Effect of Stabilizer

On

The Mechanical Properties of Rigid PVC

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by

Karl K.T. Woo, B.S.

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AUTHOR:　Karl K.T. Woo, B.S. Chem. Eng.
(Lowell Technological Institute, Mass. U.S.A.)

SUPERVISOR:　Dr. A.E. Hamielec and Dr. J. Vlachopoulos

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In this study commercial suspension polymerized polyvinyl chloride resin with different stabilizer contents was first compounded and injectioned molded into small dumbbell shape specimens. Most of the specimens after annealing were then tested on the Instron Tensile Tester while the rest on Miniature Tensile Tester for difference in mechanical properties. Four parameters from the stress-strain curves were of interest in this study: tensile yield stress, tensile modulus, elongation at fracture and ultimate fracture strength. The differences in mechanical properties were explained by the change in molecular structure of polyvinyl chloride brought about by the reaction between the stabilizer and PVC molecules. In the second part of the experiment, the effects of heat treatment and molecular weight on the mechanical properties of rigid PVC were also investigated.

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1. Introduction

Polyvinyl chloride is an important member of a large family of thermoplastics referred to as vinyls. These are polymers containing the vinyl group (CH_2=CHR) such as polyethylene and polystyrene. Through common usage, "vinyl" generally refers to polyvinyl chloride and copolymers.

Polyvinyl chloride is the leading plastic material in Europe, and second in importance after polyethylene in the United States and Japan. In the United States, the annual production is close to 3 billion pounds and the rate of growth is about 20 % per year.

Polyvinyl chloride became commercially available only prior to World War II. The factors responsible for the rapid growth of polyvinyl chloride are considered to be: (1) low cost; (2) the ability to be compounded with plasticizers to give a range of flexibility; (3) good physical, chemical and weathering properties; (4) processability by a wide variety of techniques, including extrusion, calendering, different types of moldings, solution and latex coating.

Paradoxically, polyvinyl chloride is chemically one of the least stable of the common polymers, and its utilization came about only through the development of proper technology for handling the resin and the discovery of suitable stabilizers.

Polyvinyl chloride is subject to degradation by heat and light.(1,2) The main processes of degradation are evolution of hydrogen chloride, with darkening and deterioration in physical and chemical properties. Thermal degradation starts at about 100°C.(3) The function of a heat stabilizer is to prevent discoloration and degradation caused by heat treatment during processing. After the processing operation, the requirement for heat stabilizer no longer exists for most application, except for those special cases where the product may be subjected to heat.

The major purpose of this study is to determine the effects of additives on the mechanical properties of rigid PVC. Rigid PVC is characterized by its rigidity and strength and any change in the mechanical properties of the final product caused by the different quantities of additives which must be added before processing are of extreme importance from an engineering point of view. Moreover, most research on the mechanical properties of rigid PVC has been conducted on commercial PVC resins which have stabilizer and other additives already compounded in it, and no systematic examination of influence of stabilizer or lubricant contents on the mechanical properties of the final product has been published.

Four parameters relating to the mechanical properties were of interest in this study: yield stress, tensile modulus, ultimate tensile strength and elongation at fracture.

Before rigid PVC specimens were prepared, PVC resin and additives were first dry blended in a heated mortar and pestle. Then the "Mini Max Molder" developed by Bryce Maxwell was used to prepare the specimens.

Rigid PVC is considered one of the most difficult thermoplastics to process since it has a high melt viscosity. Injection molding of rigid PVC requires very high pressure, usually in the order of [illegible],[illegible] 20,000 psi.(4) Obviously this cannot be achieved by the Mini Molding Machine in the laboratory. But the injection pressure can be reduced by increasing the temperature of the mold. After injection, the hot mold with the specimen was immediately quenched into cold water in order to minimize thermal degradation of the specimen. Rapid cooling during quenching freezes polymer chains into position. The bulky nature of the chain segments leads to difficulties in segments alignment and results in poor packing and unoccupied volume in the glassy state.(5,6) Hence before the specimens were tested on the tensile tester, they were all annealed at 110°C for 20 minutes. On the application of heat some local motion of polymer chains becomes possible and they move into lower energy configurations.

The second part of the experiment investigated the effect of heat treatment (annealing time) on the mechanical properties of rigid PVC. Lastly, PVC resins with different molecular weights were tested and their effect on mechanical properties were also investigated.

2. Literature Review

2.1 Physical Properties of PVC Homopolymer

Polyvinyl chloride is not generally classified as a crystalline polymer. As formed in the usual commercial polymerization, the polymer is highly amorphous with only a low degree of crystallinity. Together with other amorphous polymers such as polystyrene and polycarbonate, they are usually referred to as glassy polymers. The crystallinity is associated with syndiotatic sequences.(7,8) PVC prepared at 40-75°C has a crystallinity about 10 %. At lower temperature the degree of crystallinity is higher.(9)

For most commercial PVC the glass transition temperature is between 70 and 80°C.(10,11) Glass transition temperature is characterized as the temperature at which an amorphous polymer will change from its hard or glassy state to a rubbery soft material. Near this temperature certain properties undergo a remarkable change, such as specific volume, mechanical loss and shear modulus. The additions of a plasticizer to the polymer reduces the glass transition temperature significantly.(12)

PVC is soluble in many ketones and esters. It swells in aromatic hydrocarbons, but is unaffected by alcohols or aliphatic hydrocarbons. Similar to other polymers, low molecular weight PVC is more soluble than high molecular weight in the same solvent. The preferred or most widely used solvents are tetrahydrofurane (THF) and cyclohexanone.

PVC is considered one of the most difficult polymers to process because of its high melt viscosity. Low melt viscosity permits good mixing and high processing rates. Lower melt viscosities are obtained through compounding with plasticizers. The presence of low molecular weight PVC fractions also reduces melt viscosity. Fractors contributing to an increase in melt viscosity are high molecular weight, long chain branching, crosslinked structure and regularity.(13)

2.2 Rigid PVC

Besides stabilizers, the other very important additive to PVC resin is plasticizers.Plasticiers are commonly used to reduce the softening and thus the processing temperature required for PVC and to achieve flexibility of the final product. As with degradation and stabilization, there is extensive literature on the subject of plasticization in general and that of PVC in particular.(14-19) PVC plasticizers are high molecular weight nonvolatile liquids. The most commonly used plasticizers are esters of di or tribasic acids such as dibutyl, dicapryl and dioctyl phthalates; tritolyl and trioctyl phosphate.

The effects of plasticizers on properties are of prime concern in considering their use in particular manufactured products. In addition to the main effect of producing flexibility practically every other property of PVC is changed by the introduction of plasticizers.

Qualitatively, it is found that as plasticizer concentration increases, there are corresponding reductions in tensile modulus, tensile strength, hardness, density, glass transition temperature, softening temperature while at the same time there are increases in elongation at break, toughness and softness.

The plasticizer content of plasticized PVC resin is usually quite high in the order of 40 to 70 phr (parts per hundred resin). Those resins containing less than 20 phr plasticizer are referred to as 'semi-rigid' PVC. The expression 'rigid PVC' is used to describe a material which consists of a PVC resin containing very little or no plasticizer but including stabilizer and other additives.

Over the past fifteen years the use of rigid PVC has grown at a higher rate than that of PVC as a whole. Rigid PVC now has many applications the most important of which are within building and packaging industries. Rigid PVC differs from flexible plasticized PVC most markedly in rigidity and strength both of which are several-fold higher.

2.3 Lubricants

The main purpose for addition of a lubricant to PVC is to facilitate processing and permit control of processing rate. Lubrication is required to prevent excessive sticking. Processing at the usual melt temperature of 160 to 200°C leads in the absence of lubricant to sticking to the hot process equipment. Apart from the consequent loss of material, interference with removal of the PVC from equipment and general messiness, the adhering PVC will become overheated and decompose excessively, leading to deterioration of processed material and corrosion of the equipment. On the other hand, excessive lubricant will cause complete absence of adhesion between polymer and equipment which eliminates shear force for thermal plasticization and homogenisation.

The effectiveness of lubricants depends on their marginal or complete insolubility in the PVC resin. This insolubility or incompatibility results in exudation to the polymer-metal or polymer-polymer interface, reducing friction and sticking. Jacobson(20) reports that low solubility and affinity for metallic mold surfaces are vital properties for a lubricant.

It is also customary to classify PVC lubricants as 'internal' or 'external' according to their action and effects.(4) The principal function of an external lubricant is to reduce the external friction against the sticking to the surfaces of processing machinery and molds. The main function of the internal lubricant is to lower the 'internal' friction, i.e. inter-particle and inter-molecular friction of the polymer in processing, hence reducing the effective melt viscosity and frictional heat build-up. The classification of lubricants for PVC into internal and external lubricants is not a rigid one, since it is likely that most lubricants possess both properties. It is more accurate to think in terms of what predominant behavior the lubricant has.

As pointed out by Oakes(21) and Andrews et al.(22) both internal and external lubrication can improve the heat stability of rigid PVC, through the above mentioned reduction of internal or external friction; the demands on the stabilizer may thus be reduced.

The most commonly employed external lubricants(3) are stearic acid and its salts with calcium, lead, cadmium and barium; paraffin wax, low molecular weight polyethylene; and certain esters, such as ethyl palmitate. Internal lubricants are rarely necessary in plasticized PVC, but they are essential for rigid PVC commpositions. In addition to the substances listed as external lubricants, which may have internal lubrication effects the following are used; wax derivatives, such as montan wax ester derivatives; amide waxes, such as ceramide; glyceryl esters, such as those of stearic and oleic acid.

The formulation of lubricants is arbitrary. Combination of two or three different lubricants are frequently employed in rigid PVC to get the desired balance of behaviour. Little fundamental guidance can be offered for the selection of lubricants and it is usually necessary to rely on past experience and trial and error experiments on specific processing equipment.

An objectionable side effect displayed by lubricants arises from the fact that they have very low compatibility with PVC resin. As the concentration of a lubricant is increased it will often reach the point where it is exuded to the surface when subject to heat and pressure during processing, carrying with it pigments or filler particles and forming a deposit on the surface of the equipment. This phenomenon is generally known as 'plate-out'. For this reason, the total concentrations employed are usually between 0.5 and 1.0 phr, but 0.25 to 0.6 phr for stearic acid when used alone.(3)

2.4 Degradation of Polyvinyl Chloride

While decomposition of PVC can be induced by other forms of energy, thermal decomposition is by far the most important. Thermal degradation starts about 100°C with the evolution of hydrogen chloride and development of colour. Dehydrochlorination is substantially complete in 30 minutes at 300°C.(23) As the thermal decomposition proceeds, the colourless PVC becomes yellowish, then brown, and finally black.

Thermal stability to degradation varies with the method of manufacturing of the resin. Other things being equal, the stability decreases in the sequence of bulk polymer, suspension polymer and emulsion polymer. This is usually attributed to the amount of impurities present which increases in the same sequence. Generally speaking, higher molecular weight resins are more resistant to degradation than lower molecular ones, and homopolymers are more resistant than copolymers or mixed polymers.

As stated in the introduction, the main purpose of this study is to investigate the effect of stabilizer on four parameters of mechanical properties, and the differences in these four parameters were brough about by the change in molecular structure of PVC polymer chains. Thus before going into the experimental conditions, the kinetics and mechanisms of degradation and stabilization will be described briefly in the following.

It has been generally agreed that the rate of decomposition increases with time and temperature.(26) Kinetic studies of PVC decomposition are complicated by the fact that many minor differences between different samples of polymer can profoundly affect rates of decomposition. PVC prepared with different initiators will have different rates of degradation. According to Druesedow and Gibbs,(27) the decomposition of PVC in air or oxygen is different from that in an inert atmosphere or vacuum. The rate of evolution of hydrogen chloride is more rapid in an oxygen atmosphere than in nitrogen. This suggests that hydrogen chloride has an autocatalytic or pseudo-catalytic effect in the presence of oxygen. In the absence of oxygen, hydrogen chloride has generally been thought to be non-catalytic. Imoto and Otsu(28) confirmed these results. In the presence of oxygen, the rate of liberation of hydrogen chloride increases with increasing temperature, while it is practically constant in a nitrogen atmosphere.

Thermal decomposition of unstabilized PVC produces intense discolouration by the time as little as 0.1 % of hydrogen chloride is produced.(29) It is generally assumed that the colour arises from the conjugated polyene structures arising from elimination of hydrogen chloride from consecutive vinyl chloride units in the polymer chain. The colours obtained require at least seven consecutive double bonds.(29,30) This suggests that hydrogen chloride molecules are eliminated in succession along polymer chain by so called 'zipper' reaction.(31) This is due to the fact that the elimination of hydrogen chloride from the polymer chain leads to an extremely reactive allylic structure of the type -CHCl-CH=CH-, in which the chlorine atom remaining on the polymer chain is quite unstable, through resonance activation by the neighbouring double bond.(32) The exact mechanism of decomposition of PVC is still not completely understood or agreed. However, three possible mechanisms have been suggested: radical-chain theories,(25) unimolecular expulsion theory,(33) and ionic theories.(34) Although there is only small smount of kinetic evidence to support the 'zipper' unimolecular expulsion theory,(26) it is generally accepted on the basis of negative evidences which oppose other theories.

According to Smith,(35) PVC having the ideal structure of $CH_3(CH_2.CHCl)_n.CH_2.CH_2Cl$ would not be likely to evolve hydrogen chloride below 300°C. This is based on the fact that low molecular weight compounds such as 1,3,5-trichlorohexane have very good thermal stability. This suggests that initiation of the thermal decomposition of PVC must arise from departures from the idealised structure. The major four structural irregularities of PVC are:

I. Irregularities arising from initiators: Commercial polymerization of PVC involes initiation by means of peroxy or azo compounds. Hence the organic peroxides are likely to leave an acyloxy group (R.COO) at the end of polymer chains. With azonitriles, the group attached to the PVC structure will be substituted nitrile, e.g.

$(CH_3)_2(CN)C$–. The latter structure appears to lead to more rapid thermal decomposition than that derived from organic peroxides.(36,37) In general suspension polymers are more thermally stable than those emulsion polymers. This might suggest that the end-group arising from persulphate initiation, such as $-SO_4M$, is more liable to lead to decomposition than those derived from organic peroxide initiation. But the difficulties of purifying emulsion polymers from residues containing emulsifying agents and buffers make it difficult to be sure on this point.

II. Unsaturation: Chain-transfer involving monomer molecules is an important feature of PVC polymerization, and this leads to an unsaturated groups in the molecule. Similar unsaturation would arise as a result of termination by disproportionation. Unsaturation of this type would be prone to oxidation and peroxidation, which could account at least in part for the differences observed between decomposition in the presence and absence of oxygen.

III. Branching: Branching results generally from the transfer reactions to polymer during polymerization and the kinetics of PVC polymerization indicate that branching must be occurred. Commercial polymers have been shown to contain between 5 to 10 percent of long-chain branched molecules. Recently Lyngaae-Jorgensen(38) reported that the degree of branching in commercial PVC is 0.4 to 0.5 $CH_3/100\ CH_2$. Transfer reactions during polymerization could lead to the chlorine atom attaches tertiary to the carbon atom which is extremely unstable.

IV. Other structural irregularities: Although the structure of PVC is predominantly head-to-tail, it is not impossible that some head-to-head and tail-to-tail structures might occur to a small degree difficult to detect. Termination by combination would also lead to tail-to-tail structure at the point where the combination of two growing chains had occurred. It is suggested that a concentration of one tail-to-tail structure in every one thousand normal linkages is unlikely to have serious effect on the initiation of dehydrochlorination.(39)

2.5 Stabilization of Polyvinyl Chloride

Although most stabilizers for PVC react with hydrogen chloride, this is certainly not always the only or even the main function. The fact that PVC will continue to decompose if the hydrogen chloride is removed suggested that some other activity must be employed in stabilization. As has been point out, e.g. by Thacker,(40) basing on the knowledge of degradation mechanisms, an ideal stabilizer for PVC should have the following properties:

1) By reaction with liberated hydrogen chloride, especially if the resultant product is neutral to the decomposition reaction.

2) By reaction with polymer molecules at points of deviation from idealized structure so as to reduce the number of positions where decomposition might be more readily initiated.

3) By reaction with polymer molecules as to interfere the propagation reaction.

4) By reaction with oxygen as to protect the polymer from harmful oxidation attack.

5) By reaction with impurities, e.g. metals, and to form products without activating effect on the decomposition.

Besides that, the stabilizer itself and any reaction products resulting from the above functions, should ideally be innocuous, non-migratory, non-toxic, odourless, and should not impair the colour, clarity of PVC compound. In addition, from the standpoint of processing and use, the ideal stabilizer should also: (1) be readily dispersible in the PVC compound, (2) have no adverse effect on processing properties, (3) be equally effective in PVC resin of all types and from all sources and (4) be inexpensive and effective in small proportions.

The ideal universal stabilizer with above mentioned properties does not exist, however, many available stabilizers are highly effective. Practical stabilization of PVC has been reviewed frequently,[35,41,42] and trade literature is often very informative on this subject. A review of the more important stabilizers will be discussed in the following. Generally stabilizers for PVC are classified according to their chemical type:

I. Inorganic metal salts: This group of stabilizers consist of mainly basic lead compounds such as basic lead carbonate, tribasic lead sulphate and dibasic lead phosphite. Basic lead carbonate was used in the early days of PVC and is still regarded as an efficient cheap stabilizer. Unfortunately, its products are substantially opaque and the compound decomposes to yield carbon dioxide in the higher range of processing temperature especially rigid PVC. Tribasic lead sulphate is more stable and more expensive than lead carbonate and used mainly in rigid PVC. Dibasic lead phosphite has good resistance to photodegradation and is particaularly useful in outdoor application. Like all lead compounds, lead stabilizers are toxic and therefore not usable in foodstuffs packaging.

II. Metal soaps and salts of organic acids: The stearates, laurates, naphthenates of many metals have been used as stabilizers for PVC. The most important stabilizers of this class are the soaps of barium, cadmium, zinc, calcium, and magnesium. Cadmium stearate is capable of stabilizing plasticized PVC, but the stabilizing effect is not very prolonged. On the other hand, the use of barium stearate alone leads to slightly yellow colours, but the initial colour is maintained for relatively long processing times. Combining both stearates gives much better results than single stearates. Barium/cadmium complex stearates prepared by co-precipitating have been available commercially for many years.

III. Metal complexes: most of the metal soaps are effective lubricants and have limited compatibility with PVC resin. After a maximum concentration is reached, the metal soap will exude to the surface during processing. The phenomenon is known as 'plate-out'. As a result, metal complexes systems such as barium/cadmium and barium/cadmium/zinc complexes of phenates and alkylated phenates were introduced. These metal complexes do not have 'plate-out' problems with PVC and are probably the most commonly used stabilizers, after basic lead carbonate. In addition, as mentioned in II, they have better stabilizing abilities than single metal soaps.

IV. Organotin compounds: Organotin compounds are generally superior to any other PVC stabilizer both in stabilizing power and in the level of clarity. Generally speaking, organotin stabilizers can be divided into four classes. The simplest comprises butyltin compounds, the best known of which are dibutyltin dilaurate and maleate. The second type comprises dibutyltin compounds in which various kinds of sulphur-containing groups are incorporated. These are commonly known as 'thio-organotin compounds'. Examples of which are dibutyltin thiomaleate, dibutyltin dinonyl thioglycollate. These stabilizer are more powerful than those non-sulphur-containing organotin compounds. The butyltin compounds are generally toxic and cannot be used in food-packaging applications. A number of mono-butyltin compounds derived from butyl thio-stannic acid and some octyltin compounds such as dioctyltin laurate, maleate have been developed to overcome the toxicity problem.

V. Other organic and miscellaneous compounds: The stabilizers in this group may be described as secondary or subsidiary, as they are never used alone but always in conjection with the metal-based stabilizers. They are less important than the latter, although they do serve useful purposes such as ultra-violet absorbers, antioxidants and to provide synergistic effects in stabilizer mixtures.

One of the classes of stabilizers in this group is epoxy compounds. These are epoxidized oils and esters which are also plasticizers for PVC. Because of their dual stabilizer/plasticizer function, they are of particular interest in rigid PVC. Their greatest use is with synergistic mixtures, especially of barium/cadmium which they improve the 'long-term stability' considerably.

Ultra-violet absorbers are sometimes used to prevent the degradation of PVC by directly absorbing the radiation and thus preventing or reducing its absorption by the PVC. They are organic compounds, usually of one of the following types: benzophenone derivatives, benztriazole derivatives, substituted acrylonitriles, and certain aryl esters.(43,44)

2.6 Effects of Annealing on Mechanical Properties

The effects of annealing of glassy polymers have been investigated extensively. Rapid cooling during quenching freezes polymer chains into fixed position which results in poor packing and substantial unoccupied volume. It is suggested that annealing produces a greater degree of order within the amorphous regions of the glassy polymer, resulting in an increase in density. This density difference produces significant differences in mechanical properties of the glassy polymer. For example, Raha(45) prepared samples of polystyrene by quenching into iced water from 110°C, and found that the intrinsic yield stress measured in compression at 22°C was 12 % lower than the yield stress of samples annealed at 110°C and slowly cooled to room temperature over 24 hours. Golden(46) have reported increases in yield stress of polycarbonate of up to 15 % on annealing quenched samples. Golden also reported that an increase in the degree of crystallinity of the polymer can be discounted in view of the lack of change in X-ray diffraction pattern after heating. It would therefore appear probable that the increased strength is due to the changes within the amorphous region. Experiments by Ender(47) on quenched and annealed polymethylmethacrylate tested at 80°C under constant load also indicate that the yield stress is reduced by any quenching treatment.

2.7 Effect of Molecular Weight and Molecular Weight Distribution

It has been generally agreed that mechanical properties usually increase with M.W. (molecular weight) and decrease with broadening of M.D.W. (molecular weight distribution). The situation is complicated by the fact that, in some cases, M.W. and M.W.D. can affect physical properties through their effects on other material parameters such as branching, orientation, crystallinity, crystal structure, processing conditions, etc. Hence the specific effects of M.W. or M.W.D. can be determined only if all other variables are held constant or allowed for quantitatively.

The M.W. and M.W.D. dependence of PVC polymers has been rather widely studied. For example, four PVC samples which have identical values of (η) but different M.W.D. were compared by Kaminska.(48) He found that tensile strength increased as the M.W.D. was narrowed.

Pezzin and Zinelli(49) found that the tensile strength of compression molded, plasticized PVC (60 phr dibutyl phthalate) increased strongly with $\overline{M}_w$ and showed no signs of leveling off below $\overline{M}_w = 2 \times 10^5$.

Studies which relate the yield stress of amorphous polymers to M.W. are few but some work has been accomplished on polycarbonate(50) and polystyrene.(51) In both cases, it was found that flexural yield strength of samples with narrow M.W.D. increased with M.W. but leveled off at M.W. = 1.6×10^4 for polycarbonate and M.W. = 1.6×10^5 for polystyrene.

Like other low-strain properties of glassy polymers, Tensile modulus is usually not functions of M.W. or M.W.D. except at very low M.W. Thus it is not surprising that the tensile moduli of polystyrene,(52,53) and polymethylmethacrylate(54) are reported to be independent of M.W. Flexural modulus measurements on polystyrene(52,51) and polycarbonate(55) led to similar conclusions although a later test on polycarbonate(50) indicated that the modulus decreased slowly as $\overline{M}_w$ was increased over a wide range of strain rates.

Early work on vinyl chloride/vinyl acetate copolymers indicated the modulus increased with M.W. up to 6000-8000.(56,57) Further increase due to M.W. were relatively small. In a study of plasticized PVC fractions and mixtures,(58) Young's modulus was found to be constant for $\overline{M}_w$ greater than 5×10^4. It decreased slightly when $\overline{M}_w$ was reduced below this value.

3. Experimental Conditions

3.1 Mixing and Compounding of PVC

In industry, a wide variety of different machines is used for the mixing and compounding of PVC compositions. The PVC resin and other additives are pre-mixed in a blender, followed by fluxing on large mill rolls or in an internal mixer.

Some of the more common types of pre-mixers are tumble mixers, paddle mixers, ribbon blenders and 'air' mixers. In a tumble mixer, the components to be mixed are placed in a drum which is then turned end over end by mechanical means. The drum chambers are usually of very complicated shape with internal baffles eccentrically rotated. Paddle mixers are those in which the components being mixed are agitated in a vessel by means of blades, rotors rotating on vertical shafts. Ribbon blenders have probably been the most commonly employed machine for the production of premixes of PVC compositions. The mixing blades or agitators are usually in the form of strip metal mounted in spiral fashion around a horizontal shaft rotating in a trough-shaped mixing chamber. 'Air' mixer employs air to 'fluidise' the components to be mixed, thus offering very efficient dispersion and rapid mixing of the PVC resin.

For compounding of PVC compositions, heated roll mills and internal mixers are used. Heated roll mills are usually two-roll mills with one roll in fixed bearings and the other in bearings which can be moved towards and away from the fixed ones. Heating and cooling is usually provided by passing steam, hot water, or cold water through the rolls. Temperatures are controlled by steam pressure valves. The processing time and conditions on the mill depend very much on the type of resin and plasticizer. The front roll is usually 5-10°C higher than the back roll. The temperature of the rolls are usually in the range of 130-180°C. After adequate compounding, which usually takes 10-15 minutes from the time the whole batch has gelled, the crepe is removed from the rolls for cooling and granulation.

The internal mixer was originally designed by Banbury(59) for compounding rubber stocks, and machines of this type are frequently referred to as 'Banbury mixers' or 'Banburys'. At the present time most PVC is compounded in internal mixers. The mixing chamber of a Banbury mixer is a hollow regular cylinder with a cross-section shaped rather like a prone figure of eight. The upper section is closed by a ram which can be raised and lowered by hydraulic means. This in turn can apply pressure to the material being processed. The mixing chamber can be heated by steam. The mixing cycle varies considerably according to the resin and rotor speed which varies from 20 to 100 r.p.m. At rotor speed of 40 r.p.m., the mixing cycle usually takes 4 - 5 minutes.

The above industrial mixing and compounding procedures can be translated into laboratory methods. Premixing can be achieved in a heated mortar and pestle while compounding is done in the "Mini Max Molder". It is a combination of miniature mixer, extruder and injection molding machine. The details of the machine will be described later.

3.2 PVC Resin and Additives:

The commercial grade PVC resin was obtained from Esso Chemical Canada of Sarnia, Ontario. Four different grades with nominal intrinsic viscosities 0.63, 0.86, 1.00 and 1.19 (dl/g - cyclohexanone at 30°C) were investigated.

Stearic acid was used as lubricant and Mark-99 was used as stabilizer for PVC. Mark-99 is a high-efficiency barium/cadmium complex solid for the stabilization of rigid polyvinyl chloride. It is manufactured by Argus Chemical Corporation of Brooklyn, New York. Both the stearic acid lubricant and Mark-99 stabilizer were supplied by Esso Chemical Canada.

3.3 Preparation of Specimens:

A 1,000 c.c. mortar and pestle was used to blend the premix. Heating was supplied by a 6 inch diameter heating mantle made by Glas-col Apparatus Company of Indiana. A Powerstat was also used to provide variable voltage input. The procedures of blending were as following: 50 grams of PVC resin was weighed and placed in the mortar. The voltage input of the heating mantle was set at 80 per cent. Mixing started when the temperature of the resin, measured by a thermometer, reached 50°C. When the temperature reached 70°C, weighed amount of Mark-99 stabilizer and stearic acid lubricant were added to the resin while mixing continued. The voltage input of the heating mantle was reduced to 30 per cent when the temperature of the mixture reached 85°C. Mixing was continued for another 20 minutes while the temperature remained constant around 85°C. The hot premix was then removed from the mortar and cooled to room temperature before compounding. The whole process took about 40 minutes.

In this investigation, the Mark-99 stabilizer content was varied from 2 phr to 6 phr. The lower limit is set by the fact that 2 phr is around the minimum amount one has to add to PVC resin for adequate thermal stabilization. On the other hand, due to the limited compatibility of the stabilizer, it is found that when the concentration of the stabilizer was higher than 6 phr, it was very difficult to make the specimen.

As for the stearic acid lubricant, the concentration was set constant throughout the experiment at 0.536 phr. The reason for this low level is that lubricant has very low compatibility with PVC resin. As mentioned in section 2.3 the concentration employed for stearic acid when used alone ranged only from 0.25 to 0.6 phr. Thus the effect of different amounts of lubricant on the mechanical properties of PVC will be considerably small.

The PVC premix was compounded in a miniature mixing and injection molding machine. The machine was designed by Professor

Bryce Maxwell of Princeton University and manufactured by Custom Scientific Instrument, Inc. of New Jersey.(60)

Compounding PVC requires both intensive and extensive mixing so that the stabilizer and lubricant can be distributed uniformly over the PVC melt. Intensive mixing requires a high local shear stress, and therefore a high shear rate, to break down feed agglomerates. Extensive mixing requires a large magnitude of deformation of a "fold back" nature. Figure 2 illustrates the intensive mixing principle. A cylindrical rotating rotor is placed in a cup-like stator. The material to be melted, mixed and injected is entrapped between the lower surface of the rotor and the bottom of the cup, both of which are heated. As the rotor turns with an angular frequency, ω, the material between point M and N is subjected to a shear rate of

$$\dot{\gamma} = 2\pi r(\omega)/G \qquad (1)$$

where $\dot{\gamma}$ is the shear rate, r is the distance from the centre of the rotor to points M and N and G equals the gap between the two surfaces.

From equation (1), it is apparent that for a small volume of polymer sample, a small gap G and a high rotational frequency ω are required to produce a high shear rate. If the rotational frequency ω is kept constant, a smaller gap G and a larger radius r would increase the shear rate $\dot{\gamma}$.

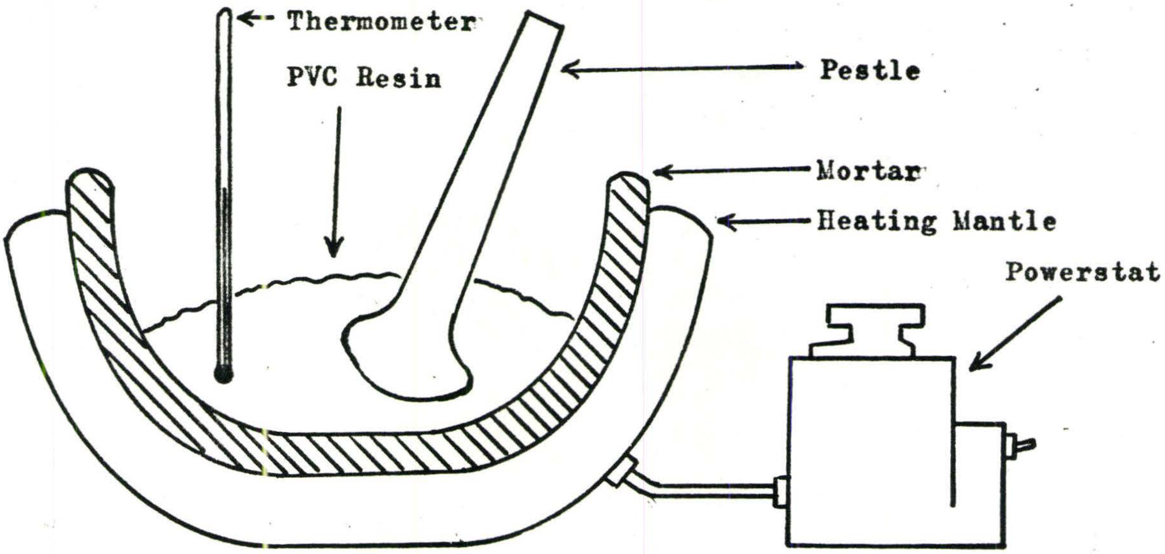


Fig. 1 Blending of PVC Premix.

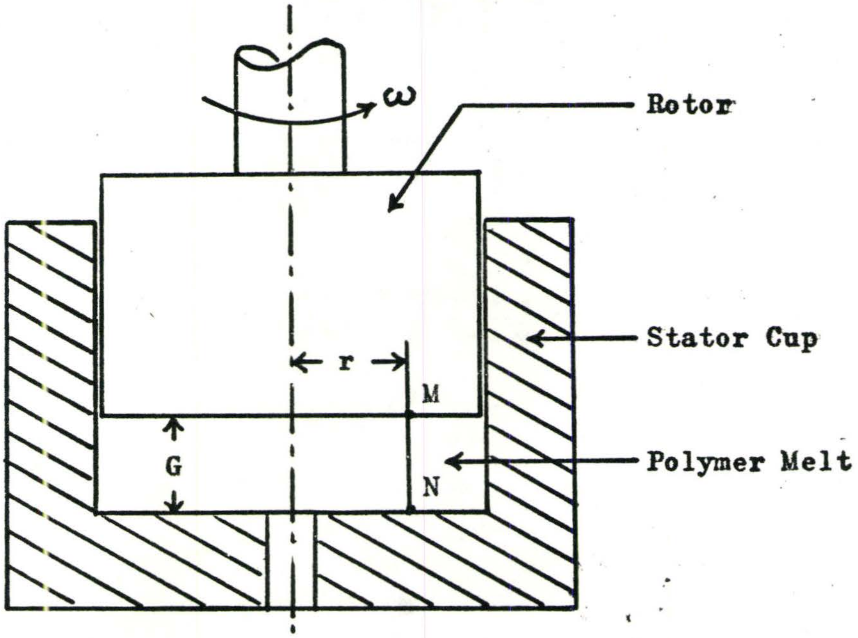


Fig. 2 Section View of Rotor and Stator Cup.

The high shear rate produces a high shear stress and thereby intensive mixing. In addition, some extensive mixing is produced by the smearing out of material along circular paths. This smearing out is greatest at the periphery of the rotor and decreases to essentially zero at the centre. Thus, in order to increase the homogeneity of the polymer melt, a method is needed to move the material near the center out to the region of high shear rate at the periphery. The principle used for this "back folding" process is illustrated in Figure 3.(60)

A relatively small diameter pin is centrally located through the rotor. It rotates with the rotor but is restrained from vertical motion. After melting and mixing has started, the rotor is raised, and because the pin is rotating, the polymer melt climbs up the pin as a result of normal force effect. Later in the cycle, the rotor moves downward, and point N of the polymer melt is scraped off the pin and moved radially outward from the axis of rotation. As a result, the "back folding" process is accomplished, as shown by the reversed position of M and N in Figure 3f. This step may be repeated several times if the residence time is not extremely short.

The relationships between shear rate, radius, and gap suggest that for a high shear rate during mixing, it is desirable for a large rotor radius and a small gap between the rotor and stator. On the other hand, since the injection pressure is developed by the downward force of the rotor, injection pressure is much reduced by the

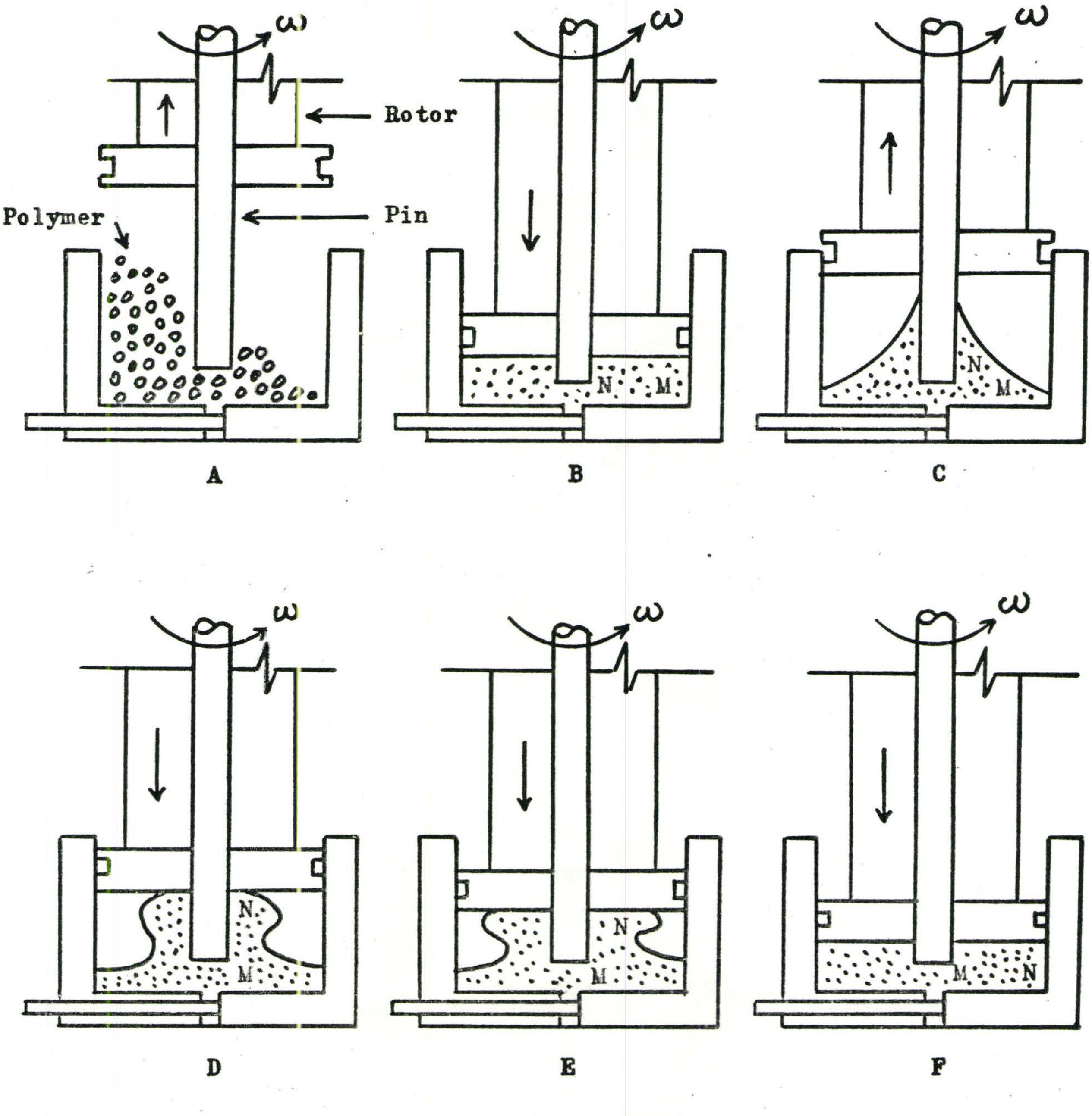


Fig. 3 Molding cycle sequence depicting extensive mixing-"back folding" process. As the rotor is raised, polymer (N) near the center of the rotor is drawn up along the pin, which is co-rotating but vertically stationary, while polymer (M) at the periphery is drawn to the bottom of the pin. As the rotor is lowered, polymer (N) is pushed into the space formerly occupied by polymer (M) at the periphery.

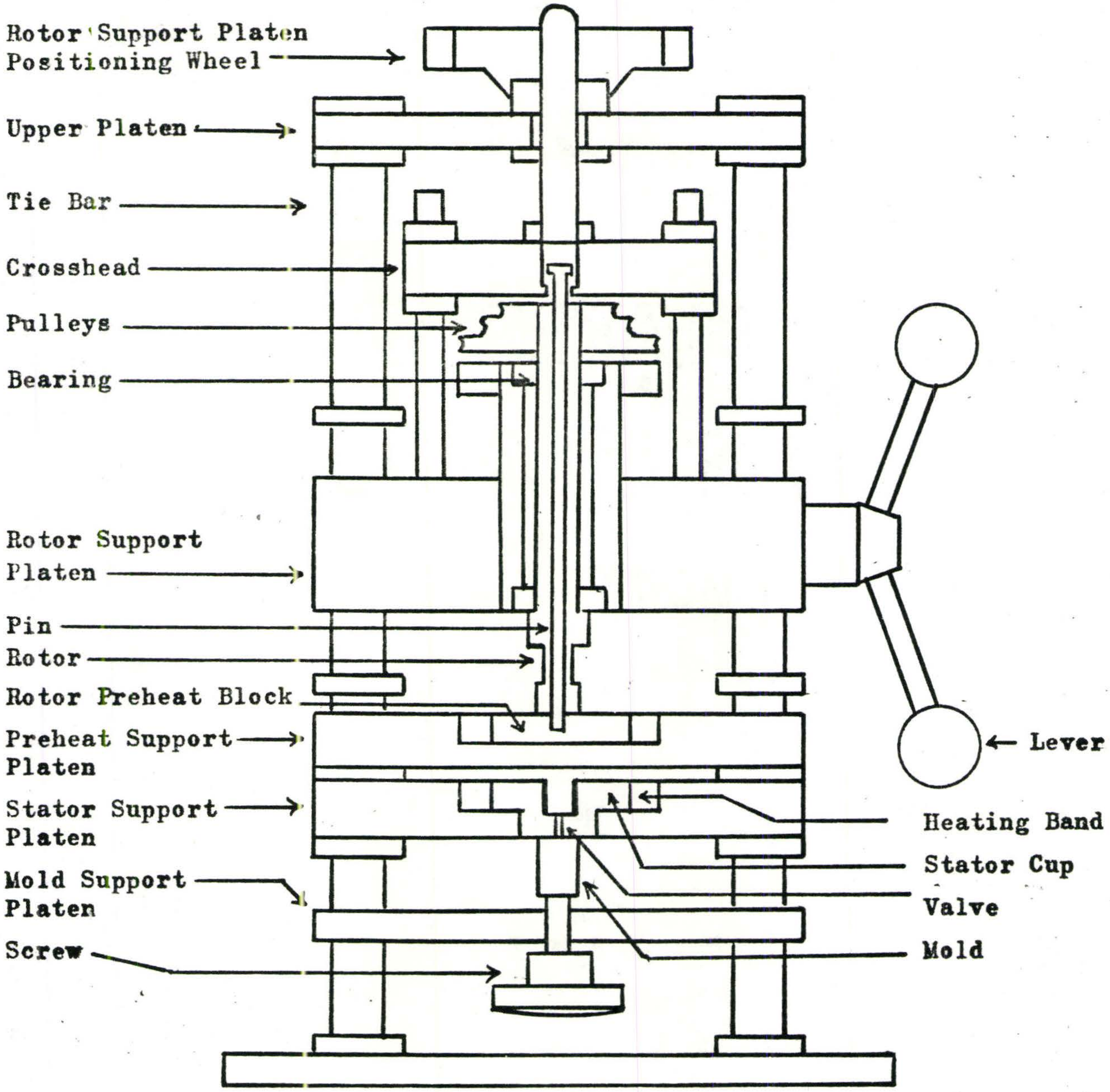


Fig. 4 Schematic Diagram of Mixing and Injection Molding Apparatus.

use of large rotor radii. A rotor diameter of 0.5 inch was chosen as a compromise in design. It provides a shear rate of approximately 100 sec^{-1} at 300 r.p.m. and an injection pressure of 4,000 psi can be developed by appling a downward force about 70 pounds on the injection lever.

As stated in the section of Introduction, rigid PVC is considered one of the most difficult polymers to process because it has a high melt viscosity. Injection molding of rigid PVC requires very high pressure usually in the order of 20,000 psi when molding takes place at room temperature.(4) This pressure is much higher than that can be developed by the miniature injection molding machine. One way to reduce the injection pressure is by increasing the temperature of the mold to the point where injection molding can be achieved with a pressure of less than 4,000 psi. After performing a series of trial and error experiments, it was found that the temperature of the mold should not be lower than 20°C below the temperature of the mixing cup and PVC melt. The temperature of the mixing cup and total time for mixing depended very much on the type of PVC resin. They varied from 180°C and 2.0 min. for high molecular weight resin ($\eta = 1.19$) to 165°C and 1.5 min. for low molecular weight resin ($\eta = 0.63$).

The procedures for making a PVC specimen by the miniature mixing and injection molding machine were as follows:

1. Before making any specimen, the stator cup and the rotor should be thoroughly cleaned and the rotating frequency of the rotor

Intrinsic Viscosity	Temperature of Mixing Cup	Mixing Time, min.
$\eta = 0.63$	165°C	1.5
$\eta = 0.86$	170°C	1.6
$\eta = 1.00$	175°C	1.8
$\eta = 1.19$	180°C	2.0

Table 1. Temperature of Mixing Cup and Mixing Time for Different Resins.

should be set at highest speed (300 r.p.m.).

2. The injection lever block was raised to the highest position by means of lift hand wheel. The rotor preheat block was swung into position under the rotor and injection lever block was lowered until rotor tip contacted the top of the rotor preheat block. In this position, the mixing rod was inside the hole of the rotor preheat block.
3. The two heater controls (rotor preheat and stator cup) were turned on and adjusted to desired temperature.
4. The mold was placed in a oven with a temperature set at 20°C less than that of stator cup.
5. When the desired temperature has been reached, the injection lever block was raised and the rotor preheat block was swung out of the way. About 0.5 gram of PVC premix was placed into the stator cup.
6. The injection lever was then lowered fully to its lower stop and the motor was turned on.

7. By means of the injection lever, the rotor tip was raised and lowered for at least 10 times to impart radial mixing by "back folding" process.
8. When proper mixing time was reached, the stator cup valve was opened and a small quantity of PVC melt was extruded out (approximately 1/4 inch).
9. After the extrudate was removed with tweezers, the hot mold was placed on the mold support wheel which was then turned to clamp the mold against the bottom of the stator cup.
10. The valve was opened and the PVC melt was injected into the mold by means of the injection lever.
11. The mold was removed from machine and quenched into cold water.
12. The injection lever block was raised again and excess PVC melt in the stator cup was removed as a whole piece with tweezers.
13. The valve was closed and the motor was then turned off.
14. The specimen was removed from the mold.
15. The cold mold was placed back into the oven.
16. When the mold reached the temperature of the oven, the above procedures could be repeated for making another specimen.

3.4 After Treatment of Specimens:

The specimens made by the miniature mixing and injection molding machine are specially designed for testing on the miniature tensile testing machine also manufactured by Custom Scientific Instrument, Inc. The specimen is relatively small and in a usual standard 'dumb-bell' shape with overal length of 3/4 inch and a 1/16 inch diameter by

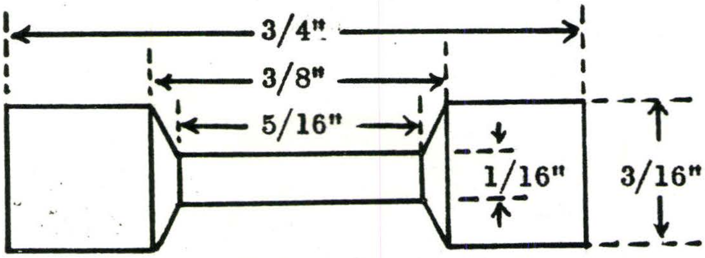


Fig. 5. Dimensions of the Specimen.

5/16 inch long test section. It weighs about 0.2 gram.

As mentioned in Introduction, rapid cooling during quenching in cold water freezes polymer chains of the specimen into fixed random position. Thus before the specimens were tested on the tensile tester, they were all annealed at 110°C for 20 minutes. At this temperature (about 35°C above the glass transition temperature) some polymer chains may move into more favoured, ordered positions and reducing free volume considerably. In the second part of the experiment, specimens were annealed at 110°C with different time intervals of 5 minutes, 10 minutes, 20 minutes, 60 minutes and 180 minutes. Their mechanical properties were compared with those which had not been annealed at all.

Five specimens were tested for each sample. This is also the number of test specimens recommended by A.S.T.M.(61) (American Society for Testing and Materials). The more specimens tested for each sample the more accurate the result would be, but injection molding of PVC is very time consumming. Five specimens for each sample would be enough, because they do provide quite reproducible results. For example, variation of yield stress is only about 0.9 % in most cases.

Although the dimensions of all the specimens are approximately the same, they are not exactly identical. The dimensions of the test section of each individual specimen were measured, since the diameter of the specimen is very critical in determination of its yield stress and ultimate tensile strength. For those specimens used in conducting the second part of the experiment, dimensions of the specimens before and after annealing were also recorded to see the amount of volume change.

3.5 Testing of Specimens:

The first set of specimens (12 samples) were tested on the miniature tensile tester. All the rest were tested on the traditional Instron tensile testing machine. Although the results obtained from both machines are comparable, it is found that the Instron tester is potentially a better machine. The variation among the five specimens are considerably smaller and testing on the Instron machine is less time consumming.

Before testing, the machine was calibrated by usual means to give a spread of 2 inch from a load of 10 pounds. The maximum load on the 10 inch wide chart was 50 pounds. Three testing speeds were selected. The different beam speeds and the corresponding recording chart speeds of both machines are listed in Table 2. All of the tests were conducted at a room temperature of $30^{\circ}C \pm 2^{\circ}C$.

In analyzing the data, the testing sections of the specimens

Instron Tester		Miniature Tester	
Beam Speed	Chart Speed	Beam Speed	Chart Speed
0.02 in/min	2 in/min	0.0225 in/min	20 sec/in
0.1 in/min	10 in/min	0.1125 in/min	5 sec/in
0.5 in/min	50 in/min	0.45 in/min	2 sec/in

Table 2. Different testing beam speeds and corresponding chart speeds.

were assumed to have constant volume initially to the region just beyond the yield point. Thus in this initial region, the instantaneous cross-section area of the specimen could be determined from the amount of elongation the specimen had, which could be obtained from the X-axis of the recording chart. The true stress at any instant is the loading force divided by the instantaneous cross-section area of the specimen at that instant. The true yield stress is the loading force at yield point divided by the instantaneous cross-section area of the testing section at yield point. Tensile modulus which is also known as Young's modulus is the straight line portion (within 50 % of the maximum yield stress region) of the true stress versus nominal strain curve. On the other hand, the ultimate tensile strength was measured on the nominal basis, that is the loading force at fracture divided by the initial cross-section area of the specimen. The reason for this is that just before fracture occurred, a weak spot developed with a cross-section area much less than the rest of testing section. Hence after breaking, the diameter at the break is smaller than the rest of testing section. It is also not consistent to take the diameter of testing section after breaking as the diameter at the instant of breaking, because the material is viscoelastic. After the yield point, the specimen goes through orientation hardening and the material changes from colourless to white. This shows voids are formed and the volume of the specimen has been changed. So the instantaneous cross-section area of the specimen cannot be determined from the amount of elongation it had.

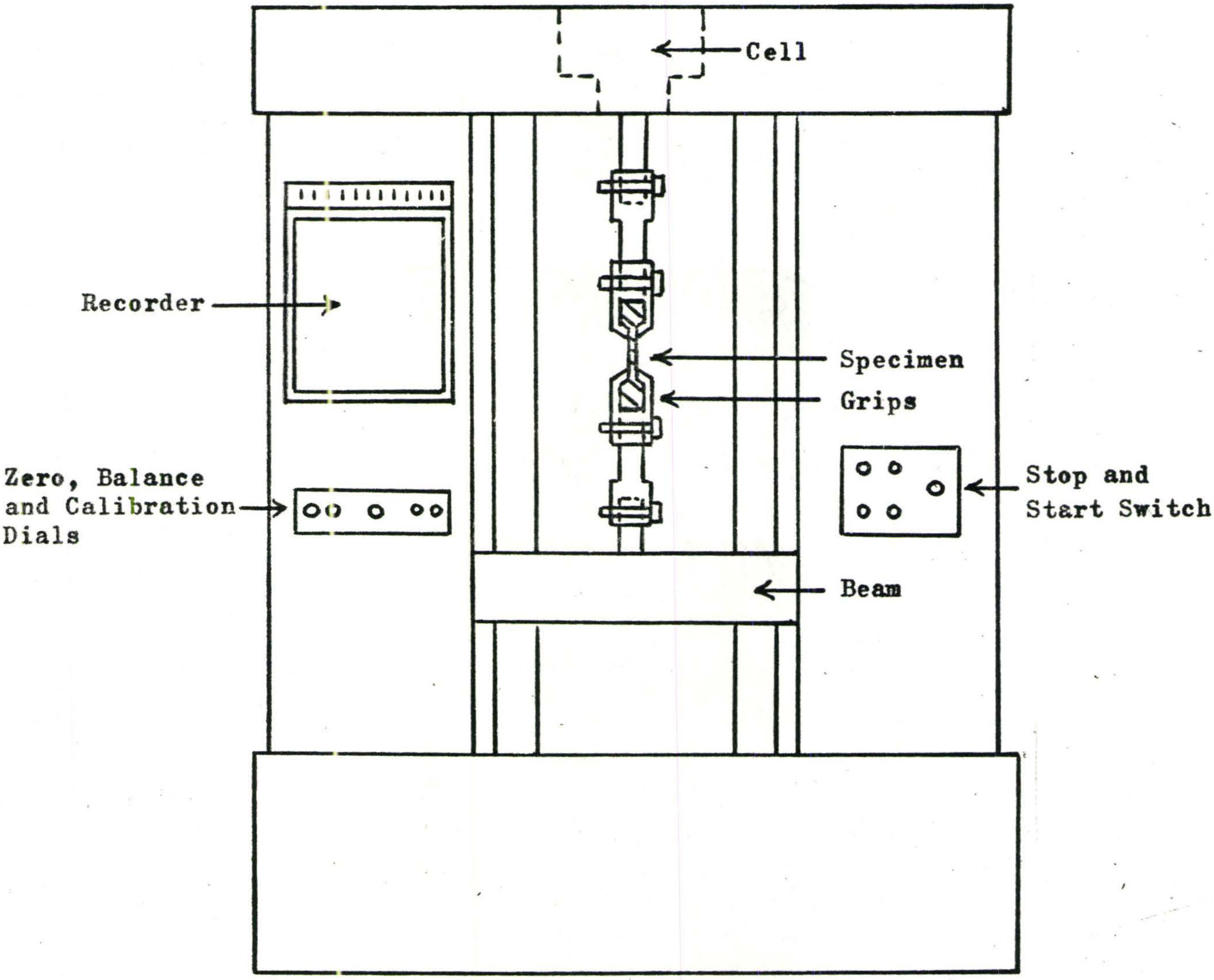


Fig. 6 The Instron Tensile Tester.

4. Results

All PVC specimens tested showed inhomogeneous deformation after yield point. The phenomenon is referred to as 'necking'. The reason why inhomogeneous deformation occurs is that homogeneous deformation has become unstable. There are many possible reasons for this instability; the most important two are:

I. Strain softening: If local strain should happen to be slightly higher than elsewhere (possible due to some stress concentration) then the material will be softer locally and it will therefore deform to a higher strain than elsewhere and becomes softer still. This process can only be stopped by the eventual orientation hardening of the material.

II. Necking: If part of the specimen should happen to be slightly thinner than the rest, then the stress there will be slightly higher. This will concentrate further deformation at that point and increase the local stress further. A neck in the specimen will be formed and a geometrical instability will result.

The phenomenon of 'necking' will be described in more detail in the next section.

12 samples of PVC resin Esso grade 369 ($\eta = 1.00$) with Mark-99 barium/cadmium complex stabilizer contents varied from 2 phr

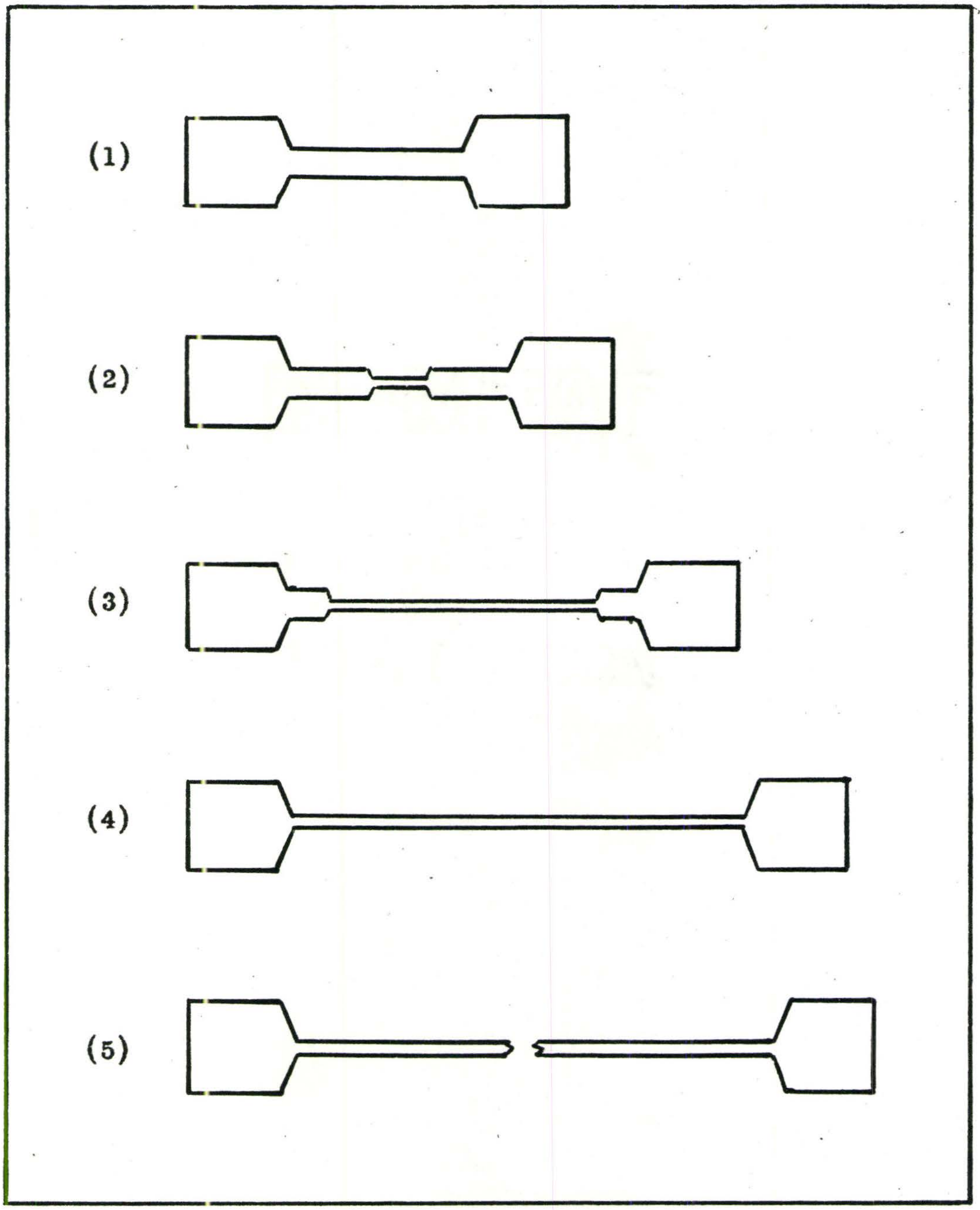


Fig. 7 Inhomogeneous Deformation Sequences of PVC Specimen after Yield Point.

to 6 phr were tested on the miniature tensile tester. It was found that the tensile yield stress decreased slightly with increase in stabilizer content. Figure 8 shows that true tensile yield stress decreases about 500 psi when the Mark-99 stabilizer content increased from 2 phr to 6 phr. The results are similar from three testing speeds (straining rates). True tensile yield stress also increases with increasing straining rate. This has been well established because increase in straining rate increases the brittle-ductile transition temperature of PVC.(62)

Tensile modulus usually increases or decreases with yield stress. But in this study, the result shows the contrary which is not expected. Figure 9 shows tensile modulus increases slightly with increase in stabilizer content for all three straining rates.

Like the true yield stress, figure 10 shows that nominal ultimate tensile strength decreases slightly with increase in stabilizer content. Comparison of the true tensile yield stress data with the nominal tensile strength indicates more scatter. This might be due to the fact that the processing conditions of the specimens were not exactly identical. As the specimens were individually produced by injection molding, the mixing temperature, time of mixing, amount of extensive mixing (back folding) were not exactly the same. These differences do not show any substantial effects before orientation hardening (necking) had occurred. But because of these differences the amount of orientation hardening the specimens would have would be different, giving large differences in the nominal ultimate tensile strength of the specimens.

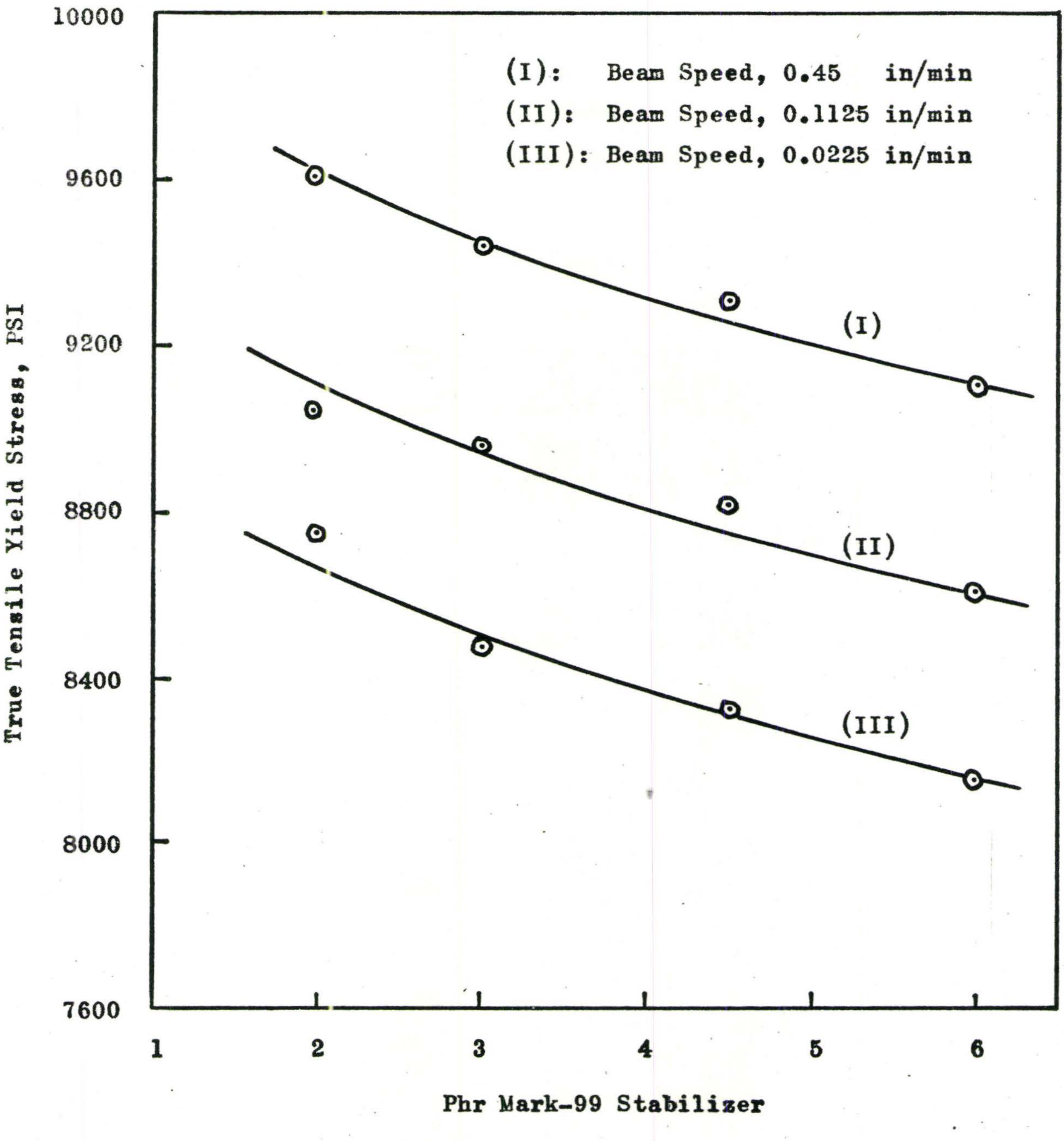


Fig. 8 Effect of Stabilizer Content on True Tensile Yield Stress. PVC Resin 369 (η = 1.00).

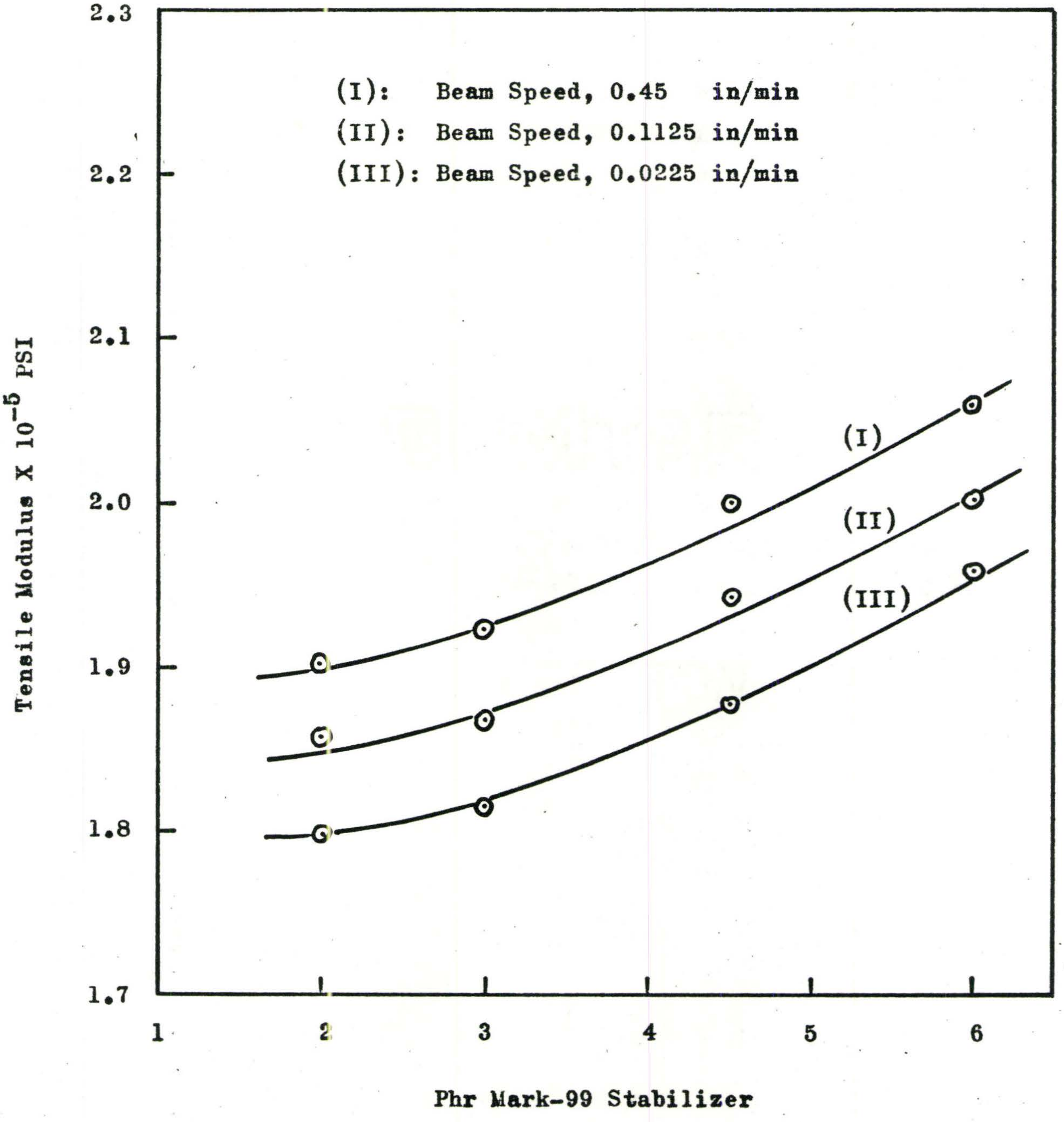


Fig. 9 Effect of Stabilizer content on Tensile Modulus. PVC Resin 369 (η = 1.00).

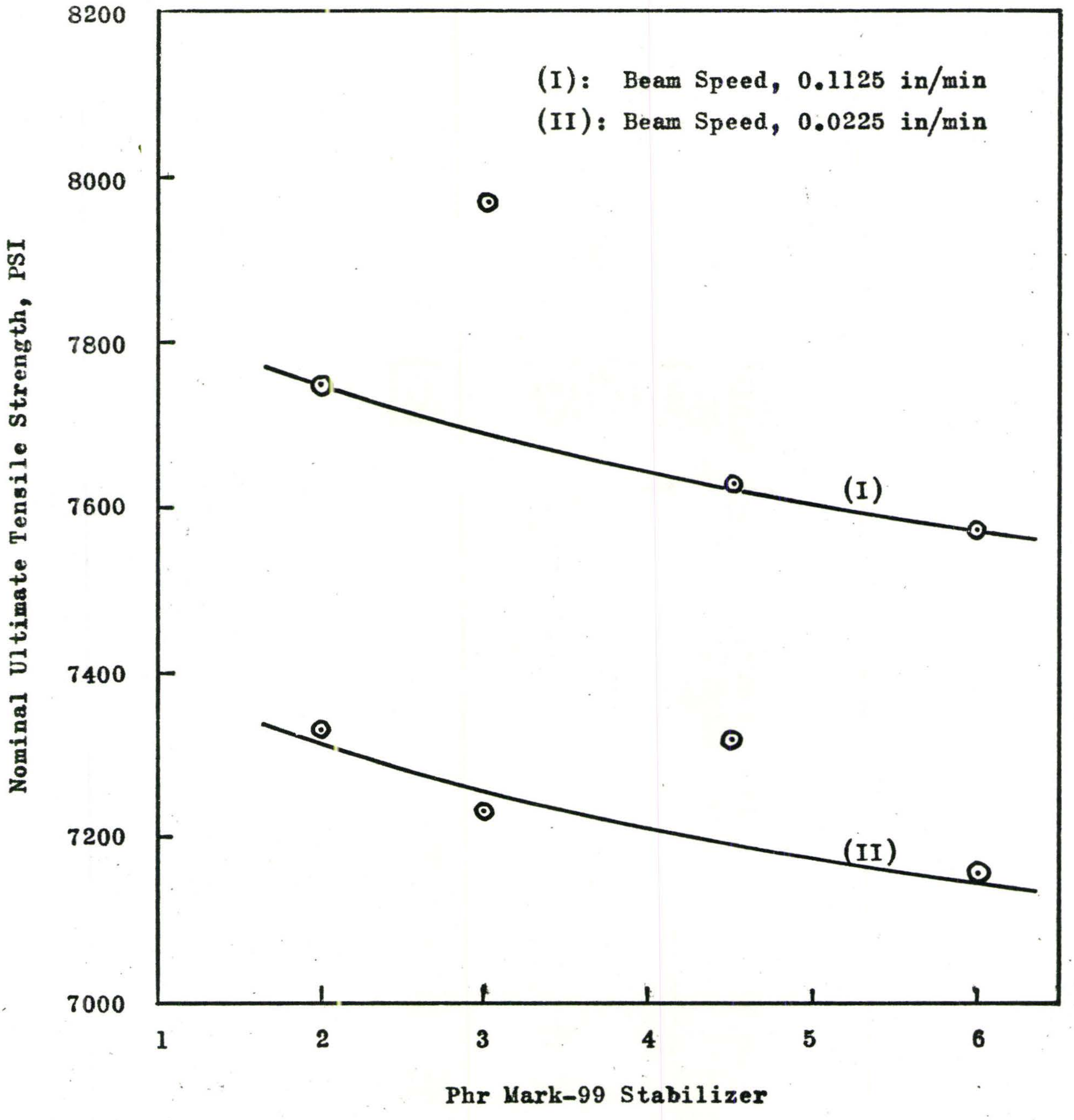


Fig. 10 Effect of Stabilizer Content on Nominal Ultimate Tensile Strength. PVC Resin 369 (η = 1.00).

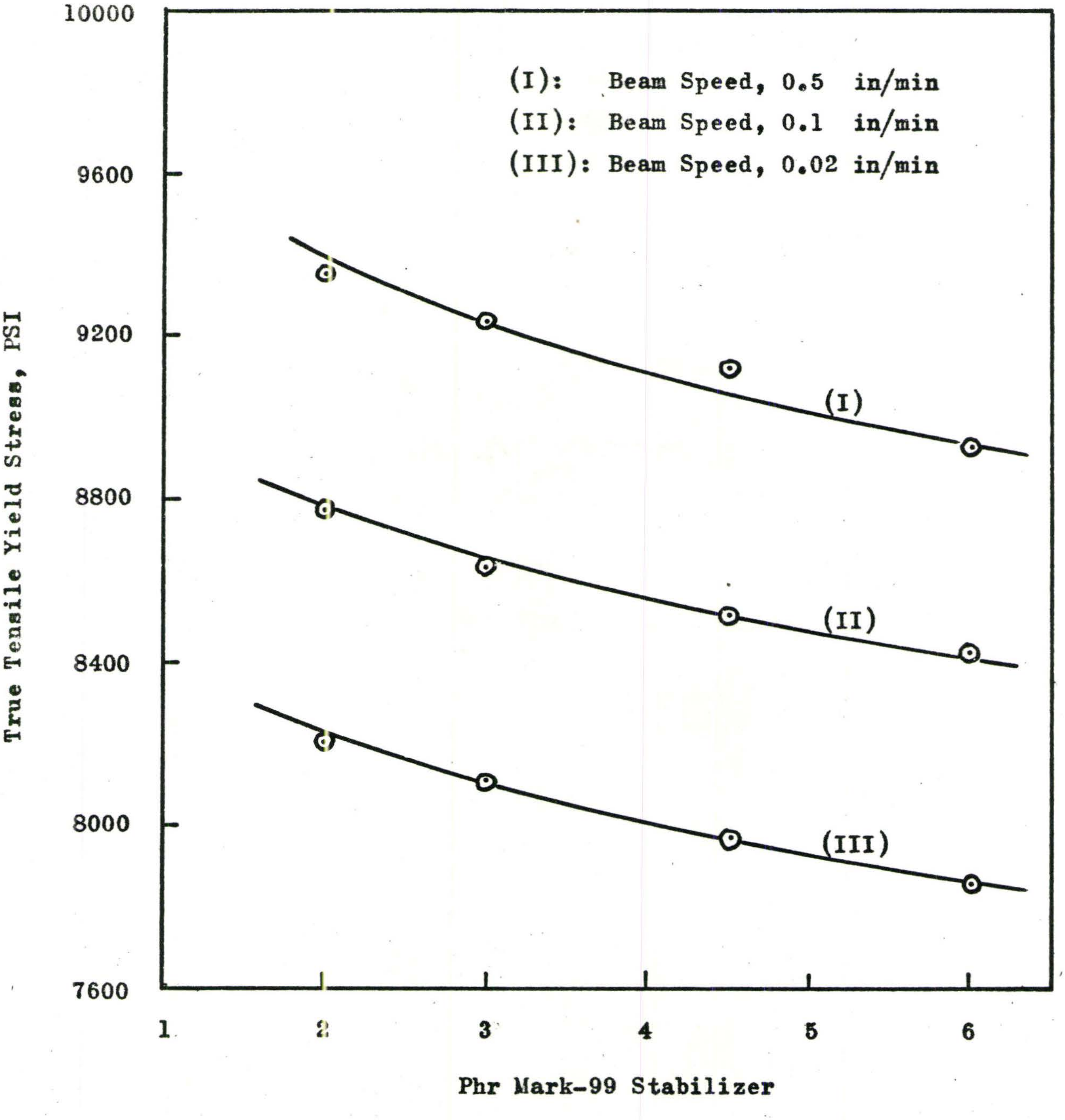


Fig. 11 Effect of Stabilizer content on True Tensile Yield Stress. PVC Resin 353 (η = 0.63).

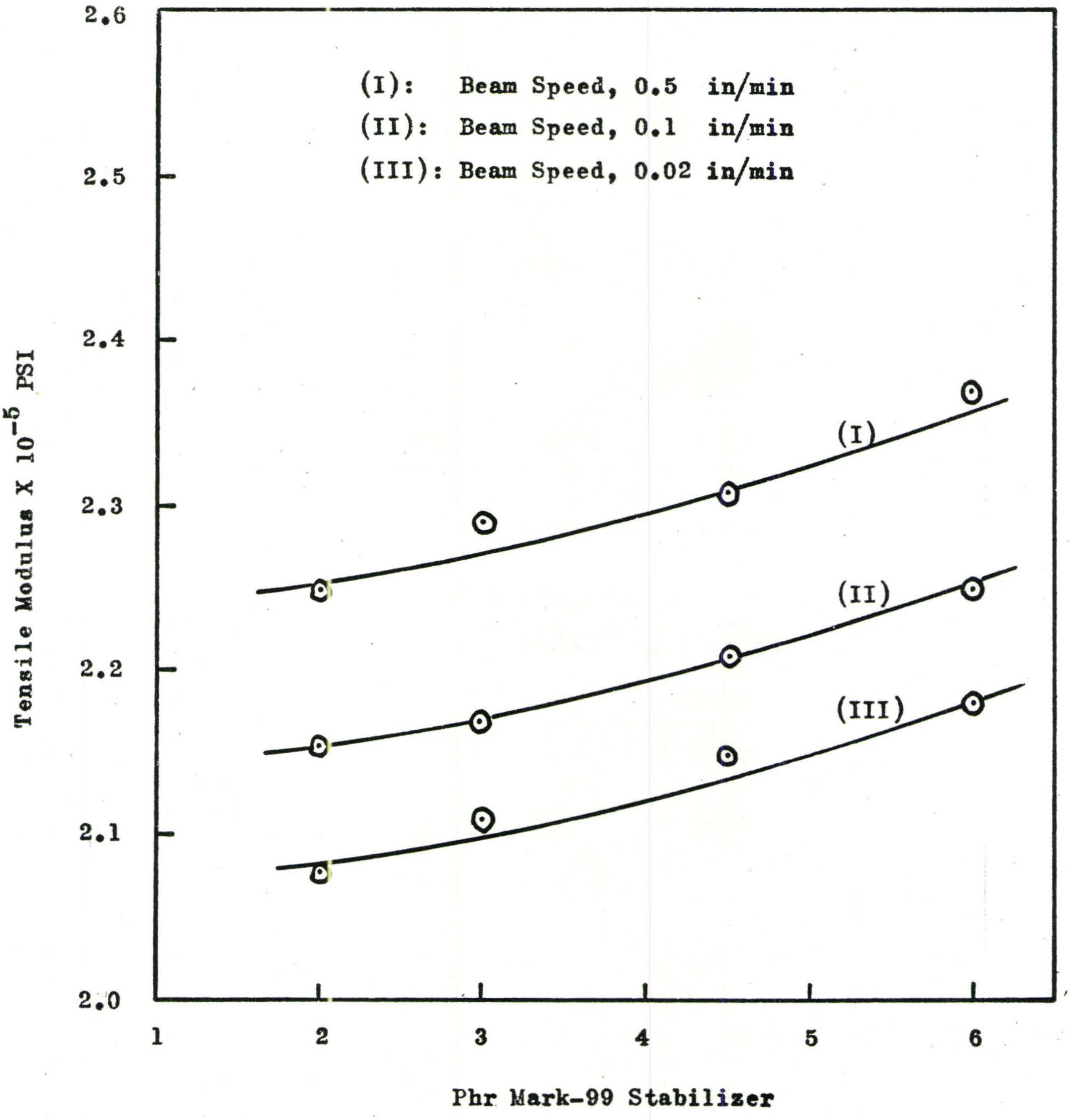


Fig. 12 Effect of Stabilizer Content on Tensile Modulus PVC Resin 353 (η = 0.63).

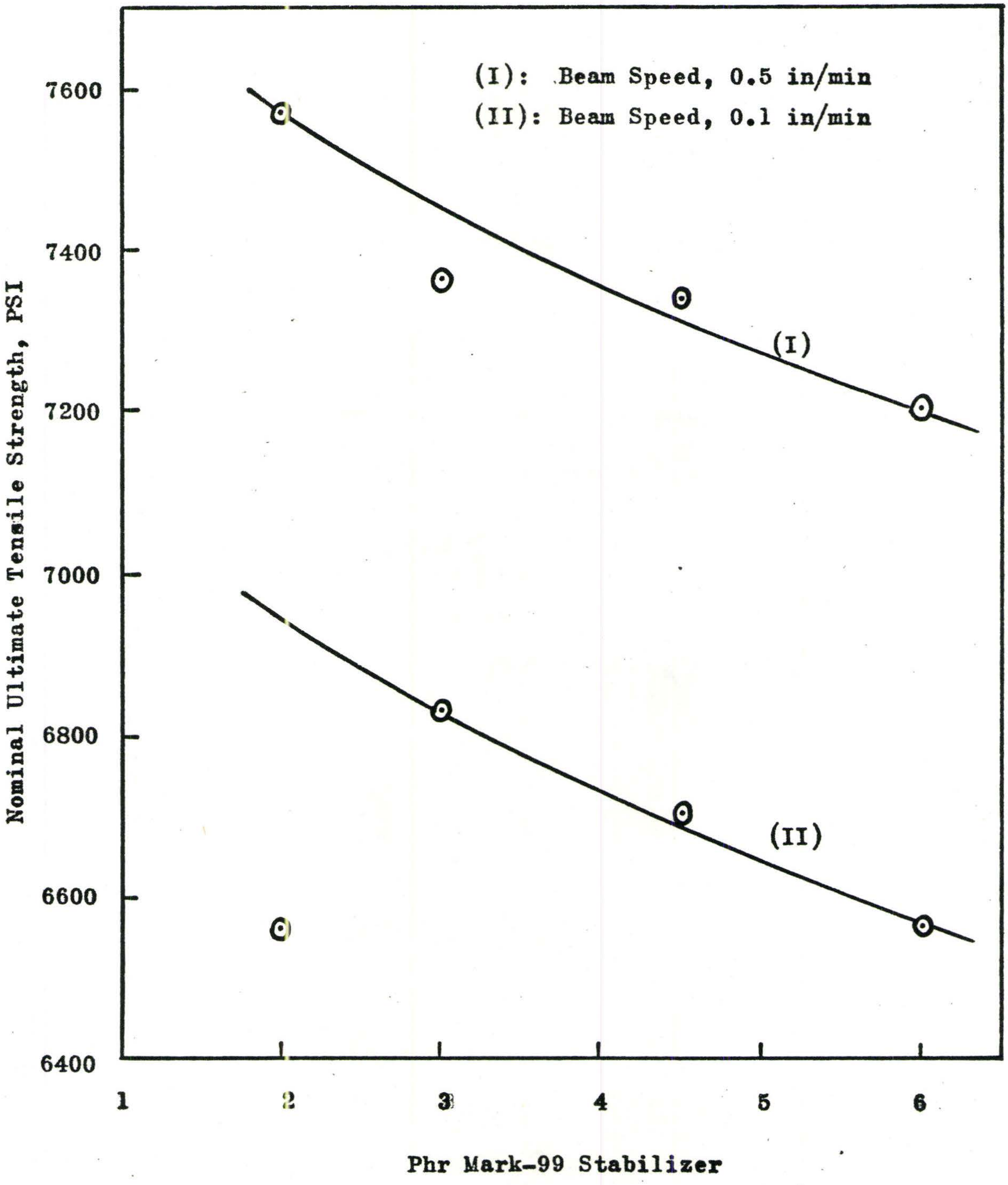


Fig. 13 Effect of Stabilizer Content on Nominal Ultimate Tensile Strength. PVC Resin 353 (η = 0.63).

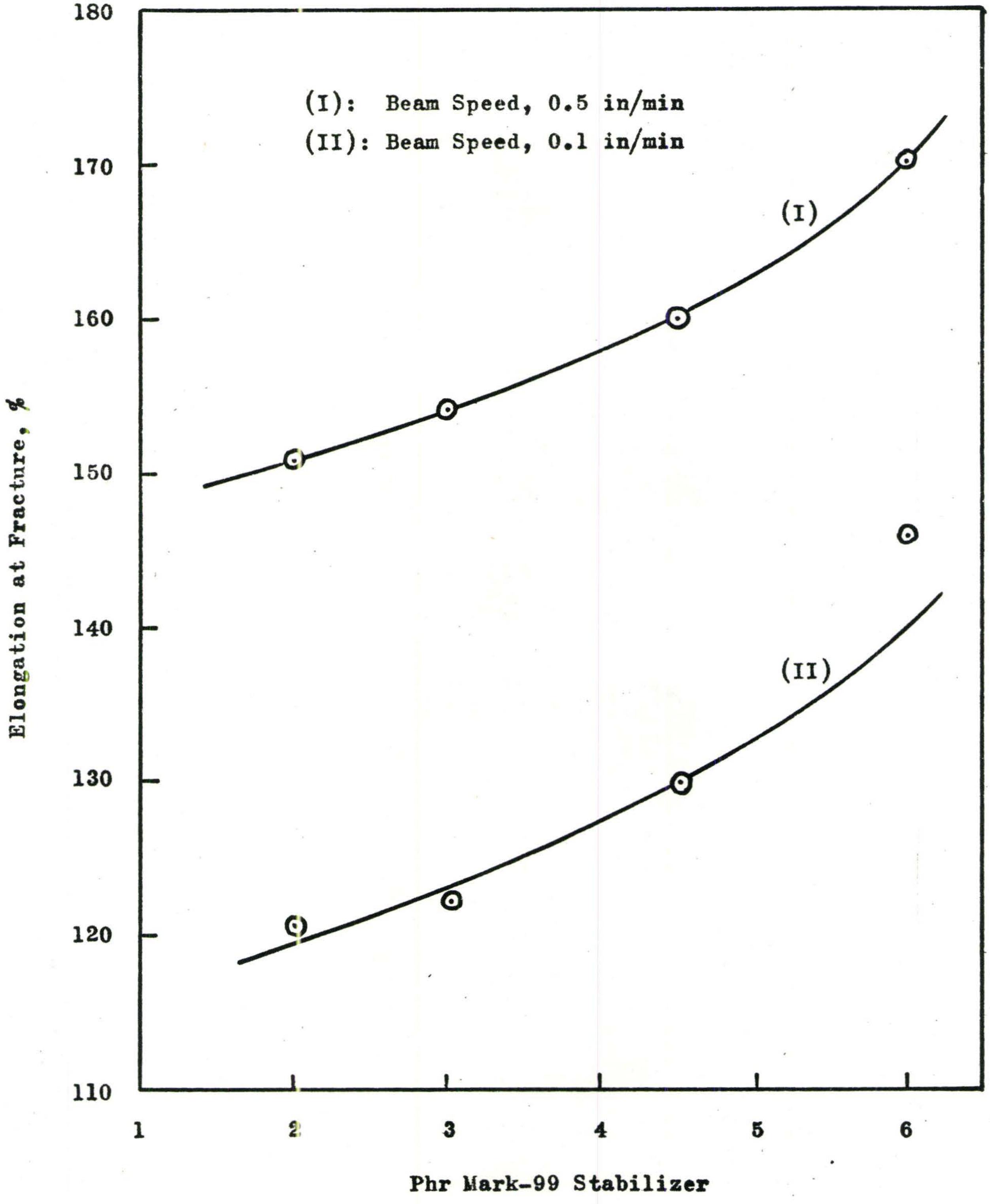


Fig. 14 Effect of Stabilizer Content on Elongation at Fracture. PVC Resin 353 ($\eta = 0.63$)

Another 12 samples of PVC resin Esso grade 353 (η = 0.63) with different contents of Mark-99 stabilizer were tested on the Instron tensile tester. As far as the effect on the amount of stabilizer is concerned, the results (figure 11 - 13) are similar to those previously mentioned. There are differences in the value of true tensile yield stress, tensile modulus and ultimate tensile strength due to the difference in molecular weight. Figure 14 shows elongation at fracture also increases slightly with increase in stabilizer content.

In the second part of the study, 5 samples of PVC resin 353 (η = 0.63) were annealed at 110°C for different time intervals of 5 minutes, 10 minutes, 20 minutes, 60 minutes and 180 minutes. All specimens contained 4.5 phr Mark-99 stabilizer. The specimens were tested on the Instron tensile tester using a beam speed of 0.1 in/min. A sample of specimens which had not been annealed at all was also tested. Figure 15 and 16 show both the true tensile yield stress and tensile modulus increase with amount of heat treatment (time of annealing) initially, but remain constant from 60 minutes and onward. Figure 17 shows nominal ultimate tensile strength also increases slightly with increase in annealing time. On the other hand, figure 18 shows elongation at fracture decreases when heat treatment increased, but also levels off at 60 minutes. The major cause of all these mechanical properties changes brought about by annealing is due to the change in free volume of the specimen after annealing. Figure 19 shows the changes in volume of the specimens after annealing at different times.

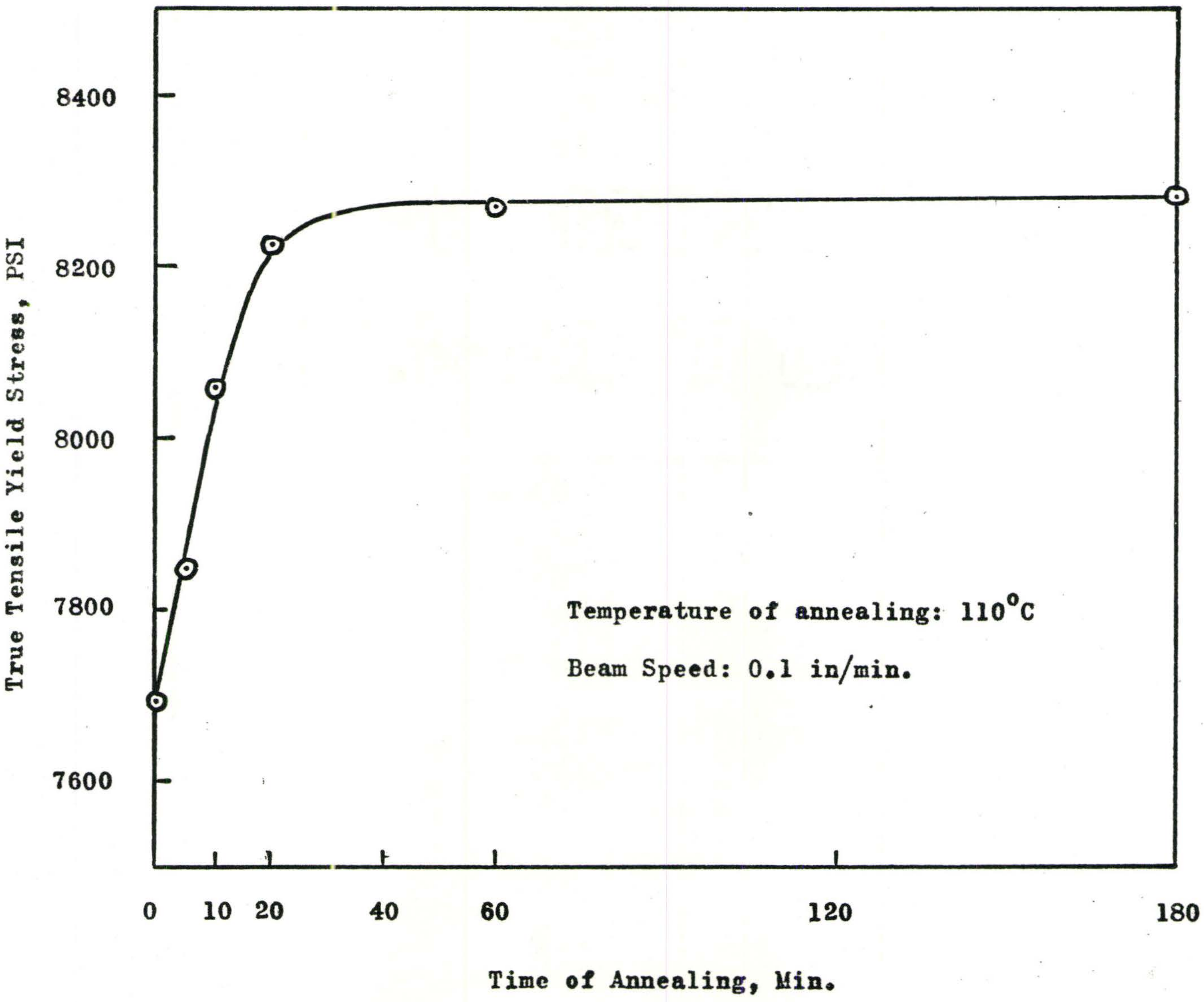


Fig. 15 Effect of Annealing Time on True Tensile Yield Stress. PVC Resin 353 (η = 0.63) with 4.5 phr Mark-99 Stabilizer.

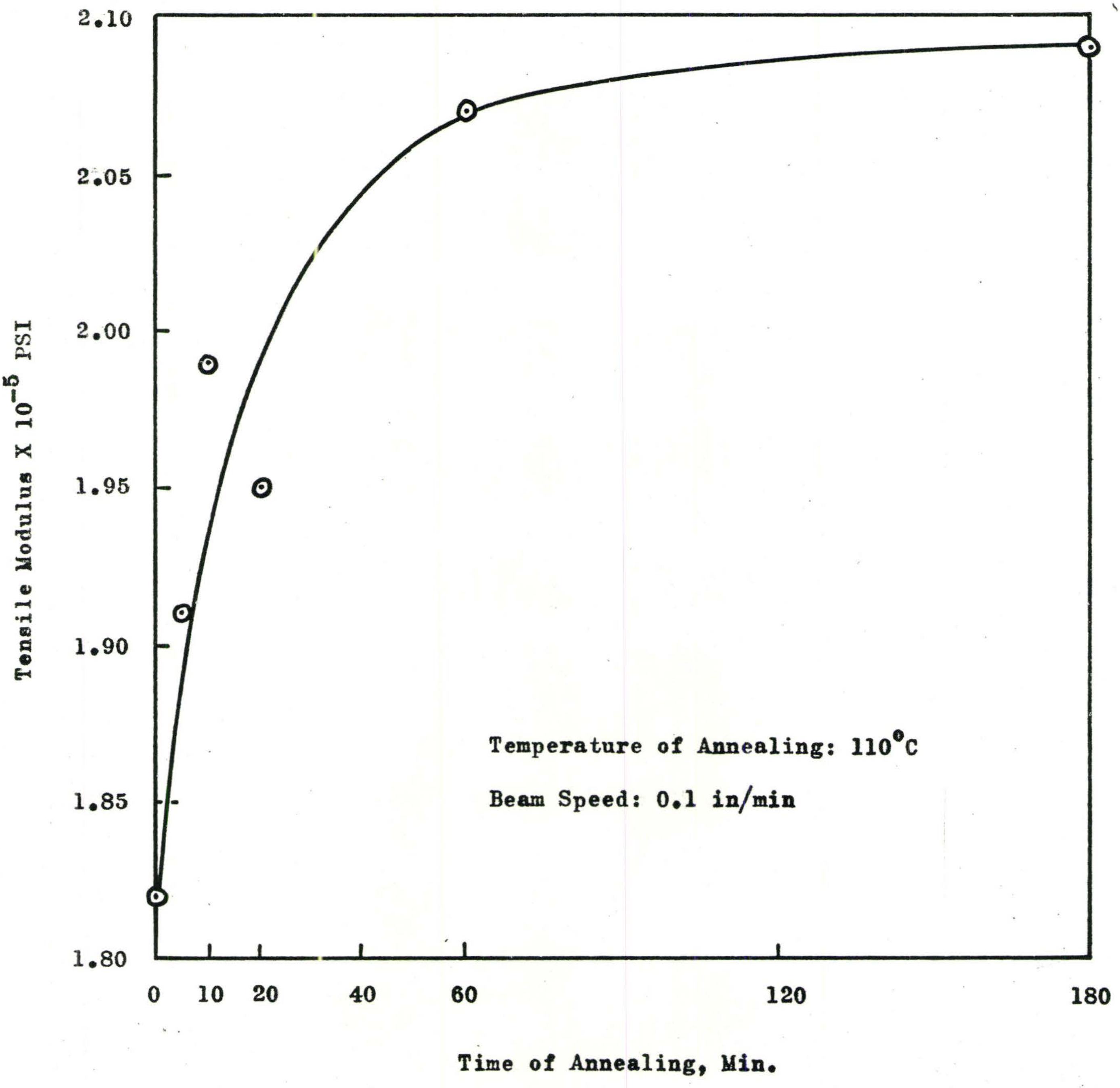


Fig. 16 Effect of Annealing Time on Tensile Modulus. PVC Resin 353 (η = 0.63) with 4.5 phr Mark-99.

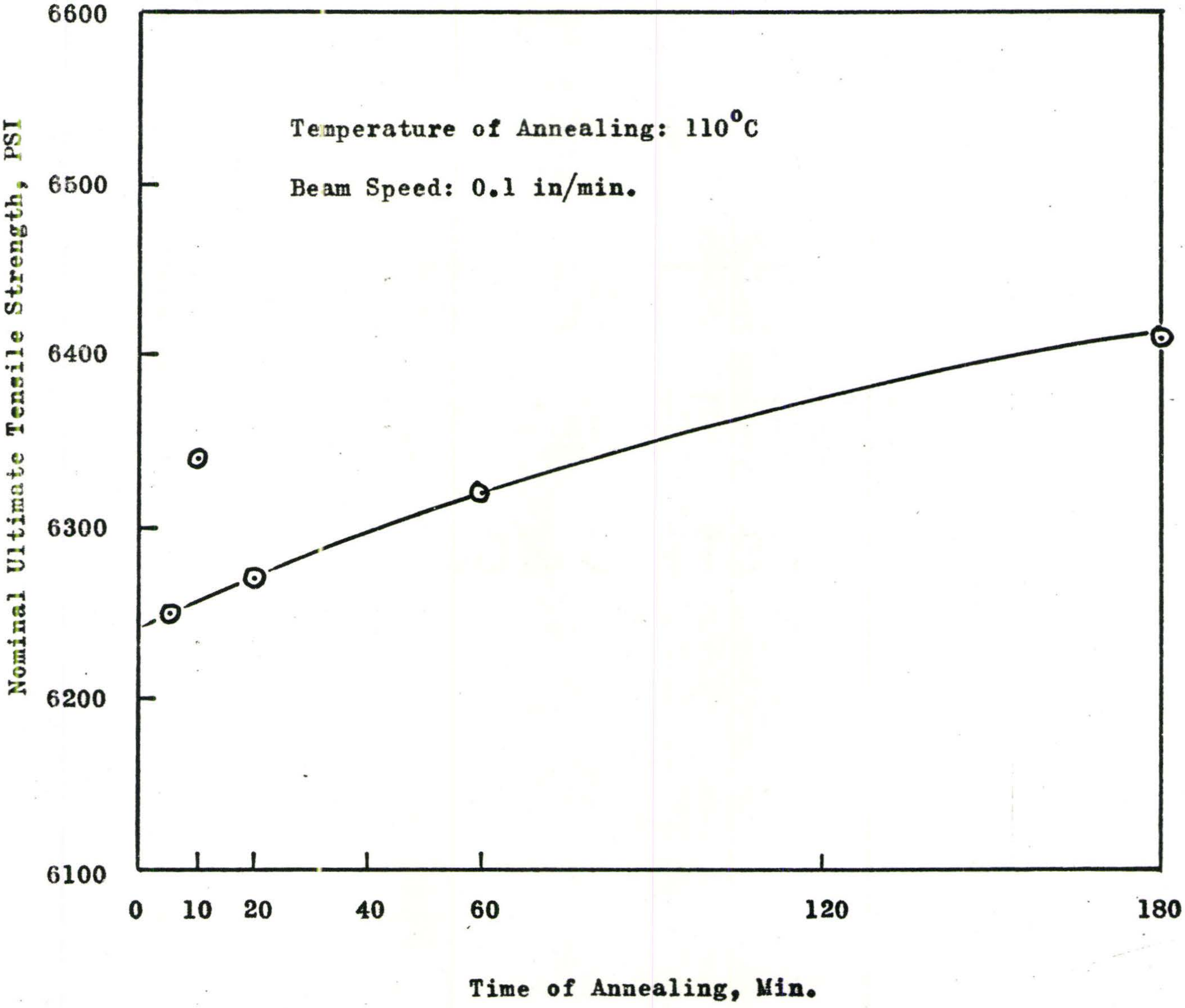


Fig. 17 Effect of Annealing Time on Nominal Ultimate Tensile Strength. PVC Resin 353 ($\eta = 0.63$) with 4.5 Phr Mark-99.

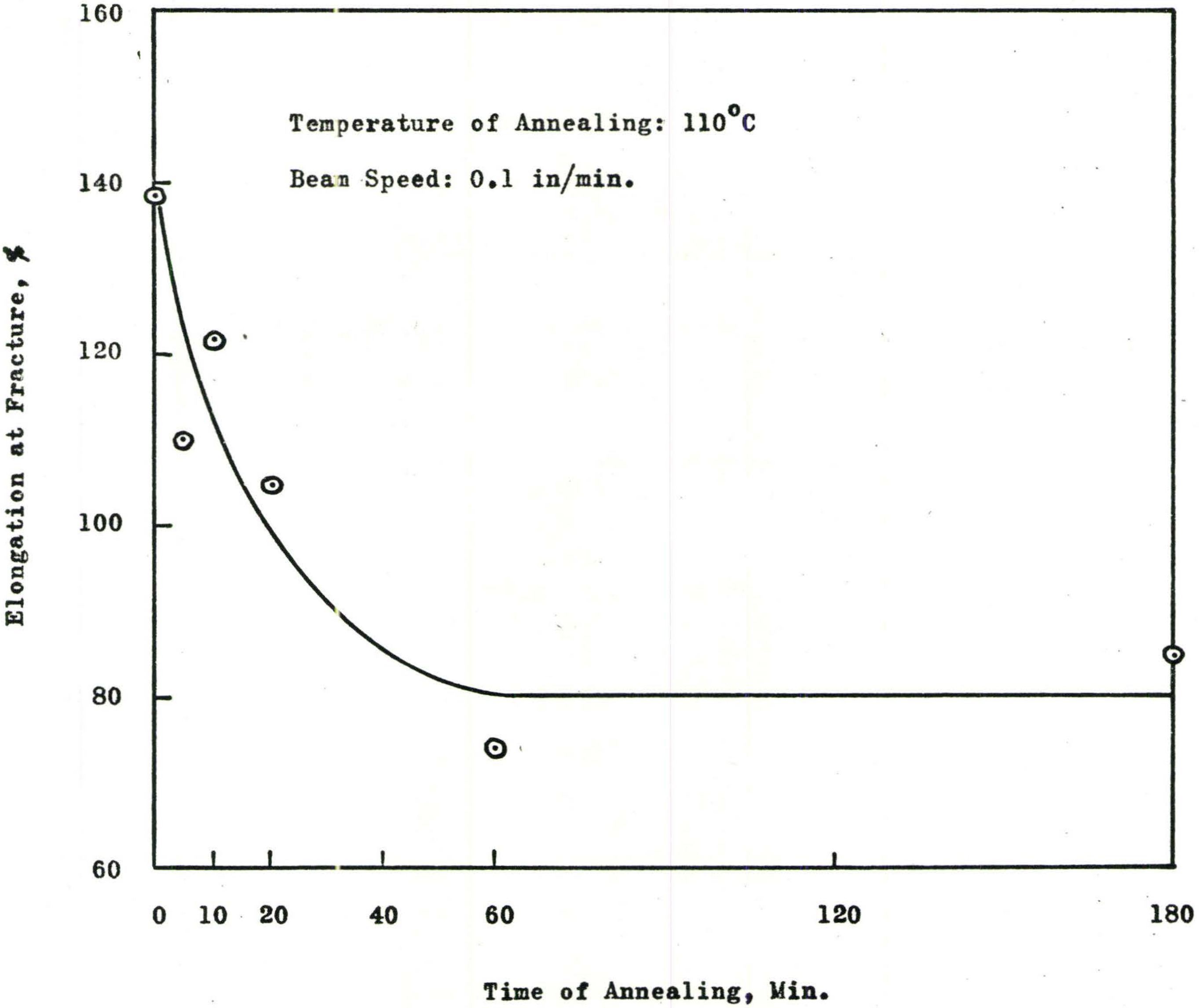


Fig. 18 Effect of Annealing Time on Elongation at Fracture.

PVC Resin 353 (η = 0.63) with 4.5 phr Mark-99.

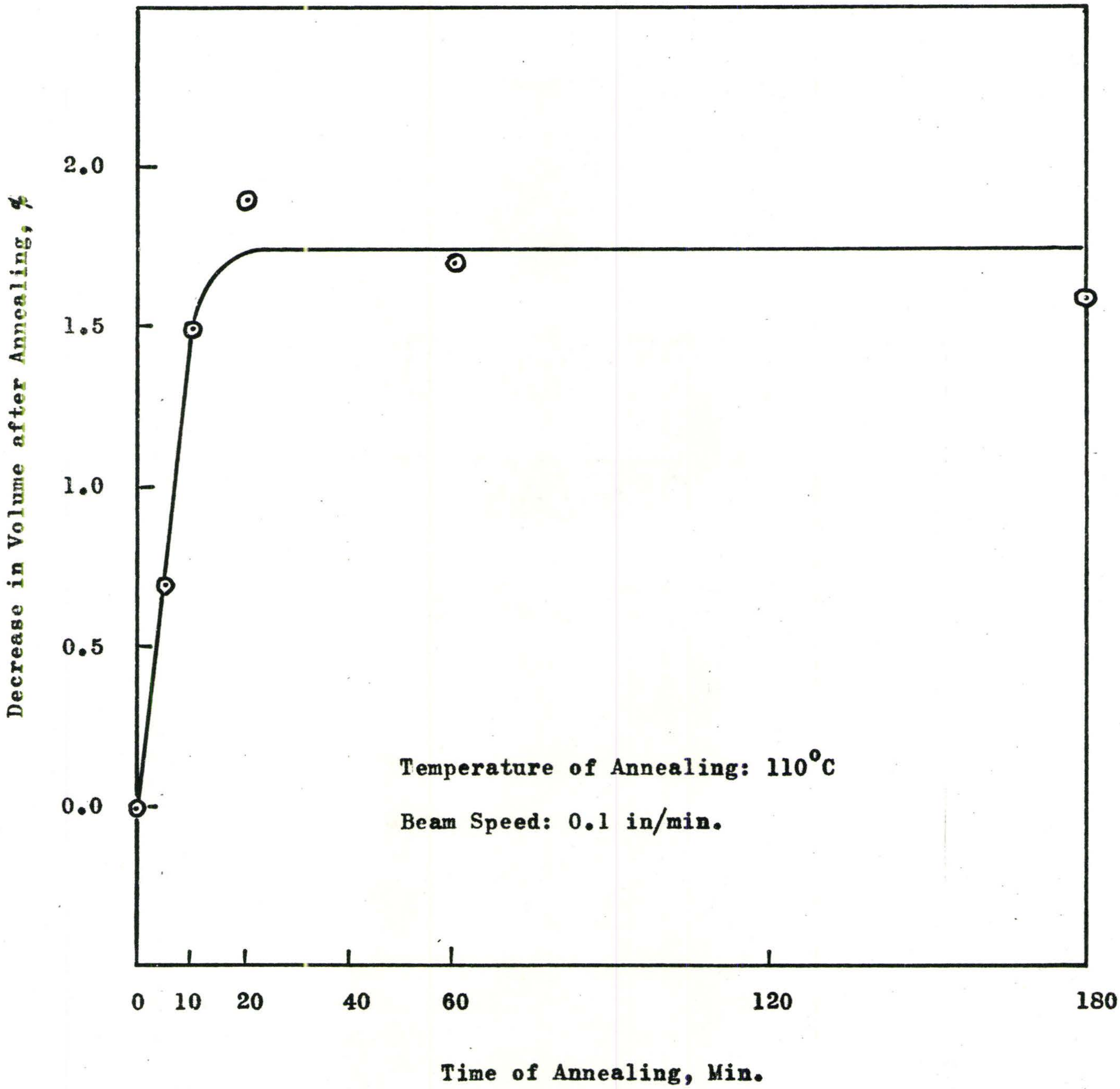


Fig. 19 Effect of Annealing Time on Density of Specimens. PVC Resin 353 (η = 0.63) with 4.5 phr Mark-99.

In the last part of the study, specimens made with PVC resin of different molecular weights were tested on the Instron Tensile Tester. The specimens contained different stabilizer contents of 3, 4.5, and 6 phr Mark-99 and they were all annealed at 110°C for 20 minutes before testing. A medium beam speed of 0.1 in/min was used for the tests. Figure 20 shows true tensile yield stress increases with nominal intrinsic viscosity which is a function of weight average molecular weight for all three different stabilizer contents. Like the yield stress, figure 22 shows ultimate tensile strength also increases with intrinsic viscosity of PVC. On the other hand, figure 21 shows tensile modulus decreases with intrinsic viscosity of the polymer.

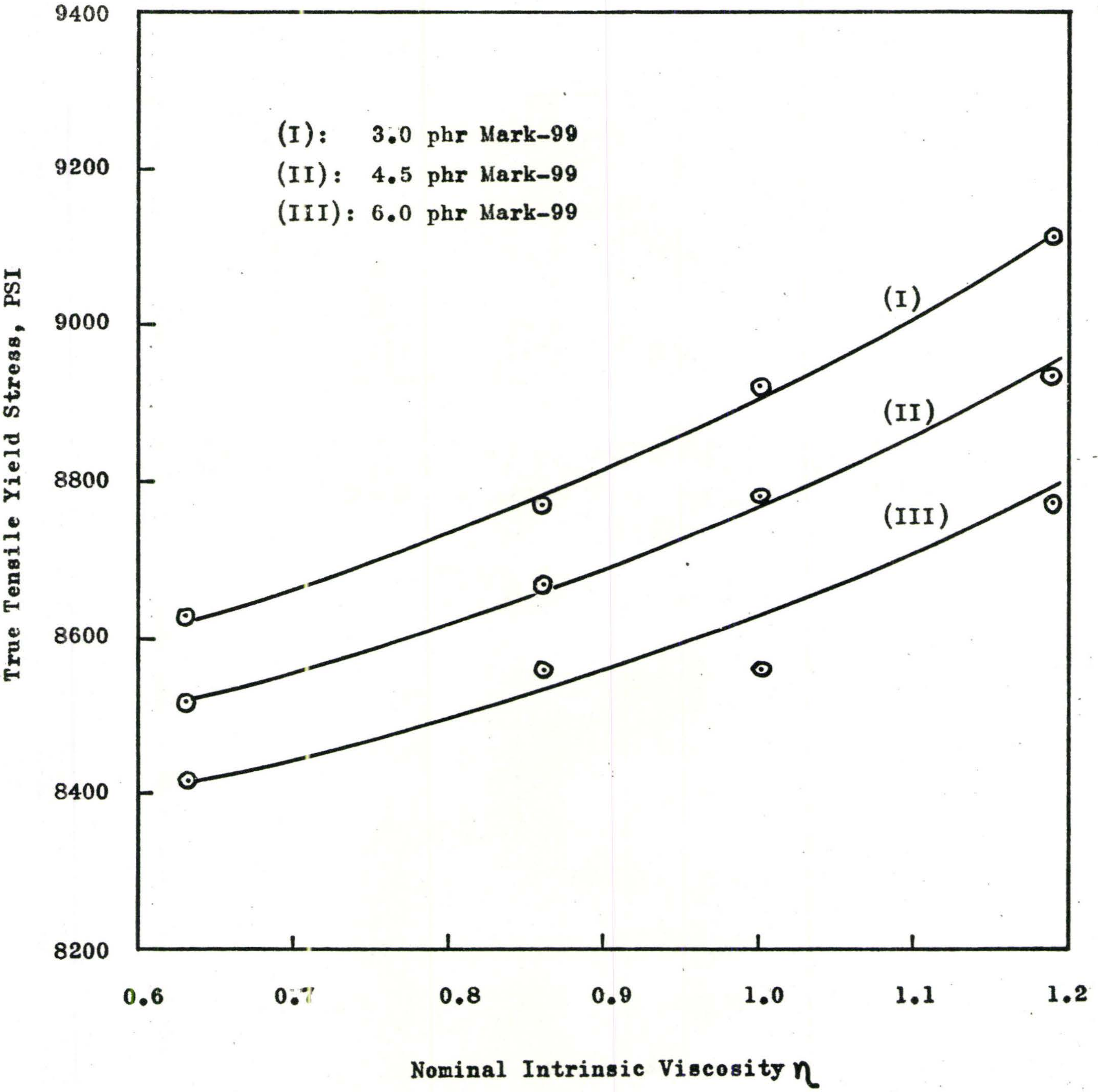


Fig. 20 Effect of Weight Average Molecular Weight (Function of Intrinsic Viscosity) on True Tensile Yield Stress. Beam Speed: 0.1 in/min.

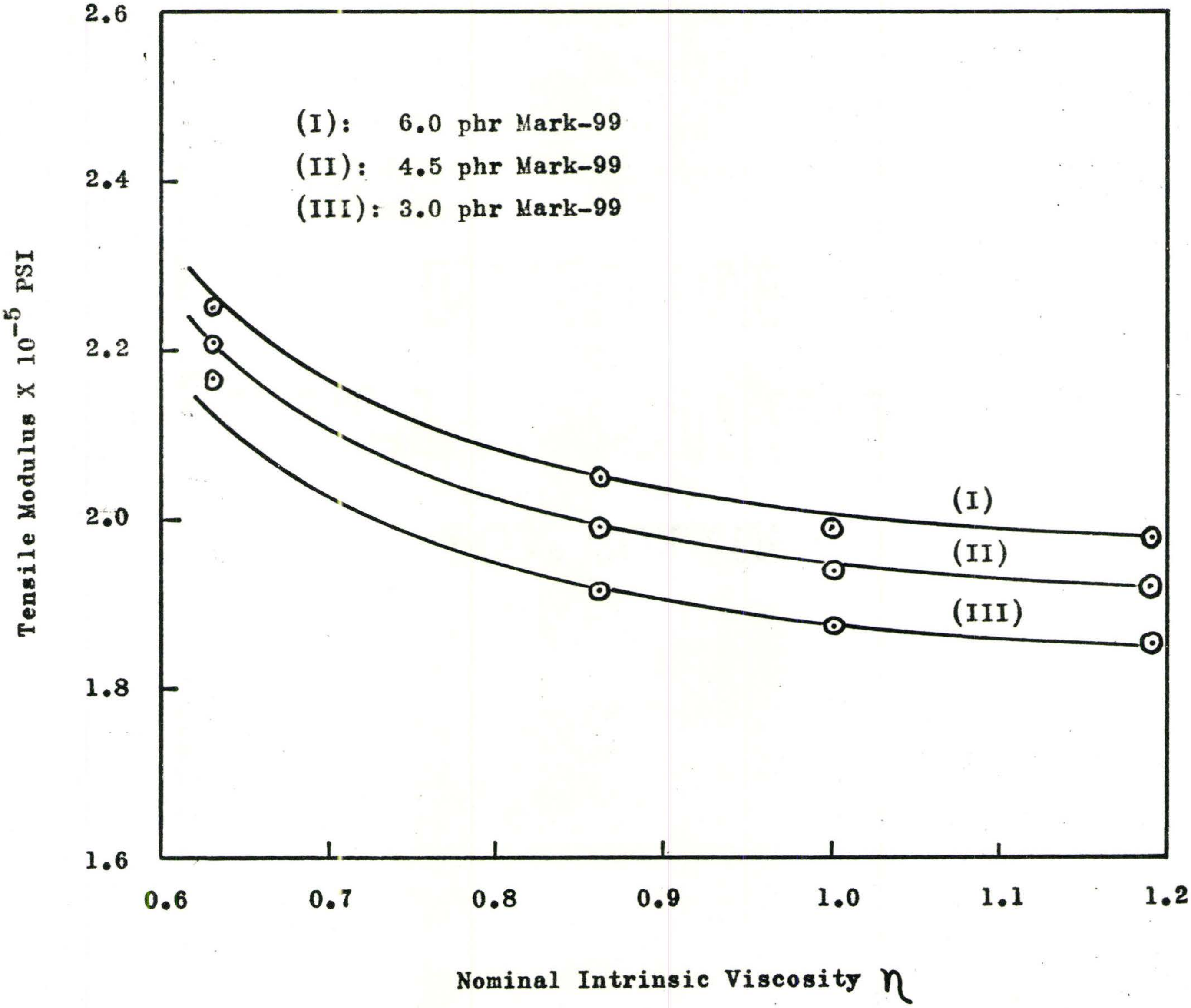


Fig. 21 Effect of Weight Average Molecular Weight (Function of Intrinsic Viscosity) on Tensile Modulus. Beam Speed: 0.1 in/min.

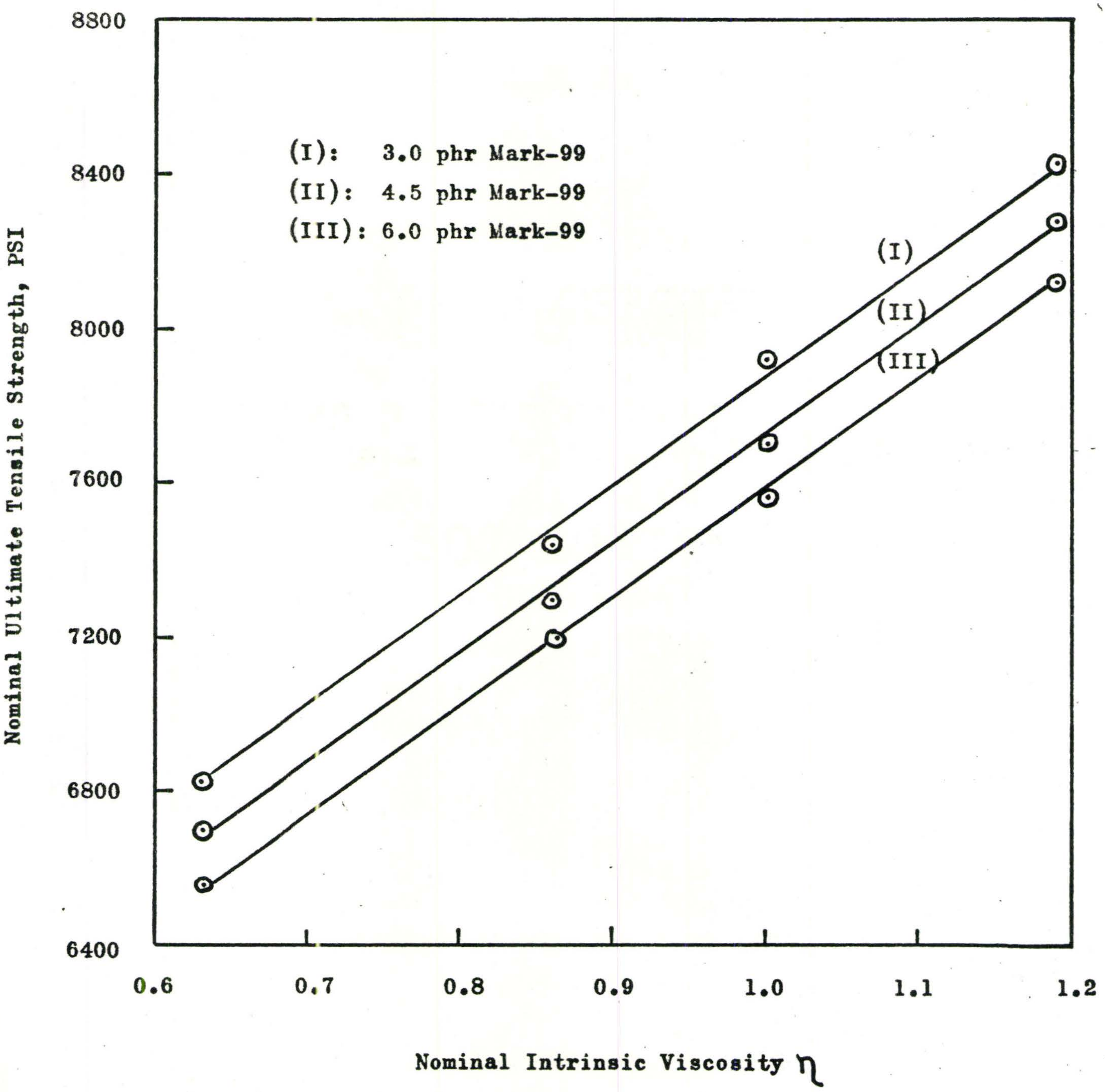


Fig. 22 Effect of Weight Average Molecular Weight (Function of Intrinsic Viscosity) on Nominal Ultimate Tensile Strength. Beam Speed: 0.1 in/min.

5. DISCUSSION OF RESULTS

5.1 Strain Softening and Necking

When a glassy polymer such as PVC starts to deform plastically under an applied stress it is said to yield. Yield leads to a long term change in the shape of the specimen as a whole. In the elastic region the material is deforming elastically and the deformation is recoverable on unloading. At some point beyond this it yields. For polymers which exhibit a stress versus strain curve with a maximum similar to that of the curve in Figure 23, the intrinsic yield point is generally defined as this maximum point.(63) The yield stress and yield strain then correspond to values at this maximum.

Tensile modulus which is also known as Young's modulus is a measurement of elasticity of the material. For most polymers the stress and strain are related linearly only at very low strain; thus tensile modulus is the slope in the initial straight line portion of the stress-strain curve. In this experiment, tensile modulus is taken within 50 % of maximum yield stress region. The corresponding strain at that point is about 2.0 %.

The sudden drop in true stress after yielding is mainly due to the intrinsic and geometric instability, i.e. strain softening and necking of the glassy polymer. Probably most plastic material show some form of strain softening, but its magnitude differs substantially from one another. Binder and Muller(64) indicate both polystyrene and polymethylmethacrylate show a substantial strain softening effect, while polyvinyl chloride and polycarbonate show smaller effect.(65) It is perhaps significant that tough materials are associated with a small amount of strain softening.(66) For example polycarbonate and rigid PVC may be compared with polystyrene and polymethylmethacrylate. The former are tougher materials and the latter relatively brittle ones.

Figure 24 (from reference 64) shows different magnitude of strain softening from different polymers. Figure 25 is a reproduction from present experimental chart of one of the specimens tested on beam speed 0.1 in./min. The specimens were made with resin 373 (η = 1.19) with 6 phr Mark-99. This curve is similar to the stress-strain curve in shape and it also shows certain strain softening effect in PVC. A true tensile stress versus nominal strain curve can be obtained when the X-axis is divided by the initial length of the testing section (0.335 in.) and the Y-axis is divided by the instantaneous cross section area of the testing section (initial diameter = 0.057 in.).

PVC specimens tested in present experiment showed plastic instability after yield point. The most well-established phenomenon associated with plastic instability in polymer glasses is that of 'necking'. It occurs with most of the well-known amorphous polymers: PVC,(67,68) polycarbonate(67) and polymethylmethacrylate.(69) Neck formation have also been reported with polystyrene when extension takes place under hydrostatic pressure.(70)

The plasticity theory of necking has been described by

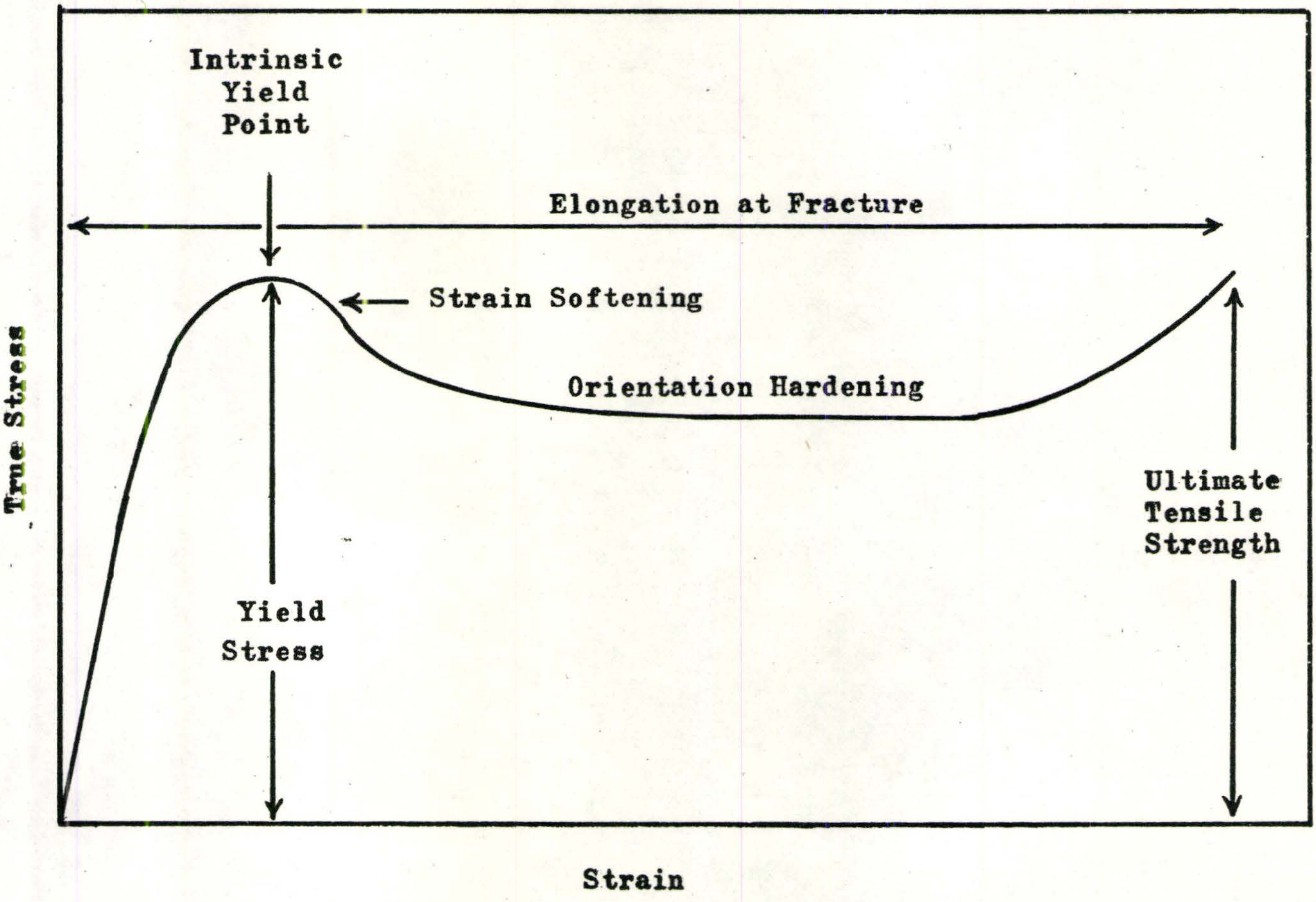


Fig. 23 Generalized True Tensile Stress-strain Curve for Amorphous Glassy Polymers.

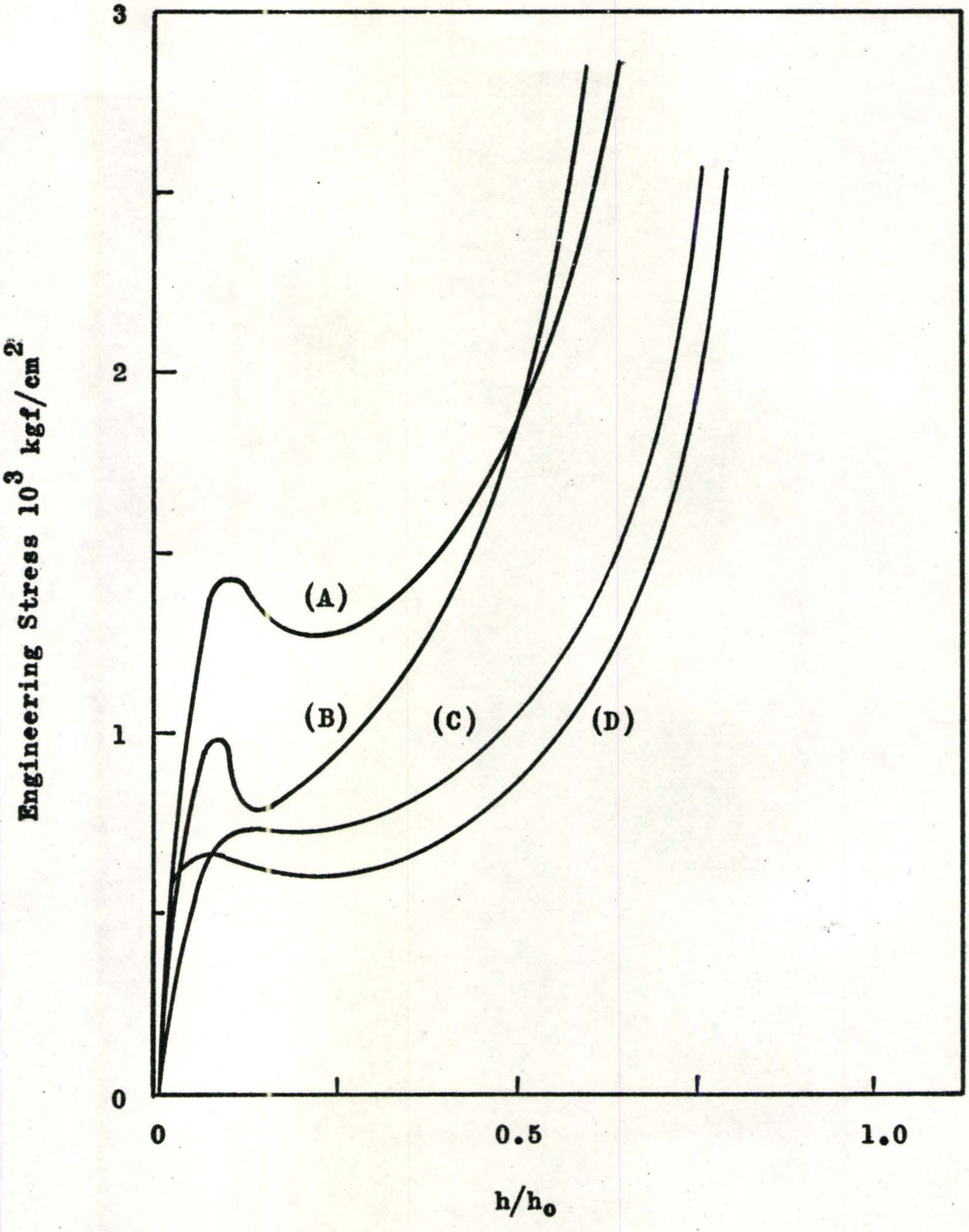


Fig. 24 Compression Curves for Different Plastics. (A) Polymethylmethacrylate; (B) Polystyrene; (C) Polycarbonate; (D) Polyvinyl Chloride. (From Ref. 64)

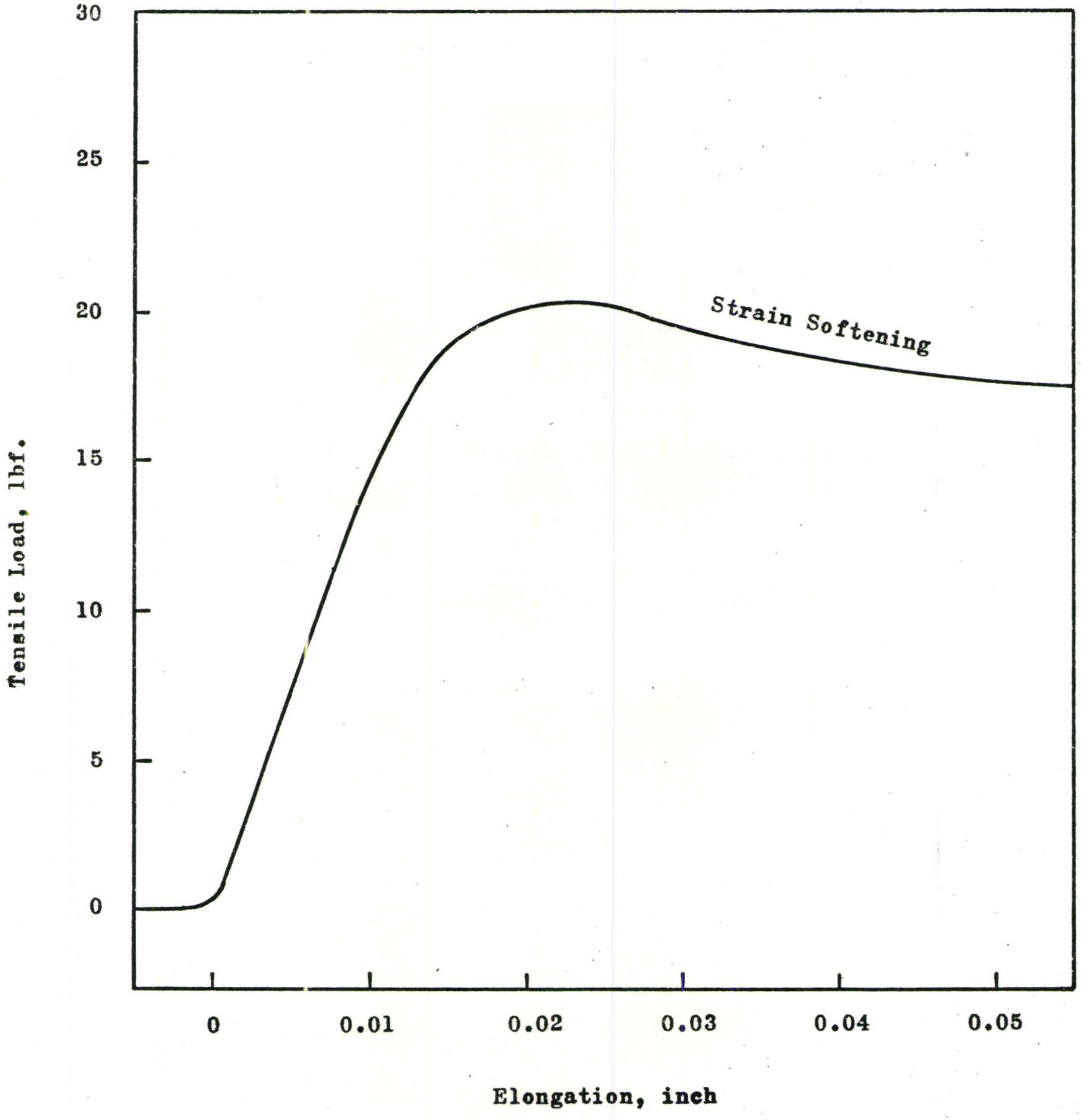


Fig. 25 Present Experimental Chart of One of the Specimens.

Beam Speed: 0.1 in/min., Resin 373 (η = 1.19) with 6 phr Mark-99.

Considere,(68) whose treatment is outlined here. When a tensile test specimen deforms plastically without change in volume then the cross-section areas A, Ao, the lengths L, Lo (where subscript o refers to the initial conditions of the test specimen) and the plastic strain ε, are related as follows:

$$\frac{A}{A_o} = \frac{L_o}{L} = \frac{1}{1+\varepsilon} \qquad (2)$$

It follows that if σ_o is the stress referred to the original cross-section of the test specimen then σ, the true stress, = $\sigma_o(1+\varepsilon)$, from which it can be shown that

$$\frac{d\sigma_o}{d\varepsilon} = \frac{1}{(1+\varepsilon)^2}\left[(1+\varepsilon)\frac{d\sigma}{d\varepsilon} - \sigma\right] \qquad (3)$$

Then at the point where σ_o is a maximum $d\sigma/d\varepsilon = \sigma/(1+\varepsilon)$ and this corresponds to the tangent to the true stress-strain curve from an origin defined by L = 0 (figure 26). Thus, the maximum of σ_o and the tangent to the true stress-strain curve occur at the same elongation, and any further increase in elongation beyond this point leads to a fall in stress σ_o.

If the test specimen had perfectly uniform cross-section and composition it would, in principle, be possible for uniform extension to take place. However, in practice this is never so; there is always a point in the test specimen where σ_o passes the maximum first, and when this happens, the stress required to extend further at this point falls. Extension therefore continues there while the stress in other points of the test specimen falls below that required to pass over the yield point. A constriction, or neck, then develops. Once such a neck is formed it may get steadily thinner, with the load decreasing up to fracture as is the case with copper, or the neck may stabilize and extend throughout the test specimen as is the case with many glassy polymers.

Thermal effects also contribute to the formation of the neck. The plastic component of the energy of deformation must lead to the heating of test specimen. Where this heat is not removed the temperature will rise and yield stress will fall so that any tendency to necking will increase. Since the yield stress increases with the strain rate it is clear that both the heat output and the rate of heating will increase at high strain rates, and for this reason necking is more likely to occur under such conditions. Figure 14 shows the elongation at fracture increases about 25 % when the strain rate increases 5 times. This indicates necking is more favourable at higher strain rates.

5.2 The Eyring Model of Plastic Flow

Figures 27 and 28 show the plots of yield stress against the logarithm of the strain rates are linear for different stabilizer contents so that the gradient $(\partial \sigma_y / \partial (\ln \dot{\varepsilon}))_T$ is a constant. It is this gradient that determines the activation volume in the Eyring equation of flow,(69) which is one of the earliest quantitative models to describe the flow of polymers. Eyring's model assumes that molecular segments are vibrating over an energy barrier of height E_o and that the

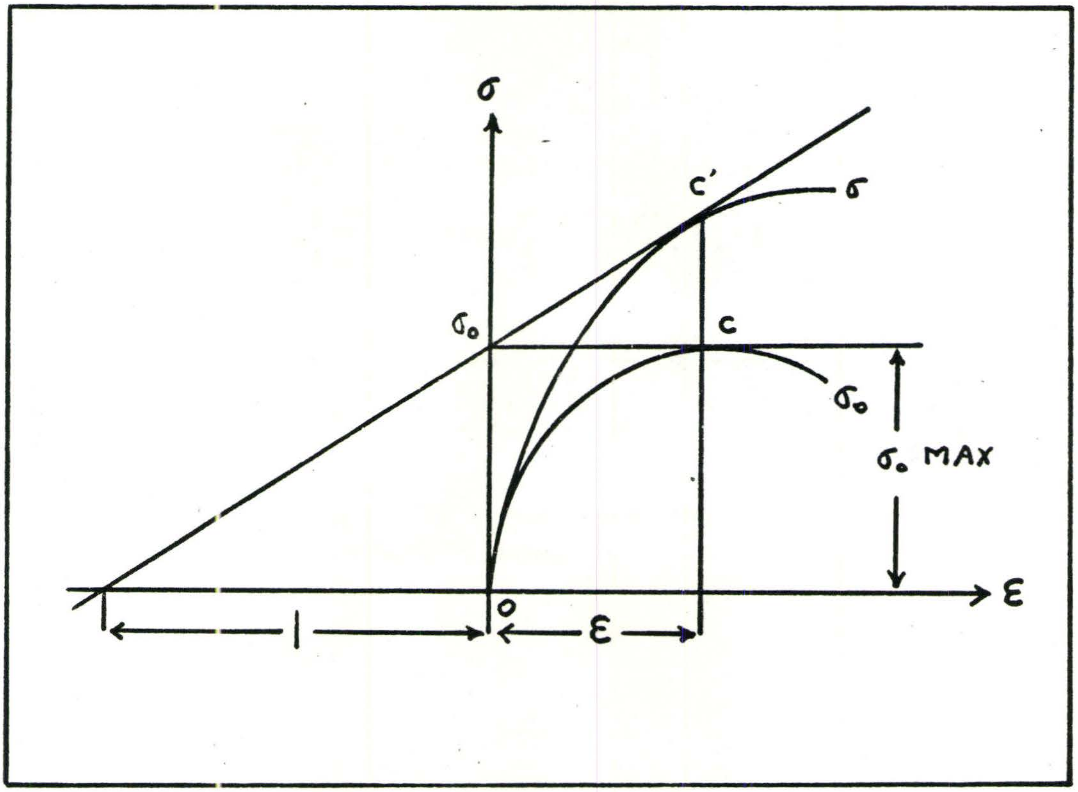


Fig. 26 Construction by Considere. The point C, which is a maximum on the engineering stress curve, (σ_o), is also a tangent from the point L = 0 on the true stress curve (σ). Reproduced from reference 70.

effect of the applied stress is to reduce the height of the barrier for a jump in the forward direction and to increase it for a jump in the reverse direction. It is further assumed that the macroscopic strain rate of the sample is proportional to the net jump rate of the segments in the forward direction. This model then predicts that the macroscopic shear strain rate is given by an equation of the form

$$\dot{\gamma} = \dot{\Gamma} \quad \exp(-\frac{E_o}{kT})\sinh(\frac{\upsilon\tau}{2kT}) \tag{4}$$

The quantity $\dot{\Gamma}$ is a constant with the dimensions of strain rate, E_o is the enthalpy of the process and υ is the activation volume. The quantity $(\upsilon\tau)$ has the dimensions of energy and is the work done on a mobile segment during a jump by the applied shear stress, τ. The Eyring equation describes a viscous process occurring at constant stress so it can be applied to yield if yield occurs at constant stress. Then equation (4) can be rearranged to give the flow stress

$$\tau = \frac{2kT}{\upsilon} \sinh^{-1} \left[\frac{\dot{\gamma}}{\dot{\Gamma}} \exp(\frac{E_o}{kT}) \right] \tag{5}$$

For flow at high strain rates and low temperatures the equation predicts that the flow stress will vary linearly with the logarithm of applied shear strain rate since $\sinh^{-1} x$ is approximately equal to log x for large x. In this region the differentiation of equation (5) leads to the prediction that the flow stress should vary linearly with the logarithm of the strain rate and that the slope of such a plot should be proportional to the absolute temperature.

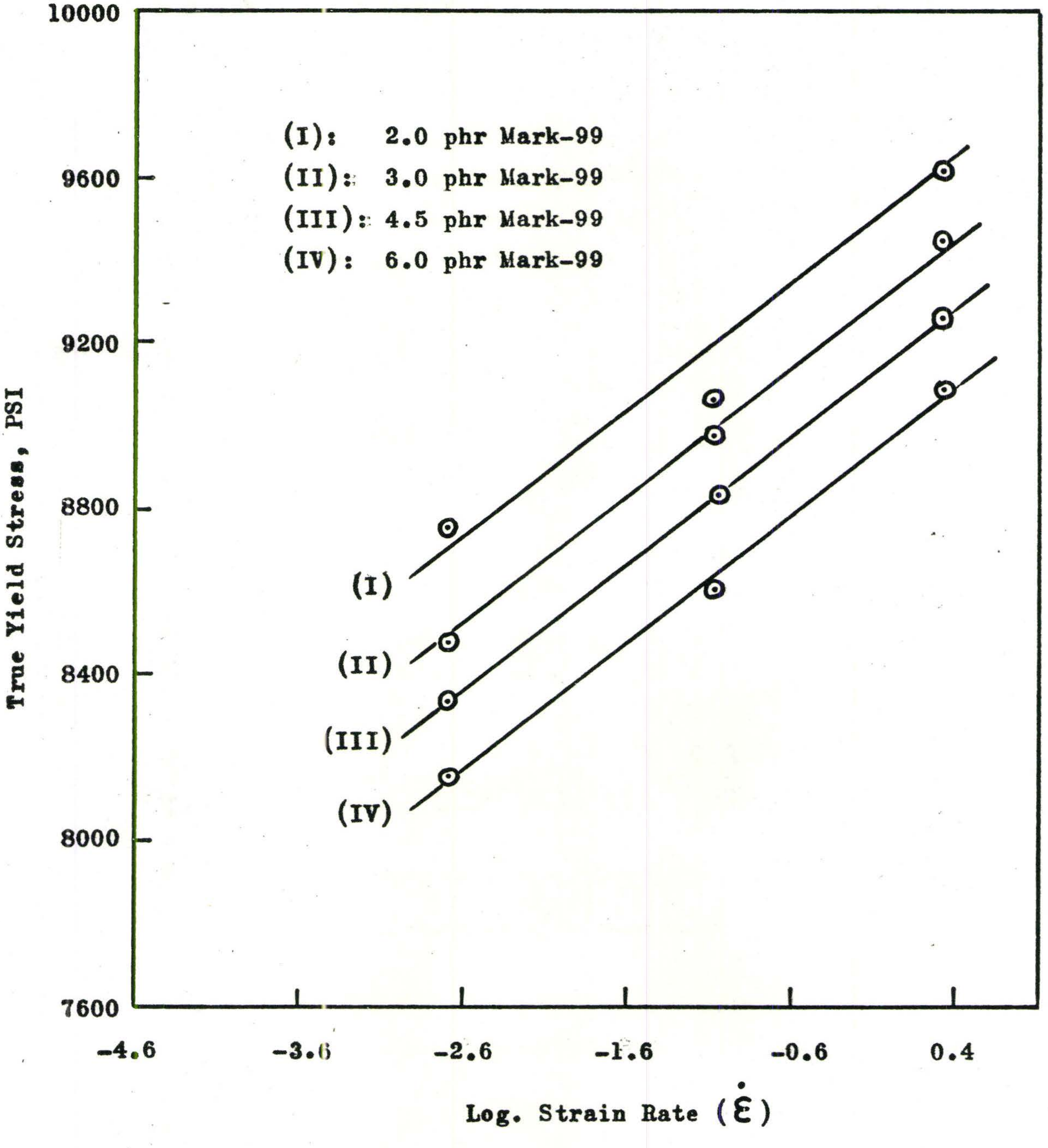


Fig. 27 Plot of Yield Stress Against Log. Strain Rates. PVC Resin 369 (η = 1.00).

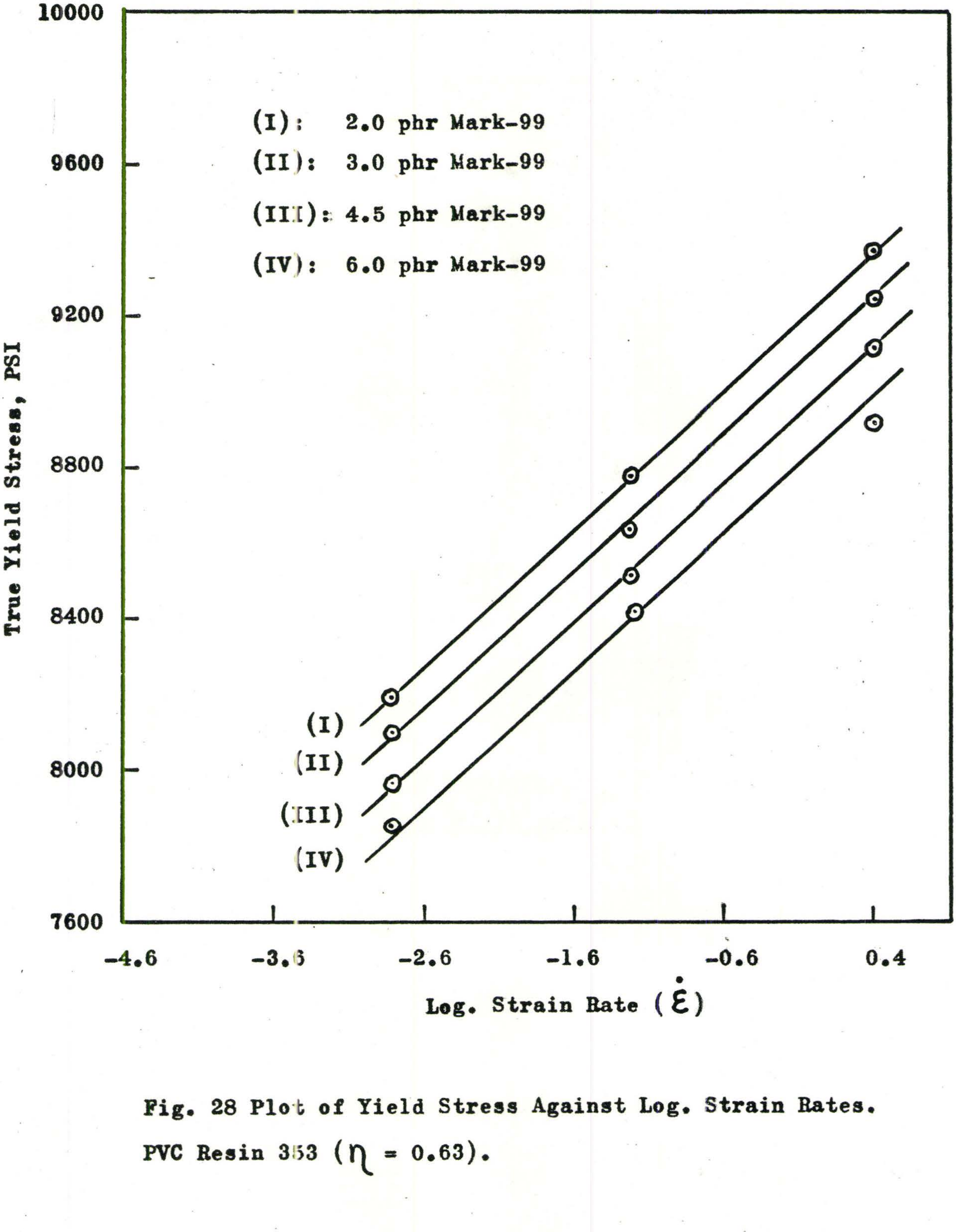


Fig. 28 Plot of Yield Stress Against Log. Strain Rates. PVC Resin 353 (η = 0.63).

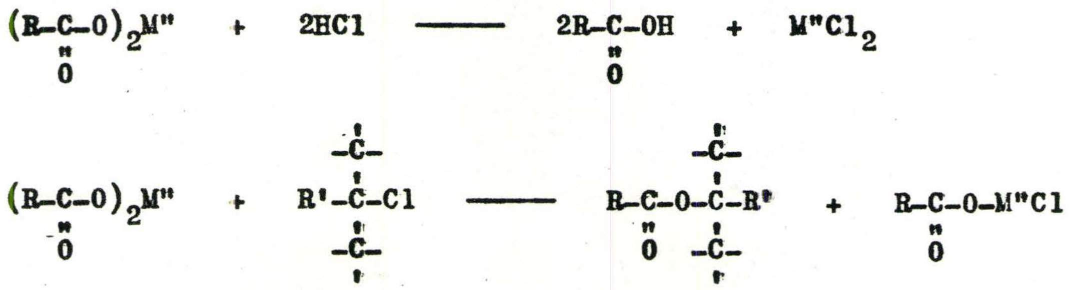
$$\frac{\partial \tau}{\partial (\ln \dot{\varepsilon})} = \frac{2kT}{\upsilon} \qquad (6)$$

Figures 27 and 28 show the slopes of stress-ln $\dot{\varepsilon}$ curves are parallel. This implies activation energy of flow is independent of the mechanism causing an increase in flow stress. In other words the mechanism in which molecular segments are vibrating over an energy barrier is the same for different stabilizer contents; although they face different redardation due to the differences in free volume which will be explained in the next section.

5.3 Effect of Stabilizer on the Mechanical Properties of PVC

Figures 8 - 14 show stabilizer acts like plasticizer in certain ways. Their presence tends to reduce the mechanical properties of PVC although the mechanisms are entirely different. The only exception is tensile modulus tends to increase with stabilizer content, but with plasticizer it tends to fall.

It has been generally agreed that besides reacting with liberated hydrogen chloride, the main functions of stabilizer are:(3) (1) Reacting with PVC molecules at points of deviation from idealized structure so as to reduce the number of positions where decomposition might be readily initiated. (2) Reacting with PVC molecules as to interfere the propagating 'zipperlike' elimination of hydrogen chloride. Frye and Horst(71,72) show that barium/cadmium complex salt stabilizer do attach to the PVC molecules after milling. Their studies were first conducted by infrared spectroscopy and then by radioactive tracer technique.



$$(\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O})_2\mathrm{M''} + 2\mathrm{HCl} \longrightarrow 2\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}OH} + \mathrm{M''Cl_2}$$

$$(\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O})_2\mathrm{M''} + \mathrm{R'{-}}\overset{\overset{|}{-\mathrm{C}-}}{\underset{\underset{|}{-\mathrm{C}-}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{{-}Cl} \longrightarrow \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O{-}}\overset{\overset{|}{-\mathrm{C}-}}{\underset{\underset{|}{-\mathrm{C}-}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{{-}R'} + \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}O{-}M''Cl}$$

The attached stabilizer on PVC molecules acts like small branches. These small branches, which increase in number with stabilizer content, tend to increase the free volume of the specimen. Before any deformation has occurred, these relatively small branches of the stabilizer form an entanglement which hinders initial molecular movement. When the molecular chains break through the initial barrier, they can move more freely in the free volume which is increased because of these small branches.

Tensile modulus is a measure of elasticity which depends on initial deformation of the polymer and for the above reason, tensile modulus will increase slightly with stabilizer content as shown in figure 9 and 12. On the other hand, large deformation parameters such as yield stress and ultimate fracture stress decrease slightly when stabilizer content increases (figures 8, 10, 11, 13). The increase in mobility due to large free volume favours necking substantially. Thus figure 14 indicates elongation at break increases with stabilizer content.

As stated before, Frye and Horst have proved that stabilizer reacts with PVC molecules especially at defect points such as chlorine atoms attached tertiary to the carbon atoms at branch points and tail-to-tail structures. Defect points have higher flexibility due to lower energy barries to rotate about the C–C bonds. When these defect points are replaced by stabilizer branches, the energy barries for rotation about the C–C bonds will be increased because of the bulky nature of the branches. During small strain deformation, only relatively small number of bonds are involved in the rotation and it is always those weakest defect points which possess the highest flexibility rotate first. Hence increase in concentration of stabilizer, which replaces those defect points, tends to increase the retardation against initial molecular movement. But on the other hand, in order for large deformation to occur, substantially large number of bond rotations have to be activated. Because the concentration of stabilizer branches along the PVC chain is quite low, this effect becomes less important in large deformation such as yield stress and ultimate fracture stress.

5.4 Effect of Annealing on the Mechanical Properties of PVC

The effects of annealing of glassy polymers have been extensively studied. Rapid cooling during quenching freezes random polymer segments into fixed position which results in poor packing and relatively large free volume. Free volume is the excess volume occupied by unit mass of the material over and above that necessary to accommodate the atoms in the closest packing permitted by the bond structure. Annealing above the glassy transition temperature allows some local segmental movement and produces a greater degree of order within the amorphous regions of the glassy polymer resulting in an reduction of free volume. After the annealed specimens have cooled to room temperature, the density change which produces a reduction in the mobility of the polymer chains changes the mechanical properties substantially. Many glassy polymers such as polystyrene,(45) polycarbonate,(46) and polymethylmethacrylate(47) have been examined. In all cases, yield stress was found to increase up to 15 % when the quenched samples were annealed.

In the present experiment, the effects of heat treatment on yield stress (figure 15), tensile modulus (figure 16), nominal ultimate tensile stress (figure 17) and elongation at fracture (figure 18) are found to be consistent with a stiffening of the PVC due to internal rearrangements.

As can be expected, the changes in mechanical properties increase with annealing time initially, but becomes almost constant after 60 minutes when annealed at 110°C, which indicates that annealing for more than 60 minutes will have little effect on the mechanical properties of PVC. The overall increase in yield stress due to annealing is about 7.5 %, while increase in tensile modulus and nominal ultimate tensile strength are 16 % and 2.4 % respectively. A reduction of 43 % in elongation at fracture, which is a measure of tendency to necking, indicates the material becomes less ductile after annealing. A decrease in volume of PVC specimens of 1.75 % after annealing at 110°C for 20 minutes is also observed in the present experiment (figure 19).

5.5 Effect of Molecular Weight on the Mechanical Properties of PVC

As for the effects of M.W. (molecular weight) and M.W.D. (molecular weight distribution) on the mechanical properties, it has been generally agreed that mechanical properties usually increase with M.W. to a certain point and then remain constant. With M.W.D. they usually decrease with broadening of M.W.D. The main reason for this is attributed to the numerous side groups and chain ends to which the low M.W. and broad M.W.D. polymer molecules are attached. These side groups and chain ends are relatively free from motions and tend to increase flexibility of the glassy polymer. The effects of the side groups and chain ends diminish when the M.W. reaches certain high level.. The situation is complicated by the fact that, in some cases, M.W. and M.W.D. can affect physical properties through their effects on other material parameters such as branching, orientation, crystallinity, crystal structure, processing conditions, etc. Hence the specific effects of M.W. or M.W.D. can be determined only if all other variables are held constant or allowed for quantitatively.

In the present study, tensile strength of rigid PVC increases strongly from 6800 psi to 8400 psi when the intrinsic viscosity increases from 0.63 to 1.19 (figure 24); while the yield stress increases from 8600 psi to 9100 psi in the same region (figure 20). On the other hand, tensile modulus decreases slightly with increase in M.W. over different strain rates (figure 21).

The increase in tensile strength and yield stress with M.W. is consistent with those results found in literature, although the material, method of specimen preparation and testing conditions are different. Since only four different M.W. were investigated in this experiment, the point where these mechanical properties will be leveling off cannot be determined.

Many researchers concluded that tensile modulus is independent of M.W. or M.W.D. except at very low M.W., but Golden (50) indicated that the modulus of polycarbonate decreased slowly as $\overline{M}_w$ was increased over wide range of strain rates. The present result is similar to Golden's finding and tend to approach asymptotic values from about an intrinsic viscosity of $\eta = 1.0$. As stated before, this might or might not be due to the direct effect of M.W., because M.W. and M.W.D. can effect physical properties through their effects on other material parameters.

6. Conclusions

An Instron Tensile Tester and a Miniature Tensile Tester have been used to study the mechanical properties of injection molded PVC specimens with different Mark-99 barium/cadmium stabilizer contents. Based on the result of the experiment, the following conclusions could be made:

1) Besides reacting with liberated hydrogen chloride, the major functions of the stabilizer is to react with the PVC molecules at points of deviation from idealized structure so as to reduce the number of positions were decomposition might be more readily initiated and to interfere the propagation of 'zipperlike' elimination of hydrogen chloride. The attached stabilizer branches on PVC molecules tend to increase the free volume of the glassy polymer resulting in greater mobility of the PVC segments especially in large deformation. Thus tensile yield stress and ultimate fracture strength decrease slightly with increase in stabilizer content, while elongation at fracture and tensile modulus increase slightly with increase in stabilizer content. As the stabilizer reacts with PVC molecules first at those weakest defect points which have high flexibility, increase in stabilizer content tends to increase the low strain properties such as tensile modulus. This effect becomes less important in large deformation such as yield stress.

2) On the other hand, annealing of quenched specimens tends to

reduce the free volume of the glassy polymer. This is because on the application of heat, some local motion of polymer chains becomes possible and they move into more favoured and ordered positions. Thus tensile yield stress, tensile ultimate fracture strength and tensile modulus increase with annealing time to 60 minutes and then remain constant; while elongation at fracture and volume of testing section decrease with annealing time to 60 minutes and then also remain constant. These also show annealing at 110°C for more than 60 minutes has very little effect on the mechanical properties of PVC.

3) The result of this experiment also indicates tensile yield stress and ultimate fracture strength increase with molecular weight while tensile modulus decreases slightly with molecular weight.

7. Recommendations

Although premixing can be achieved in a heated mortar and pestle, an electrically heated mechanical blender is more desirable in obtaining a higher degree of homogeneity of PVC resin mixture. Mechanical blender can also provide a longer mixing time if necessary.

In order to get a clearer picture of mechanism of stabilization, and the effect of stabilizer on tensile modulus, other kinds of stabilizers such as organotin compounds should be used for investigation. At the same time, the specimens should be annealed at different temperatures so that the effect of annealing could be better understood. Further work could be devoted to investigate the effect of molecular weight and molecular weight distribution on the mechanical properties of rigid PVC.

The effect of stabilizer on the mechanical properties of rigid PVC can also be explained in terms of glass transition temperature. Thus it is worthwhile to measure the glass transition temperature of the specimens with different stabilizer contents.

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APPENDIX

Experimental Results

Tester: Miniature Tensile Tester

PVC resin 369 (η = 1.00)

Mixing time: 1.8 min. Temperature: 175°C

All specimens annealed at 110°C for 20 min.

All specimens contained 0.536 phr stearic acid lubricant.

Phr Mark-99	C.S. sec/in	B.S. in/min	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi
6.0	20	0.0225	8160 ± 140	1.96 ± 0.17	7160 ± 690
6.0	5	0.1125	8610 ± 290	2.00 ± 0.07	7570 ± 340
6.0	2	0.45	9100 ± 350	2.06 ± 0.11	-
4.5	20	0.0225	8330 ± 340	1.88 ± 0.04	7320 ± 470
4.5	5	0.1125	8830 ± 90	1.95 ± 0.07	7630 ± 600
4.5	2	0.45	9260 ± 110	2.06 ± 0.07	-
3.0	20	0.0225	8480 ± 300	1.82 ± 0.01	7230 ± 400
3.0	5	0.1125	8970 ± 230	1.87 ± 0.12	7970 ± 100
3.0	2	0.45	9460 ± 220	1.92 ± 0.09	-
2.0	20	0.0225	8740 ± 180	1.80 ± 0.12	7330 ± 240
2.0	5	0.1125	9060 ± 310	1.86 ± 0.07	7750 ± 240
2.0	2	0.45	9610 ± 75	1.91 ± 0.15	-

Tester: Instron Tesile Tester

PVC resin 353 (η = 0.63)

Mixing time: 1.5 min. Temperature: 165°C

All specimens annealed at 110°C for 20 min.

All specimens contained 0.536 phr stearic acid lubricant.

Phr M-99	C.S. in/min	B.S. in/min	True yield stress,psi	Ten.modulus X 10^{-5}, psi	Fracture stress,psi	Elongation at frac. %
6.0	50	0.5	8920 ± 110	2.37 ± 0.19	7200 ± 300	170 ± 14
6.0	10	0.1	8420 ± 70	2.25 ± 0.04	6560 ± 260	146 ± 1
6.0	2	0.02	7860 ± 70	2.18 ± 0.11	-	-
4.5	50	0.5	9124 ± 130	2.31 ± 0.11	7340 ± 250	160 ± 11
4.5	10	0.1	8520 ± 50	2.21 ± 0.05	6700 ± 130	130 ± 5
4.5	2	0.02	7970 ± 50	2.15 ± 0.06	-	-
3.0	50	0.5	9240 ± 20	2.29 ± 0.05	7360 ± 316	154 ± 5
3.0	10	0.1	8630 ± 66	2.17 ± 0.05	6830 ± 110	122 ± 5
3.0	2	0.02	8115 ± 67	2.11 ± 0.04	-	-
2.0	50	0.5	9360 ± 50	2.25 ± 0.04	7570 ± 446	151 ± 35
2.0	10	0.1	8776 ± 65	2.16 ± 0.12	6560 ± 156	121 ± 10
2.0	2	0.02	8205 ± 50	2.08 ± 0.05	-	-

Tester: Instron Tensile Tester

PVC resin 353 (η = 0.63)

Mixing time: 1.5 min. Temperature: 165°C

Mark-99 stabilizer: 4.5 phr. Stearic acid lubricant: 0.536 phr

Beam speed: 0.1 in/min., Chart speed: 10 in/min.

Temperature of annealing: 110°C

Annealing time, min.	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi	Elongation at frac. %
0	7695 ± 90	1.82 ± 0.14	-	139 ± 11
5	7850 ± 180	1.91 ± 0.08	6250 ± 150	110 ± 10
10	8060 ± 20	1.99 ± 0.09	6340 ± 100	112 ± 17
20	8230 ± 80	1.95 ± 0.06	6270 ± 200	105 ± 31
60	8270 ± 150	2.07 ± 0.08	6320 ± 120	74 ± 20
180	8280 ± 80	2.09 ± 0.17	6412 ± 130	85 ± 20

Tester: Instron Tensile Tester

PVC resin 353 (η = 0.63)

Mixing time: 1.5 min.   Temperature: 165°C

Mark-99 stabilizer: 4.5 phr.   Stearic acid lubricant: 0.536

Beam speed: 0.1 in/min.,   Chart speed: 10 in/min

Annealing: 110°C for 20 min.

Phr Mark-99	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi	Elongation at frac. %
6.0	8420 ± 70	2.25 ± 0.04	6560 ± 260	146 ± 1
4.5	8520 ± 50	2.21 ± 0.05	6700 ± 130	130 ± 5
3.0	8630 ± 66	2.17 ± 0.05	6830 ± 110	122 ± 5

Tester: Instron Tensile Tester

PVC resin 363 (η = 0.86)

Mixing time: 1.6 min.   Temperature: 170°C

Phr Mark-99	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi	Elongation at frac. %
6.0	8560 ± 50	2.05 ± 0.12	7200 ± 130	-
4.5	8670 ± 70	1.99 ± 0.06	7300 ± 80	-
3.0	8770 ± 60	1.91 ± 0.03	7440 ± 90	-

Tester: Instron Tensile Tester

PVC resin 369 (η = 1.00)

Mixing time: 1.8 min. Temperature: 175°C

Phr Mark-99	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi	Elongation at frac. %
6.0	8560 ± 90	1.99 ± 0.08	7560 ± 280	-
4.5	8780 ± 80	1.94 ± 0.07	7700 ± 340	-
3.0	8920 ± 100	1.87 ± 0.09	7920 ± 240	-

Tester: Instron Tensile Tester

PVC resin 373 (η = 1.19)

Mixing time: 2.0 min. Temperature: 180°C

Phr Mark-99	True yield stress, psi	Ten. modulus X 10^{-5}, psi	Fracture stress, psi	Elongation at frac. %
6.0	8770 ± 56	1.98 ± 0.04	8120 ± 150	-
4.5	8930 ± 62	1.92 ± 0.07	8280 ± 230	-
3.0	9110 ± 160	1.85 ± 0.05	8430 ± 160	-

Material Tested

PVC Resin: Commercial grade suspension polymerized. Manufactured and supplied by Esso Chemical Canada of Sarnia, Ontario. The four different grades which have been tested are:

Esso Resin Grade	Lot No.	Nominal Intrinsic Viscosity (η) (dl/g)(Cyclohexanone at 30°C)
353	70G051	0.63
363	73G014	0.86
369	73G027	1.00
373	72D066	1.19

Stabilizer: Barium/Cadmium complex salt - trade name Mark-99. Manufactured by Argus Chemical Corporation of Brooklyn, New York. Supplied by Esso Chemical Canada of Sarnia, Ontario.

Lubricant: Stearic Acid. Supplied by Esso Chemical Canada, Sarnia, Ontario.

Testing Machines

I. Miniature Mixing and Injection Molder - Model CS-183MM. Manufactured by Custom Scientific Instruments, Inc. Whippany, N.J., U.S.A.

II. Miniature Tensile Tester - Model CS-183TE. Manufactured by Custom Scientific Instruments, Inc. Whippany, N.J., U.S.A.

III. Instron Tensile & Compression Tester - Model TTCL. Manufactured by Instron Engineering Corporation, Canton, Mass. U.S.A.

Glossary

1) **Intrinsic Viscosity:** Intrinsic viscosity $[\eta]$ is obtained by plotting the reduced viscosity, $(\eta - \eta_o)/\eta_o C$, as a function of concentration C, and extrapolating to infinite dilution. In this expression, η is the viscosity of the solution and η_o is the viscosity of the solvent. The concentration is usually expressed in grams per deciliter. For dilute solutions, the intrinsic viscosity and molecular weight are related by the Mark-Houwink equation:

$$[\eta] = K\,M_w^a \tag{7}$$

where M_w is the weight average molecular weight and K and a are constants. Nakazawa and Matsuo(73) reported that for PVC, K is equal to 1.41×10^{-4} and a is euqal to 0.82 for intrinsic viscosities measured in cyclohexanone at 30°C. The approximate weight average molecular weight is in the range of $2 - 13 \times 10^4$.

2) **Phr:** Parts per hundred resin by weight.

3) **Percentage Elongation at Fracture:** Percentage increase in length of the test section of the specimen at fracture from initial length. The length of the test section at fracture is measured from the recording chart of tensile tester.

4) **Tensile Modulus:** In this study, tensile modulus is taken as the slope of the initial straight line portion (within 50 % of the maximum yield stress region) of the stress-strain curve.

5) Nominal Tensile Yield Stress: The loading force at yield point divided by the initial cross-section area of the test section.

6) True Tensile Yield Stress: The loading force at yield point divided by the instantaneous cross-section area of the test section at yield point . The instantaneous cross-section area of the specimen at yield point is determined from the amount of elongation the specimen had at that point assuming the test section have constant volume in this region.

7) Nominal Ultimate Tensile Strength: The loading force at fracture divided by the initial cross-section area of the specimen.