

CORRELATION OF THE EXPERIMENTAL CRYSTALLINITY WITH THE
MECHANICAL PROPERTIES OF ISOTACTIC POLYPROPYLENE

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ABSTRACT

The degree of crystallinity of variously heat treated samples of isotactic polypropylene were measured at room temperature using an X-ray diffractometer. The tensile strength and Young's modulus of the same samples were also determined at room temperature and the results correlated with the degree of crystallinity.

The percentage crystallinity is found to increase with reduction in cooling rate of the samples. Annealing at different temperatures shows a linear increase in crystallinity with increase in annealing temperature. But increase in the annealing time leads to a logarithmic relationship between annealing time and crystallinity.

The study shows that the tensile strength and Young's modulus are linearly related to the degree of crystallinity for samples cooled at different rates. For the annealed samples, tensile strength and Young's modulus are linearly related to the degree of crystallinity only at low levels of crystallinity. At high levels of crystallinity, the relationship is not linear. This was unexpected. Lack of linearity is attributed to the large spherulites, which may have

developed at the high annealing temperature and long periods of annealing, with interspherulitic boundaries that act as stress concentrators and thus weaken the material.

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CHAPTER ONE

INTRODUCTION

Polymeric materials have become increasingly popular in many areas of technological developments in the world today. This is because of the ease with which they are processed into often quite intricate shapes at relatively low temperatures. They are usually low cost compared to other types of materials and yet have desirable properties that make them be used in some cases as metal substitutes.

One of the industrially versatile polymers is isotactic polypropylene. This is due to its outstanding properties such as high tensile strength, high Young's modulus, low density and high distortion temperature. These properties have made it suitable for unlimited number of applications.

Though extensive studies have been done on the mechanical properties of polymers as a function of temperature {1,2,3} and degree of orientation {4,5} the relationship between the mechanical properties and the degree of crystallinity has not been widely studied particularly for isotactic polypropylene. One of the earliest studies done on the mechanical properties as a function of the degree of crystallinity was by Micheala {6}. He found that Young's modulus of rubber increases with increase

in degree of crystallinity. For instance an increase of 24% in degree of crystallinity increased the Young's modulus by a factor of 100. There was no explanation given for this high increase in Young's modulus for a relatively small change in crystallinity.

Greensmith and coworkers' studies on polyethylene samples {7} showed that crystalline or semicrystalline samples had a consistently higher modulus and yield stress at a given temperature than amorphous samples of the same polymer. Chin, Gent and White {8} showed that with low density polyethylene, tensile properties did not change significantly with changes in the degree of crystallinity. They however showed that with medium and high density polyethylene, the breaking elongation and the energy required to break the specimen were drastically reduced by increase in degree of crystallinity. Similar work on the effect of crystallinity on mechanical properties of nylon moldings was done by Starkweath and Brooks {9}. It was observed that an increase in degree of crystallinity increased the elastic modulus and yield stress but decreased the impact strength particularly above 35% crystallinity.

It is not certain that these effects of crystallinity on the mechanical properties of polymers are general. It would therefore be interesting to investi-

gate how the tensile strength and Young's modulus of isotactic polypropylene vary with changes in degree of crystallinity as a result of different thermal treatments. The study therefore, involved:-

- (i) Measurement of the degree of crystallinity (by X-ray diffractometer) of isotactic polypropylene samples subjected to different thermal treatments.
- (ii) Determination of the tensile strength and Young's modulus of samples whose degree of crystallinity had been measured.
- (iii) Correlation of the tensile strength and Young's modulus with the degree of crystallinity.

1.1 Molecular Structure and Uses of Isotactic Polypropylene

The repeat unit that characterizes polypropylene is the propylene monomer shown in fig. 1.

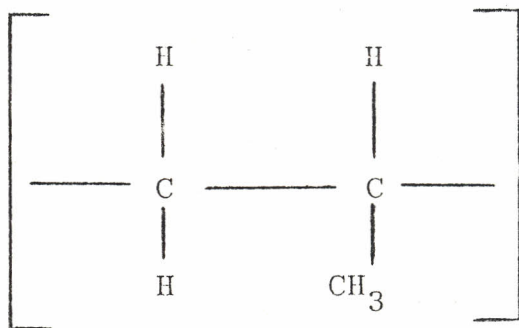
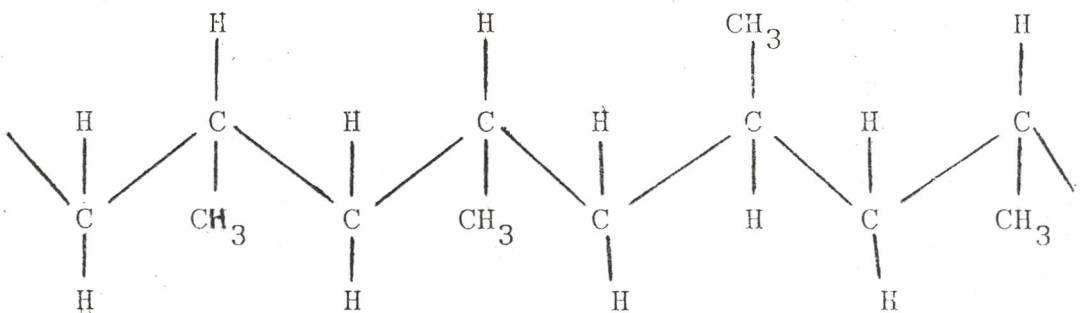


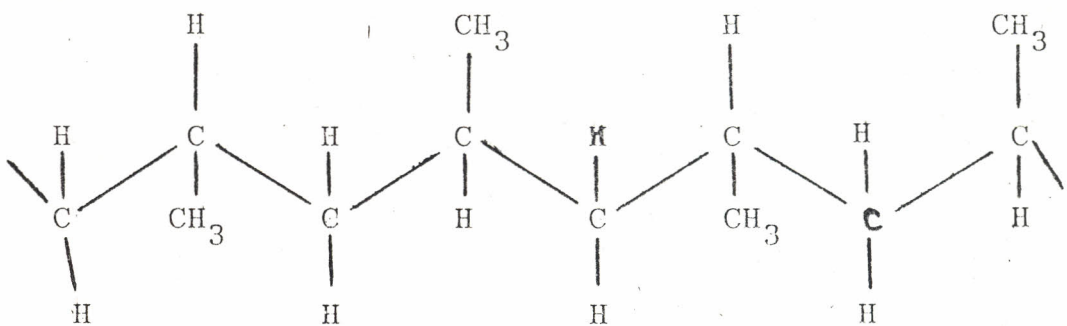
Fig. 1. Propylene monomer

Polypropylene is prepared through addition polymerization of propylene monomers, (Polymerization is the reaction of one or more monomers to form a chain like structure of high molecular weight). During the polymerization process molecular chains of different molecular weight are formed. The published data on the commercial polypropylene {10} indicates that the molecular weight are in the range $\bar{M}_w = 200,000-700,000$. A given range of molecular weight^s has properties which are different from those of other ranges of molecular weights.

The chains configuration can either be atactic, syndiotactic or isotactic. This depends on the arrangement of the methyl ($-\text{CH}_3$) group along the chain.



(a)



(b)

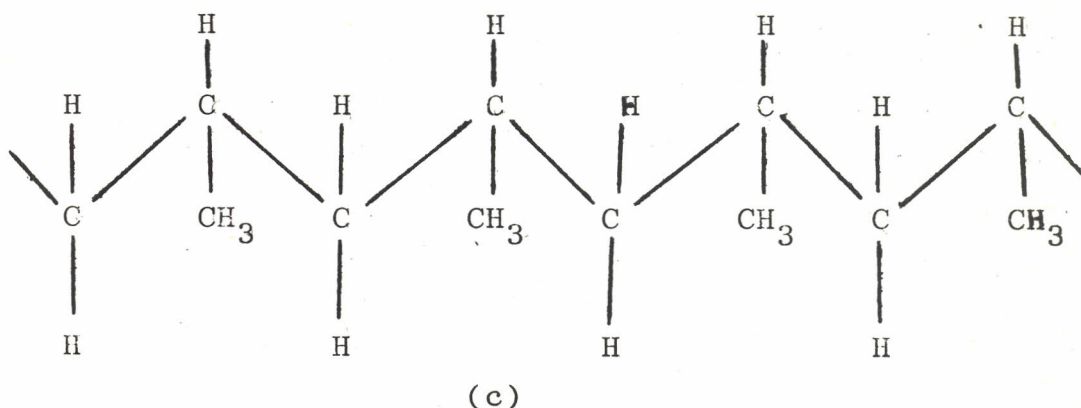


Fig. 2. Different configurations of polypropylene molecules.

(a) Atactic (b) Syndiotactic (c) Isotactic.

In the atactic form, the methyl groups arrange themselves randomly along the chain (Fig. 2a). This leads to poor molecular symmetry and hence little or no crystallinity. Atactic form of polypropylene is therefore of limited commercial importance.

The use of sterio-specific (Ziegler) catalysts [11] has been found to control the ordering of the methyl groups along the chain. When the methyl groups are alternating from one side to the other, (Fig. 2b) the polymer is said to be syndiotactic. The arrangement of the methyl groups on the same side of the chain form the isotactic polypropylene (Fig. 2c), and molecules assume a helical conformation. This is the form of polypropylene that is important commercially. The superior mechanical properties of this form is attributed to its structural regularity which in turn favours high levels of

crystallinity in the bulk material.

The commercial polypropylene is 95-97% isotactic [12] and is potentially crystallizable. However in the extruded form, not more than 65-70% of the material has been found to actually crystallize. This shows clearly that the fabrication processes affect the extent of crystallization of the material which do in turn affect the mechanical properties of the final products. Isotactic polypropylene has a glass transition temperature of about -18°C , a softening temperature of 150°C and a melting temperature of 172°C . Some of its present applications include; piping, hospital equipment, packaging materials, filaments and fibres for ropes and carpets etc. It is also replacing traditional materials like steel in many load-bearing applications.

CHAPTER TWO

Literature Review

The polypropylene mode and extent of crystallization under different thermal conditions have been extensively studied, particularly for isothermal crystallization {13,14}. It's mechanical properties as a function of either temperature or degree of orientation have also been widely studied {15,16}.

The variation of the degree of crystallinity with temperature was studied by Miller {17} using the infrared spectrophotometer. The study showed that the degree of crystallinity decreased as the sample temperature was raised from the room temperature to melting temperature where the crystallinity was zero.

In another study by Joanne and Turnbull {18} the rate of crystallization of polypropylene melt subjected to different cooling rates was investigated. Fast cooling rate was found to lower the temperature of the highest rate of crystallization. For instance with a cooling rate of 0.84°C per minute, the highest rate of crystallization occurred between 82.5°C and 76.5°C . Slower cooling rate lowered the overall rate of crystallization but raised the temperature range of the highest crystallization. On crystallizing isotactic polypropylene, Miller {17} found that it formed spherulites

only if the crystallization temperature was above 115°C . Below this temperature it formed a nonspherulitic structure.

Detailed work on the spherulitic crystallization of polypropylene was however studied by Padden and Keith [19]. They observed that in the temperature range of 110° - 143°C , polypropylene crystallized in four types of spherulites. The classification of the spherulites is on the crystallization temperature and the birefringence they exhibit. The size and distribution of the spherulites depend on the crystallization time and distribution of the nucleating agents.

Kardos et al. [20] and Pae et al. [21] studied the form of crystallization of isotactic polypropylene and established that depending on the molecular weight and crystallization pressure, polypropylene crystallized in either monoclinic (α) or triclinic (γ) or hexagonal (β) forms. Sauer and Pae [22] showed that on annealing the triclinic form (γ) at high temperature, it transformed into monoclinic form (α).

In the study done by Gilbert and Brigg [23] on the ethylene-propylene copolymer, the variation of the degree of crystallinity with the storage temperature and duration of storage time was investigated. They found that on fixing the storage time, the X-ray

determined crystallinity increased with an increase in the storage temperature. On fixing the storage temperature, the degree of crystallinity gradually increased with time until it became constant.

Ruland {24} and Samuel {25} independently investigated the degree of crystallinity of isotactic polypropylene samples as a function of cooling rates. Ruland's samples were melted and then quenched in water at room temperature. Some of the quenched samples were annealed for half an hour at 160°C . The crystallinity of the quenched samples was 31% while that of the quenched and annealed samples was 65%. Samuel's samples treatment involved compression moulding at 280°C , then air cooling them to 210°C and then quenching in tap water at room temperature. Other samples were allowed to cool in the press. The quenched samples had a crystallinity of 48.5% and the press cooled one 64.3% crystallinity. It is evident from these observations that even a slight variation in the heat treatment during the processing of the polymer melt may have a considerable change in the crystallinity of the material.

Among the studies done on mechanical properties of polypropylene is the dynamic mechanical properties investigated by Flocke {26}. The study involved the variation of loss modulus as a function of temperature on samples of different degree of crystallinity. In

all cases the results showed the loss modulus as a very pronounced peak in the temperature range of -10°C to 20°C (β relaxation). The height of the peak decreased with the increase of the crystallinity of the samples. Similar studies by Frank {27} showed that the storage modulus of isotactic polypropylene decreased with increase in temperature and was higher in samples with higher degree of crystallinity.

The effect of polymorphism and degree of lamella orientation on the dynamic mechanical properties of polypropylene was studied by Crissman {28}. The samples were crystallized from melt and exhibited the monoclinic (α) and hexagonal (β) form of crystallization in addition to varying degrees of orientation. The morphology of the samples ranged from unoriented sample showing only the monoclinic crystallites to one highly oriented having approximately 90% the hexagonal crystallites (β). For samples of nearly equal overall per cent crystallinity, it was observed that in both logarithmic decrement and loss modulus as functions of temperature, the peak occurring at -75°C decreased in height and that at 0°C increased in height as the fraction of hexagonal form of crystallinity present increased.

Owen and Ward {29} have also studied the mechanical behaviour of oriented isotactic polypropylene. The

samples were prepared by cold drawing followed by annealing at selected temperatures, and others by hot drawing. The modulus measurements were made in $0^\circ(E_0)$, $45^\circ(E_{45})$ and $90^\circ(E_{90})$ directions with respect to the sample draw direction. The moduli were studied as functions of temperature. It was observed that for all temperatures, $E_0 > E_{45} > E_{90}$ for both cold and hot drawn specimens. On annealing the samples at 145°C , an increase of E_{90} relative to E_0 and E_{45} giving $E_0 > E_{90} > E_{45}$ above 20°C was observed. Annealing at 158°C gave $E_{90} > E_0 > E_{45}$ above 40°C .

From the above review, it is evident that a number of studies done on isotactic polypropylene in recent years have concentrated on either the forms and structure of crystallization under different thermal conditions or dynamic mechanical properties of both isotropic and anisotropic specimens at different temperatures. There is little emphasis given to the degree of crystallinity and its effect on the mechanical properties of isotactic polypropylene. To the best of the author's knowledge, no model relating the mechanical properties with the degree of crystallinity has been reported. An attempt is therefore made in this study to establish if a generalized relationship exists between the mechanical properties (Young's modulus and tensile strength) and the degree of crystallinity of isotactic polypropylene at room temperature.

CHAPTER THREE

Theory of Crystallization and Mechanical Properties

3.1 Introduction

Polymeric materials are made of long flexible chain molecules. Each chain molecule interacts with other chain molecules in the bulk material. The arrangements and interactions of the chain molecules have a profound effect on the properties of the material. One of the most significant structural factors is whether the material is crystalline or amorphous. Since polymers cannot be completely crystalline (ie. cannot have a perfectly regular crystal lattice) the concept of degree of crystallinity has been introduced. The degree of crystallinity of material is not a unique parameter. It depends on the thermal history of the material. Those properties that depend on the degree of crystallinity of a material are therefore not unique also.

3.2 Crystallization of Polymers

There are many factors that determine whether a polymer melt will crystallize and to what extent it crystallizes. A necessary but not sufficient condition is geometrical regularity of the chemical structure. Absolute regularity is however not essential. Approximate regularity is often sufficient. Assuming

that the polymer is sufficiently regular and its thermodynamics are adequate for crystallization, there is nevertheless no assurance that it will crystallize. Conditions must be kinetically favourable for crystallization to occur within the experimental time.

Environmental factors such as the temperature of the melt and the time the melt remains at that temperature affects the number of heterogeneous nuclei present during the crystallization process. This in turn controls the overall rate at which crystallinity develops. The temperature at which the degree of crystallinity is determined and the cooling rate of the polymer melt also affect the degree of crystallinity of a sample. At high temperatures the molecules of the polymer are highly mobile and therefore there are few regions with regularly packed molecules. Fast cooling does not give the disorganized polymer melt molecules enough time to pack regularly. This is clearly shown (Fig. 3.) by the study of specific volume (a reciprocal of crystallinity) as a function of temperature and cooling rate {30}. In the figure, T_m represents the melting point and T_{g_1} , T_{g_2} the glass transition temperature obtained at various (decreasing) rate of cooling.

The polymer crystallization involves the nucleation and the growth processes. According to Avrami {31}

and Evans [32], the process of isothermal crystallization of the polymer melt can be expressed as

$$\frac{d\chi_t}{d\chi_t^1} = 1 - U_t \dots\dots\dots 3.1$$

where χ_t is the crystallized mass at a time t , χ_t^1 is the mass that would have crystallized at a time t if the material was monomeric, and U_t is the effective fraction transformed at a time t .

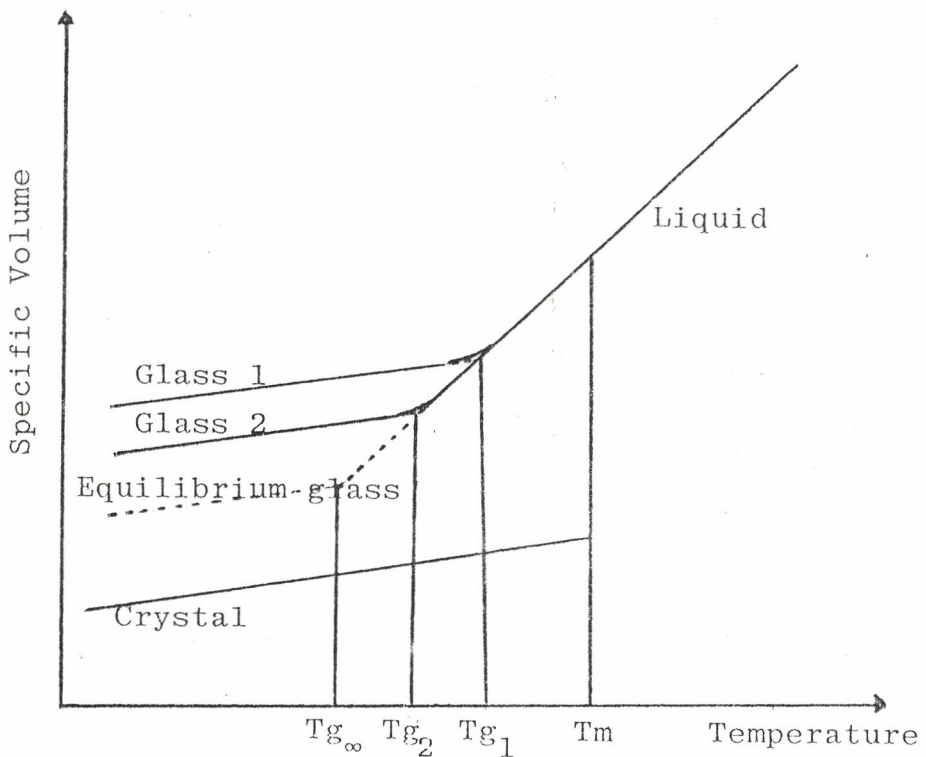


Fig. 3. Specific volume of polymer melt cooled at various rates.

The effective fraction is the total mass into which

further crystal growth cannot occur. It includes both the crystallized mass and amorphous chain segments which are in uncrystallized state at time t . Taking the effective fraction crystallized to be proportional to the actual mass fraction crystallized and the proportionality factor to be

$$\frac{1}{1-\lambda(\infty)}$$

where $\lambda(\infty)$ is the uncrystallized mass at $t = \infty$ then

$$U_t = \frac{\chi_t}{1-\lambda(\infty)} \dots\dots\dots 3.2$$

Substituting eq. (3.2) into eq. (3.1) and integrating we get,

$$\ln \frac{1}{1-\chi/(1-\lambda(\infty))} = \frac{1}{1-\lambda(\infty)} \chi_t^1 \dots\dots\dots 3.3$$

Substituting the value χ_t^1 obtained by Johnson and Mehl (33) for monomeric material, equation 3.3 becomes

$$\ln \frac{1}{1-\chi/(1-\lambda(\infty))} = \frac{1}{1-\lambda(\infty)} kt^n \dots\dots\dots 3.4a$$

$$\text{or } \chi = [1-\lambda(\infty)] \left[1 - e^{-\frac{k t^n}{1-\lambda(\infty)}} \right] \dots\dots\dots 3.4b$$

where k is a factor depending on the nucleation concentration and temperature of crystallization. n is a constant depending on the growth habit. For instance, for three dimensional linear growth and homogeneous nucleation, n has a value of 4. Equation 3.4 is called Avrami equation and it gives the general

result of isothermal crystallization {31}. It shows that the actual crystallized mass χ is a function of time and temperature. When equation (3.4) is expressed in measurable qualities such as the specific volume, it becomes {34}.

$$\ln \frac{V_{\infty} - V_t}{V_{\infty} - V_0} = - \frac{1}{1 - \lambda(\infty)} kt^n \dots\dots\dots 3.5$$

where V_0 is the initial specific volume, V_{∞} is the final specific volume, and V_t is the specific volume at time t . By defining $\frac{1}{1 - \lambda(\infty)} kt^n$ as τ , then $\tau^{1/n}$ is directly proportional to the time. Isothermal crystallization of $\frac{V_{\infty} - V_t}{V_{\infty} - V_0}$ against $\tau^{1/n}$ can then be plotted {35}.

3.3 Annealing of Polymers

Annealing is a process of holding a solid material at an elevated temperature for some length of time. If a sample is crystallized and then subjected to an annealing treatment, metastable conditions such as residual strains, nonequilibrium crystals, dislocations and vacancies will tend to be eliminated as the system strives to attain thermodynamic equilibrium. The experimental crystallinity of such samples will tend to increase after such treatment.

Another effect of annealing is the thickening of the polymer crystals, when annealed isothermally. The

thickening is believed to be an irreversible phenomenon. The general thermodynamic principles of irreversible processes can be applied to study the thickening rate. Consider a lamellar crystal that is undergoing an annealing process (Fig. 4).

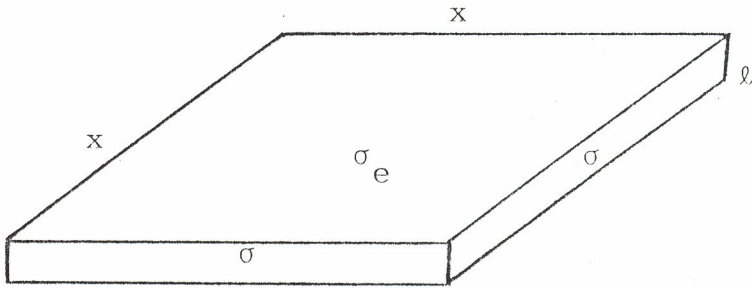


Fig. 4. Schematic drawing of the geometry of a lamellar crystal.

By taking the thickening rate to be proportional to the surface free energy gradient, Colson, and Eby { 36 } developed the equation,

$$x^2 \frac{d\ell}{dt} = - k \frac{dG_S}{d\ell} \dots\dots\dots 3.6$$

where x is the lateral dimension of the crystal, ℓ is thickness, G_S is the surface energy, t is the time and k is the proportionality constant that depends on the annealing temperature .

The surface free energy G_S of a lamellar crystal with square cross section is given as {37},

$$G_S = 4x\ell\sigma + 2x^2\sigma_e \dots\dots\dots 3.7a$$

$$\text{or } G_S = 4(lv)^{\frac{1}{2}} \frac{\sigma + 2v\sigma_e}{l} \dots\dots\dots 3.7b$$

where σ_e is the surface free energy for the basal surface, σ is the surface free energy of the lateral surface and $V = x^2 l$ is the volume of the crystal.

For polymeric materials $\sigma_e > \sigma$ {36}. This means that the crystal will reduce its surface free energy by thickening in the chain direction, i.e. l will increase and x decrease. As the thickening continues, we shall come to a thickness l^* where the surface free energy gradient will be zero.

$$\text{For thickness } l^*, \frac{dG_S}{dl} = 0 \dots\dots\dots 3.8$$

The crystal will have attained its equilibrium dimensions l^* and x^* . Assuming that the volume of the lamella remains constant then,

$$l^* = \frac{\sigma_e^2 V}{\sigma^2}^{1/3} \text{ and } x^* = \frac{\sigma V}{\sigma_e}^{1/3} \dots\dots\dots 3.9$$

From equations (3.8) and (3.9) it is observed that the thickening of a polymer lamella does not continue indefinitely. It stops as soon as the equilibrium dimensions are attained.

3.4 Crystallinity and Mechanical Properties

The mechanical properties of semi-crystalline polymeric material is studied by assuming a two-phase model in which one phase is the crystalline and the other

amorphous. Each phase has its own intrinsic properties that are different from those of the other phase. The properties of the composite material was predicted by Takayanagi {38} using the series and parallel models. Assuming the crystalline phase was in parallel arrangement with the amorphous phase, the Young's modulus of the composite was given as;

$$E_{\text{composite}} = \chi E_{\text{crystalline}} + (1-\chi) E_{\text{amorphous}} \dots 3.10$$

where χ is the fraction of the crystalline phase of the composite. In the series model, the result was:

$$\frac{1}{E_{\text{composite}}} = \frac{\chi}{E_{\text{crystalline}}} + \frac{1-\chi}{E_{\text{amorphous}}} \dots \dots \dots 3.11$$

As the Young's modulus of a crystalline phase is superior to that of the amorphous phase, it is evident from equations (3.10) and 3.11) that the Young's modulus of the composite would be expected to increase with an increase of the fraction of the crystalline phase. According to Nielsen {39} and Leitner {40}, equation (3.10) gives the maximum modulus of the composite while equation (3.11) gives the lowest value of modulus. Halpin and Kardos {41}, however, suggested that values of a composite should fall between the bounds set by these equations irrespective of the composite's crystallite morphology.

CHAPTER FOUR

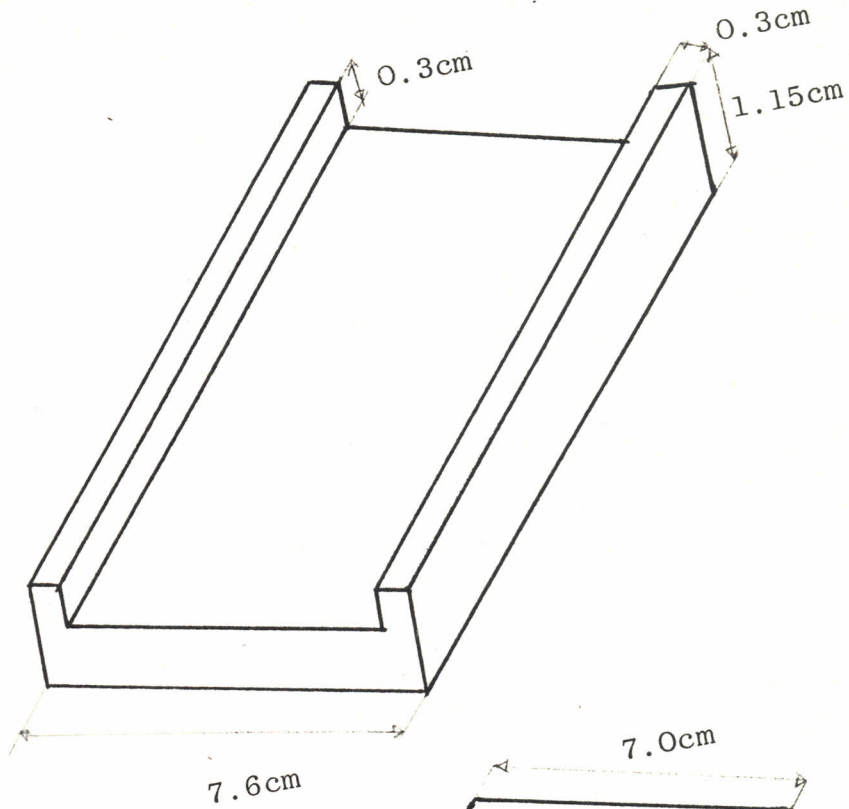
Experimental Apparatus and Method

4.1.0 Experimental Apparatus

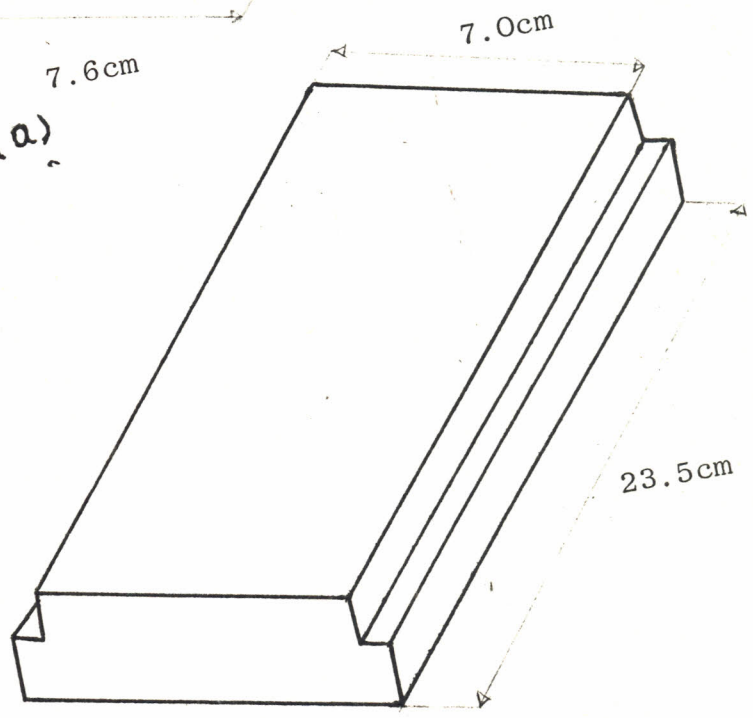
Several pieces of equipment were used in this study. These included the mold, an insulating box, oven, press, X-ray diffractometer, density measurement equipment, planimeter, and the mechanical properties test equipment (Hounsfield tensometer). The use of each equipment will be briefly discussed below.

4.1.1 The Mold

This was made to prepare the polypropylene films from the granules. It consists of two aluminium plates whose surfaces were smoothed by machining and polishing. The polishing was done with emery papers starting with grade 220 (coarse) and finishing with grade 600 (finest). To ensure production of films with smooth surface in the compression molding process, aluminium foils were put between the polymer melt and the mold plates. The dimensions of the plates were as shown in Fig. 5. The mold had clamps made of brass strips and bolt. The compression molding of the films was done by either clamping the mold or by pressing it with the pressing machine.



(a)



(b)

Fig. (a) Mold (b) Cover plate

4.1.2 Insulating Box

The insulating box was made from a frame of timber and plywood. Its dimensions were 35cm x 30cm x 30cm. It was used to minimize the cooling rate of the mold and its contents by mainly convectional currents and conduction. This was achieved by lining it with layers of glass fibre and cotton which are used as lagging materials.

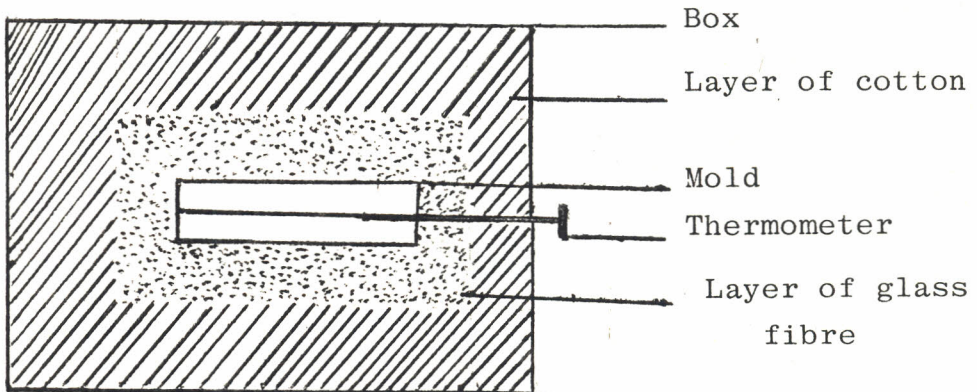


Fig. 6. Cross-section of the insulating box.

4.1.3 The Oven and the Press

This equipment is at Civil Engineering Department of the University of Nairobi. The oven was used to heat polypropylene granules to melting temperature and for annealing the molded films. Its maximum temperature was 250°C and could maintain a given temperature thermostatically with a fluctuation of $\pm 2^\circ\text{C}$.

The oven had a motor that rotated a disc in the

heating compartment. This eliminated the problem of hot spots during the air annealing of the samples in the oven.

The press was the Denison Compression Testing Machine type. It has a marked capacity of 180 tons on a 29.2 cm ram and was used for compression molding of the films.

4.1.4 X-ray Diffractometer

The wide angle X-ray diffraction measurements were made using a Phillips Norelco Diffractometer, at the mines and geological department of the Ministry of Environment and Natural Resources. The diffractometer was equipped with a nickel monochromator. The Cu K_α radiation used was from a stabilized source that was maintained at an anode voltage of 40kV and a filament current of 20mA. The intensity was monitored with a proportional counter detector system. Samples whose typical thickness was 0.5mm were scanned from $2\theta = 5^\circ$ to $2\theta = 31^\circ$ at a scanning speed of 2° per 1.5 minutes.

4.1.5 Density Measurement

The mass and volume of the samples were determined with a 50ml specific gravity bottle and an analytical balance that had an accuracy of 0.0001g. A vacuum

desiccator was used to remove any entrapped air when filling the density bottle with water.

4.1.6 Planimeter

This instrument was used to measure the area under a closed loop. It is calibrated by tracing the path of a loop whose enclosed area is known once. It was used to measure the areas under the X-ray diffraction patterns.

4.1.7 Mechanical Properties

The tensile test was done with the Table Hounsfield Tensometer, Model W3344, at the strength of materials laboratory in the department of mechanical engineering, University of Nairobi. It had a capacity of 20kN. When motorized, the machine gave a constant straining speed. The grips used to hold the test pieces were the 'wedge action' type. Other equipment like the instron testing machine could not be used because its cross head could not effectively hold the specimen tightly.

4.2.0 Sample Treatment and Experimental Procedure

The polymer used in this study was isotactic polypropylene. It was obtained from East African Bag and Cordage industry in Juja, one of the indigenously owned polymer using industries. The material was in

granular form and was converted into film form as explained below. It is from these films that the experimental specimens were cut.

4.2.1 Film Molding and Thermal Treatments

To make the film, the oven was switched on and allowed to attain a steady temperature of 240°C . The mold was then put in the oven and given 15 minutes to attain the steady temperature of the oven. 20g of isotactic polypropylene granules were then evenly spread on the mold when it was still in the oven. The mold and its content were kept in the oven for 10 more minutes for the granules to melt. After the granules had melted, the mold was either clamped when still in the oven or quickly removed from the oven and taken to the pressing machine. For the cases where the mold was clamped, the following treatments were done:

Case I acetone/Dry ice quenching

The mold and its contents were quickly placed into a mixture of acetone, dry ice and tap water whose temperature was below -20°C . The mold cooled to a temperature of -10°C which took about two minutes. It was then removed from the mixture and the film tested for at room temperature which was about 26°C . The samples were termed as acetone-dry ice quenched. (A/Q).

Case II - Tap water quenching

The mold and its contents were quickly placed into tap water whose temperature was 20°C. The water was kept flowing to prevent a high rise in temperature due to the heat lost by the mold. The cooling to room temperature took about eight (8) minutes. These samples were termed as tap water quenched (T/Q).

Case III - Air cooling

The mold and its contents were placed on the bench in the open air and allowed to cool normally. The cooling from the melting to room temperature took about 1½ hrs. The samples were termed as air cooled (A).

Case IV - Insulation/Air cooling

The mold and its contents were placed in the insulated box and allowed to cool slowly. The cooling from the melting to room temperature took about 4½ hours. These were termed as insulation/Air cooling (I/A).

Case V - Tap water quenching & annealing

Some of the samples in case II were annealed at 125°C for 16 hours. The oven was switched off and the annealed samples allowed to cool in there. These samples were termed as quenched and annealed (A/An).

The films made using the pressing machine were subjected to a pressure of 25 tons per square inch. They were allowed to cool to room temperature under this pressure. These films were then divided into two sets and subjected to the following heat treatment:

Set I: The films were annealed for a fixed time of three hours at different temperatures of 50°C , 75°C , 100°C , 125°C and 145°C .

Set II: The films were annealed at a fixed temperature of 125°C for different times of 1 hour, 3 hours, 6 hours, 16 hours, 22 hours and 48 hours. After these heat treatments, the samples were reserved for degree of crystallinity measurements and the tensile test.

4.2.2 Determination of Degree of Crystallinity

There are many methods for estimating the degree of crystallinity of polymeric materials. The principal ones are: Density method {42}, Nuclear magnetic resonance method {43}, Differential thermal analysis {44}, Differential scanning calorimetry {45}, The infrared spectroscopy {46}, and the X-ray diffraction method {47}. Detailed explanation of the methods can be obtained in the given references. In this study X-ray method was used because of the ease of availability of equipment.

The X-ray diffraction pattern of a semi-crystalline polymeric material shows sharp peaks superimposed on a broad diffuse scattering region. The sharp peaks are due to the periodic structure (crystalline regions) that scatter the X-ray coherently, while the broad region is due to unperiodic structure (amorphous regions) of the sample. This method assumes that the total area under the sharp peaks is proportional to the total intensity scattered by the crystalline regions which in turn is proportional to the mass of the sample in the crystalline phase. The assumption applies to the broad diffuse scattering region and amorphous phase also. The calculation of the degree of crystallinity of a polymeric material uses these areas of the sharp peaks and the broad diffuse scattering regions. From each film of the variously heat treated samples, a specimen of typical dimensions 4cm x 2.5cm x 0.5mm was cut. This was fixed on a glass slide of 5.0 x 3.0cm x 1.0mm using cello tape along the edges. The glass slide acted as a specimen holder. This was then mounted in the diffractometer and scanned from $2\theta = 5^\circ$ to $2\theta = 31^\circ$. The diffraction patterns obtained for different specimens are shown in the result section.

The diffraction patterns of isotactic polypropylene are expected to show four main peaks superimposed on a broad diffuse scattering [14]. The peaks occur at

- (i) $2\theta = 14^\circ$ (due to diffraction in the (110) plane
- (ii) $2\theta = 16.8^\circ$ (due to diffraction in the (040) plane
- (iii) $2\theta = 18^\circ$ (due to diffraction in the (130) plane
- (iv) $2\theta = 21.5^\circ$ (due to diffraction in either the
(111), (140) or (131) planes.

In calculating the degree of crystallinity the diffraction patterns were resolved into three zones. According to Herman[48] a straight line is drawn from $2\theta = 7^\circ$ to $2\theta = 29^\circ$. This separates from the amorphous curve the contribution of the scattered radiation, on account of thermal agitation and incoherent radiation (White and Compton radiation). The zone below this base line is neglected in the calculation of crystallinity because it is not from either amorphous or crystalline phases. The zone above the base line was resolved into the amorphous halo and sharp crystalline peaks. This was done using the method suggested by Natta and Corradini[49] for the polypropylene crystallinity measurement.

The method suggests that the maximum intensity of the amorphous halo is taken to be equal to the minimum intensity between the peaks (110) and (040). This lies at the angle $2\theta = 16.3^\circ$. It coincides with the angle at which the maximum of the diffraction curve of a wholly amorphous sample occurs(48). In order to plot as exactly as possible the amorphous curve in the

region of maximum intensity, Kakundo and Ullman {50} suggested the plotting of a symmetrical amorphous curve about the maximum intensity. This method was also confirmed by Aggarwall, and Tilley {51} and Venk {52}. It is the method that was used to resolve the diffraction patterns in this study; (see the resolved regions in the result section Fig. 7, 8 & 9).

After resolving the diffraction patterns, the area of each region was estimated using the planimeter. Appropriate factors were applied to each peak to correct for atomic scattering, absorption, temperature and diffraction angle (polarization factor) so as to equalize the scattering power of different peaks. The total radiation diffused by the sharp peaks in the polypropylene diffraction pattern {47} is given by Equation 4.1.

$$C=3.06A_{(110)}+5.18A_{(040)}+6.98A_{(130)}+3.10A_{(111)(140)(131)} \dots\dots\dots 4.1$$

The numerical values are the correction factors while $A_{(hkl)}$ denote the area of the peak from the reflection in the (h k l) plane. The contribution of the amorphous region is given as $6.21A_a$ where A_a is the area under the amorphous curve. The percentage of crystallinity was calculated from the equation {53},

$$\chi = \frac{C}{C+6.21 A_a} \times 100 \dots\dots\dots 4.2$$

4.2.3 Tensile Tests

The tensile strength and the Young's modulus of the variously heat treated samples were determined with a Hounsfield Tensometer.

From the sheets where the specimen for crystallinity measurements were cut, dumbbell shaped specimens were marked and carefully cut using a sharp penknife.

Typical dimensions of the specimen within the gauge length of 5cm were of a thickness of 0.5mm and a width of 13.50mm. The thickness and width were measured to an accuracy of ± 0.02 mm. When mounting the test specimen in the gripping system, the following precautions were taken. The insertion of the test piece was aligned in the direction of strain to avoid any bending or shearing component. To ensure that the specimen was held without any slippage, an emery paper was inserted between the jaw face of the grip and the test specimen, with the rough paper surface facing the test specimen. The tensometer was motorized and a force-elongation curve plotted. The curves are shown in the result section.

From the force-elongation curve, the maximum load was obtained. The tensile strength was calculated from equ. 43.

$$\text{Tensile Strength} = \frac{\text{maximum load}}{\text{cross-section area (Nominal)}} \dots\dots\dots 4.3$$

The load-elongation curves contain the deflection of the loading beam of the machine. To get the true specimen extension, this machine deflection must be subtracted from the force-elongation curves. The machine deflection was determined by inserting a 7mm diameter high tension steel rod in place of the specimen in the tensometer and loading up to the capacity of the loading beam. This gave a steep straight line (machine characteristic line) whose deflection was subtracted from the curve of each specimen. The Young's modulus was calculated from equ. 4.4.

$$\text{Young's modulus (E)} = \frac{\text{Stress}}{\text{Strain}} \dots\dots\dots 4.4$$

From the load-elongation curve,

$$\text{Young's modulus E} = \frac{\Delta F}{\Delta l} \cdot \frac{l}{A} \dots\dots\dots 4.5$$

where $\Delta F/\Delta l$ is the slope of the linear section of the load-elongation curve, l is the gauge length of the specimen and A is the nominal cross-section area of the specimen in the gauge length.

4.2.4 Density Measurement

The set of samples whose density was evaluated was that annealed at 125°C for different periods of time. The films were cut into small pieces that could fit into 50ml specific gravity bottle. The empty bottle was weighed and the mass denoted as ω_1 . These film pieces were put into the density bottle and the mass

taken again (ω_2). The bottle was partially filled with distilled water and then connected to a vacuum pump for 10-15 min to evacuate any entrapped air. The half filled bottle was then completely filled with distilled water and reweighed ω_3 . The bottle was emptied of its content and filled with distilled water only (ω_4).

The density was calculated from the equation

$$\text{Density} = \frac{\omega_2 - \omega_1}{(\omega_4 - \omega_1) - (\omega_3 - \omega_2)} \quad \dots\dots\dots 4.6$$

CHAPTER FIVE

Experimental Results and Discussion

5.0 Introduction

From the samples subjected to varying cooling rates and annealing treatments specimens were cut for the determination of degree of crystallinity and tensile tests. Several crystallinity measurements and tensile test measurements were made but only some representative diffraction patterns and load-extension curves have been included in the result section. The density was determined for only those samples that were annealed for different periods of time at 125°C.

5.1 X-ray Diffraction Patterns

The diffraction patterns obtained after scanning the samples using the X-ray diffractometer are shown in the following figures.

- (i) Figures 7(a-c) are the patterns of the samples cooled at different rates.
- (ii) Figures 8(a-c) are the patterns of the samples compression molded and annealed at different temperatures for equal annealing time of three hours.
- (iii) Figures 9(a-c) are the patterns for the samples

annealed at a temperature of 125°C for different periods of annealing time.

All the patterns show four main peaks in the scan range done from $2\theta=5^{\circ}$ to $2\theta=31^{\circ}$. The peaks are approximately at $2\theta=14^{\circ}$ (A), $2\theta=16.8^{\circ}$ (B), $2\theta=18.5^{\circ}$ (C) and $2\theta=21.5^{\circ}$ (D).

It was observed that for the air cooled samples, insulated box cooled samples, and annealed samples, the peaks positions shifted slightly towards bigger values of 2θ as compared with the quenched or unannealed samples. The maximum shift was about 0.1° . Quenching the samples in either acetone dry ice mixture or tap water at room temperature did not split peak D (Fig. 7a) as was the case in the slowly cooled samples patterns (Fig. 7b). Quenching in tap water at room temperature followed by air annealing showed peak D as a doublet and improved the sharpness (Fig. 7c). In the samples annealed at different temperatures the peaklets of peak D become sharper as the annealing temperature was raised.

In the samples that were molded with the compression machine, there appears a small peak at $2\theta=16^{\circ}$ splitting from the peak at $2\theta=16.8^{\circ}$ in the unannealed sample (Fig. 8a). This peak's intensity decreases with the increase in the annealing temperature, and with increase in the annealing time. Annealing at

125°C and 145°C for three hours got rid of this peak completely (Fig. 8c & 9c). In general all the peaks became sharper as the annealing temperature was raised. The samples annealed at 125°C for different periods of times showed similar features to those that were annealed at different temperatures.

5.2 The Tensile Test Curves

The load-extension curves obtained for different specimens are shown in the following figures:

- (i) Figures 10(a-c) show the curves for samples cooled at different rates.
- (ii) Figures 11(a-c) show the curves for samples annealed at different temperatures for three hours.
- (iii) Figures 12(a-c) show the curves for samples annealed at different periods of time at a constant annealing temperature of 125°C.

The curves for the quenched samples (Fig. 10a) and the unannealed samples (Fig. 11a) show more necking tendency than the rest of the curves. A tendency towards brittle failure is observed when either annealing temperature was raised, or annealing time was increased or the cooling rate was reduced. The curves are varying in the vertical scale. This is

because of the differences in their cross-sectional area, in addition to the effect of the different thermal treatment.

5.3 Degree of Crystallinity

After resolving the diffraction patterns as is explained in section 4.2.2, the areas of different regions were obtained using the planimeter. With these areas the degree of crystallinity of the samples was calculated using equations 4.1 and 4.2. The results obtained are as shown in the tables below.

Table 1. Percentage crystallinity of samples cooled at different rates

Sample Treatment	Mean percentage Crystallinity
Quenched in acetone/dry ice mixture	41.9 ± 0.3
Quenched in tap water	44.4 ± 0.6
Air cooled	47.3 ± 0.3
Cooled in an insulated box	49.9 ± 0.3
Quenched in tap water & Annealed	55.5 ± 0.5

Table 2. Percentage crystallinity of samples annealed at different temperatures for 3 hours.

Sample Treatment	Mean Percentage Crystallinity
Not annealed	48.2 ± 0.8
Annealed at 50°C for 3 hours	50.3 ± 0.2
" " 75°C " "	52.7 ± 1.0
" " 100°C " "	55.5 ± 0.4
" " 125°C " "	58.8 ± 0.5
" " 145°C " "	63.9 ± 0.9

Table 3. Percentage crystallinity of samples annealed at a fixed temperature of 125°C for different times.

Sample Treatment	Mean Percentage Crystallinity
Not annealed	48.2 ± 0.8
Annealed at 125°C for 1 hour	53.8 ± 0.2
" " " " 3 "	56.9 ± 0.5
" " " " 16 "	60.8 ± 0.3
" " " " 22 "	63.2 ± 0.8
" " " " 48 "	65.2 ± 0.3

5.4 Tensile Strength and Young's Modulus

From the measurements of the thickness and width of the specimen in the gauge length, the cross-section area was calculated. Using the load-extension curves and equations 4.3 and 4.5, the tensile strength and the Young's modulus of the specimens were determined. The results obtained are summarized in the tables below.

Table 4. Tensile strength and Young's modulus of specimen cooled at different rates.

Sample Treatment	Mean Tensile Strength $\times 10^7$ N/m ²	Mean Young's Modulus $\times 10^8$ N/m ²
Quenched in acetone/dry ice mix	1.66 \pm 0.05	2.51 \pm 0.21
Quenched in tap water	1.71 \pm 0.03	3.01 \pm 0.15
Air cooled	1.83 \pm 0.12	3.65 \pm 0.27
Cooled in an insulated box	1.99 \pm 0.10	4.68 \pm 0.27
Quenched in tap water & Annealed	2.27 \pm 0.11	5.34 \pm 0.32

Table 5. Tensile strength and Young's modulus of samples annealed at different temperatures for 3 hours.

Sample Treatment	Mean Tensile Strength $\times 10^7$ N/m ²	Mean Young's Modulus $\times 10^8$ N/m ²
Not annealed	2.36 \pm 0.05	3.08 \pm 0.15
Annealed at 50°C for 3 hours	2.47 \pm 0.05	4.01 \pm 0.06
" " 75°C " "	2.64 \pm 0.11	4.44 \pm 0.16
" " 100°C " "	2.85 \pm 0.05	4.91 \pm 0.10
" " 125°C " "	2.87 \pm 0.14	5.08 \pm 0.12
" " 145°C " "	3.00 \pm 0.38	5.14 \pm 0.21

Table 6. Tensile strength and Young's modulus of samples annealed at a fixed temperature of 125°C for different time intervals.

	Mean Tensile Strength x 10 ⁷ N/m ²	Mean Young's Modulus x 10 ⁸ N/m ²
Not annealed	2.36 ± 0.05	3.08 ± 0.15
Annealed at 125°C for 1 hr	2.59 ± 0.08	3.79 ± 0.04
" " " " 3 hrs	2.88 ± 0.20	4.00 ± 0.14
" " " " 6 hrs	3.00 ± 0.06	4.30 ± 0.15
" " " " 16 hrs	2.95 ± 0.09	4.34 ± 0.06
" " " " 22 hrs	2.61 ± 0.15	4.48 ± 0.22
" " " " 48 hrs	2.83 ± 0.05	3.71 ± 0.12

5.5 Density Measurements

The density of the samples annealed at 125°C for different periods of time were determined using equation 4.6. The results obtained are shown in table 7.

Table 7. Density of samples annealed for different times.

Sample Treatment	Mean Density g/cm ³
Not annealed	0.8911
Annealed for 1 hr at 125°C	0.8937
" " 3 hrs " "	0.8968
" " 6 " " "	0.8995
" " 16 " " "	0.9044
" " 22 " " "	0.9024
" " 48 " " "	0.9048

The table shows that there is a slight increase in the mean density with an increase in annealing time. This is in agreement with the crystallinity results obtained for the sample. This is expected result because degree of crystallinity is proportional to the density of the sample.

5.6 Discussion

One of the observations made in the diffraction patterns was the slight shift of the peaks and the sharpening of the peaks of samples cooled slowly. Increasing the annealing time and raising the annealing temperature had a similar effect. These observations may be attributed to increased crystallite perfections. Defects such as screw or edge dislocations, stacking disorders, chain entanglements and imperfect folds are reduced when the polymer is cooled slowly or annealed. This improves the crystal lattice and hence the planes. The slight shift of the peaks to higher values of the diffraction angle reflects this change in the plane spacing (i.e. smaller d). The samples prepared by compression molding using the press were molded at high pressures (25 tons per square inch). When polypropylene is molded at high pressures, it exhibits some triclinic form of crystallization. On annealing such samples at high temperatures the triclinic form of crystals convert into monoclinic form of crystals. It is possible that the small peak at $2\theta=16.8^\circ$ which disappeared on annealing the samples at 125°C and 145°C indicated the presence of triclinic form of crystallization in the unannealed samples. This may be confirmed by X-ray study of the crystallite form of the unannealed samples and those annealed at 125°C and 145°C for three hours and over.

Table 1 shows that quenched samples had the least X-ray

determined degree of crystallinity. The trend of the increase in degree of crystallinity with respect to the cooling conditions is as expected from the theory. Fast cooling (quenching) does not give the polymer melt enough time for the molecular chains to organize in an orderly fashion (crystallize) and therefore the degree of crystallinity of such samples is less than that of slowly cooled samples, in which the melt has a longer time for molecules to arrange themselves in a crystalline form. The samples that were quenched and annealed show the highest degree of crystallinity. This may have resulted from the recrystallization of the material when residual strains, nonequilibrium crystals and defects such as point dislocations, acquired during the fast crystallization in quenching, are eliminated in the annealing treatment. Figure 13 shows the relationship between the degree of crystallinity and the annealing temperature. A probable reason for the linear relation would be that when the annealing temperature is raised, there are higher chances of more defective regions in the material to be eliminated and give way to crystalline regions. Recrystallization of the amorphous regions in the sample also increases as the annealing temperature is raised. From the differences in values of crystallinity obtained by X-ray diffraction and thermal analysis methods on Ethylene-propylene samples, Gilbert and Briggs {23} argued that there were some

crystallite sizes that the X-ray scattering may not distinguish from that of amorphous materials. Probably on annealing the samples the small crystals undergo a thickening process and reach a size detectable by X-ray as a crystalline phase, and hence the increasing crystallinity with the annealing temperature.

A plot of the degree of crystallinity against annealing time is shown in figure 14. The percent crystallinity does not increase linearly with annealing time. The percentage crystallinity reaches a certain asymptotic value when annealed at a temperature of 125°C. A plot of the density against annealing time for the same samples gave a similar curve (Fig. 15). This confirms the crystallinity-annealing time graph because the crystallinity is proportional to density. This observation could be explained by the fact that for a given annealing temperature there is a thermodynamically stable number of defects and amorphous regions that will not recrystallize. Further more the establishment of the thermodynamic equilibrium from the metastable condition by annealing takes a finite time. Once the equilibrium between the crystallized and uncrystallized phases is attained, further annealing will not have any effect. This is why the degree of crystallinity reaches an asymptotic value after a certain period of annealing. Similar observations were made ^{by} Howard {54} on the density of shock cooled polyethylene stored at a temperature of 70°C.

To establish the relationship between the tensile strength and Young's modulus with the degree of crystallinity the following graphs were plotted.

- (i) Tensile strength against per cent crystallinity for samples cooled at different rates (Fig. 16).
- (ii) Young's modulus against per cent crystallinity for samples cooled at different rates (Fig. 17).
- (iii) Tensile strength against per cent crystallinity for samples annealed at different temperatures for 3 hours (Fig. 18).
- (iv) Young's modulus against per cent crystallinity for samples annealed at different temperatures for 3 hours (Fig. 19).
- (v) Tensile strength against per cent crystallinity for samples annealed for different periods of time at 125°C (Fig. 20).
- (vi) Young's modulus against per cent crystallinity for samples annealed for different periods of time at 125°C (Fig. 21).

Straight line graphs were obtained for the samples cooled at different rates (Fig. 16 and 17). The linear graphs show that the tensile strength and Young's modulus are linearly related to the degree of crystallinity of the samples. Tensile strength versus degree of crystallinity gave a correlation coefficient

(γ) of 0.99 and Young's modulus versus degree of crystallinity gave a correlation coefficient of 0.98. This shows that for samples cooled at different rates both tensile strength and Young's modulus are positively and highly correlated to the degree of crystallinity.

A possible reason would be that the crystallites are acting as effective reinforcements of the bulk material. In that case higher degree of crystallinity would mean higher extent of reinforcement and therefore more improved mechanical properties of the bulk polymer. Considering the theory of the molecular chain interactions, the forces of interaction in the crystalline phase are found to be not only of short range order but also of long range order while only the short range order forces dominate the amorphous phase. It is therefore expected to be easier to deform an amorphous material than a crystalline material. This is what the experimental results do confirm. Though the samples might have been having crystallites of different sizes and morphology due to the difference in cooling rates the results show that the extent of crystallization had a greater effect on the mechanical properties than the structure of the crystallites present in the specimens.

In the samples annealed at different temperatures and different annealing times, the tensile strength and

Young's modulus do not show a linear relationship with the degree of crystallinity in the whole range of degree of crystallinity measured. Those annealed at different temperatures at a fixed time showed a linear relationship below 56% crystallinity (Fig. 18 and 19). This range of per cent crystallinity corresponds to an annealing temperature of 100°C and below. Samples annealed for different periods of time at a fixed temperature of 125°C showed a linear relationship between the mechanical properties and per cent crystallinity below 61% crystallinity. This range corresponds to an annealing period of below 16 hours (Fig. 20 and 21). Above these values of crystallinity, the tensile strength and Young's modulus increase gradually and finally decrease. For the samples annealed at different temperatures, tensile strength versus degree of crystallinity gave a correlation coefficient of 0.96 and Young's modulus versus degree of crystallinity gave a coefficient of 0.88. Samples annealed for different periods of time gave correlation coefficients of 0.63 and 0.69 for tensile strength versus degree of crystallinity and Young's modulus versus degree of crystallinity respectively. These coefficients are less than those for samples cooled at different rates. There seems to be another factor that checks the reinforcement role of crystallites in the mechanical properties of the specimens. It is

probable that at annealing temperature of above 125°C and beyond 16 hours of annealing, the annealing process develops large spherulites with interspherulitic boundaries that act as stress concentrators and thus weaken the material. Another possible reason is that the large spherulites may have left few molecules to tie the separate spherulites together. The spherulites are therefore held together largely by the secondary forces between the spherulites and thus the material is much more prone to rupture at low stresses. This is partially evidenced by the tendency towards brittle failure exhibited by the load-extension curves of the samples annealed at high temperatures and for long periods of time (Fig. 11c and 12c). Attempt to confirm this from the microscopy study using the polarized light transmission microscope failed to yield any definitive result due to the thickness of the samples.

From the theory (section 3.4), the Young's modulus of a semicrystalline polymer was given by equations 3.10 & 3.11.

$$E_{\text{specimen}} = \chi E_{\text{crystalline}} + (1-\chi) E_{\text{amorphous}} \quad \text{and}$$

$$\frac{1}{E_{\text{specimen}}} = \frac{\chi}{E_{\text{crystalline}}} + \frac{1-\chi}{E_{\text{amorphous}}}$$

These two models of mechanical properties and degree of crystallinity by Takayanagi [10] give the theoretical upper and lower bounds of the Young's modulus. Due to

lack of data for the E-purely crystalline material and E-purely amorphous for the grade of isotactic polypropylene used in this study, it was not possible to plot the theoretical curves of the studied properties to compare with the experimental curves. It is however observed that the graphs for the samples cooled at different rates would have an equation similar to the upper bound equation.

The slope of the linear sections (Fig. 17, 19 and 21) would give the Young's modulus of the crystalline phase and the intercept would give the modulus of the amorphous phase. Comparing the slopes of the three curves, they were found to be different, though expected to be the same. This indicated that different sample treatment had different crystallites or different crystallite distribution and thus the different slopes.

5.7 Conclusion and Recommendation

The measurement of the degree of crystallinity of isotactic polypropylene samples that were subjected to varying crystallization and annealing treatments were made at room temperature. The tensile tests were also carried out at room temperature. The X-ray determined per cent crystallinity and tensile test results obtained show that:

- (i) The percentage crystallinity of samples increases with reduction in cooling rate and on increasing the annealing temperature.
- (ii) Increasing the annealing time for a fixed annealing temperature resulted in a logarithmic relationship between percentage crystallinity and annealing time.
- (iii) The tensile strength and Young's modulus are linearly related to the percentage crystallinity for samples cooled at different rates.
- (iv) Samples annealed at different temperatures for a fixed period of time, and those annealed for different periods of time at fixed temperature, do not show a well defined relationship between the mechanical properties (tensile strength and Young's modulus) and percentage crystallinity in the whole range of crystallinity determined.

The observations made by correlating the mechanical properties and the degree of crystallinity demonstrate that it would not be reasonable to expect the mechanical properties of semicrystalline polymers in general and isotactic polypropylene in particular to relate simply with the measure of degree of crystallinity. It is not enough to determine only the degree of crystallinity to be able to predict the mechanical properties of the polymeric material. It is necessary to take account also of the way in which crystallinity was achieved and probably the detail of the texture of the crystallites. It is not enough to say that the higher the crystallinity, the higher the mechanical properties. The thermal history of the material which determines the nature of the crystallites is important.

The tensile strength and Young's modulus have not changed significantly in all the three sets of sample treatments. This is as a result of the narrow range of the degree of crystallinity in the sample treatment. It may be necessary to extend the crystallinity of the samples to below 40% and above 70% crystallinity.

The study focused on the effect of the quantity of crystallinity on the mechanical properties. It is recommended that further study be done on the effects of the type, size and distribution of crystallites on the mechanical properties of isotactic polypropylene. Other methods of crystallinity determination could be used to compare the results with the X-ray determined crystallinity.

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APPENDIX 1Calculation of the Correlation Coefficient Between Two Variables

The correlation coefficient measures the amount of linear relationship between two variables. For the variables x and y , the correlation coefficient (γ) is given as;

$$\gamma_{(x,y)} = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\{\Sigma(x_i - \bar{x})^2 \Sigma(y_i - \bar{y})^2\}}}$$

$$\text{where } \bar{x} = \frac{1}{n} \Sigma x_i$$

$$\text{and } \bar{y} = \frac{1}{n} \Sigma y_i$$

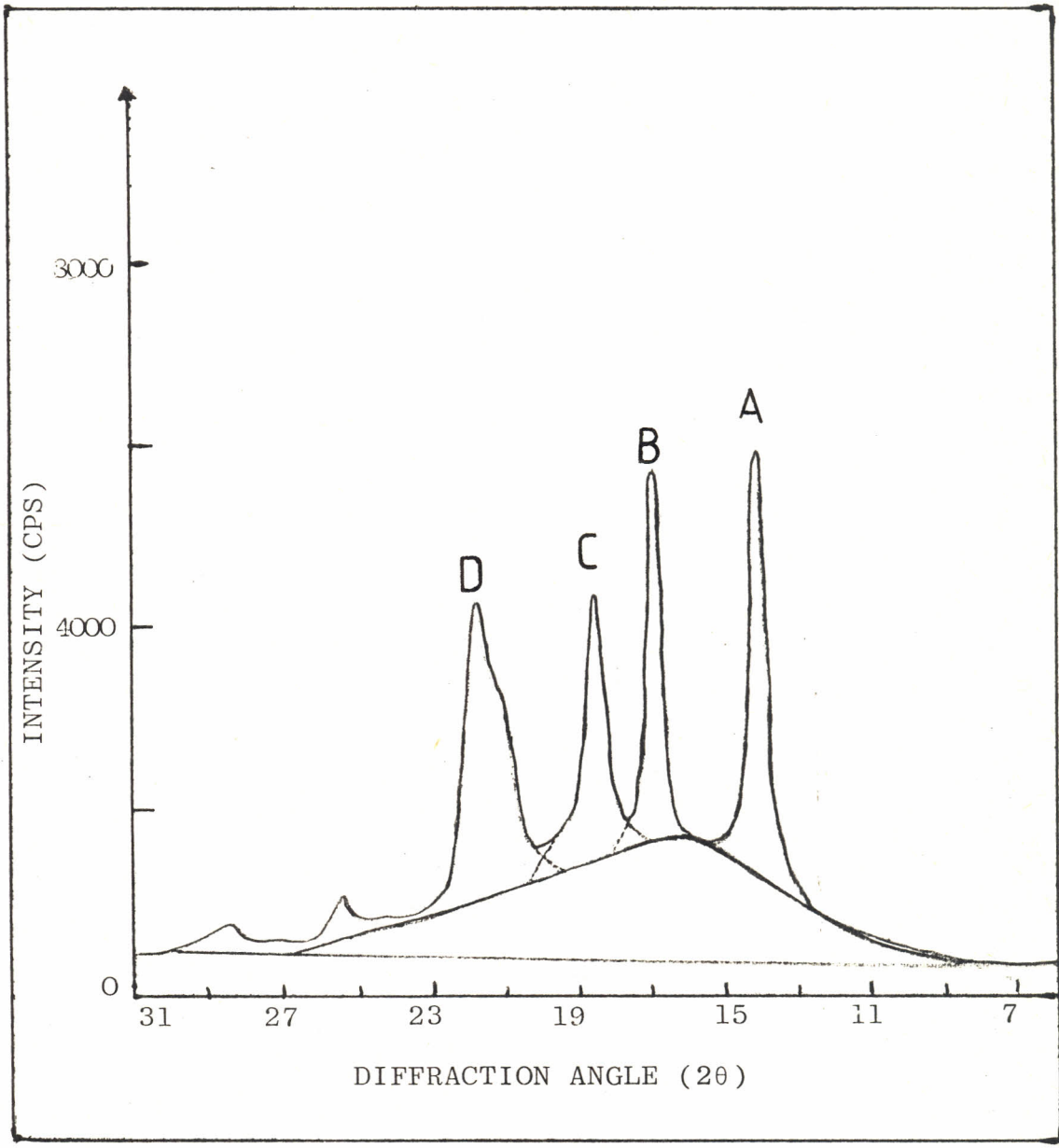


FIG 7a. Diffraction curve for sample quenched in acetone-dry ice mixture below -20°C .

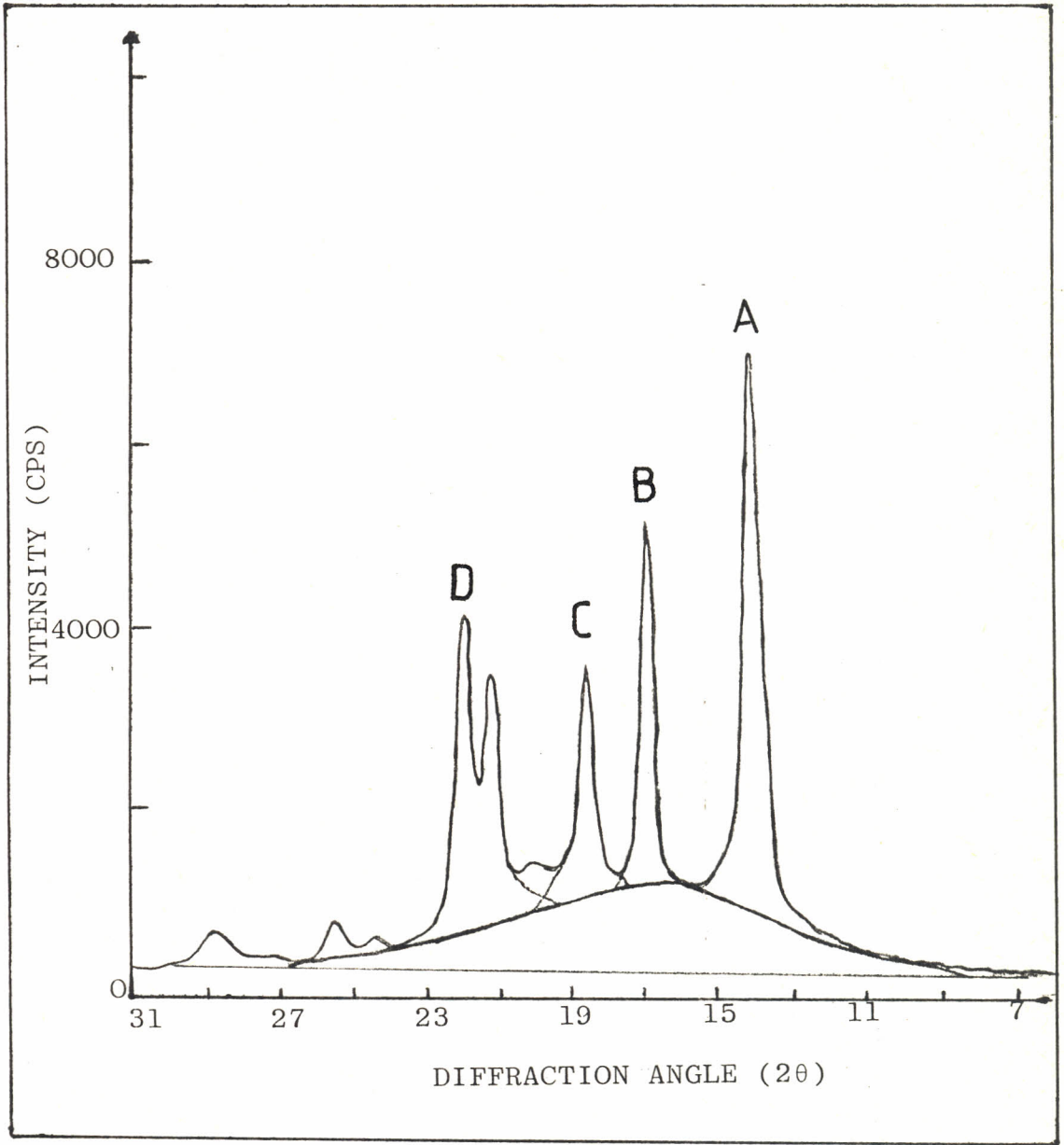


FIG 7b. Diffraction curve for sample cooled in an insulated box.

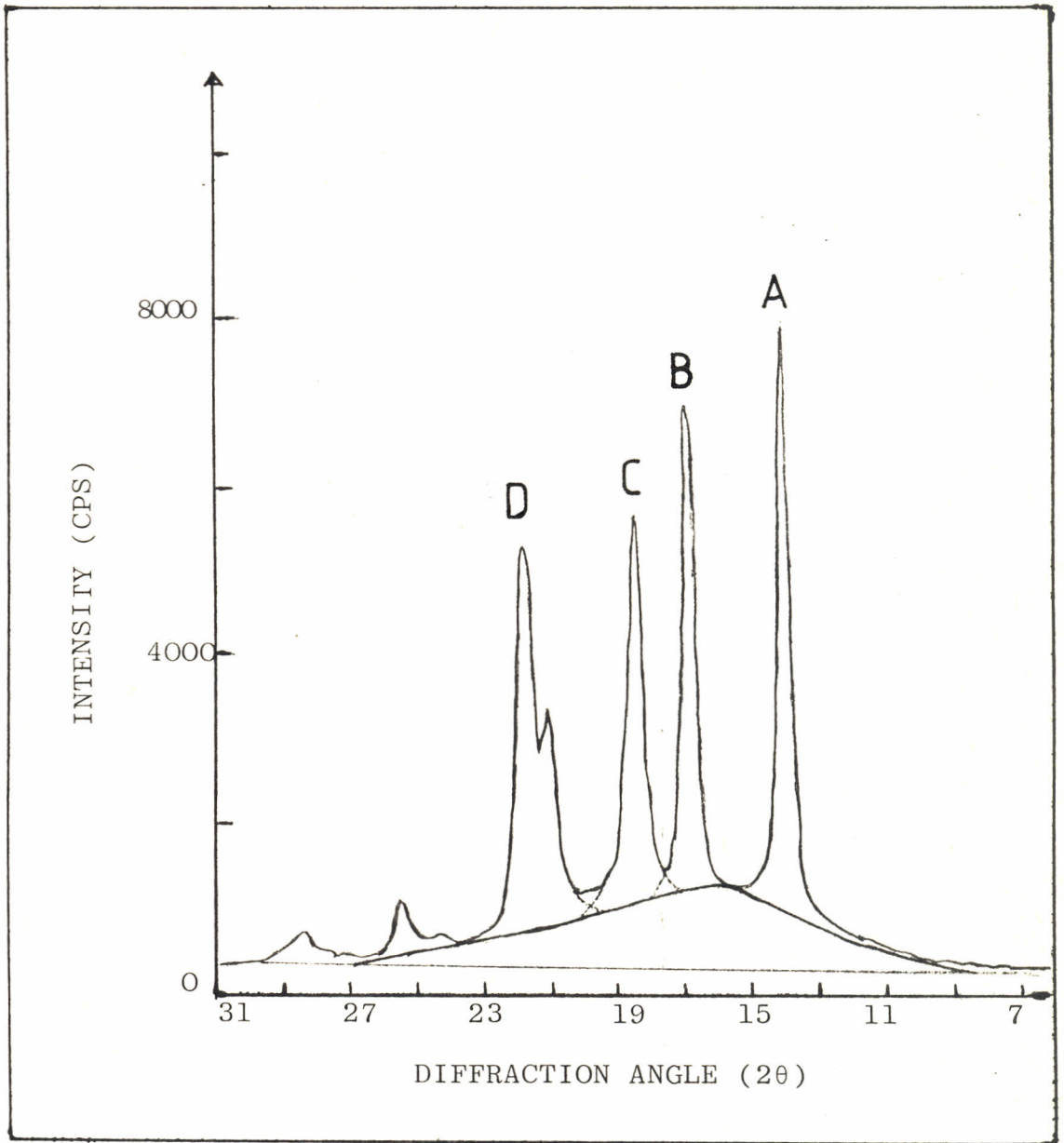


FIG 7c. Diffraction curve for sample quenched in tap water at room temperature and annealed at 125°C for 16 hours.

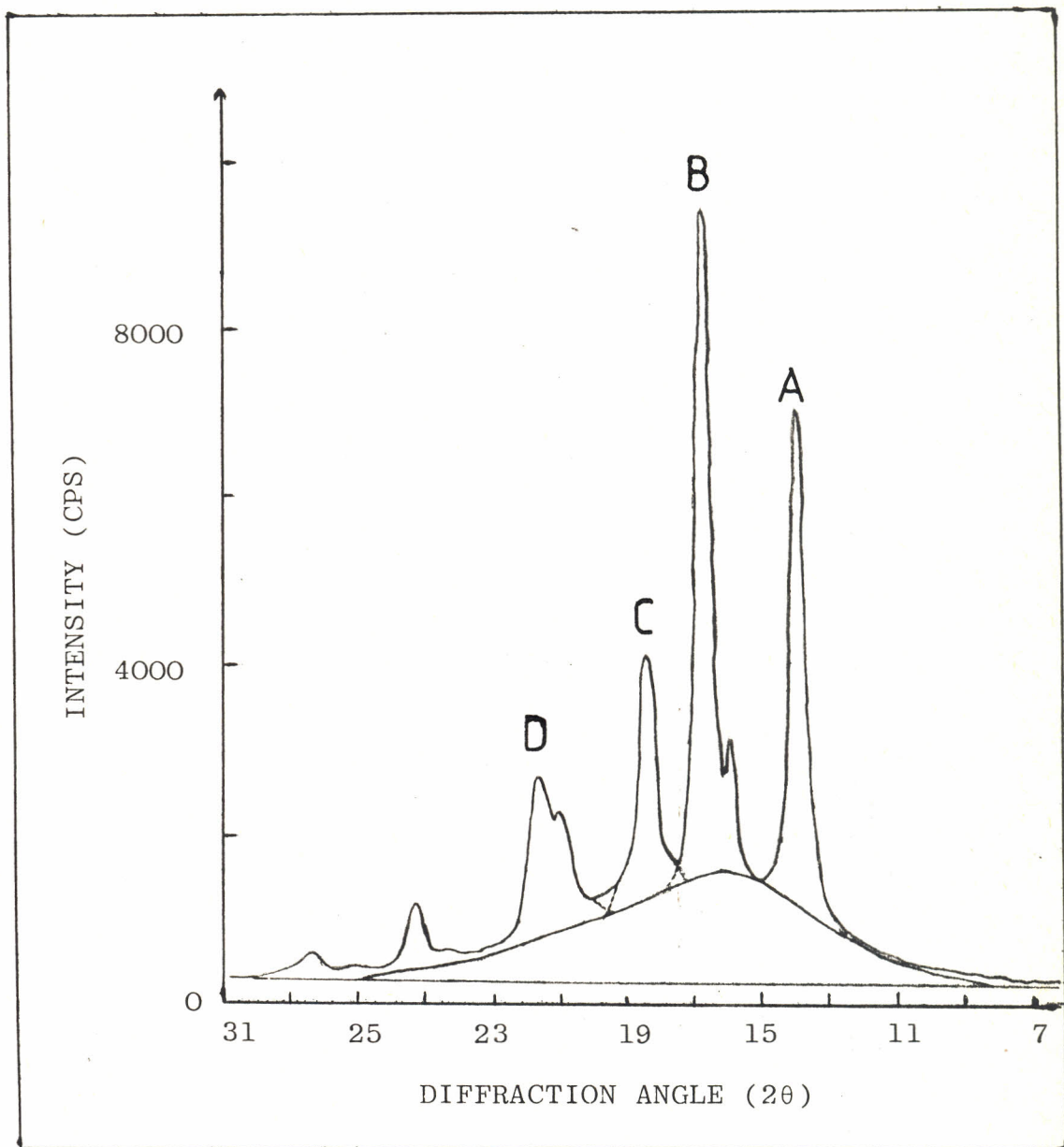


FIG 8a. Diffraction curve for sample not annealed.

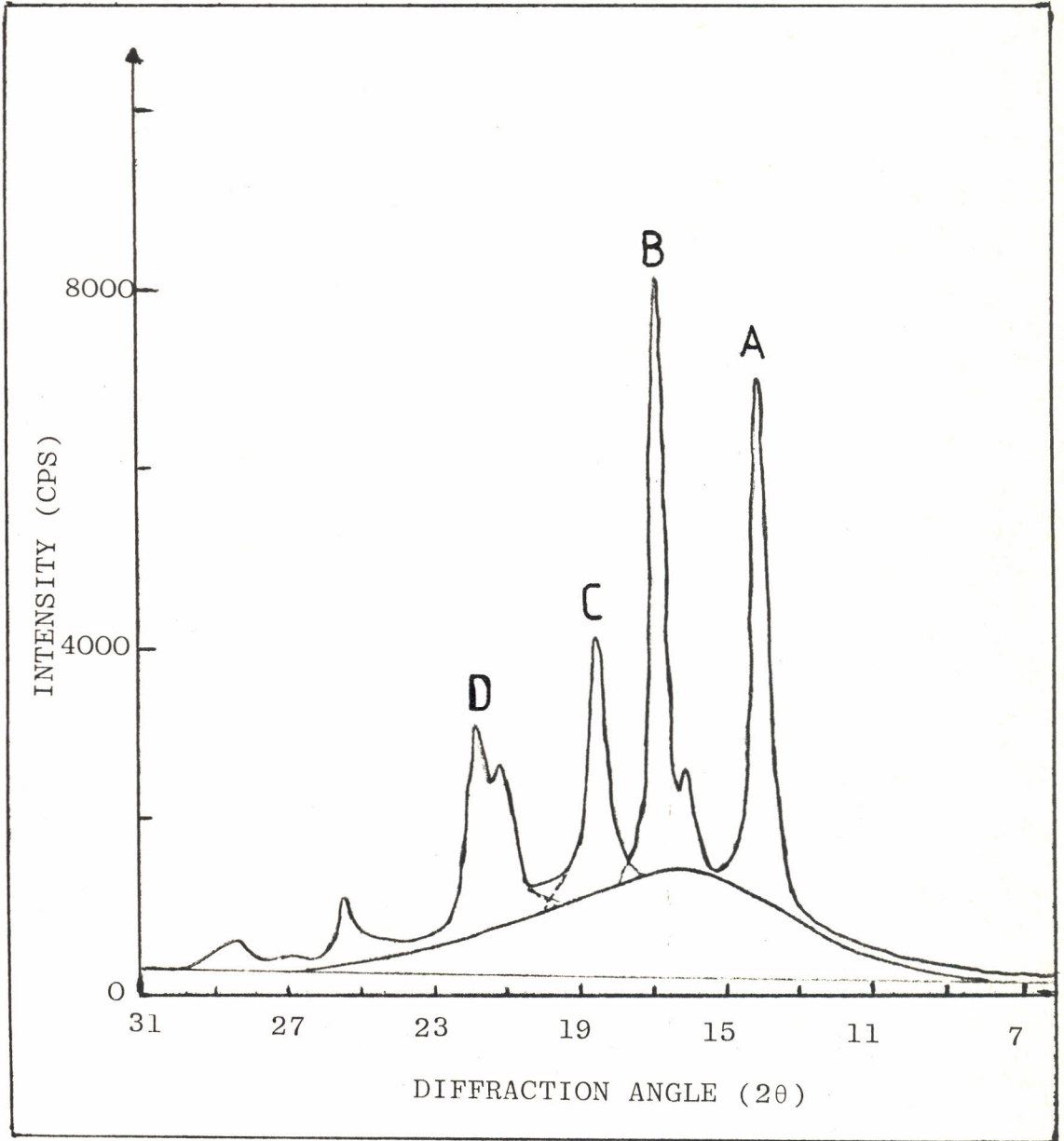


FIG 8b. Diffraction curve for sample annealed at 75°C for 3 hours.

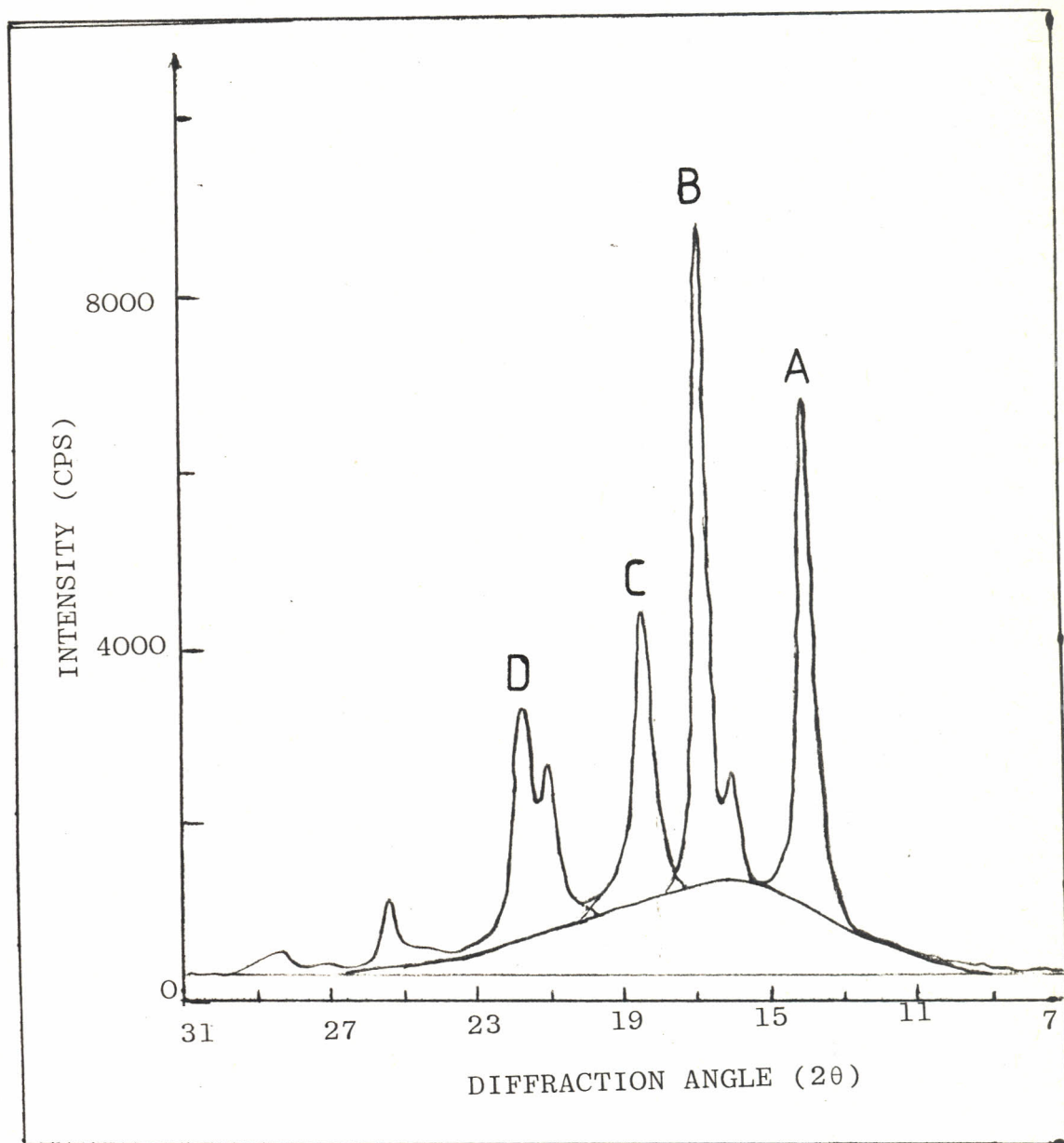


FIG 9a. Diffraction curve for sample annealed at 125°C for 1 hour.

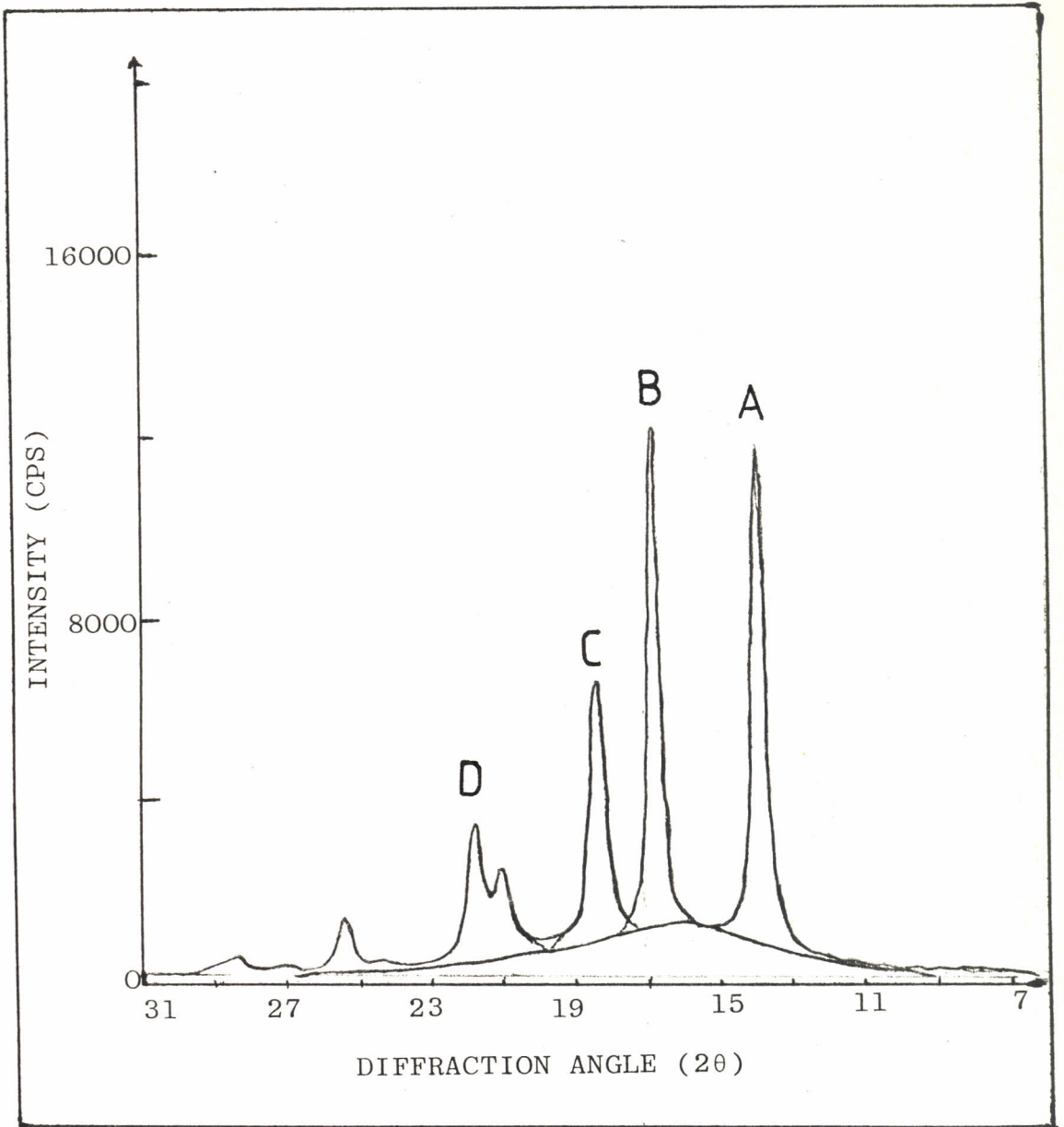


FIG 9b. Diffraction curve for sample annealed at 125°C for 16 hours.

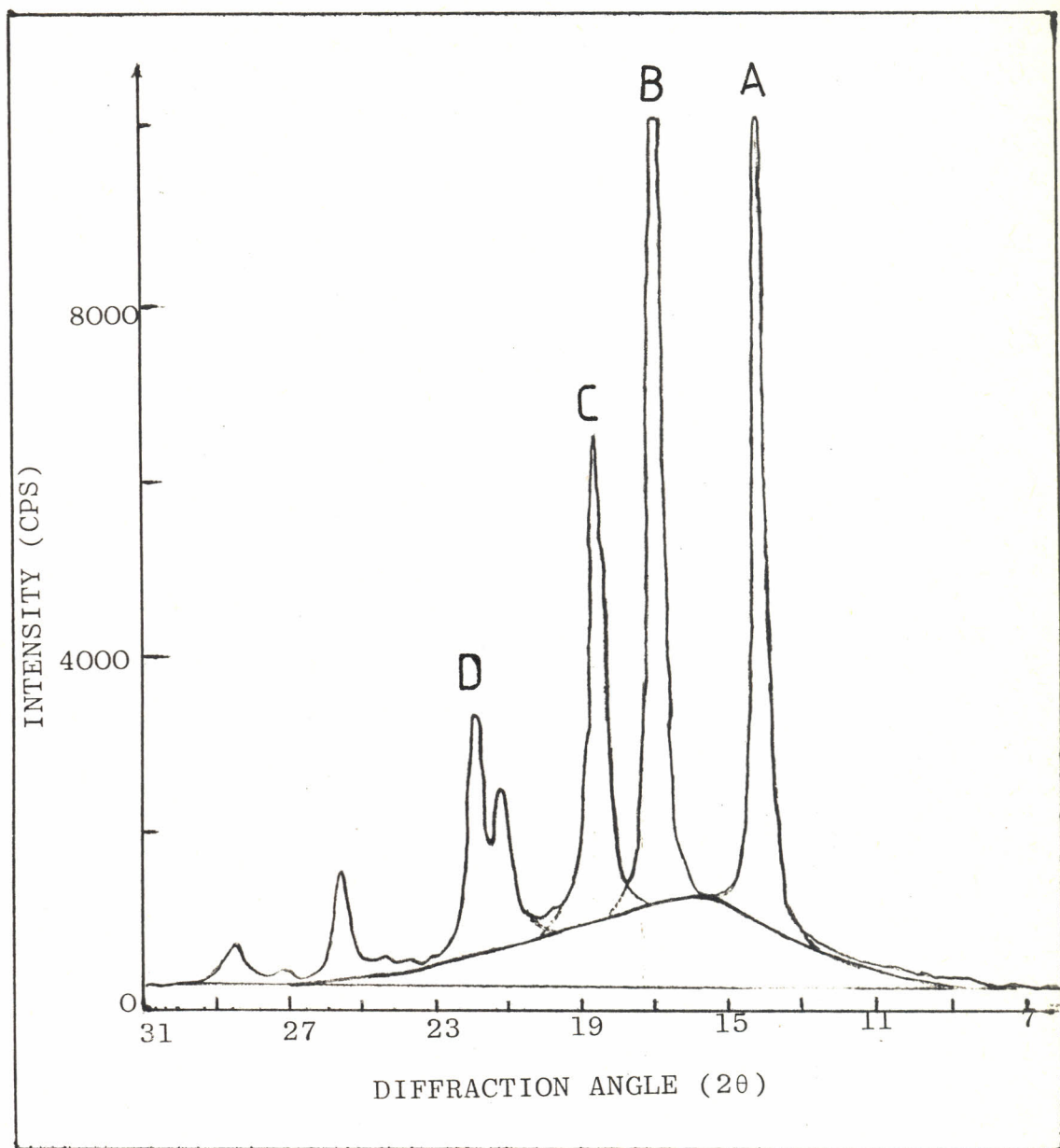


FIG 9c. Diffraction curve for sample annealed at 125°C for 22 hours.

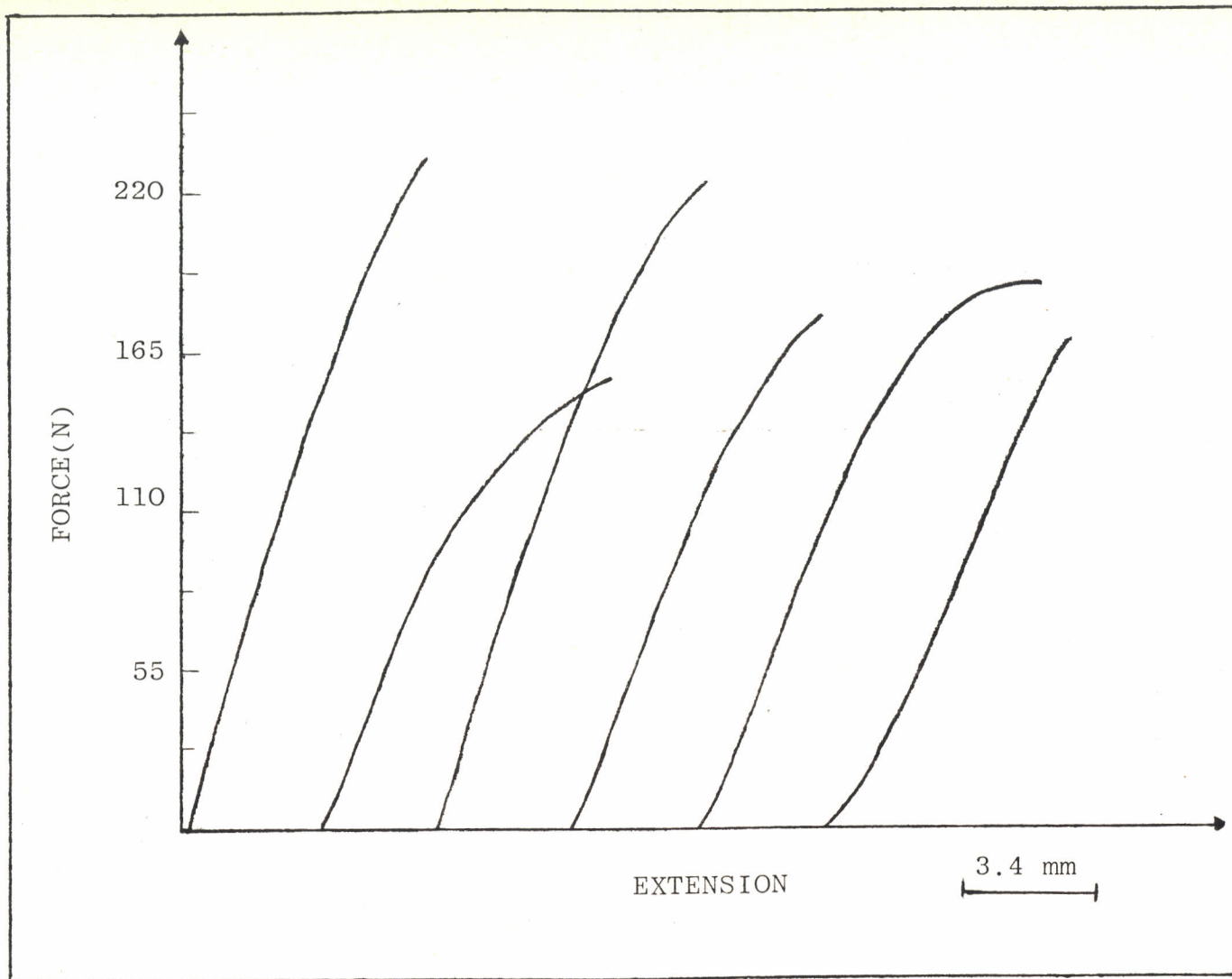


FIG 10a. Force-Extension curves for samples quenched in tap water.

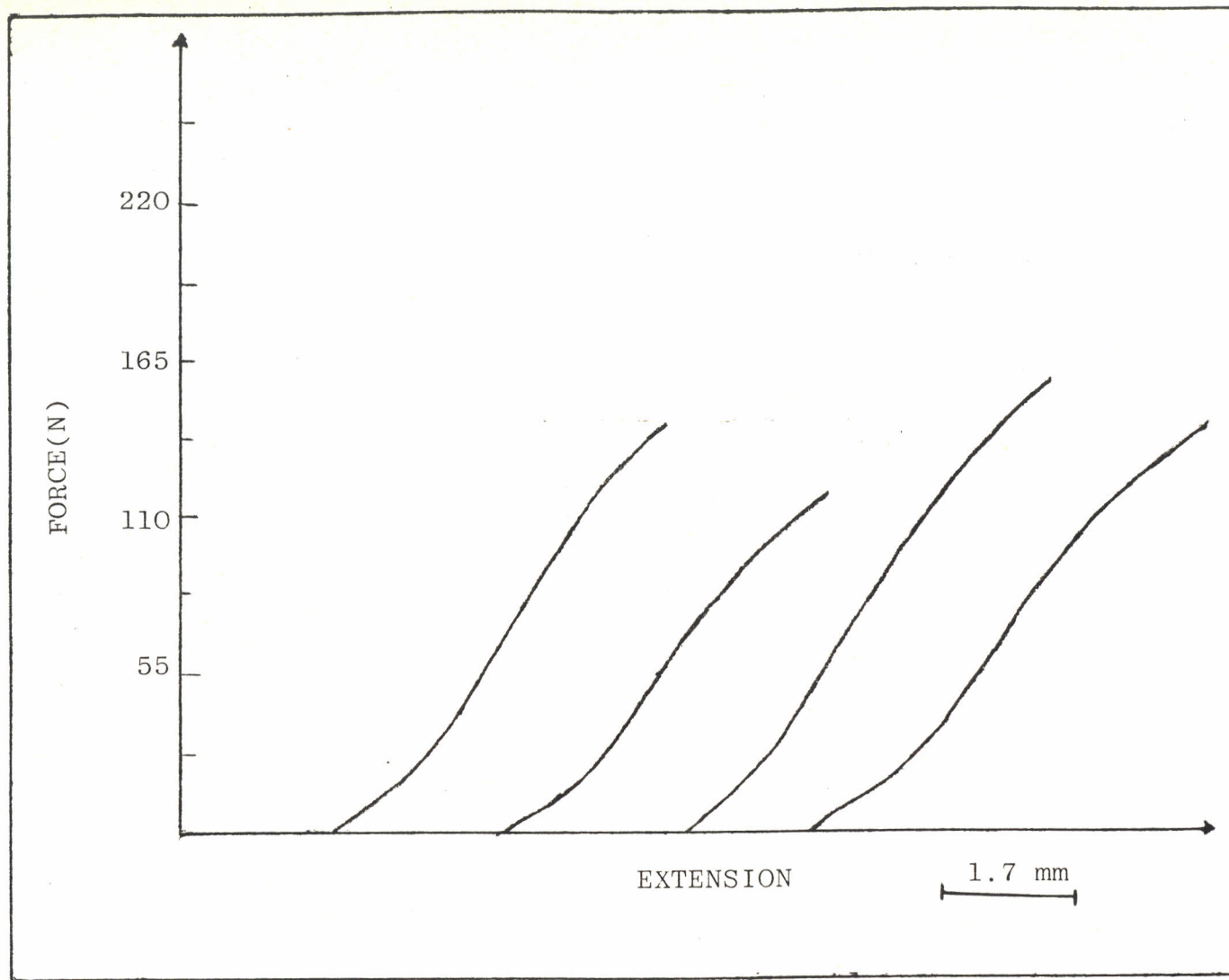


FIG 10b. Force-Extension curves for samples cooled in an insulated box.

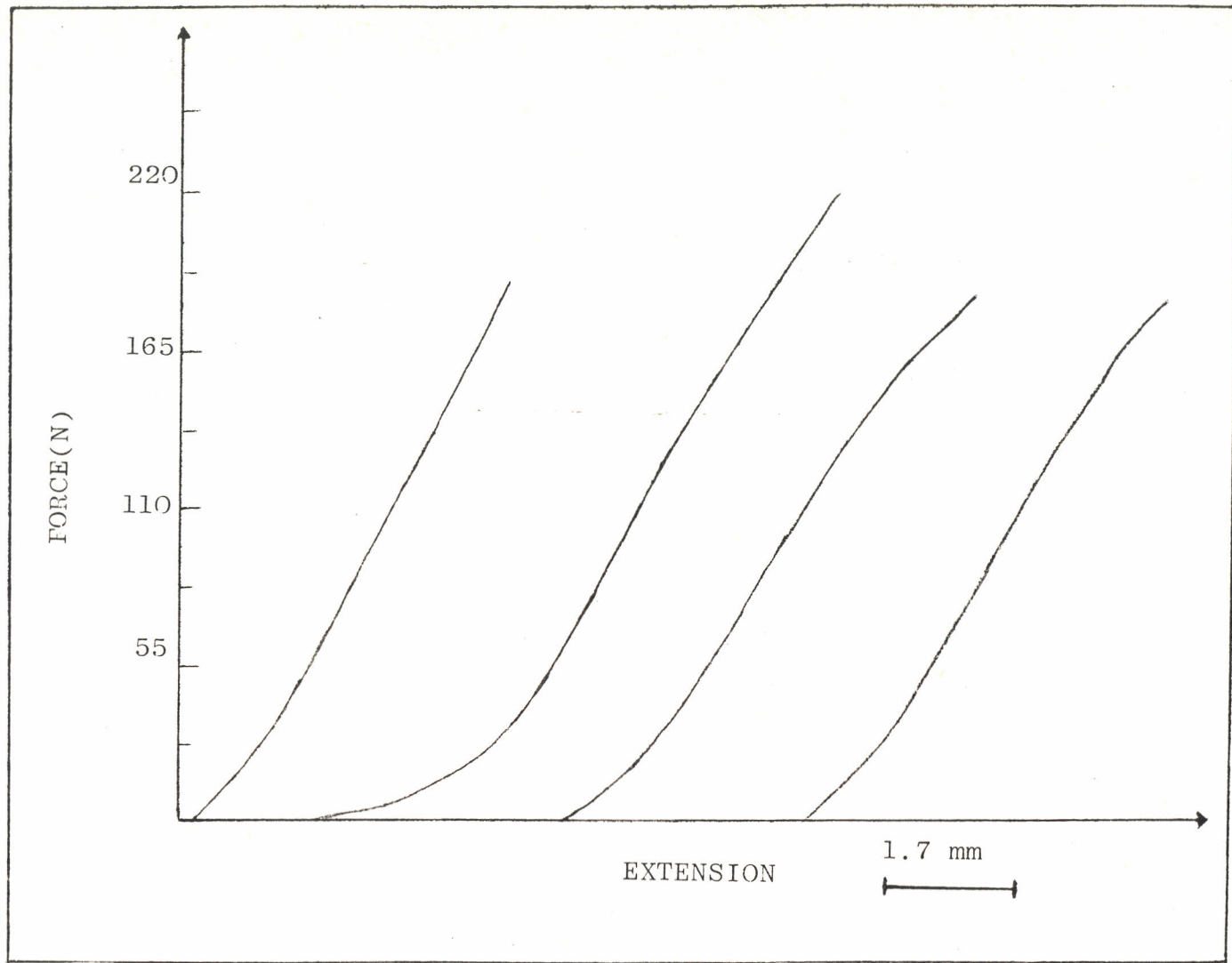


FIG 10c. Force extension curves for samples quenched in tap water and annealed at 125°C for 16 hours.

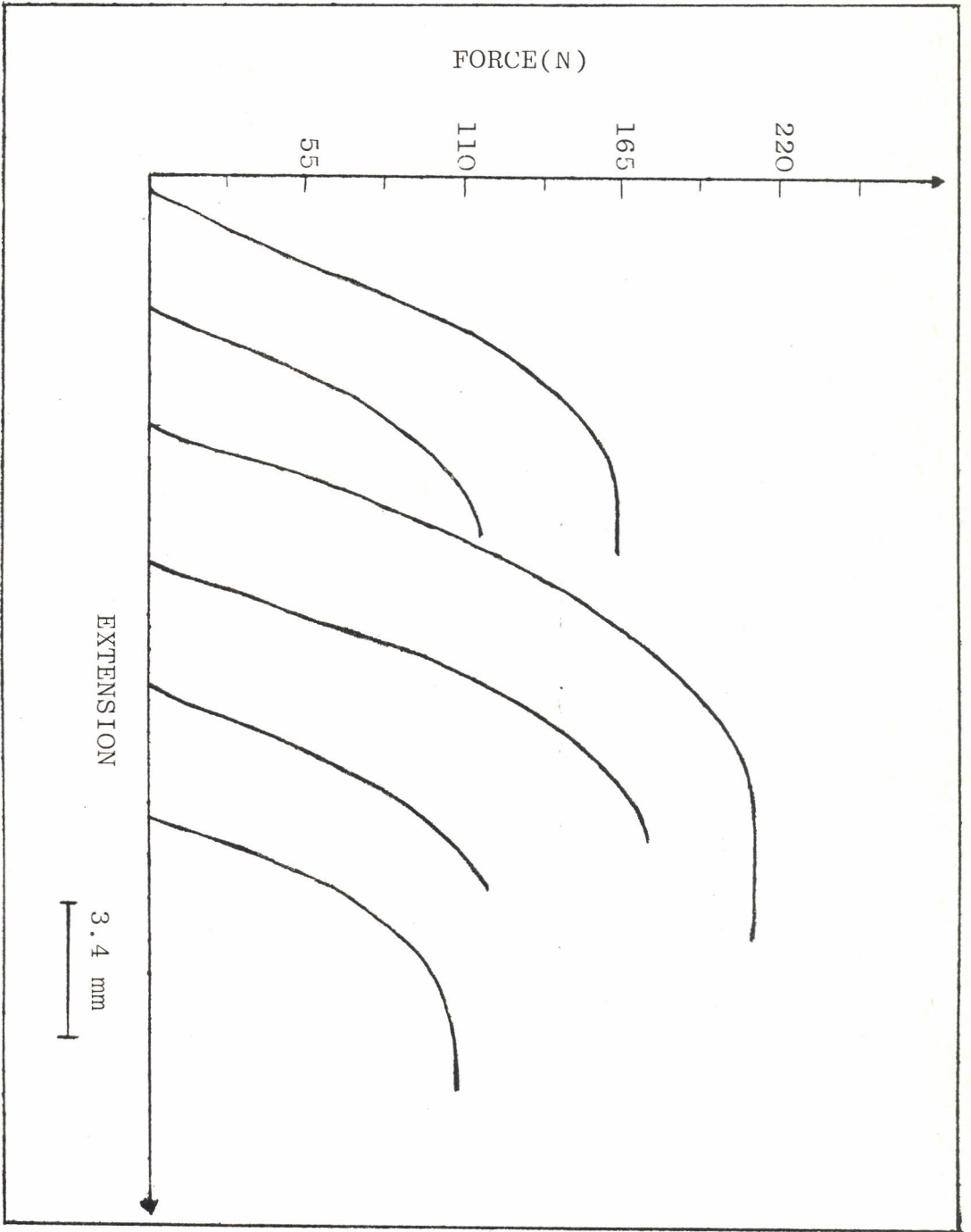


FIG 11a. Force-Extension curves for samples not annealed.

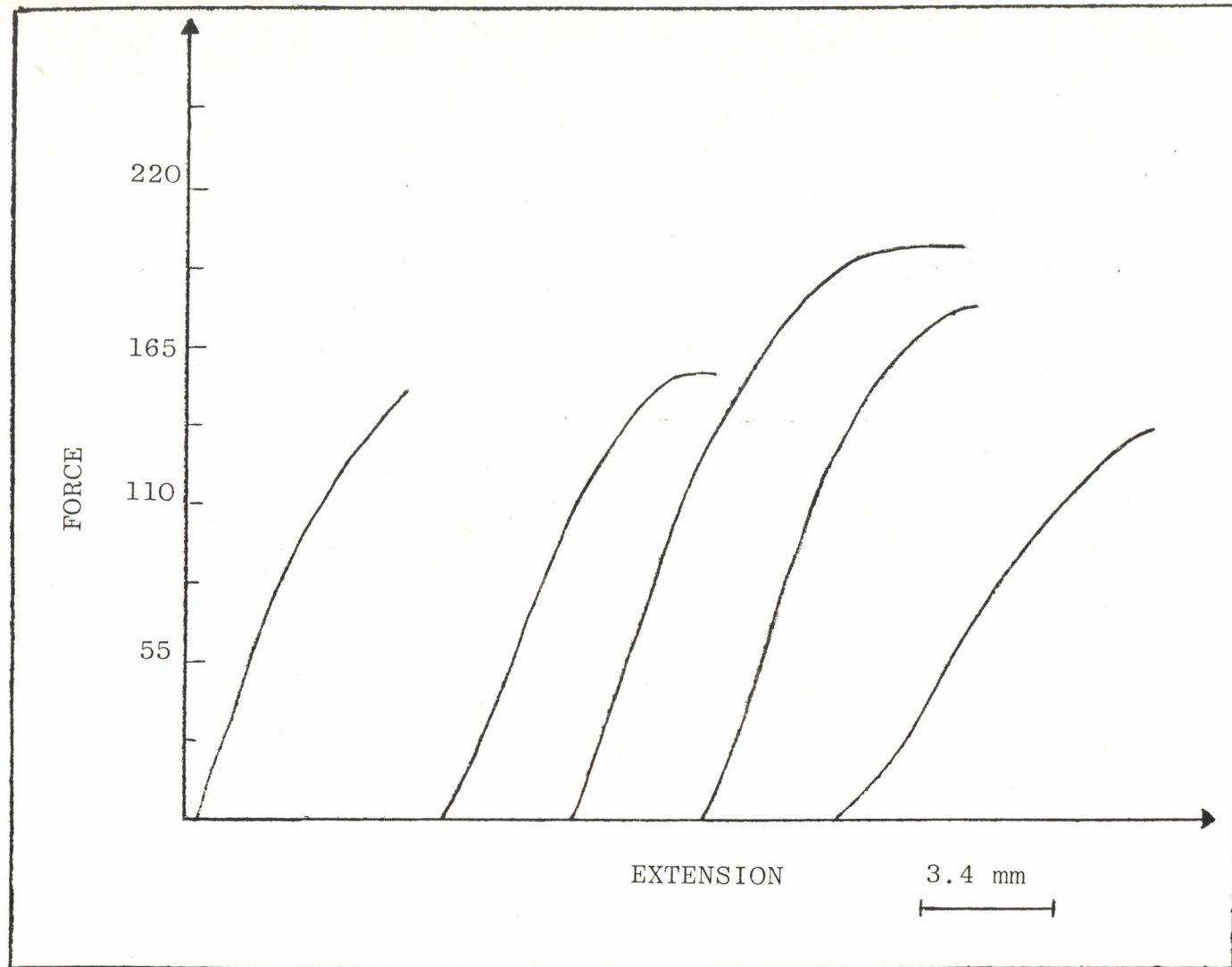


FIG 11b.. Force-Extension curves for samples annealed at 75°C for 3 hours.

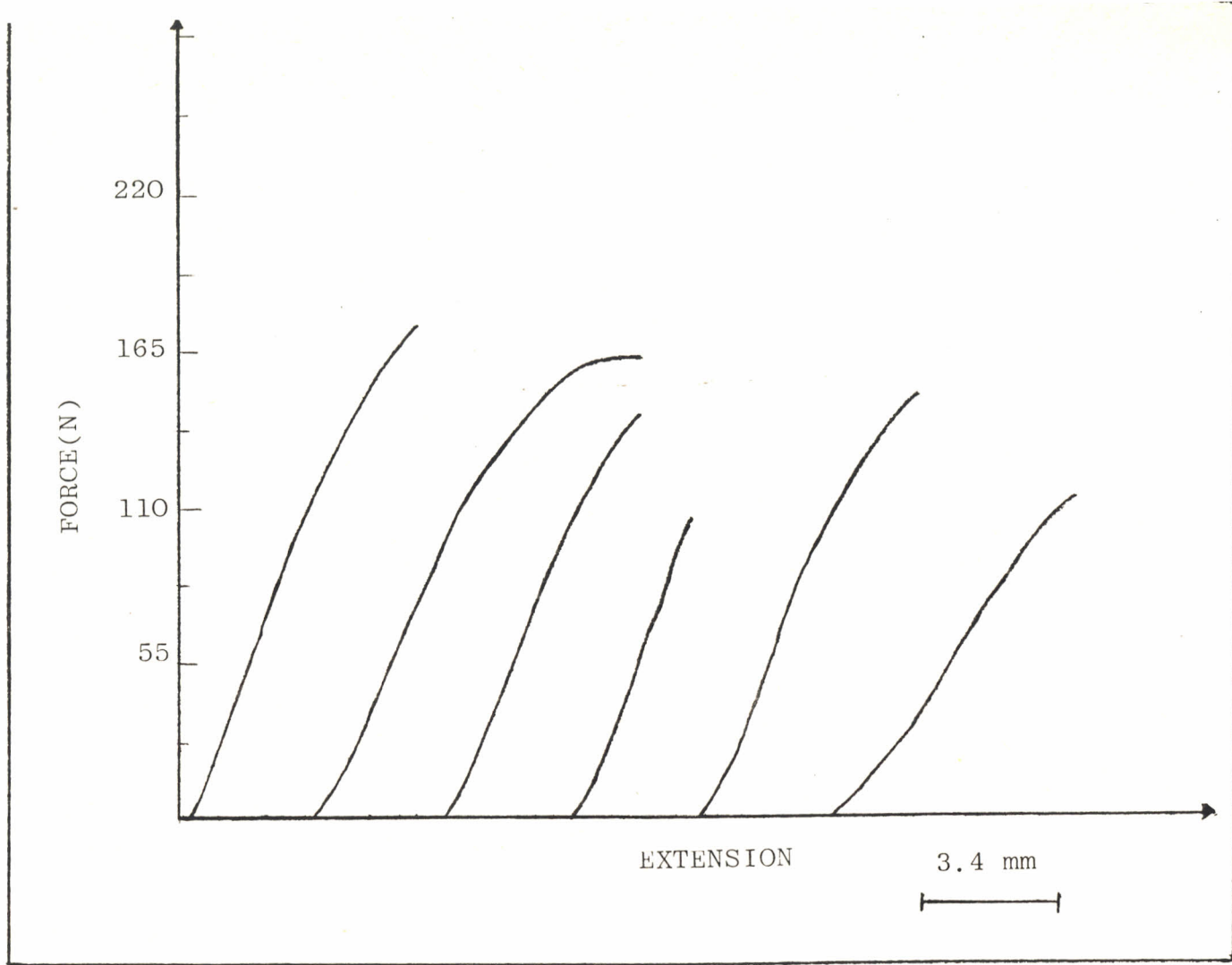


FIG 11c.. Force-Extension curves for samples annealed at 125°C for 3 hours.

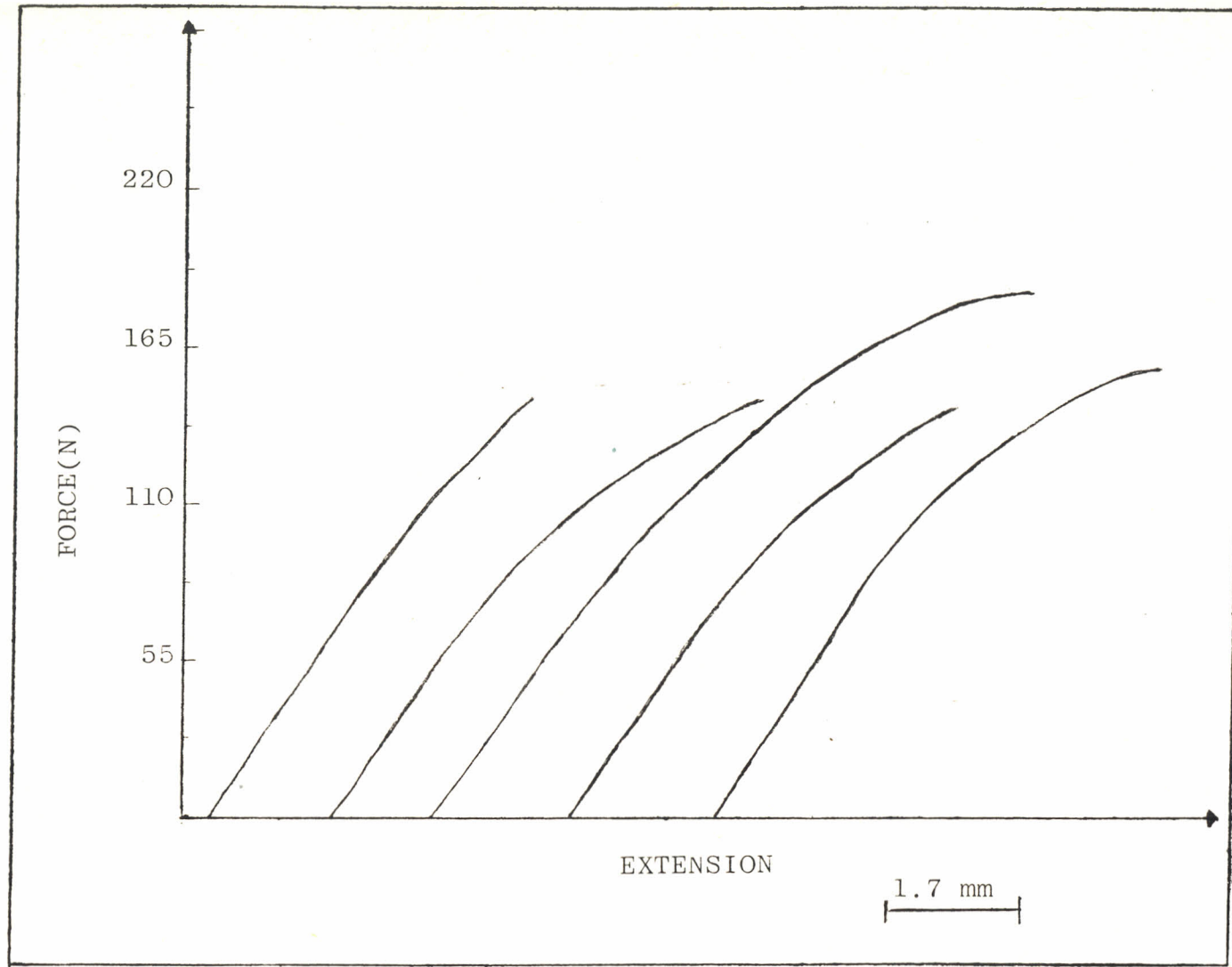


FIG 12a. Force-Extension curves for samples annealed at 125°C for 1 hour.

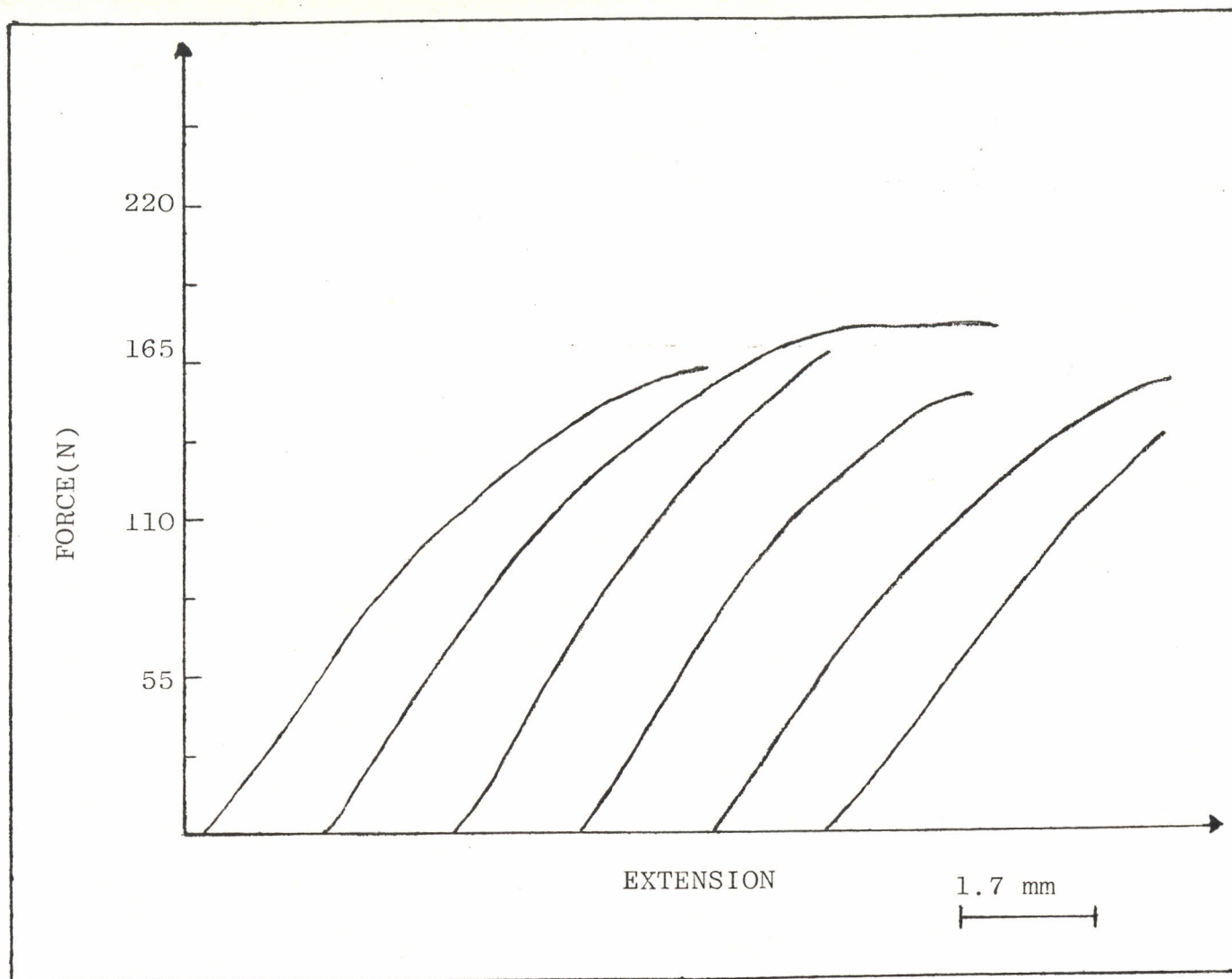


Fig 12b. Force-Extension curves for samples annealed at 125°C for 6 hours.

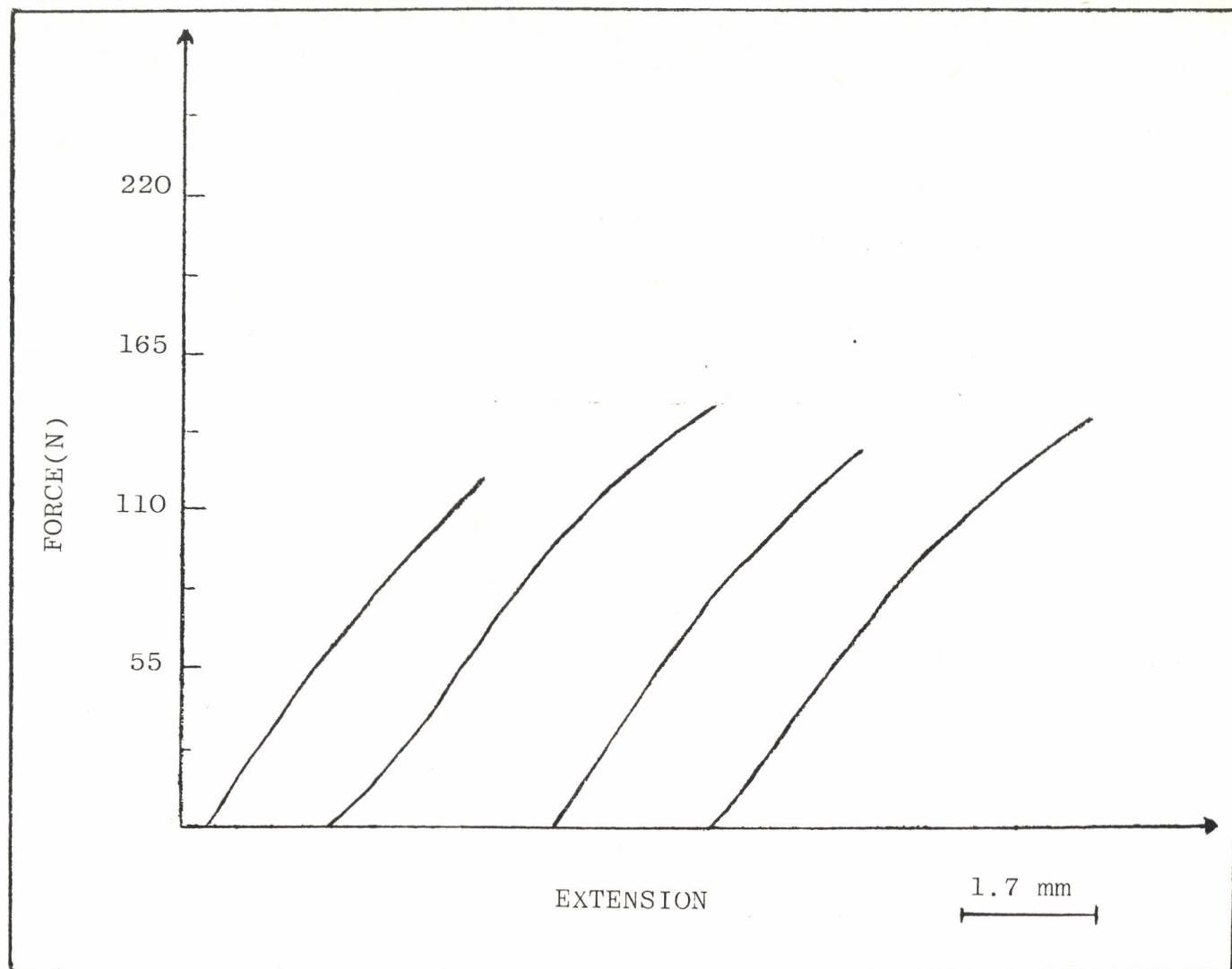


Fig. 12c. Force-extension curves for samples annealed at 125°C for 16 hours.

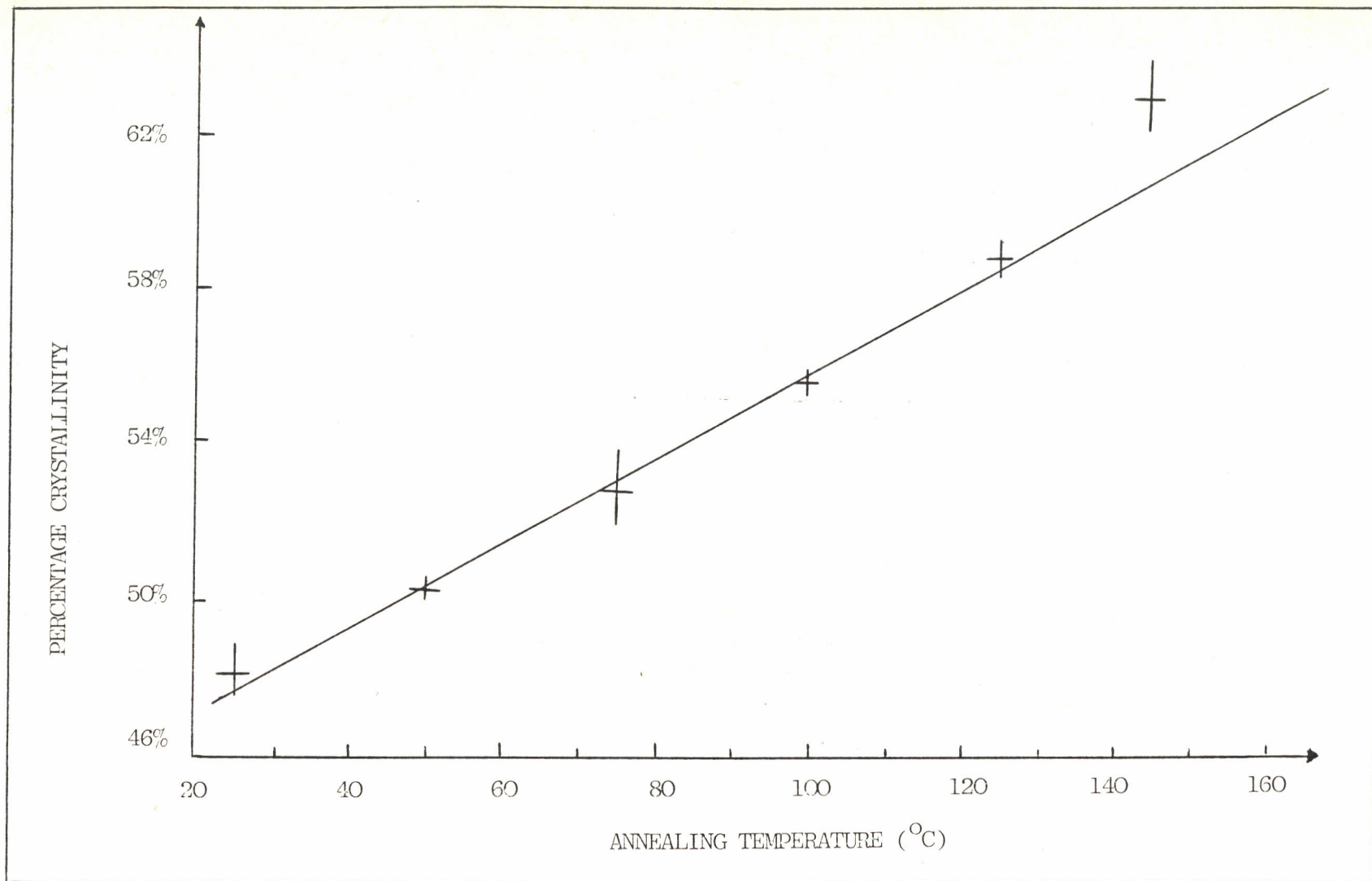


FIG. 13. PERCENT CRYSTALLINITY AGAINST THE ANNEALING TEMPERATURE, FOR FIXED ANNEALING TIME.

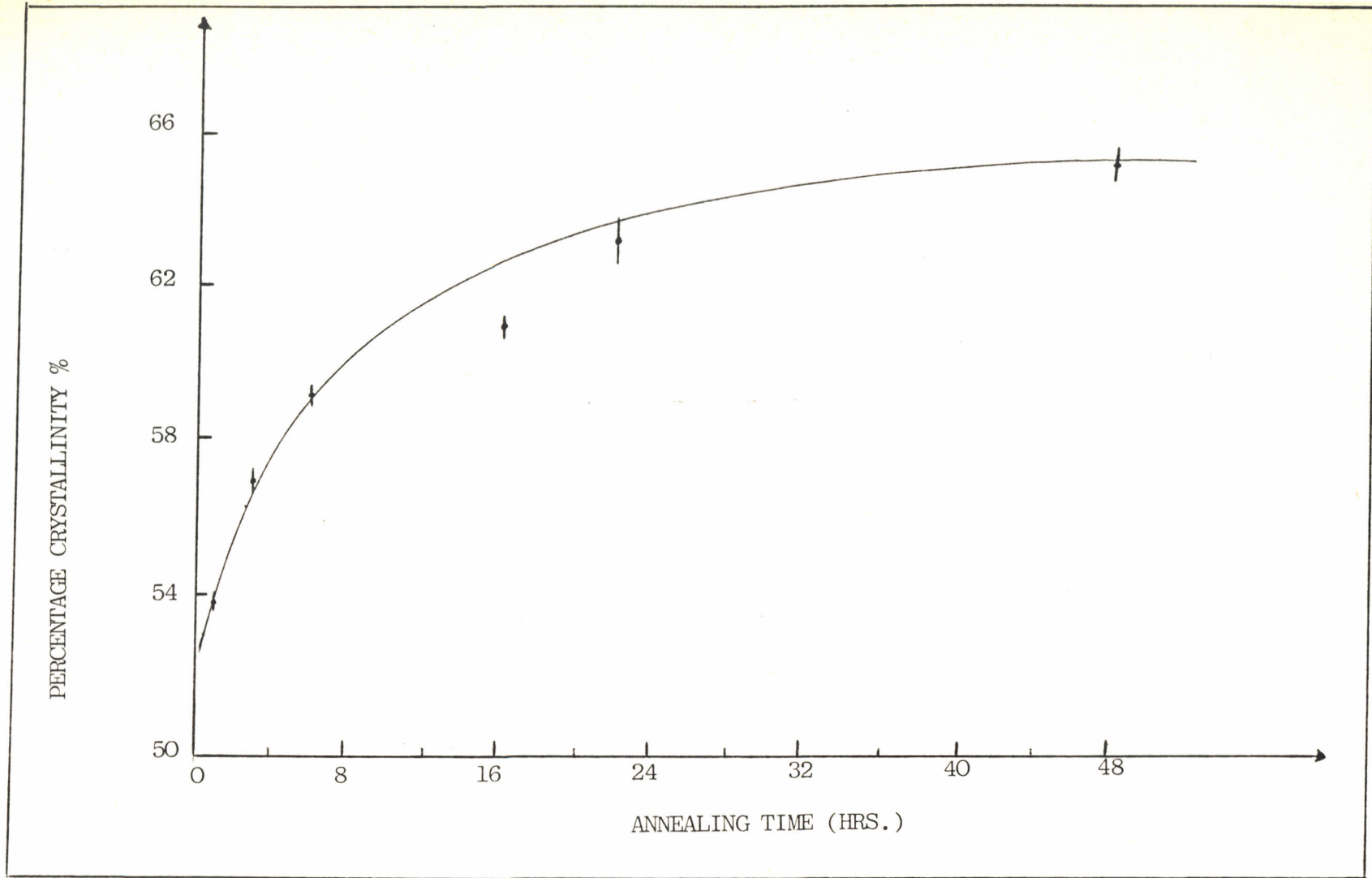


FIG. 14. % CRYSTALLINITY AGAINST THE ANNEALING TIME (ANNEALING TEMPERATURE CONSTANT).

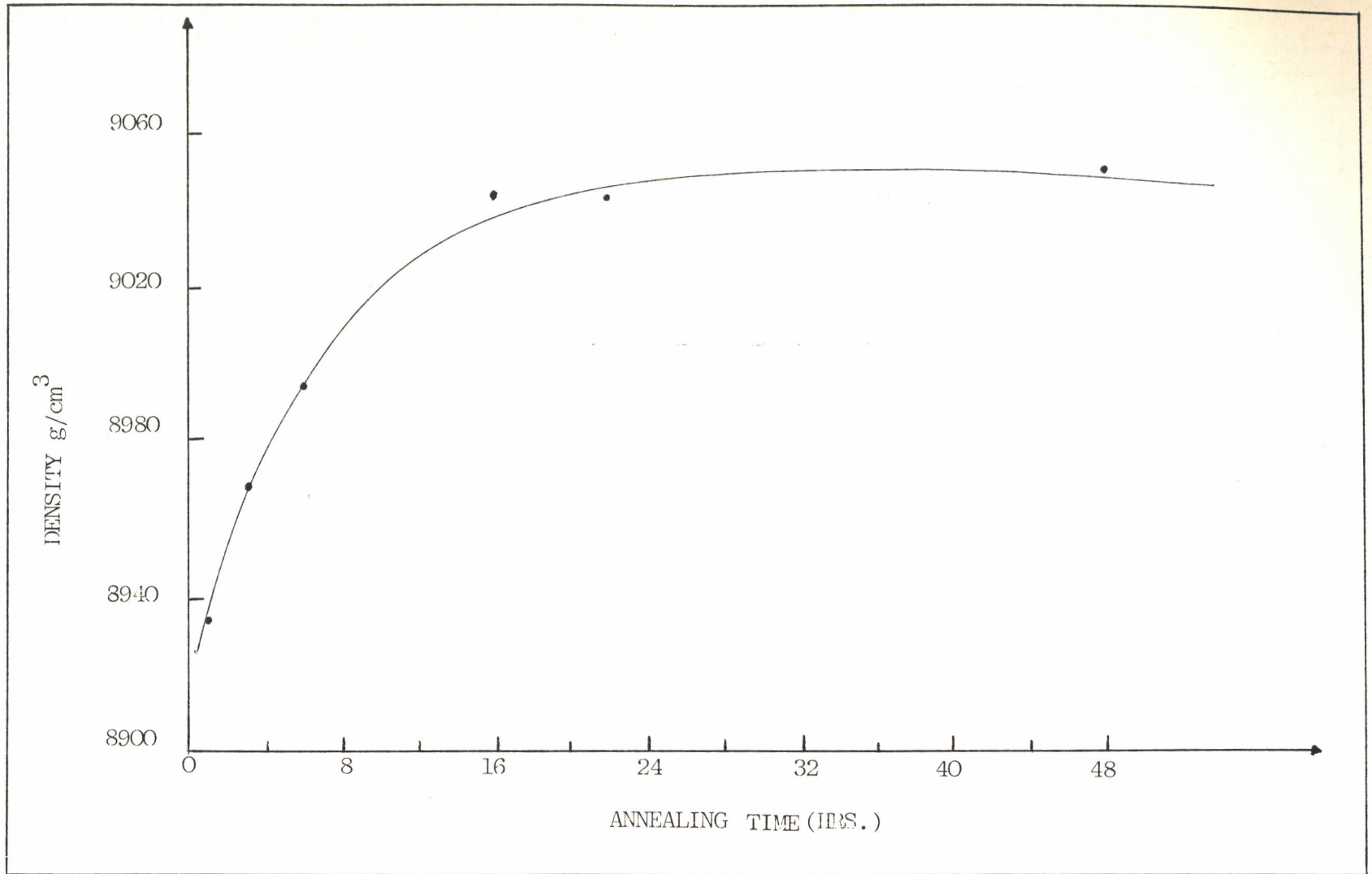


FIG 15. DENSITY AGAINST ANNEALING TIME FOR SAMPLES ANNEALED AT DIFFERENT TIMES.

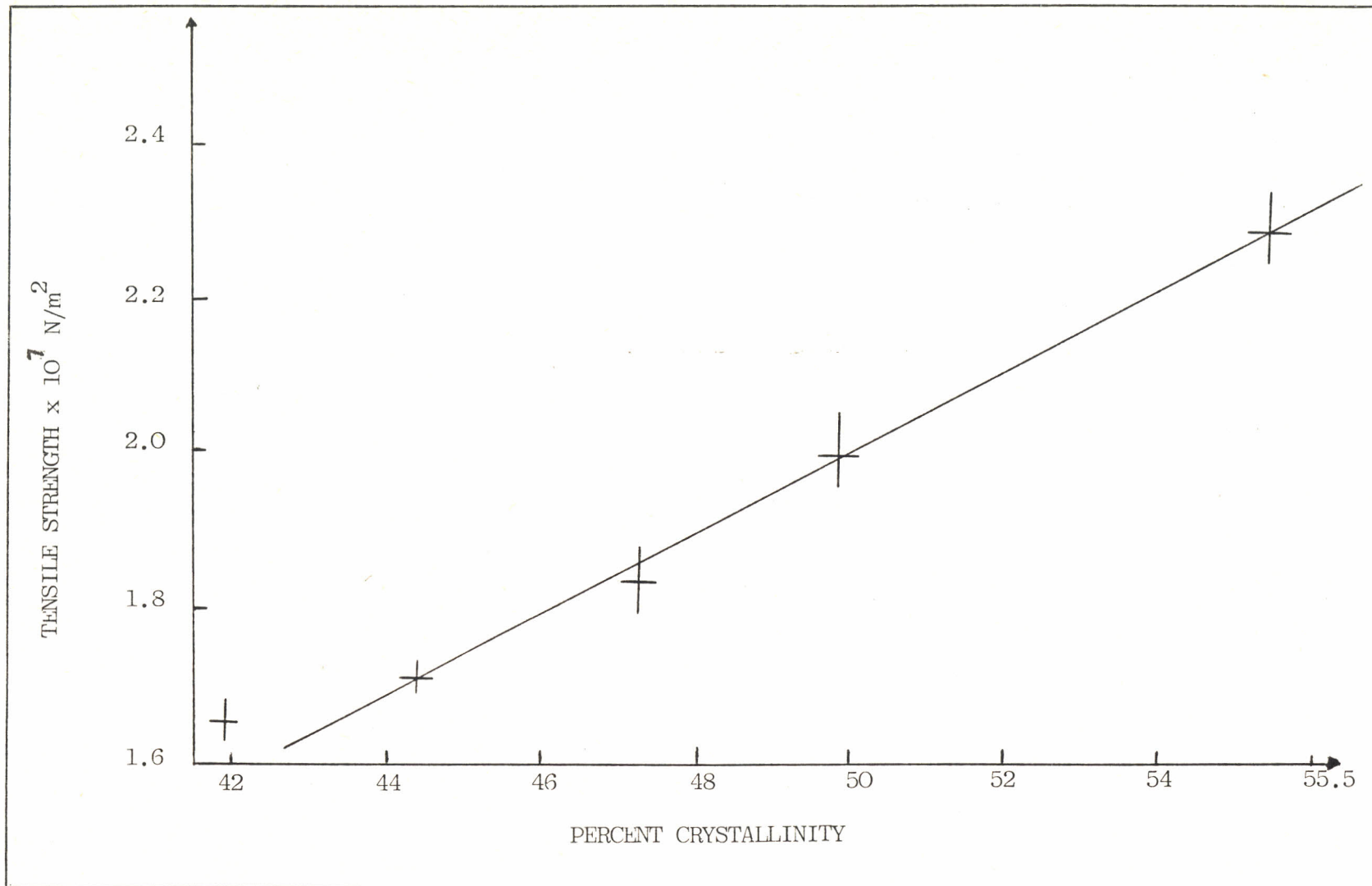


FIG. 16. TENSILE STRENGTH AGAINST CRYSTALLINITY FOR SAMPLES COOLED AT DIFFERENT RATES.

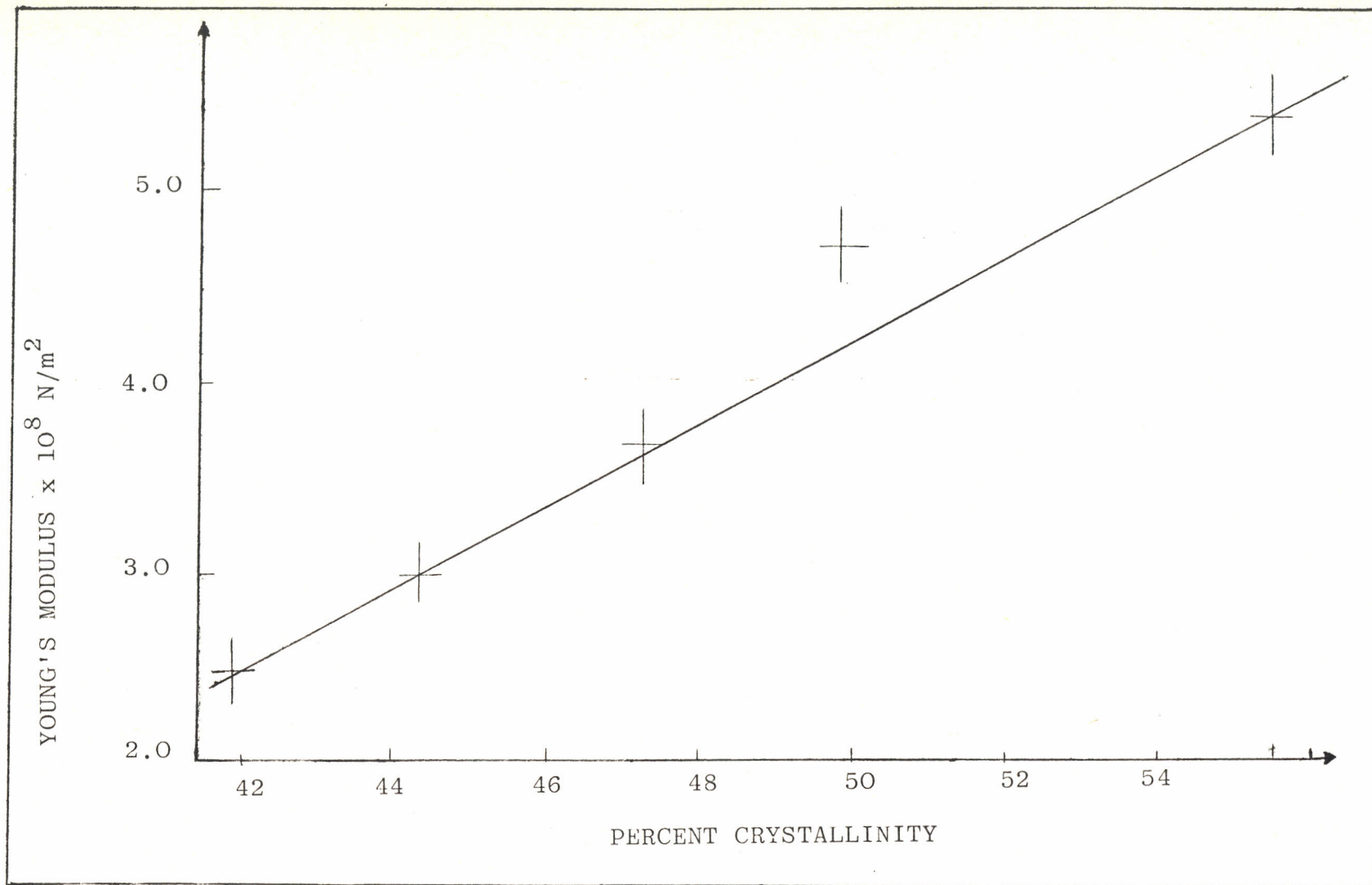


FIG. 17. YOUNG'S MODULUS AGAINST % CRYSTALLINITY OF SAMPLES COOLED AT DIFFERENT RATES

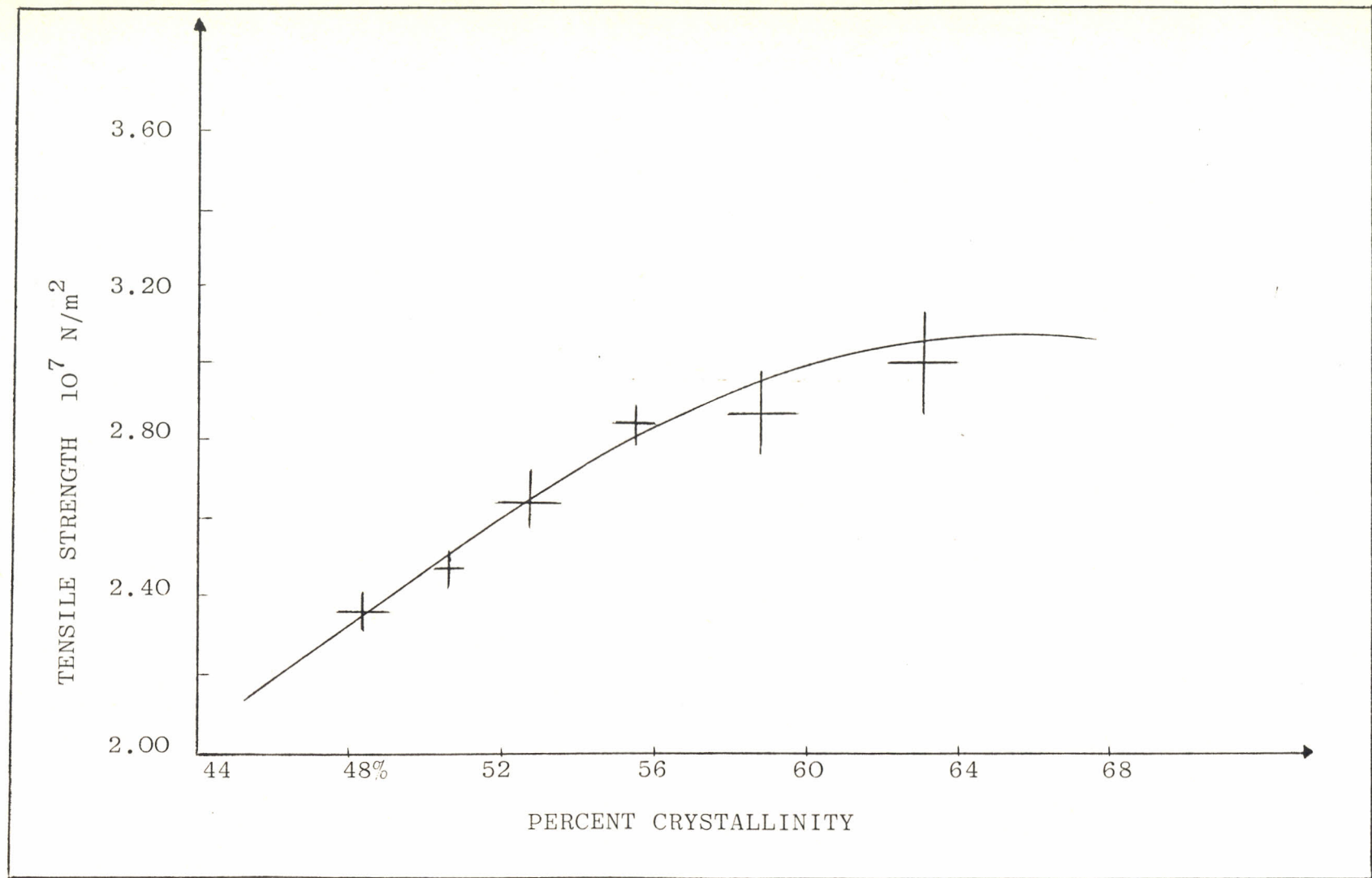


FIG. 18. TENSILE STRENGTH AGAINST PERCENT CRYSTALLINITY FOR SAMPLES ANNEALED AT DIFFERENT TEMPERATURES.

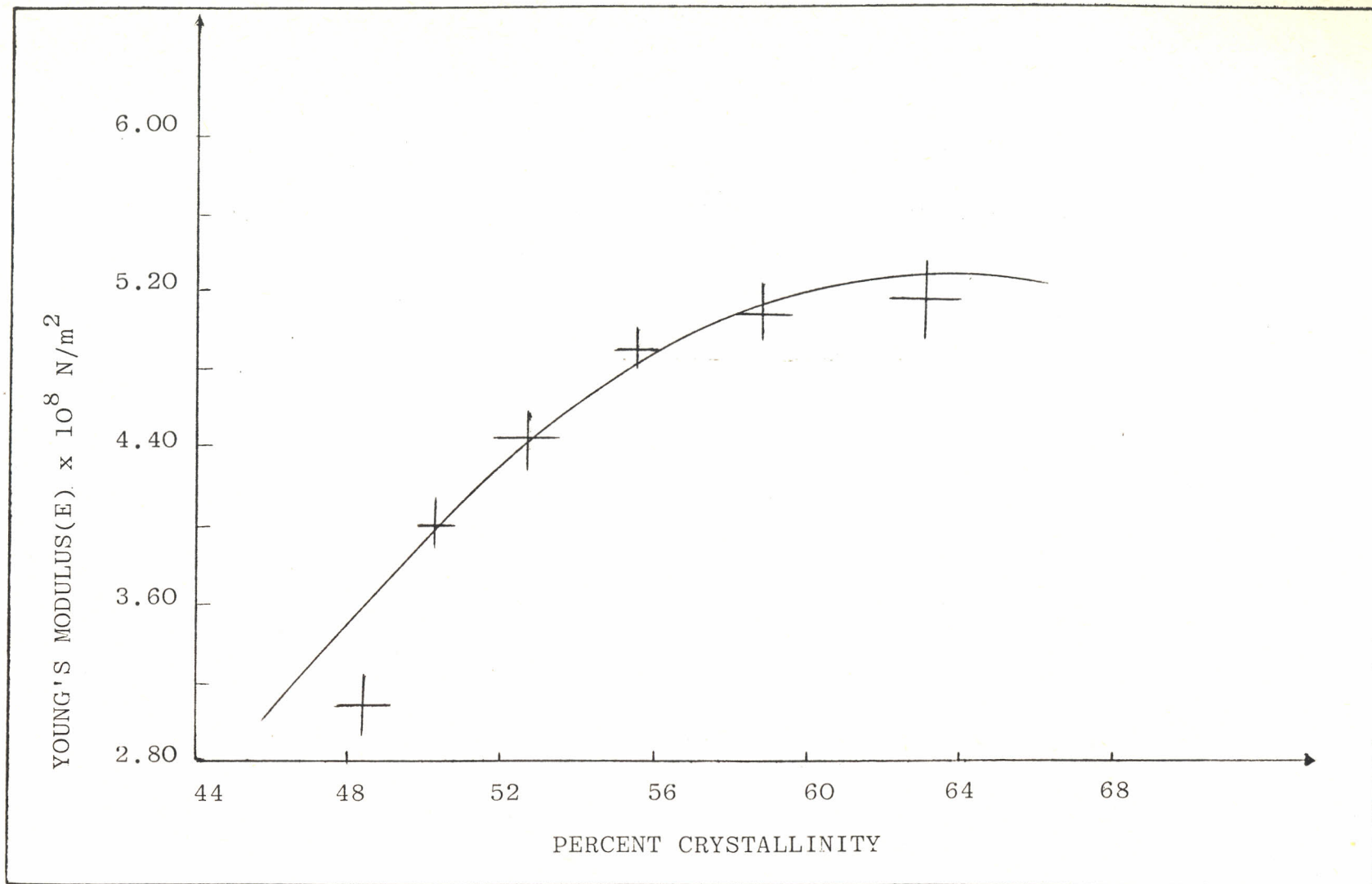


FIG. 19. YOUNG'S MODULUS AGAINST PERCENT CRYSTALLINITY OF SAMPLES ANNEALED AT DIFFERENT TEMPERATURES.

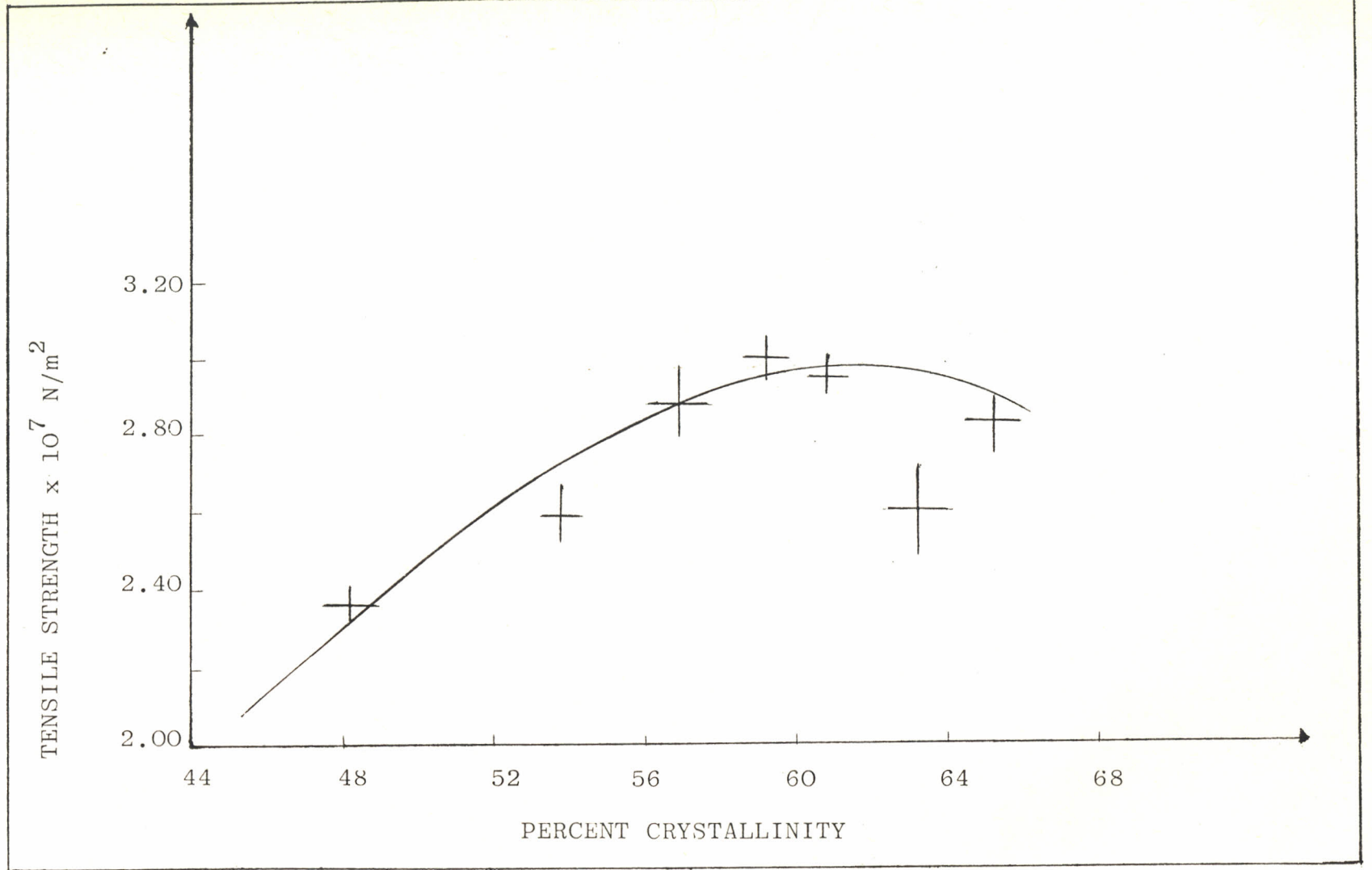


FIG. 20. TENSILE STRENGTH AGAINST PERCENT CRYSTALLINITY OF SAMPLES ANNEALED FOR DIFFERENT TIMES.

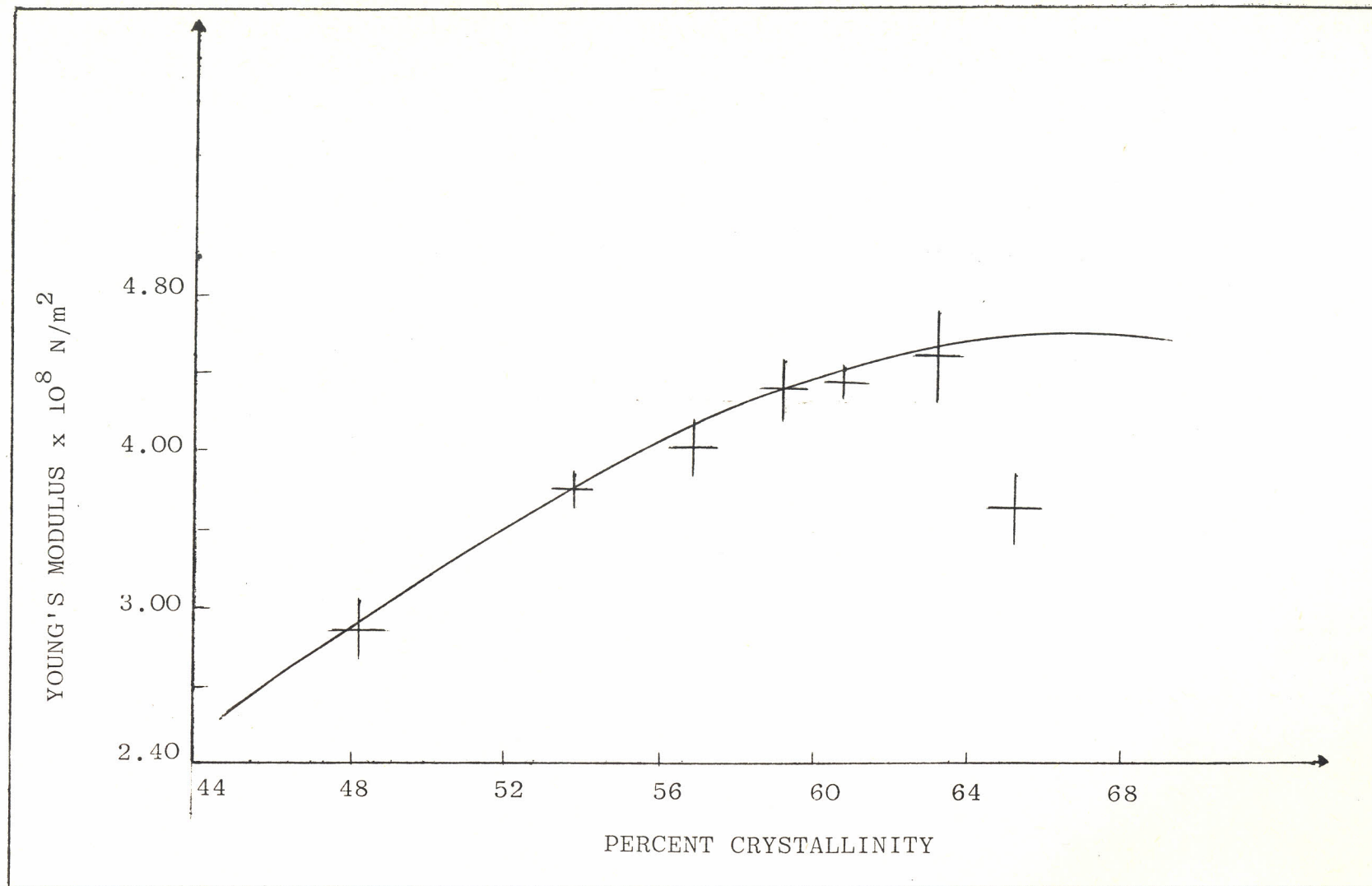


FIG. 21. YOUNG'S MODULUS AGAINST PERCENT CRYSTALLINITY OF SAMPLES ANNEALED FOR DIFFERENT PERIODS OF TIME.