratios, but at higher draw ratios winding speed plays an important role in determining the birefringence properties of filaments.

FIGURE 17

INFLUENCE OF DRAW RATIO ON DENSITY AT CONSTANT MELT SPINNING CONDITIONS.



3.4 Influence of Draw Ratio on Physical Properties of Fibre

Three draw ratios were selected (i.e. 2:1, 3.5:1 and 5:1), and keeping all the experimental conditions constant their effect on the physical properties of fibres were studied. Filament (1:1 draw ratio) was also passed over the hot pin and hot plate, without drawing, in order to obtain all the samples in similar conditions.

3.41 Influence of Draw Ratio on Density

The density of the polymer in the form of a "candle" was found to be 1.387 gm./cm.^{3}, while the density of fibre, at different draw ratios, varied from 1.383 to 1.385 gm./cm.^{3}. This suggests that there is a slight fall in density during melt spinning (see Table XI).

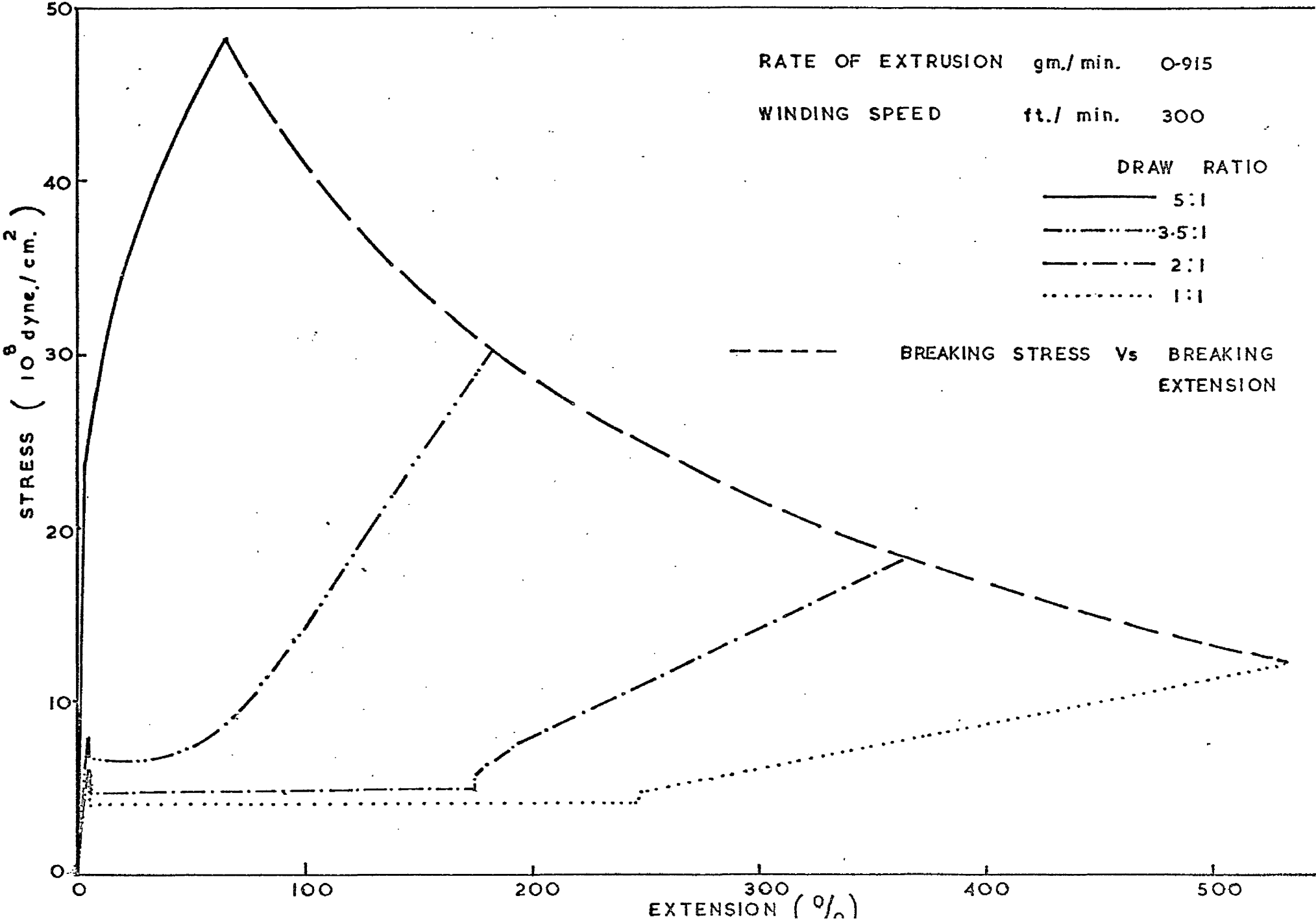
Density is plotted against draw ratio in Figure 17. With increase in draw ratio the density decreases very slightly and then remains constant. If all the readings of density, obtained at each draw ratio, are averaged out and plotted against draw ratio, the same type of curve is obtained as shown in Figure 17.

There seem to be two logical explanations for

/this

FIGURE 18

STRESS / STRAIN CURVES AT DIFFERENT DRAW RATIOS AND CONSTANT MELT SPINNING CONDITIONS



this drop of density with increase in draw ratio. Firstly, at higher draw ratios microscopic voids have been reported to appear, on occasion decreasing the density.[70] Secondly, the forces applied during the drawing process can compress the polymer to a fixed extent, quite apart from the increase in density due to induced crystallisation as indicated by Ward.[96]

Thompson and Woods[70] and Farrow and Ward[36] have also reported, for polyethylene terephthalate filaments, that density slightly decreases with increase in draw ratio, confirming these results.

3.42 Influence of Draw Ratio on Tensile Properties

Stress/strain curves of filaments spun under the same conditions but with different draw ratios are plotted in Figure 13. If a fixed length of material (1:1 or 2:1 draw ratio) is stretched at constant rate, material starts extending uniformly and then suddenly a neck will form at some point, then propagate along the sample until the entire sample is again geometrically uniform. Further extension will occur uniformly through out the sample length.

/During

During straining of the sample the formation of the neck occurs as stress passes through a maximum (i.e. yield point). The stress during propagation of the neck then slowly rises to its maximum value when the sample breaks.

The stress/strain curve has three distinct regions:

(1) An initial linear portion or high modulus region where the specimen stretches uniformly. When the force is applied to the fibre extensions will occur for two reasons:

a. A slight stretching of chain molecules themselves

b. A straightening of molecules in non-crystalline regions with resultant straining of the entanglements between them. The magnitudes of the distortion of the molecules and entanglements will be proportional to the applied force. So the stress/strain curve is linear. At the yield point the specimen necks down in one region and stress drops to

/a nearly

a nearly constant value as the stretching continues. This relaxation of stress could be explained as follows:

(i) the stress that is set up when a fibre is stretched is divided between the molecules and the entanglements. There is every possibility that entanglements will give way in forming new positions thereby reducing the stress

(ii) during stretching heat is generated which might bring down the viscosity of polymer and so relaxation of stress occurs, or

(iii) the rate of relaxation is faster than the rate of plastic flow, so when the Instron cross-head speed was increased to 20"/min. (i.e. 10 times faster) this relaxation of stress was not observed.

(2) In the second region, when applied force becomes larger some of the most highly strained entanglements in the amorphous region may break because they can not support the force applied to them. This permits greater straightening of the

/molecules.

molecules. Consequently extension becomes much easier. In this region the stress/strain curve is contained between two yield points, separated from each other by a long horizontal portion. The cold drawn region grows at the expense of undrawn ones, until all of the specimen is in the drawn state. Necking appears at the first yield point and disappears at the second yield point.

(3) The third region of the stress/strain curve involves further straining of cold drawn polymer. This last region is characterised by a rapid increase in stress as the drawn material has a high modulus and is very strong. Stiffness in the chain contributes to this high modulus in the fibre. In this region, extension is again uniform but non-recoverable.

Figure 18 clearly shows that yield stress increases with increase in the draw ratio of the fibre, i.e. at higher draw ratios the first yield point is shifting upwards, indicating that Young's modulus increases and

/the second

and the second yield point disappears. In fibres of 5:1 draw ratio, at about 12% extension, the yield point disappears and a slight inflexion appears in its place. With increase in the draw ratio of the fibre relaxation of stress decreases until, finally, no relaxation of stress occurs.

The breaking points of the fibres of all draw ratios have been joined by dotted lines in Figure 18 giving a curve of breaking stress against breaking extension. This indicates that with increase in draw ratio the locus of the breaking point moves upwards, i.e. breaking stress increases with decrease in breaking extension.

A similar stress/strain curve for undrawn filament has been reported by Meredith,[97] Marshall and Thompson[48] and Williams and Bender.[58]

Roth and Schroth[46] have studied the stress/strain behaviour for fibre with draw ratios from 2.9:1 to 4:1. These curves were obtained using only the hot pin in the drawing apparatus initially and then inserting the hot plate at 140°C for

/later

FIGURE 19

INFLUENCE OF DRAW RATIO ON INITIAL MODULUS AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.

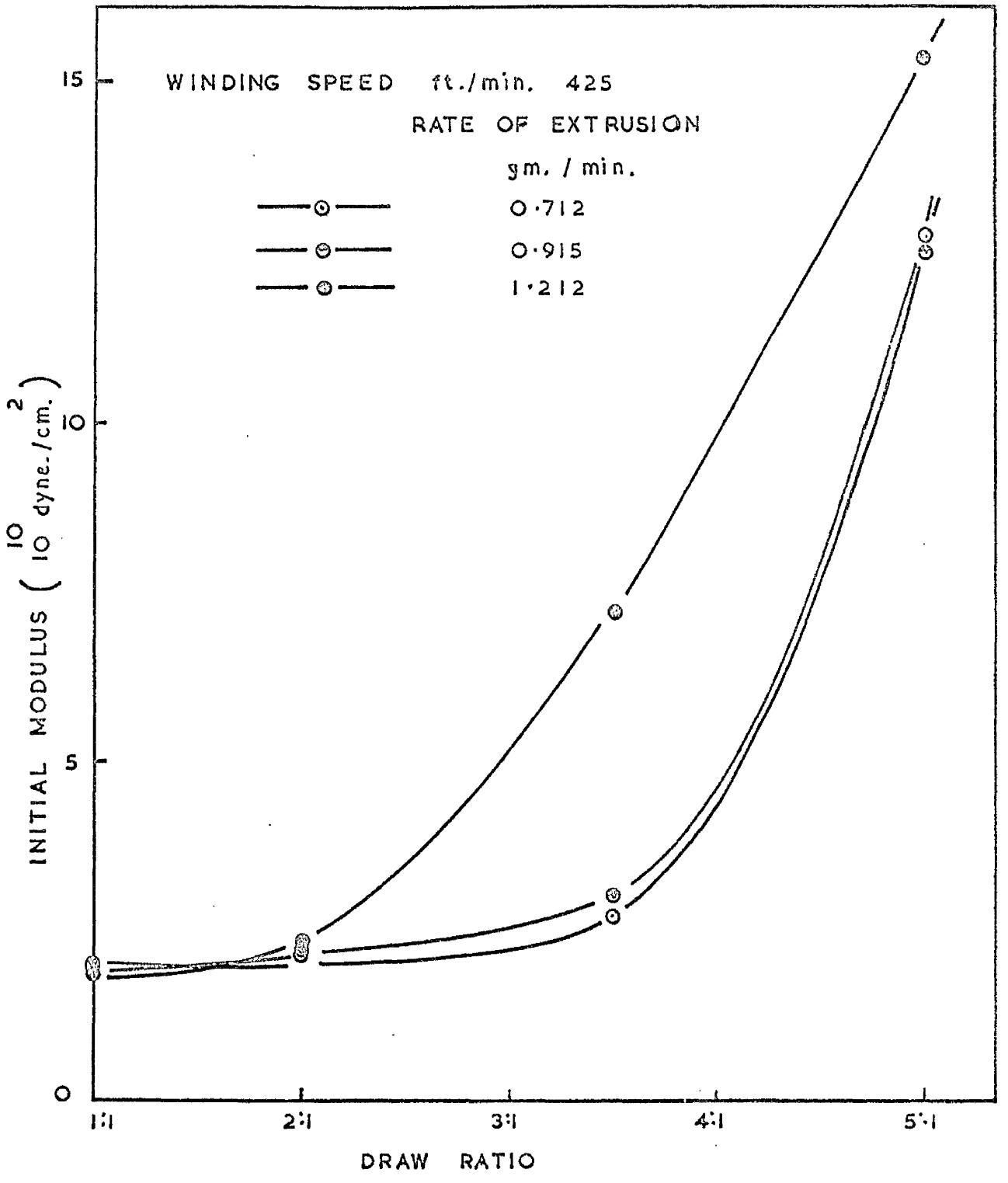
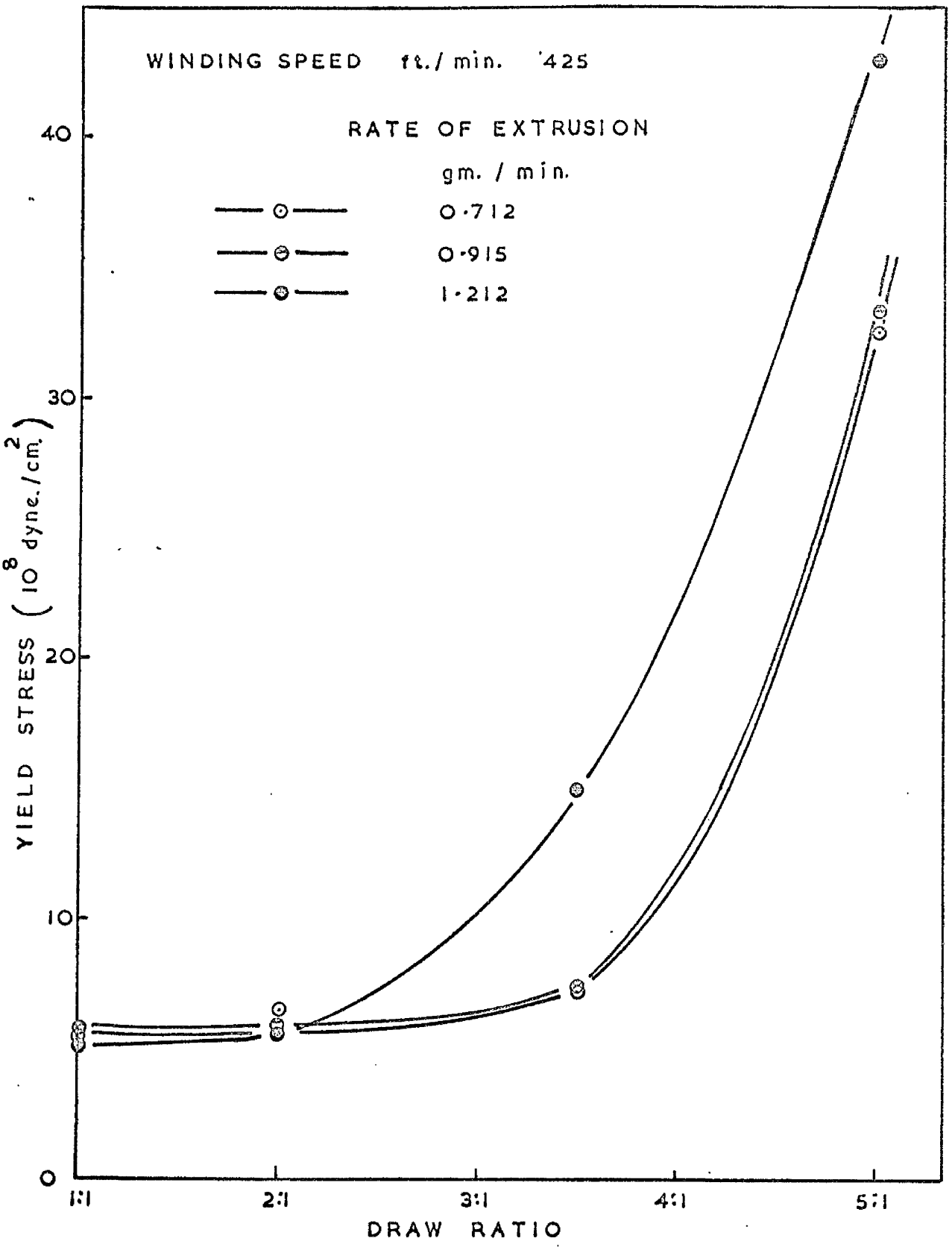


FIGURE 20

INFLUENCE OF DRAW RATIO ON YIELD STRESS AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.



later experiments. At this high hot plate temperature necking was eliminated from the stress/strain curve. This shows that the stress/strain curves of polyethylene terephthalate can be varied according to the temperature of the hot pin and hot plate used during drawing, and on the draw ratio obtained.

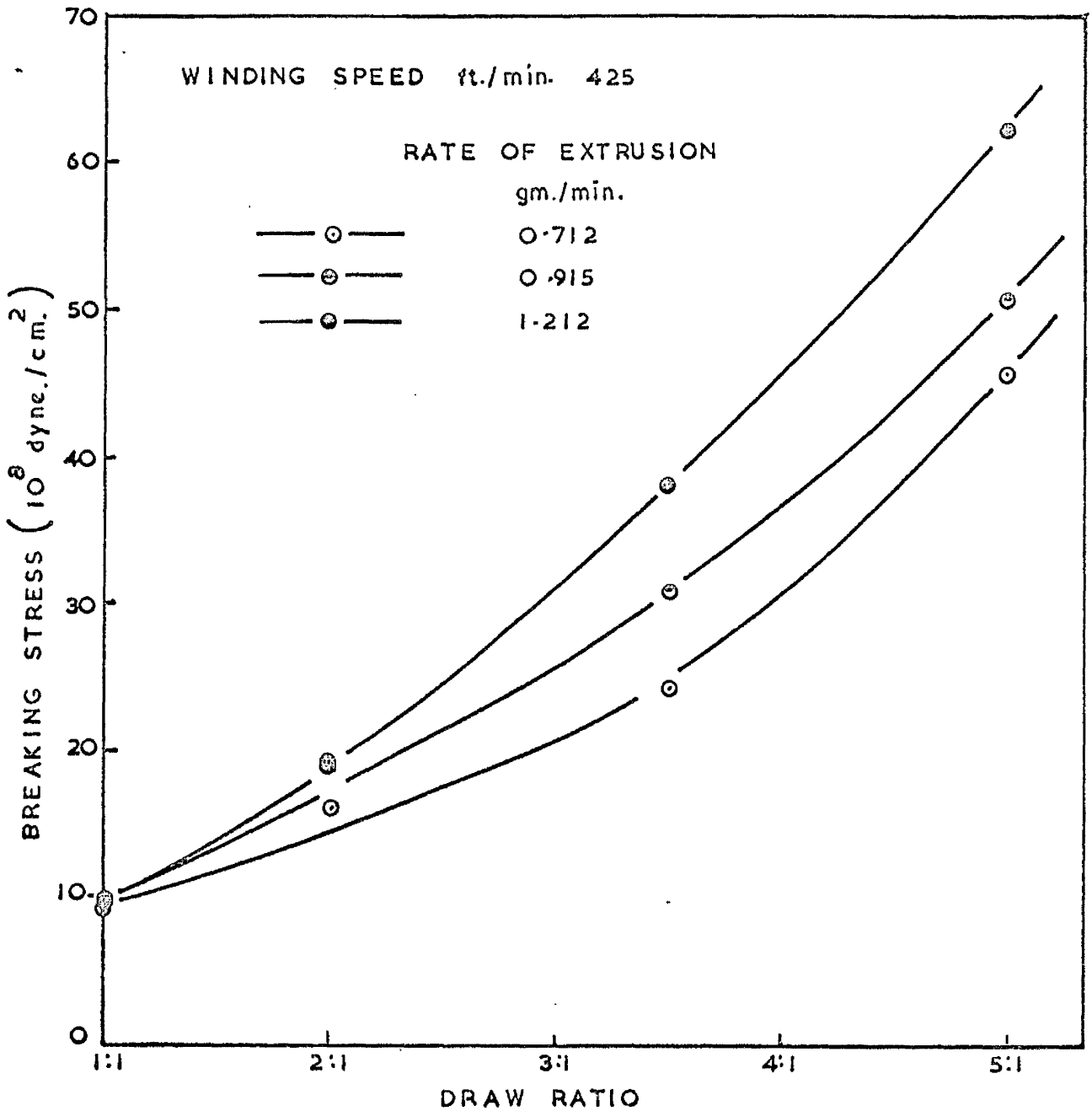
Initial modulus and yield stress are plotted against draw ratio at constant winding speed and different rates of extrusion in Figure 19. and Figure 20 respectively and from Tables V and VI. These figures show very similar trends. Initial modulus and yield stress are substantially unaffected by increase in draw ratio below a draw ratio of 2:1. Above this value both properties show an increasingly great dependence on draw ratio, and increase rapidly. Moreover, both initial modulus and yield stress are rather more sensitive to changes in draw ratio, below draw ratio of 3.5:1, at the higher rate of extrusion than at the lower rates.

Breaking stress increases as draw ratio increases irrespective of melt spinning conditions. This

/can

FIGURE 21

INFLUENCE OF DRAW RATIO ON BREAKING STRESS AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.



can be seen in Figure 21 and Table VII. The essential difference between Figures 19, 20 and 21 is that there is an increase in breaking stress with increase in draw ratio, even at lower draw ratios. At constant draw ratio, as has been pointed out earlier, the higher the rate of extrusion, the higher is the breaking stress.

When initial modulus, yield stress and breaking stress are plotted against draw ratio at constant rate of extrusion and varying winding speed, similar curves are obtained.

This concludes that at high rate of extrusion and winding speed, if the filament is drawn at a higher draw ratio, higher values of initial modulus, yield stress and breaking stress can be obtained. This is because molecular orientation increases with increase in draw ratio

Roth and Schroth,[46] in studying the effect of breaking stress on draw ratio, have also observed that as the draw ratio or molecular orientation increases breaking stress also increases.

/The variation

FIGURE 22

INFLUENCE OF DRAW RATIO ON BREAKING EXTENSION AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.

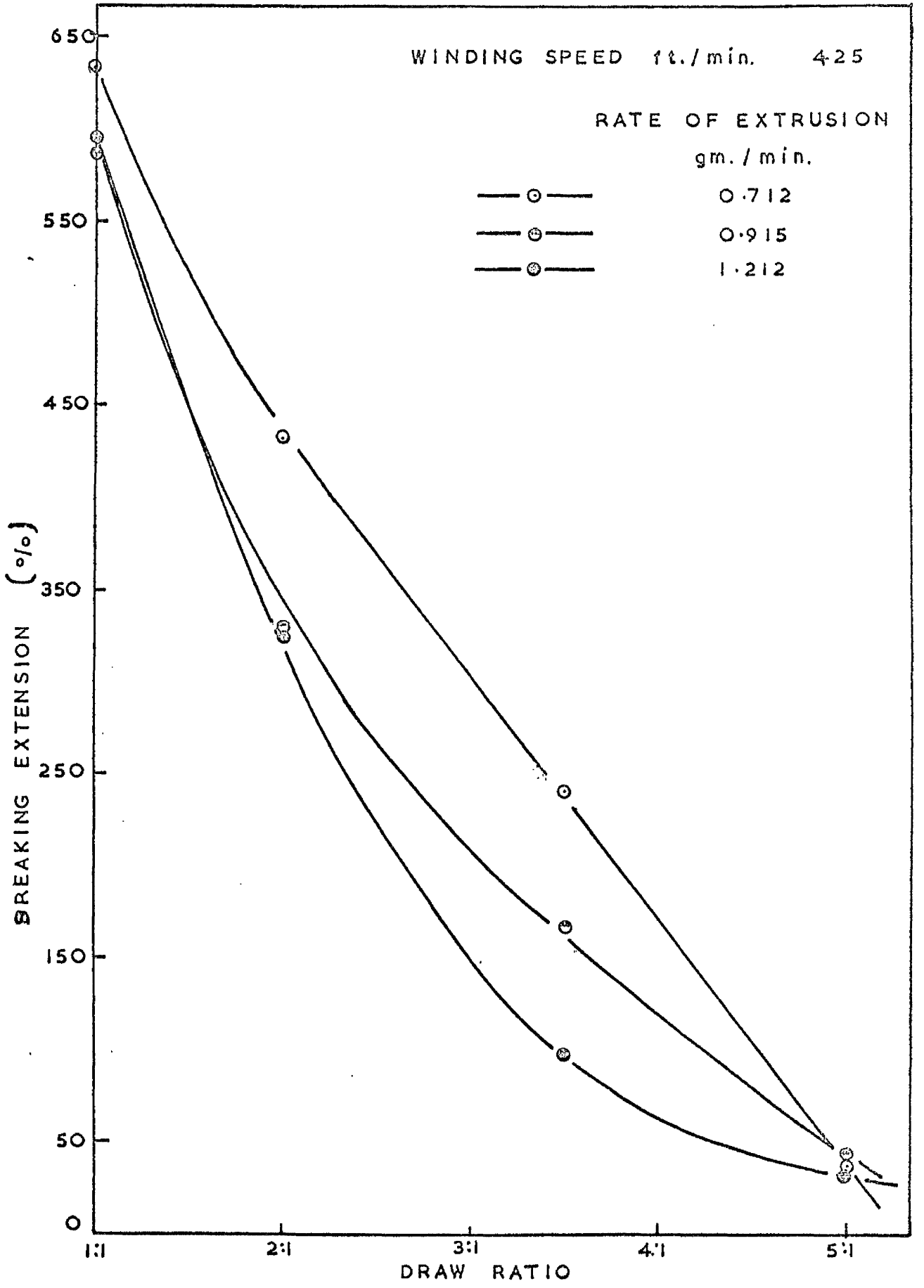


FIGURE 23

INFLUENCE OF DRAW RATIO ON MODULUS OF RIGIDITY AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.

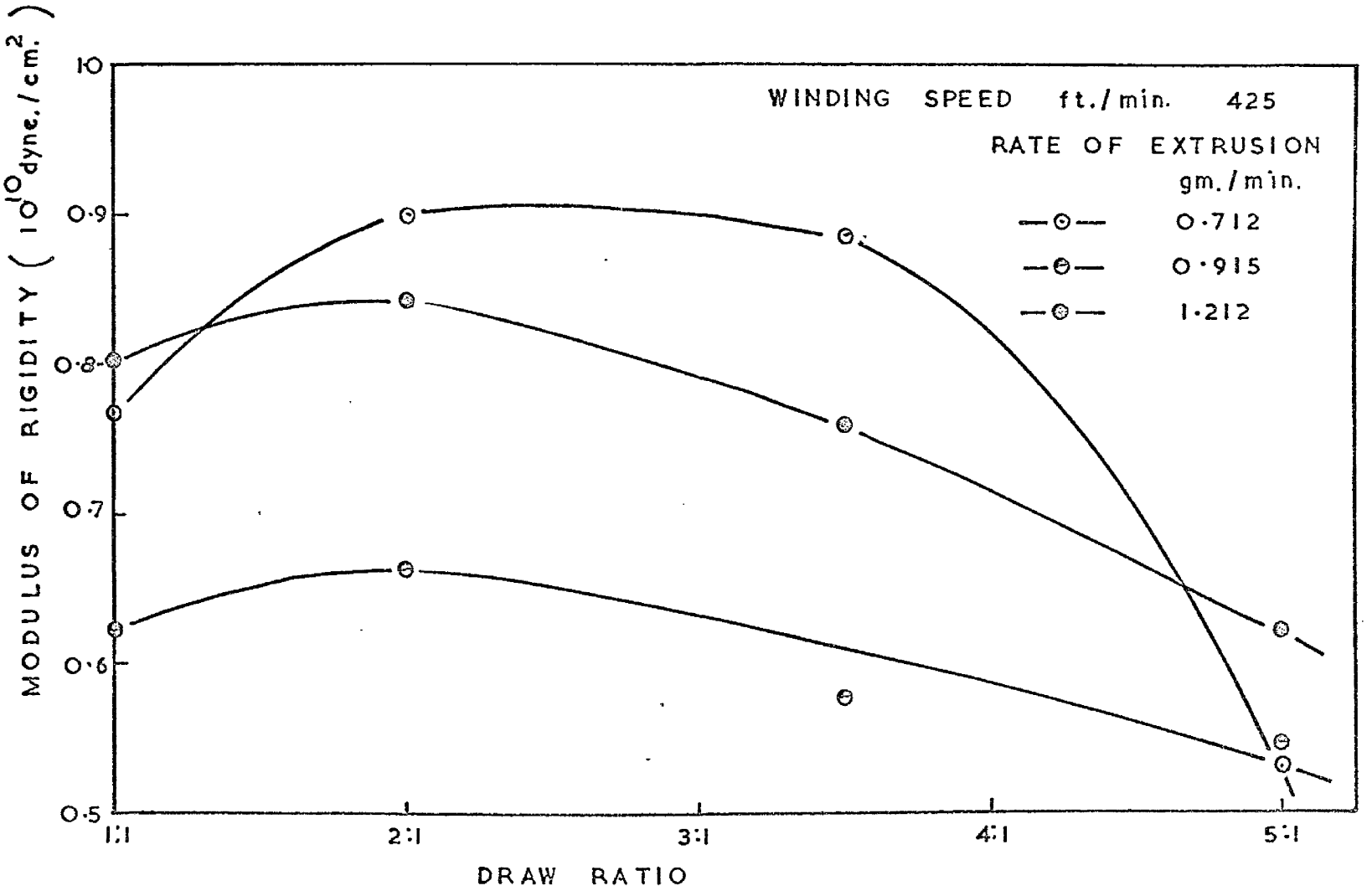
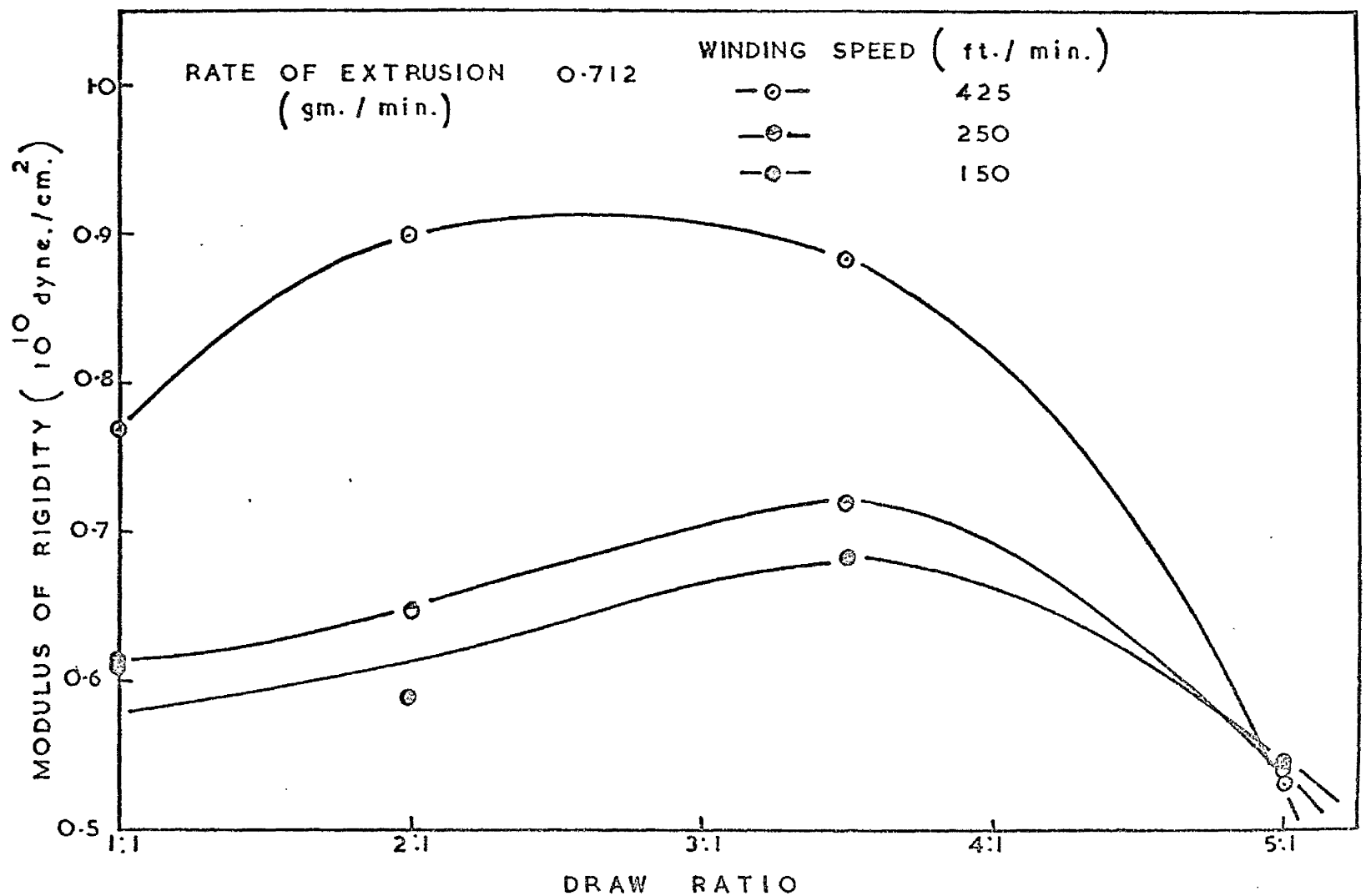


FIGURE 23(a)

INFLUENCE OF DRAW RATIO ON MODULUS OF RIGIDITY AT CONSTANT RATE OF EXTRUSION AND VARYING WINDING SPEED.



The variation of breaking extension with draw ratio, at constant winding speed and different rates of extrusion, is shown in Figure 22 and Table VIII. With increase in draw ratio, breaking extension decreases irrespective of the melt spinning conditions.

When breaking extension is plotted against draw ratio at constant rate of extrusion and varying winding speed, once again curves are obtained similar to those shown in Figure 22. These curves also indicate that at constant draw ratio, if the winding speed is high, low breaking extensions are obtained.

3.43 Influence of Draw Ratio on Modulus of Rigidity

The variation of modulus of rigidity with draw ratio is shown in Figures 23 and 23(a) and Table IX. Figure 23 shows that with increase in draw ratio the modulus of rigidity increases until 2:1 draw ratio and then decreases. This maximum is shown at all three rates of extrusion indicating that while there are some apparent inconsistencies in the results, the maximum is, in fact, genuine.

Figure 23(a) shows the same types of curves as

/shown

shown in Figure 23. At lower winding speeds viz: 150 and 250 ft./min., with increase in draw ratio, the modulus of rigidity increases until about 3.5:1 draw ratio and then drops to lower values with further increase in draw ratio. The trend of the curve remains the same at a winding speed of 425 ft./min., but the maximum occurs at a lower draw ratio. At the 5:1 draw ratio a virtually constant value of modulus of rigidity is obtained, irrespective of winding speed.

The average of five measurements were taken as a mean value for modulus of rigidity, but large experimental variations amongst these results were noticed. However, even the lowest value of modulus of rigidity in undrawn filament is significantly higher than the highest value obtained at the 5:1 draw ratio. Thus, at the highest draw ratio the modulus of rigidity is even lower than in the undrawn filament.

The cause of this rise and then fall in modulus of rigidity with increase in draw ratio is very difficult to explain on a molecular level. If it is assumed that the value of shear strain

/remains

remains constant during the experimental determination then the value of shear stress must have decreased at the highest draw ratio, thereby decreasing the value of modulus of rigidity.

The undrawn fibre is unoriented with random entanglements and no significant crystallinity. At draw ratio of 2:1 to 4:1 a midway point in the orientation has been reached in which the molecules are partially oriented, the intermolecular entanglements are strained but not necessarily reduced in number, and some degree of crystallinity has been achieved. This would suggest that the force required to deform the fibre by twisting would be rather higher than the force needed in the internally unstrained undrawn filament. At the highest draw ratio attained, i.e. 5:1, the molecules are arranged in a very much more parallel configuration with a fairly high degree of crystallinity. Under these circumstances it might be anticipated that resistance to strain by twisting would be rather less than in the intermediate draw ratio.

/3.44

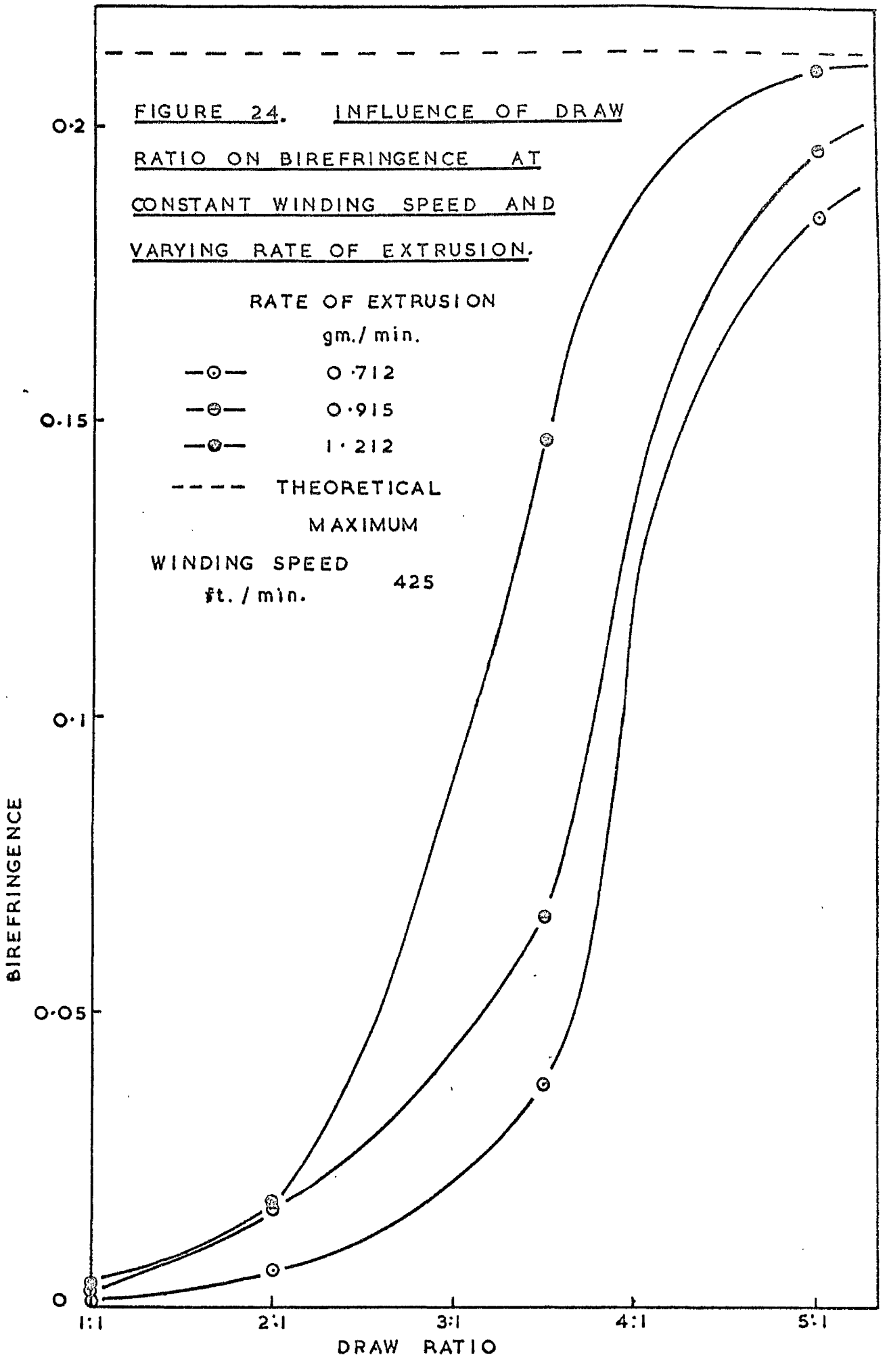


FIGURE 24. INFLUENCE OF DRAW RATIO ON BIREFRINGENCE AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.
RATE OF EXTRUSION gm./min.
0·712
0·915
1·212
THEORETICAL MAXIMUM
WINDING SPEED ft./min. 425
BIREFRINGENCE
0·2
0·15
0·1
0·05
0
1:1
2:1
3:1
4:1
5:1
DRAW RATIO

3.44 Influence of Draw Ratio on Birefringence

The values of birefringence are plotted against draw ratio at constant winding speed and varying rates of extrusion in Figure 24 from Table X. Sigmoidal curves are obtained. With increase in draw ratio, birefringence (a measurement of orientation) first increases slowly between 1:1 and about 2.5:1 draw ratio and then increases at a much faster rate, levelling off below the theoretical maximum. This suggests that drawing orientates the fibre molecules. As has been shown previously (see Page 82), at constant draw ratio, if the rate of extrusion is high, higher values of birefringence are obtained.

The same relationship is obtained when birefringence is plotted against draw ratio at constant rate of extrusion and varying winding speed.

Farrow and Dagley[69] have suggested that it is the non-crystalline orientation which changes with draw ratio.

Ward[96] has plotted birefringence against draw ratio, from 2.7:1 draw ratio onwards. In the present study, the birefringence/draw ratio curves (see Figure 24) from 2.7:1 draw ratio onwards, show

/exactly

exactly the same behaviour as obtained by Ward.

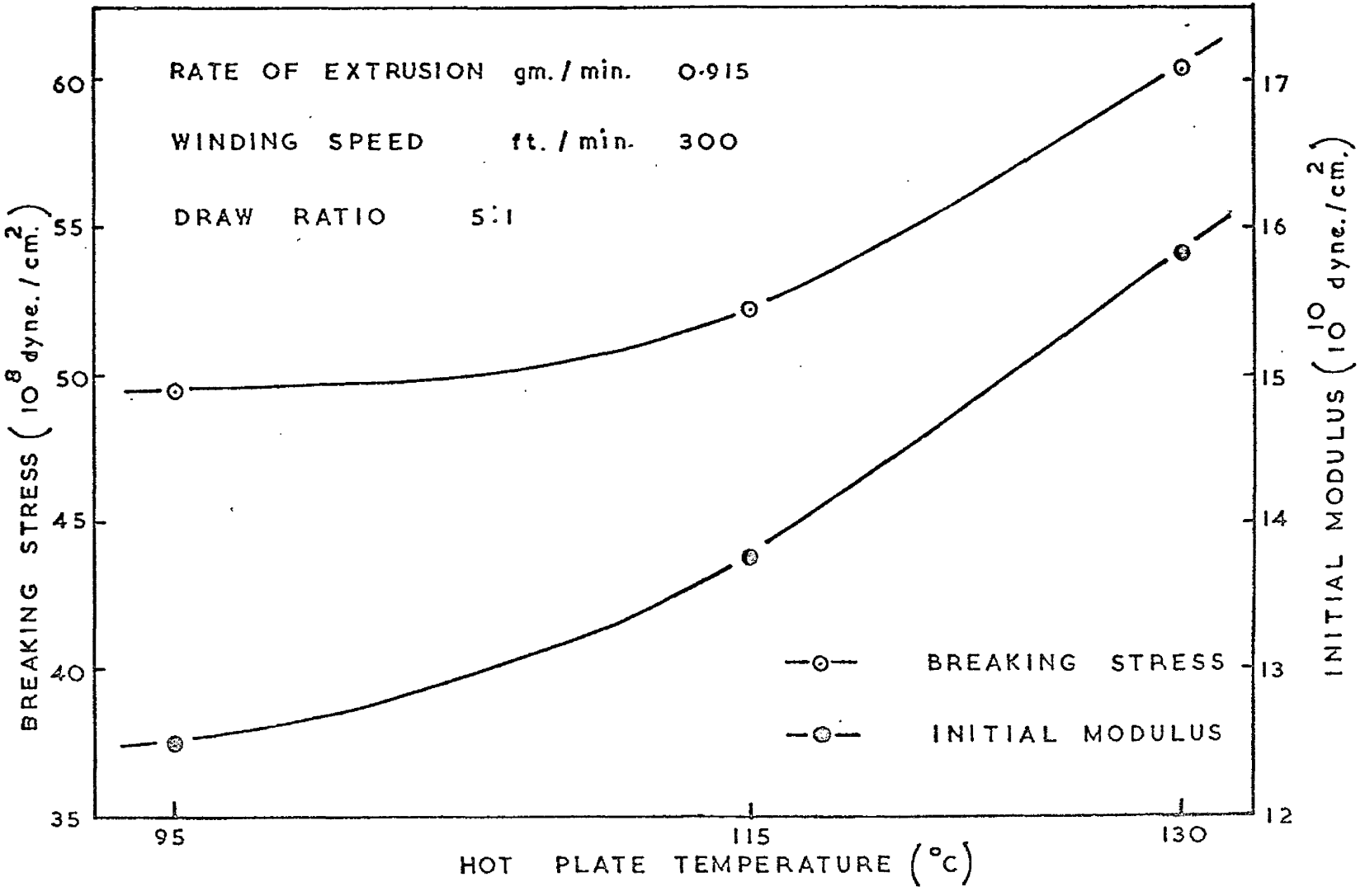
3.45 Influence of Drawing on Orientation and Crystallinity

The X-ray pattern of an extruded polyethylene terephthalate sample is poorly defined and shows a characteristic amorphous halo with no evidence of crystalline reflections.(see Plate IV). The extruded sample of polyethylene terephthalate, therefore, possesses a very low degree of molecular orientation.

The X-ray reflections given by a drawn filament of 5:1 draw ratio are shown in Plate V. These reflections are of short arcs showing that orientation and crystallinity have been induced by the drawing process. The length of the arcs gives an indication of maximum dispersion of molecular axes of the crystals from ideal parallelism with the fibre axis. The production of orientation and crystallinity by the drawing process is, of course, fairly well known, and this experiment served only to confirm that it was in fact occurring in the samples.

FIGURE. 25

INFLUENCE OF HOT PLATE TEMPERATURE ON BREAKING STRESS AND INITIAL MODULUS AT CONSTANT MELT SPINNING CONDITIONS.



3.5 Influence of Hot Plate Temperature on Physical Properties of Fibre

The temperature of the hot plate was increased from 95°C to 115°C and 130°C, keeping all other factors constant. Filament produced at a rate of extrusion of 0.915 gm./min. and a winding speed of 300 ft./min. was drawn at a 5:1 draw ratio at each of these three hot plate temperatures. The hot pin temperature was, of course, kept constant.

3.51 Influence of Hot Plate Temperature on Tensile Properties

Breaking stress and initial modulus are plotted against hot plate temperature in Figure 25 from Table XII. The curves are convex to the hot plate axis. With increase in temperature of the hot plate breaking stress and initial modulus also increases. This is to be expected since a greater amount of the drawing takes place at the hot plate and less at the hot pin, as the hot plate temperature increases. The net result would be an increase in orientation with a subsequent increase in breaking stress and initial modulus.

Roth and Schroth[46] have observed that by

/increasing

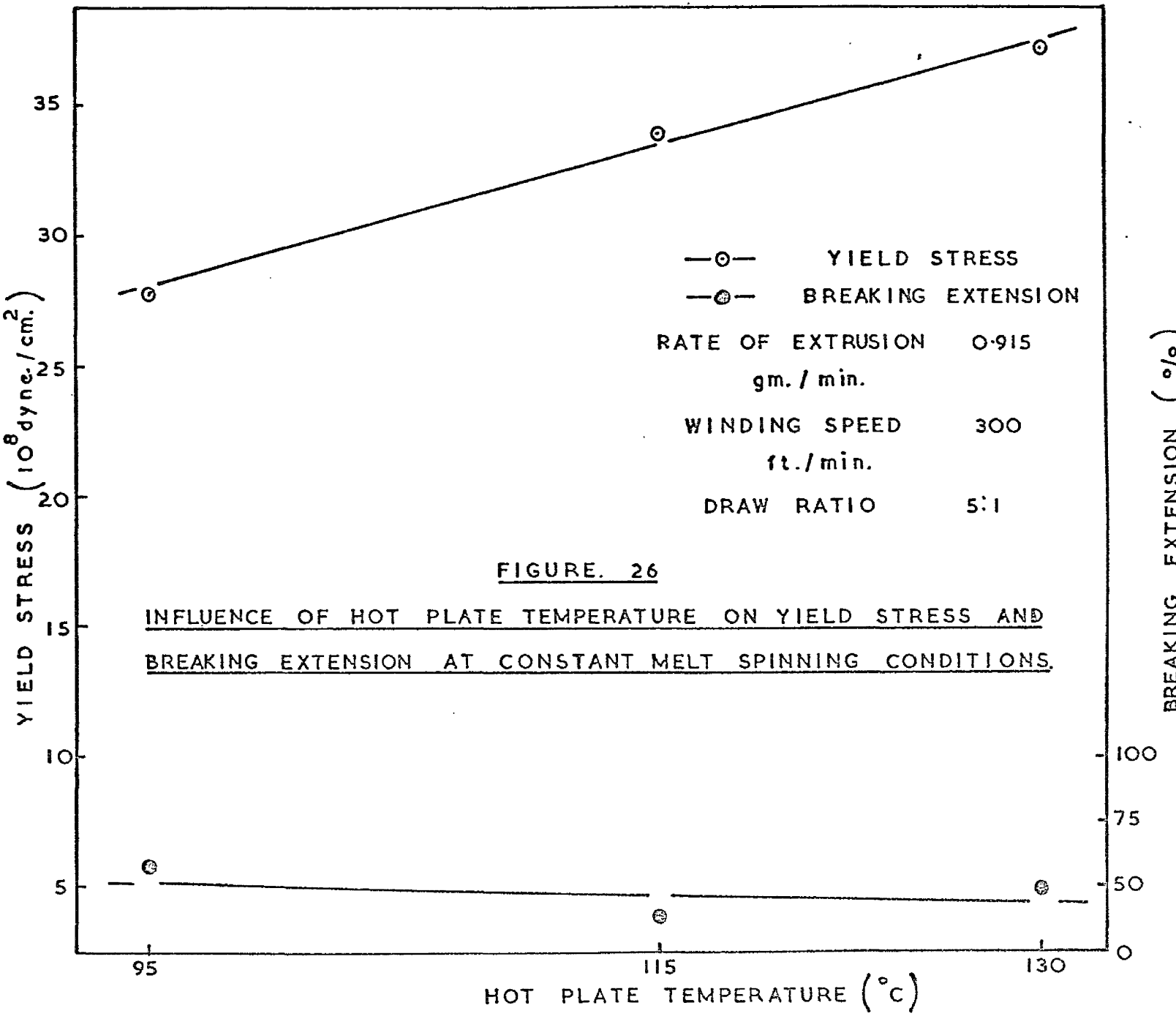
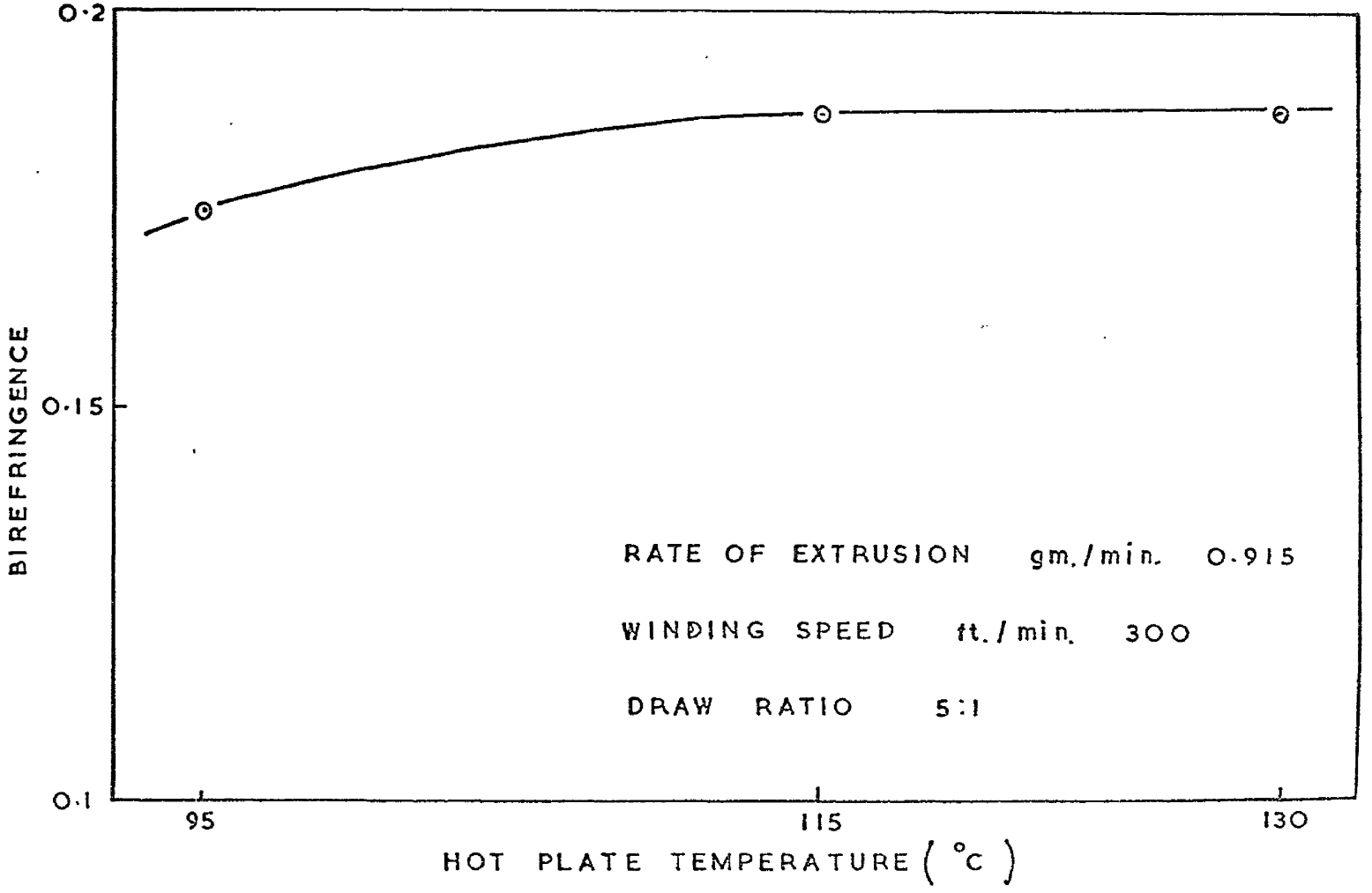


FIGURE. 26

INFLUENCE OF HOT PLATE TEMPERATURE ON YIELD STRESS AND BREAKING EXTENSION AT CONSTANT MELT SPINNING CONDITIONS.

FIGURE 27

INFLUENCE OF HOT PLATE TEMPERATURE ON BIREFRINGENCE AT CONSTANT MELT SPINNING CONDITIONS.



increasing the temperature of the hot plate, breaking stress can be increased.

Yield stress and breaking extension are plotted against hot plate temperature in Figure 26 from Table XII. Yield stress seems to increase linearly with increase in hot plate temperature; but there is a slight fall in breaking extension with increase in hot plate temperature.

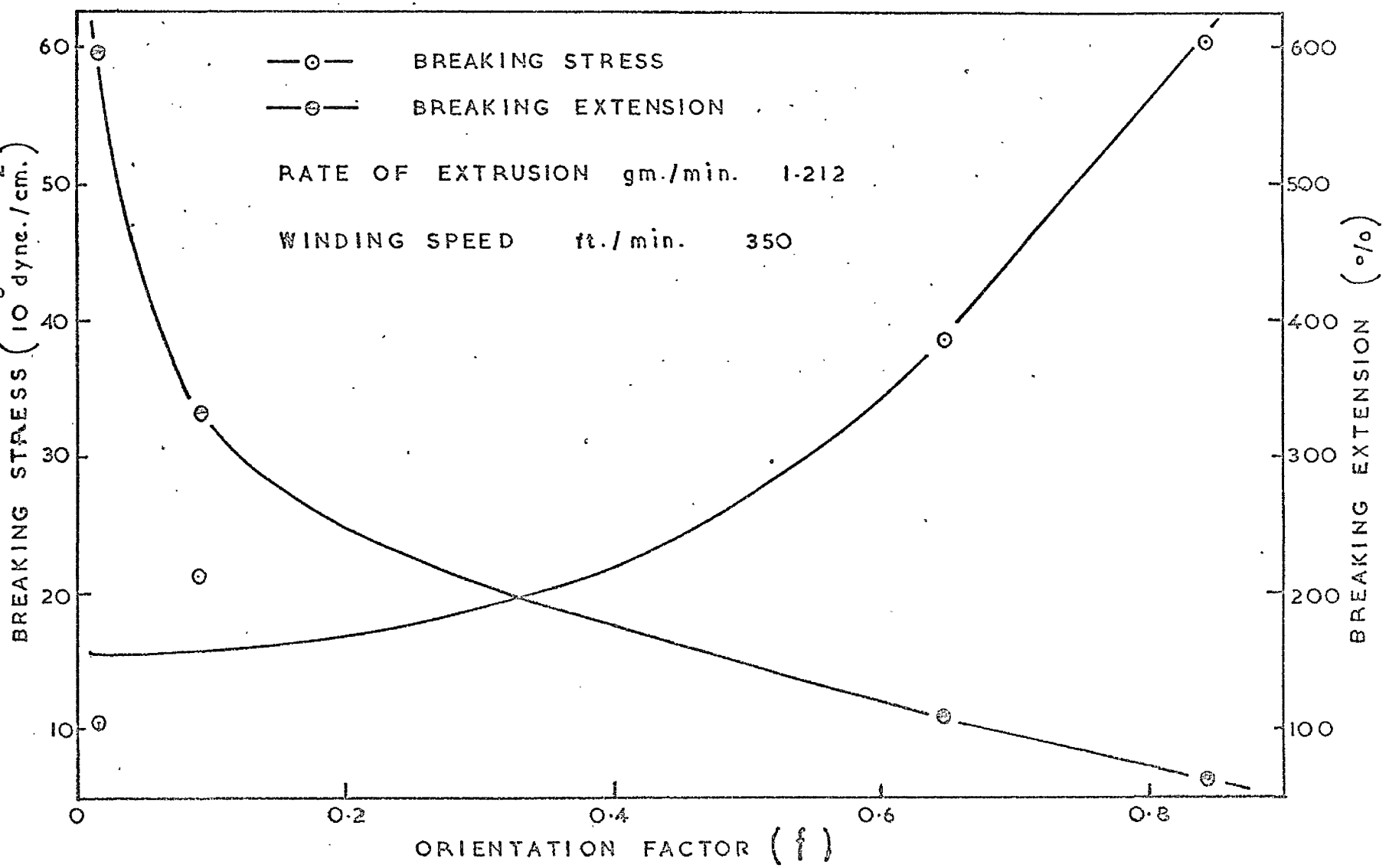
In general then, by increasing hot plate temperature initial modulus, yield stress and breaking strength increase and breaking extension falls only slightly, if at all.

3.52 Influence of Hot Plate Temperature on Birefringence

Birefringence is plotted against hot plate temperature in Figure 27 from Table XII. Birefringence increases slightly with increase in hot plate temperature and then remains steady. This confirms that molecular orientation can be increased at higher hot plate temperature although only to a limited extent.

FIGURE 28

INFLUENCE ON BREAKING STRESS AND BREAKING EXTENSION OF ORIENTATION FACTOR.



3.6 Relationship between Orientation Factor and Tensile Properties

In Figure 28, breaking stress and breaking extension are plotted against orientation factor. The curves obtained show that as the orientation factor increases, i.e. as the orientation of the chain molecules increases, breaking stress rises and breaking extension falls. This, of course, would be expected from the birefringence results. Even in the undrawn filaments Figure 28 shows that some orientation exists indicating that complete relaxation of the molecules has not occurred between the molten polymer leaving the spinneret and solidifying.

FIGURE 29

DENIER Vs BREAKING STRESS AT CONSTANT

WINDING SPEED AND VARYING RATE OF EXTRUSION.

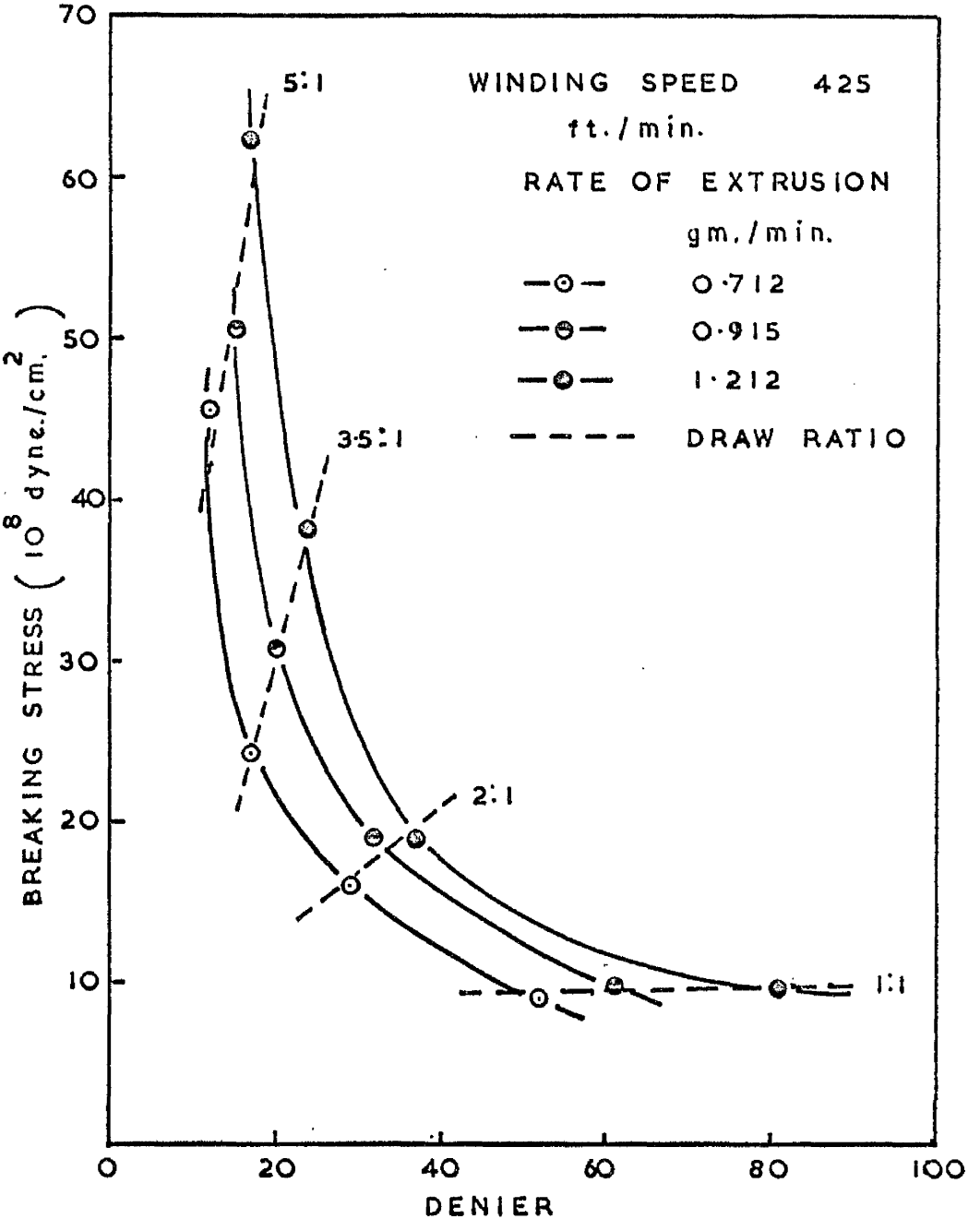


FIGURE 30

DENIER Vs BREAKING STRESS AT CONSTANT RATE OF EXTRUSION AND VARYING WINDING SPEED.

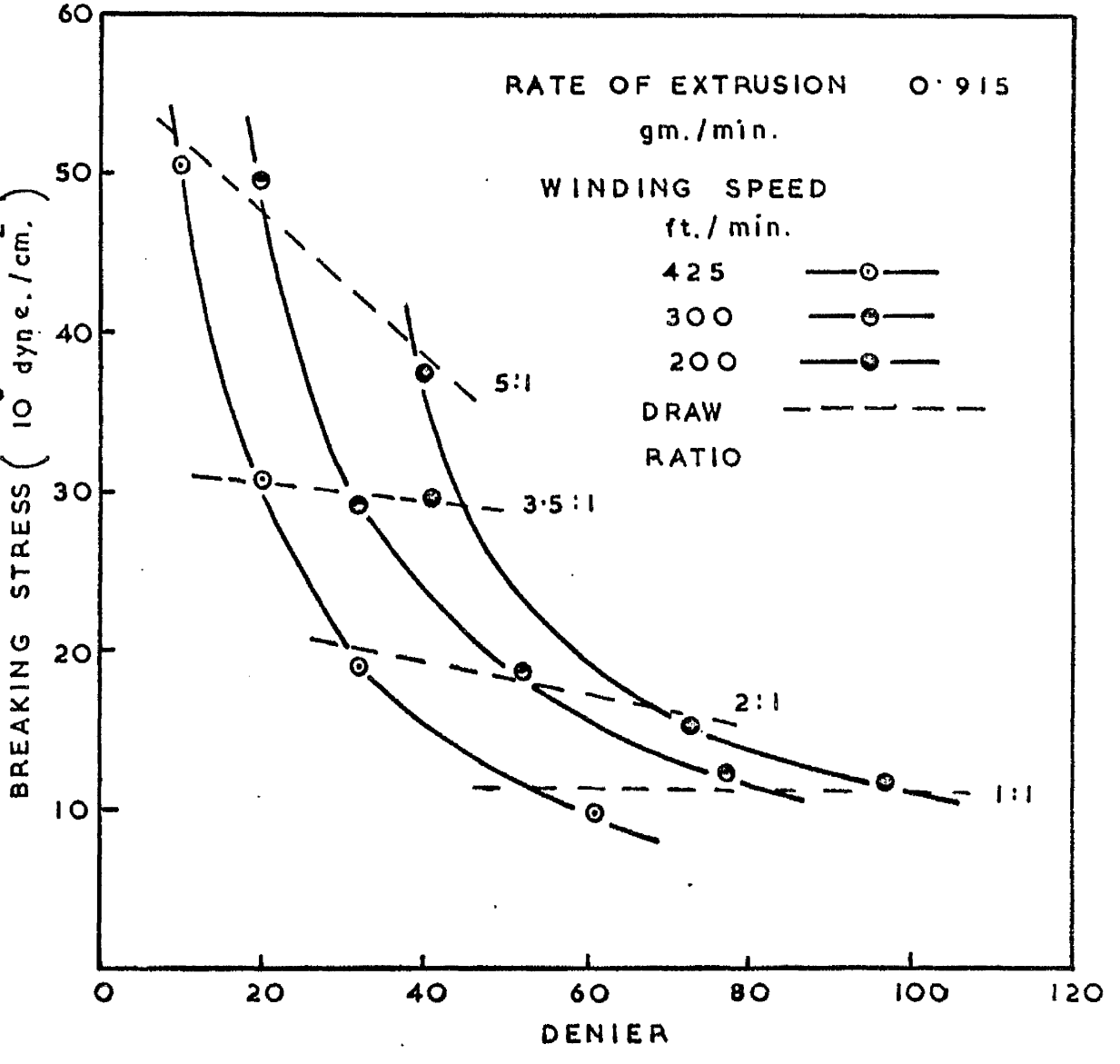


FIGURE 31

DENIER Vs BREAKING EXTENSION AT CONSTANT WINDING SPEED AND VARYING RATE OF EXTRUSION.

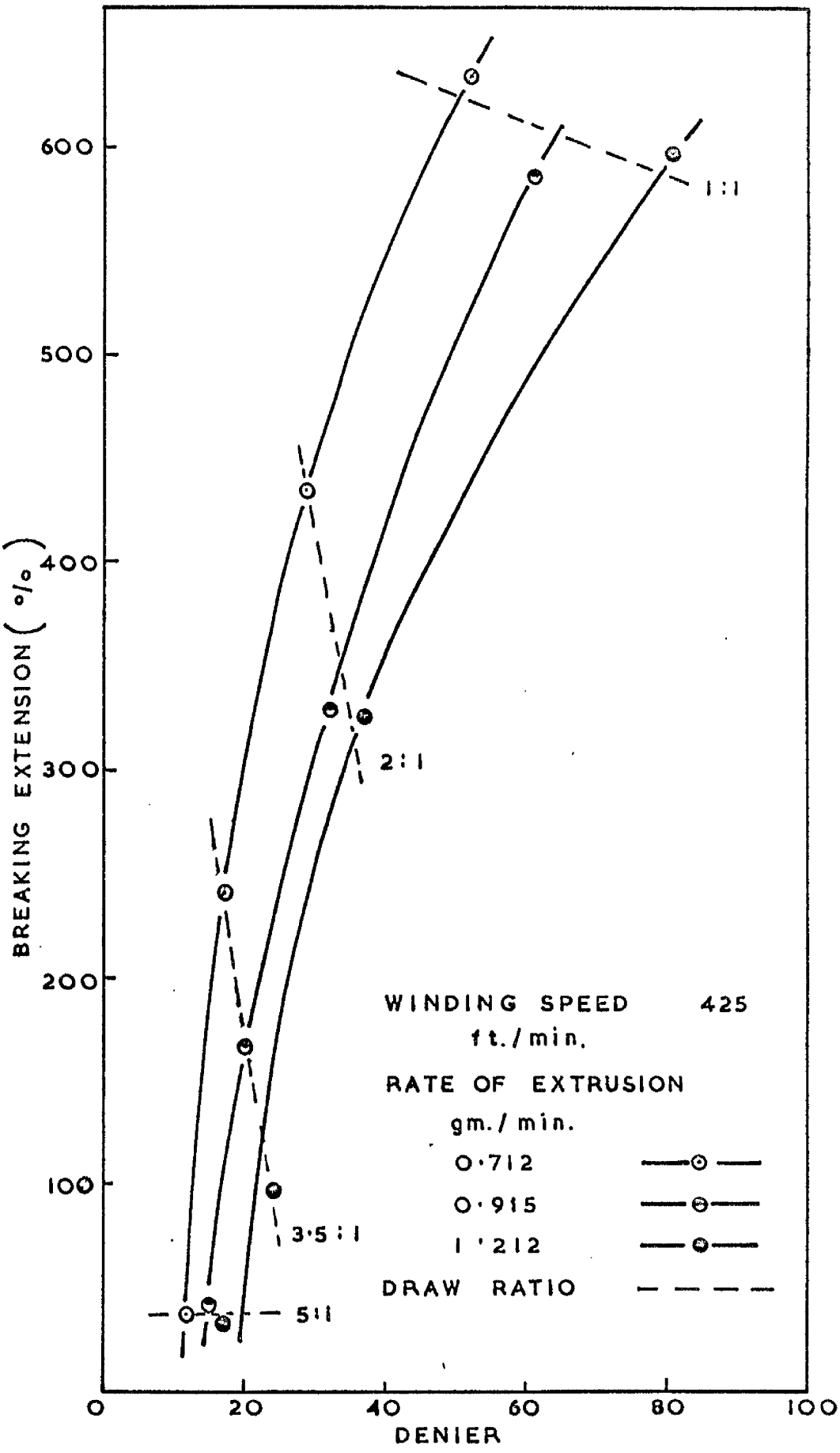
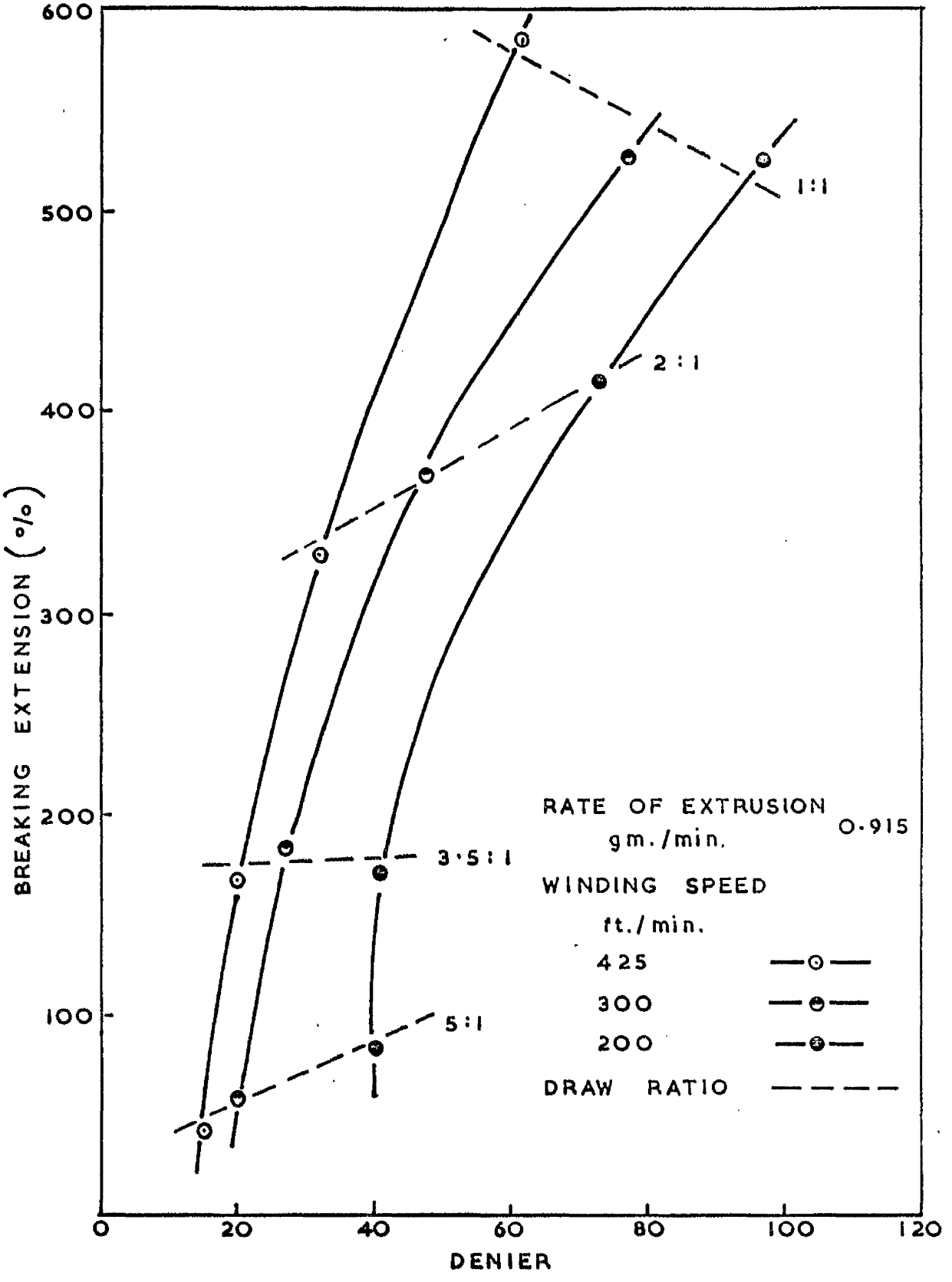


FIGURE 32

DENIER Vs BREAKING EXTENSION AT CONSTANT RATE OF EXTRUSION AND VARYING WINDING SPEED.



3.7 Influence of Denier on Tensile Properties

So far in this thesis the results have been examined from the point of view of the influence of spinning and drawing conditions on properties without actually taking into consideration the denier of the filament produced. However, it is of importance to consider the results from more than one point of view. For example, the data can be used to find the range of physical properties obtainable at any required denier, and whether or not there is more than one method of actually attaining that denier. The practical advantages of this approach are, of course, obvious.

In Figures 29-32 inclusive, denier is plotted against various physical properties under a variety of spinning conditions, from Tables VII, VIII and XIII. In Figure 29, for example, breaking stress is plotted against denier at three rates of extrusion, with constant winding speed, from Tables VII and VIII. By joining points of equal rates of extrusion three almost parallel curves, roughly hyperbolic in shape, are obtained. The broken lines join points of equal draw ratio. This Figure shows that breaking stress is much more dependent on denier at low values than at high values of denier. This means that when rate of

/extrusion

extrusion is varied from 0.712 gm./min. to 1.212 gm./min. at 50 denier, breaking stress increases from 9.5×10^8 dyne/cm.^{2} to 14×10^8 dyne/cm.^{2}. The same increase in rate of extrusion at 20 denier produces an increase in breaking stress from 21.5×10^8 dyne/cm.^{2} to 49.5×10^8 dyne/cm.^{2} In other words, as regards breaking stress, extrusion rates are much less critical for high denier filaments than for low denier filaments (spinneret orifice being kept constant).

Where a particular breaking stress is required, e.g. 40×10^8 dyne/cm.^{2}, Figure 29 shows that it can be obtained in a variety of ways. Once denier is also specified, however, the point becomes fixed in space and only one set of spinning/drawing conditions will achieve it at constant winding speed. These conditions can be found by interpolating in Figure 29. Variation in winding speed introduces yet one more degree of freedom. For example, a filament of 20 denier and 40×10^8 dyne/cm.^{2} can be produced (see Figure 29) at a winding speed of 425 ft./min., a rate of extrusion of approximately 1.1 gm./min., and a draw ratio of approximately 4:1. An identical denier and breaking stress could also be achieved (see Figure 30) at a rate of extrusion of 0.915 gm./min., using a

/winding

winding speed of approximately 350 ft./min., and a draw ratio of approximately 4.3:1.

The broken lines, in Figures 29-32 inclusive, show the effect of denier on physical properties at constant draw ratio. The actual effect varies with the particular property being considered. Figure 29 shows that in filament spun by keeping winding speed constant and varying the rate of extrusion, denier has no effect on breaking stress in undrawn filament. As draw ratio increases, however, breaking stress becomes increasingly dependent on denier.

In Figure 30 similar curves are obtained. It is interesting to note that at constant denier breaking stress is higher, the lower the winding speed. This agrees with Figure 29, in that both increasing the rate of extrusion and decreasing the winding speed increases the denier at constant draw ratio. In both cases then, draw ratio must be increased to keep denier constant, and hence breaking stress increases.

There is an apparent disagreement between the results shown in Figures 29 and 30 in that the lines of constant draw ratio give a positive slope in Figure 29 but a negative slope in Figure 30. This can be explained by referring to Figures 7 and 13 respectively.

/Figure 7

Figure 7 shows that, as the rate of extrusion increases (i.e. denier increases) breaking stress increases for drawn filament providing winding speed is kept constant. Figure 13, on the other hand, shows that at constant rate of extrusion breaking stress increases as winding speed increases (i.e. denier decreases) at constant draw ratio.

Breaking extension is plotted against denier at constant winding speed and constant rate of extrusion in Figures 31 and 32 respectively from Tables VIII and XIII. The results show rather more experimental variation than those for breaking stress. Breaking extension is extremely sensitive to denier over the entire range of deniers obtained. This accounts for the experimental variation of results, and a slight variation in denier produces a very large variation in breaking extension. Figures 31 and 32 can also be used to find, by interpolation, the spinning and drawing conditions necessary to give any required breaking extension.

C H A P T E R I V

CONCLUSIONS

4 - CONCLUSIONS

Melt filaments of polyethylene terephthalate are amorphous, relatively weak and highly extensible, irrespective of melt spinning conditions. A separate drawing process greatly improves their ultimate physical properties.

Rate of extrusion and winding speed have no significant effect on tensile properties and birefringence at lower draw ratios, but they play an important role in determining these properties at higher draw ratios. With increase in rate of extrusion, winding speed or draw ratio; yield stress, initial modulus, breaking stress and birefringence increase, while breaking extension decreases. The increase in birefringence with increase in draw ratio suggests that drawing orientates the fibre molecules. Thus, fibre with a high degree of molecular orientation will have good ultimate tensile properties.

From molecular weight determinations, it appears that polymer is only very slightly degraded during melt spinning. Polymer density also falls during this period. With increase in draw ratio there is a slight fall in fibre density, until it reaches a steady value.

Rate of extrusion, winding speed and draw ratio

/are

are important factors in determining the modulus of rigidity. Modulus of rigidity appears to pass through a minimum with increase in the rate of extrusion and through a maximum with increase in draw ratio. Also it seems to increase with increase in winding speed; except that 5:1 draw ratio filaments are less affected. This different behaviour of modulus of rigidity with rate of extrusion, winding speed and draw ratio is very difficult to explain on a molecular level, and it would be necessary to carry out some more experimental work on modulus of rigidity before arriving at a definite conclusion.

With increase in hot plate temperature initial modulus, yield stress and breaking stress increase but breaking extension decreases slightly. Birefringence slightly increases initially and then remains steady with further increase in hot plate temperature.

It has been found that where any particular value of a physical property is required at a stated denier it is possible to obtain this at more than one set of spinning conditions. Thus, although spinning and drawing apparati are limited in their performance, virtually any required fibre property value may be obtained by a suitable selection of spinning and drawing conditions within the physical limits of the material.

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TABLE I.

Variation in rate of extrusion during spinning:

Ram speed (in./min.)	Weight extruded in 10 seconds during time interval from start of extrusion			
	10 to 20 sec.	20 to 30 sec.	30 to 40 sec.	50 to 60 sec.
0.8	-	124.3	-	119.9
1.0	176.1	-	172.4	167.2

TABLE II.

Influence of ram speed on mean rate of extrusion at various winding speeds:

Ram speed (in. / min.)	Winding speed (ft. / min.)	Mean rate of extrusion (gm. / min.)
0.8	425	
0.8	250	0.712
0.8	150	
1.0	425	
1.0	300	0.915
1.0	200	
1.25	425	
1.25	350	1.212
1.25	250	

TABLE III.

Intrinsic viscosity of polyethylene terephthalate fibre and polymer "sample."

Sample	Concentration (gm./100 ml.) c	Time of flow of solvent (Sec.) η_0	Time of flow of solution (Sec.) η	Relative viscosity $\eta_r = \left(\frac{\eta}{\eta_0}\right)$	Specific viscosity $\eta_{sp} = (\eta_r - 1)$	Reduced viscosity $\eta_{red} = \left(\frac{\eta_{sp}}{c}\right)$	Intrinsic viscosity $[\eta]$
Polyethylene terephthalate fibre	0.450	120.2	160.1	1.33	0.33	0.740	0.57
	0.225	120.2	137.9	1.15	0.15	0.659	
	0.112	120.2	128.5	1.07	0.07	0.615	
Polymer "sample"	0.447	120.2	160.7	1.38	0.38	0.754	0.60
	0.223	120.2	138.2	1.15	0.15	0.671	
	0.112	120.2	128.7	1.07	0.07	0.625	

Temp. = 20°C. Solvent = Equal volumes of tetrachloroethane and phenol.

TABLE IV.

Moment of inertia of inertia bars.

No.	Moment of inertia by theoretical calculations ($gm.\ cm^2\ 10^{-3}$)	Moment of inertia compared with bar of known length and weight ($gm.\ cm^2,\ 10^{-3}$)	Moment of inertia compared with bar of known moment of inertia ($gm.\ cm^2,\ 10^{-3}$)
1	63.0	61.5	62.5
2	48.9	48.5	49.4
3	63.0	62.6	63.7
4	63.0	60.6	61.7
5	56.5	56.2	57.1
6	48.9	50.2	49.9

TABLE V.

Influence of melt spinning conditions on initial modulus n = 10

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Initial modulus at 1% extension (10^{10} dyne./cm.^{2}) at draw ratio of 1 : 1	2 : 1	3.5 : 1	5 : 1
0.712	425	2.0	2.2	2.8	12.7
0.712	250	2.5	2.1	2.5	13.3
0.712	150	1.8	2.3	4.0	10.1
0.915	425	2.0	2.2	3.1	12.5
0.915	300	2.3	2.3	4.3	12.5
0.915	200	2.3	2.3	3.8	8.2
1.212	425	1.9	2.3	7.2	15.4
1.212	350	2.1	2.3	6.8	10.9
1.212	250	1.7	2.2	3.5	8.9

NOTE: n denotes number of samples tested to obtain each value quoted.

TABLE VI.

Influence of melt spinning conditions on yield stress

n = 10

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Yield stress (10^8 dyne/cm^2) at draw ratio of 1 : 1	2 : 1	3.5 : 1	5 : 1
0.712	425	5.4	6.5	7.5	32.5
0.712	250	6.4	5.5	6.1	33.9
0.712	150	5.3	6.1	9.1	22.5
0.915	425	5.8	5.0	7.5	33.5
0.915	300	5.1	6.6	8.7	27.7
0.915	200	6.5	6.0	8.3	17.4
1.212	425	5.2	5.7	14.9	42.9
1.212	350	5.6	6.3	14.1	25.5
1.212	250	5.1	6.1	7.9	19.3

TABLE VII.

Influence of melt spinning conditions on breaking stress.

n = 10

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Breaking stress, (10^8 dyne/cm^2) at draw ratio of 1 : 1	2 : 1	3.5 : 1	5 : 1
0.712	425	9.0	16.1	24.4	45.5
0.712	250	10.7	15.9	20.3	48.4
0.712	150	10.5	17.9	32.1	42.1
0.915	425	9.7	19.1	30.0	50.5
0.915	300	12.3	18.6	29.3	49.6
0.915	200	11.8	15.3	29.7	37.3
1.212	425	9.9	19.0	38.2	62.9
1.212	350	10.5	21.2	38.6	60.4
1.212	250	8.7	15.6	22.0	39.5

Table XXII.

Influence of melt spinning conditions on breaking extension.

n = 30

Rate of extrusion (gms./min.)	Winding speed (cms./min.)	Breaking extension (%) at draw ratio of 1 : 1	2 : 1	2.5 : 1	3 : 1
0.712	425	693	439	210	37
0.712	250	626	378	208	49
0.712	350	581	328	189	75
0.925	425	587	326	167	41
0.925	300	527	268	104	59
0.925	200	525	425	172	64
1.212	425	596	325	97	30
1.212	350	596	291	106	62
1.412	250	648	347	240	81

Table XX.

Influence of melt spinning conditions on modulus of rigidity

n = 5

Rate of extrusion (gms./min.)	Winding speed (cms./min.)	Modulus of rigidity (10^{10} dyne/cm^2) at draw ratio of 1 : 1	2 : 1	2.5 : 1	3 : 1
0.712	425	0.77	0.90	0.89	0.83
0.712	250	0.68	0.65	0.72	0.84
0.712	350	0.62	0.59	0.60	0.84
0.925	425	0.62	0.66	0.80	0.83
1.212	425	0.80	0.81	0.76	0.62

TABLE X.

Influence of melt spinning conditions on birefringence

n = 2

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Birefringence, at draw ratio of 1 : 1	2 : 1	3.5 : 1	5 : 1
0.712	425	0.0011	0.006	0.038	0.185
0.712	250	0.0021	0.014	0.070	0.172
0.712	150	0.0062	0.020	0.075	0.161
0.915	425	0.0029	0.017	0.066	0.196
0.915	300	0.0062	0.021	0.058	0.175
0.915	200	0.0055	0.009	0.089	0.166
1.212	425	0.0029	0.017	0.147	0.209
1.212	350	0.0028	0.038	0.130	0.170
1.212	250	0.0031	0.012	0.074	0.150

TABLE XI.

Influence of melt spinning conditions on density.

n = 2

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Density (gm/cm^3) at draw ratio of 1 : 1	2 : 1	3.5 : 1	5 : 1
0.712	425	1.385	1.389	1.389	1.384
0.712	250	1.384	1.384	1.389	1.389
0.712	150	1.384	1.389	1.389	1.389
0.915	425	1.385	1.384	1.384	1.384
0.915	300	1.385	1.384	1.389	1.389
0.915	200	1.384	1.384	1.389	1.389
1.212	425	1.384	1.389	1.384	1.389
1.212	350	1.384	1.389	1.389	1.389
1.212	250	1.385	1.389	1.384	1.384

TABLE XII.

Influence of hot plate temperature on filament properties as constant melt spinning conditions

Temperature of hot plate °C	Filament diameter μ	Yield stress (10^8 dyne/cm^2)	Breaking stress (10^8 dyne/cm^2)	Initial modulus at 3% extension (10^{10} dyne/cm^2)	Breaking extension (%)	Birefringence
95	40.9	27.7	49.6	12.5	58.6	0.175
115	42.0	33.9	52.3	20.1	12.8	0.187
130	42.0	37.2	60.4	49.0	15.9	0.187

Rate of extrusion gm./min. 0.935. Winding speed ft./min. 300. Draw ratio : 5 : 1.

TABLE XIII.

Influence of melt spinning conditions on denier.

Rate of extrusion (gm./min.)	Winding speed (ft./min.)	Denier at draw ratio of 2 : 1	2 : 1	3.5 : 1	5 : 1
0.722	425	52	29	17	12
0.712	250	67	46	27	18
0.712	150	113	65	37	22
0.935	425	61	32	20	15
0.935	300	77	47	27	20
0.935	200	97	73	48	40
1.212	425	81	37	24	17
1.212	350	90	49	29	24
1.212	250	127	64	38	35