THE EFFECT OF TEMPERATURE AND STRAIN RATE ON THE TENSILE PROPERTIES OF SOME NEW TEXTILE YARNS

by

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SUMMARY

The tensile properties of some new textile yarns have been studied with particular reference to the effect of temperature and rate of strain application on the stress-strain behaviour. The work has been split into two parts covering different types of material.

In part 1, an Instron tensile tester was used to investigate the effect of strain rate and temperature on the stress-strain properties of two samples of polypropylene yarn. Differences in behaviour occurring between the samples were explained by measurements of structural properties such as isotactic index and average molecular weight. Results were compared with data from the literature on an isotactic polypropylene yarn. The method of reduced variables has been used to apply time-temperature superposition and obtain composite curves reduced to a standard reference temperature. This was done for the ultimate stress and strain values and values of stress at lower strains expressed as the tensile modulus. A similar superposition was obtained from stress relaxation data.

In part 2, five samples of synthetic polyurethane elastomeric yarns and one sample of natural rubber yarn have been studied under different conditions. The stress-strain curve, toughness, Schwartz value, elastic recovery and stress relaxation properties have been measured and compared. The stress-strain curve of one of the synthetic yarns was studied at different temperatures and initial strain rates. Unlike polypropylene, the same superposition could not be applied to all the data in this case. The equivalence of changes in time and temperature alters with increasing strain as the molecular orientation alters.

Yarns of completely different structure have been studied and it has been shown that time-temperature superposition can be applied, in a restricted form, to a non-linear semi-crystalline material. It is therefore possible to obtain data necessary to characterise the behaviour of a material over several decades of logarithmic time using a single instrument of a type used in normal tensile testing procedure.

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PART I POLYPROPYLENE

I.I INTRODUCTION

Textile fibres have been used for many centuries for a wide variety of purposes. The ancient Egyptians knew how to weave satisfactorily and, in fact, some fine examples of their work are preserved to this day. Until recently however, the manufacturing processes have been developed and carried on in what can only be described as ignorance of the fundamental properties of the materials being handled. Even in the present day, when we consider research techniques to have reached an advanced stage, many processes in the field of textile technology are not fully understood or do not reap the benefit of the fundamental knowledge already available.

Certainly one reason for this slow progress is the number of outside influences which can affect the behaviour of a fibre. Most fibre-forming materials are viscoelastic crystalline polymers with preferential orientation of the crystallites along the fibre axis. The physical properties of such materials are often inter-related and are affected by such variables as

(1) Temperature. Heat causes a change in the internal viscosity or flow properties and will affect relaxation

and creep and associated dynamic mechanical properties. The basic microcrystalline structure of such polymers is affected and a change in density due to re-orientation or changes in crystallinity may result. The thermal history of the material is therefore important.

(2) Humidity. By far the largest percentage of fibres used commercially are hydrophilic and are therefore affected by moisture in the surrounding air. In some cases small changes in relative humidity have a greater effect on properties than small changes in temperature.

(3) Time. Both the previous variables affect rate processes within the material. Superimposed on this is the external time factor applied by the measuring instrument and governed by the method used. Not only is the rate at which the test is carried out and its duration important, but the speed with which a measurement can be made or the response time of the recorder must be borne in mind.

(4) Sample variability. This is an obvious cause of an apparent change in behaviour, yet it is the one most often ignored or given least attention. Natural textile materials in particular are notoriously variable. Their growth is affected by their geographical situation, climate, disease and other environmental conditions. Man has

greater control over the synthetic materials and they are generally more uniform, though still far from perfect. It is, therefore, necessary to take precautions against obtaining an unrepresentative result when measuring the properties of these materials. Statistical methods must be used for both sampling and analysis of results.

Thus the measured value of a property affected by the viscoelastic nature of textile materials has little meaning unless the conditions under which the measurement was made are known or taken into account.

Such is the case when measuring the tensile properties. Strength, whether it be tensile, loop, tear, burst, yield or ultimate, is one physical property which has found wide application as a measure of uniformity and a tool of quality control for textile materials in fibre, yarn and fabric form. It was not until control limits became more precise, with the advent of new materials, improved methods and increasing competition, that the effect of test conditions on the values obtained became important enough to be significant. The initial problem was avoided by standardising the test conditions but interest developed in measuring quantitatively the changes caused by variations in these conditions.

The time effect was the first to be studied since it can be easily controlled and measured over a limited range on standard testing equipment.

Peirce[1,2,3] and co-workers did some of the early work related particularly to cotton and found that the breaking load increased in proportion to the logarithm of the rate of loading. This relationship was established, over the restricted range of three decades of logarithmic time, in fibre, yarn and fabric form. Both Bellinson[4] and Entwistle[5] noted a similar relationship in viscose rayon yarns.

Special techniques have been used to extend the time range over which the effect can be measured beyond that possible using conventional testing machines. Constant loading[6] and high speed impact methods have been used to obtain information at very long and very short times respectively. There are a wide variety of methods by which impact loads can be applied totextile yarns and fabrics. Among them are longitudinal impact by a freely falling weight,[7] by a weight pneumatically or hydraulically propelled[8,9] or by direct impact of a flywheel[10,11,12] or a ballistic pendulum[13,14] Transverse impact[15] by a bullet or similar missile has also been used successfully to measure tensile properties at high speed.

Meredith[6,16] made measurements on cotton yarn at normal test speeds, producing results in agreement with Peirce. Then, using high speed techniques, he found that the same relationship held over 10 decades of logarithmic time with only slight differencies due to the various test methods used. In a later paper,[10] viscose and acetate rayon, silk and nylon yarns were studied at high strain rates. With the exception of acetate rayon, the initial modulus was found to increase linearly with the logarithm of the rate of elongation.

Smith[17] and co-workers obtained stress-strain curves at rates of straining of up to 7000 per cent per second for several textile yarns and compared them with curves produced at conventional testing speeds. Generally, it was found that the yield stress was approximately proportional to the logarithm of the rate of elongation in agreement with Meredith.[10] It has also been shown[18] that this relationship holds for stress at a given strain beyond the yield point. Although most writers note a similar trend in the breaking stress, with the exception of cotton it has not been correlated, probably due to the effect of apparently unpredictable variations in the breaking strain. Bellinson,[4] however, did establish a direct relation between the breaking stress and the rate of loading for viscose rayon yarn by using a simple regression equation.

Thus, with a few exceptions, a simple general relationship has been established between the time factor and stress in a textile material, although the proportionality may differ between materials.

It was realised that, while the rate of testing affected the stress in a material by external means, temperature would affect it by altering the rate processes within the fibre. An increase in the rate of stressing or straining causes a corresponding increase in stress at a given strain because less time is allowed for relaxation to take place. An increase in temperature, however, will increase the rate of relaxation and therefore cause a decrease in stress at a given strain, provided the speed of testing remains unaltered. An increase in temperature therefore has a similar effect to a decrease in the rate of stressing or straining.

This was clearly illustrated by Kaswell[19] who used the combined effect of low temperature and high speed testing to obtain data on tensile properties of drawn, partially drawn and undrawn nylon, silk and vinyon yarns under extreme conditions. A reduction in temperature or an increase in strain rate produced an increase in the stress at a given strain and generally led to an increase in breaking stress but a decrease in the energy required to cause rupture due to a drop in the breaking elongation. In certain cases at high test speeds the reduction in the breaking strain was marked and the breaking stress also showed a decrease.

Hall[20] carried out a more detailed study using isotactic polypropylene yarn. Tensile tests were made to investigate the effect on the stress-strain curve of passing through the glass transition region. The glass transition temperature for this polymer has been given as 253°K[21] and 255°K[22] measured by dilatometry, and a temperature range of 90°K to 308°K was used for the first series using a single strain rate. These tests showed a rapid drop in breaking strain and little change in the breaking stress in the range 260°K to 290°K followed by a more gradual fall in breaking strain and rise in breaking stress at lower temperatures. A second series was carried out at room temperature using strain rates above that used in the previous tests and covering a range of six decades of logarithmic time. A similar trend was observed, the transition effect showing at rates between 4×10^{-3} and 3×10^{-1} sec^{-1} and the gradual fall in breaking strain with accompanying rise in breaking stress occurring at higher strain rates. Thus structural changes caused by changes in temperature appear to be closely related to, if not the same as, those due to changes in the rate of straining.

This leads to the concept of time-temperature superposition. If changes in viscoelastic properties caused by an alteration in the time scale can be related, as in, say, a material whose properties vary linearly with time, and this is equivalent to an alteration in temperature, then one measurement should complement the other. It has already been shown that a decrease in temperature is apparently equivalent to an increase in the time scale or vice-versa. Thus, by varying both the temperature and the time scale, it would be possible to extend the scale of measurement outside the normal experimental limits by converting temperature data to their equivalent position on the time scale.

I.2 THE TIME-TEMPERATURE SUPERPOSITION PRINCIPLE

The principle, whereby viscoelastic data at one temperature may be translated to their values at another temperature by a simple horizontal shift of the time scale, was first introduced by Tobolsky and Andrews[23] and by Leaderman[24] in 1943.

Tobolsky and his co-workers used the statistical theory of rubber elasticity[25] as the basis of their method. The theory predicts that

$$\sigma = nkT \left\{ \frac{l_1}{l} - \left(\frac{l}{l_1} \right)^2 \right\} \quad \text{-------} \quad (1)$$

where σ is the stress calculated on the original cross-section, n is the number of network chains per cubic centimeter, k is Boltzmann's constant, T is the absolute temperature and l and l_1 are the unstretched and stretched lengths of the specimen. For stress relaxation experiments l and l_1 are fixed and σ is proportional to n and T. The temperature effect can be eliminated by relating all the stress values to some arbitrary reference temperature T_0. Thus the reduced stress $\sigma_R = {}^{T_0}/T \cdot \sigma$ is a direct function of n and since n should change only slightly with temperature, curves of reduced stress against time measured at different temperatures should superpose by a horizontal translation along the time axis. This method assumes that rubber elasticity increases with absolute temperature and that the viscoelastic behaviour of the system is linear.

By this means composite stress relaxation curves have been obtained for several amorphous polymers. The combination of time and temperature dependence has made it possible to determine the viscoelastic behaviour over a much wider time scale than would be obtainable otherwise. Tobolsky and his co-workers[26-31] used the stress relaxation method to obtain composite curves covering up to 12 decades of logarithmic time for polysulphide rubbers,[26] polyisobutylene,[27] polymethyl acrylate,[28] polymethyl methacrylate,[29] polystyrene,[28] plasticised polyvinyl chloride[30] and certain gum vulcanates.[31]

In 1950 Ferry[32] developed his method of reduced variables along similar lines. If a material is characterised by a generalised Maxwell model, changes in concentration and temperature will multiply all relaxation times by the same factor. Assuming that the rigidity associated with each element in the model is proportional to the absolute temperature and the polymer concentration, it is possible to bring data to a standard reference state by use of reduced variables. The principle remained in an empirical form until 1953 when it was given a sound theoretical basis with the introduction of a flexible-chain theory by Rouse.[33] This was supplemented in the following year by a similar theory by Bueche.[34] Both analysed the motion of long chain molecules in a viscous medium. The theories describe a viscoelastic material in terms of a modulus E(t) and a characteristic relaxation time τ_K. The modulus is proportional to the number of effective network chains per unit volume and the absolute temperature (cf. n and T in equation (1)). The characteristic relaxation time is determined primarily by the zero shear viscosity and is inversely proportional to the number of effective network chains per unit volume and the absolute temperature. This corresponds to the assumptions made by Ferry.

The polymer density replaces the concentration term when the theory is applied to undiluted polymer and, when expressed in terms of the shear relaxation spectrum H, it predicts

$$H = \frac{\rho RT}{M} \Sigma \tau_p \, \delta(\tau - \tau_p) \quad \text{---------} \quad (2)$$

where $$\tau_p = \frac{a^2 Z^2 \zeta_0}{6\pi^2 p^2 kT} \quad \text{------------} \quad (3)$$

where ρ is the polymer density, R, the gas constant, M the molecular weight, δ, the Dirac delta, τ, the relaxation time, p, an integer, a, the root-mean-square end-to-end distance per square root of the number of monomer units, Z, the degree of polymerisation and ζ_0 is the average friction coefficient per monomer unit. Temperature dependence enters in several ways, the factors T and ρ in equation (2) and the primary effect in ζ_0 in equation (3) which is also affected by T and a, which may change slightly. Ferry[35] linked the factors in equation (3) together to form the horizontal shift factor a_T while the

$$a_T = \frac{[\tau_p]_T}{[\tau_p]_{T_0}} = \frac{[a^2 \zeta_0]_T T_0}{[a^2 \zeta_0]_{T_0} T} \quad ---- \quad (4)$$

factors in equation (2) form the small vertical adjustment $\rho T / \rho_0 T_0$ where ρ_0 is the polymer density at an arbitrary reference temperature T_0.

There is only a slight difference between the method of Ferry and that of Tobolsky. The latter omits the density term from the vertical correction factor. This detail, however, has been found to be insignificant in work reported in the literature on amorphous polymers since their density remains almost constant over a wide range of temperature and the correction is negligible.

Ferry[36] and his co-workers found that, within a limited temperature range, the ratio a_T of mechanical relaxation times at temperature T to those at a reference temperature T_o could be expressed by

$$\log a_T = \frac{-C_1 (T-T_o)}{C_2 + T - T_o} \text{ - - - - - - - - - } (5)$$

and, by selecting T_o to be approximately 50° above the glass transition temperature and restricting the range of T to $T_o \pm 50^\circ$, the same constants, $C_1 = 8.86$ and $C_2 = 101.6$, were found to apply to a wide variety of polymers, polymer solutions, organic glass-forming liquids and even inorganic glasses, although the transition temperature for the last group is in a much higher range than the others. The lower limit of application of this precise form of equation (5) is due to the fact that the variation in free volume above and below the transition point is different. Curves of specific volume against temperature show an inflection at this point, a fact which is often utilised to measure the transition temperature. However a different form of equation (5) may be applicable below this temperature. The upper limit is due to a decrease in the non-specific behaviour allowing the effect of structure to play an increasing role and causing a variation in the behaviour of different polymers. Thus a single empirical function was established to describe the temperature dependence of all mechanical relaxation processes, in the range 100° immediately above the glass transition temperature. This function, now known as the W.L.F. equation, has since been used by various writers. Recently Tobolsky[28,30,37] has used a modified form incorporating characteristic parameters which had been established in his earlier work. Brettscheider[38] and Smith[39] have both used the exact form described in equation (5) to characterise the behaviour of solid rocket fuels and a GR-S rubber respectively. Both papers describe the application of the superposition principle to the ultimate tensile properties, breaking stress and strain, over a wider range of temperatures than indicated in the theory. The application to ultimate properties is interesting since linear viscoelastic behaviour found in amorphous materials may not apply to the full stress-strain curve but may be restricted to the initial portions only.

There is not an equivalent superposition principle for crystalline polymers which can be applied in such a general form. The principle for the amorphous materials already discussed assumes a reversible temperature effect and linear viscoelastic behaviour. The validity of both these assumptions in relation to crystalline polymers, which are the main fibre forming polymers, is questionable, but with no alternative available their application was attempted.

Tobolsky[40,41] tried, without success, to extend his method to include polymers with a crystalline structure. In studies of polytrifluorochloroethylene[40] and polyethylene[41] it was found that the transition region extended over a much wider temperature range and specific structural features appeared to have a continuous effect on the behaviour. It was concluded that the general equivalence of time and temperature and the simple time-temperature superposition were not valid, but that some additional vertical shift factor would have to be introduced to correct for the structure effect before any superposition could be achieved. It should be pointed out that a very wide range of temperatures was used in each case (over 160°) and if any changes in microcrystalline structure are going to occur it is a distinct possibility that they will occur to some extent within this range.

More recently Nagamatsu[42,43] and his co-workers, using stress relaxation measurements have successfully applied Ferry's method and produced composite relaxation curves for polytetrafluoroethylene[42] and polytrifluorochloroethylene.[43] To achieve this, non-linear viscoelastic effects were avoided by using strains of less than 1% and the effect of temperature on the structure was minimised by selecting a restricted temperature range in which little or no change took place. When the same technique was used to study polyethylene[44] it was found that there was a marked increase in crystallinity as the temperature decreased, and the simple superposition principle could not be applied. A composite curve was obtained when the degree of crystallinity was introduced in the vertical shift factor.

Polyethylene, in fibre and plastic form, has received more attention than other crystalline polymers. Methods similar to that of Nagamatsu have been used successfully in studies of stress relaxation behaviour of a commercial plastic[45] and of the ultimate tensile behaviour of a yarn.[46] In the latter study ultimate stress and strain obtained at different strain rates and temperatures were reduced to composite curves although this material is known[47] to have distinctly non-linear viscoelastic behaviour. This would appear to add strength to the argument that linear viscoelastic behaviour is not a necessary criterion for the successful application of the superposition principle.

Considerable ambiguity was found in the results of different writers[45,47] for the same polyethylene plastic. In one case[45] a correction was used to compensate for a rapid change in crystallinity, particularly between 0° and 90°C. In the other[47] the crystallinity was reported to be constant over the range from 0° to over 80°C and the simple time-temperature superposition was found to apply. Such a pronounced difference is surprising and inexplicable, although it has been recognised in recent years that the crystallinity of many polymers remains constant or nearly so over a considerable range of temperature.

The only other fibre material to have received much attention is nylon, a hydrophilic material with a moisture regain of about 4% under standard atmospheric conditions. It is therefore affected by humidity as well as temperature, and both time-temperature and time-humidity superposition have been applied to the viscoelastic behaviour of this polymer, which is unique in that it is almost linear at small strains. Simple time-humidity superposition of stress relaxation data[48] of nylon 6 has been achieved using a form of the W.L.F. equation. Stress relaxtion of nylon 6 film specimens[49] has been measured in torsion at several different temperatures and three humidities and all the data reduced to a common curve covering 21 decades of logarithmic time. In another paper[50] the real and imaginary parts of the complex dynamic modulus were obtained from vibrational experiments on nylon 66 using several different humidities and two temperatures. Again a single composite curve was obtained from all the data for each part of the modulus by applying the method of reduced variables.

It is seen that what little work has been done on the application of the superposition principle to crystalline polymers does not present a very clear picture of the behaviour of these materials. Briefly it has been found that the principle cannot be applied to data covering unlimited ranges of time or temperature in some cases, while in others it can only be applied when modified to take structural changes due to changes in temperature into account. It has also been found that it can be used to describe data obtained in a limited temperature range at small strains, yet can also be applied (in the modified form) to data at high strains to describe the ultimate tensile properties of yarns made from these polymers.

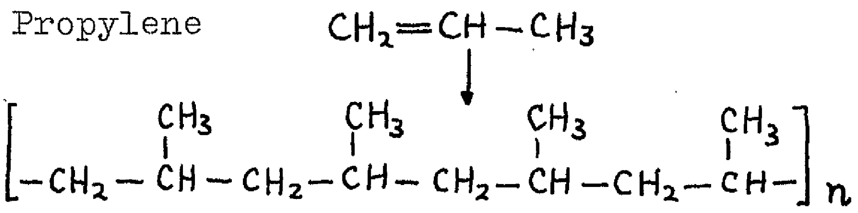
In the present study the tensile properties of polypropylene, a close relative of polyethylene, have been investigated. It has been assumed that the simple superposition principle could be used to reduce data obtained for this non-linear, crystalline material in an attempt to describe more precisely the relationship between temperature and the time factor for this type of polymer.

I.3 EXPERIMENTAL

1.3.1 The Material

Polypropylene was chosen as the material to be studied in the first part of the work for several reasons. It is the most recently developed high tenacity textile yarn and shows considerable potential due to its low density and high strength. It has already found a market in light weight blanketing and is being developed for use in carpet yarns. It is hydrophobic and is therefore unaffected by moisture in the atmosphere. This makes the study of its properties relatively simpler by eliminating one variable. Finally the polymer itself is of some interest because of certain structural peculiarities not normally found in fibre forming materials which affect its physical properties and their interpretation.

Propylene is a member of the olefin family of unsaturated hydrocarbons and, as such, is capable of polymerisation by addition. Depending on conditions and the catalyst used varying mixtures of three known types may be formed. Of these the isotactic form is by far the most common. It is produced by the normal head-to-tail polymerisation process and has all the methyl side-groups on the same side of the chain. The atactic form is known to exist in commercial polypropylene yarns to a small extent. It is produced by a random polymerisation and shows no ordered arrangement of the side groups. The syndiotactic form is less common and is not normally found in commercial yarns. It is the result of head-to-head, tail-to-tail polymerisation which gives an alternate arrangement of the side groups on each side of the chain. The three types are illustrated in Fig. 1.1.

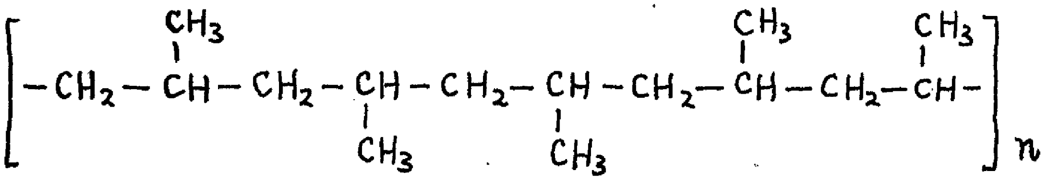


Propylene $CH_2{=}CH-CH_3$

$$\downarrow$$

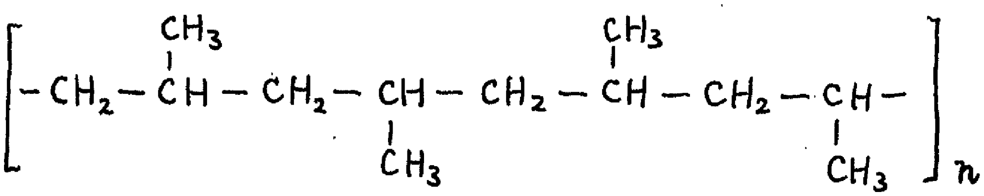
$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-\right]_n$$

Isotactic Polypropylene or



$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-\right]_n$$

Atactic Polypropylene or



$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-\right]_n$$

Syndiotactic Polypropylene

Fig. 1.1. Chemical Structure of Polypropylene.

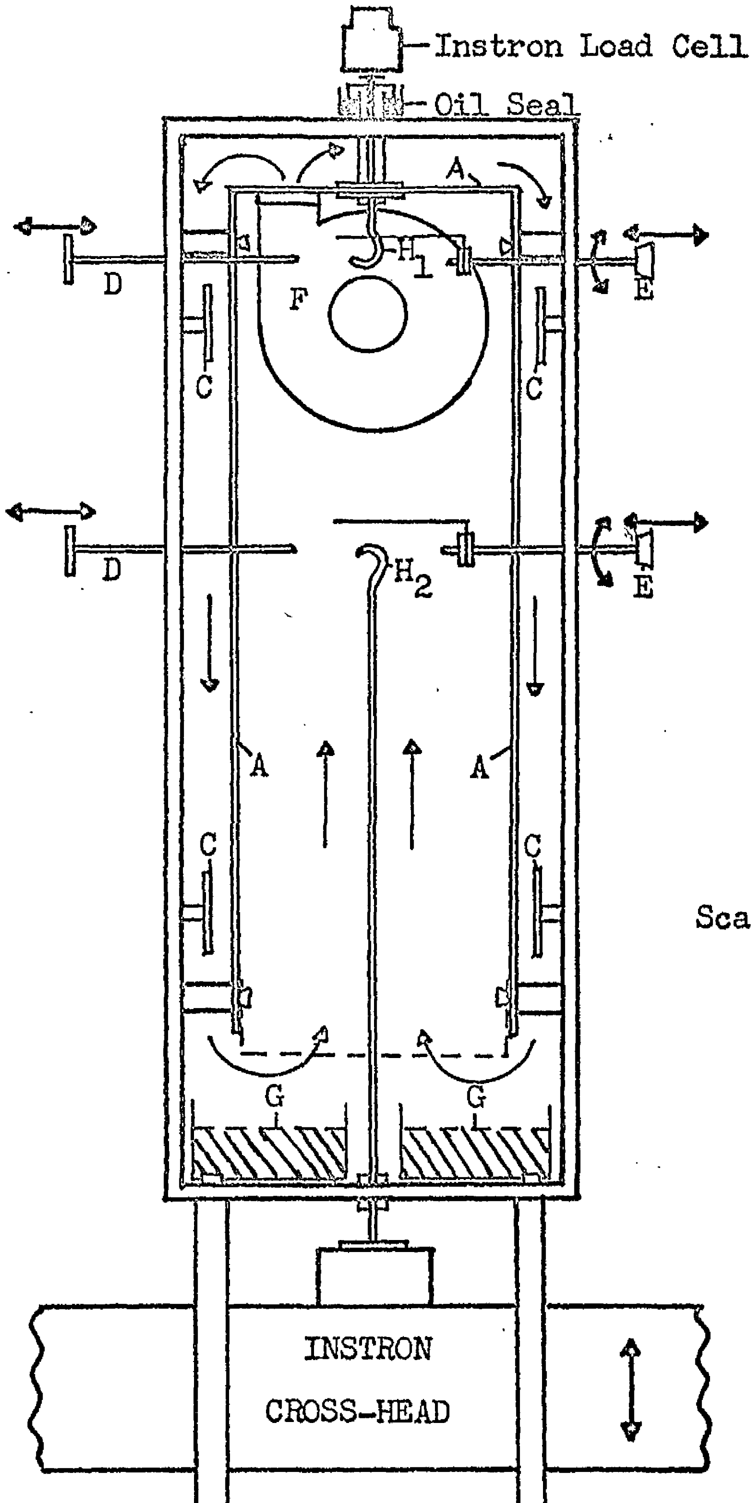
It is conceivable that a co-polymer of the isotactic and atactic forms exists to a measurable extent. Molecules containing the two forms may serve as a link between one region of high order (crystalline region), in which the isotactic form is predominant, and another, with areas of low order (amorphous regions), in which the atactic form is found, situated between the crystalline regions. Thus a polymer with a high isotactic content is capable of better ordering and should have a higher degree of crystallinity.

Two commercial yarn samples from different sources were used in this investigation. They are referred to as A and B throughout. Both were multifilament yarns, sample A being 26.4 tex, 70 filament, untwisted and sample B 21.9 tex, 40 filament, 0.5 turns/inch. They were supplied as 230 denier (25.6 tex) and 200 denier (22.2 tex) respectively.

1.3.2 Apparatus

A table model TTM Instron tensile testing machine, giving a range of test speeds covering up to three decades of logarithmic time, was used.

To permit tests to be carried out under various conditions a cabinet was designed and built for use in conjunction with the Instron tester, at temperatures up to 100°C. A face view is shown in Fig. 1.2. Tufnol 5/16" thick was used in the construction of the outer casing to give reasonable heat insulation. A 1/8" glass plate acted as the face and a removeable window. To facilitate sealing



Scale 1 : 2

FIG 1.2
Conditioning Cabinet designed for use with the Instron Model TTM Tensile Tester.

the cabinet the regular jaws were replaced by hook members. The upper hook H_1 was screwed into an attachment to fit load cell 'B', the cell used for these tests. Since the cell displacement is very slight an inverted cup oil seal was used to close the gap and still allow slight lateral movement of the hook. This was necessary to avoid frictional contact with the top, which might lead to false load readings. The lower hook H_2 was screwed into a fitting on the cross-head of the machine, and was thus capable of moving with it. Friction was unimportant here and a greased rubber bung was used to seal this entry point. Baffle walls A of 1/16" Tufnol were used to direct the circulation of air from fan F (as shown by the arrows) over the heaters C to the testing area. They also give the test specimens protection against radiated heat. Although it was not necessary for the present work, provision was made for humidity control by glycerine, sulphuric acid or saturated salt solutions placed in dishes at G just before the air stream passed up to the specimens.

The four 100-Watt heaters C were connected in parallel to give even heat distribution throughout the chamber. A thermostat was originally included, but in the conditioned test room, the temperature outside the cabinet varied little and a finer adjustment could be obtained using a rheostat to control the heat input. The heat distribution in the test area was checked using copper-constantan thermocouples in conjunction with a constant temperature junction and a multi-point potentiometric recorder. Slight heat pockets were found to exist within 1/2" of the baffle walls in the vicinity of the heaters due to conduction of heat through the walls and 1/2" spacers had to be placed on the rods D to avoid this hazard. The temperature gradient over the rest of the area was not more than 0.7°C even at elevated temperatures and was generally less than half this figure. After equilibrium had been reached, the rheostat was able to control the temperature to within 0.5°C. The cumulative temperature variation was, therefore, just over 1°C at its maximum and temperatures could be quoted with a tolerance of ± 1°C. During testing a mercury thermometer was found to give sufficient accuracy to measure temperature.

To enable tensile tests to be carried out specimens were attached to fibre washers. The prepared specimens were mounted on the moveable brass rods D for conditioning purposes before being transferred to the hooks by means of the probes E. Thus several specimens may be conditioned and tested without disturbing the conditions. The cabinet can accommodate a gauge length of up to 10 inches for materials with less than 30% ultimate elongation and Fig. 1.2 shows the arrangement for a 5 inch gauge length as used in the present work where extensions up to 80% were encountered.

1.3.3 Polypropylene A - Sample Preparation and Test Procedure

The behaviour of each sample was studied under several conditions in a preliminary investigation to establish the likely limits of the full testing programme. This was necessary to ensure correct sampling for the whole programme. Polypropylene A was studied first, and it was decided to take measurements at seven temperatures using seven strain rates at each temperature. The temperature range chosen was from 25°C to 85°C in even steps of 10°. The range of strain rates and precise values were dictated to a large extent by the capabilities of the test machine. Cross-head speeds of 0.2, 0.5, 1, 2, 5, 10 and 20 inches per minute gave effective strain rates of 4, 10, 20, 40, 100, 200 and 400 % per minute using a 5 inch gauge length.

Since the quantity of yarn was limited, only five tests could be carried out at each of the 49 test conditions. A suitable sampling scheme was therefore drawn up. The cut-skein method was chosen as the simplest in the circumstances. This method eliminates short term variations in the yarn and reduces the effect of variations between intermediate lengths although long term variations may still occur between skeins.

In this case the last difficulty was overcome by preparing extra specimens to serve as cross-checks. Seven skeins, each containing five loops of yarn of sufficient length to provide nine sections six inches long, were wound. One skein thus consisted of seven sections to be used for all the tests at one temperature and two sections for use as cross-checks between each temperature. The exact arrangement is outlined in Table 1.1 below, the letters representing different skeins and the numbers indicating the section of the skein involved.

TABLE 1.1 Order of Sampling by the Cut-Skein Method

STRAIN RATE (%/MIN)	TEST TEMPERATURE (°C)						
	25	35	45	55	65	75	85
4	A_1	B_1	C_1	D_1	E_1 G_8	F_1 G_9	G_1
10	A_2	B_2	C_2	D_2 F_8	E_2	F_2	G_2 F_9
20	A_3	B_3 E_8	C_3 E_9	D_3	E_3	F_3	G_3
40	A_4 D_8	B_4	C_4	D_4	E_4	F_4	G_4 D_9
100	A_5	B_5	C_5	D_5	E_5 C_8	F_5 C_9	G_5
200	A_6 B_8	B_6	C_6	D_6 B_9	E_6	F_6	G_6
400	A_7	B_7 A_8	C_7 A_9	D_7	E_7	F_7	G_7

To enable hooks to be used in place of the regular jaws, each length of yarn was attached at both ends to fibre washers of the following dimensions:-

External diameter	½ inch
Internal diameter	3/16 inch
Thickness	1/16 inch
Weight	0.20 G.

The specimens were threaded through holes of 20 thou diameter specially drilled in the washers which were then placed on a jig consisting of 1/4" diameter brass rods reduced to just under 3/16" diameter at the top and screwed into a Tufnol base. The rods were arranged to give a gauge length of approximately 5 inches between the ends of the washers. A side view of the frame is shown in Fig. 1.3.

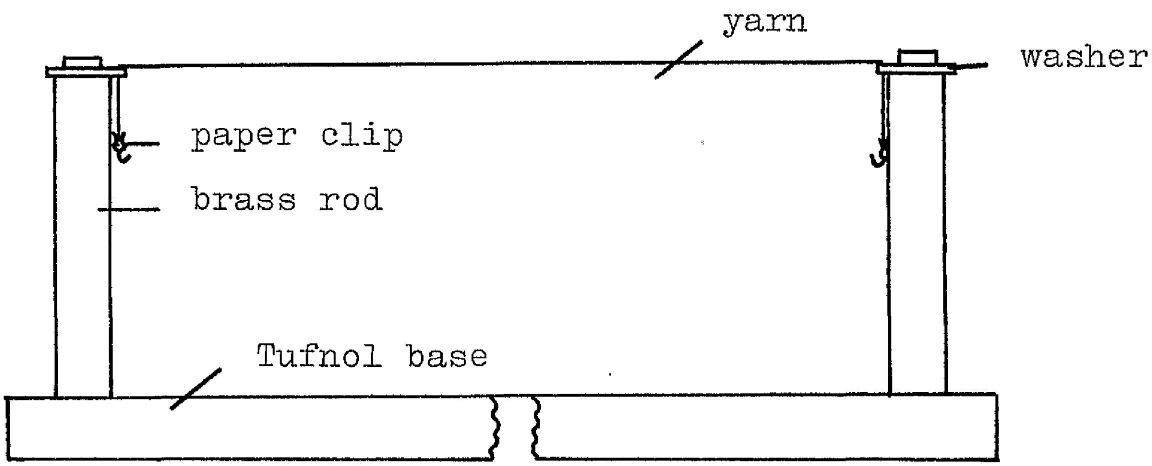


Fig. 1.3. - Sample Preparation Jig

Miniature paper clips weighing 0.33 gm were used to hold the yarn in position under slight tension while it was cemented to the washers. This was done by spotting each end with a mixture of Araldite 105 and hardener 951, a warm setting resin adhesive of high tensile strength. The jig was then placed in an oven at 100°C for 2 hours to cure the Araldite completely. (The manufacturers recommend a minimum time of 20 minutes at this temperature). This treatment also served to anneal the yarn and minimise the effect of thermal history on the results.

It should be noted at this point that the yarn was held on the jig throughout the annealing process and was not allowed to relax. Specimens were conditioned in the relaxed state in a standard atmosphere for at least 48 hours following the heat treatment.

Up to 10 specimens were mounted in the cabinet at any one time and allowed to condition for at least one hour at the test temperature before being transferred to the hooks. Since the jig gives only an approximate length, the exact gauge length was measured on the hooks under a load of 0.01 g/denier immediately before each test. This was found to vary between 4.95 and 5.25 inches, the average length being 5.13 inches. Over 75% of the lengths were within 1% of the average value. Individual lengths were taken into account when measuring the tensile data but calculations of strain rate and other time factors were based on the average value for each series.

The temperature was noted frequently during conditioning and before each test, adjustments being made when necessary.

The Araldite adhesive penetrates the yarn and washer when applied and becomes hard and rigid when cured. If it is not mixed correctly or is prevented from penetrating properly by, say, an air bubble, the yarn will be allowed to slip out. This occurred occasionally during testing, and where it was detected the values were omitted. Good penetration caused its own trouble in the form of brittle jaw breaks characterised by abnormally low breaking elongation and load. These were also eliminated and this meant that the average values for some conditions were calculated from 3 tests only. Thus the accuracy of these results is low and this must be borne in mind when their interpretation is attempted.

1.3.4.

Polypropylene B. - Preparation and Procedure

The sample preparation and test procedure for polypropylene B was very similar to that for the first yarn with only slight modifications resulting from experience gained in the course of the first series of tests.

A larger quantity of the second yarn was available and ten specimens were prepared for test at each condition to allow for the possibility of slippage and abnormally low breaks, and to improve the accuracy of the results. The breaking elongation was expected to increase rapidly at the higher end of the time scale and to study this effect in more detail it was decided to use a slightly lower range of strain rates. The cross-head speeds chosen gave effective strain rates of 1, 4, 10, 20, 40, 100 and 200 % per minute for a 5 inch gauge length. Although the same effect could have been achieved by increasing the highest test temperature it would have meant approaching very close to the annealing temperature. The same range of temperature was therefore used.

When washers were re-ordered it was found that the outside diameter had been reduced to 7/16 inch and the weight was only 0.14 g. The weight was insignificant in any case but the diameter change reduced the effective surface available for attaching specimens by a third as shown in Fig. 1.4.

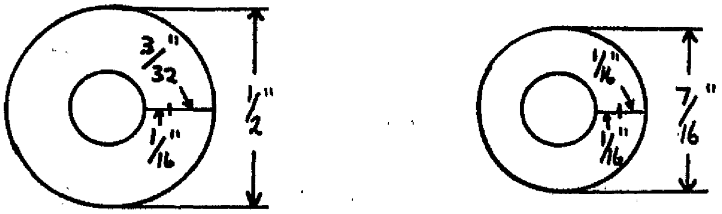


Fig 1.4.

This caused a slight increase in the number of specimens which slipped from the washers during test. Also, using the same jig the average gauge length was slightly greater. It was expected to increase by 1/16th of an inch (0.0625 inches) and in fact it was found to vary between 5.00 and 5.35 inches with an average value of 5.20, an increase of 0.07 inches.

To apply time-temperature superposition to the results the glass transition temperature (Tg) should be known. The fact that the relationship between volume and temperature shows a marked discontinuity at Tg is used to measure this temperature. The method, called dilatometry has been used to determine Tg for several polymers of the olefin family and has led to considerable difference of opinion due to large variations in values quoted by different authors. Tg for polyethylene has been given as 143°K[21] and 193°K[51] by this method. Values for polypropylene are more consistent (253°K[21] and 255°K[22] for example) but measurements have not been made using filament specimens. Since polymer properties are affected by the high temperatures involved in the melt spinning process[52] it was felt necessary to determine Tg for polypropylene in filament form.

The fact that filaments, in equilibrium under load, show a change in length with temperature which is positive below Tg and negative above this temperature was utilised. Single filament specimens of each sample were loaded to approximately 15 g/tex and left for four days at 20°C to reach an equilibrium strain of about 8%. Changes in length with temperature were then measured over the temperature

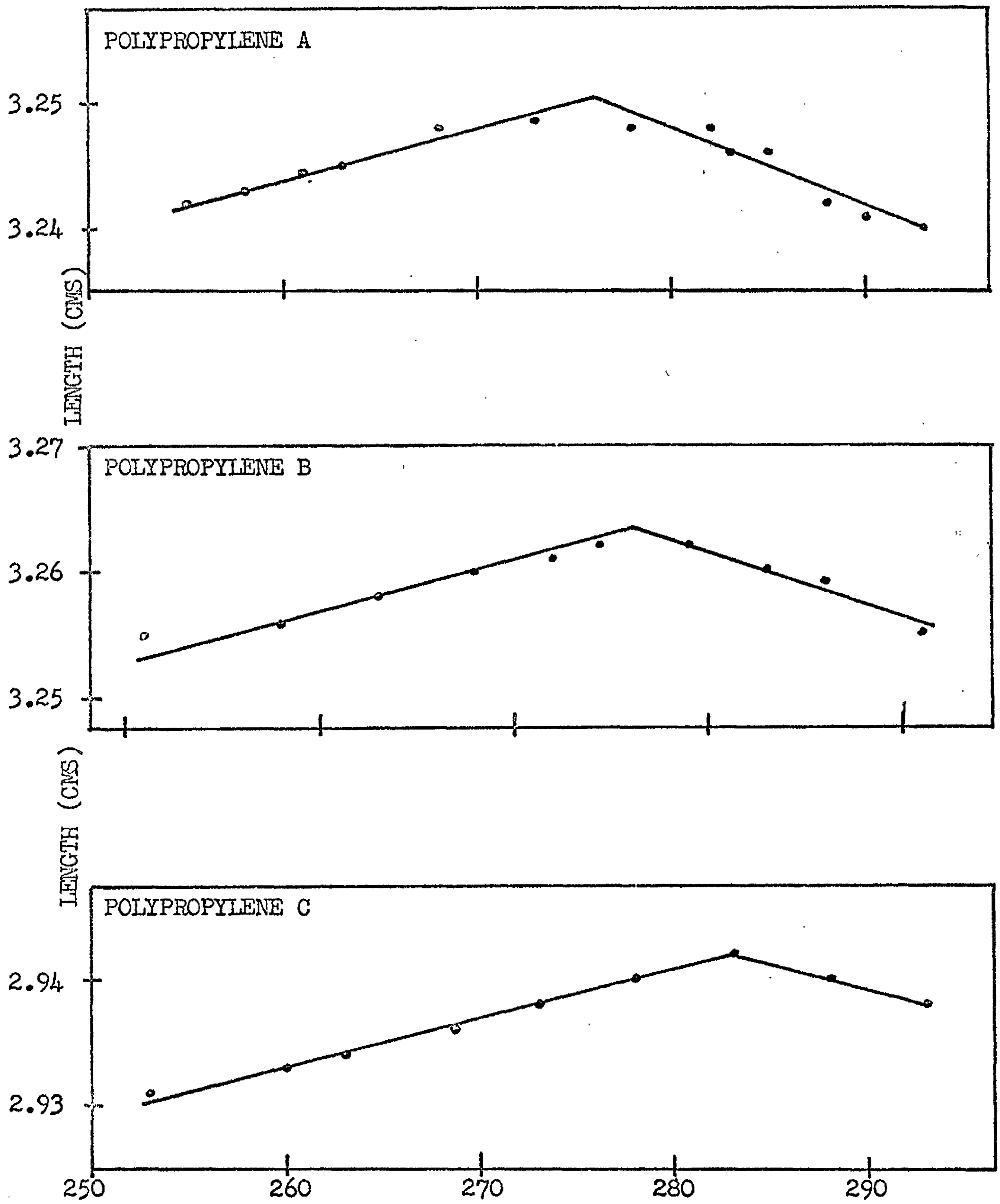


FIG 1.5 Determination of the Glass Transition Temperature.

range 250°K to 293°K, 30 minutes being allowed for conditioning at each temperature. Readings were taken while the temperature was both decreasing and increasing using a cathetometer accurate to ± 0.001 cm. A sample of isotactic polypropylene identical with that used by Hall[20] and designated as sample C was also included in these measurements. Fig. 1.5 shows the result of plotting length against temperature. It is seen that the transition point can be readily determined within ± 1°C by this method. The values obtained are shown in Table 1.2 (a). They are much higher than the values recorded for block polymer using dilatometry.

The density of each sample was also measured using a density gradient column similar to that described by Jones[53]. Xylene was used as the low density liquid and a mixture of xylene and carbon tetrachloride constituted the high density liquid, the densities of each being known from hydrometer measurement. Glass floats of known density were used to check the calibration of the column so prepared, a theoretical calibration being obtained using the formula

$$P_h = e^{-Ah/v} \text{ - - - - - - - - - } (6)$$

where P_h is the proportion of low density liquid in the column at a point h from the top, A is the column cross-sectional area and v is the initial volume of low density liquid in the mixing chamber.

TABLE 1.2 Measurement of Density and Transition Temperature

(a)		(b)	
SAMPLE	GLASS TRANSITION TEMPERATURE	DENSITY AS RECEIVED	(G/CC) ANNEALED
A	276°K	0.915	0.918
B	276°K	0.911	0.914
C	283°K	0.900	0.904

(c) SAMPLE B	
TEMP (°C)	DENSITY (G/CC)
20	0.914
30	0.913
40	0.912
50	0.911
60	0.908
70	0.905

Measurements were made at 20°C on specimens as received and after annealing for two hours at 100°C and at different temperatures on annealed specimens of sample B. The specimens were prepared carefully by the following procedure:-

1) A 3-minute rinse in alcohol
2) A 3-minute rinse in ether
3) Drying
4) A 5-minute wash in a 1% solution of Teepol at 60°C
5) Thorough rinse in distilled water
6) Conditioning in a desiccator at 0% R.H. for 24 hours.

The prepared specimens were thus free from oils, surface finish and moisture.

The measured values are shown in Table 1.2 (b and c). It is seen that the values remain in the same order but are slightly higher after annealing and that the density of sample B falls very slightly at first with increasing temperature, the effect becoming greater at higher temperatures.

1.3.5

Stress Relaxation Measurements.

As already mentioned the accuracy of data taken from the stress-strain curves is not high and correlation with tensile stress relaxation measurements was attempted. In relaxation experiments a large part of the time scale is covered by measurements on a single specimen at one temperature and relative rate changes can be determined more precisely although the absolute values of stress and the effect of temperature is still affected by the sample variation. On the other hand exact correlation cannot be expected since the stress-strain data are obtained at a constant rate of strain while the tensile stress relaxation measurements are made at a constant strain.

Stress relaxation from 6% strain was carried out at 25°C, 55°C and 85°C for two and a half hours on samples A and B. Two specimens of each sample were tested at each condition using the Instron tester and conditioning cabinet as described previously. The strain was imposed on the 5 inch long specimens at the rate of 3.20×10^{-2} sec^{-1} and took just under 2 seconds to reach its constant value.

I.4 RESULTS

The initial slope of the stress-strain curve for polypropylene is not uniform and shows a slight decrease at low extensions before increasing again to almost its original value. The point at which this discontinuity occurs varies with strain rate and temperature. This is reflected in the values of the tensile modulus $E(t)$, calculated, at 3, 6, 9 and 15% strain, from the equation

$$E(t) = S(t)\; l/_{A\Delta\ell} \qquad - - - - - - - - - (7)$$

where $S(t)$ is the tension at time t, l is the specimen length, $\Delta\ell$, the imposed elongation and A is its cross-sectional area. This reduces the measured tension at any time to comparable values and, if the slope of the curve was constant the calculated modulus would also be constant. A lower modulus value at higher times indicates that the slope is decreasing, while a higher value shows an increase. The 15% value is generally lower than the others since the slope of the curve is again decreasing as the yield point is approached.

In addition to the modulus, the breaking stress and strain were measured at each condition and the results are shown in Tables 1.3 and 1.4.

TABLE 1.3 POLYPROPYLENE A.

1	2	3	4	5	6	7	8	9
A1	25	6.54	3.95	25.9	2.24	2.22	2.08	1.96
A2	25	16.3	4.04	28.3	2.26	2.28	2.16	2.04
A3	25	32.7	4.10	25.9	2.46	2.40	2.26	2.08
A4	25	65.4	4.14	25.6	2.68	2.48	2.34	2.14
A5	25	165.	4.48	26.2	2.68	2.56	2.44	2.22
A6	25	330	4.63	26.5	2.78	2.68	2.54	2.26
A7	25	658.	4.73	27.2	2.52	2.56	2.44	2.26
D8	25	65.8	4.23	25.2	2.60	2.46	2.34	2.14
B8	25	329.	4.62	28.2	2.70	2.54	2.44	2.22
B1	35	6.55	3.50	28.6	1.94	1.93	1.91	1.78
B2	35	16.2	3.84	28.3	2.08	2.06	2.02	1.91
B3	35	32.2	3.90	26.2	2.34	2.26	2.14	2.00
B4	35	65.5	3.94	24.0	2.56	2.36	2.28	2.08
B5	35	164.	4.28	25.9	2.60	2.48	2.36	2.16
B6	35	325.	4.24	23.9	2.52	2.48	2.34	2.22
B7	35	645.	4.48	26.2	2.52	2.52	2.40	2.22
E8	35	32.4	4.06	30.4	2.44	2.32	2.20	2.02
A8	35	645.	4.42	26.1	2.44	2.46	2.38	2.22

TABLE 1.3 (CONTINUED)

1	2	3	4	5	6	7	8	9
C1	45	6.50	3.38	28.8	1.73	1.78	1.82	1.69
C2	45	16.2	3.63	36.4	1.89	1.94	1.93	1.82
C3	45	32.4	3.83	38.1	2.18	2.18	2.10	1.95
C4	45	65.8	3.94	23.7	2.54	2.44	2.30	2.08
C5	45	162.	4.22	26.4	2.40	2.44	2.30	2.14
C6	45	322.	4.32	24.6	2.54	2.46	2.36	2.16
C7	45	649.	4.31	24.0	2.48	2.46	2.34	2.16
E9	45	32.4	3.72	29.5	2.06	2.02	1.98	1.90
A9	45	647.	3.97	22.9	2.22	2.26	2.18	2.06
D1	55	6.50	2.77	24.6	1.57	1.57	1.63	1.51
D2	55	16.3	2.95	24.8	1.70	1.67	1.71	1.59
D3	55	32.9	3.32	32.2	1.81	1.84	1.87	1.71
D4	55	65.4	3.46	26.5	1.94	1.96	1.93	1.78
D5	55	161.	3.71	28.4	1.92	1.97	1.97	1.85
D6	55	324.	3.87	23.9	2.18	2.18	2.08	1.93
D7	55	650.	3.89	25.5	2.18	2.22	2.18	2.00
F8	55	16.2	3.29	34.5	1.86	1.84	1.82	1.64
F9	55	324.	3.83	25.6	2.22	2.16	2.08	1.93

TABLE 1.3 (CONTINUED)

1	2	3	4	5	6	7	8	9
E1	65	6.50	2.54	29.8	1.35	1.35	1.39	1.34
E2	65	16.3	2.74	26.5	1.57	1.57	1.57	1.46
E3	65	32.9	2.90	29.4	1.67	1.67	1.65	1.53
E4	65	65.4	3.20	26.9	1.81	1.88	1.85	1.68
E5	65	161.	3.26	24.8	1.92	1.90	1.90	1.74
E6	65	324.	3.57	25.7	1.81	1.88	1.87	1.82
E7	65	650.	3.42	20.7	1.93	2.02	1.99	1.87
G8	65	6.54	2.60	35.8	1.24	1.17	1.26	1.27
C8	65	163.	3.34	23.9	1.86	1.90	1.85	1.80
F1	75	6.56	2.55	60	1.16	1.16	1.21	1.17
F2	75	16.4	2.79	54	1.19	1.20	1.27	1.24
F3	75	32.5	2.84	47	1.32	1.34	1.41	1.32
F4	75	64.5	2.95	49	1.49	1.47	1.48	1.42
F5	75	163.	3.04	34.6	1.46	1.50	1.55	1.50
F6	75	325.	3.21	20.7	1.62	1.66	1.71	1.62
F7	75	655.	3.32	26.1	1.65	1.75	1.80	1.70
G9	75	6.56	2.37	47	1.05	1.64	1.11	1.09
C9	75	163.	3.01	33.3	1.46	1.52	1.57	1.54

TABLE 1.3 (CONCLUDED)

1	2	3	4	5	6	7	8	9
G1	85	6.60	2.31	71	0.95	1.00	1.09	1.02
G2	85	16.3	2.38	54	1.08	1.09	1.17	1.09
G3	85	32.4	2.42	45	1.13	1.15	1.22	1.14
G4	85	65.0	2.41	31.2	1.00	1.00	1.00	1.08
G5	85	162.	2.79	42.	1.08	1.08	1.14	1.20
G6	85	325.	2.89	35.0	1.16	1.20	1.29	1.30
G7	85	649.	2.96	29.0	1.24	1.34	1.42	1.44
E9	85	16.4	2.37	49.	1.11	1.12	1.16	1.11
D9	85	65.0	2.44	34.6	1.11	1.17	1.23	1.23

KEY:-

COLUMN 1. - Sample number.

" 2. - Test temperature. ($^{\circ}$C)

" 3. - Strain rate. (sec.$^{-1}$ x 10^{-4})

" 4. - Ultimate stress. (dynes/cm.^{2} x 10^{9})

" 5. - Ultimate strain. (%)

" 6, 7, 8, and 9. - Tensile modulus, E(t), measured at 3, 6, 9, and 15% strain respectively. (dynes/cm^{2} x 10^{10})

TABLE 1.4 POLYPROPYLENE B

1	2	3	4	5	6	7	8	9
A1	25	1.60	2.46	21.9	1.78	1.65	1.59	1.37
A2	25	6.40	3.35	24.5	2.30	2.12	2.02	1.76
A3	25	16.2	3.65	25.2	2.48	2.28	2.16	1.90
A4	25	31.8	3.79	22.4	2.72	2.54	2.40	2.10
A5	25	64.4	4.06	24.4	2.72	2.54	2.42	2.12
A6	25	160.	4.33	23.6	2.92	2.70	2.58	2.26
A7	25	318.	4.55	25.8	3.10	2.88	2.70	2.32
B8	25	6.45	3.39	26.0	2.32	2.14	2.04	1.79
D8	25	31.8	3.85	21.6	2.78	2.56	2.42	2.14
B1	35	1.62	2.32	22.2	1.70	1.56	1.50	1.31
B2	35	6.35	2.78	21.3	1.97	1.85	1.78	1.56
B3	35	16.0	3.12	22.8	2.32	2.10	2.00	1.70
B4	35	31.8	3.41	22.9	2.46	2.34	2.14	1.85
B5	35	63.7	3.58	22.6	2.60	2.40	2.26	1.94
B6	35	159.	3.85	22.7	2.70	2.52	2.38	2.10
B7	35	320.	4.23	25.4	2.76	2.62	2.42	2.14
A8	35	1.60	1.93	18.2	1.57	1.45	1.44	1.29
E8	35	63.7	3.61	22.7	2.72	2.48	2.32	1.97

TABLE 1.4 (CONTINUED)

1	2	3	4	5	6	7	8	9
C1	45	1.60	1.73	21.9	1.24	1.13	1.11	1.02
C2	45	6.34	2.14	21.9	1.49	1.45	1.41	1.24
C3	45	15.9	2.58	21.5	1.92	1.81	1.74	1.46
C4	45	32.0	3.00	25.1	2.14	1.96	1.86	1.60
C5	45	63.4	3.24	23.7	2.34	2.20	2.08	1.80
C6	45	160.	3.78	26.0	2.48	2.32	2.18	1.90
C7	45	320.	3.89	24.7	2.68	2.50	2.36	2.02
A9	45	1.62	1.57	18.5	1.44	1.13	1.12	1.07
E9	45	64.1	2.71	17.9	2.42	2.24	2.08	1.79
D1	55	1.60	1.44	17.2	1.05	0.93	0.91	0.89
D2	55	6.34	1.56	16.7	1.30	1.21	1.20	1.02
D3	55	16.2	1.68	16.2	1.35	1.25	1.24	1.13
D4	55	32.3	2.10	20.7	1.54	1.43	1.41	1.22
D5	55	64.4	2.44	22.5	1.81	1.72	1.65	1.40
D6	55	161.	2.69	20.7	2.06	1.92	1.85	1.61
D7	55	322.	3.13	24.7	2.00	1.95	1.88	1.62
B9	55	6.37	1.50	15.8	1.30	1.21	1.19	1.08
F8	55	160.	2.67	20.5	2.02	1.91	1.85	1.60

TABLE 1.4 (CONTINUED)

1	2	3	4	5	6	7	8	9
E1	65	1.60	1.38	26.2	0.86	0.74	0.72	0.70
E2	65	6.34	1.48	20.6	1.03	0.91	0.90	0.85
E3	65	16.3	1.69	18.1	1.11	1.02	1.03	1.01
E4	65	32.2	1.90	19.1	1.38	1.32	1.31	1.17
E5	65	64.4	2.23	21.2	1.51	1.48	1.47	1.29
E6	65	163.	2.34	19.4	1.73	1.71	1.66	1.44
E7	65	322.	2.73	25.8	1.70	1.65	1.64	1.45
C8	65	16.1	1.62	16.4	1.08	1.02	1.04	1.01
G8	65	320.	2.12	17.3	1.59	1.60	1.55	1.36
F1	75	1.62	1.13	47	0.65	0.55	0.52	0.46
F2	75	6.45	1.28	32.8	0.78	0.69	0.64	0.62
F3	75	16.1	1.40	22.1	0.86	0.78	0.77	0.76
F4	75	32.0	1.51	22.4	0.97	0.91	0.91	0.87
F5	75	63.9	1.81	22.8	0.97	0.91	0.92	0.91
F6	75	160.	2.16	21.3	1.19	1.16	1.18	1.16
F7	75	322.	2.12	21.2	1.22	1.26	1.29	1.24
C9	75	16.1	1.49	24.4	0.86	0.75	0.73	0.74
G9	75	322.	1.75	18.6	1.11	1.09	1.13	1.13

TABLE 1.4 (CONCLUDED)

1	2	3	4	5	6	7	8	9
G1	85	1.60	1.07	86.	0.49	0.42	0.38	0.33
G2	85	6.48	1.33	44.	0.59	0.52	0.48	0.45
G3	85	16.0	1.32	43.	0.62	0.51	0.48	0.50
G4	85	31.7	1.13	25.4	0.62	0.59	0.54	0.51
G5	85	63.4	1.20	20.4	0.76	0.67	0.65	0.67
G6	85	161.	1.48	22.4	0.89	0.85	0.85	0.85
G7	85	320.	1.61	20.8	0.95	0.95	0.98	0.91
D9	85	32.2	1.25	26.3	0.70	0.63	0.60	0.61
F9	85	160.	1.73	31.5	0.73	0.73	0.74	0.80

Key:- See Table 1.3

For both samples it is seen that the breaking stress decreased as the temperature was increased or the strain rate was decreased, the effect being apparently greater in sample B. There was little change in the breaking strain except at the highest temperatures and the lowest strain rates where a rapid increase took place. This corresponded to the appearance in the stress-strain curve of a flow region beyond the yield point where the stress was almost constant.

The isotactic sample of Hall[20] showed a similar flow region at a much lower temperature corresponding closely to the glass transition temperature values given for the polymer by dilatometry. It has, however, been shown[54] that commercial samples of this yarn, containing generally a small percentage of atactic material do not necessarily exhibit such a marked flow region associated directly with the transition temperature.

It has been stated that the reduction method of time-temperature superposition is only applicable to crystalline polymers if the structure of the material does not change within the range of temperature used and strains do not exceed the limit of linear viscoelastic behaviour.

The slight fall of density with increasing temperature indicates a slight change in crystalline structure. The linearity can be checked using the formula

$$\sigma/R = \int_{-\infty}^{\infty} \tau M(\tau)\left(1 - e^{-\epsilon/R\tau}\right) d \ln \tau \quad -- \quad (8)$$

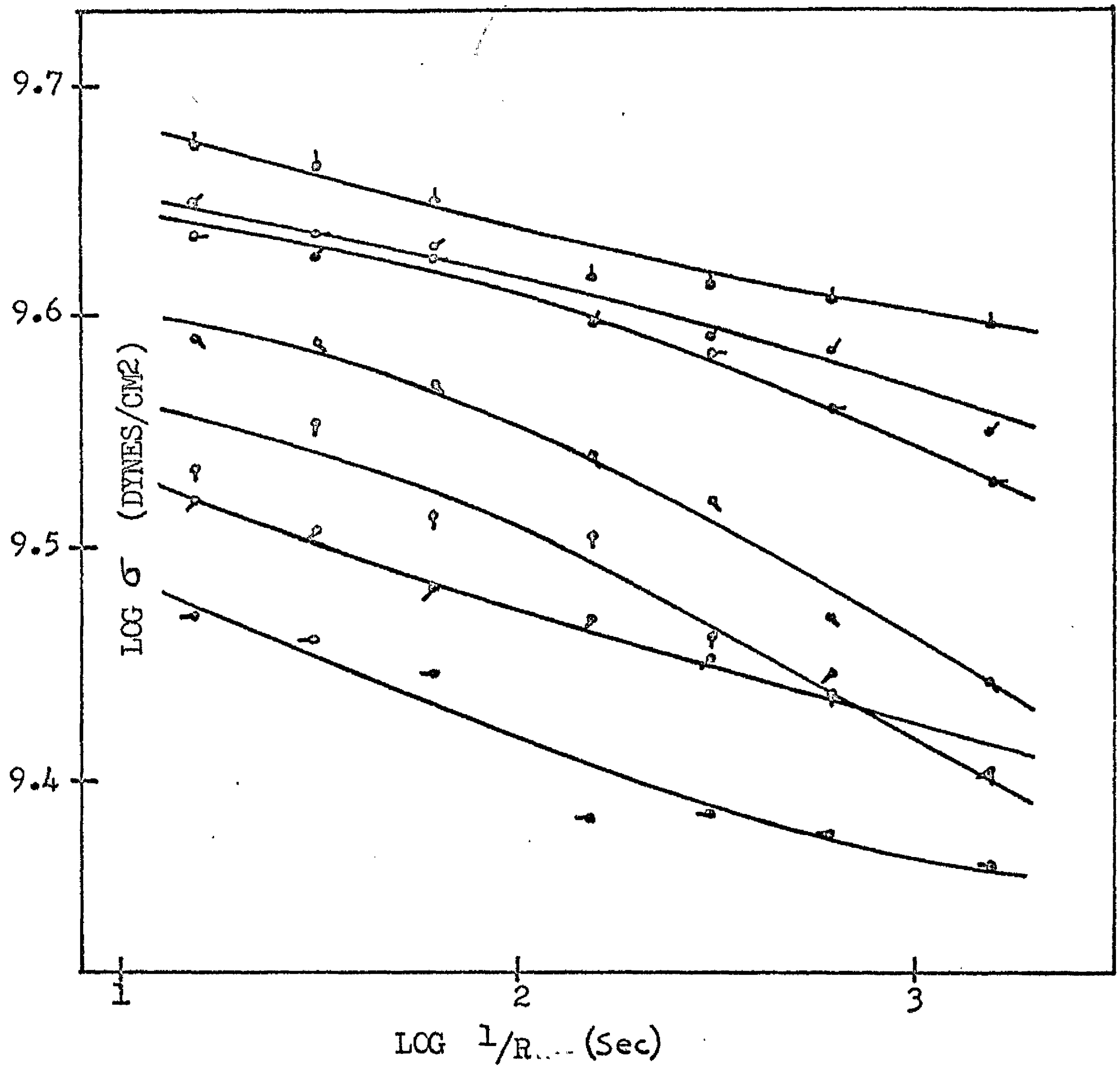
where σ is the stress, R the rate of strain, ϵ the strain and $M(\tau)$ is the relaxation distribution function. σ/R is a function of ϵ/R and by plotting σ/R against time a single master curve should result if the material is linear. Samples A and B were tested in this way at extreme conditions of temperature and strain rate. In no case was a single curve obtained. Even at small strains a slight divergence occurred although this only became marked above 3% strain.

Thus, as expected, polypropylene cannot be termed a linear material while it is felt that its molecular structure changes only slightly in the range of temperature used.

To study the temperature dependence of the results plots of log (breaking stress) against log (strain rate) and log (tensile modulus) against log (time), for the 6% and 15% levels, were drawn at each temperature. These are shown in Figs. 1.6 to 1.11. The breaking strain was not included at this stage since it changed little at the lower temperatures and did not give a clear picture of any trends which might have assisted the interpretation of the results. The same general trend is seen in all the figures and it appeared possible that superposition of the data could be achieved by reducing them to a standard reference temperature. Accordingly all the stress values were reduced to 326°K, the chosen reference temperature, this being 50° above the measured glass transition temperature. Using the general form of equation (5),

$$\log a_T = \frac{-8.86\,(T-T_0)}{101.6 + T-T_0} \quad ------\ (9)$$

and plotting $\log \sigma . T_0/T$ against $\log 1/Ra_T$ and $\log E(t)\, T_0/T$ against $\log t/a_T$, a good 'fit' of the data was not obtained. Consequently an empirical shift was used to reduce the results to the standard temperature $T_0 = 326^\circ K$. The composite curves thus produced are shown in Figs. 1.12 to 1.19 and include curves describing the effect of temperature on the breaking strain using strain and $\log 1/Ra_T$ as the co-ordinates. The curve of equation (9) and the shift factors used in this case are compared in Fig. 1.20. This reveals a linear relationship between the shift factors and the temperature.



TEMPERATURE KEY

298°K
308°K
318°K
328°K
338°K
348°K
358°K

FIG 1.6 The Effect of Strain Rate and Temperature on the Breaking Stress of Polypropylene A

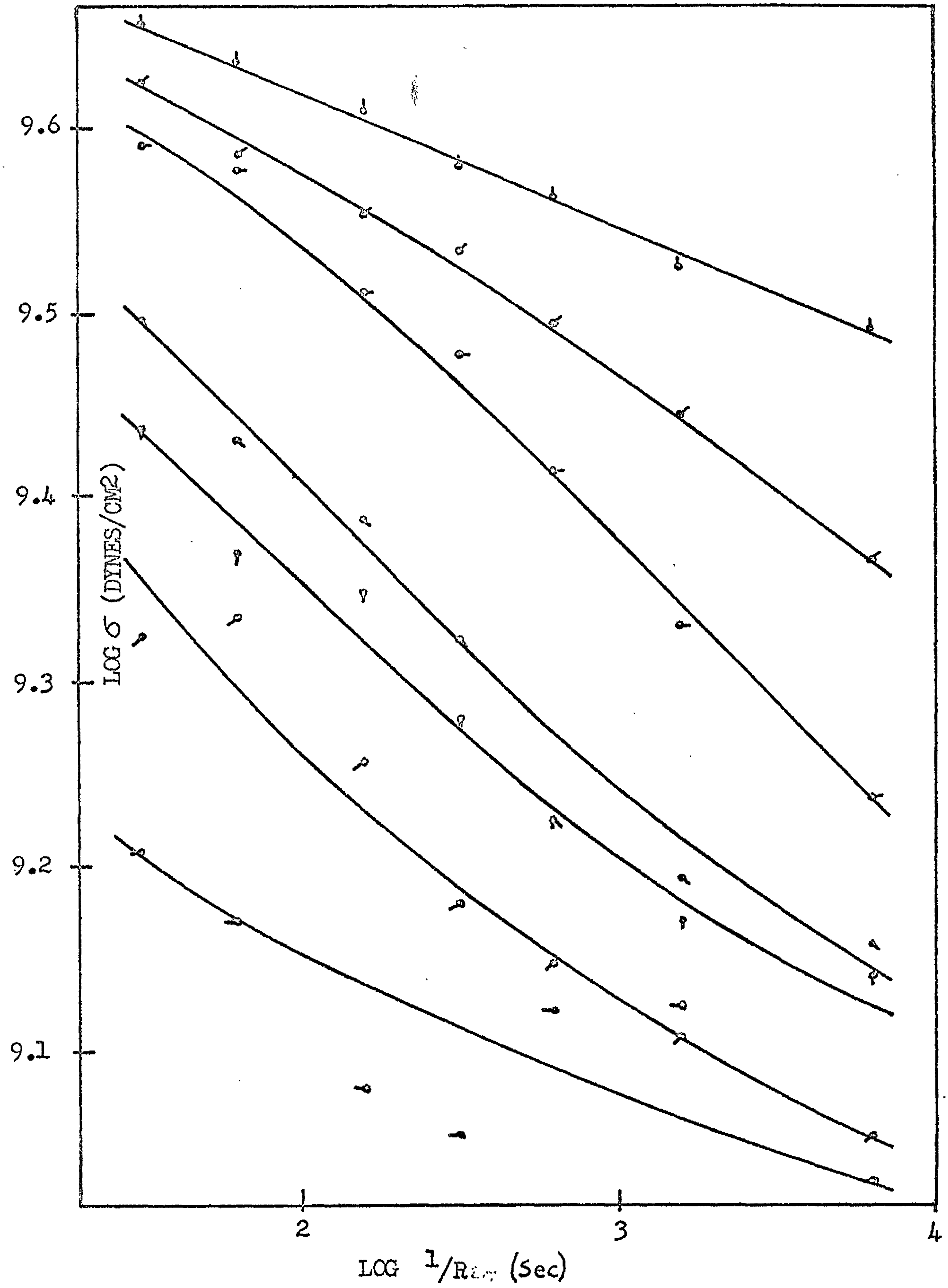


FIG 1.7 Polypropylene B. Key as FIG 1.6

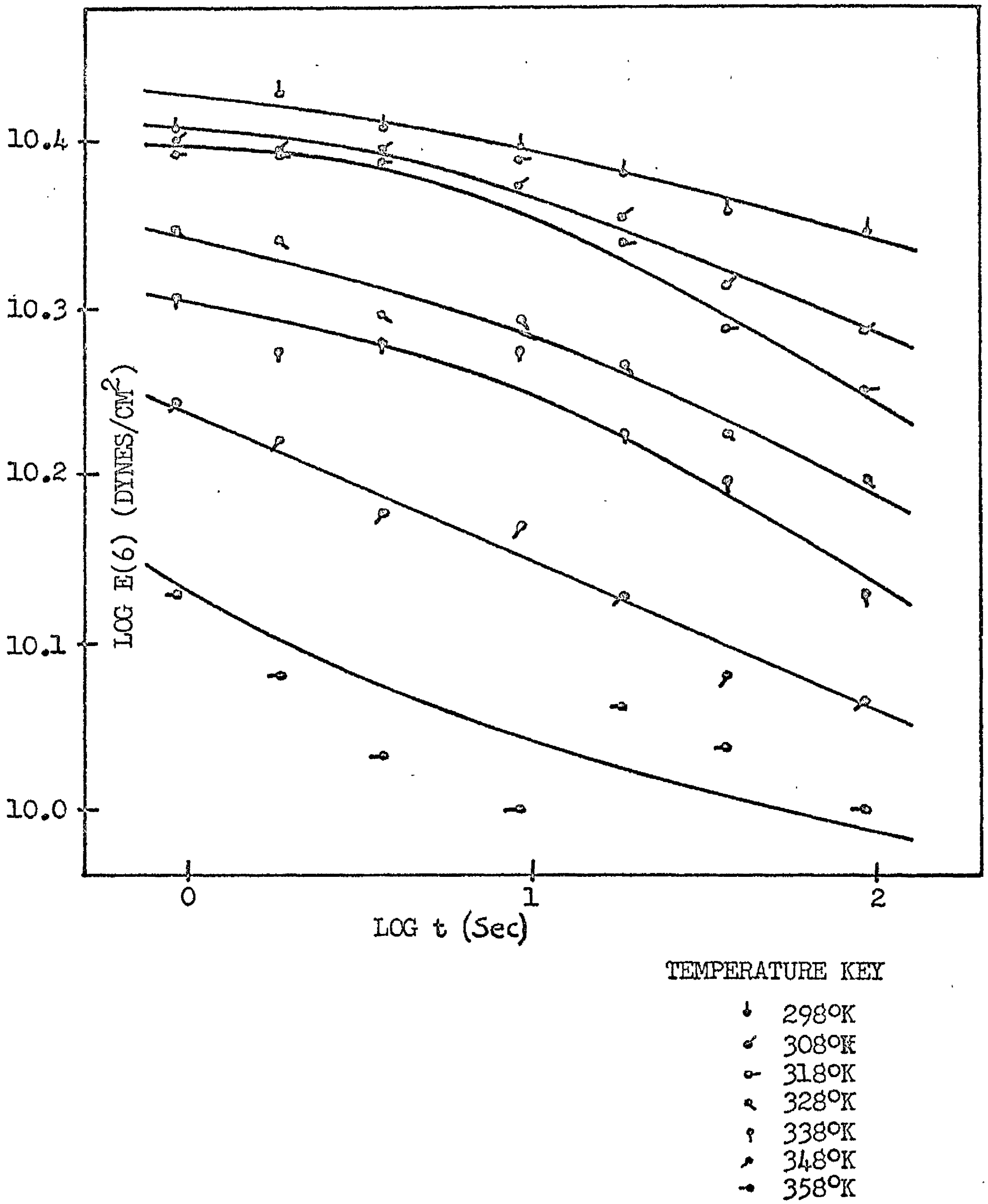


FIG 1.8 The effect of Strain Rate and Temperature on the Tensile Modulus of Polypropylene A measured at 6% strain

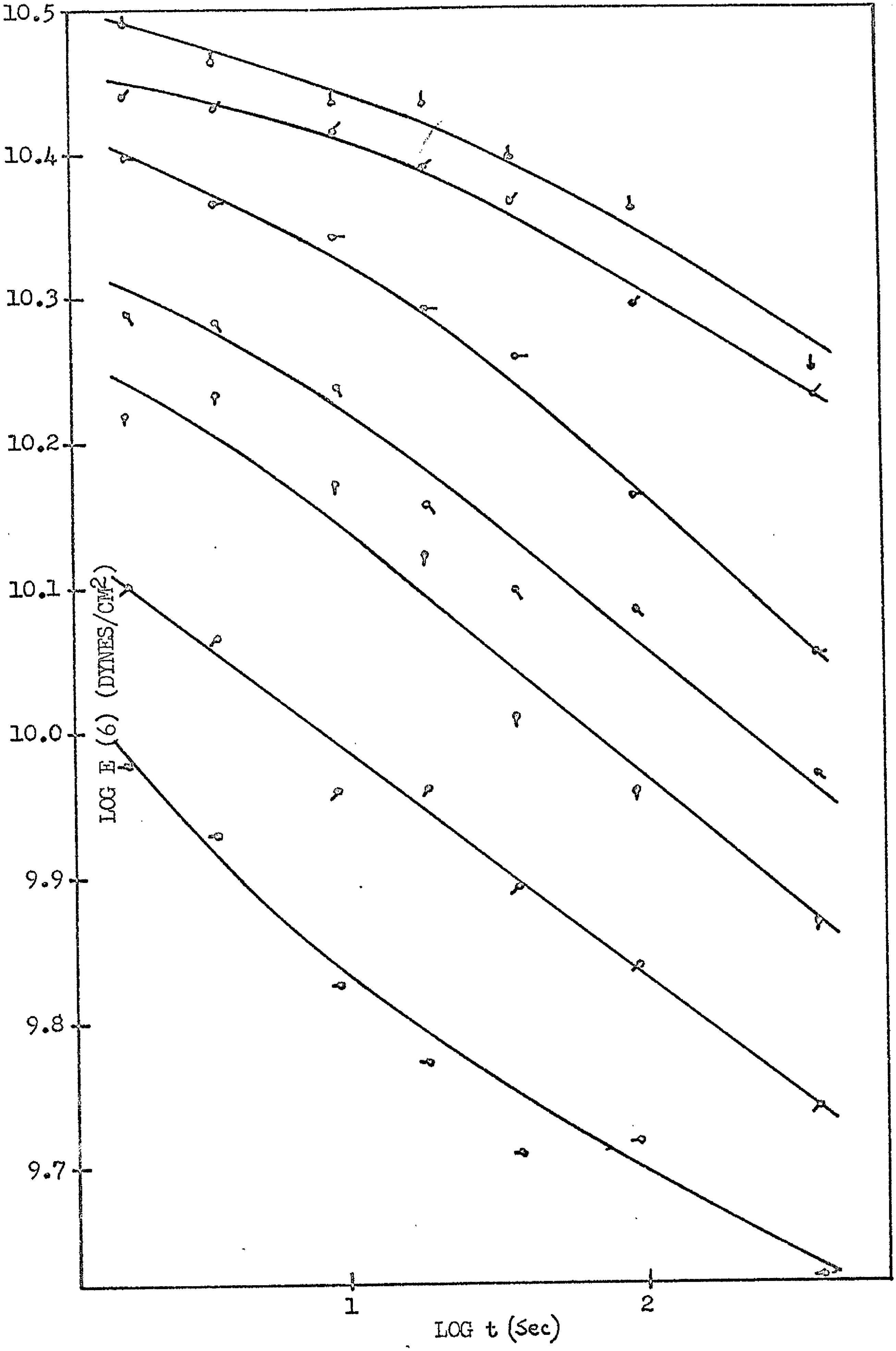


FIG 1.9 Polypropylene B Key as FIG 1.8

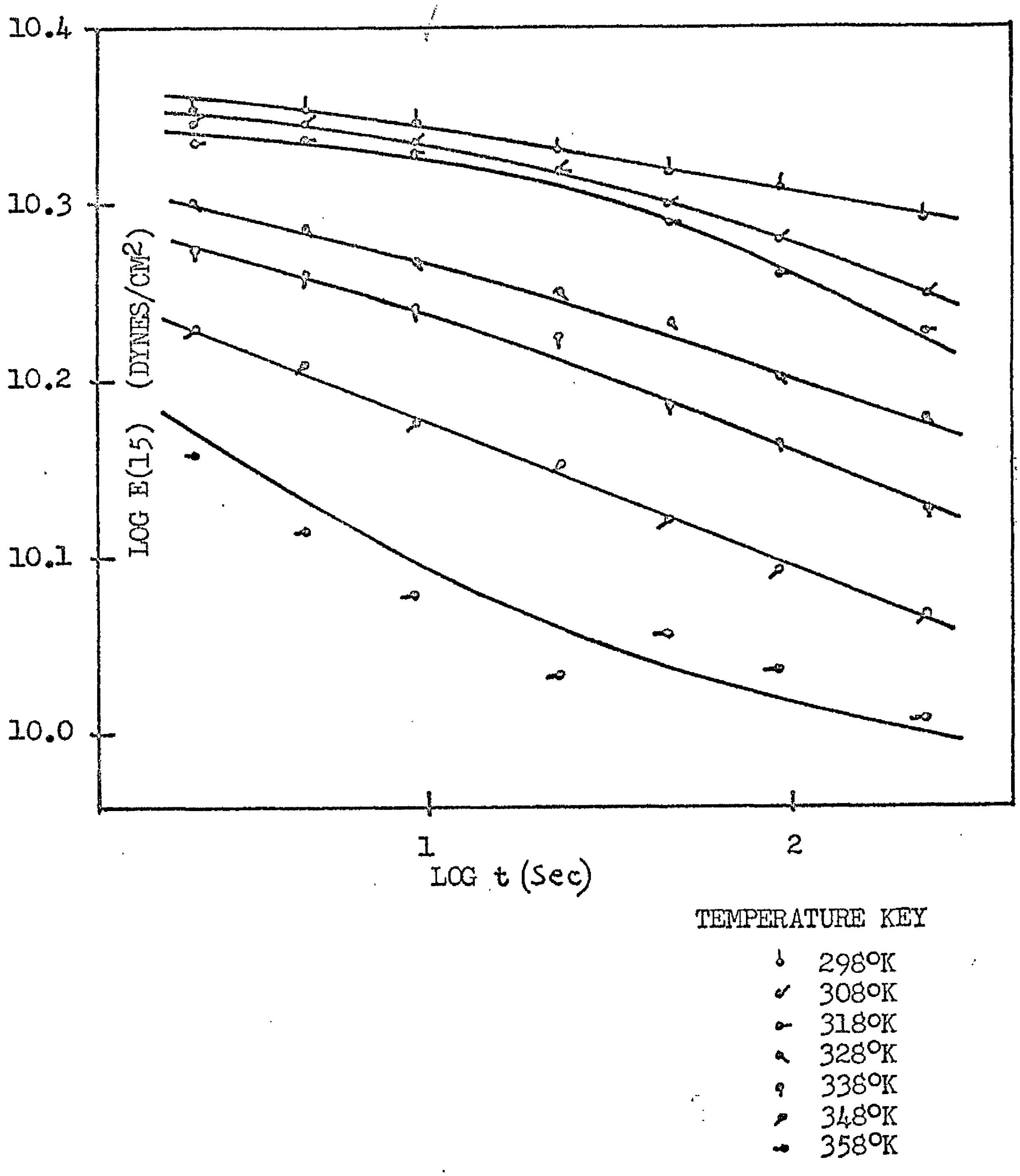


FIG 1.10 The Effect of Strain Rate and Temperature on the Tensile Modulus of Polypropylene A measured at 15% Strain

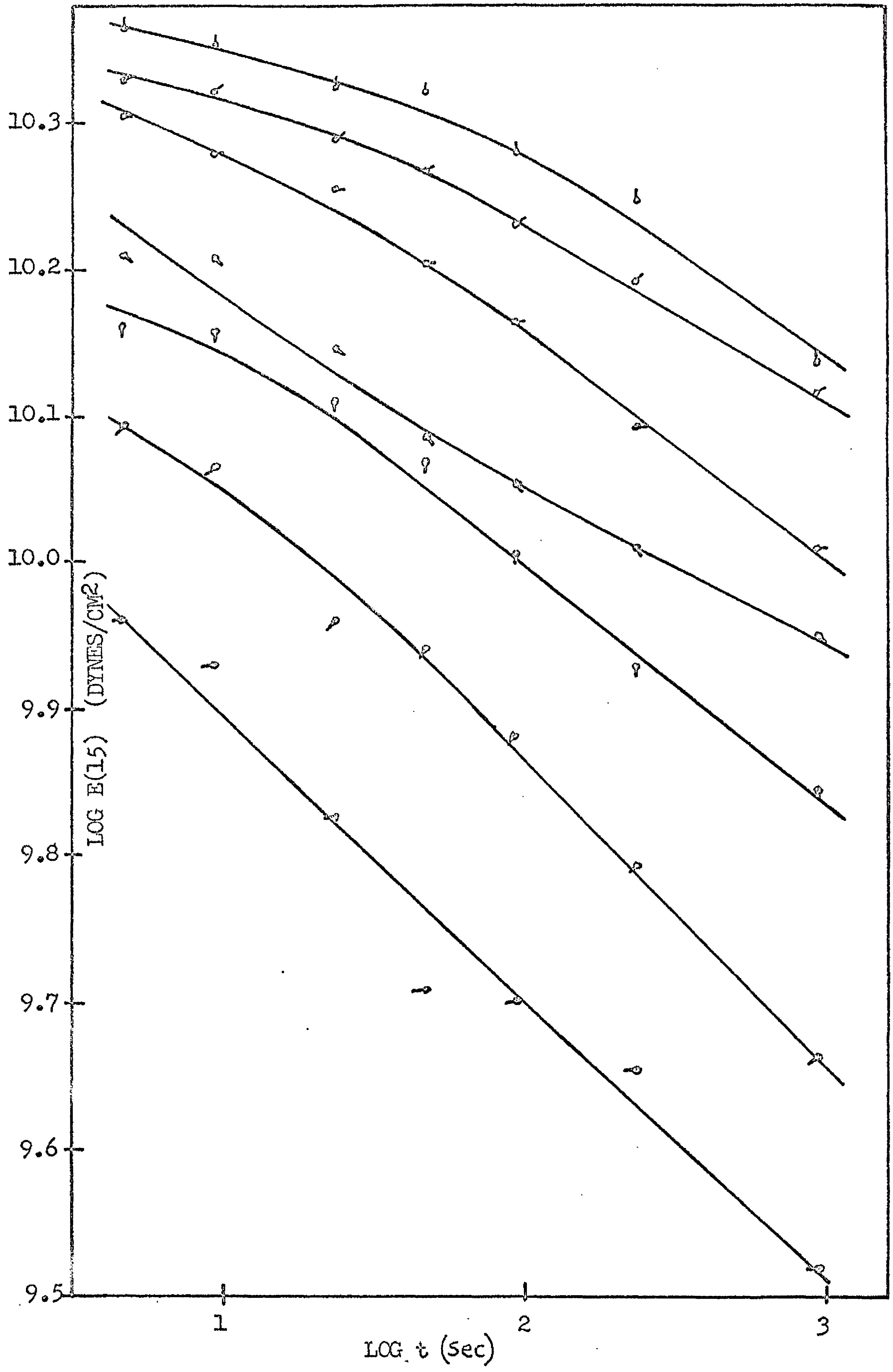


FIG 1.11 Polypropylene B Key as FIG 1.10

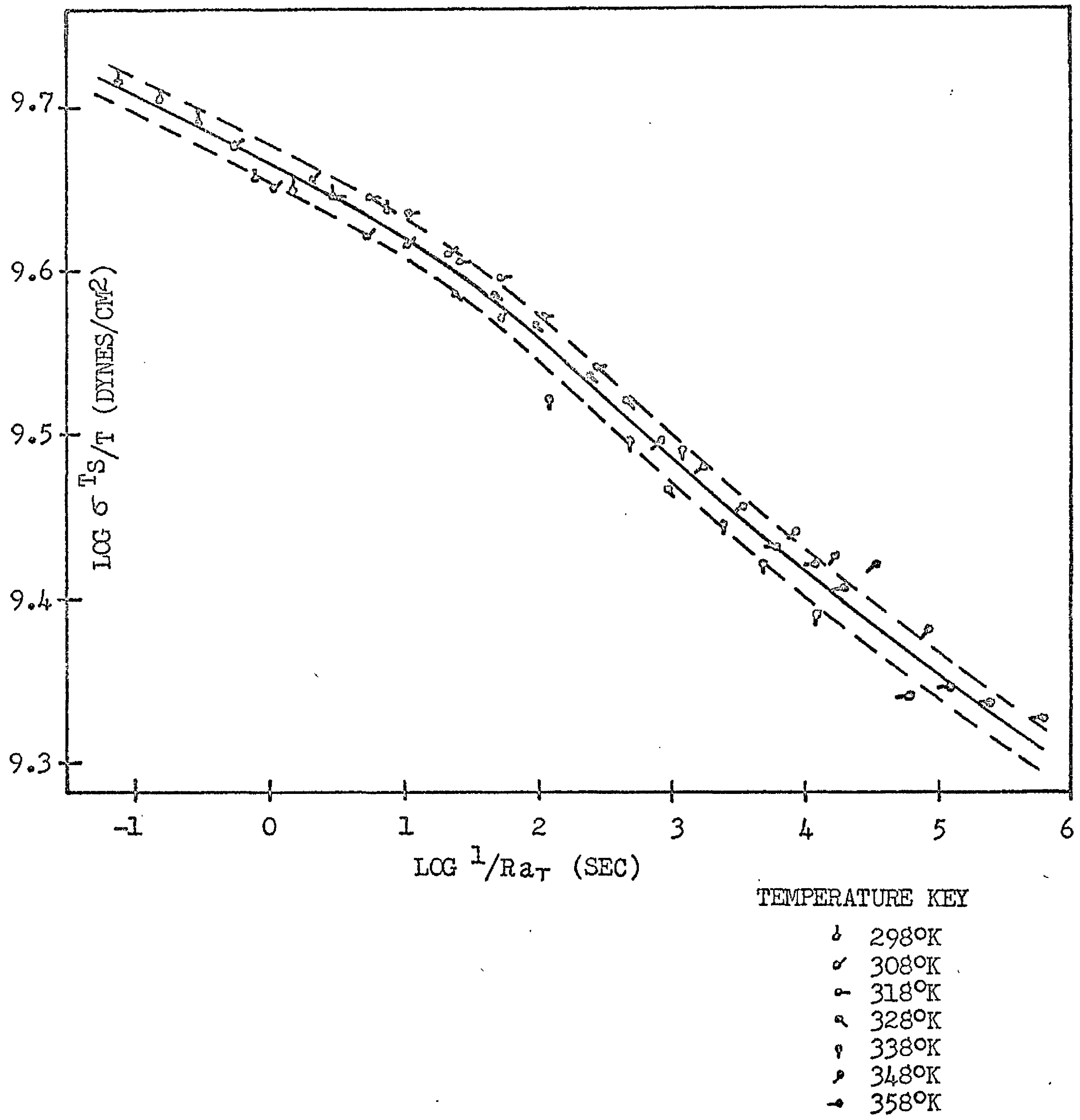


FIG 1.12 Composite Curve showing the Effect of Strain Rate and Temperature on the Breaking Stress of Polypropylene A

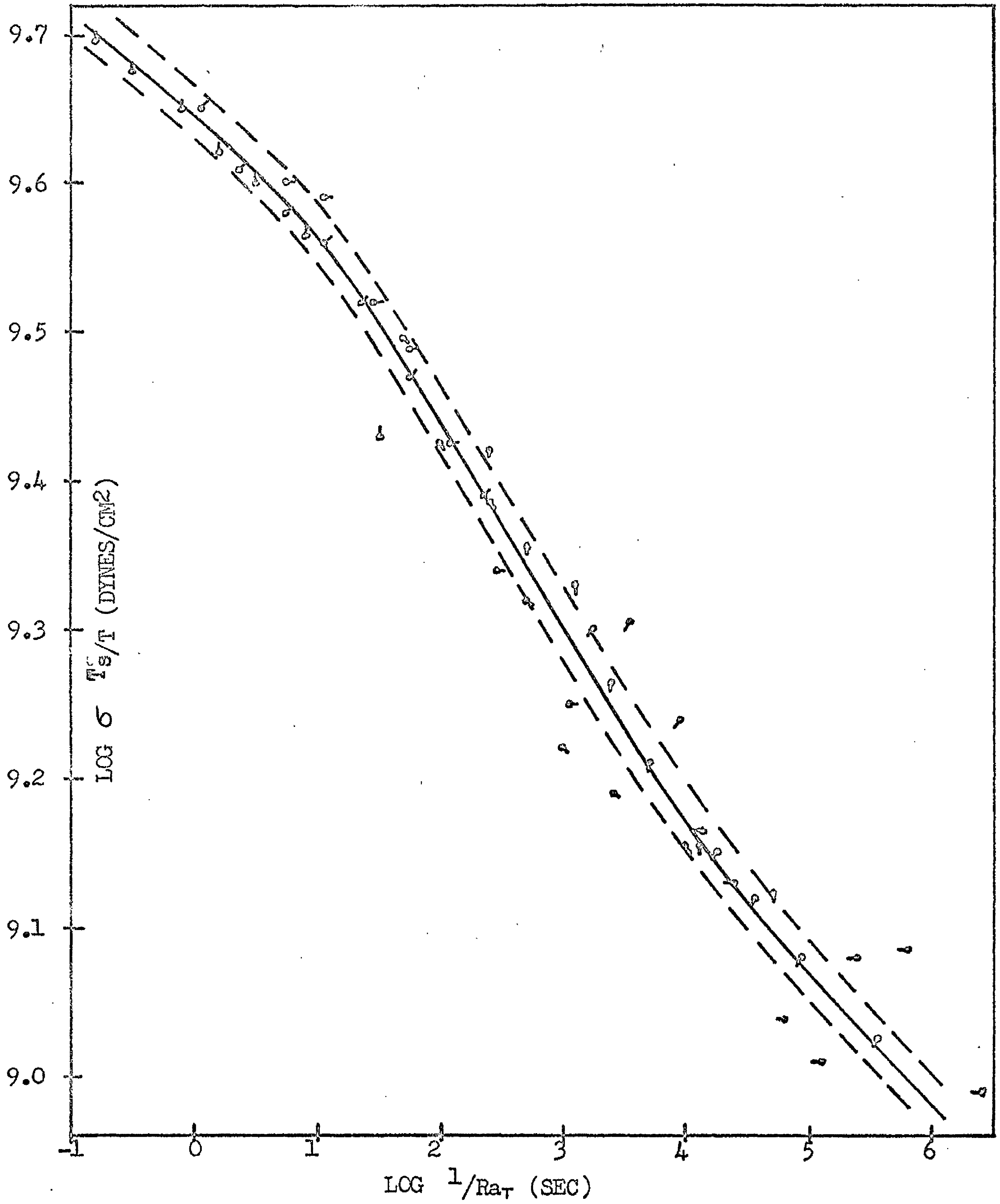


FIG 1.13 Polypropylene B Key as FIG 1.12

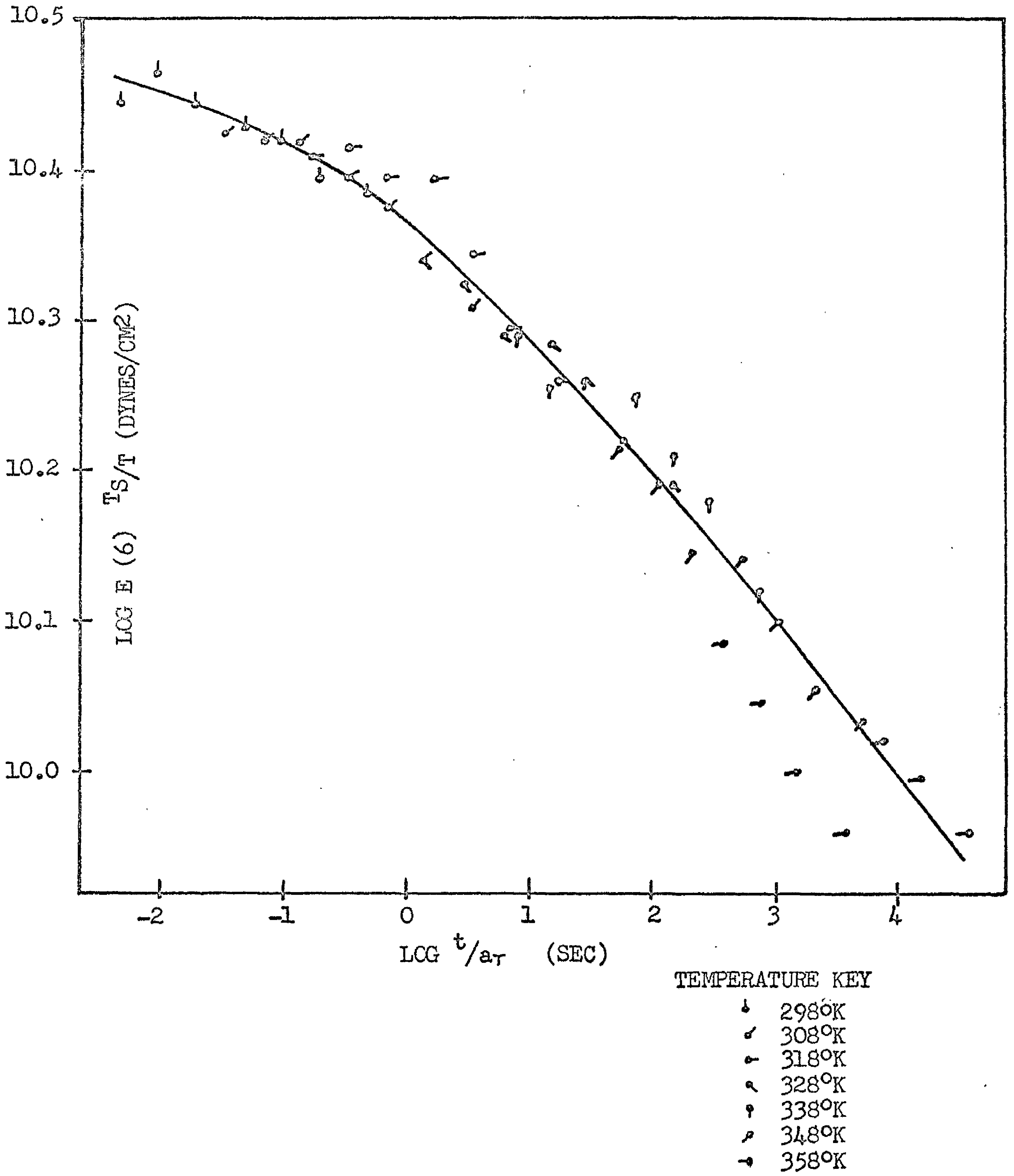


FIG 1.14 Composite Curve showing the Effect of Strain Rate and Temperature on the Tensile Modulus of Polypropylene A measured at 6% strain

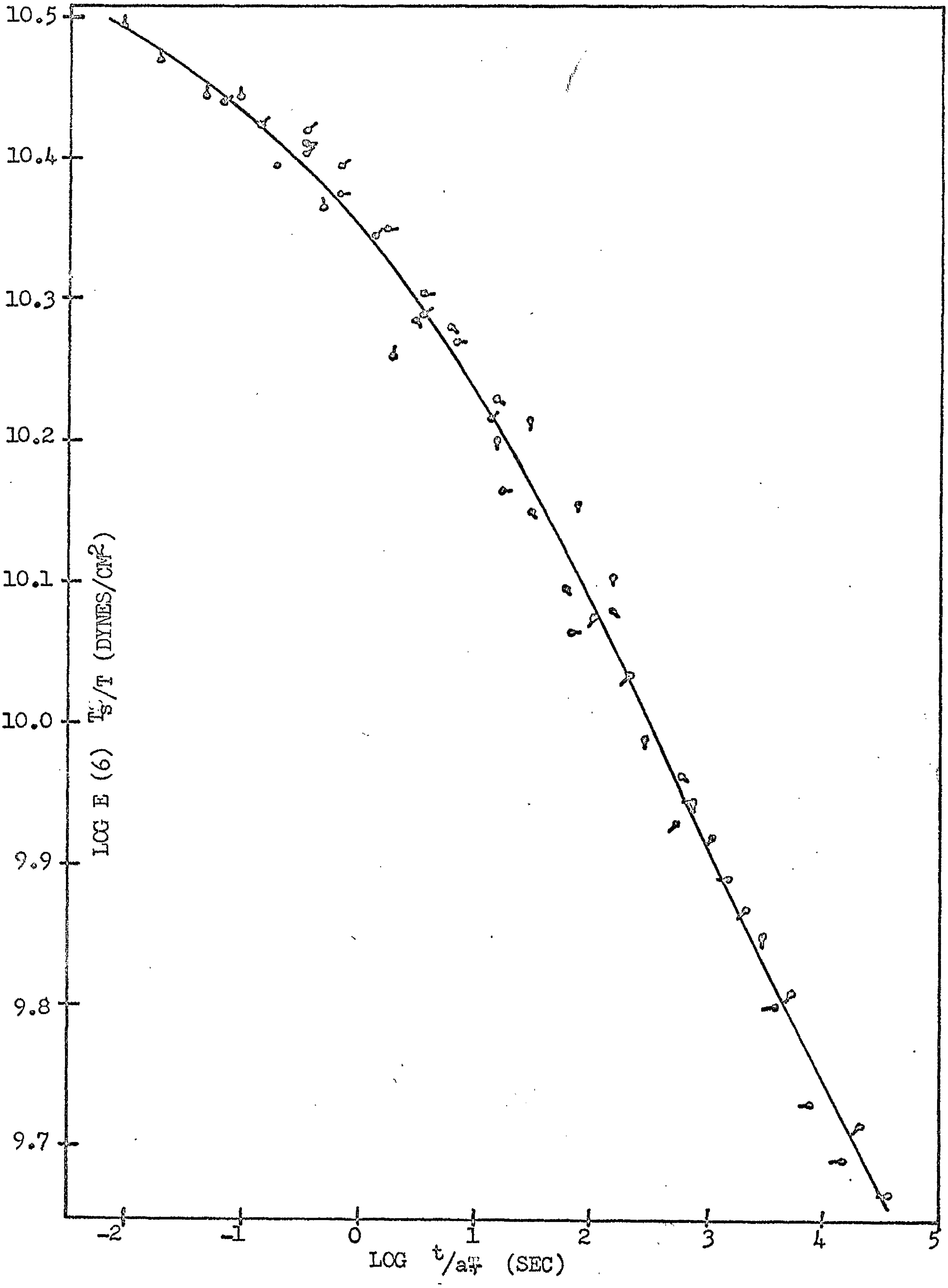


FIG 1.15 Polypropylene B Key as FIG 1.14

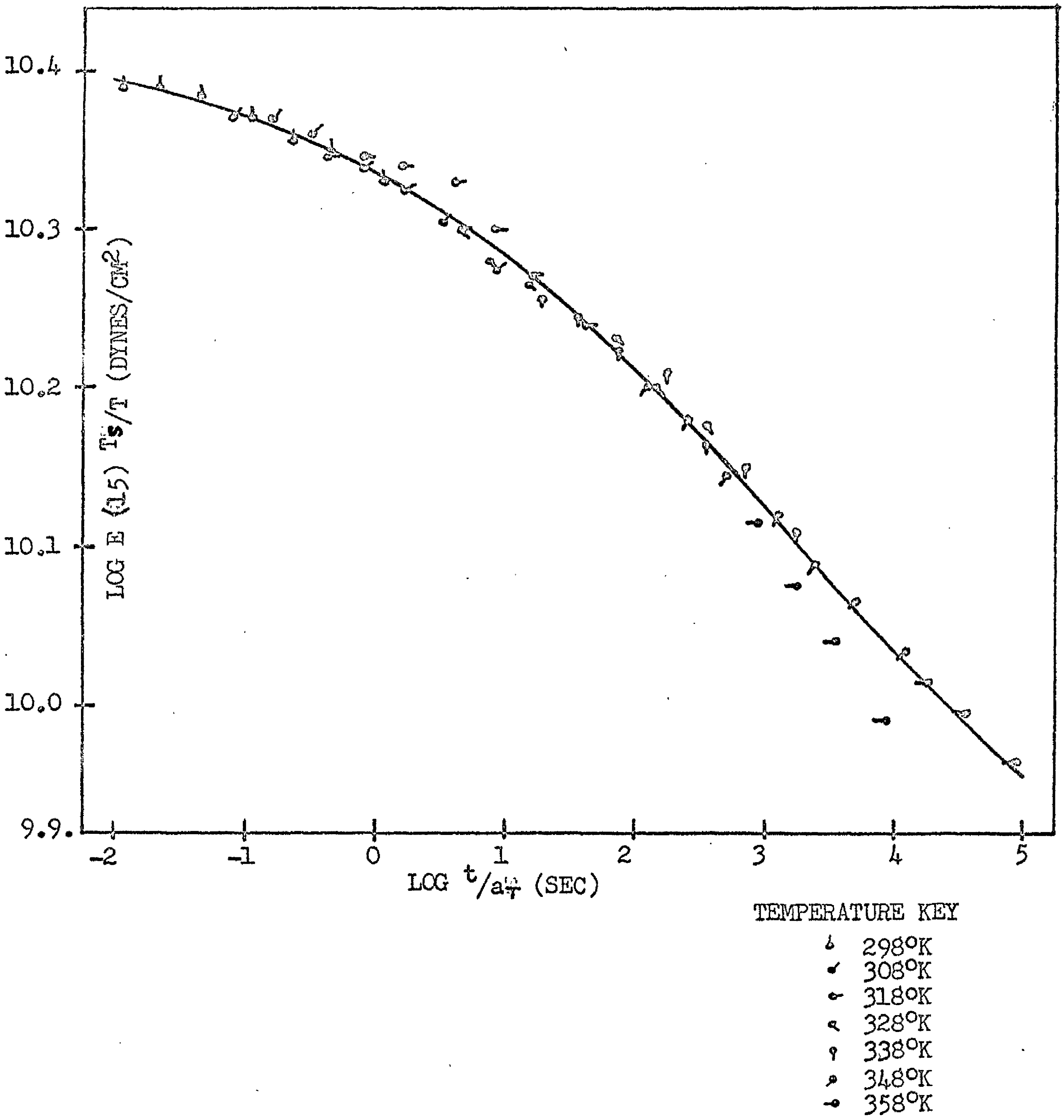


FIG 1.16 Composite Curve showing the Effect of Strain Rate and Temperature on the Tansile modulus of Polypropylene A measured at 15% strain

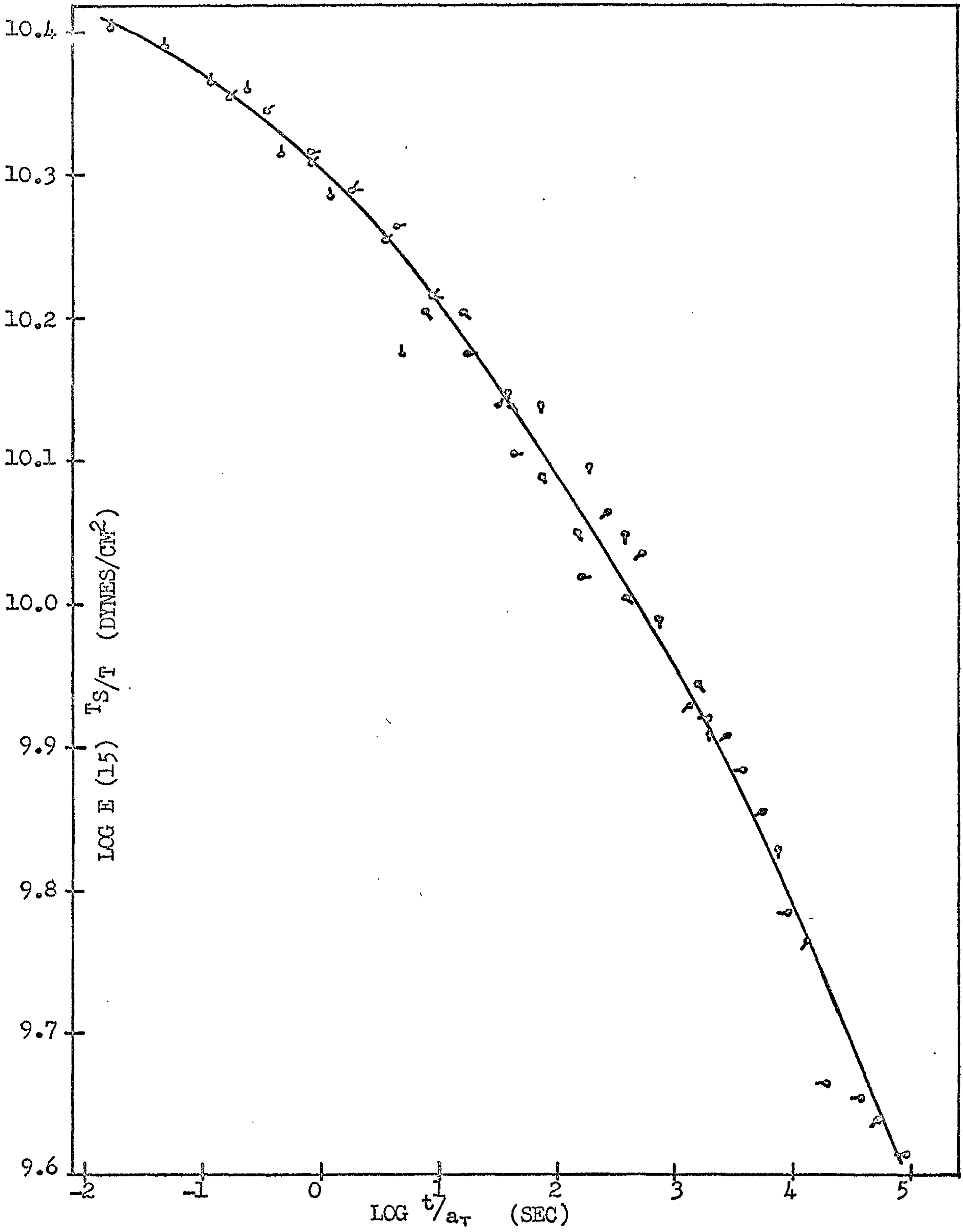


FIG 1.17 Polypropylene B Key as FIG 1.16

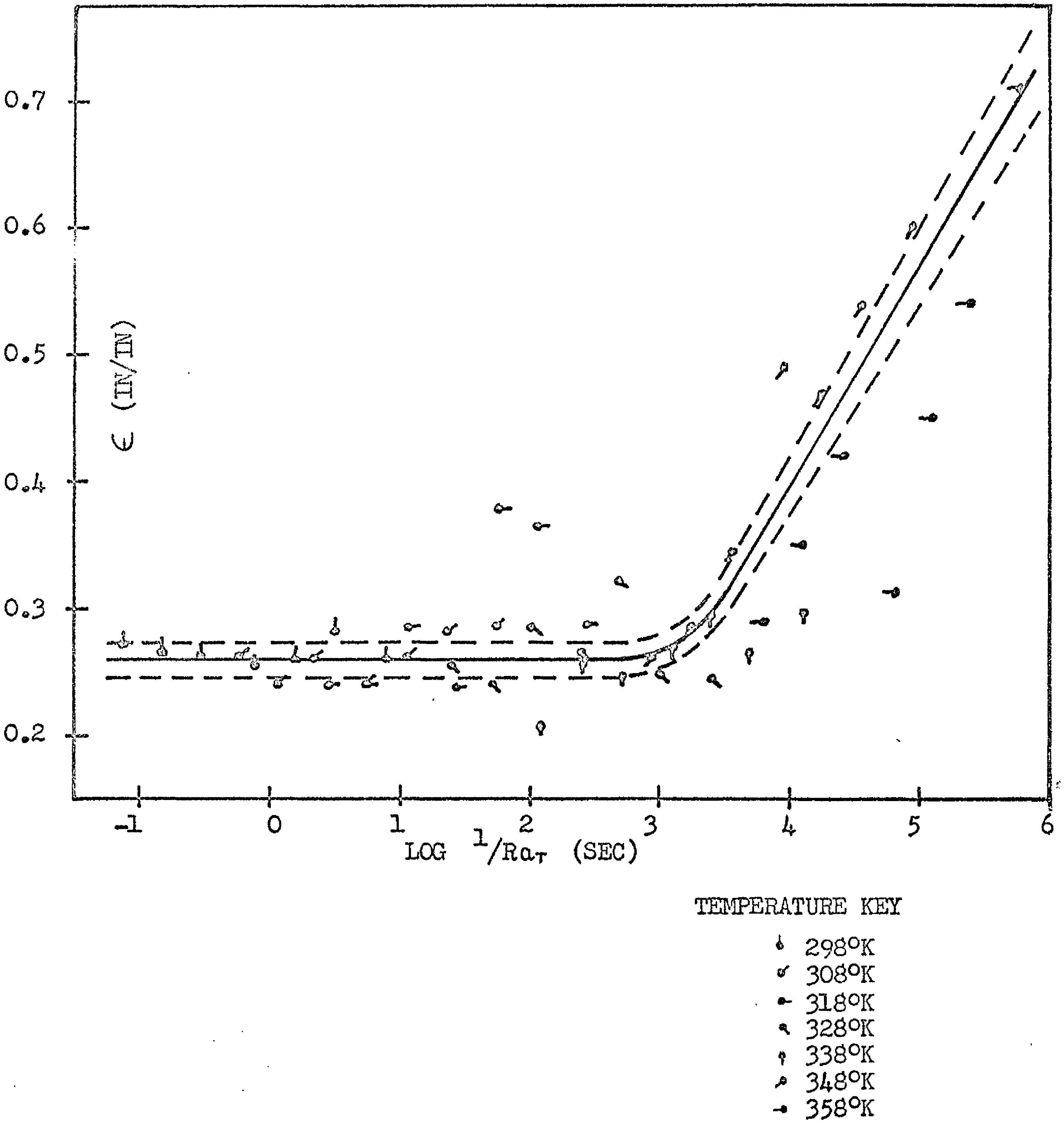


FIG 1.18 Composite Curve showing the Effect of Strain Rate and Temperature on the Breaking Strain of Polypropylene A

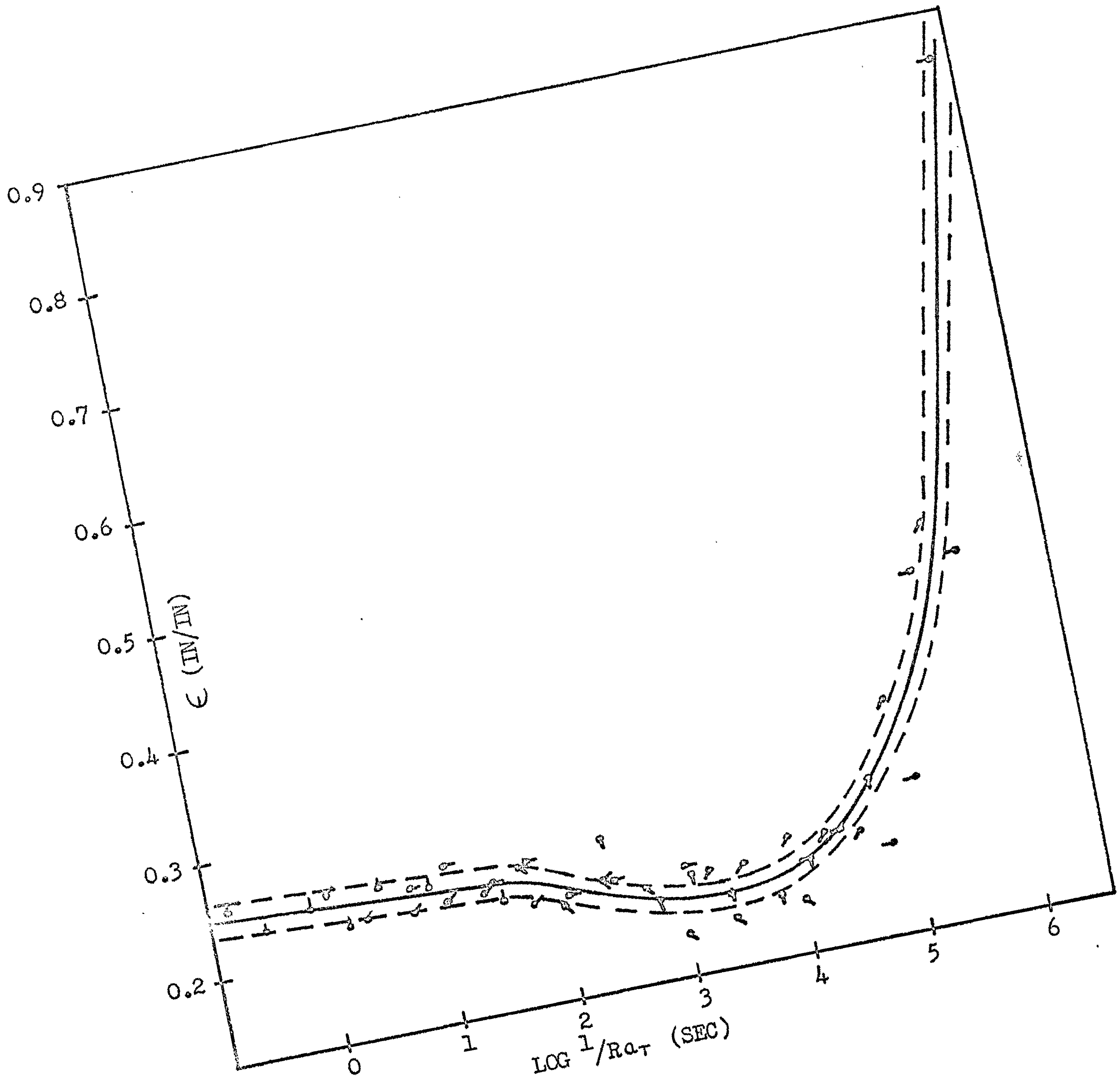
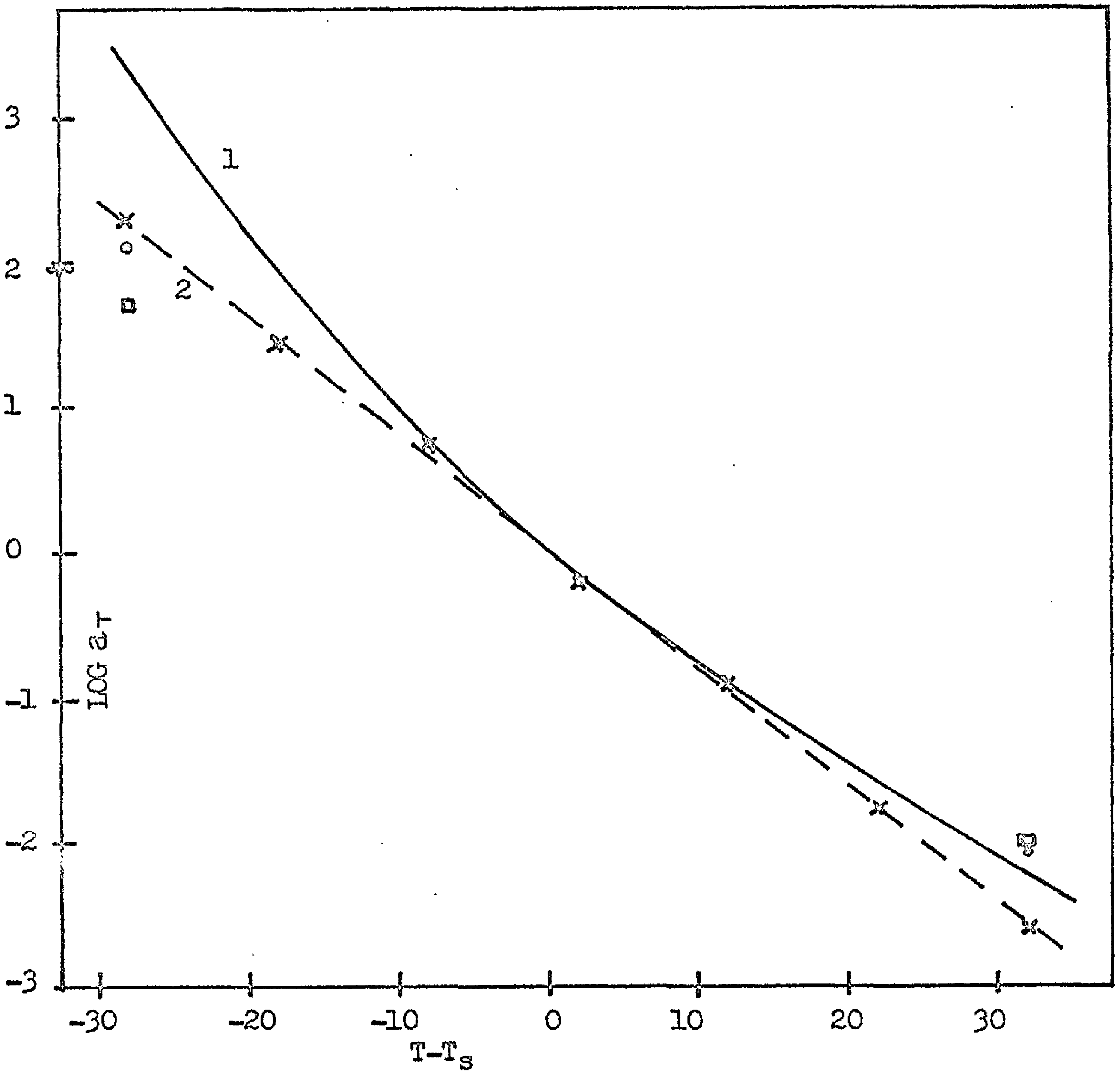


FIG 1.19 Polypropylene B Key as FIG 1.18



(1) Curve of the W.L.F. equation $\text{Log } a_T = \dfrac{-8.86\,(T-T_s)}{101.6 + T-T_s}$

(2) × Shift Factors used for Stress-Strain Data
• Shift Factors used for Relaxation Data - Polypropylene A
▫ Shift Factors used for Relaxation Data - Polypropylene B

FIG 1.20 Horizontal Shift Factors for Polypropylene A and B

This, together with the fact that the same shift could be applied to all the data from both samples, suggests that the superposition is reasonable.

The variation of the results was, however, high, particularly where ultimate properties were involved. The average standard error of each mean value was about the same for both samples indicating that the benefit of testing more specimens of sample B was offset by a higher inherent variability in this sample. The average coefficients of variation are shown in Table 1.5.

PROPERTY	COEFF. OF	VARIATION
	A.	B.
σ	3.5%	5%
ϵ	5%	7%
E(6)	4%	6.5%
E(15)	3%	6%

TABLE 1.5

COEFFICENT OF VARIATION

Although these values are reasonable a few individual values for breaking strain had a coefficient of variation of 15% or over and several values for breaking stress had a coefficient of 10% or over for sample B. When the temperature variation of ± 1°C is taken into consideration an error is introduced along the time axis and the overall coefficient becomes higher. If this average variation is applied to the composite curve a good indication of the accuracy of the data and the limits of the true curve are given. This is shown by the dotted lines in Figs. 1.12, 1.13, 1.18 and 1.19.

Data from tensile stress relaxation experiments (Table 1.6) were treated in the same way as the stress-strain data. The stress was converted to the tensile modulus and measurements at different temperatures compared on a log-log plot of modulus with time. (Figs. 1.21 and 1.22). Once again it was seen that temperature had a greater effect on sample B. Exact superposition could not be achieved using the previous shift factors. In fact slightly different factors had to be used for each sample as shown in Table 1.7.

TABLE 1.7. HORIZONTAL SHIFT FACTORS ($\mathrm{Log}\, a_T$)

TEMPERATURE SHIFT FACTOR FROM	25°C	55°C	85°C
STRESS-STRAIN CURVES	2.3	$\bar{1}.8$	$\bar{3}.4$
STRESS RELAXATION - SAMPLE A	2.1	$\bar{1}.8$	$\bar{3}.9$
STRESS RELAXATION - SAMPLE B	1.7	$\bar{1}.8$	$\bar{2}.0$

TABLE 1.6 STRESS RELAXATION

LOG TIME (SEC)	SAMPLE A			SAMPLE B		
	25°C	55°C	85°C	25°C	55°C	85°C
0.477	2.48	1.87	1.30	2.44	1.74	1.02
0.778	2.37	1.71	1.19	2.23	1.46	0.78
0.954	2.30	1.63	1.13	2.15	1.35	0.71
1.079	2.24	1.57	1.08	2.08	1.28	0.67
1.322	2.18	1.49	1.03	1.97	1.15	0.62
1.477	2.09	1.44	1.00	1.87	1.08	0.58
1.778	2.00	1.31	0.95	1.70	0.93	0.54
2.079	-	1.23	0.89	1.55	0.82	0.50
2.255	1.84	-	-	-	-	-
2.380	1.77	1.15	0.84	1.37	0.73	0.46
2.623	-	1.08	0.83	1.27	0.66	0.43
2.778	1.64	1.05	0.81	1.19	0.62	0.42
2.954	-	1.00	0.79	1.10	0.59	0.40
3.176	1.47	-	-	-	-	-
3.322	1.41	0.92	0.74	0.94	0.54	0.38
3.519	1.33	0.89	0.70	0.89	0.51	0.36
3.653	-	0.88	-	0.84	0.49	-
3.708	1.27	0.87	0.69	-	-	0.35
3.756	-	-	-	0.79	0.47	-
3.839	-	-	-	0.75	0.46	-
3.875	-	0.83	0.66	-	-	0.34
3.954	-	-	0.64	0.71	-	-
4.000	-	0.81	-	-	0.44	0.32

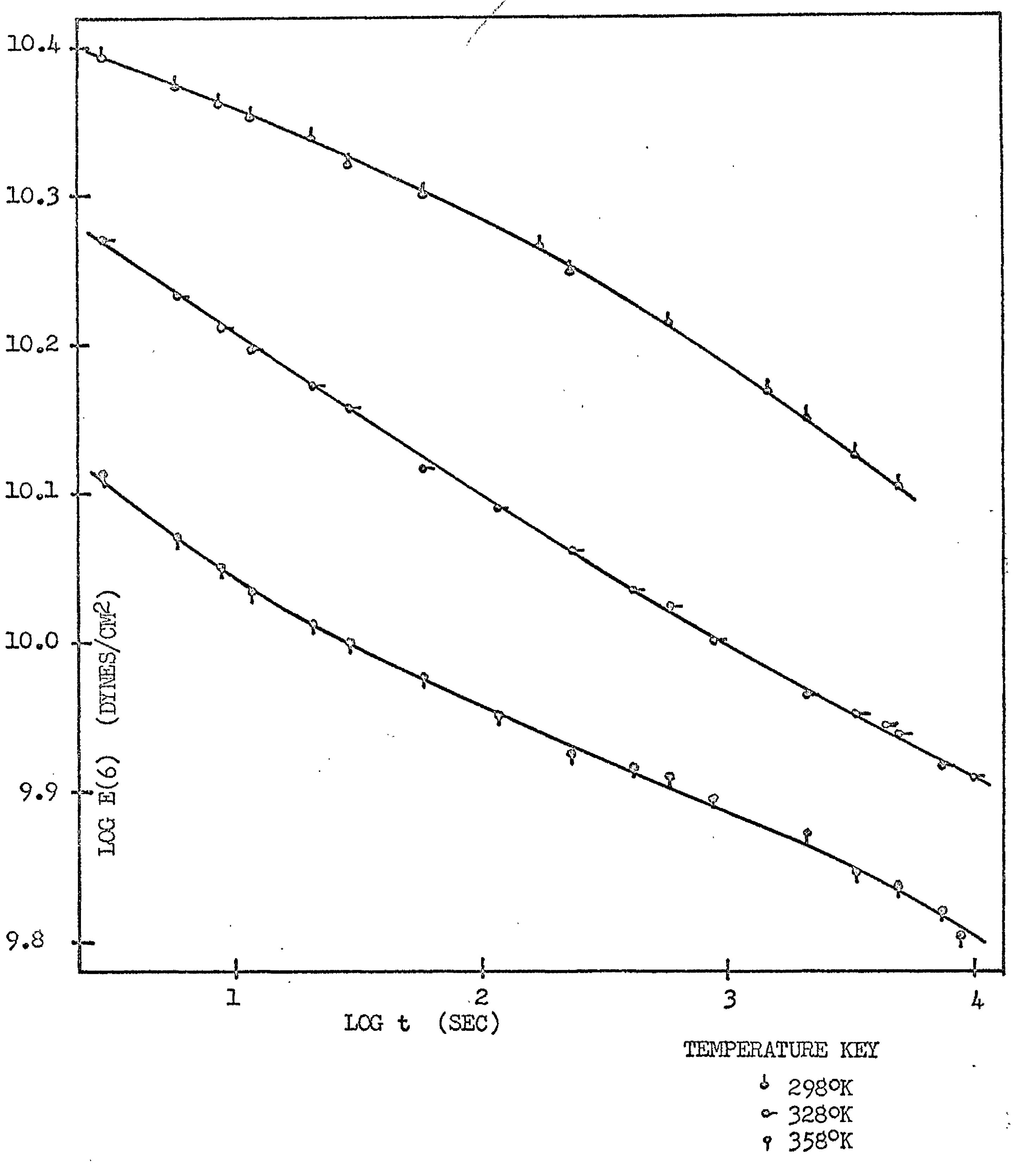


FIG 1.21 The Effect of Temperature on the Relaxation of Stress in Polypropylene A from 6% extension. (Data expressed in terms of the Tensile Modulus.)

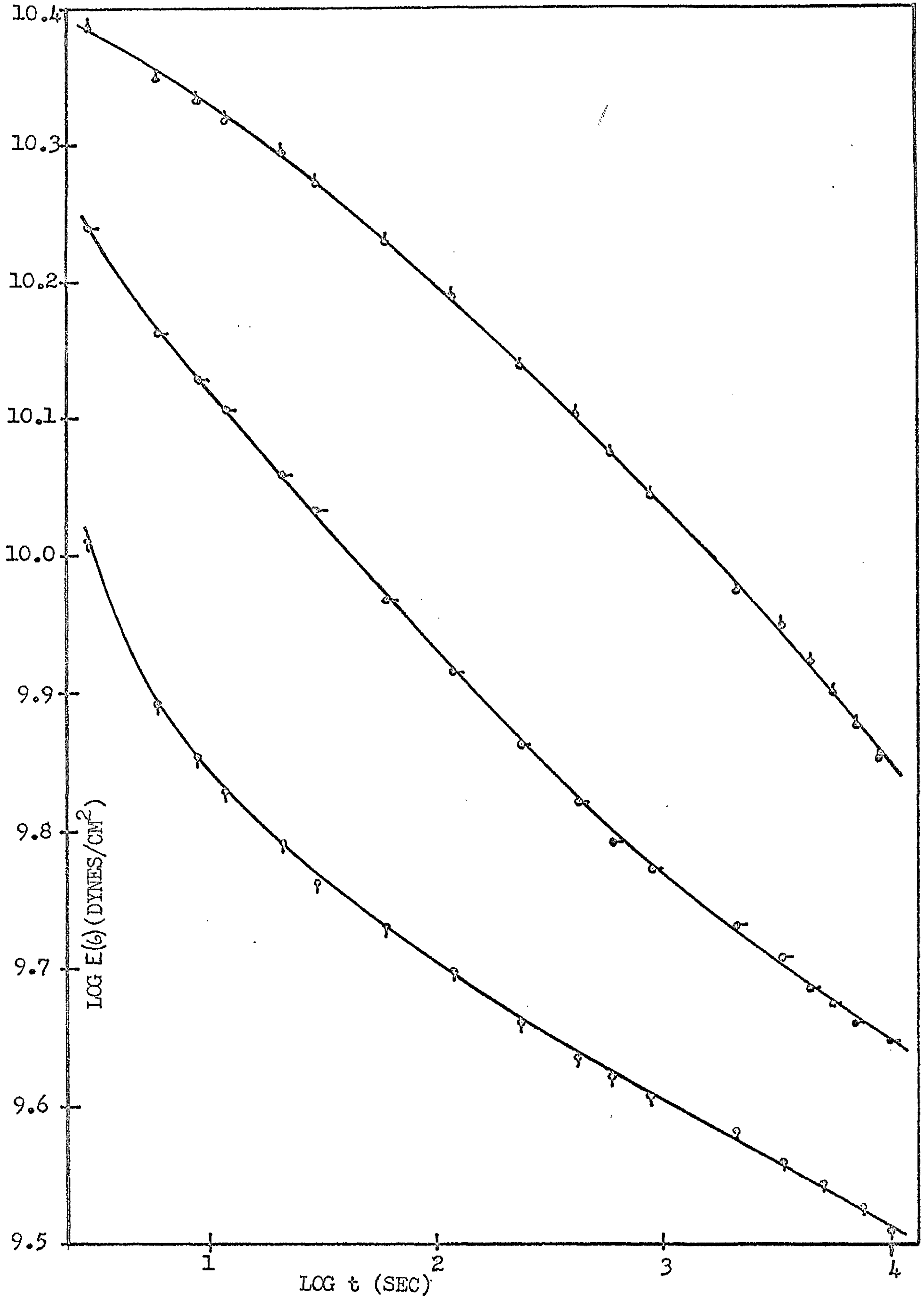


FIG. 1.22 Polypropylene B. Key as FIG 1.21
Stress Relaxation from 6% extension at different temperatures.

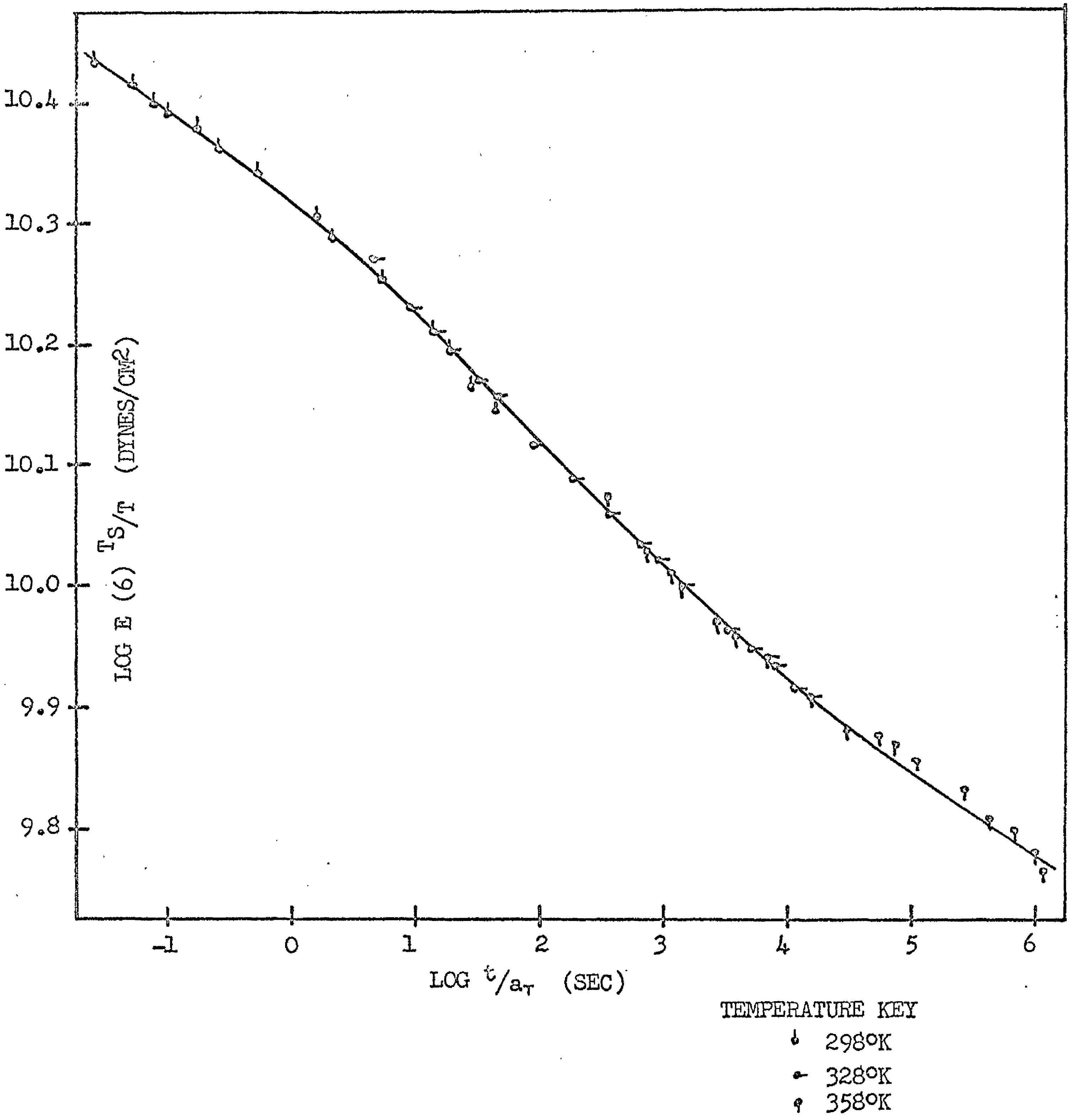


FIG 1.23 Composite Curve showing Effect of Strain Rate and Temperature on the Tensile Modulus of Polypropylene A, taken from Stress Relaxation Data.

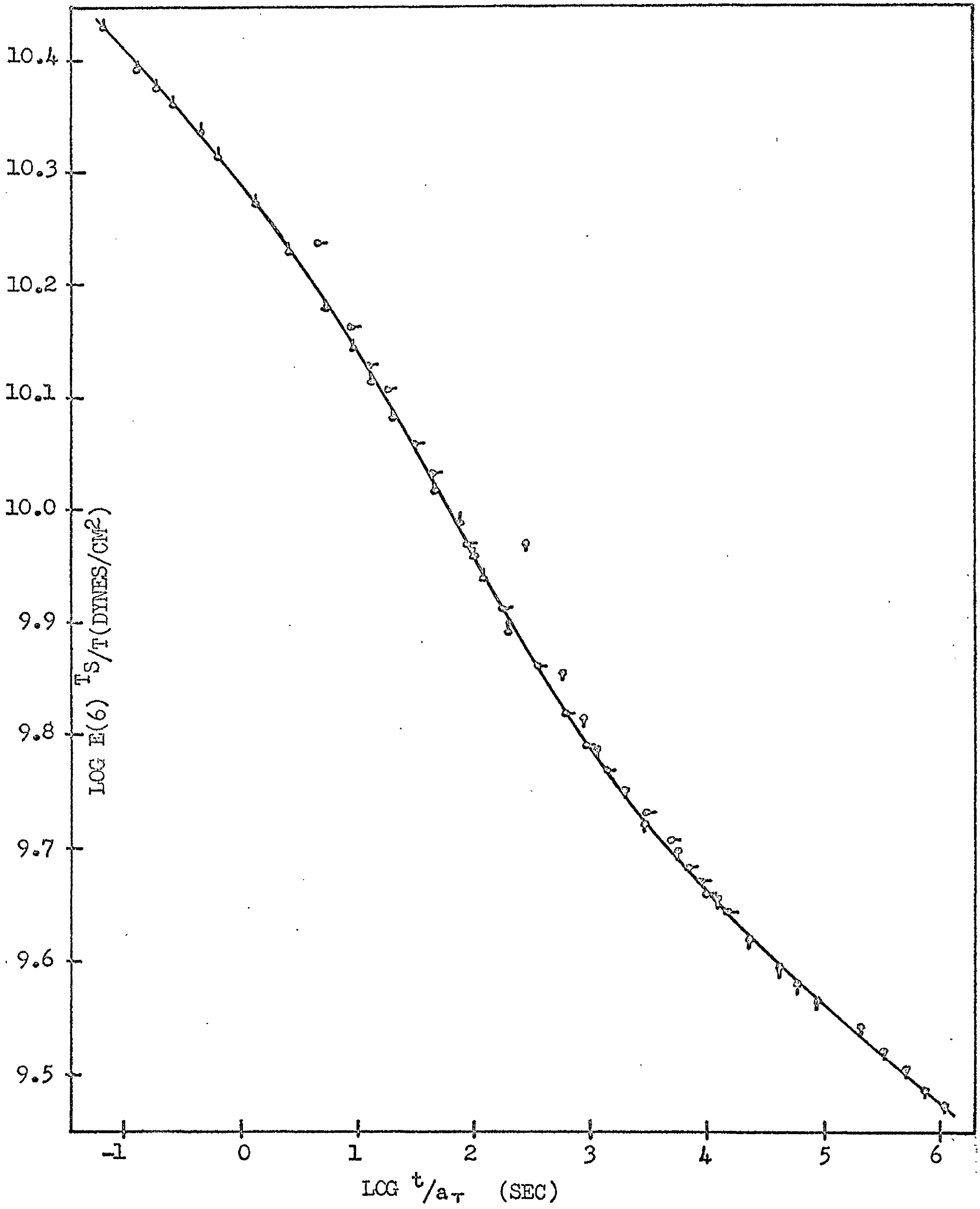


FIG 1.24 Polypropylene B Key as FIG 1.23

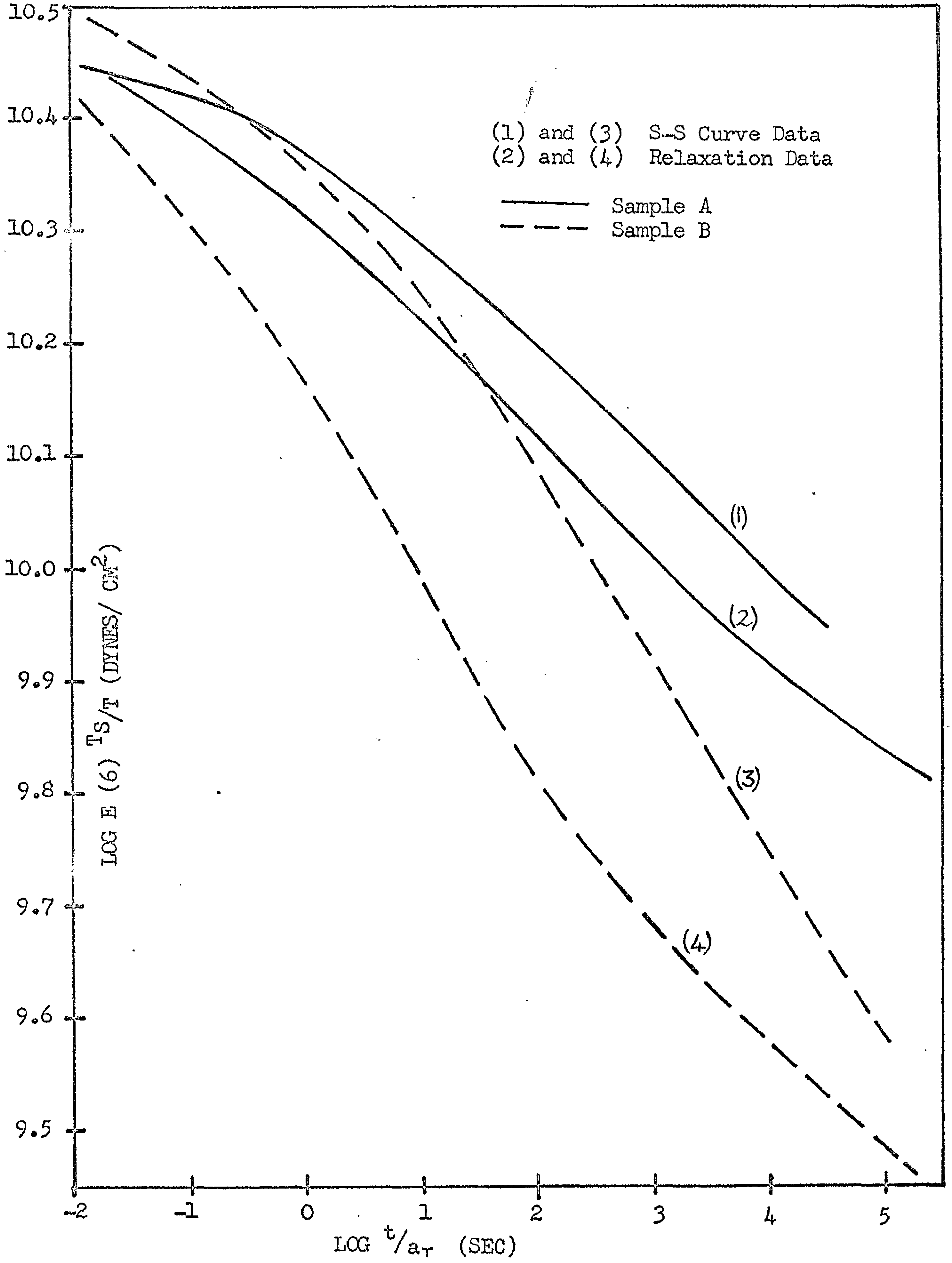


FIG 1.25 Comparison of the Tensile Modulus calculated from the Stress-Strain Curve with that calculated from Stress Relaxation Data for two samples of Polypropylene

These differencies may well arise from the fact that only two specimens of each sample were tested at each temperature, making the absolute value of stress doubtful although the relative values are reliable and give good "fit" in the composite curves (Figs. 1.23 and 1.24) with the exception of values measured in the first 10 seconds of relaxation of sample B.

When the data from the stress-strain curves are compared directly with the relaxation results (Fig. 1.25) it is seen that the former have the higher stress values at any particular time, the difference between the two sources being greater in the case of sample B. Both curves, for either sample, have similar slopes, indicating that the same rate processes are involved and there is merely a change in the time scale due to the different methods used. Although any one point on the time scale in Fig. 1.25 corresponds to the same strain and time in all the curves this equality was achieved in different ways. If the strain has been imposed for some time, as in stress relaxation at constant strain, the total stress has been relaxing for the duration of the test. If the strain is only attained for the first time at the moment of measurement, as in stressing at constant rate of strain, new stresses are being introduced continuously and some have therefore been relaxing for a shorter period than others. The average effect of this is to produce a higher stress since the average relaxation time is shorter, and the effect is greatest in materials which have higher relaxation rates (sample B in this case).

1.5 ANALYSIS OF RESULTS

When the composite curves are compared directly (Figs. 1.26 and 1.27), the marked differences between the behaviour of samples A and B are clearly seen. Also, although previous data on sample C does not lend itself to superposition and was obtained using a different temperature range and time scale, it differs again from the other two, if it is compared where the data overlap. Thus there is a considerable variation in the tnesile properties of different samples of polypropylene.

This unusual situation was investigated further in an effort to correlate tensile behaviour with other physical properties. Degree of crystallinity and orientation are known[55] to be important in

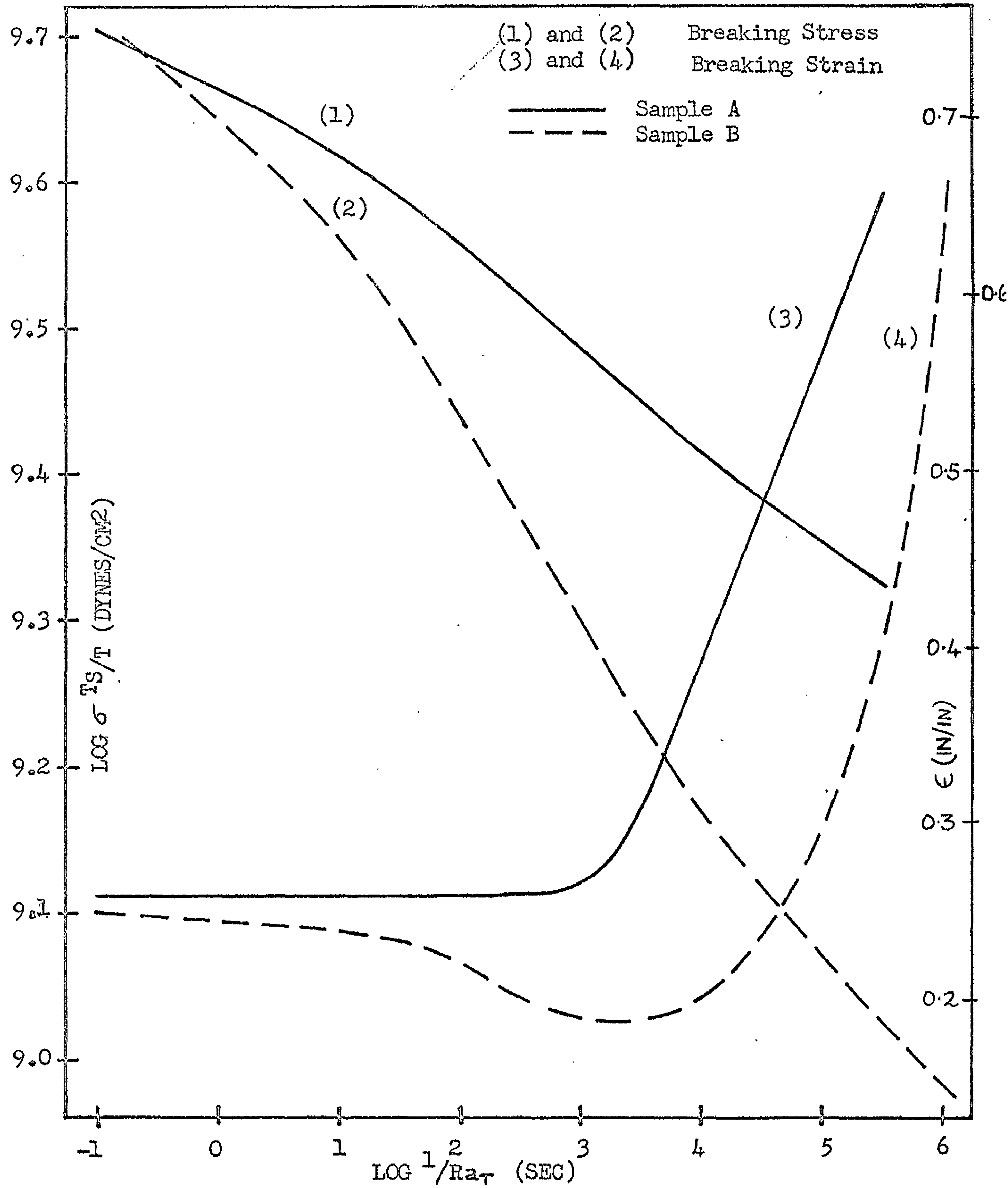


FIG 1.26 Comparison of the Breaking Stress and Strain of Two Samples of Polypropylene

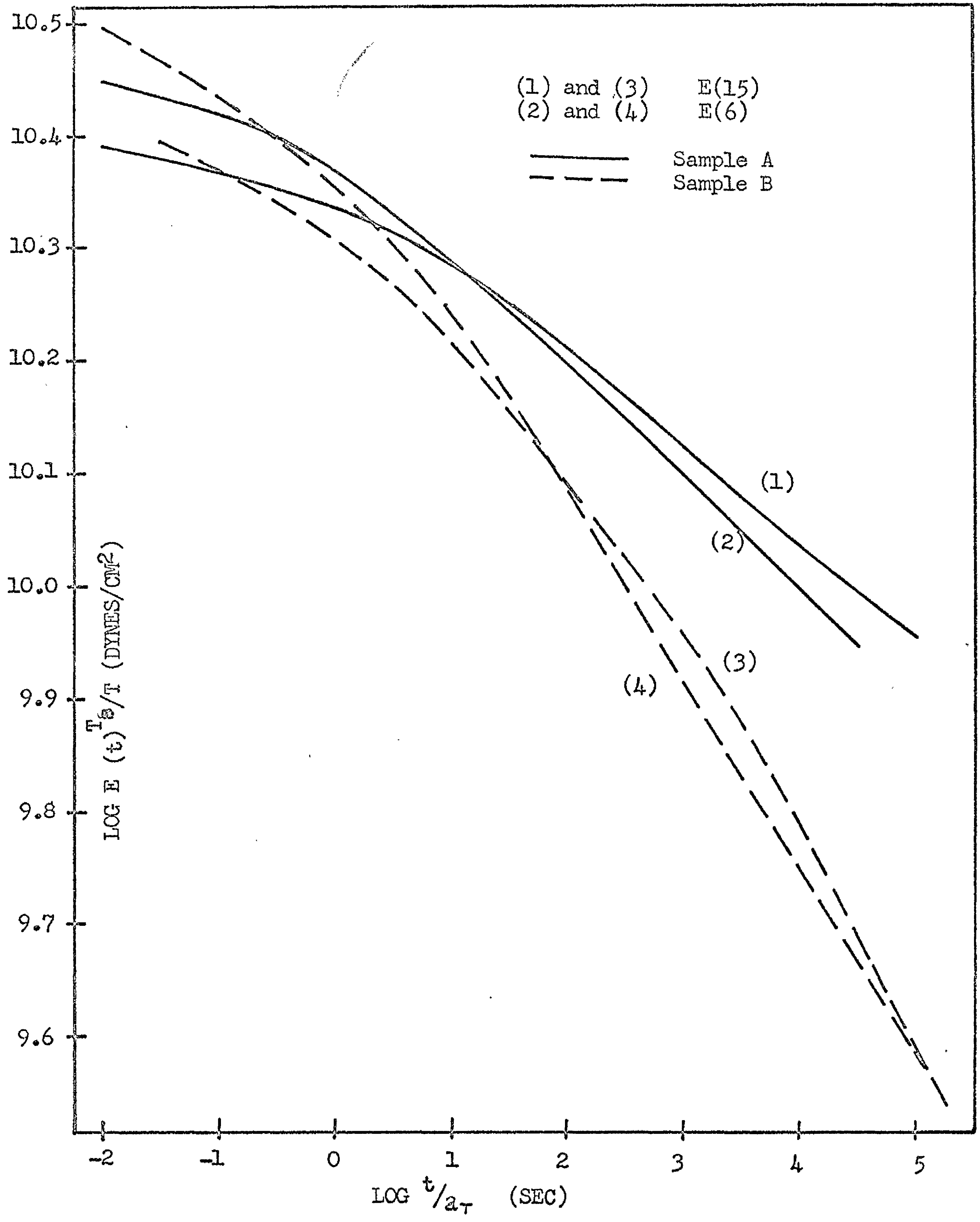


FIG 1.27 Comparison of the Tensile Modulus of Two Samples of Polypropylene

determining the behaviour of polypropylene under small deformations, while the average molecular weight and molecular weight distribution are important factors governing the brittleness or flow properties in which large deformations are involved. The atactic content of the polymer, normally indicated in reverse by the isotactic index expressed as a percentage by weight, is related to the degree of crystallinity since it is unlikely that this form is capable of crystallization. In fact the presence of atactic polymer has been found[56] to have a greater effect on mechanical properties, including tensile, than molecular weight or molecular weight distribution. Finally the crystalline melting point is of some significance in connection with high temperature properties. Consequently, in addition to density and glass transition temperature already mentioned, the isotactic index, crystalline melting point, birefringence, intrinsic viscosity and hence the weight average molecular weight were measured. To provide further evidence in support of the values of the transition temperature the dynamic loss tangent, tan δ , was also measured. All the measurements were carried out on finish-free yarn after annealing unless otherwise stated.

The isotactic index was determined by extraction in 2.2.4 - trimethyl pentane (iso-octane) for 4 hours. The index was expressed as a percentage of the weight remaining after extraction to the original weight, both readings being taken in the desiccator dried state. The crystalline melting point was determined visually with the aid of a polarising microscope. The intrinsic viscosity was measured in decalin at 135°C, three specific viscosity readings being taken at each concentration. The weight average molecular weight $\overline{M}w$ was then calculated using the folmula

$$[\eta] = \overline{M}_w^{0.8} \times 10^{-4} \quad \text{\_ \_ \_ \_ \_ \_ \_} \quad (10)$$

where $[\eta]$ is the intrinsic viscosity. Birefringence was determined by the Becke Line method of refractive index measurement using polarised light. The dynamic loss tangent (tan δ) was measured on specimens as received and in the annealed state over a wide range of temperature. A forced lateral vibration method similar to that described by Meredith and Hsu[57] was used.

Data for these properties are summarised in Table 1.8. The specific viscosity-concentration plot from which $[\eta]$ was measured is shown in Fig. 1.28 and the temperature dependence of tan δ is shown in Fig. 1.29.

Annealing caused a shift in the loss tangent peak for samples A and B to a slightly lower temperature, the peak for sample C remaining almost unchanged. The maximum values of the dynamic loss tangent therefore occur at temperatures slightly higher than the measured glass transition temperatures of the materials and in the same order as these measurements. It would therefore seem certain that there is no difference in the transition temperature of samples A and B while sample C has a higher value.

The calculated molecular weight of material B is less than half that of the other two samples, C having the highest value. Examination of Fig. 1.28 shows that the viscosity-concentration lines of samples A and B have a similar slope while that of sample C is much steeper. This indicates the possibility, in the latter case, of a more rigid molecular structure. It must be borne in mind, however, that this depends on only 3 or 4 measurements at different concentrations. In the case of sample B only two points were obtained because small portions tended to precipitate out in the later stages of the viscosity measurement and interefere with the rate of flow. This less stable behaviour suggests that cross linking is taking place due to the presence of peroxide used to degrade the material to the required molecular chain length. This is therefore consistent with the low molecular weight value obtained.

TABLE 1.8 Structural Properties

SAMPLE	A	B	C
Isotactic index	96.8	94.2	100
Crystalline Melting Pt. (°C)	172	172	170
Intrinsic viscosity ($[\eta]$)	2.01	1.13	2.11
Molecular weight ($\times 10^{-5}$)	2.39	1.16	2.54
Birefringence ($n_{\parallel} - n_{\perp}$)	0.025	0.025	0.029
Loss tangent peak (°C)			
(as received)	22	22	22
(annealed)	18	18	23

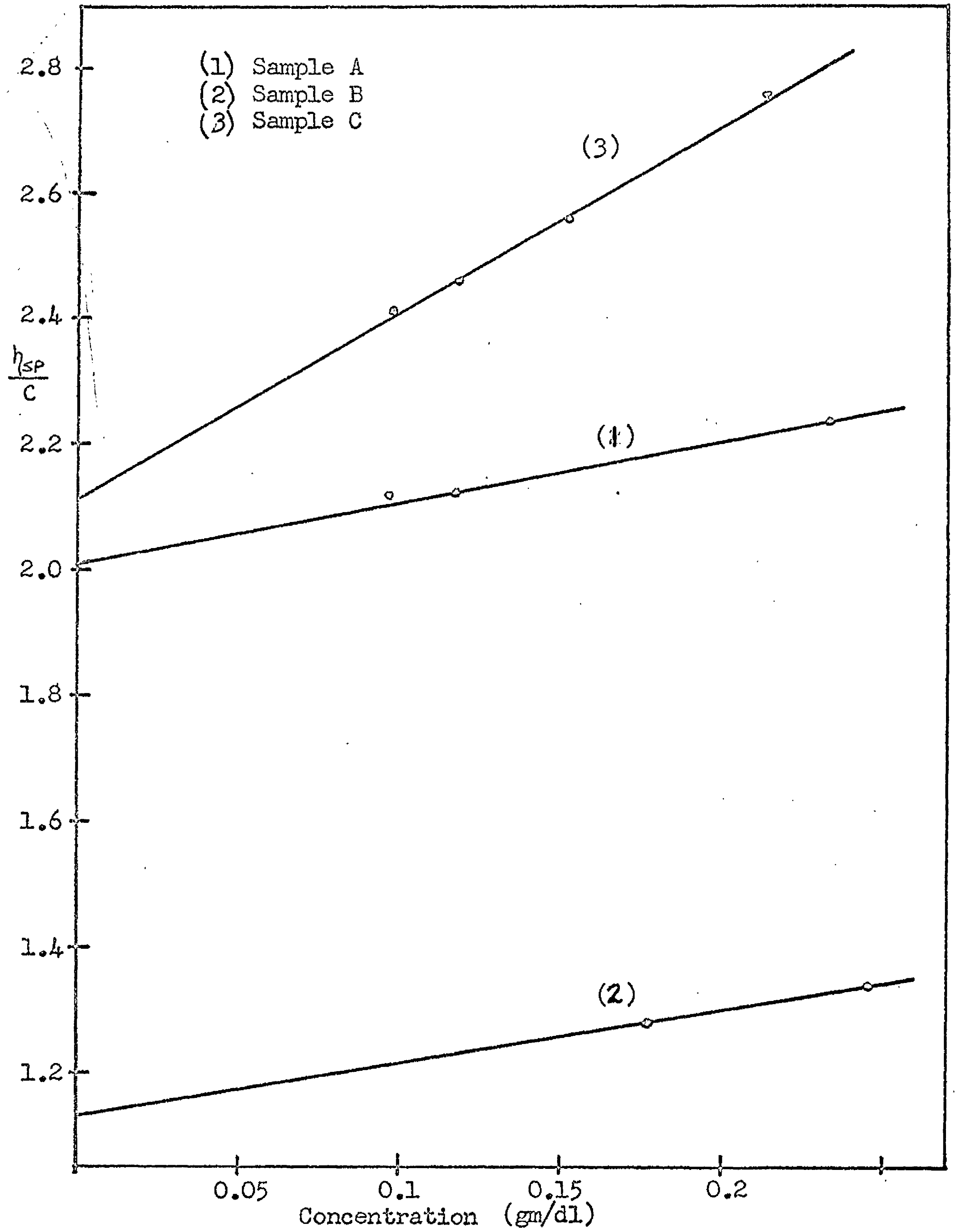


FIG 1.28 Determination of Intrinsic Viscosity for Three Samples of Polypropylene

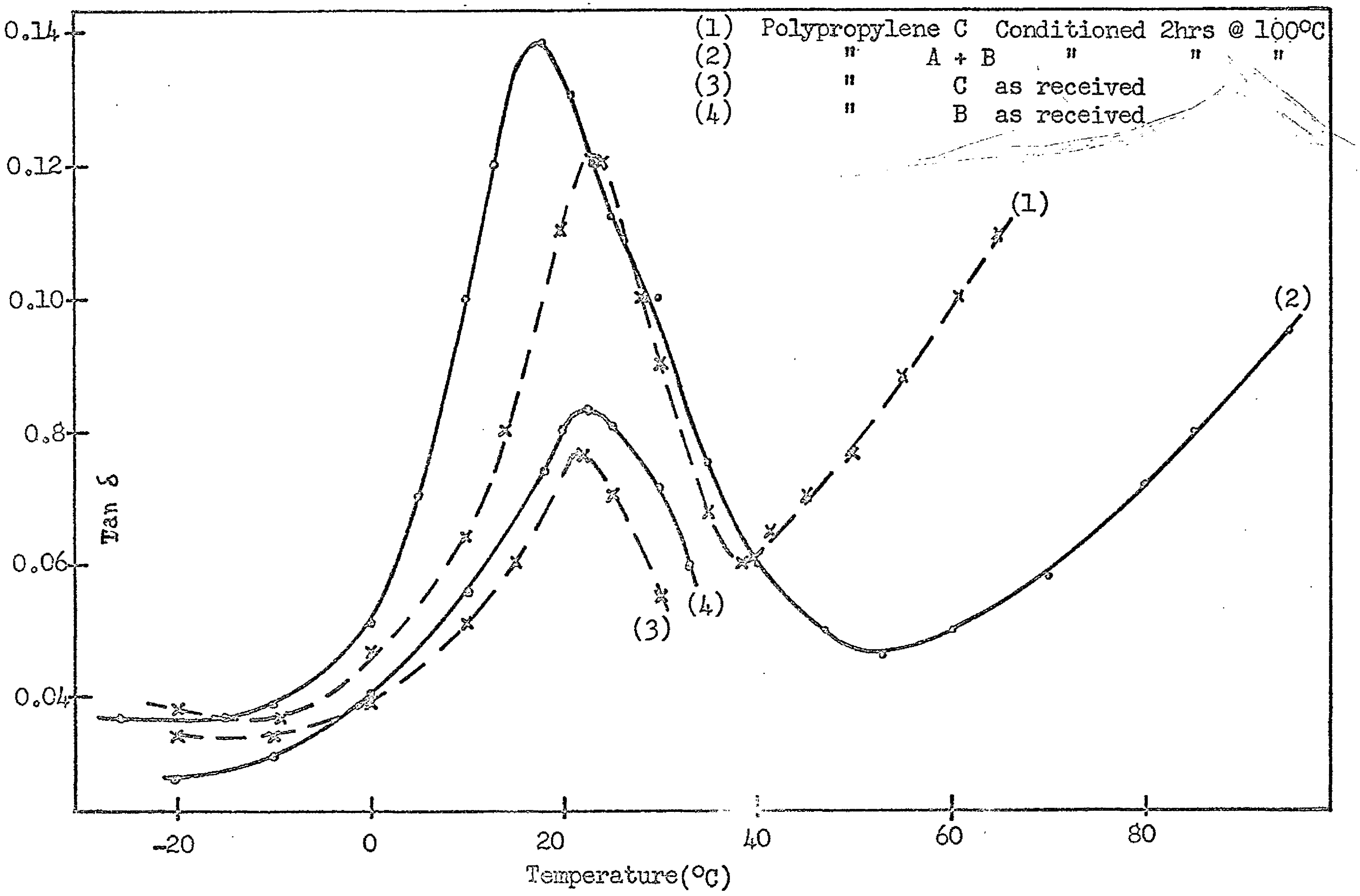


FIG 1.29 The Effect of Temperature on the dynamic loss tangent of Three Samples of Polypropylene

The higher molecular weight and rigidity, together with the apparent absence of atactic material which allows better orientation as indicated by the higher birefringence, would certainly account for the higher tensile strength of sample C. The low density of this material is, at first sight, contrary to that expected since it indicates a lower crystallinity. However this might explain the higher extensibility at room temperature, since if it is assumed that crystalline and amorphous polypropylene have densities of 0.936 and 0.850 g./c.c. respectively a density of 0.904 shows that over 35% of this sample is amorphous.

The presence of atactic material in samples A and B results in a lower birefringence indicating a poorer orientation than sample C although the density values reflect a considerably higher crystallinity (80% for A and 75% for B). This would suggest that small changes in atactic content play a more important role in determining physical properties than corresponding changes in crystallinity. The crystalline melting points of all three samples are very similar and no conclusion can be drawn from them.

The combined effect of high atactic content and low molecular weight in sample B goes a long way to explaining the greater temperature dependence of this yarn. In fact, of all the properties measured, the average molecular weight and the isotactic index appear to have the greatest effect on the tensile properties, a conclusion reached by Crespi and Ranalli[56] using a plastic form of polypropylene.

1.6 CONCLUSIONS

Differences in tensile behaviour between samples of polypropylene can be explained by differences in structural properties.

The higher tensile strength of sample C^{20} may be attributed to the absence of atactic material which allows a higher orientation of the crystallites along the filament axis. Although sample B had a higher atactic content than sample A, these materials have the same birefringence. Since their tensile properties were similar at the lower end of the time scale, where less time was allowed for relaxation to take place, the actual amount of atactic polymer present does not appear to be of prime importance. A small percentage is sufficient to limit the orientation and hence the tensile strength.

The viscoelastic behaviour of a material depends on its rigidity. This is determined to a large extent by the type of molecular chain comprising the linear polymer but is affected by the molecular weight and, in this case, the isotactic index. Sample A had a higher weight average molecular weight and isotactic index than sample B. Both these factors would be expected to make the latter less rigid and make it more sensitive to the effect of temperature and strain rate in tensile tests. This was found to be the case. Sample C cannot be compared directly, since Hall's data[20] only overlap slightly, but it had a higher average molecular weight and isotactic index than either of the other materials and would therefore be expected to be less sensitive to changes in temperature or strain rate than these samples.

Although sample B was more sensitive to factors affecting the rate processes of the material than sample A, time-temperature superposition can be applied in both cases using the same shift factors for each. Although the data for sample C were limited Hall[58] attempted to reduce the breaking strain results at different temperatures to room temperature and showed that the sudden drop in the values as the temperature decreased corresponded to a similar drop as the strain rate increased. The shift factors used in this paper agree closely with those used in the present investigation and suggest that superposition can be applied to all three samples using the same factors, provided suitable limits are chosen.

Composite curves of the type described could be used to characterise different samples of polypropylene or detect changes in behaviour occurring as a result of structural changes caused by alterations in conditions at some stage in polymer production or filament formation.

PART 2 ELASTOMERIC YARNS

2.1 INTRODUCTION

Until very recently elastic threads have been produced either by cutting vulcanised rubber sheet or by extruding latex or rubber solutions through a spinnaret and vulcanising after spinning. In either case the raw material used was rubber. It was inevitable that chemists would try to develop synthetic fibres with the same high degree of elasticity, which is the outstanding feature of rubber, but with a higher modulus and tensile strength.

The "Vulkollan principle" [59] by which the addition polymerisation of diisocyanates was made possible provided the break through and various methods based on this process have now been perfected. These fall into two broad classifications, chemical spinning and solvent spinning. In both cases polyglycols, either esters or ethers, are first produced from dialcohols and aromatic or aliphatic acids, a wide range of which are suitable. These are then reacted with a diisocyanate to form a macrodiisocyanate. This has still a fairly low molecular weight and, in chemical spinning it is allowed to react with a polyamide, introduced in a carefully measured quantity, during fibre formation. By causing further polymerisation, the amide hardens the filaments which can then be handled for further processing. In solvent spinning the macrodiisocyanate is dissolved in a suitable solvent such as dimethylformamide and treated with a calculated amount of a polyamine again to extend the polymer and produce a spinnable viscous solution. This must be coagulated after extrusion in the normal way.

The resultant material is a high polymer which can be cross-linked by free isocyanate groups to form a network structure with a high rubberlike elasticity. These polyurethanes, as they are called, are characterised by a higher tensile strength and elastic modulus than natural rubber, the energy required to break them being 2-4 times greater. The new spinning methods permit finer counts to be produced and rubber yarns can be replaced by much finer yarns of equivalent modulus and tensile strength. The synthetic polyurethanes can be dyed successfully and have good resistance to oxidation, abrasion, perspiration and cosmetic oils. They can therefore be used more readily on their own without being coated or covered.

All the yarns produced by these methods qualify under the generic name of "Spandex", the general classification adopted in America to identify synthetic elastic yarns containing at least 85% of a segmented polyurethane. However a Dutch company uses the trade mark "Spandon" for wool yarn and cloth giving rise to some confusion in Europe. To clarify the situation the term Elastomeric Yarn is being used and a definition is under review by the American Society for Testing Materials which reads as follows:-

> Elastomeric Yarn - a continuous filament or spun yarn which, by virtue of the chemical structure of the fibre, is characterised by a high break elongation, a low modulus of extension and a high degree and rate of recovery from a given elongation.

Natural rubber yarns, a sample of which is included in the present investigation, can be included in this definition which thus covers all the yarns studied in this section.

2.2 EXPERIMENTAL

2.2.1. Materials

Five samples of synthetic polyurethane yarns and a sample of natural rubber yarn were included in the first series of tests to investigate the effect of various physical treatments on the mechanical properties of the new elastomeric yarns in relation to similar data on a rubber yarn.

The yarn dimensions, count (tex) and number of filaments, are detailed in Table 2.1. The multifilament yarns were all partially fused, some to a greater degree than others, and an exact measure of the filament count or number of filaments in the yarn was impossible. Spanzelle was known to consist of 27 filaments and an estimate of the number in Lycra and Blue C was made by determining the count of short lengths extracted from the yarn. Glospan was too highly fused for this to be done and, in fact, this yarn behaved like a monofilament in the subsequent tests programme.

TABLE 2.1.

MATERIAL	COUNT (TEX)	NO. OF FILAMENTS	DENSITY G /CC.	MOISTURE REGAIN (%) AS RECEIVED	FINISH-FREE
Blue C	46	ca 20	1.21	1.8	1.2
Glospan	62	MULTIFIL	1.27	1.8	1.1
Lycra	51	ca 27	1.15	1.6	0.8
Spanzelle	46	27	1.26	1.9	1.2
Vyrene	50	1	1.32	2.3	0.9
Rubber	54	1	1.10	1.9	0.6

2.2.2 Experimental Procedure

The moisture regain and density were the first physical properties to be measured. The regain at 65% relative humidity was measured on samples as received and with the surface finish removed. In each case the dry weight was taken after oven drying at 105°C until no change was observed. The finish was removed by boiling in a 2% solution of Teepol for ten minutes.

The finish-free yarns all had a regain of about 1% while the figure for the samples as received was about 2%.

The density was measured using the graded density column method of Jones as already described with xylene and carbon tetrachloride as the miscible liquids. Again, finish free yarn was prepared, the Teepol wash being followed by boiling in xylene for 3 minutes to remove the moisture. Three specimens of each sample were measured and all 3 gave identical values in each case with the exception of the natural rubber material which varied considerably. This may have been due to the presence of zinc oxide filler in this yarn, it being used to add weight and give the almost white appearance which makes it more presentable as a textile yarn. In the very small specimens used, less than a centimetre, a variation in the filler content would give a considerable difference in the density reading.

The density and moisture regain are given in Table 2.1. It is seen that the densities of the synthetic yarns differ considerably. The values for Blue C and Vyrene compare with values of 1.26 and 1.29 respectively claimed by the manufacturers. The latter value was obtained in zinc sulphate solution by the simple floatation method. This was checked and it was found that Vyrene did have a density of 1.29 g/cc in zinc sulphate solution and all the other synthetics, including Blue C, gave lower values than those shown in Table 2.1. This suggests that the values obtained in the gradient column were high, due to absorption of the high density liquid i.e. carbon tetrachloride. If this were so it would be expected to take place over a considerable period of time until equilibrium was reached and would thus cause a change in the density reading with time. This did not occur over a period from 10 minutes after insertion until 48 hours later in any of the samples and suggests that the values measured in the column are accurate and that the lower values in zinc sulphate solution might be due to moisture absorption. The value for Blue C quoted by the manufacturers is certainly high.

Tensile tests were carried out at different conditions to investigate the general effect of moisture, heat and heat ageing on the properties. Textile jaws are not normally used to test rubber yarns since they appear to cause damage and result in premature breaks with, in particular, low values of breaking elongation. The capstan type of jaw, on the other hand, requires the use of bench marks and elongation cannot be recorded automatically since the gauge length is unknown. It was found that textile jaws, lined with a fine rubberised silk fabric acting as a masking tape and minimising the possibility of jaw breaks, were suitable for testing the synthetic materials and these were also used for the natural rubber yarns although it was felt that they were still imposing a slight restriction and causing jaw breaks in rubber specimens.

Tests were carried out to measure

(1) the stress-strain curve
  (a) at standard conditions
  (b) in water at 20°C
  (c) in water at 90°C
  (d) at standard conditions after heat ageing for 24 hours at 105°C in the relaxed state.
  (e) at standard conditions after heat ageing for 24 hours at 130°C in the relaxed state.
  (f) at standard conditions after heat ageing for 24 hours at 100°C and 150% extension

(2) the elastic recovery
  (a) at standard conditions
  (b) in water at 20°C

(c) in water at 90°C

(d) at standard conditions after extension at 35°C

(3) the stress relaxation at standard conditions.

(4) the "Schwartz value" *

(a) at standard conditions

(b) at standard conditions after heat ageing for 24 hours at 100°C and 150% elongation.

All tests at standard conditions were carried out on an Instron tester using load cell B with the regular jaws lined as described. The initial gauge length had to be restricted to not more than 2 inches to allow for the extremely high elongations encountered with these materials. The apparent elongation was higher than the true value due to a creep back in the jaws as the strain was increased, particularly beyond about 200%. This was caused by the considerable reduction in diameter at the higher strains and meant that the gauge length did not remain constant but increased as the test proceeded. To determine the true breaking strain the jaw effect had to be measured and a correction applied. This was done by using two different gauge lengths, one being twice the other,

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* For definition see Page 106.

to measure the stress-strain curve at the same strain rate.

If L and 2L are the gauge lengths and λ_1 and λ_2 are the respective observed apparent extensions, assuming the "slippage" S to be the same in each case, the true fractional extension ϵ is given by

$$\epsilon = \frac{\lambda_1}{L+S} = \frac{\lambda_2}{2L+S} \quad ----- (11)$$ from which

$$S = \frac{L(2\lambda_1 - \lambda_2)}{\lambda_2 - \lambda_1} \quad ------ (12)$$

and substituting for S in (11) we obtain.

$$\epsilon = \frac{\lambda_1}{L + \frac{L(2\lambda_1 - \lambda_2)}{\lambda_2 - \lambda_1}} \quad -- (13)$$ which reduces to

$$\epsilon = \frac{\lambda_2 - \lambda_1}{L} \quad -------- (13a)$$

This equation can be rearranged in a more convenient form as follows:-

$$\epsilon = \frac{\lambda_2}{2L} - \left(\frac{\lambda_1}{L} - \frac{\lambda_2}{2L}\right) \quad ----- (13b)$$

i.e. the true fractional extension is the difference between the apparent fractional extensions subtracted from that measured with the larger gauge length. If necessary the "slippage" can be calculated from equation (12). After the initial tests using 2 inch and 1 inch gauge lengths the remaining tests were made using a 2 inch length. An initial strain rate of 1.67×10^{-1} $\sec^{-1}$ was used throughout. It should be noted at this point that, although the traverse rate was constant, since the gauge length increases as the strain increases, the strain rate decreases. This decrease is not uniform and depends on the gauge length, the smaller length resulting in the greater decrease if the amount of slippage remains the same. Table 2.2 shows the effect of increasing (true) strain on the strain rate and slippage in Spanzelle yarn. Even at 500% strain the difference between the rates at the two gauge lengths is only 15% and is unlikely to cause a significant difference in the slippage or the values of breaking stress and strain obtained.

TABLE 2.2

STRAIN (IN/IN)	SLIPPAGE (IN)	STRAIN RATE (% OF ORIGINAL)	
		2" GAUGE LENGTH	1" GAUGE LENGTH
0	0	100	100
1	0.04	98	96
2	0.09	96	92
3	0.15	93	87
4	0.28	88	78
5	0.64	76	61

To enable tests to be carried out in water a jacketed glass cylinder was constructed for use in conjunction with small steel jaws, lined as before. The arrangement is outlined in Fig. 2.1. The lower jaw A_2 was fixed to a weight W, which was considerably heavier than the largest expected breaking load, and rested on the base plate B of the cylinder C which in turn was mounted on the cross-head of the Instron tester and moved with it. Hook members were used to connect the upper jaw A_1 to the load cell to avoid introducing any stresses other than longitudinal tensile in the specimen. Rigid piano wire hooks P were used to support the lower assembly during mounting of the specimen to allow the gauge length to be set with the cylinder removed. The traverse of the instrument was reduced by about half by this arrangement and a 1" gauge length was used. Slippage was also measured in water using a ½" gauge length and was found to be similar to that measured in air.

A thermostatically controlled immersion heater and circulator pump unit, placed in a large capacity water tank adjacent to the tester, was used to maintain the test temperature in the cylinder jacket.

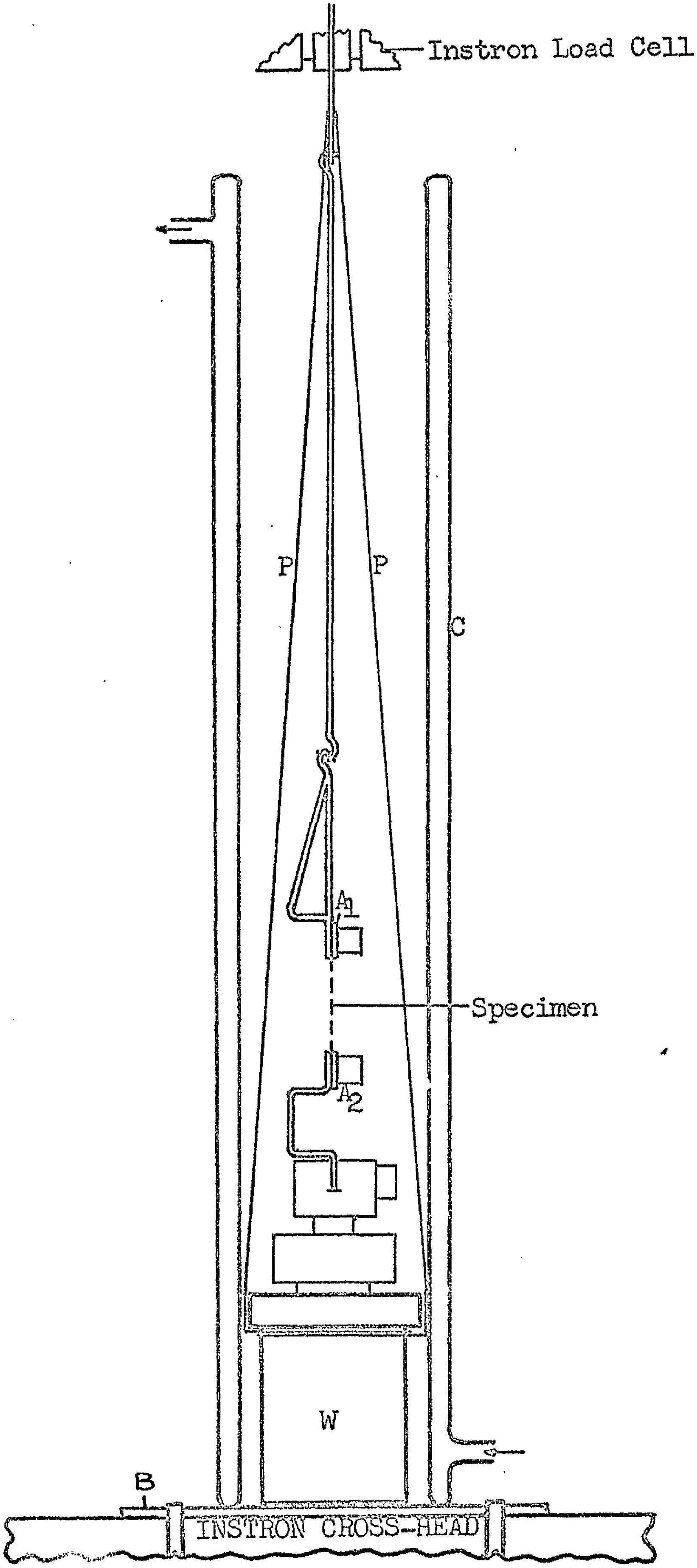

FIG 2.1

ASSEMBLY FOR TENSILE TESTS OF ELASTOMERIC YARNS IN WATER

Scale 1 : 2

FIG 2.1

Heat ageing at 150% extension was done by stretching 4" loops over pegs fixed in a piece of Sindanyo board which are unaffected by heat. All the aged specimens were allowed to condition for a further 24 hours in a standard atmosphere before being tested.

The elastic recovery from true strains of 50%, 100%, 200%, 300% and 400% was measured under condition (a), (b) and (c) by a cyclic loading technique, 2 inch and 1 inch gauge lengths being used in air and water respectively as before. Each specimen was extended to the lowest strain, held for 10 seconds and allowed to recover for 1 minute under no load. This was then repeated with the strain being increased progressively. The elastic recovery from each strain was thus measured on a single specimen, readings being taken immediately after removal of the stress and 1 minute later.

Condition (d) was chosen to simulate the recovery cycle which might be expected during wear and give some indication of the long-term recovery properties. Specimens of each yarn were extended in a stretching frame to strains of 200% and 400%

approximately and held extended for 16 hours at 35°C, i.e. around body temperature. Recovery was measured by cathetometer 15 minutes and 8 hours after removal of the stress.

Stress relaxation from strains of 400%, 200% and 50% was carried out for 2 hours at standard conditions on the Instron tester. The long term stress relaxation is important since elastomeric yarns are used for long periods in a stretched condition. The Sindanyo board was utilised for this test, 4" loop specimens being held at 150% strain in a standard atmosphere. A fine spring balance was used to measure the stress over a period of 14 days.

The Schwartz value of an elastomeric yarn is used as a measure of the "power" of the yarn after repeated stretching. In the rubber thread industry a special Schwartz board is used to measure this value.[60] A length of thread is coiled into several loops each containing 4 inches of thread and knotted. This multiple loop is then "massaged" by repeated extension up to a set value by hand, placed on the board and, after several more extension cycles the stress is measured at some value below the maximum extension on both the extension and retraction cycles. The mean of these two values gives the Schwartz value. It was found that knotting was unsatisfactory for the synthetic yarns at higher strains, although this method was used at 150% extension on the Sindanyo board. To avoid the possibility of slippage at the knot the Schwartz test was simulated on the Instron tester using a single thread specimen, with a 2 inch gauge length. Each thread was "massaged" by hand several times increasing the extension each time until it reached 300%. A further 10 cycles to 300% were then carried out on the Instron at a rate of 1000% / minute, before the stress was measured at 200% in both directions.

For all the tensile tests a simple cut-skein method of sampling was again used. A 6 strand skein, sufficiently long to provide specimens for every test, was prepared from each sample and cut as required. Five specimens were measured in all cases except for the Schwartz value, where values were highly reproducible, stress test required a long time to complete. In these cases three specimens were tested at each condition.

Correction - Replace last two lines with:-

"stress relaxation and long-term elastic recovery, where each test required a long time to complete. In these cases three specimens were tested at each condition."

Elastomeric yarns are frequently covered with a textile yarn for use in wearing apparel. The cover yarn or yarns are wound on while the elastic yarn is stretched, the cover being overfed. This has the effect of stricting the recovery and means that the core yarn is always under tension. This also tends to control the breaking elongation.

Thus the properties are modified considerably and, for comparison, the stress-strain curve of a Vyrene yarn covered with two fine nylon multi-filament threads was measured at standard conditions. The yarn was made up as follows:-

Vyrene core - 24 Tex monofilament
Nylon cover - 2.2 Tex seven filament

The Vyrene was stretched during winding and therefore had a negative uptake of 15%. The uptake of both the nylon yarns was almost 300%. The effective counts were thus 21 Tex and 6.5 Tex for the Vyrene and Nylon respectively and the final yarn count was 34 Tex.

The stress-strain curve of each component was also measured so that their contributions to the curve of the combined yarn could be determined.

Correction - Line 5

for "stricting" read "restricting"

2.3 RESULTS AND DISCUSSION

The tensile properties are summarised in Table 2.3 and are detailed in Figs. 2.2 to 2.7. In addition to the properties at break, the initial "power" is measured by the stress at 0.5 and 2.0 in/in strain; the toughness is measured by the area under the stress-strain curve and is a measure of the engery required to break a unit mass of the fibre when expressed in the form of joules/g; the Schwartz values is a measure of the stress retained by the yarn in what might be described as the mechanically conditioned state.

Condition 1 in the Table refers to standard conditions of 20°C and 65% R.H., the stress-strain curves for which are shown in Fig. 2.2. In general the elastomeric yarns have an extremely low initial modulus or power, a relatively low breaking stress and a very high extensibility as compared with conventional textile yarns. There are, however, considerable differencies between the elastomeric materials, the power and breaking stress varying by a factor of 4 between the weakest and the strongest. All the synthetic materials are stronger than the natural rubber thread.

Condition 2 in Table 2.3 corresponds to that used in measuring the stress-strain curves at 20°C in distilled water and shown in Fig. 2.3. The power and breaking stress are slightly lower under these conditions resulting in a drop of about 20 - 25% in the toughness in most cases. Changes in breaking strain are relatively small. The stress-strain curves at 90°C in water (condition 3 in Table 2.3) show marked changes as seen in Fig. 2.4. The breaking stress is reduced to a quarter, or less, of its value under normal conditions and the power is also much lower. The toughness is reduced, on average, to about a third of its original value. Natural rubber is the exception. The power is virtually unchanged and the other properties show smaller changes but it should be remembered that this yarn had very low stress values originally, compared with the other materials.

Heat ageing at 105°C for 24 hours (condition 4 in Table 2.3) has little effect on the breaking stress, as shown in Fig. 2.5, but may, in fact, result in a slight increase in value for multifilament yarns where this treatment appears to fuse the filaments together more e.g. Lycra, Spanzelle and Blue C. An increase in the breaking strain results in a general increase in the toughness in spite of the lower power values. The exception is again the natural rubber yarn. The values of its breaking properties are lower and its toughness is therefore reduced although the power is still unchanged. Condition 5 refers to heat ageing at 130°C, also for 24 hours. This relatively small increase in the ageing temperature has remarkable effect on the tensile properties as shown in Fig. 2.6. The rubber is almost in a state of disintegration after this treatment and only Vyrene and Spanzelle show good resistance, retaining their high breaking strain and 50% of their breaking stress. The remaining yarns all have very low breaking stress and power and their breaking strains are also greatly reduced. Their resulting toughness values are therefore very low.

Heat ageing under strain is said to improve the power and Schwartz value of a rubber thread. In condition 6 heat ageing was carried out at 100°C for 24 hours under a strain of 1.5 in/in. As might be expected the breaking strain is reduced, by over 50% in some cases, as shown in Fig. 2.7. With the exception of Vyrene the stress at a given strain is higher than at any other condition if the initial part of the stress-strain curve is excluded. The breaking stress is, however, much lower in most cases than normal and the toughness values are also considerably reduced. The rubber yarn shows only a slight reduction in breaking stress and the toughness is comparable with its values at other conditions.

A typical Schwartz value measurement is shown in Fig. 2.8. It is seen that the loading curve of the measuring cycle is very different from the initial loading curve of the yarn although the unloading curve is similar. Thus, although the elastic recovery is good a large percentage of the work done in stretching the yarn is lost and the power suffers as a result. The Schwartz value is therefore very much lower than might be expected from the stress-strain curve. At standard conditions all the synthetic yarns have higher values than the natural rubber. After heat ageing under strain, however, the rubber yarn shows a slight increase and of the remainder only Lycra and Blue C have values which are appreciably higher than that for rubber.

TABLE 2.3 TENSILE PROPERTIES

ELASTOMER	Condition	Breaking stress ($X10^8$ dynes/cm^2)	Breaking strain ($X10^2$ in/in)	Power at ($X10^7$ dynes/cm^2) STRAIN		Toughness (Joules/gm)	Schwartz Value (lb/in^2)
				50%	200%		
LYCRA	1	9.5	580	3.6	12.2	149	486
	2	8.9	610	3.1	10.2	132	
	3	2.5	640	2.6	6.1	58	
	4	9.8	610	2.5	12.2	161	
	5	1.7	360	1.6	7.7	28	
	6	6.7	455	2.2	16.8	98	353
SPANZELLE	1	5.0	640	3.4	8.9	107	372
	2	4.9	580	3.4	7.8	76	
	3	1.3	640	1.7	4.0	32	
	4	6.1	780	2.2	6.7	156	
	5	2.6	700	1.1	4.0	61	
	6	3.0	355	1.4	11.3	31	233
BLUE C	1	8.2	525	4.3	11.8	106	418
	2	6.8	520	4.3	10.7	75	
	3	1.7	575	3.2	6.4	36	
	4	8.8	605	3.2	7.5	106	
	5	0.4	340	1.1	2.2	6	
	6	5.3	335	2.1	15.0	57	309

TABLE 2.3 (CONTINUED)

ELASTOMER	Condition	Breaking Stress (X10^8 dynes/cm^2)	Breaking Strain (X10^2 in/in)	Power at (X10^7 dynes/cm^2)		Toughness (Joules/gm)	Schwartz Value (lb/in^2)
				50%	200%		
				STRAIN			
VYRENE	1	8.1	660	2.3	4.7	98	294
	2	6.1	610	2.4	4.7	68	
	3	1.1	680	0.9	1.7	20	
	4	6.9	690	1.8	4.1	89	
	5	4.3	740	1.6	2.9	72	
	6	2.0	410	1.3	3.9	16	176
GLOSPAN	1	6.1	620	3.9	10.8	123	341
	2	5.4	630	3.4	7.9	101	
	3	1.6	690	2.3	4.4	43	
	4	5.7	670	3.4	10.8	133	
	5	0.8	470	1.6	4.4	19	
	6	1.5	205	2.0	14.1	13	220
RUBBER	1	2.3	530	1.0	2.5	32	211
	2	2.2	470	1.0	2.8	26	
	3	1.3	480	1.0	2.8	20	
	4	1.9	450	1.0	2.8	22	
	5	–	–	–	–	–	
	6	2.1	440	0.8	3.2	23	219

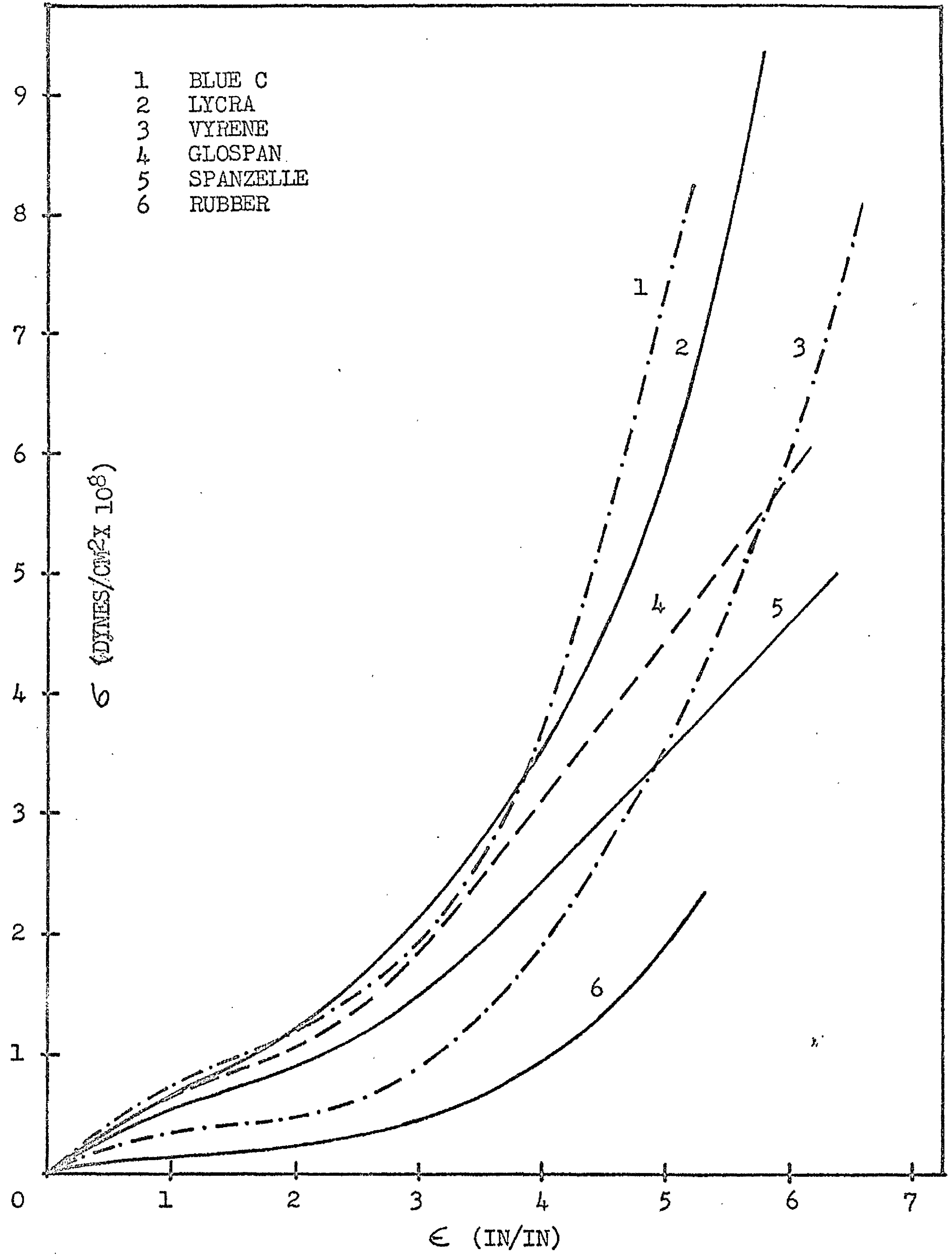

FIG 2.2 The Stress-Strain Curves of Elastomeric Yarns at Standard Conditions

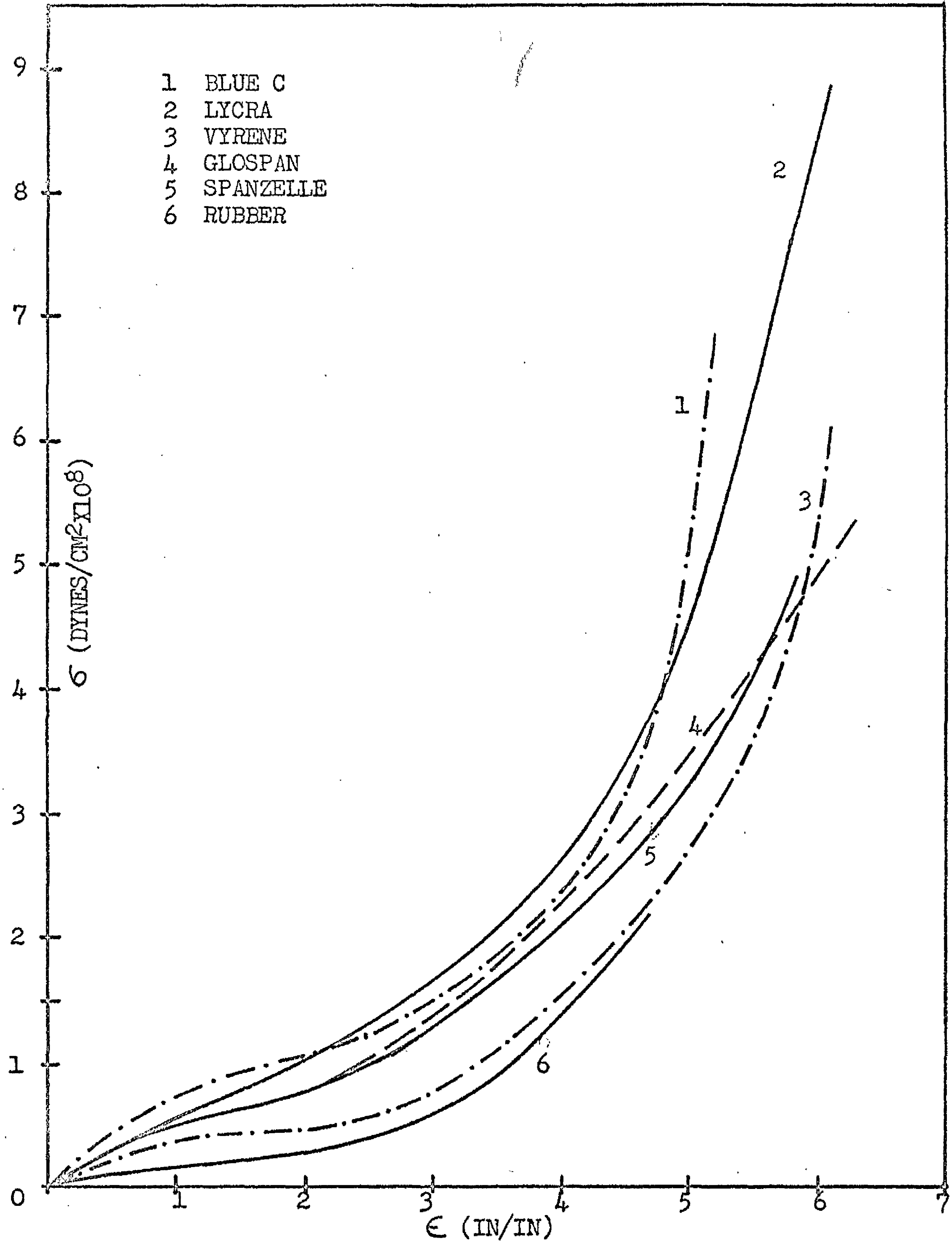

FIG 2.3 The Stress-Strain Curves of Elastomeric Yarns in Water at 20°C

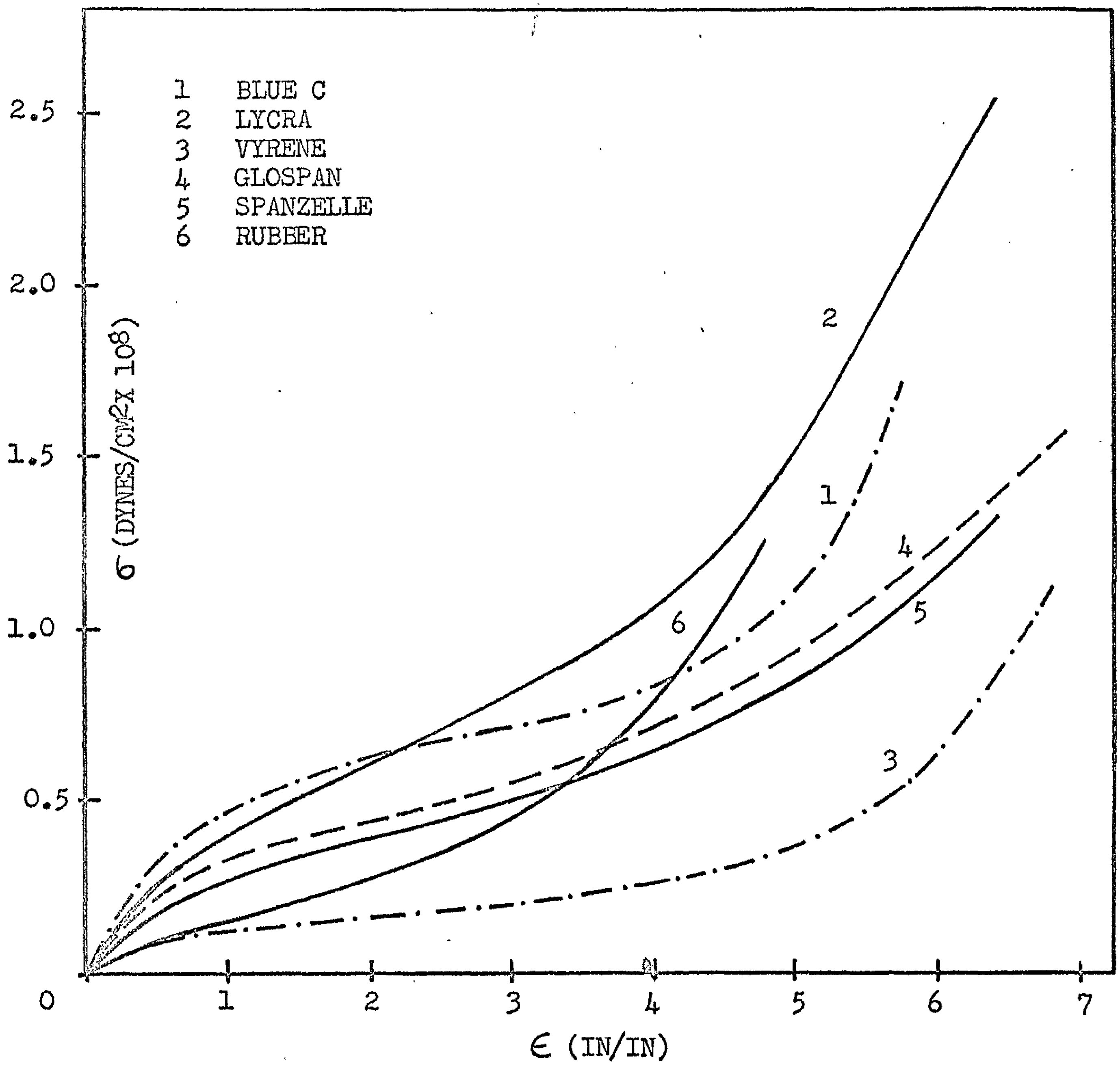

FIG 2.4 The Stress-Strain Curves of Elastomeric Yarns in Water at 90°C

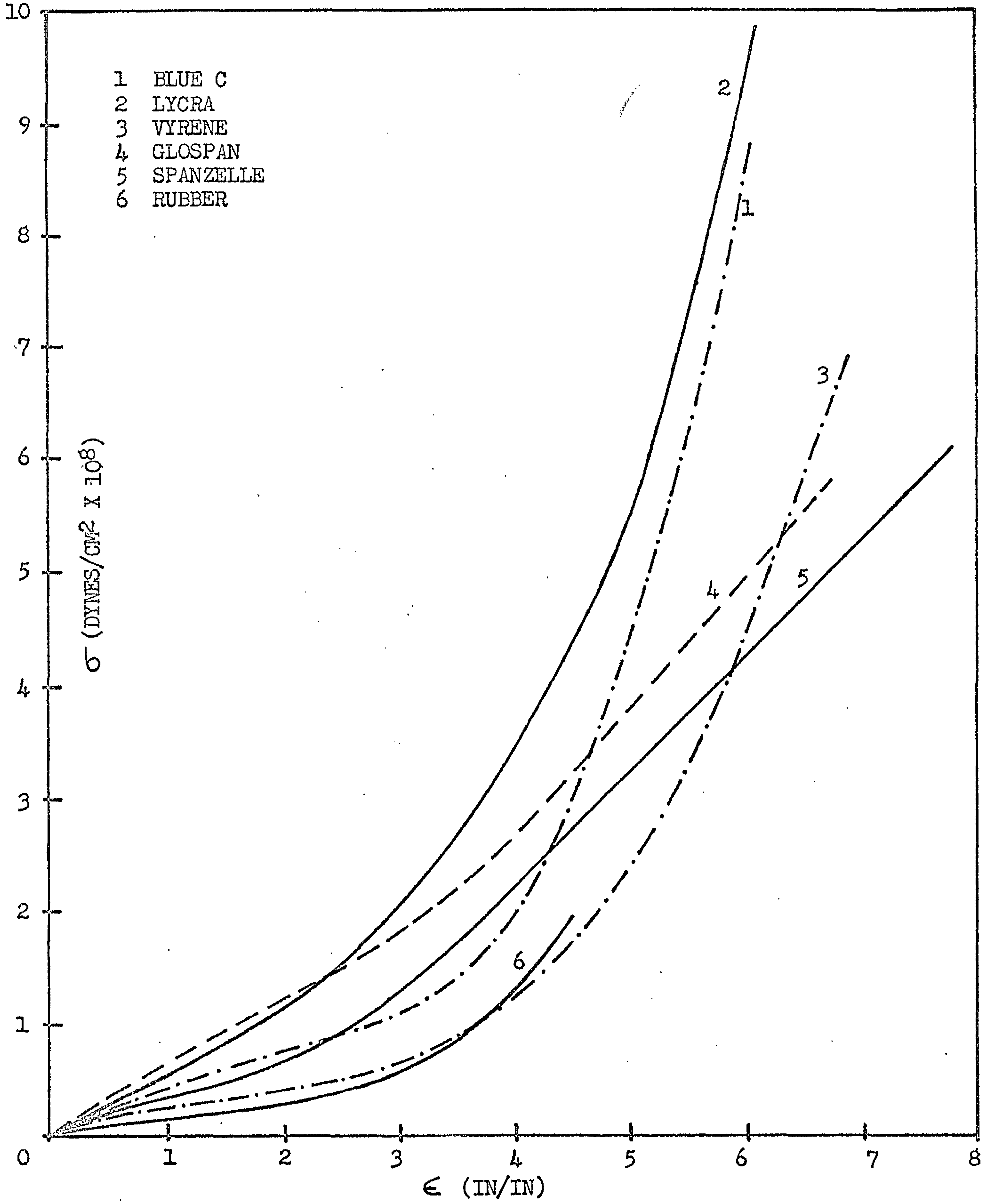

FIG 2.5 The Stress-Strain Curves of Elastomeric Yarns at Standard Conditionsafter Heat ageing at 105°C for 24 hours

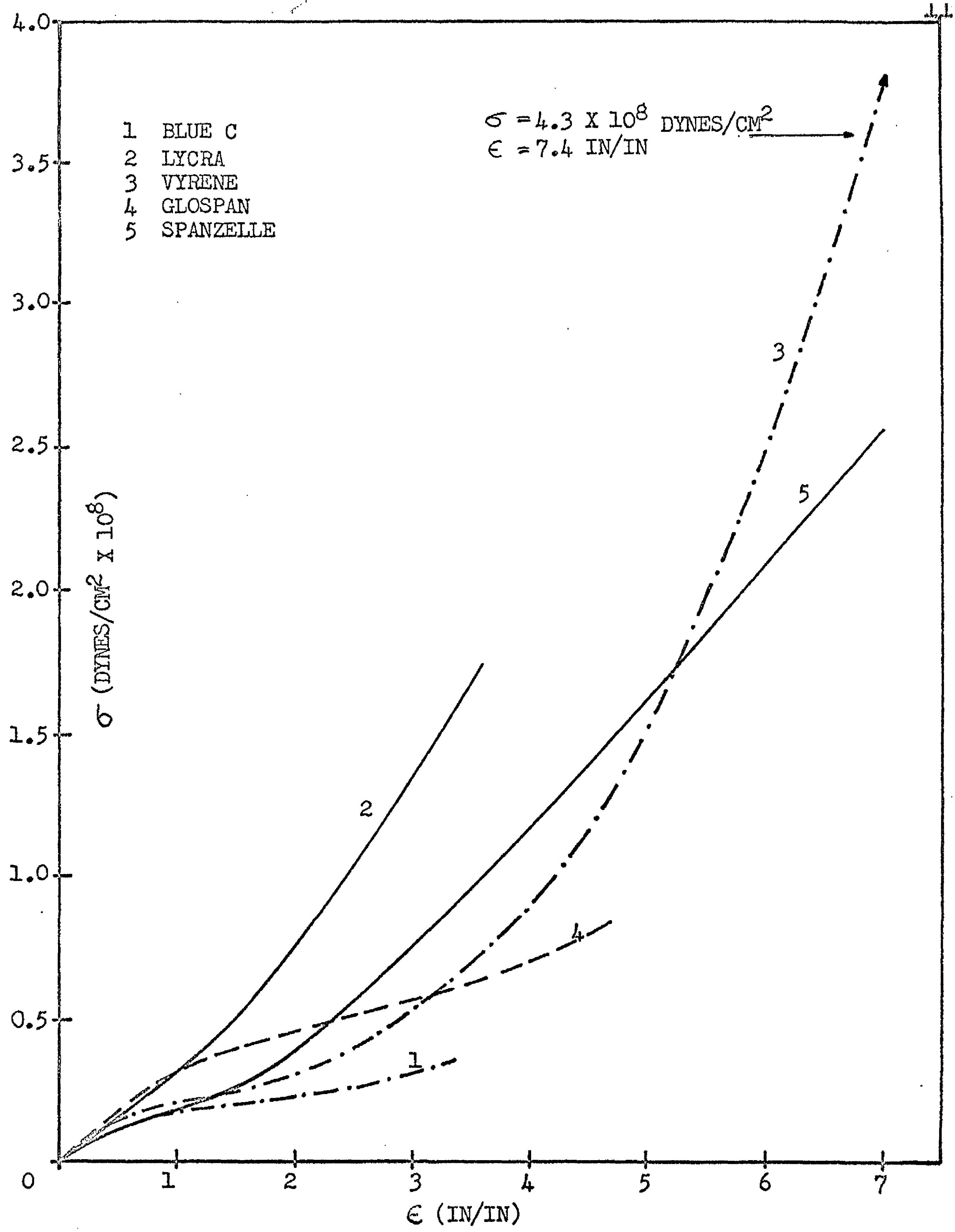

FIG 2.6 The Stress-Strain Curves of Elastomeric Yarns at Standard Conditions after Heat ageing at 130°C for 24 hours.

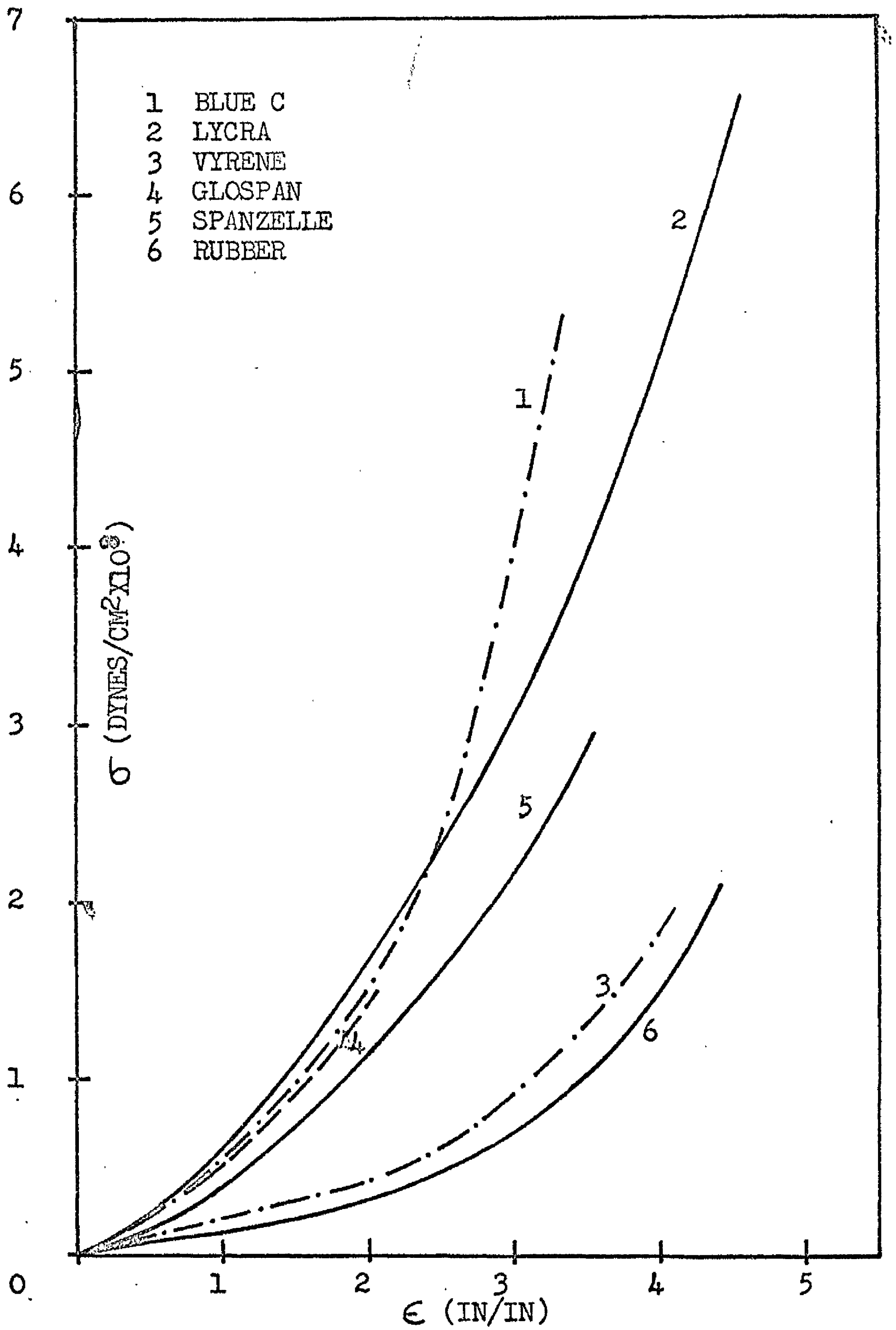

FIG 2.7 The Stress-Strain Curves of Elastomeric Yarns at Standard Conditions after Heat ageing for 24 hours at 100°C and 150% Elongation

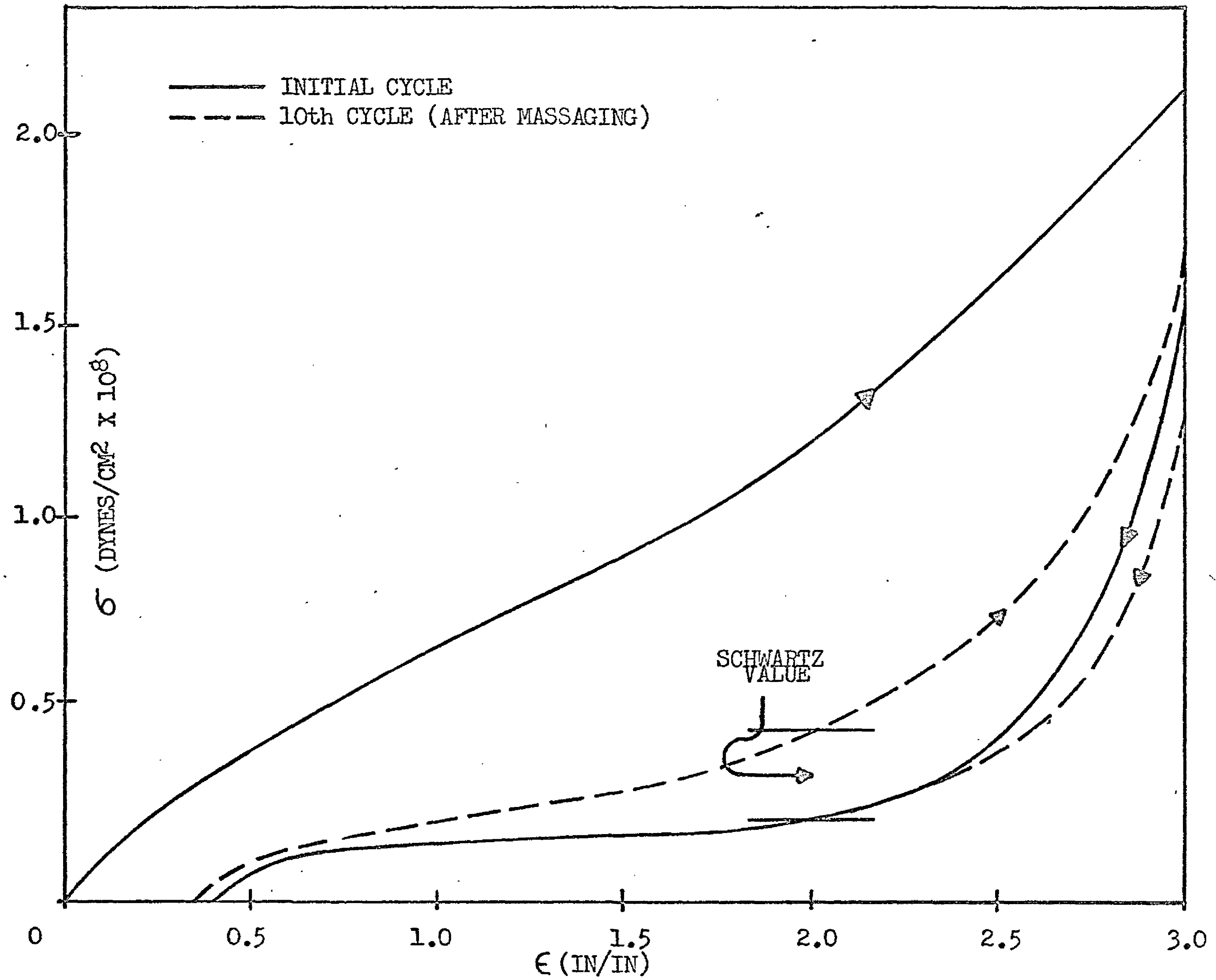

FIG 2.8 Determination of the SCHWARTZ value of LYCRA

The elastic recovery properties are condensed in Table 2.4. Values are given as the ratio of the recovered strain to the imposed strain expressed as a percentage. All the yarns show excellent properties under all the conditions tested. At standard conditions none of the samples has an immediate recovery of less than 85% and after one minute 90% or more of the strain has been recovered. The slight differences occurring between values measured at standard conditions and those measured in water at 20°C are not significant since readings were only accurate to ± 1% but there is an indication that the recovery is slightly less or slower im water. In both these cases rubber and Vyrene show slightly superior properties. In water at 90°C there is a pronounced reduction in the values, particularly at the higher strains with the exception of rubber which stands out above the synthetics in this test, only Vyrene and possibly Spanzelle approaching it. In the test of long-term recovery after prolonged straining at or near body temperature there is little to choose between any of the synthetics but, good as their properties are , rubber still shows itself to be superior in this case also.

TABLE 2.4 ELASTIC RECOVERY

EXTN.	1		2		3		4	
(%)	A	B	A	B	A	B	C	D
LYCRA								
50	100	100	100	100	100	100	-	-
100	97	98	95	98	94	97	-	-
200	94	95	94	96	90	95	92	95
300	91	94	91	94	87	92	-	-
400	87	90	88	92	83	88	92	94
SPANZELLE								
50	100	100	98	100	96	100	-	-
100	99	99	97	99	92	98	-	-
200	97	98	95	97	91	95	91	94
300	93	95	92	95	89	93	-	-
400	89	92	90	92	87	91	90	92
BLUE C								
50	98	99	97	98	93	95	-	-
100	95	99	95	97	91	95	-	-
200	95	98	94	97	89	93	87	92
300	93	96	93	95	87	91	-	-
400	88	92	89	93	84	88	90	93
VYRENE								
50	97	100	95	100	91	100	-	-
100	96	100	95	100	90	97	-	-
200	95	99	95	99	90	94	88	95
300	95	99	95	98	89	94	-	-
400	92	97	93	97	88	93	92	95

TABLE 2.4 (CONTINUED)

EXTN. (%)	1		2		3		4	
	A	B	A	B	A	B	C	D
GLOSPAN								
50	95	98	94	98	94	98	-	-
100	94	98	92	98	91	95	-	-
200	92	96	91	95	86	90	92	96
300	89	94	89	94	83	87	-	-
400	86	92	86	90	78	83	90	94
RUBBER								
50	100	100	99	100	100	100	-	-
100	98	100	98	100	98	99	-	-
200	97	99	96	99	97	98	98	100
300	97	98	97	99	97	97	-	-
400	96	98	96	97	95	96	98	99

KEY:-

Condition 1 - Standard Conditions
" 2 - In Water at 20°C
" 3 - In Water at 90°C
" 4 - Held Under Strain at 35°C and allowed to recover at Standard Conditions

A - Immediate Recovery
B - Recovery after 1 minute
C - Recovery after 15 minutes
D - Recovery after 8 hours

The stress relaxation curves were measured at constant strains of 0.5, 2.0 and 4.0 in/in for 2 hours at standard conditions. This served to provide information on the amount of stress, or power retained by an elastomeric yarn when held under strain for long periods of time.

It was found that the stress decayed very rapidly initially, then more and more slowly as time progressed. When stress was plotted against time on a log-log basis a straight line relation was found to exist fitting the simple relaxation formula

$$f_t = f_t \ (1-2{\cdot}3k)^{t/t_0} \qquad (14)$$

$$f_t = f_{t_0}(1-2{\cdot}3k)^{t/t_0} \text{ — — — — — — — } (14)$$

whe:

at where f_t is the stress at time t, f_{t_0} is the stress log at any reference time t_0 and k is the gradient of the relaxation behaviour can thus be dscribed completely if k and f_{t_0} are known. The behaviour is presented in this form in Table 2.5 where values of k and f for t = 30 secs are given.

TABLE 2.5 STRESS RELAXATION

Elastomer	Relaxation from					
	0.5		2.0 Strain (in/in)		4.0	
	− k	f	− k	f	− k	f
Lycra	0.023	3.2	0.070	8.2	0.110	17.1
Spanzelle	0.041	2.7	0.050	6.5	0.072	15.7
Blue C	0.039	3.6	0.062	7.1	0.170	13.7
Vyrene	0.035	1.9	0.047	3.5	0.050	8.5
Glospan	0.039	3.3	0.047	7.4	0.050	17.2
Rubber	0.023	0.9	0.038	2.1	0.040	7.6

(f given in dynes/cm^2 x 10^7)

It should be emphasized that equation (14) does not hold at short times at higher strains (below 10 seconds at strains above 1 in/in). The values in Table 2.5 are taken from Figs. 2.9 to 2.11, k, a negative number, is a direct indication of the rate of relaxation or loss of power, the higher the value of k, the higher the rate. Thus Blue C and Lycra lose their power more rapidly than the other samples at high strains. These yarns, however, have more power initially and can, perhaps, afford to lose more as seen in Fig. 2.11. "Elasticated" garments are required to maintain their power as near a constant level as possible over a long period of time in normal wear and

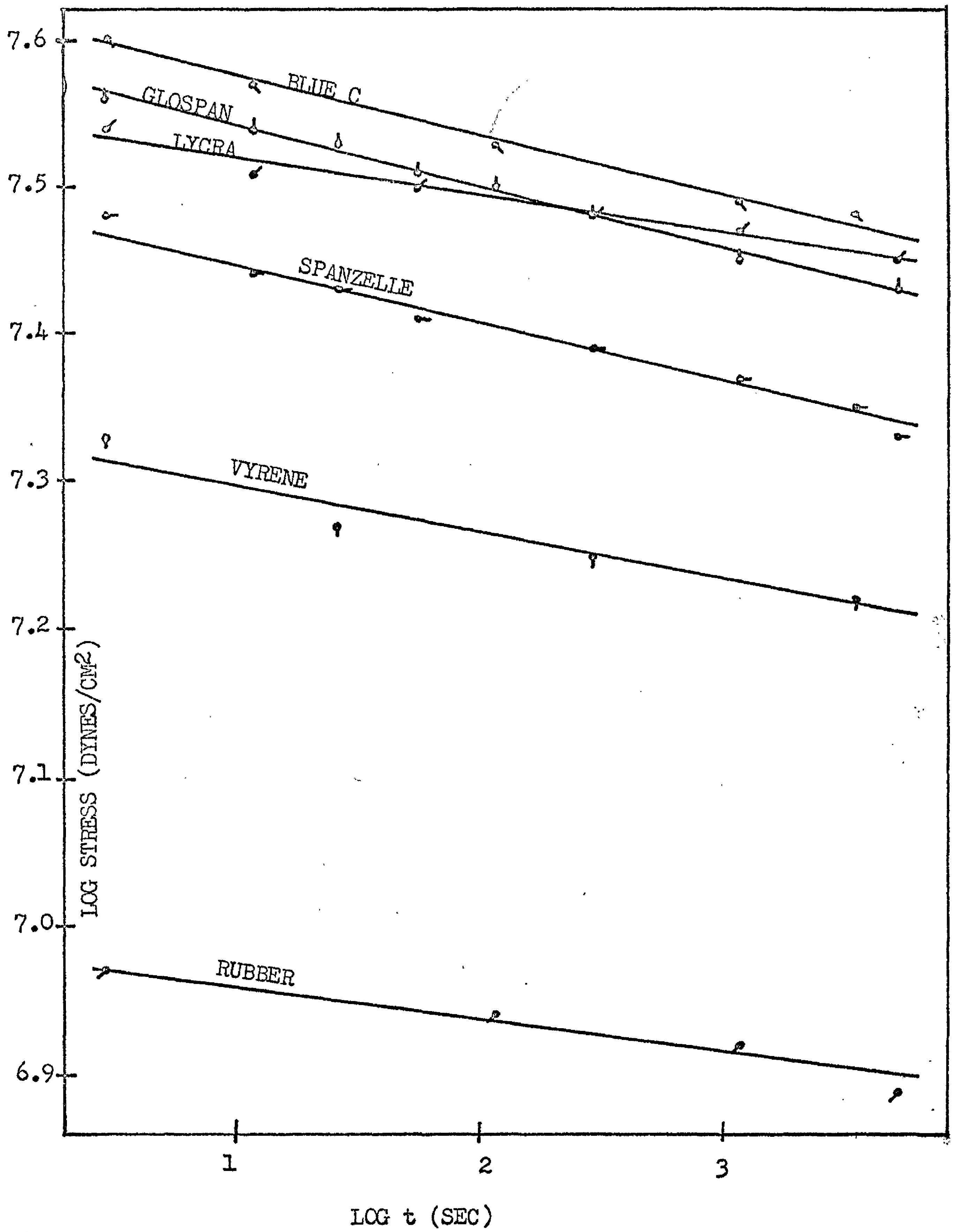

FIG 2.9 Stress Relaxation of Elastomeric Yarns from Strain at Standard Conditions. (0.5 IN/IN)

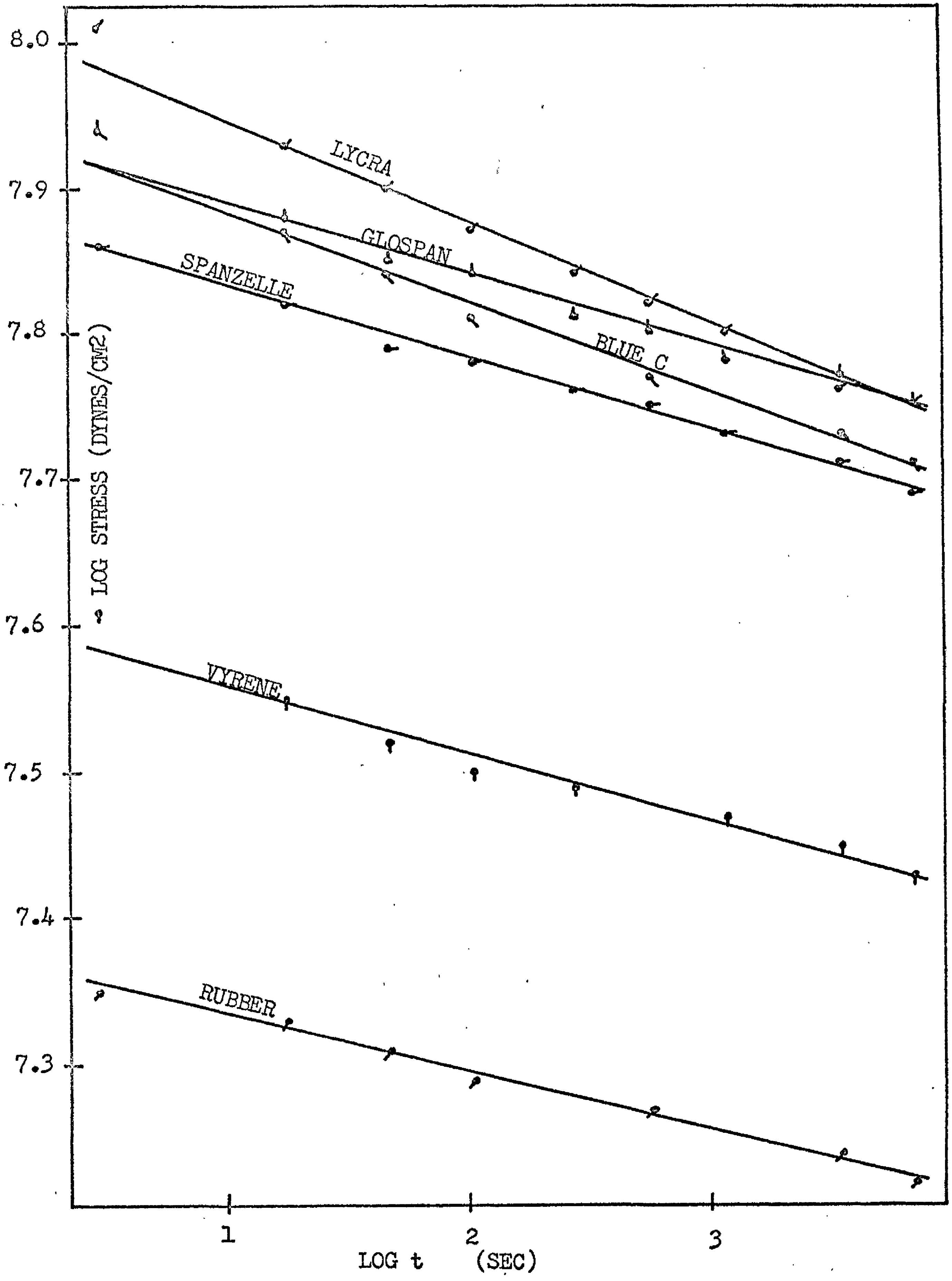

FIG 2.10 Stress Relaxation of Elastomeric Yarns from 2 IN/IN Strain at Standard Conditions.

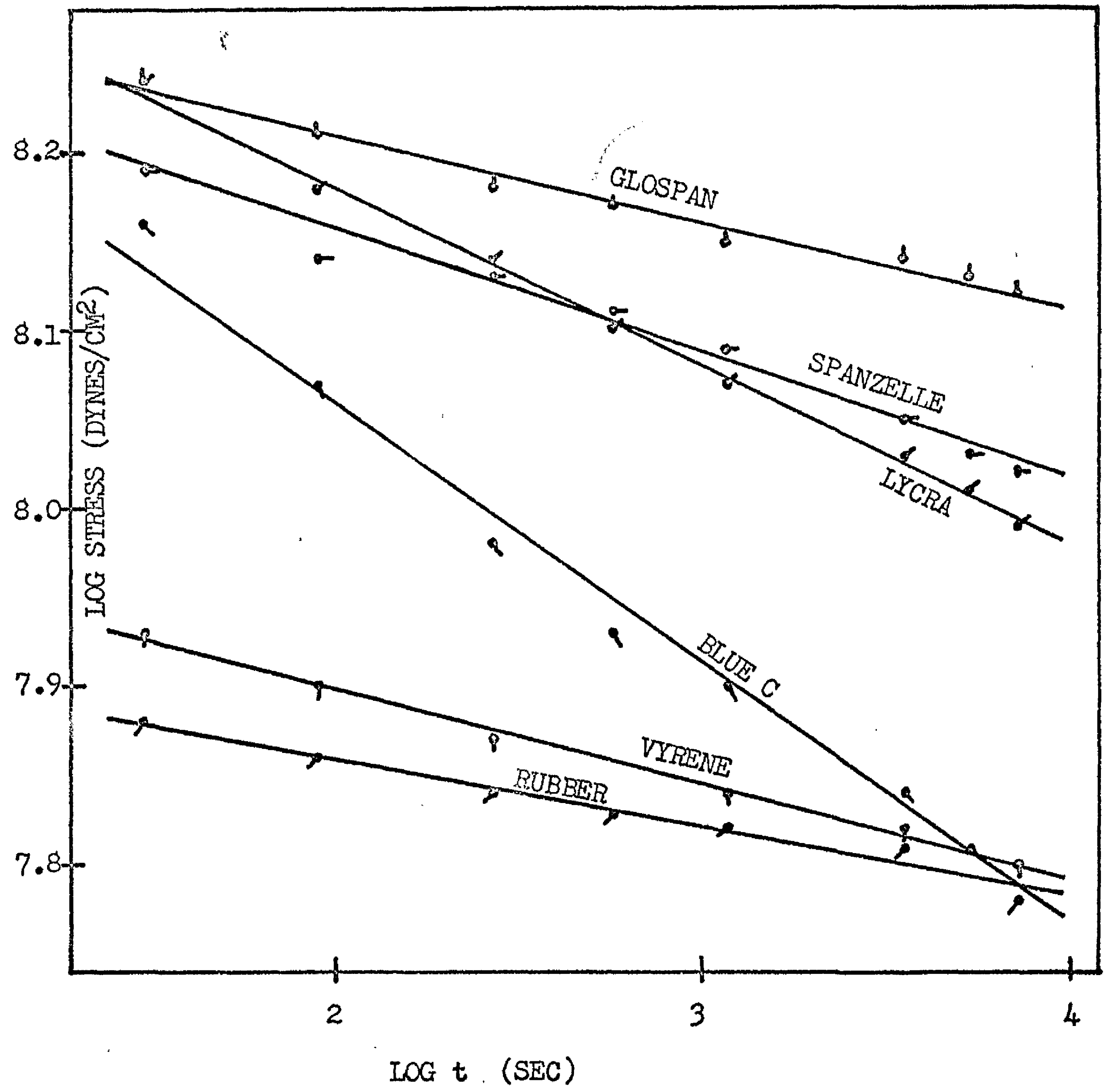

FIG 2.11 Stress Relaxation of Elastomeric Yarns from 4 IN/IN Strain at Standard Conditions

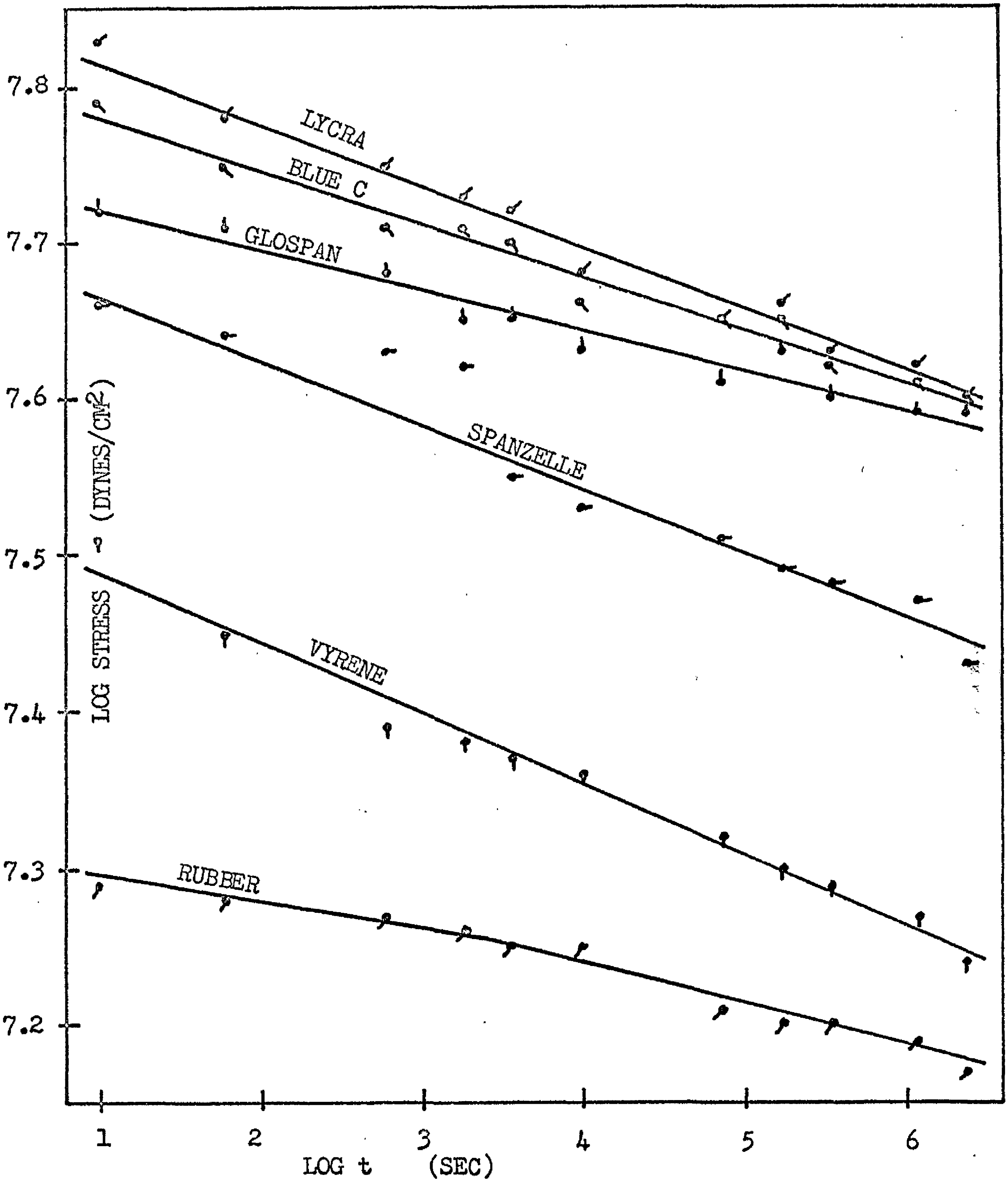

FIG. 2.12 Stress Relaxation of Elastomeric Yarns from 150% Strain at Standard Conditions, using 4" Loop Specimens

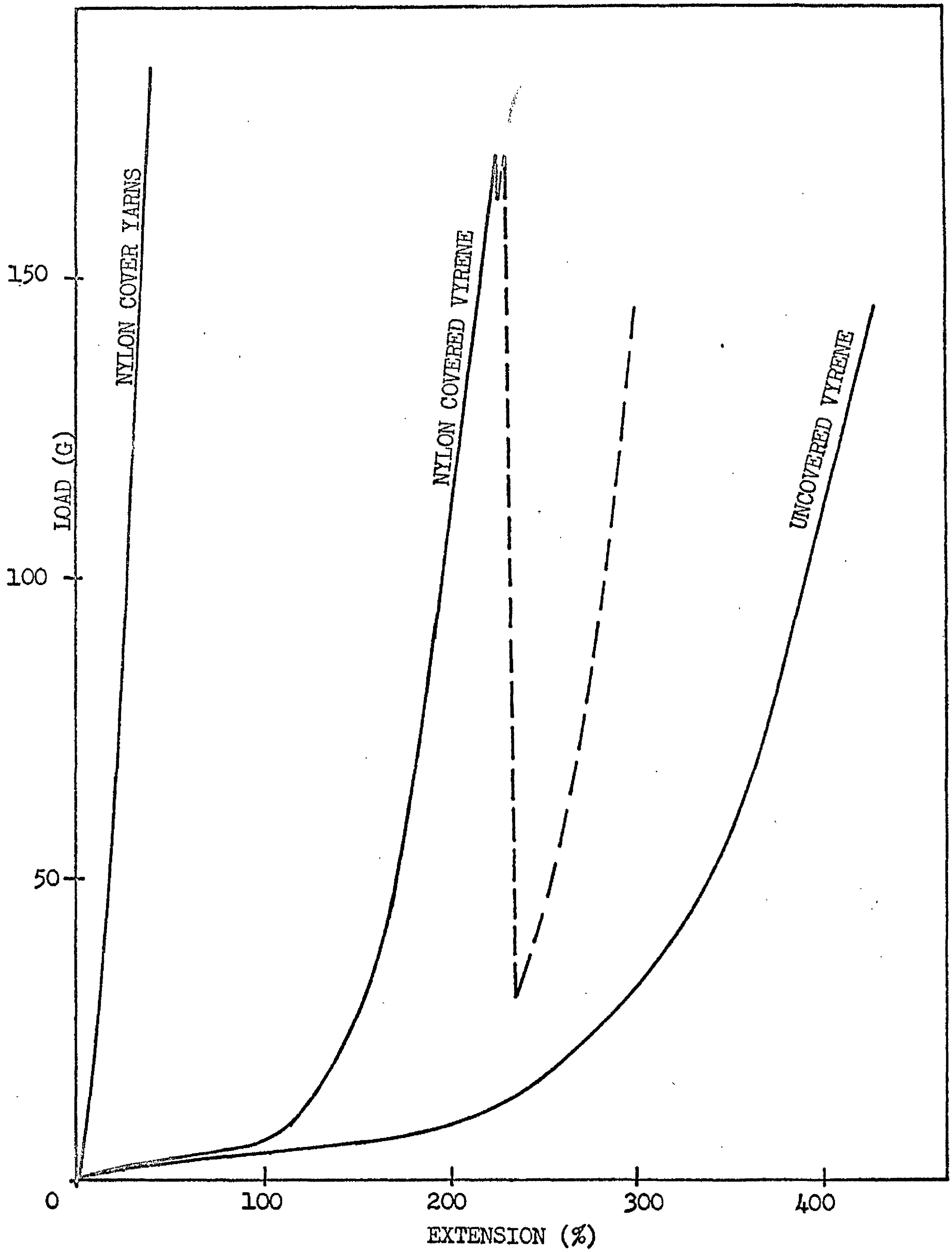

FIG 2.13 The Load - Extension Curves of a Covered Elastomeric Yarn and its Component Threads.

yarns with a low k value may therefore be favoured although their initial power is lower.

Fig. 2.12 shows the long term relaxation curves measured by spring balance for a period of 14 days and verifies that equation (14) holds beyond a mere 2 or 3 decades of logarithmic time except possibly in the case of rubber where the slope increases at longer times. k values calculated from these curves agree reasonably well with the previous data even with the different measuring technique used. The values for Glospan and Blue C are lower than expected.

As mentioned in Chapter 2.2 elastomeric yarns are often used as the core of a plied yarn. The load-extension curves of a covered Vyrene yarn of the Vyrene core and of the double nylon cover are shown in Fig. 2.13. The Vyrene component has a curve typical of the material although the breaking extension is low, probably because it does not recover completely after being held under strain for a prolonged period. The nylon cover has a higher breaking load with an extension of 40%. The curve of the combined yarn follows that of the elastomer for the first 100% with a slightly higher initial power. Up to this point the nylon is uncoiling loosely on the surface and contributes little resistance to the applied strain but as it reaches its limit no more uncoiling takes place, the nylon presses against the Vyrene core and takes over as the main load-bearing component. The load now increases rapidly until the nylon threads break at a slightly lower value than that recorded for nylon alone since the weaker of the two threads initiates the break and the outward pressure of the elastomer plays a part applying forces other than true tensile load to the cover yarns. If the test is carried beyond this point the core yarn will extend to about 300% before breaking at the point where the cover yarns ruptured, the extension being restricted by the presence of the loose nylon yarn on the surface and the fact that the elastomeric yarn is in a stretched condition at the commencement of the test. This also affects the initial power and a truer comparison over the first section of the curves would be obtained if the curve of the covered yarn was started at 15% elongation, i.e. if it was shifted 15% relative to the curve of the Vyrene core in which case it would almost superpose up to 100% elongation.

The extensibility of covered elastomeric yarns has been investigated more fully by Treloar [61] using a simple theoretical model consisting of a cylindrical core of high extensibility covered by a single inextensible filament of zero thickness. It is apparent that the properties in the initial region, while the cover yarn is coiled loosely on the surface, will be very similar to those of the elastomer. As the cover yarn or yarns take more stress, there is a region in which the extensibility drops from the high value of the core to the low value of the cover. Beyond this, the extensibility and the breaking properties of the composite yarn are almost entirely dependent on the properties of the cover yarn.

2.4 TIME - TEMPERATURE SUPERPOSITION.

The elastomeric yarns represent a completely different class of materials, both in chemical structure and properties compared with these of the olefin family discussed in the first section of this work. They are interesting in that, although they are high polymers with, generally, some degree of cross-linking, X-ray diffraction patterns taken on the unstretched material exhibit amorphous rings. Signs of crystallisation only appear on stretching,[62] although not in all cases, due to a straightening of the molecules which causes an increase in orientation rather than actual crystallite formation. Thus from a stress bearing point of view these materials show amorphous behaviour at low strains but become more like crystalline structures in their behaviour at higher strains.

A study of the tensile properties of one of these yarns at different strain rates and temperatures is therefore of particular interest as a means of investigating the general applicability of the superposition principle discussed in Chapter 1.2.

Early work by Tobolsky and his associates[26,30,31,37] on amorphous polymers with a rubberlike structure has already been mentioned in a more general context. The more direct application of the W.L.F. equation by Brettscheider,[38] to rubberlike rocket fuels, and Smith,[39] to a GR-S rubber, have also been discussed. Landel and Smith,[63] in work on rubberlike propellants and filled elastomers, pointed out that superposition was only applicable in some cases and other workers[64] have been unable to find any time-temperature dependence in similar materials. There is, therefore, some doubt concerning the applicability of the reduction method to elastomeric materials.

The yarn chosen for the present study was Glospan. It was selected because its tensile properties were fairly representative of the group already tested and the highly fused nature of the filaments meant that a precise breaking point could be observed. The latter factor was important in that the variability of the ultimate tensile properties was lower than that of materials in which individual filaments tended to break separately yet maintaining the higher strength of the multifilament yarn as compared with a monofil. The coefficient of variation of Glospan was 6% as compared with 9% for Lycra for example.

Tests at different temperatures could not be made using the Tufnol conditioning cabinet as before due to the exceptional extensibility of the sample. Araldite adhesive could not be used to fix specimens to washers since the contraction in diameter which occurred on stretching caused the yarn to slip out of the hardened resin. To overcome this difficulty these tests were carried out in distilled water using the jacketed cylinder already available as described in Chapter 2.2.

Care was taken in the preparation of the specimens to ensure that results obtained under different conditions were comparable. A simple cut-skein sample containing 6 strands was divided into 18 sections of sufficient length to provide specimens for test using a 1" gauge length. Each section was boiled in distilled water for 2 hours in the relaxed state and then left in a standard atmosphere for at least 24 hours. Final conditioning for a further period of one hour was allowed in distilled water at the test temperature immediately prior to testing. Five specimens were tested at each of seven temperatures ranging from 20 to 80°C and two initial strain rates. (3.3×10^{-1} and 3.3×10^{-2} sec^{-1}). In addition tests were carried out at 6°C and 10°C using the highest strain rate only.

From the load-extension charts obtained on the Instron tester the tensile modulus at 0.5, 2 and 4 in/in strain and the breaking stress and strain were measured. These data are shown in Table 2.6. Since a linear increase of stress with strain is required to maintain a constant modulus figure it is seen immediately that this is not so, that in fact beyond 0.5 in/in strain the stress increases more slowly for a time and at lower temperatures the 2 in/in modulus value is lowest, the stress increasing more rapidly again by the time a strain of 4 in/in is reached. At higher temperatures the modulus only starts to increase more rapidly beyond 4 in/in strain and this value is the lowest. The tensile modulus therefore shows a greater variation with temperature as the strain is increased. This is in

TABLE 2.6.

Temp. (^{o}C)	Initial Strain Rate (sec^{-1}) (x 10^{-2})	Tensile Modulus (dynes /cm^{2} x 10^{7}) 0.5 in/in Strain	2 in/in Strain	4 in/in Strain	Breaking Stress (dynes/ cm^{2} x 10^{8})	Breaking Strain (in/in)
6	33	5.6	4.6	7.4	6.3	6.40
10	33	5.6	4.3	6.6	5.7	6.30
20	33	5.2	3.7	5.2	5.4	7.00
	3.3	4.8	3.2	4.5	4.5	6.90
30	33	4.8	3.0	3.7	4.3	7.40
	3.3	4.8	2.9	3.4	3.8	7.50
	0.33	4.4	2.6	3.4	3.5	7.45
40	33	4.8	2.9	3.2	3.6	7.40
	3.3	4.4	2.7	3.0	3.3	7.60
50	33	4.8	2.8	2.8	3.1	7.70
	3.3	4.4	2.5	2.4	2.8	7.85
60	33	4.4	2.6	2.3	2.7	8.00
	3.3	4.4	2.3	2.0	2.3	8.00
70	33	4.4	2.5	2.0	2.4	8.20
	3.3	4.0	2.2	1.8	2.0	8.20
80	33	4.0	2.2	1.7	2.0	8.40
	3.3	4.0	2.1	1.6	1.7	7.90

agreement with the idea that the orientation increases as the molecular chains become straightened and causes a change in the stress bearing mechanism. This in turn would alter the temperature dependence of the modulus as the strain was increased.

The linearity of Glospan was tested by the method used for polypropylene using equation (8). The test was applied to the curves obtained at 30°C and once again linear viscoelastic behaviour could not be said to exist at any strain although the deviation was small up to almost 1 in/in strain.

Using the general W.L.F. equation in the form of equation (9) each set of data was reduced to a reference temperature of 47°C (320°K) as before. The resulting curves are shown in Figs. 2.14 to 2.17. The curve of the modulus measured at 0.5 in/in strain (Fig. 2.14a) shows considerable scatter. This is because the actual stress at this point is very low and the accuracy of measurement was correspondingly poor. The curve is covered by a change in load measurement of only 4 grammes on a scale of 400 grammes. When this is taken into consideration

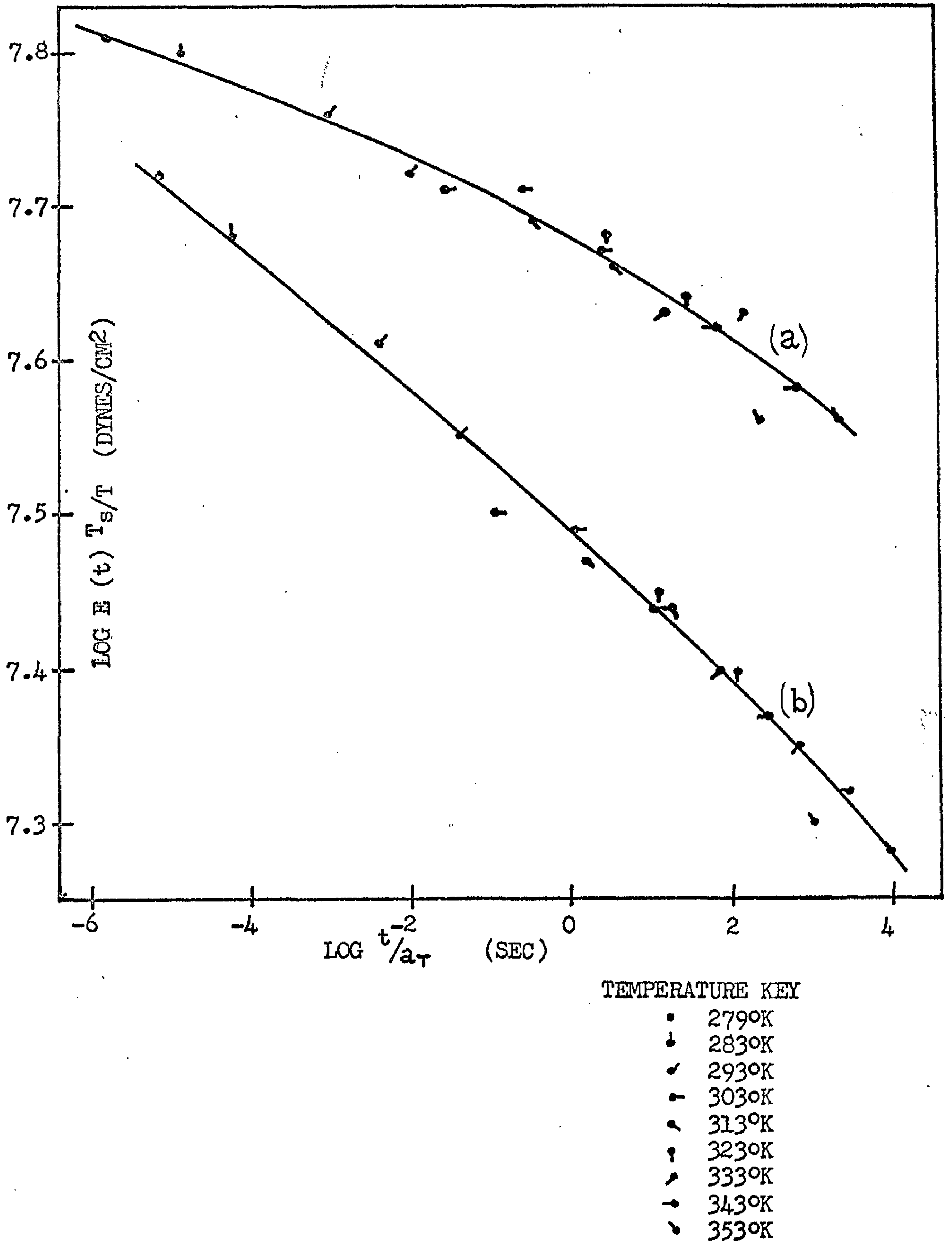

FIG 2.14 The Effect of Strain Rate and Temperature on the Tensile Modulus of Glospan measured at
(a) 0.5 IN/IN Strain
(b) 2 IN/IN Strain

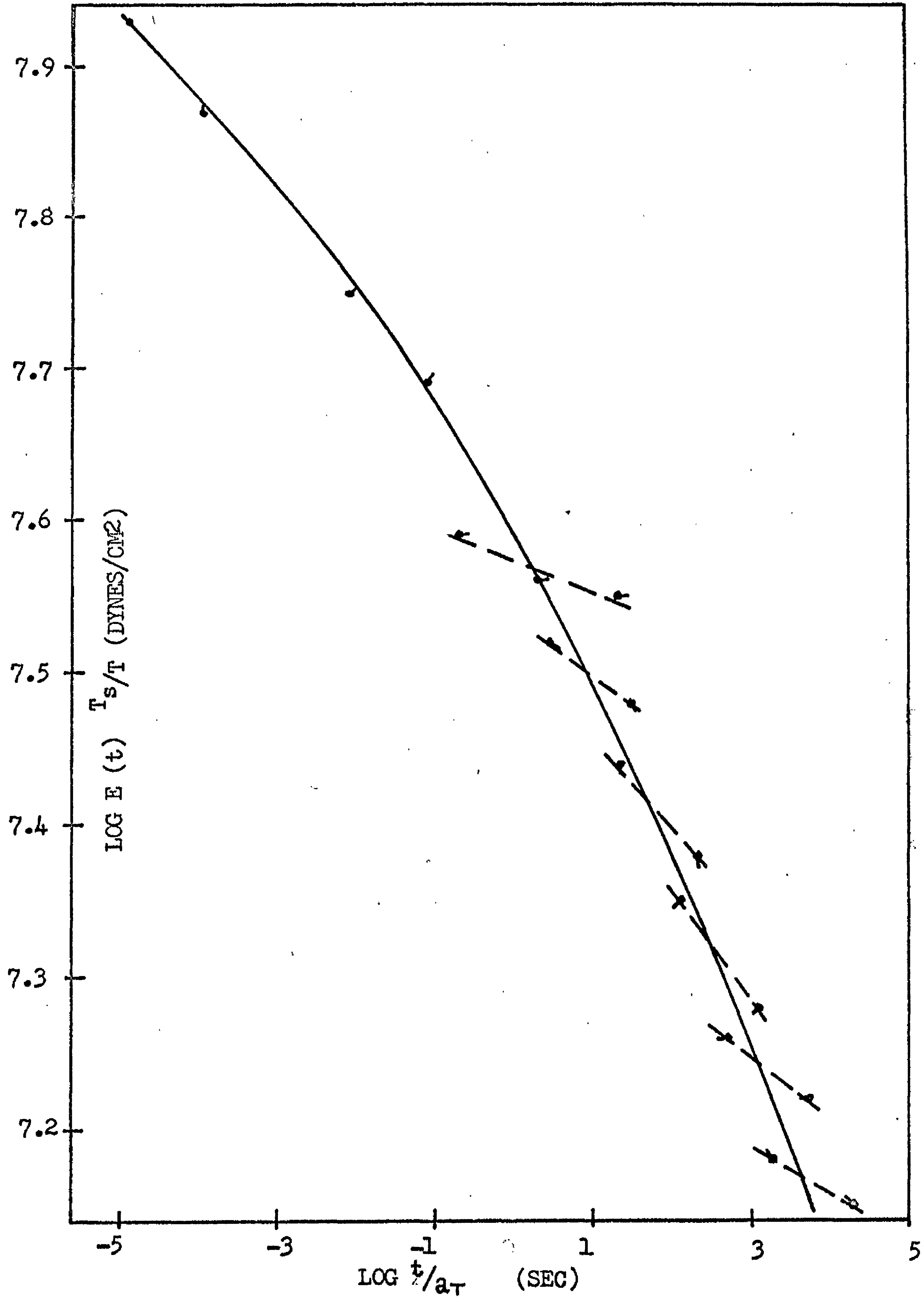

FIG 2.15 The Effect of Strain Rate and Temperature on the Tensile Modulus of Glospan measured at 4 IN/IN Strain. Key as FIG 2.14

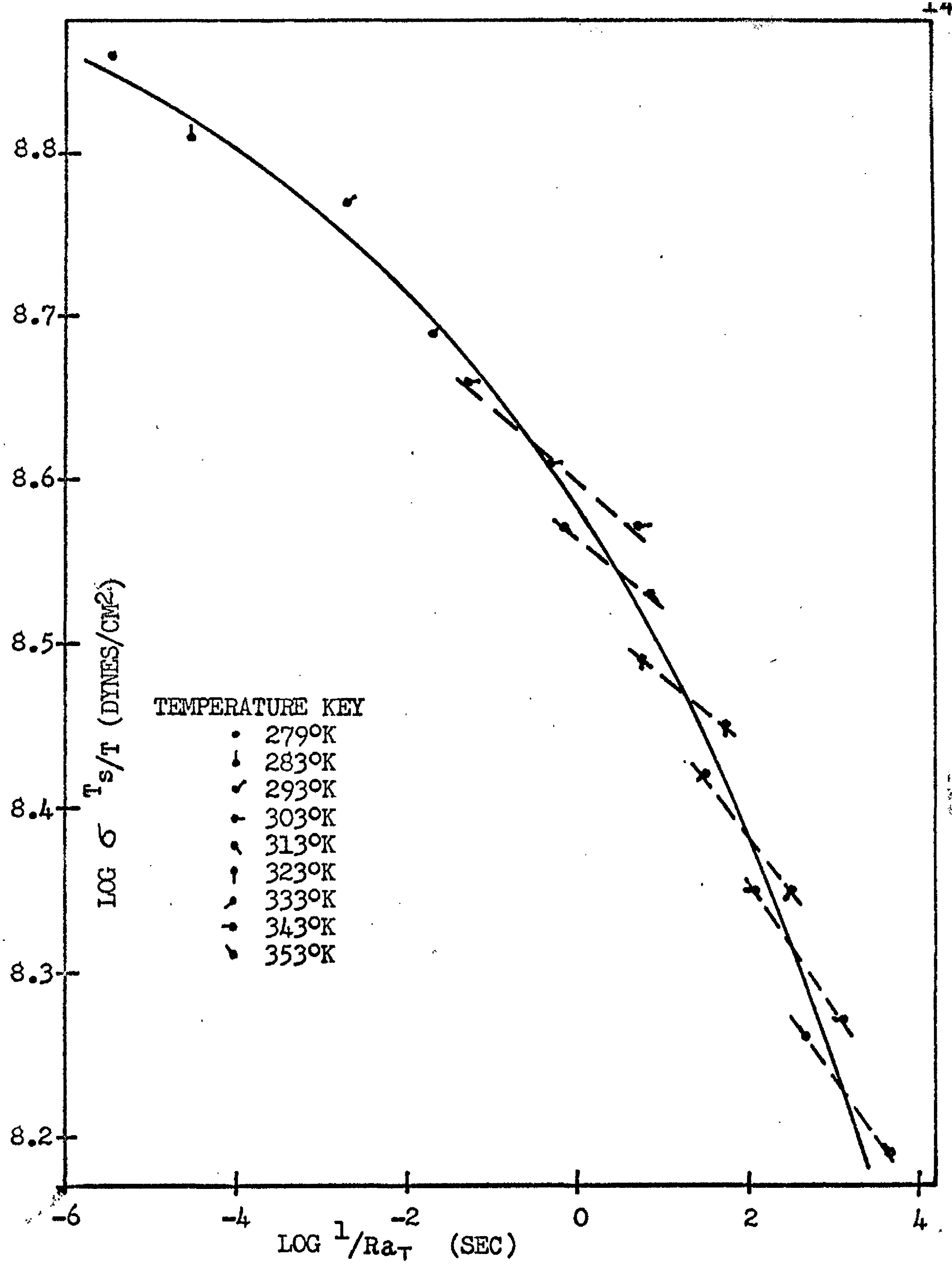

FIG 2.16 The Effect of Strain Rate and Temperature on the Breaking Stress of Glospan

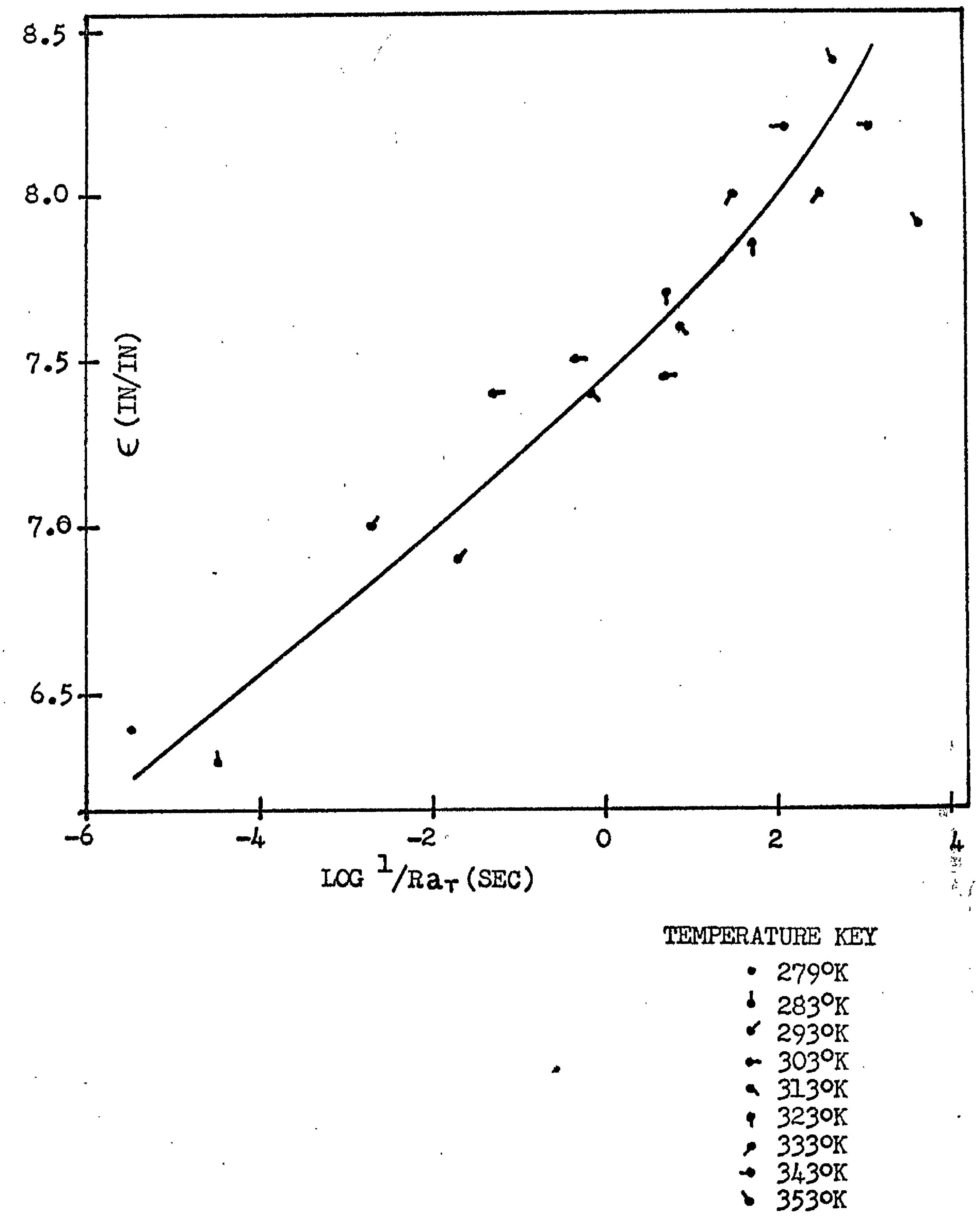

FIG 2.17 The Effect of Strain Rate and Temperature on the Breaking Strain of Glospan.

the superposition is reasonable. The curve of the modulus measured at 2 in/in strain (Fig. 2.14 b) shows excellent correlation with the expected shift, due mainly to the increased accuracy of the points. Thus, although the strain in this case is appreciable, and the modulus shows a greater variation with temperature, the time dependence has changed in conjunction with it and the superposition is still valid at this stage.

The reduced data for the modulus measured at 4 in/in strain (Fig. 2.15) presents a somewhat different picture. The first few points, corresponding to results obtained at the lower temperatures, appear to follow the same trend as those measured at lower strains. Beyond 20°C, however, it is found that the modulus is changing at a greater rate due to changes in temperature than it is due to changes in time. The continuous line in Fig. 2.15 thus shows the temperature dependence and the broken lines, joining points measured at the same temperature, show the relative time dependence. The equivalence of changes in time and changes in temperature has thus altered and it would appear that perhaps some vertical translation factor, taking the rearranged molecular structure into account, might be required. An examination of the curves for the ultimate properties (Figs. 2.16 and 2.17) adds strength to this argument. Again the superposition is not complete when equation (9) is applied to the data for the breaking stress. Although the error is perhaps slightly less than in the previous case, it follows the same pattern and indicates that beyond 4 in/in strain changes occurring in molecular structure are almost independent of temperature.

A simpler application of time-temperature superposition was used by Smith[65] to obtain a characteristic failure envelope for an elastomer. His method follows directly from Figs. 2.16 and 2.17. If the logarithm of the reduced breaking stress and the breaking strain are both related to the same time scale they should be inter-related. Smith plotted the logarithm of the reduced breaking stress against the logarithm of the breaking strain and obtained a composite curve describing the ultimate properties of two SBR gum vulcanates.

This is a more critical test of the application of the superposition method since two parameters are involved, each carrying a considerable experimental error in the case of filament yarn materials.

The shift factor on the time axis does not enter into this relationship, however, and the method was used to produce a failure envelope for Glospan. This is shown in Fig.2.18 and it is seen that, bearing in mind the high scale magnification and the coefficient of variation of 6% in both the stress and strain values, a reasonable curve is obtained. This suggests that superposition of the ultimate stress and strain data for Glospan is possible and that it is merely a question of adjusting the shift factors to take into account molecular orientation occurring at higher strains as already mentioned.

The corresponding failure data for polypropylene samples A, B and C are shown in Figs. 219, 2.20 and 2.21 respectively. All three show the same general trends and the curve of sample C, reduced to a reference temperature of 333^{o}K, is in a form which is more directly comparable with the other two. The surves for samples A and B are similar in shape to those in Figs. 1.18 and 1.19 showing the effect of strain rate and temperature on the breaking strain alone. This is because the relation between the logarithm of the reduced breaking stress and time is almost linear over several decades of logarithmic time. Failure data for sample A (Fig. 2.19) show poor agreement while sample B (Fig. 2.20) shows reasonable agreement. The results for sample C (Fig. 2.21) were taken from measurements by Hall[20] made at different temperatures. Measurements at different strain rates only agree at lower rates and are not shown.

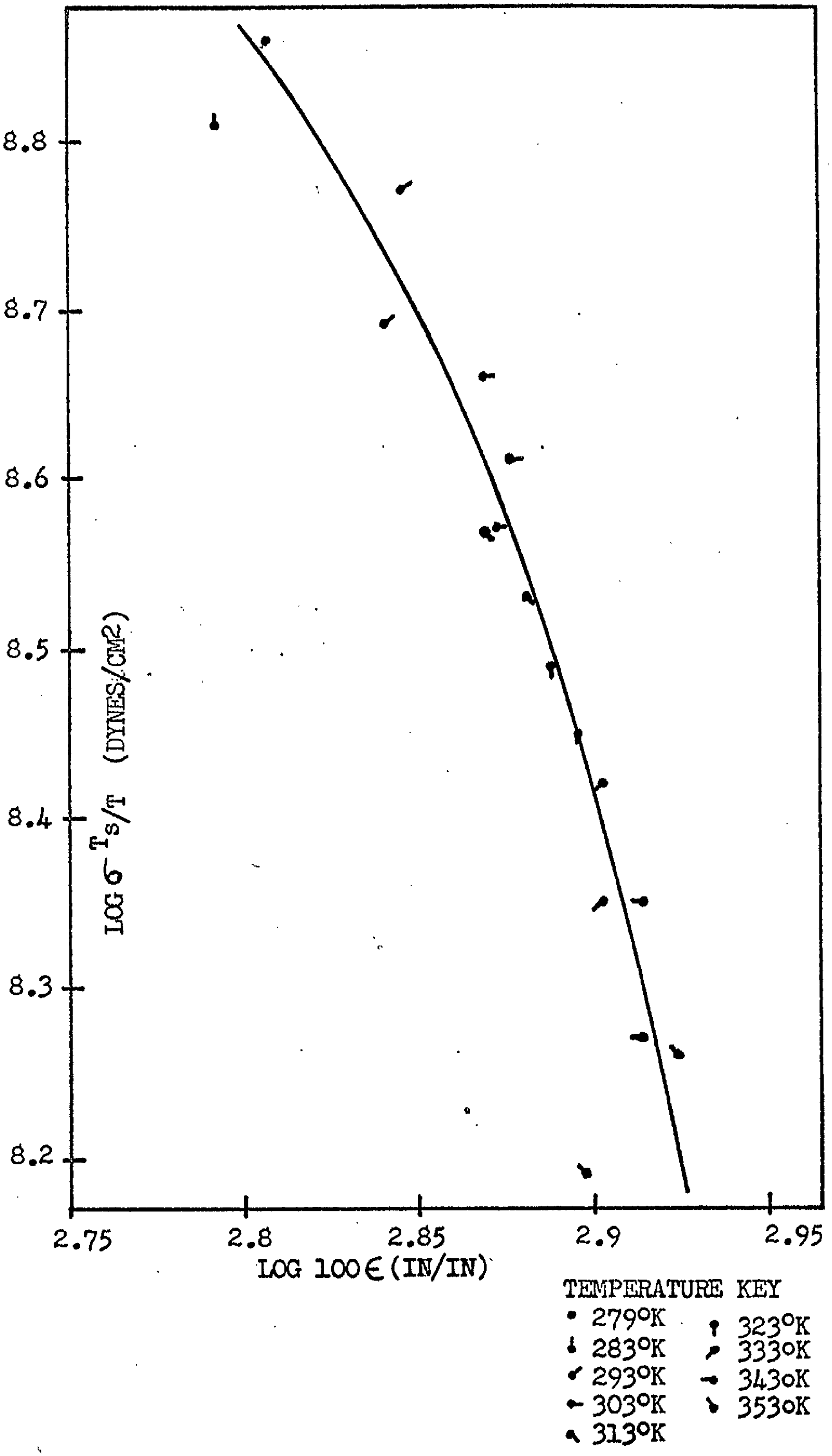

FIG 2.18 Failure Envelope for Glospan

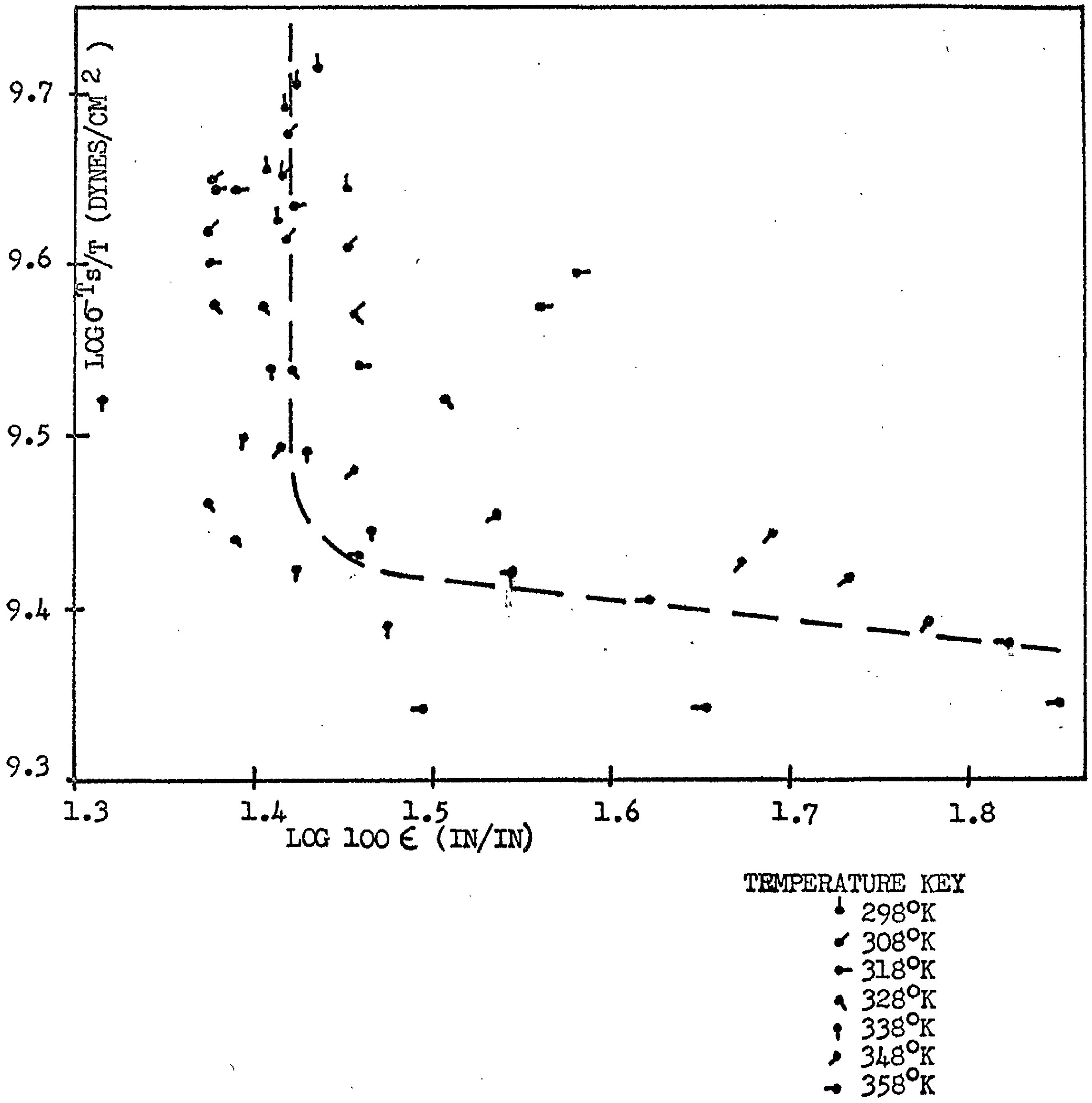

FIG 2.19 Failure Envelope for Polypropylene A

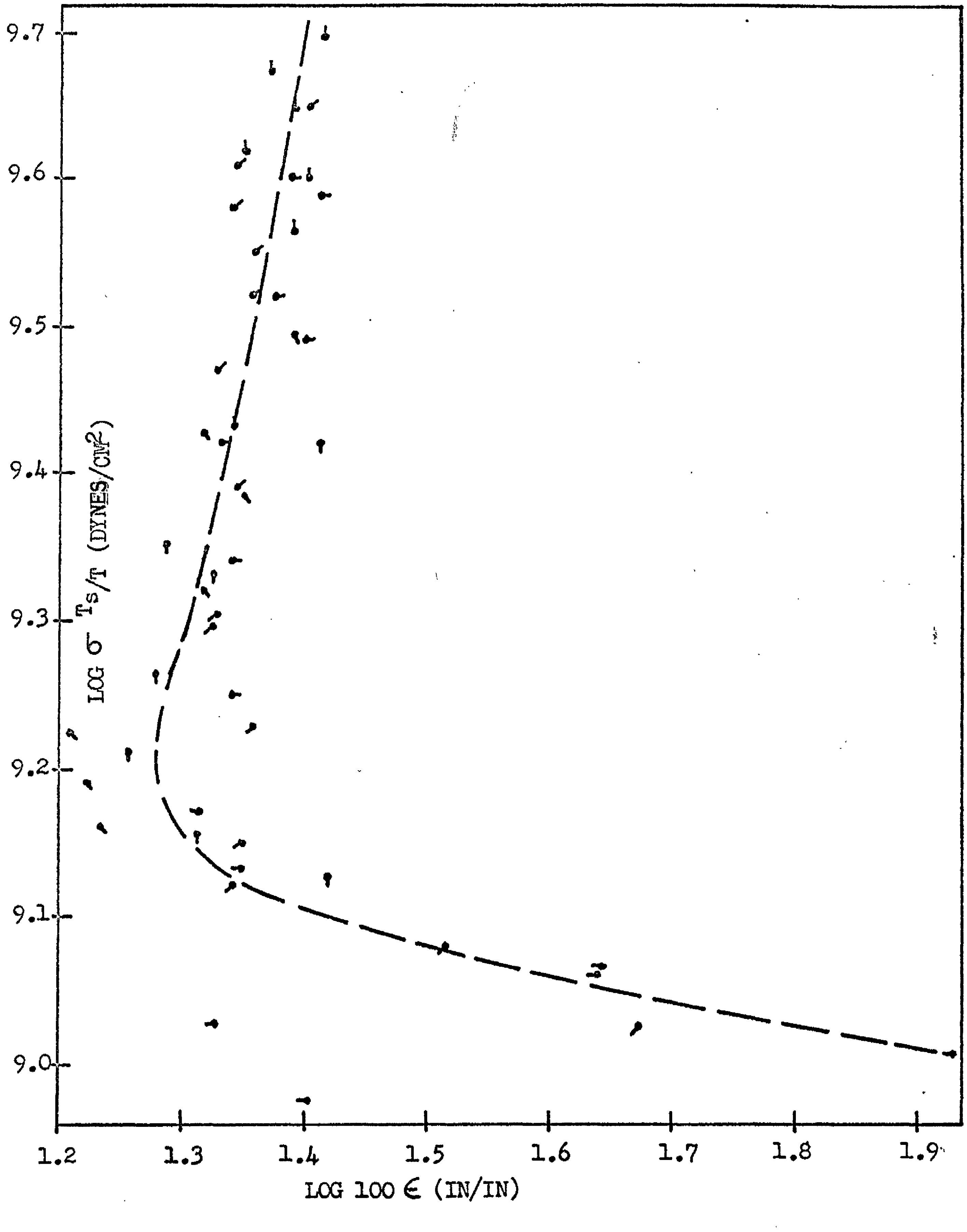

FIG 2.20 Failure Envelope for Polypropylene B **Key as Fig 2.19**

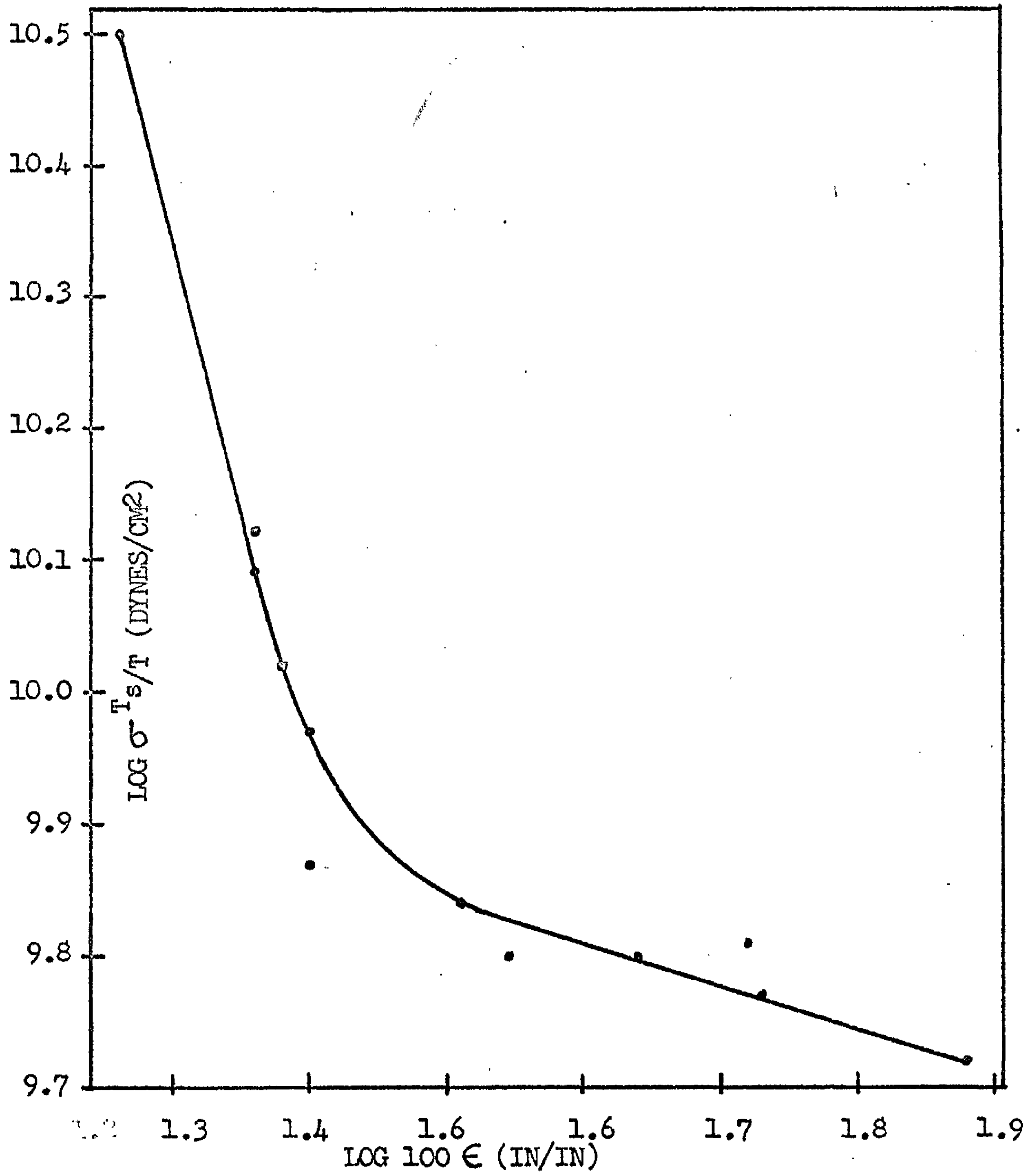

FIG 2.21 Failure Envelope for Polypropylene C

(From HALL[20])

2.5 CONCLUSIONS

The tensile behaviour of a number of synthetic polyurethane elastomeric yarns has been compared with that of a natural rubber yarn under different conditions. All the yarns had a low initial modulus and tensile strength, a high extensibility and elastic recovery, and a large loss of energy in repeated stretching compared with normal textile yarns. They exhibited a constant rate of stress relaxation over several decades of logarithmic time.

Considerable variation was found, within the general range outlined above, between different elastomeric yarns due to differences in chemical structure which are evident from the wide range of density values obtained for these materials. All the synthetic materials had a higher modulus and ultimate strength than the rubber but the latter had a lower rate of stress relaxation and a slightly higher elastic recovery.

In the covered state these materials are held under continuous tension by the covering yarns in the "relaxed" or, more appropriately the equilibrium position. The tensile properties of the plied yarn were found to be dependent on the elastomeric component at strains up to 1.0 to 1.5 in/in. At higher strains the outer yarns took over as the main stress-bearing components and the ultimate properties were controlled by the covering material.

The general W.L.F. equation has been applied to Glospan at strains up to 2.0 in/in using a reference temperature of 320°K. At higher strains the equivalence of time and temperature was found to alter due to increased orientation along the yarn axis and reasonable composite curves could not be obtained using the same shift factors.

An orthodox high tenacity textile material of recent development (polypropylene) and a less orthodox elastomeric yarn have been studied. It has been shown that time-temperature superposition can be applied, in a restricted form, to a non-linear semi-crystalline polymer. The resulting composite curves were independent of temperature and could be used to characterise the behaviour of a material over several decades of time using a single instrument to obtain the necessary data. The method was found to be sensitive enough to distinguish between different types of the same material.

APPENDIX - LIST OF SYMBOLS

a	The root-mean-square end-to-end distance per square root of the number of monomer units.
a_T	Shift factor (time).
c	Concentration.
	Base for natural logarithms.
f	Relaxed stress.
h	Height.
k	Boltzmann's constant; relaxation rate constant.
l	Length. Δl Fractional increase in length.
n	The number of network chains per cubic centimeter.
$n_{\parallel}$	The refractive index measured parallel to the fibre axis.
$n_{\perp}$	The refractive index measured perpendicular to the fibre axis.

p	An integer.
t	Time.
v	Volume.
A	Cross-sectional area.
C	Constant.
$E(t)$	Tensile modulus.
$E(6)$	Tensile modulus measured at 6% strain.
$E(15)$	Tensile modulus measured at 15% strain.
H	Shear relaxation spectrum.
L	Gauge length.
M	Molecular weight.
$\overline{M}_w$	Weight average molecular weight.
P	Proportion integer.
R	Strain rate; the gas constant.
S	Slippage.
$S(t)$	Tension.
T	Absolute temperature.
T_s	Standard reference temperature (absolute).
Z	Degree of polymerisation.
δ	Dirac delta.
$\mathrm{Tan}\,\delta$	Dynamic loss tangent.

ϵ	Strain.
ζ_o	The average friction coefficient per monomer unit.
η_{sp}	Specific viscosity.
$[\eta]$	Intrinsic viscosity.
λ	Apparent extension.
ρ	Density. (ρ_o Density at temperature T_o)
σ	Stress.
σ_R	Reduced stress.
τ	Relaxation time.
τ_K	Characteristic relaxation time.

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SUMMARY

The tensile properties of some new textile yarns have been studied with particular reference to the effect of temperature and rate of strain application on the stress-strain behaviour. The work has been split into two parts covering different types of material.

In part 1, an Instron tensile tester was used to investigate the effect of strain rate and temperature on the stress-strain properties of two samples of polypropylene yarn. Differences in behaviour occurring between the samples were explained by measurements of structural properties such as isotactic index and average molecular weight. Results were compared with data from the literature on an isotactic polypropylene yarn. The method of reduced variables has been used to apply time-temperature superposition and obtain composite curves reduced to a standard reference temperature. This was done for the ultimate stress and strain values and values of stress at lower strains expressed as the tensile modulus. A similar superposition was obtained from stress relaxation data.

In part 2, five samples of synthetic polyurethane elastomeric yarns and one sample of natural rubber yarn have been studied under different conditions. The stress-strain curve, toughness, Schwartz value, elastic recovery and stress relaxation properties have been measured and compared. The stress-strain curve of one of the synthetic yarns was studied at different temperatures and initial strain rates. Unlike polypropylene, the same superposition could not be applied to all the data in this case. The equivalence of changes in time and temperature alters with increasing strain as the molecular orientation alters.

Yarns of completely different structure have been studied and it has been shown that time-temperature superposition can be applied, in a restricted form, to a non-linear semi-crystalline material. It is therefore possible to obtain data necessary to characterise the behaviour of a material over several decades of logarithmic time using a single instrument of a type used in normal tensile testing procedure.