

Rheological Breakdown in the Continuous Shearing of Plasticized Poly(vinyl Chloride)

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Synopsis

The melt behavior under continuous simple laminar shearing of two poly(vinyl chloride) compositions plasticized with different proportions of di-2-ethylhexyl phthalate, has been studied in a cone-and-plate rheometer. In tests at constant shear rates between 0.09 and 9.8 sec.⁻¹, tangential stress was measured as a function of shear over a range of temperatures which was extended by the application of hydrostatic pressure to prevent break-up of the sample. When no hydrostatic pressure was applied, the normal stress difference $p_{11} - p_{22}$ was also determined, and shear recovery was measured. In tests at constant tangential stress in the range 0.4-34 g./cm.², shear was measured as a function of time. During constant-rate shearing, the melts—in common with other polymers—generally showed a reversible reduction in stress and recoverable strain (rheological breakdown) which increased with the stress. At sufficiently low stresses, however, the stress and strain recovery increased with shearing, and this was attributed to recovery from rheological breakdown suffered during the original milling. It is considered that shearing at first disrupts the network formed by secondary cross linkages between the molecules, and then progressively reduces the molecular entanglements to an equilibrium level determined by the conditions. There is an intervening stage in which the decline in shear recovery is temporarily arrested, for which no entirely satisfactory explanation can be offered. At moderate and high shears the strain recovery decreases with increasing shear rate.

INTRODUCTION

Despite the extensive use of extrusion and molding processes in the manufacture of plasticized poly(vinyl chloride) (PVC) products, involving the flow properties of the melt, there is very little published work relating to the fundamental characteristics of this class of material under conditions of continuous shearing. The reason may well be the chemical instability of the material at temperatures used in processing, though this is not the only difficulty inherent in such studies.

The work to be described relates to the behavior of PVC (this contraction is used throughout to indicate the plasticized polymer) when subjected to continuous simple laminar shearing at constant rates in the range 0.09-9.8 sec.⁻¹, or in a few instances at constant shear stresses up to 0.034 kg./cm.²

METHOD

Apparatus

To ease the task of interpreting non-Newtonian behavior an apparatus to give a substantially uniform rate of shear is to be preferred. Accordingly the cone-and-plate rheometer described by Pollett and Cross¹ was used, but with the leaf spring for measuring the thrust on the plate sufficiently stiff to limit axial movement to about $50\ \mu$, which was small enough to have an insignificant effect on the geometry with the angle of about 5° between cone and plate employed in this work. Even with this small displacement it was necessary to disregard readings taken during fairly rapidly changing thrusts, on account of pressure gradients associated with radial flow.² No attempt was made to introduce a correction for these in the present work.

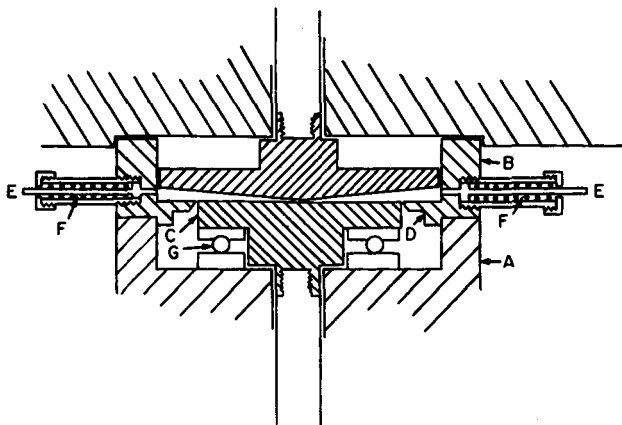


Fig. 1. Modified arrangement for tests under hydrostatic pressure.

Two variations of this set-up were also used. There is a strong tendency for the sample to break up in the early stages of shearing and to leave the test space, if high recoverable strains develop. This imposes a lower limit on the temperatures at which tests can be carried out which is only a few degrees below the maximum set by the thermal instability, but the break-up can be avoided if the test is carried out with an applied hydrostatic pressure. Unfortunately this interferes with the measurement of thrust for normal stress evaluation. The arrangement for such tests is shown in Figure 1, where B is an extension to the rheometer muff A and incorporates a guard ring D. There is a radial gap of about $25\ \mu$ between this and the plate C, which is supported by a thrust bearing G. During molding of the sample the pistons EE are forced back against helical springs FF, and serve to maintain pressure during the test. The leakage between the plate and guard ring, also between the cone and muff extension, is only slight except at high temperatures, and then hydrostatic pressure is no longer needed. It has been shown³ that in these enclosed tests the cylindrical retaining surface

interferes with the uniform shear field only in a region opposite the guard ring, and the same technique has indicated that uniform laminar shearing, without slip at the boundaries, persists at least down to 160°C. at the highest rate of shear. The actual hydrostatic pressure varied during a test, but this was shown to have no significant effect on the torque. At low stresses (e.g., <0.1 kg./cm.²) the friction in the thrust bearing assumed importance, but over a certain range of conditions the arrangement is considered to represent an improvement over existing methods of determining the shear stress-rate of shear relationship in viscoelastic materials.

For tests at constant tangential stress, instead of constant shear rate, the driving clutch was disengaged and a drum attached to the cone spindle. Around this were wound two cords arranged to apply a known couple by means of weights and a system of pulleys. The shear was measured by an optical lever employing a mirror on the cone spindle or, for higher values, by the movement of a scale on the driving drum past a stationary pointer.

Materials

Two compositions incorporating different proportions of di-2-ethylhexyl phthalate as plasticizer were used, details being given in Table I. Mixing occupied 15 min. on a laboratory mill at 155–160°C. The main purpose of the highly plasticized composition 228 was to extend the temperature range in which tests could be performed without application of hydrostatic pressure.

TABLE I
PVC Compositions

	Parts by weight	
	Composition 6343	Composition 228
PVC Geon 101	100	—
PVC Corvic D 65/8	—	100
Di-2-ethylhexyl phthalate	55	100
Litharge	4	4
Ethyl palmitate	1	1

Test Procedure

The correct weight of material to fill the test space was molded between the cone and plate, previously heated to the test temperature, and an interval of 5–6 min. was normally allowed between mold closure and the commencement of shearing, this having been shown to be sufficient for the samples to attain a uniform temperature. Temperatures were controlled to within about $\pm 0.5^\circ\text{C}$. Shear recovery was measured in separate tests from those for stress determination by cone recoil on disengaging the drive while the motor was running, and normally a fresh sample was used for each measurement.

Tests on composition 6343 were at constant shear rates, usually of 0.1, 1.0, and 9.8 sec.⁻¹ in the open tests and slightly lower values in the enclosed tests. The former covered the temperature range 190–207°C. and the latter 150–200°C. Composition 228 was tested only in the absence of applied hydrostatic pressure, usually at constant shear rates of 0.1, 0.28, 1.0, 2.8, and 9.8 sec.⁻¹ in the temperature range 173–203°C. It was also sheared at constant stresses between 0.44 and 34 g./cm.² at temperatures of 174–182°C. Determinations of shear recovery were made at 191 and 196°C. on composition 6343, but only at 187°C. on composition 228.

Validity of Results

On account of the instability of the polymer at the test temperatures, measurements were made of the induction periods before evolution of HCl could be detected by litmus paper for the crumbed compositions alone, and admixed with iron powder (because of a possible catalytic effect of the steel-rheometer plates). Also the loss of plasticizer (including ethyl palmitate) was checked after periods of heating in the rheometer. The results are shown in Tables II and III. The plasticizer loss is considered sufficiently

TABLE II
Loss of Plasticizer from PVC Compositions at 190°C.

Composition	Heating period, min.	Plasticizer content, % ^a
6343	0	35.15
	30	34.90
228	0	49.94
	19	49.60
	26	49.10

^a Includes ethyl palmitate.

TABLE III
Evolution of HCl from PVC Compositions on Heating

Composition	Temperature, °C.	Iron powder	Induction period, min.
6343	200	Absent	25
	200	Present	15
228	185	Present	60
	195	Present	45

low to be unimportant; in the enclosed tests it would of course be negligible. Even under the worst conditions a period of approximately 20 min. was available for test before the commencement of HCl evolution. Although it is likely that some decomposition occurred at an earlier stage, the HCl being absorbed, there is evidence that it had little effect on the rheological

properties, and in general the point at which chemical changes interfered was marked by a fairly rapid rise in stress. In any case, such decomposition is an essential feature of the material's behavior which is relevant to factory processing, even if it interferes with the determination of fundamental characteristics.

Determination of Stress Components

If a rectangular system of coordinates x_1, x_2, x_3 is so chosen that the x_1 axis is parallel to the direction of shear and the x_2 axis is perpendicular to the shear planes, we put:

$$p_{12} \equiv p_s$$

$$p_{11} - p_{22} \equiv p_t$$

For shearing in the cone-and-plate system these quantities are obtained from the relationships:

$$p_s = 3M/2\pi R^3$$

$$p_t = 2F/\pi R^2$$

where M is the torque and F the thrust acting on the plate of radius R .

The complete evaluation of stress in the melt during laminar shearing requires the determination of one additional normal stress difference, but for molten polyethylene^{2,4} and well-masticated natural rubber⁵ as well as for several polymer solutions^{6,7} it has been shown that $p_{22} - p_{33}$ is, at any rate to a first approximation, zero. Markowitz⁸ and Lodge⁹ have questioned the equality of p_{22} and p_{33} . Attempts to measure $p_{22} - p_{33}$ for plasticized PVC melt by the method previously used² gave inconclusive results, owing to experimental errors associated with the long relaxation times for the material.

EXPERIMENTAL RESULTS

Typical curves showing the variation of p_s with applied shear σ at a series of temperatures but constant shear rate are given in Figure 2 for enclosed tests on composition 6343 and in Figure 3 for open tests on composition 228, while Figure 4 gives similar curves for a series of different shear rates $\dot{\sigma}$ at about the same temperature. The variation of p_t with applied shear is shown in Figure 5 for a series of different temperatures and in Figure 6 for several rates of shear, both sets referring to the less plasticized composition.

Figure 7 shows the effect of various intervals between successive periods of shearing at 0.92 sec.^{-1} on the tangential stress developed by composition 6343 in enclosed tests at 173°C . In other tests at low shear rates the time between molding the sample and commencement of shearing was varied, and Figure 8 shows the effect of this on the stress components for composition 6343.

In recoil measurements the shear recovery continued at a diminishing rate for periods up to about 30 min. In Figure 9 the recovery values ultimately reached are plotted against applied shear at 196°C. for composition 6343 at three different rates.

The preceding curves all apply to tests at constant shear rates. Representative results for the increase in shear with time for tests at constant stress are shown in Figure 10.

DISCUSSION OF RESULTS

Rheological Breakdown

At the commencement of shearing at constant rate p_s and p_t , as well as recovery, increased, usually to well defined maxima, at a shear of about 15 (Figs. 9 and 11). In only a small proportion of the present tests was it possible to make reliable stress measurements at low enough shears to characterize these maxima accurately, but this is readily done on the commercially available Weissenberg rheogoniometer. In one such test, carried out by King¹⁰ on a composition similar to composition 228 at 180°C. and 10 sec.⁻¹, a peak was reached by p_s at a shear of 13 and by p_t at 18, and this appears to be fairly representative.

Beyond these maxima the values of p_t and shear recovery tended to decrease. In the case of p_s a similar tendency was sometimes partly obscured by what appeared to be a superimposed temporary increase in shear stress at shears within the range 50–500 (cf. Figs. 3 and 4) and a comparable effect, but at higher shears, has been reported for polyethylene.² The reduction in

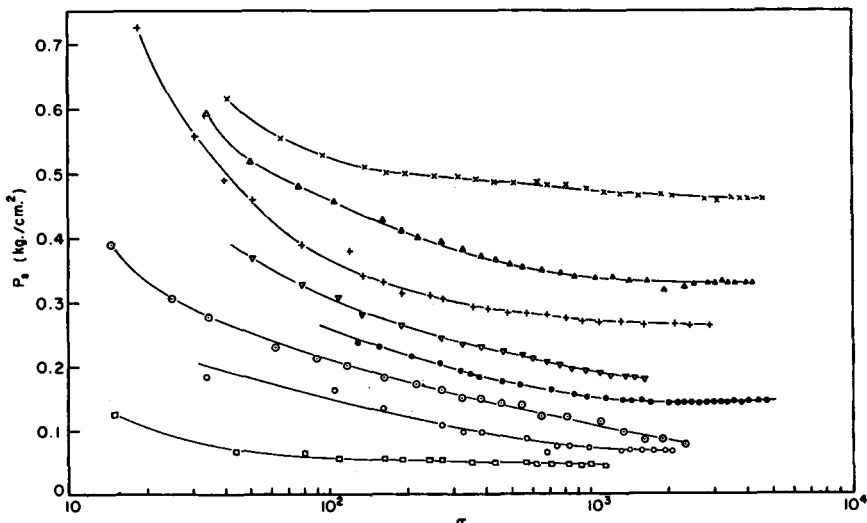


Fig. 2. Enclosed tests on composition 6343 at various temperatures: (×) 151.5°C.; (Δ) 161°C.; (+) 168.5°C.; (∇) 173°C.; (●) 178.5°C.; (⊙) 181°C.; (○) 189°C.; (□) 194.5°C. Shear stress as function of shear at 0.92 sec.⁻¹.

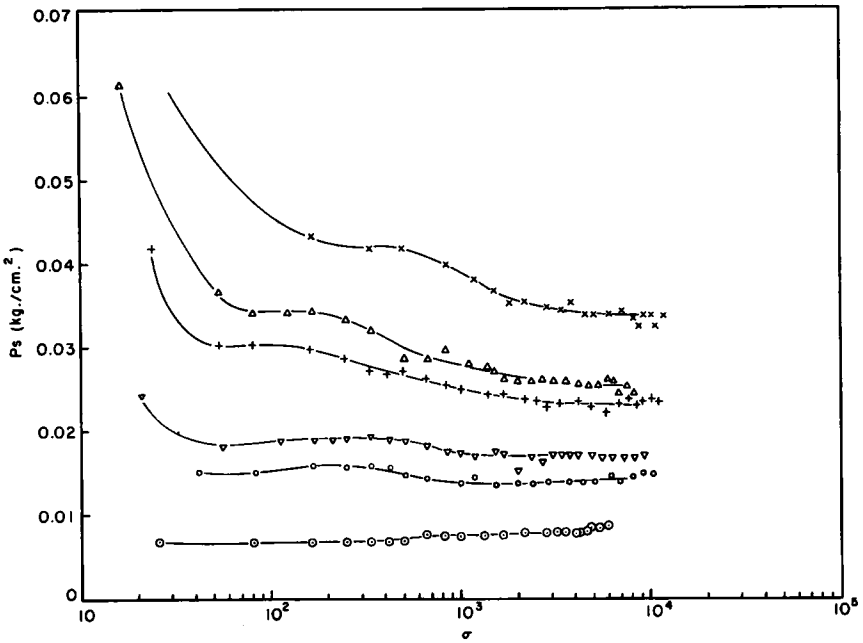


Fig. 3. Open tests on composition 228 at various temperatures: (X) 177.5°C .; (Δ) 179.5°C .; (+) 181°C .; (∇) 184°C .; (O) 186.5°C .; (\odot) 192°C . Shear stress as function of shear at 2.8 sec.^{-1} .

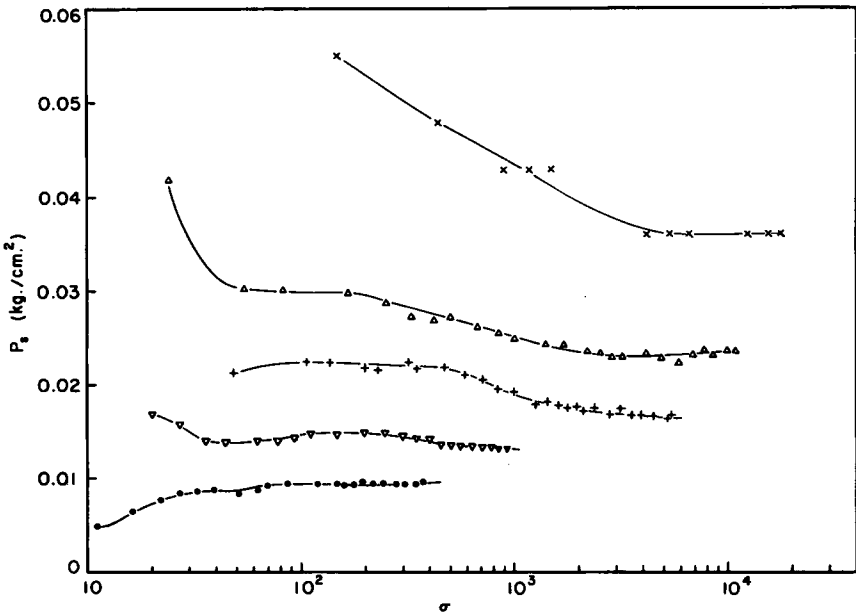


Fig. 4. Open tests on composition 228 at various shear rates: (X) 9.8 sec.^{-1} , 180.5°C .; (Δ) 2.8 sec.^{-1} , 181°C .; (+) 1.0 sec.^{-1} , 180°C .; (∇) 0.28 sec.^{-1} , 180.5°C .; (\bullet) 0.10 sec.^{-1} , 180°C . Shear stress as function of shear.

shear recovery with increasing shear was also interrupted, but over a relatively short range of shears. In the case of composition 228, tested at 187°C. the interruption was made apparent only by a subsequent abrupt increase in slope at a shear of 35-55, depending on the shear rate; there was no second peak similar to those in Figure 9.

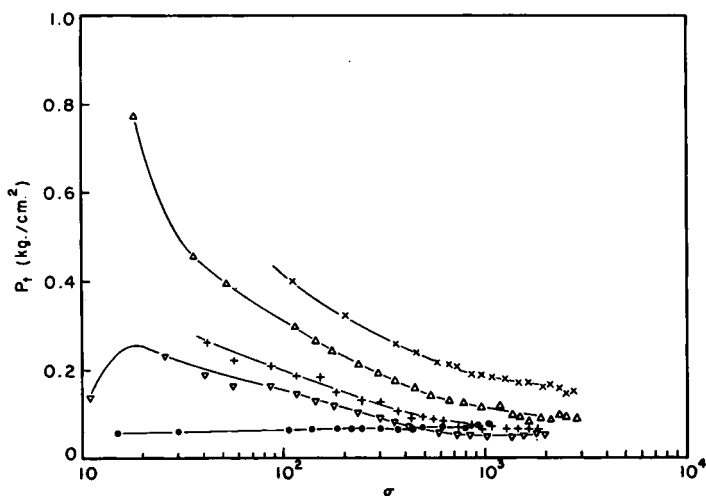


Fig. 5. Normal stress as function of shear at various temperatures for composition 6343 sheared at 1.0 sec.⁻¹: (X) 191.5°C.; (Δ) 193°C.; (+) 196°C.; (∇) 198.5°C.; (●) 205.5°C.

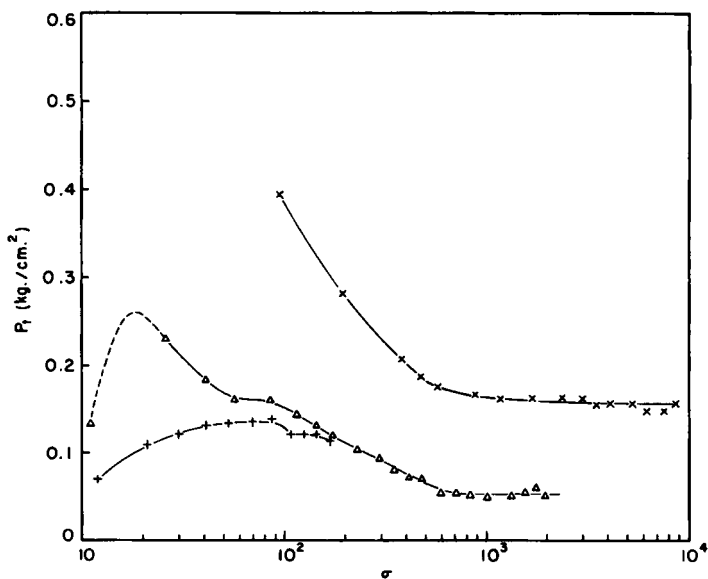


Fig. 6. Normal stress as function of shear for composition 6343 for various shear rates at 198°C.: (+) 0.1 sec.⁻¹; (Δ) 1.0 sec.⁻¹; (X) 9.8 sec.⁻¹.

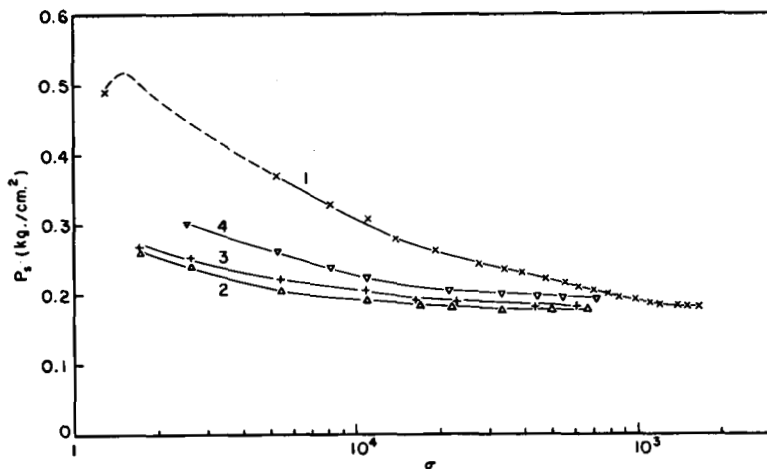


Fig. 7. Effect of resting on shear stress for composition 6343 sheared at 0.92 sec.^{-1} and 173°C. : interval between 1 and 2 = 10 min.; interval between 2 and 3 = 20 min.; interval between 3 and 4 = 56 min.

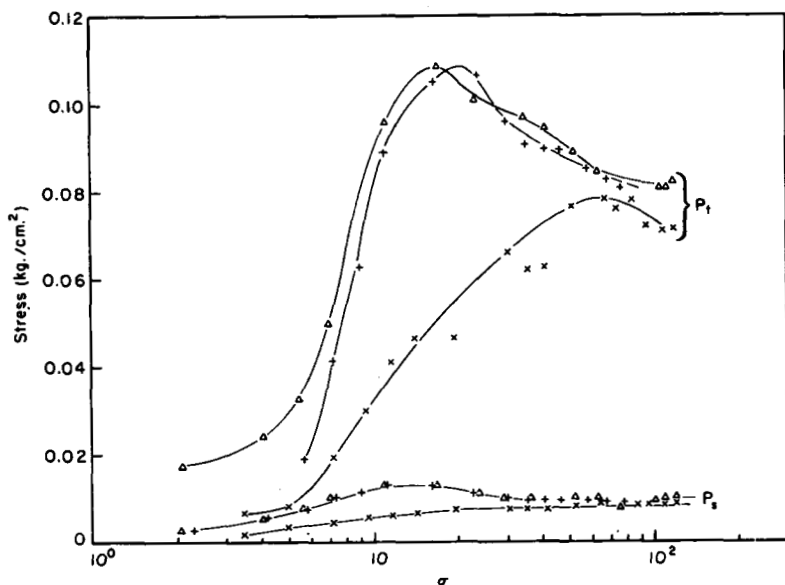


Fig. 8. Effect of interval between molding and shearing for composition 228 sheared at 0.093 sec.^{-1} and 181°C. : (X) 5.5 min.; (Δ) 15 min.; (+) 30 min.

There was rather indefinite evidence in some instances that the decline of p_1 was interrupted in the same way as that of the shear recovery (Fig. 11). For the moment this interruption of the general trend will be disregarded so that attention may be focussed on the reduction in stress and recoverable strain accompanying shearing at a constant rate—a phenomenon which has

previously been observed with other polymers.^{2,11} It is clear from Figure 7 that the reduction in p_s on shearing is reversed if the PVC is rested at the same temperature, and similar evidence is available in respect to p_i and shear recovery. Although reversion to the unworked condition was not

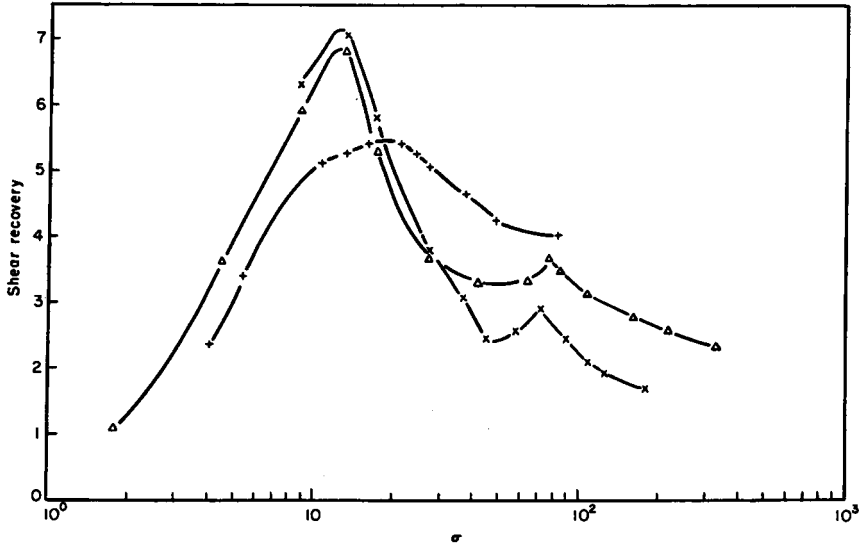


Fig. 9. Effect of shear at various rates on recovery for composition 6343 at 196°C.: (+) 0.093 sec.⁻¹; (Δ) 0.93 sec.⁻¹; (\times) 9.1 sec.⁻¹.

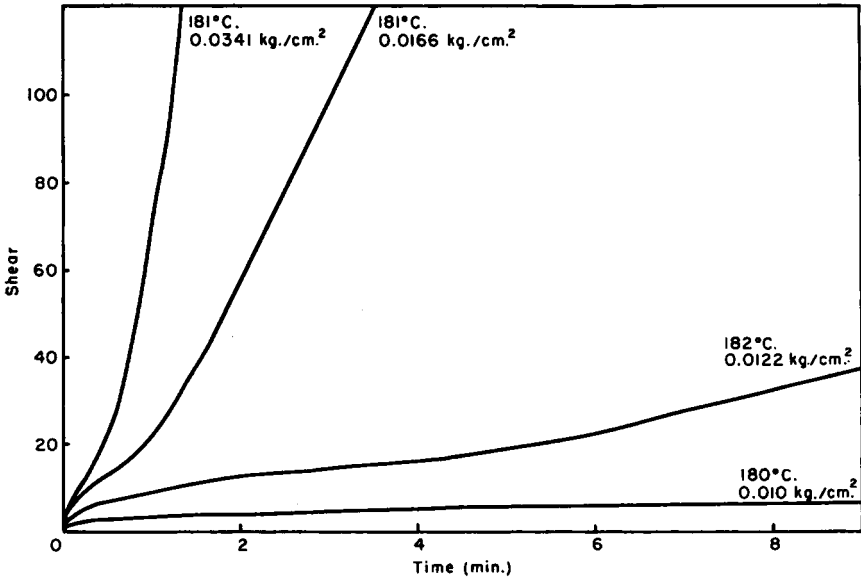


Fig. 10. Shear as function of time at various shear stresses for composition 228 sheared at constant stress.

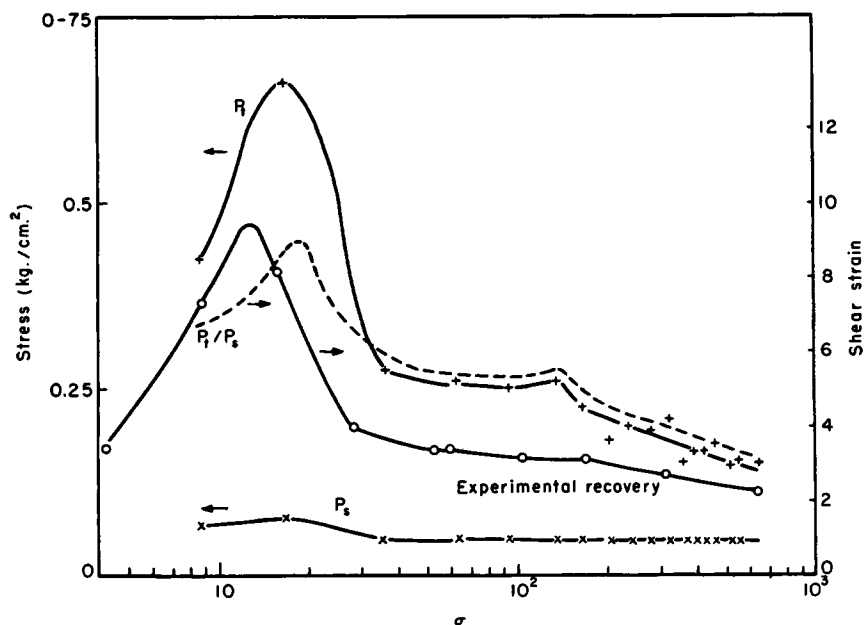


Fig. 11. Comparison of experimental shear recovery for composition 6343 sheared at 0.35 sec.^{-1} and 191°C. with ratio p_s/p_t .

complete, it was more nearly approached the longer the rest period, and, by analogy with polyethylene² it is reasonable to suppose that it would have been complete if a sufficiently long rest period had been possible. Since substantially the same stress was ultimately reached in each cycle of shearing, it is unlikely that there was any significant permanent change in the material. The term "thixotropy" is inadequate to describe this reversible reduction in stress and recoverable strain by shearing, and in this laboratory it has been designated "rheological breakdown"—without any implication, however, that it is attributable to a single mechanism. The extent of rheological breakdown increases with stress, as well as with amount of shearing.

Exceptions to the pattern of behavior already considered occurred when the value of p_s was below about 0.05 kg./cm.^2 for composition 6343, or 0.01 kg./cm.^2 for 228 (see Figs. 4 and 6). Under these conditions p_s and p_t continued to rise at shears well above that at which they normally passed through maxima.

The preparation of the compositions in the first place involved working on a mill, and this must have produced appreciable rheological breakdown. During testing, the material would consequently have had a tendency to recover from this, as well as for further rheological breakdown to occur, but only at sufficiently low stresses would the former have been preponderant, so that p_s and p_t progressively rose. If the PVC were allowed to stand at the test temperature for a longer period before commencement of shearing,

the recovery from rheological breakdown should progress further before the start of the test, and the curves in Figure 8 confirm that this does happen. In this instance a standing time of 15 min. at 181°C. for composition 228 allowed substantially complete recovery, since a further 15 min. made little difference to the stress. In the case of composition 6343 at 199°C., however, a longer period was required.

Shear Recovery

It has already been pointed out that the shear recovery-log σ curves consist of a steeply increasing region for low shears followed by a region of diminishing negative slope interrupted by a temporarily reduced rate of decline or actual increase in recovery at moderate shears of the order of 100. These general characteristics are shown with variations by polyethylene² and other polymer melts,¹¹ but a feature not previously reported is that the recovery decreases with increasing rate of shear for both compositions 6343 and 228 for shears greater than about 30.

According to Weissenberg¹² the recoverable shear is given by p_i/p_s , though Pollett² has pointed out that the experimental recovery is likely to be less. Lodge¹³ gives the ultimate recovery, constrained to a simple shear, as $p_i/2p_s$. Unfortunately in the present work the shear rates were usually slightly lower in the recovery determinations than in the tests for stress measurement, so that a direct comparison with theory was not possible, but this difficulty did not arise with the results in Figure 11. Here the ratio of shear recovery to p_i/p_s was less than unity, except at low shears where the radial pressure gradients associated with the rapidly changing

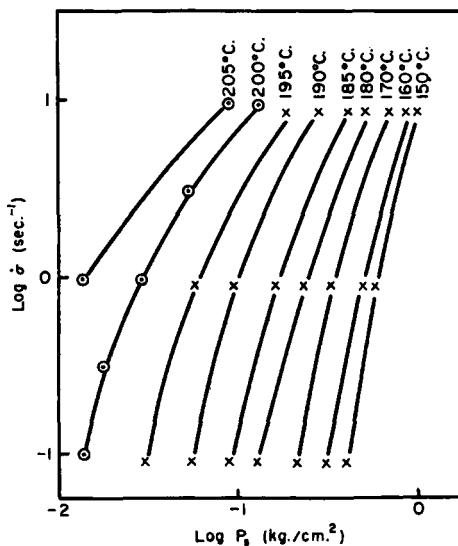


Fig. 12. Rate of shear-shear stress relationships for composition 6343 at applied shear of 100: (×) enclosed tests; (○) open tests.

value of p_i probably vitiated its determination. For shears above 20 the ratio varied between about 0.6 and 0.75, which is higher than required by Lodge's theory, but it is doubtful whether the PVC composition can be regarded as coming within his category of concentrated polymer solutions.

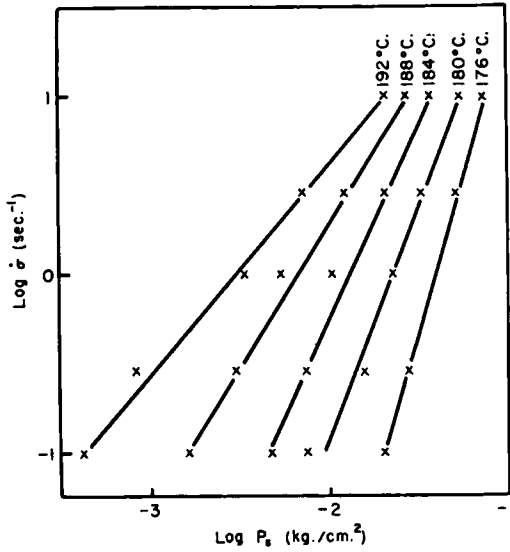


Fig. 13. Rate of shear–shear stress relationships for composition 228 at applied shear of 100.

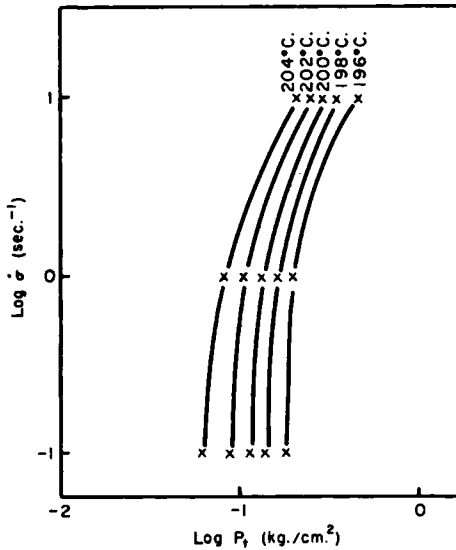


Fig. 14. Rate of shear–normal stress relationships for composition 6343 at applied shear of 100.

Stress-Rate of Shear Relationships

In order to reduce errors resulting from the very high temperature sensitivity of the stress developed by PVC at a given rate of shear and the rather low degree of temperature control ($\pm 0.5^\circ\text{C}$.) attainable, the stress components were plotted against temperature at each rate of shear for

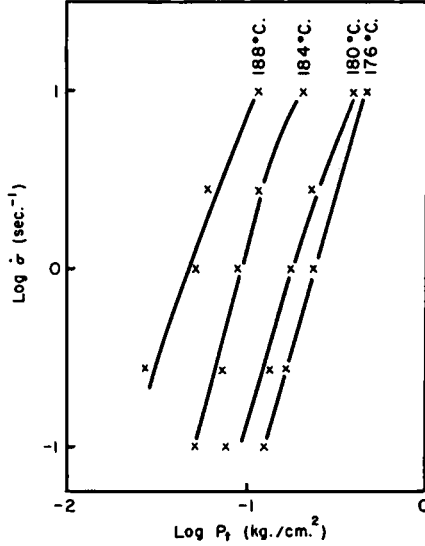


Fig. 15. Rate of shear-normal stress relationships for composition 228 at applied shear of 100.

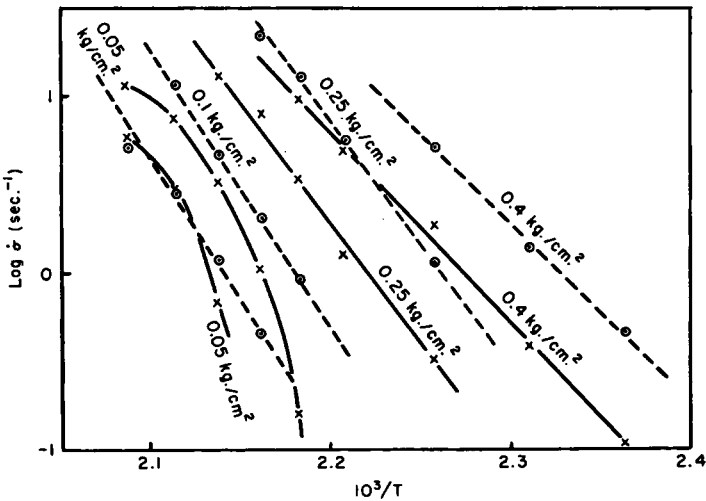


Fig. 16. Arrhenius plots at constant shear stress and applied shear, for estimation of activation energy of composition 6343: (—X—) applied shear = 100; (---O---) applied shear = 1000.

several different applied shears. The smoothed curves were then used for subsequent evaluations. The plot of $\log \dot{\sigma}$ against $\log p_s$ at constant shear, gave a series of practically linear curves for composition 228 (Fig. 13), but for composition 6343 (Fig. 12) they were convex to the $\log \dot{\sigma}$ axis instead of concave, as is usual for polymer melts. This may be due to the presence of the plasticizer, since polymer solutions give curves which change from concave to convex with increasing rates of shear. Similar plots for p_t instead of p_s are given in Figures 14 and 15.

Apparent Activation Energy for Viscous Flow

The dependence of viscosity on amount, as well as rate, of shear introduces a complication in the determination of activation energy for viscous flow. In the case of polyethylene it was shown² that equal values of p_s/T , where T is absolute temperature, at equal applied shears corresponded to equivalent conditions for estimation of the activation energy, but a similar justification for this criterion could not be established in the case of PVC, and it is doubtful whether a satisfactory basis for determination of an activation energy exists. The procedure adopted for composition 6343 was to plot $\log \dot{\sigma}$ against $1/T$ at constant p_s and σ , but is quite arbitrary, so that values obtained are of doubtful physical significance. Reasonable straight lines were obtained (Fig. 16) except at low shears and shear stresses, when the rheological breakdown during milling was likely to have interfered. Composition 228, on the other hand, did not yield straight lines, but did so if $\log (p_s/\dot{\sigma})$ was plotted against $1/T$ at constant p_t and σ .

The apparent activation energies obtained from the slopes of these curves are shown in Table IV. Even when account is taken of the arbitrary procedures for their estimation the values are extremely high and are unlikely to have a quantitative fundamental meaning, but they are nevertheless a true reflection of the high temperature dependence of the viscosity of the PVC melts. It may perhaps be significant that the apparent activation energies are independent of applied shear, but decrease with increasing stress, also that the values are very much higher for the softer composition.

TABLE IV
Apparent Activation Energies for Viscous Flow

Composition	p_s , kg./cm. ²	p_t , kg./cm. ²	σ	Activation energy, kcal./mole
6343	0.05	—	1000	70
	0.1	—	1000	70
	0.25	—	100	62.5
	0.25	—	1000	62.5
	0.4	—	100	49
	0.4	—	1000	47
228	—	0.05	100	168
	—	0.1	100	159
	—	0.2	100	131

Structural Changes During Shearing

Whereas the shearing of PVC under constant stress proceeded at a diminishing rate for shears below about 15, above this critical value the rate increased again (Fig. 10), as though some kind of yielding of the structure had occurred. This effect is matched by the occurrence of peak values for the stress components at about the same shear, applied at a constant rate, though at low stress levels this pattern may be modified by rheological breakdown. Furthermore, the shear recovery and the ratio p_i/p_s pass through maxima at about this same shear. These phenomena have been noted previously with other polymer melts,^{2,11,14} and the present results serve only to strengthen the view already expressed¹¹ that the molecular network formed by secondary crosslinkages disrupts at the critical shear almost catastrophically. At somewhat lower temperatures or higher shear rates catastrophic breakdown does occur at this stage, as evidenced by macroscopic cracking: failure of crosslinkages throws additional stress on those remaining at a higher rate than can be relieved by relaxation. Recently de Vries and Tochon¹⁴ have expressed a somewhat similar view, but report that the structure is reformed in 5–10 sec. after cessation of flow. In the experience of the present authors, although an interval of this order after moderately prolonged shearing—may be sufficient for the stress to pass through a peak again when it is resumed at not too low a rate, the stress level is lower than on the first shearing. It is likely, therefore, that a much more open network is formed at this stage, and that recovery from rheological breakdown is still far from complete. It is considered unlikely that the initial network is produced mainly by entanglements, as its disruption would then be expected to be more gradual.

The subsequent decline in stress components and in shear recovery has also been observed in other polymer melts.^{2,11} Not only is it reversible, which rules out chain scission, but it persists when milled material, or sheared polymer removed from the rheometer,² is remolded and tested. It cannot therefore be due to macroscopic effects such as that described by Hutton.¹⁵ Network rupture cannot continue up to very high shears except perhaps as breaking down of gel fragments which, even if it occurs, seems incapable of explaining the observed behavior. The only explanation which appears to fit the facts is that previously suggested tentatively: that the molecular entanglements are progressively eliminated by the sliding of the molecules over one another until an equilibrium is set up between this effect and the tendency for thermal agitation to produce fresh entanglements. The greater the molecular orientation, the less effective the thermal agitation will be in producing entanglements, and the greater will be the rheological breakdown.

If entanglements can be regarded effectively as crosslinkages of greater stability than those formed by secondary bonds, they will tend to increase N_2 relative to N_1 in Lodge's theory,¹³ where these are proportional respec-

tively to the second and first moments of the junction age distribution. According to this theory the normal stress varies as N_2 , and the tangential stress as N_1 . Hence elimination of entanglements would be expected to reduce p_t more than p_s , and lessen the constrained shear recovery, as is observed. Molecular entanglements would be unlikely to have much effect on the activation energy for viscous flow, but to increase the magnitude of the entropy of activation. Although the exact significance of the measured activation energies for the PVC compositions is uncertain, it may be noted that the degree of rheological breakdown, as represented by amount of shear at a given stress, had no effect on the value. Also, since the viscosity generally diminished with increasing shear it may be inferred that the magnitude of the entropy of activation decreased. On the other hand, increasing stress at constant shear resulted in a reduction in apparent activation energy, which might seem to be opposed to the idea that rheological breakdown is simply an elimination of entanglements. However, it seems reasonable to suppose that associations which exist between plasticizer and polymer molecules will be broken down to an increasing extent as the stress rises, and this may account for the effect. In the case of polyethylene, where this complication does not exist, and where the activation energy is likely to have a more definite significance, its value was shown² to be substantially independent both of amount of shear and of the stress. Howells and Benbow¹⁶ have likewise attributed the reduction in viscosity of a polyethylene melt on shearing to a decrease in molecular entanglements.

The interruption in rheological breakdown which occurs at intermediate shears, and which is best seen in the recovery/applied shear curves (Fig. 9), is the most difficult of the sequence of changes to explain adequately. The tentative hypothesis¹¹ that it is due to steric interference between branch chains does not seem to explain the sharpness of the maxima. This objection possibly applies also to an alternative suggestion that, following the near-catastrophic disruption of the original network, the increased concentration of secondary crosslinking sites results in their reuniting at an increased rate. This produces a second network in which the crosslinks were formed at about the same time, so that they also break down at about the same time. Also it might be thought that the second peak in the recovery/ $\log \sigma$ curves would be displaced to higher shears with increasing shear rate, if this explanation were correct.

It therefore appears that no very satisfactory explanation of the interruption of the process of rheological breakdown can yet be offered.

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Résumé

On a étudié la comportement rhéologique de deux chlorures de polyvinyle plastifiés par du phthalate de di-2-éthylhexyle à l'aide d'un rhéomètre à cône. Le cisaillement durant l'expérience est du type laminaire continu. On a effectué plusieurs expériences à vitesse de cisaillement constante variant depuis 0.09 jusqu'à 9.8 s⁻¹. On a mesuré la tension tangentielle en fonction du cisaillement à différentes températures. On a artificiellement étendu le domaine des mesures en appliquant une pression hydrostatique, qui empêche la rupture de l'échantillon. On a également déterminé en l'absence de pression hydrostatique la différence $p_{11} - p_{22}$ entre les tensions normales et le recouvrement. Dans une série de tests où la tension tangentielle était maintenue constante (entre 0.4 et 34 g/cm²), on a mesuré le cisaillement en fonction du temps. À vitesse de cisaillement constante, les polymères montrent, comme les autres polymères à l'état fondu, une diminution réversible de la tension et de la déformation recouvrable (rupture rhéologique) qui augmente avec la tension. Cependant, on constate que lorsque les tensions sont suffisamment petites, il se produit une augmentation de la partie recouvrable de la tension et de la déformation avec le cisaillement. On attribue ce phénomène à une rupture rhéologique introduite lors de la préparation de l'échantillon. On pense que le cisaillement perturbe d'abord le réseau formé par les ponts physiques entre les molécules et réduit ensuite les entrelacements moléculaires à un équilibre déterminé par les circonstances. À un stade intermédiaire, la décroissance du recouvrement est momentanément arrêtée. On ne possède pas encore une explication plausible de ce phénomène. À des cisaillements moyens et élevés, le recouvrement diminue lorsque la vitesse de cisaillement augmente.

Zusammenfassung

Das Schmelzverhalten von zwei mit verschiedenen Anteilen an Di-2-äthylhexylphthalat weich gemachten Polyvinylchloridproben wurde unter kontinuierlicher, einfacher, laminarer Scherung in einem Kegel-Plattenrheometer untersucht. Bei den Tests bei konstanter Schergeschwindigkeit zwischen 0,09 und 9,8 s⁻¹ wurde die Tangentialspannung als Funktion des Schubs in einem Temperaturbereich gemessen, welcher durch die Anwendung von hydrostatischem Druck zur Verhinderung des Aufbrechens der Probe noch erweitert wurde. Ohne Anwendung von hydrostatischem Druck wurde auch die Normalspannungsdifferenz $p_{11} - p_{22}$ bestimmt und die Schererholung gemessen. Bei den Tests bei konstanter Tangentialspannung im Bereich 0,4 bis 34 g/cm² wurde der Schub als Funktion der Zeit gemessen. Während einer Scherung mit konstanter

Geschwindigkeit zeigten die Schmelzen in Übereinstimmung mit anderen Polymeren im allgemeinen eine reversible Herabsetzung der Spannung und der rückbildbaren Verformung. (Rheologischer Zusammenbruch), welche mit der Spannung zunahm. Bei genügend niedriger Spannung nahm jedoch die Spannungs- und Verformungsrückbildung mit der Scherung zu, was einer Erholung vom während des ursprünglichen Walzens aufgetretenen rheologischen Zusammenbruch zugeschrieben wurde. Es wird angenommen, dass die Scherung zuerst das durch sekundäre Vernetzung zwischen den Molekülen gebildete Netzwerk zerstört und dann allmählich die Molekülverschlingungen auf eine durch die Versuchsbedingungen bestimmten Gleichgewichtswert herabsetzt. Es besteht ein Zwischenstadium, bei welchem das Abklingen der Scherungsrückbildung zeitweilig unterbrochen wird; für diese Erscheinung kann keine vollständig befriedigende Erklärung gegeben werden. Bei mässiger und hoher Scherung nimmt die Verformungsrückbildung mit steigender Schubgeschwindigkeit ab.

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