Influence of Processing Parameters and Molecular Weight on the Mechanical Properties of PVC

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Synopsis

The role of a variety of processing parameters in determining the mechanical properties of solid PVC has been examined. Annealing pretreatment has been shown to increase both the yield stress and the modulus. It was found that the density of the material similarly increased as the annealing progressed, and when the density reached a limiting value, the yield stress and modulus also reached a limiting value. The molecular weight of the resin, as measured by its intrinsic viscosity, also affected the various mechanical properties measured. However, the yield stress increased while the modulus decreased as the molecular weight increased. This unusual behavior was thought to be a secondary effect. Finally, the addition of increasing amounts of stabilizer to the PVC resin resulted in an increase in modulus and a decrease in yield stress. This was consistent with a model for plastic deformation in which the stabilizer acted as small hard particles. The activation strain volume did not change with different concentrations of stabilizer, further supporting a model for a two-phase structure.

INTRODUCTION

Processing and Mechanical Properties

There has been increasing interest recently in the detailed deformation mechanisms in glassy polymers.[1–3] The accurate measurement of mechanical properties such as yield stress and modulus has, therefore, become important. In many cases, commercially obtained sheet material has been used for these measurements. However, the role of processing parameters in affecting the mechanical behavior of these materials has not always been reported. Parameters such as molecular weight, annealing pretreatment, and additive content may have a significant effect on the mechanical behavior. In careful studies related to deformation mechanisms, it is necessary to compare the processing parameters when comparing mechanical behavior.

Stabilization Behavior of PVC

Poly(vinyl chloride) (PVC) is one of the most important commercial plastics in use. It is chemically one of the least stable of the common polymers, and commercially obtained specimens must contain some additives needed to sta-

bilize the molecules. The use of additives of many different types is common in plastics, but very little information has been presented about the role of these additives in their mechanical behavior. Various commercially obtained materials which have been used by investigators in the past have not necessarily contained the same additives. Studies of yield point and mechanisms of flow in glassy polymers, particularly where PVC is concerned, may be influenced by the type and quantity of heat stabilizer used.

PVC is subject to degradation by heat at temperatures above about 100°C. The stabilizer usually falls into one of several groups of compounds. For example, commonly used ones are (1) inorganic metal salts, (2) metallic soaps and salts of organic acid, (3) metal complexes, and (4) organotin compounds. The chemical reactions by which these compounds stabilize the plastic are not known with certainty.[4] However, it is generally agreed that the barium–cadmium salt complexes used in these studies serve three main functions. First, they react with the hydrogen chloride produced by the thermal degradation process. Secondly, they react with PVC molecules at points of deviation from the idealized structure to reduce the number of positions on the molecule where decomposition might easily initiate. Finally, they react with the molecule to interfere with the "zipper-like" decomposition of the molecule. It has been shown that the barium–cadmium complex does attach itself to the PVC molecules after milling.

The modification of the molecular architecture in this way is expected to affect the mechanical behavior of the solid plastic.

Molecular Weight

Molecular weight is one of the important parameters in processing polymers. Changes in molecular weight have a direct effect on the mechanical properties of the solid polymer.[5] However, the greatest changes in deformation behavior with molecular weight occur at low molecular weights, and the relatively minor changes at higher molecular weights typical of commercial PVC resins have not been examined previously. In addition, the combined influence of stabilizer content and molecular weight has not been studied.

Annealing

In processing polymers, annealing pretreatment has a significant influence on the mechanical behavior of the final solid.[6] Parameters such as yield stress and modulus are affected strongly by the temperature and time of annealing. This is generally well known in that mechanical studies of glassy polymers usually are preceded by some kind of annealing. The purpose behind this heat treatment is to standardize the initial "structure" of the polymer to eliminate this "structural" variable. The quantitative relationship between these mechanical parameters and the annealing pretreatment has never been elucidated in PVC.

EXPERIMENTAL

PVC resin was obtained from Esso Chemical Canada Limited. Four different grades with nominal intrinsic viscosities of 0.63, 0.86, 1.00, and 1.19 (dl/g, cyclohexanone at 30°C) were tested. Stearic acid was used as a lubricant, and Mark

99 as a stabilizer (a high-efficiency barium–cadmium complex solid). The stabilizer is manufactured by Argus Chemical Corporation of Brooklyn, New York.

The premix of resin, stabilizer, and lubricant was blended in a heated mortar and pestle at a temperature of about 85°C. The blended premix was compounded in a miniature mixing/injection molding machine. Specimens suitable for a standard tensile test were injection molded from the same machine at temperatures which were adjusted according to the melt viscosity of the material. The specimens were approximately $3/4$ in. long with a $5/16$ in. gauge length which was $1/16$ in. in diameter.

A series of specimens was annealed at 110°C for various times (5, 10, 20, 60, and 180 min). These were mechanically tested, and the parameters of interest were measured as a function of annealing time. In addition, the density was measured. From this, a consistent thermal pretreatment was derived for the subsequent test.[5]

The stabilizer content range which was tested was 2–6 parts per hundred resin by weight (phr). The lower limit was fixed by the minimum amount necessary for thermal stabilization. The upper limit was fixed by the difficulty encountered in processing higher concentrations.

The stearic acid lubricant concentration was 0.54 phr for all specimens. For each sample of given stabilizer content, five tensile specimens were molded and tested. The variation in yield stress over the five specimens at the same strain rate was less than 1%. All tests were performed at room temperature, 23° ± 2°C.

EXPERIMENTAL RESULTS

Annealing Pretreatment

As expected, the various parameters of interest changed in the early stages of annealing but reached a saturation value after some time of annealing (about 20 min at 110°C). Figures 1–3 show the change in tensile yield stress, tensile modulus, and elongation at fracture as a function of annealing time. The density of the material also shows dependence on annealing time (Fig. 4). After about 20 min, the density has increased by about 1.7%. All specimens contained 4.5 phr Mach 99 stabilizer. The results show that 20 min of annealing at 110°C should be sufficient to standardize the specimen microstructure for the subsequent tests.

In general, it is expected that annealing will affect the mechanical properties of glassy polymers. The thermomechanical processing of the polymer specimen introduces internal stresses into the material which are a result of the inhomogeneous structure. The subsequent annealing will relax the internal stresses, effectively removing some local inhomogeneities in the structure, regions of low density, or high defect concentration. The reduction in density of the specimen suggests this may occur over the first 20 min of annealing at 110°C. The removal of some of the inhomogeneities or regions of high defect concentration will affect the mechanical properties.[5] In general, it is expected that the regions of highest defect concentration will anneal out first, since the driving force is highest. These are the regions which would yield first according to either of the recently pos-
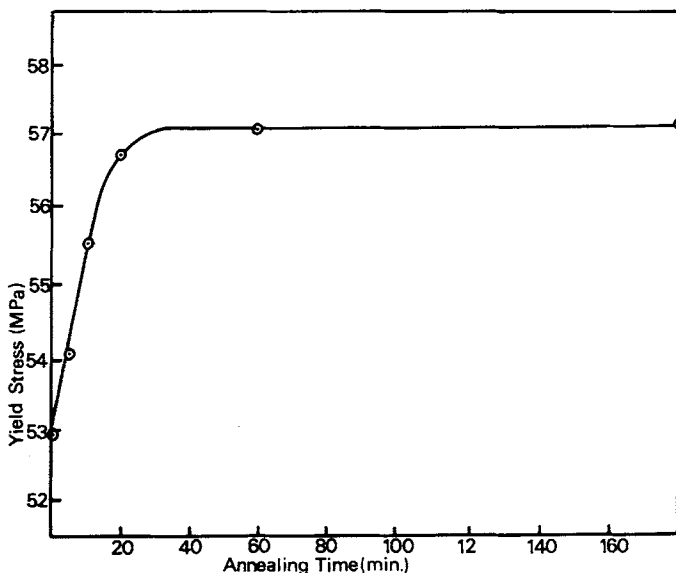
Fig. 1. Variation of tensile yield stress as a function of annealing time at 110°C. Stabilizer content 4.5 phr Mark 99.

tulated models for glassy flow.[4,5] Hence, the removal of these regions on annealing would result in an increase in yield stress and also in an increase in tensile modulus. The simultaneous saturation of density and these mechanical parameters are therefore consistent with both Argon's and Sternstein's views on plastic flow mechanisms.

Molecular Weight Dependence of Properties

Increases in nominal intrinsic viscosity (η) result in measurable changes in mechanical properties. The yield stress increases and the modulus decreases (Figs. 5 and 6). Changes in stabilizer content shifted each of the curves, but the shape of the curves remained similar.

There have been relatively few studies of the influence of molecular weight upon the mechanical properties of glassy polymers.[5] Both modulus and yield stress change only slightly with molecular weight at those values of molecular weight typical of commercially obtainable polymers. These relationships between the mechanical parameters and molecular weight appear to depend upon the type of polymer examined.

The changes in yield stress seen in PVC in these experiments amount to a negligible amount (approximately 4%), in agreement with the small changes seen in other polymers. However, the tensile modulus decreases with increasing molecular weight by a significant amount (approximately 15%). In most polymers, the modulus varies with molecular weight only at very low molecular weights.[6] The tensile moduli of polystyrene, poly(dichlorostyrene), and poly(methyl methacrylate) (PMMA) have been shown to be almost independent of molecular weight at typically high molecular weights. Polycarbonate may show a slight decrease in modulus as molecular weight increases, while the modulus of PMMA increases slightly with log $\overline{M}_V$. In a study of plasticized PVC,[7] Young's modulus was constant for $\overline{M}_w > 5 \times 10^4$, and it decreased rapidly when $\overline{M}_w$ was reduced below this value.
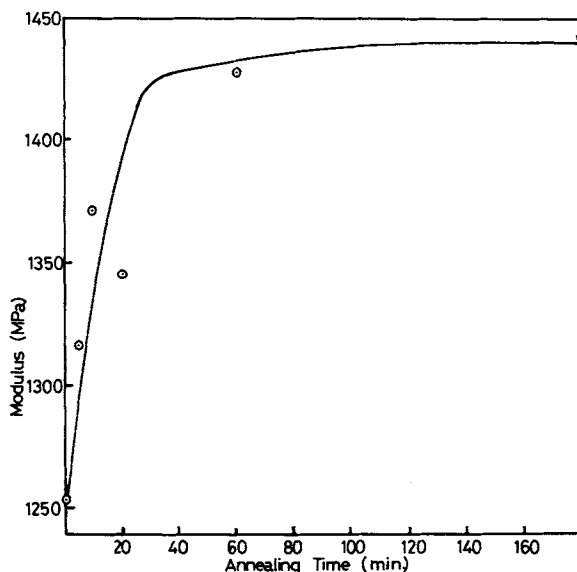
Fig. 2. Variation of tensile modulus as a function of annealing time at 110°C. Stabilizer content 4.5 phr Mark 99.

As $\overline{M}_w$ increases, it is expected that the modulus should increase if it changes at all. The decreasing modulus can be best rationalized as a secondary effect. This may arise from a number of causes, one of which is the degree of syndio-tacticity in the molecules. If this varies with $\overline{M}_w$ as a result of the polymerization conditions, then the degree of crystallinity in the PVC also changes. The modulus is then the composite modulus of a two-phase material, depending on $\overline{M}_w$ only indirectly as the syndiotacticity varies.

The final parameter of interest is the nominal ultimate tensile strength (UTS), which is the maximum load reached in the tensile test, divided by the initial cross-sectional area. The change in the nominal UTS is to be expected. The
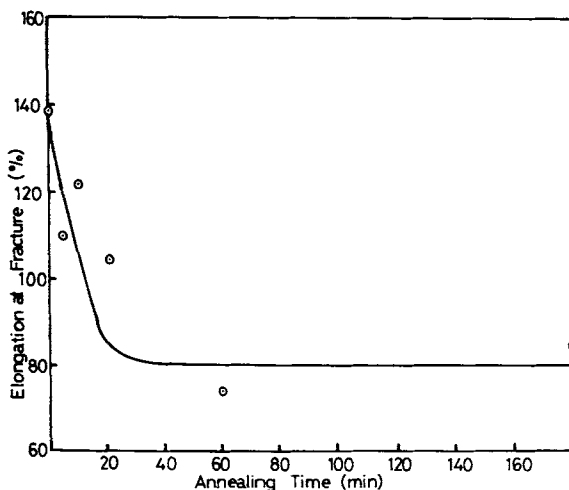

Fig. 3. Elongation at fracture as a function of annealing time at 110°C. Stabilizer content 4.5 phr Mark 99.
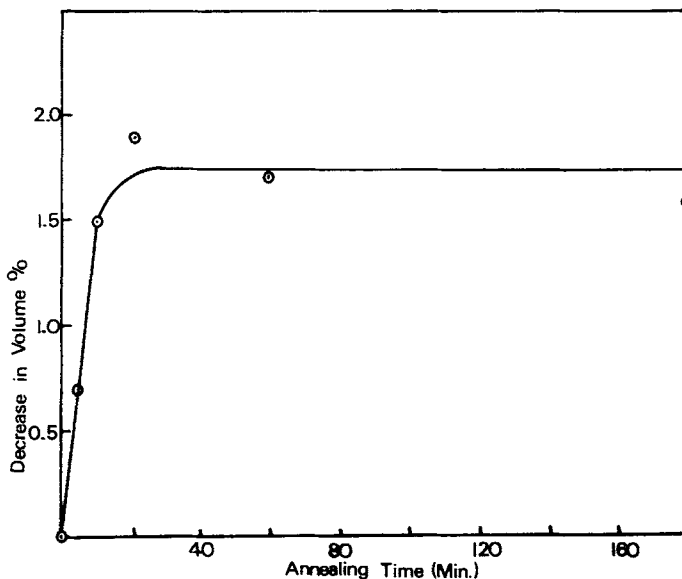
Fig. 4. Change in specific volume with annealing time.

higher $\overline{M}_w$ material will have a higher elongation to fracture, which implies a larger strain hardening capacity. In amorphous polymers, one work hardening mechanism is orientation hardening. The greater the elongation which a given specimen can withstand, the greater the degree of orientation in that specimen before failure. Hence, the higher $\overline{M}_w$ specimens will elongate further and be more highly oriented on a molecular scale. The UTS is, therefore, higher in these specimens.

Stabilizer Content

Figures 7 and 8 show the effect of changes in stabilizer content on the tensile yield stress and tensile modulus. The data presented here are for PVC resin with a nominal intrinsic viscosity of $\eta = 0.63$ and $\eta = 1.00$. The yield stress decreases and the modulus increases with increasing stabilizer content over a range of strain rates.

There are two distinct effects which might be expected from the addition of a nonpolymeric substance such as a barium–cadmium complex. It depends upon the distribution of the additive on a molecular scale.

If the stabilizer is distributed through the compounded plastic on a molecular scale and attaches itself chemically to the PVC molecule,[7,8] then the stabilizer molecule would primarily act to stiffen the molecule. The stabilizer molecules would act as branches, and the modulus and yield stress would simultaneously increase with increasing branch content. Alternatively, the effect of the greater concentration of such branches to the PVC molecule would be to increase the free volume and therefore simultaneously decrease the modulus and yield stress. In any case, the general effect would be the simultaneous change in modulus and yield stress in the same sense, either increasing or decreasing.

If the stabilizer is distributed in the form of second-phase particles in a PVC matrix, the effect expected is quite different. The dispersion of small, hard particles in the PVC matrix would result in an increase in modulus of the com-
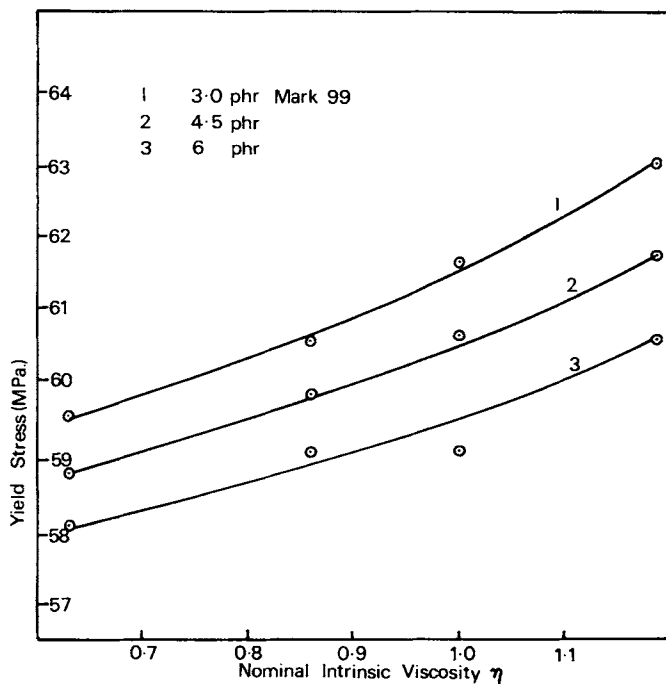
Fig. 5. Change in yield stress with nominal intrinsic viscosity at different stabilizer contents.

posite material with increasing concentration of second-phase particles. However, the yield stress will decrease. According to models for deformation in glassy polymers,[1,2] both dilatational and shear mechanisms of flow are initiated at points of stress concentration. Structurally, these are not clearly defined but
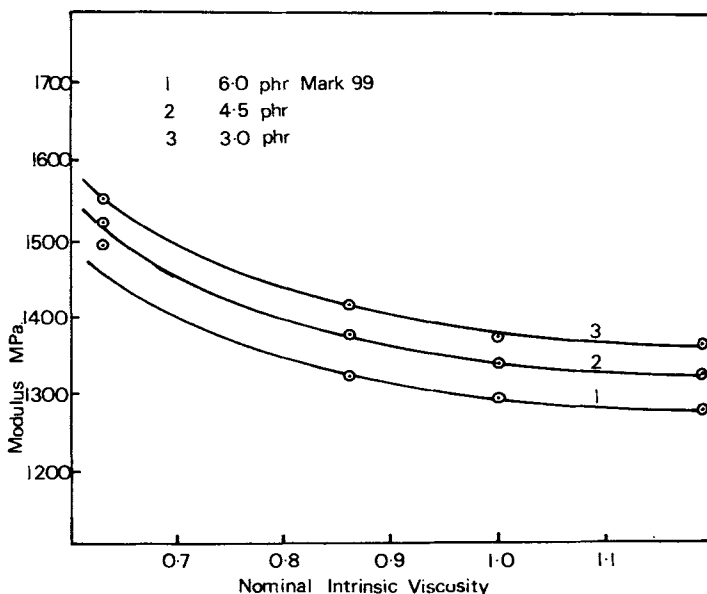

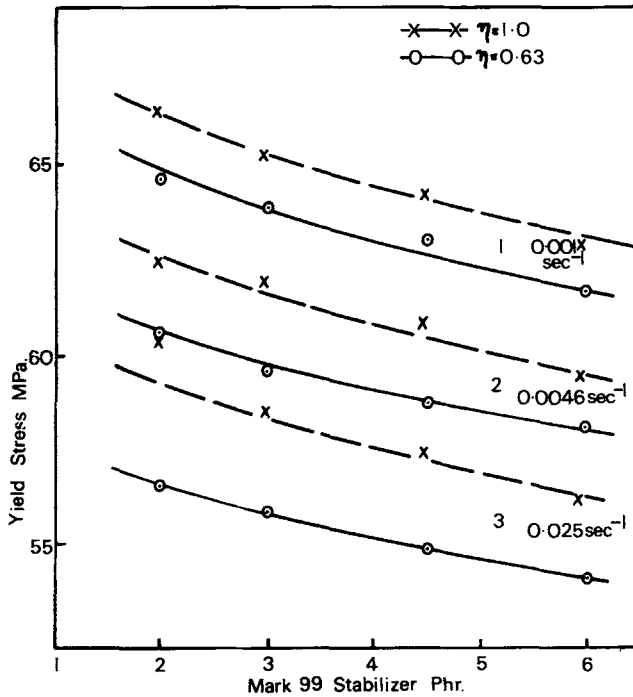Fig. 6. Change in tensile modulus with nominal intrinsic viscosity at different stabilizer contents.

Fig. 7. Effect of stabilizer content on tensile yield stress at different strain rates for two different viscosity resins.

obviously refer to any local inhomogeneities in density or stiffness. The presence of a dispersed second-phase results in local inhomogeneities which act as stress concentrators. Such local stress concentrations are necessary to activate the local shear processes which form the microcavities, the precursor to the crazes.[2] The changes in modulus and yield stress with increasing stabilizer content are, therefore, consistent with the stabilizer acting as a dispersed second phase.

Deformation Mechanisms and Stabilizer Content

The influence of stabilizers on the mechanical properties can be examined directly by measuring the activation parameters of plastic flow. If we assume an activated rate process for flow,[9] the strain rate of the form

$$\dot{\epsilon} = \dot{\epsilon}_c \exp\left(-\frac{\Delta F}{\kappa T}\right)$$

where $\dot{\epsilon}_c \equiv$ fastest attainable strain rate, $\Delta F \equiv$ standard free energy of activation, $\kappa =$ Boltzmann constant, and $T =$ temperature, where the tensile strain volume of activation is given by

$$\Omega_\sigma = -\left(\frac{\partial \Delta F}{\partial \sigma}\right)_{T,P}$$

$$= \kappa T \left(\frac{\partial \ln \dot{\epsilon}}{\partial \sigma}\right)_{T,P}$$

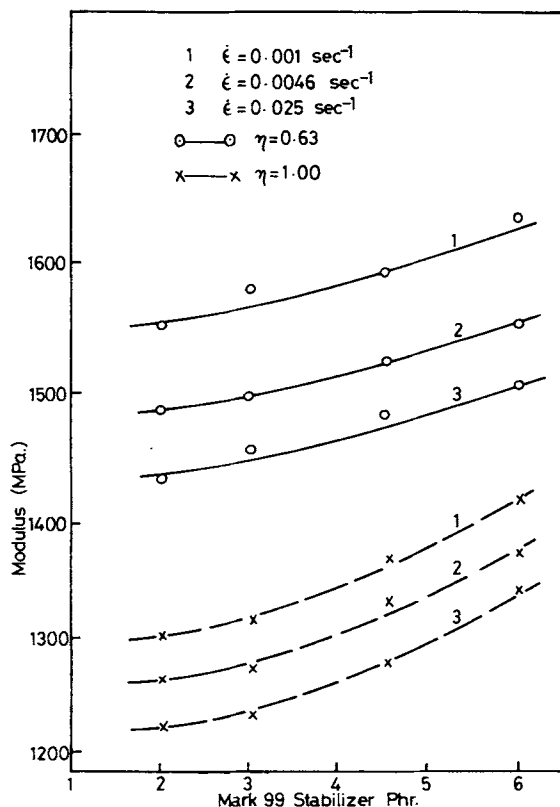Fig. 8. Effect of stabilizer content on tensile modulus at different strain rates for two different viscosity resins.

The term Ω_σ is the strain volume of the reaction, or the local additional tensile strain produced in an activation process, integrated through the specimen.[9] This remains constant over the range of strain rates used (Fig. 9).

However, for increasing molecular weight (increasing viscosity η), the tensile strain volume of activation increases. This suggests that the molecular size has a direct influence on the yielding process—larger molecules require a larger activation strain volume. In addition, stabilizer content changes do not affect the activation process. The implication is that changes in stabilizer content do not substantially affect the flow process in yielding. If the primary role of the stabilizer were to attach itself to the polymer molecule and thereby affect the yielding process, then different concentrations of stabilizer should affect the activation volume for yielding. Since they do not, the role of stabilizer additives in affecting the yielding process is more likely that of second-phase particles.

The changes in yield stress, modulus, and tensile strain volume of activation are, therefore, consistent with a model that distributes stabilizer as a second-phase particle in the PVC matrix.

For PVC with nominal intrinsic viscosity of $\eta = 1.00$, the tensile strain activation volume is approximately $\Omega_\sigma = 1.8 \times 10^{-21}$ cm^3, while for $\eta = 0.63$, $\Omega_\sigma = 1.5 \times 10^{-21}$ cm^3. These agree approximately with the typical values reported by Li.[9]
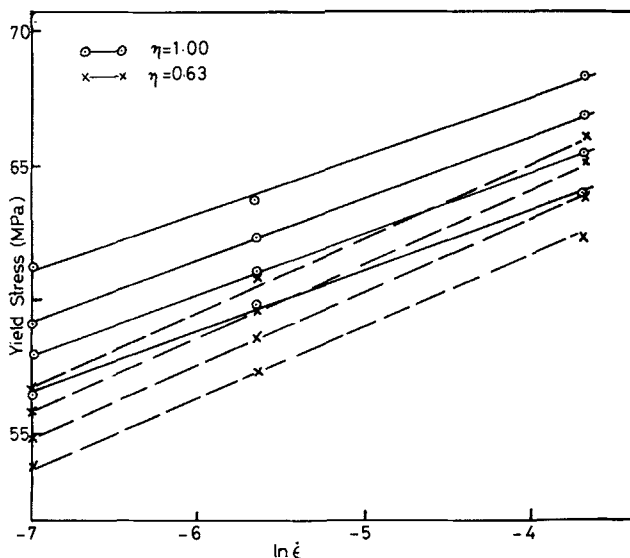
Fig. 9. Effect of strain rate on yield stress for two different viscosity resins.

CONCLUSIONS

It is clear that processing parameters such as molecular weight, thermal pre-treatment, and additive content play a significant role in determining the mechanical behavior of glassy polymers such as PVC.   In any discussion of mechanical properties, it is important that the material used in tests be prepared in a consistent manner which takes such factors into account.   In particular, it is expected than an examination of deformation mechanisms would be affected by these variables.

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