

THE RHEOLOGY OF PVC - AN OVERVIEW

Edward A. Collins

B.F. Goodrich Chemical Company, Technical Center, Avon Lake, Ohio 44012, USA

Abstract - Three aspects of the rheological behavior of PVC are considered. These are (a) particulate flow which occurs below the true crystalline melting point, (b) true melting flow which occurs at or above the melting point and (c) the flow of PVC compounds. The effect of structural differences, resulting from different polymerization temperatures employed in preparing different molecular weight polymers, on the melt viscosity and flow activation energy is reexamined and new data presented to unconfound the effect of syndiotacticity and molecular weight. The three flow behaviors of PVC is shown to be presented by three distinct flow regions. Because of thermal instability, the true melt flow region is only achieved with difficulty. However, in commercial operations this latter state is seldom, if ever, achieved in rigid formulations. The effect of compounding additives, especially lubricants and plasticizers and the importance of thermal and mastication history on the flow behavior is discussed with reference to the flow mechanism.

INTRODUCTION

There are many facets to the rheology of polyvinyl chloride unlike most other commonly used thermoplastic polymers. Indeed, the study of PVC rheology encompasses the whole field of rheology.

For all polymeric materials there are basically three aspects of rheology of interest both theoretically and practically. In simple terms of practical interest, these are: (a) rate (b) appearance, and (c) performance. Translated these become processability, elasticity and ultimate or mechanical properties respectively. Each of these are topics in this symposium.

For all thermoplastic polymers all three of these properties have a dependence on molecular factors, such as molecular weight and molecular weight distribution, structural factors, such as branching and stereoregularity and morphology. To fully understand the relationships of all of these parameters for any polymer is a monumental task as is well known. However, for PVC the situation is considerably more complicated not only because PVC is seldom, if ever, used or even studied in a pure state, but also because in almost all practical operations, PVC is processed under conditions where its particulate nature plays a dominant role. In view of this, it becomes immediately apparent then, that the true melt flow behavior of PVC is primarily of academic interest.

Looking further into the rheology of PVC one finds a unique importance of particle size, particle structure, porosity and surface characteristics which strongly influence the behavior not only in rigid formulations where compounding additives add further complexity, but also in semi-rigid or flexible applications where plasticizer adds yet another dimension. In addition, plastisols or suspensions provide still another aspect to the many facts of PVC rheology where particle structure is of primary importance.

MELT VISCOSITY

While the melt rheology of PVC has not been studied as extensively as polyethylene or polystyrene, the other major thermoplastics, sufficient investigations have been carried out to establish the effect of molecular weight; polymerization temperature and measurement temperature on the shear rate dependence of the viscosity. The expected dependence of the flow behavior of these parameters can be changed or masked by particulate (supermolecular) flow effects and complicated by shear heating, thermal degradation and slip.

The melt flow behavior of PVC can be subdivided into three parts, namely particulate flow (below the melting point) of pure PVC, true melt flow (at or above the M.P) and flow of compounds. Early studies of Fukasawa (1), Sieglaff (2), Mayrick and Sieglaff (3) and Collins and Krier (4) revealed the non-Newtonian nature of the viscosity-shear rate and viscosity-

temperature curves. In the latter study the flow of pure PVC (with only stabilizer added) was found to have two different flow activation energies in the range of temperature from 160°C to 230°C, both at constant shear rate and at constant shear stress, providing independent evidence for the presence of two distinct flow mechanisms. Activation energies of 10 and 20 k cal/mole for the low and high temperature regions respectively were reported. It was also shown that a master curve of shear stress versus reduced shear rate could be prepared for PVC when proper precautions were taken to avoid or prevent thermal degradation and due consideration was given to particulate nature of the flow.

Subsequent work of Sieglaff (5), Hoffman and Choi (6), den Otter (7) and Collins and Metzger (8) added additional support to the earlier work of Collins and Krier (4). In addition, it was shown that the dual valued nature of the activation energy was not confined to PVC polymer prepared by emulsion technique but was also common to suspension polymer providing even further supporting evidence for the particulate flow mechanism. Two excellent reviews on PVC melt flow properties have appeared in the literature (9) (10).

The effect of molecular weight on the shear rate and temperature dependence of the viscosity was reported by Collins and Metzger (8) for PVC with added stabilizer. However, while this work covered the molecular weight above and below the commercial range and has practical significance, the effect of structural differences arising as a result of the different polymerization temperatures employed in preparing such a wide range of molecular weights was not considered in that study.

Results of experiments carried out to establish this relationship are listed in Table 1.

TABLE 1. Activation Energy $\Delta E\gamma$

Sample	Polym. Temp. °C	LVN*	$\Delta E\gamma$ (k cal/mole)		
			10 sec ⁻¹	100 sec ⁻¹	1000 sec ⁻¹
A-2	5	0.131	-	36.01	32.22
B-2	5	0.693	45.89	28.60	14.38
C-2	5	0.909	39.54	24.64	12.95
D-2	5	1.750	10.38	7.28	7.26
E-2	40	0.640	42.63	24.56	12.89
F-2	40	0.682	37.60	25.12	10.74
G-2	40	1.225	25.94	13.78	8.27
H-2	70	0.495	35.28	23.17	12.51
I-2	70	0.680	30.30	20.14	10.41

* Cyclohexane 30°C.

Examination of these results indicates that at a constant polymerization temperature, the flow activation energy at constant shear rate, decreases with increasing molecular weight. The flow activation energy at constant shear rate also decreases with increasing polymerization temperature for a given molecular weight level.

Collins and Daniels (11) were able to separate the effect of molecular weight and order on the shear rate dependence of the viscosity. They showed that polymers of constant molecular weight polymerized at temperatures between 40°C and 70°C had the same flow behavior over three decades of shear rates, while a polymer of the same molecular weight prepared at 5°C and hence having an increased syndiotacticity gave rise to a nearly ten-fold increase in viscosity at low shear rates. More recently (12) viscosity shear rate data at various temperatures has been reported for PVC polymerized in the range 25°C to 110°C.

PARTICULATE FLOW

The earliest experimental evidence for the existence of domains or rheological flow units which consist of many molecules operating as a single body was reported by Mooney and Wolstenholme (13) in their classic ink migration experiment. Although earlier references suggesting particulate flow were reported by Rochow and Rowe (14), Eirich and Mark (15), Hsiao and Sauer (16) and George (17) and some later work by Rockow (18), Bender (19) and others (20-24), it was not until the work of Berens and Folt (25-27) that the particulate nature of PVC prepared by emulsion polymerization conclusively established the relationship between morphology and rheology.

Other morphological and rheological studies on rigid formulations (28-37) and those on plasticized systems (38-40) have shown that the particulate flow mechanism in PVC is a satisfactory model to account for the observed anomalous flow behavior and physical property characteristics. Some recent studies (41-45) and earlier studies (14-24) have also indicated particulate mechanisms are operative in systems other than PVC and, indeed, the concept may well be far more general than is currently realized. It may well be one of the main reasons why, for example, it has not been possible to arrive at a unique equation of state for different polymer systems over a wide operating temperature range. It should be pointed out that the changes in flow behavior resulting from temperature, shear or work history (mixing, milling, kneading) have been observed for amorphous (polystyrene (19)(41)(44)(46)(47), polymethylmethacrylate (18)(74), polyisobutylene (48), polyacrylonitrile (14), and semi-crystalline (PVC (29-35)(49)), crystalline polymers (polypropylene (42)(45)), high density polyethylene (43)(50)(51) and for compounds (two phase systems (33)(47)(49)(52)).

What are the effects of particulate flow? The major effect is the observed decrease in the apparent viscosity of the system. It has also been observed that at constant shear rate, post extrusion die swell of PVC increases with increasing temperature contrary to other thermoplastic polymers. There are other anomalous aspects of PVC rheology such as a higher viscosity for a given molecular weight than expected in comparison to other common polymers, such as polyethylene or polystyrene and anomalous elastic behavior which have been ascribed to association and/or the effect of micro-crystallinity.

Numerous workers (5)(34)(36)(53)(54)(55) have observed dramatic changes in mechanical behavior in the vicinity of 190-200°C. These have been interpreted as resulting from crystallinity even though the melting point has been reported to be considerably higher (220 to 260°C) (56)(57). While the possible effect of crystallinity is recognized, the contribution of crystallinity has not as yet been unconfounded with the effect of particulate structure.

The viscosity of virgin material increases with work history or higher temperature history in absence of mechanical or thermal degradation (34)(58). The presence of two flow activation energies has been interpreted (8) as resulting from morphological changes and indeed this has been observed by examining samples which were subjected to increasing thermal history (25-27). To establish the change in rheology with morphology, Sample D, (Ref. 8) was reexamined according to the following scheme as suggested previously (8). The sample was first extruded at 190°C where the apparent viscosity falls on the curve of lower activation energy (point a, Fig. 1). The morphology of this extrudate which was fractured in liquid

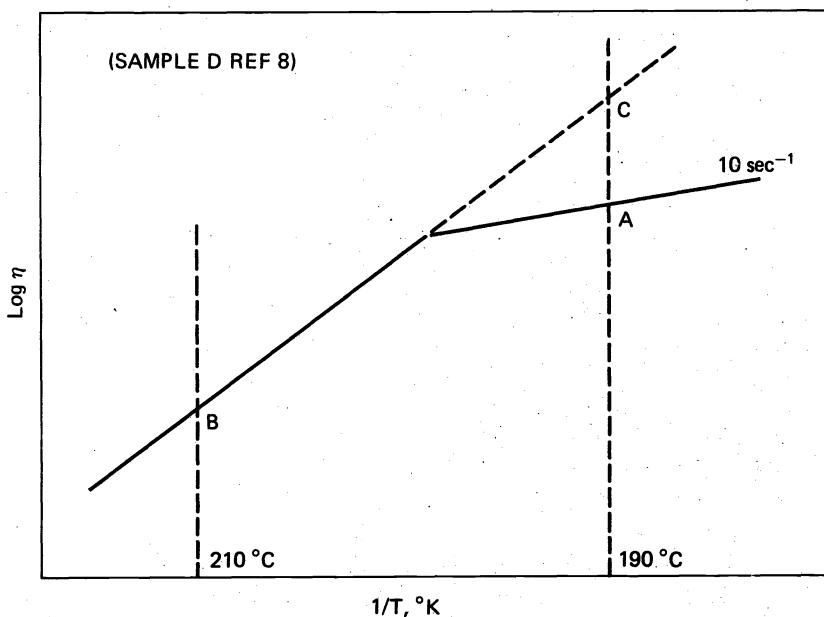


Fig. 1. Viscosity at 10 sec^{-1} vs. Reciprocal Absolute Temperature for Sample D, Ref. (8).

nitrogen and examined by electron microscopy clearly reveals the particulate nature of the sample. Extruding virgin material at 210°C where the apparent viscosity falls on the curve of higher activation energy (point b, Fig. 1) shows much less clear particulate boundaries as expected from previous studies (25-27). Upon reextruding sample b at 190°C, the apparent viscosity is now significantly higher (by 20%) than found for the virgin material extruded under the same conditions at the same temperature (point c, Fig. 1); and indeed when the sample is reexamined at other temperatures below the critical temperature above which particulate boundaries begin to disappear, the data is found to be governed by the higher flow activation energy being consistently higher than the virgin material at any temperature. The morphology of the sample extruded at 210°C and subsequently reextruded at 190°C is much the same as the morphology at 210°C.

It has also been shown previously (7)(8) that the activation energy decreases with increasing shear stress and that the break point in the curve viscosity vs. reciprocal absolute temperature shifts to higher temperature as the shear stress is reduced. This break point in the plot of shear stress vs. reciprocal absolute temperature has been used as a measure of the crystalline melting point (59).

There appears to be overwhelming evidence as to the presence of particulate domains of supermolecular structure which changes with temperature and/or shear history for both emulsion and suspension PVC (25-27)(33)(34)(35)(36)(60)(61). The decrease in apparent viscosity with increasing particle size which has been reported (27) is in fact consistent with behavior of suspensions and other systems. However, the relationship between particle size or domain size and melt rheology is still somewhat of an open question. For example, in a study (7) of the flow properties of molten unplasticized PVC with lubricants, particulate flow was excluded even though a break in the viscosity at constant shear stress vs. reciprocal absolute temperature which could be interpreted to be caused by a change in the flow mechanism was observed. An important consideration which must be taken into account is that thus far there have been no morphological studies carried out under the same conditions as the rheological measurements. This leaves open the question of possible reversible changes which could occur in particulate structure with change in temperature as suggested by Munstedt (36) and others (33)(34).

It is very unlikely that the anomalous behavior of PVC can be explained by slip. However, while early studies (2)(62) reported slip to occur in rigid PVC, it was concluded in a more recent study (7) that negligible slip was found for lubricated PVC. In a collaborative study (63) this same conclusion was reached for temperatures above 180°C but below 180°C slip was cited as a possible mechanism to explain the lack of agreement among the data obtained in various laboratories. In view of the mounting evidence that the particulate nature is quite sensitive to temperature and work history and also the instrument and geometry employed (29,33,34,36,58), it is suggested that it is highly possible that this can adequately account for the observed discrepancies.

At lower temperatures lubricants can also contribute to peculiar behavior. Under these conditions lubricants decrease the viscosity. They are added mainly to reduce viscous shear heating. Lubricants also restrict fusion (1,7,26,64,65,66). It is this restriction of fusion (due to increased particle-particle slip (26)) that could well account for the observed decrease in viscosity and the lack of good agreement among the various laboratories.

TRUE MELT FLOW

The major problem in obtaining a true melt flow curve for PVC is having adequate thermal stability for the required time to perform the measurements. High temperatures in excess of 220°C and low shear rates are necessary to reach the Newtonian region. Early attempts to estimate the limiting zero shear viscosity, η_0 , have been reported (1)(8)(67) and measurements made on a low molecular weight sample at 220°C with a capillary rheometer approached Newtonian behavior (11). Recently (68)(69) measurements on a cone and plate rheometer were carried out over a temperature range of 228°C to 244°C, and in the shear rate range 10^{-2} to 10^2 sec^{-1} , for a PVC sample with stabilizer at a level of 0.03 weight fraction. Measurements were also carried out for various levels of plasticizer to yield limiting zero shear viscosities.

While it appears that true melt flow and η_0 have indeed been achieved, the data were too limited to reveal the total range of behavior. It was found that the limiting zero shear viscosity for pure PVC (as well as the plasticized samples) could not be described by a single Arrhenius type dependence and indeed the data was best described by two activation energies. For the pure PVC sample the data were too limited to define the two regions of flow behavior; however, the temperature at the break point in the curve was estimated to be 226°C. This was interpreted to be the melting temperature of the microcrystalline regions. Lyngae-Jorgenson (59) also using a rheological method reports a value of 230°C for T_M which is in reasonable agreement considering different samples were used.

To explore the whole region from the true melt to the region where particulate flow predominates, a sample of PVC prepared at 40°C having an LVN (measured in cyclohexanone at 30°C) of 0.381 was examined over the temperature range 170°C to 230°C and shear rate range 0.1 sec⁻¹ to 3000 sec⁻¹ using both a capillary and a cone and plate rheometer. The results of these measurements are shown in Fig. 2. The data can be represented by three distinct

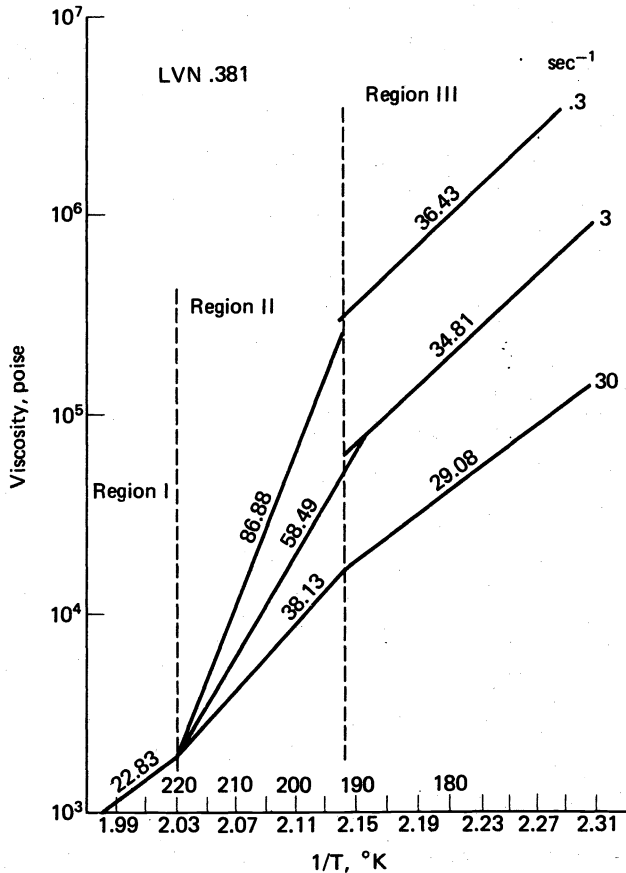


Fig. 2. Viscosity vs. $\frac{1}{T}$ at Varying Constant Shear Rates.

regions. A break in the curve at about 190°C is consistent with previously reported data (8). However, these data are at lower rates of shear and as expected the activation energies increase with decreasing shear rate. The second break which occurs at 220°C is interpreted as the crystalline melting point and is in good agreement with the value measured by infrared spectroscopy (56) for this sample. Initial measurements at 210°C and higher and at low shear rates were kindly made by Dr. J. Lyngae-Jorgensen and were subsequently rechecked by the author. At temperatures of 220°C and higher, the viscosity is Newtonian below a shear rate of 0.3 sec⁻¹. Activation energies at constant shear rate for this sample are listed in Table 2.

TABLE 2. Activation Energy ΔE k cal/mole

Shear Rate (sec^{-1})	Region I	Region II	Region III
.3	22.83	86.88	36.43
3	-	58.49	34.81
30	-	38.13	29.08

The activation energies in Regions II and III are consistent with data reported previously (8). The value in Region II at 0.3 sec^{-1} also falls in line with the value of 150 k cal/mole estimated (69) for the limiting zero shear value since the activation energy decreases with increasing shear rate.

FLOW BEHAVIOR OF COMPOUNDS

As already stated, the rheology of PVC compounds is of much greater practical importance than the rheology of pure PVC. However, additives complicate the rheology considerably and thus, even though far more studies have been carried out on compounds, the flow behavior of compounds is, in general, less well understood; each study being somewhat specific to the compound and conditions used. Studies on compounds have been carried out with the Brabender Plasticorder (70-77), capillary viscometers (5)(52)(61)(63)(64)(65), cone and plate viscometers (34)(61)(68)(69) and extruders (3,55,78-81).

Additives in PVC compounds can be classified into three major categories, namely: (1) those which are used to overcome processing deficiencies and include lubricants, stabilizers, processing aids; (2) those which modify properties or cost, such as plasticizers, impact modifiers or reinforcing fillers and opacifiers, antioxidants, etc.; and (3) those which satisfy government regulations, such as flame retardants and smoke reducers. A thorough review of additives and their effect on rheology of PVC goes beyond the intended purpose of this communication. However, some brief comments are germane to the subject under consideration since some additives especially lubricants and plasticizers have a pronounced effect on fusion, on the nature of the flow unit and, hence, the resulting flow behavior.

EFFECT OF LUBRICANTS ON FLOW

Lubricants are added primarily to control viscous shear heating and, hence, the thermal stability of PVC. Lubricants decrease the rate of fusion (64)(82-84) in a complicated way especially when used in combination with other lubricants as is often the case in practice (66,85). While the exact mechanism of lubrication behavior is still subject to question, it is generally agreed that lubricants reduce the internal polymer friction and friction between the polymer and the metal surface. The effect of lubricants on control of temperature and viscous shear heating are not considered further but have been discussed in other publications (7,65,78).

A second feature of lubricants is the effect they have on the apparent viscosity. Lubricants reduce the viscosity (1)(64)(78). At low shear and low temperatures, lubricants reduce the viscosity as illustrated in Fig. 3. At high shear rates or at high temperatures (where lubricants can become solubilized (5)(65)), their effect on viscosity is much reduced as indicated in Fig. 4.

The mechanism for the viscosity reduction of lubricants is also still subject to question. Slip has been used to explain the viscosity decrease (2, 62) but in another study (7) slip was ruled out as the major mechanism. More recently (63) the work of the IUPAC Working Committee on PVC has revealed no evidence of slip above 180°C ; however, below 180°C slip was not ruled out as a possible explanation for the lack of agreement of the different workers. This lack of agreement of flow data could well be explained by changes in particulate structure resulting from temperature and/or work history variations considered earlier. The very location of lubricants at the particle-particle interface which prolongs particulate flow is consistent with the observed decreased rate of fusion.

The viscosity-shear rate curves at various temperatures obtained with a capillary rheometer for a typical PVC compound are shown in Fig. 5. A plot of viscosity at a fixed shear stress as a function of reciprocal absolute temperature for this same compound is shown in Fig. 6. With most polymer melts, this type of plot results in straight lines with a slope which is independent of stress or two straight lines when examined over a wide temperature range (7)(8). For this compound, however, there appears to be a transition between 175°C and 180°C .

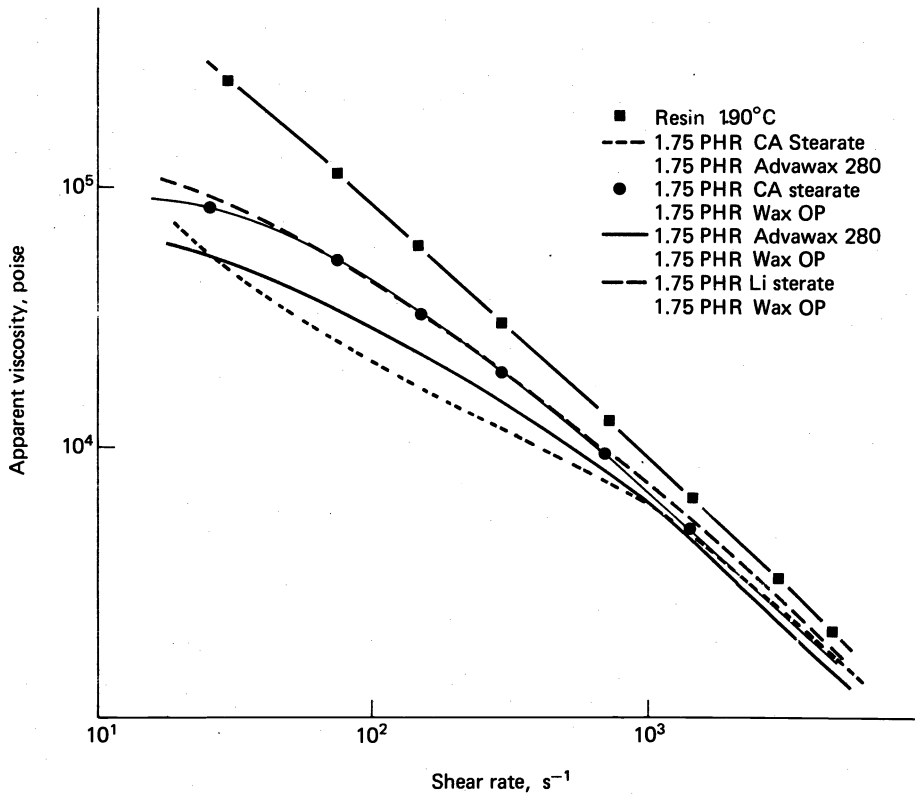


Fig. 3. Effect of Lubricants on Flow Curve at 190°C.

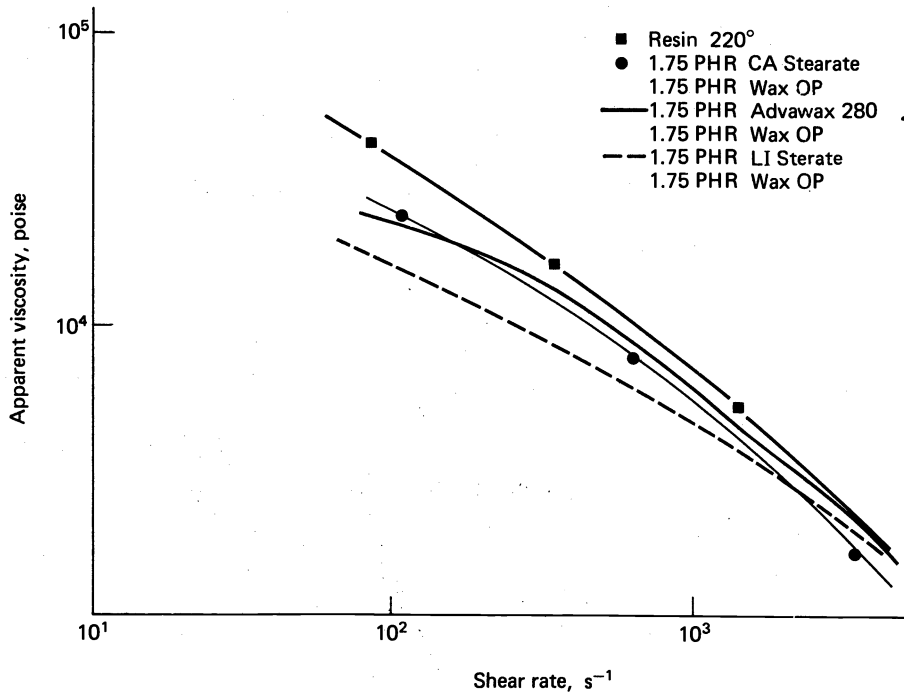


Fig. 4. Effect of Lubricants on Flow Curves at 220°C.

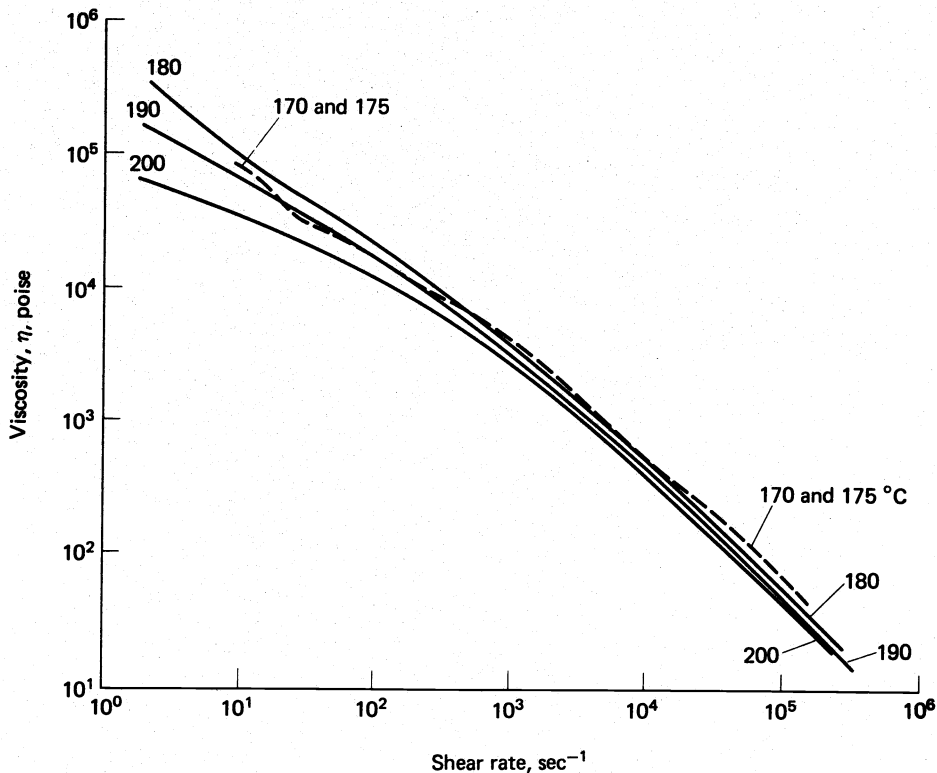


Fig. 5. Viscosity Shear Rate Flow Curves for PVC Compound with Rahinowitsch Correction Applied.

Below this the viscosities are independent of temperature, at the transition the viscosities tend to increase and above this transition the viscosity decreases and the temperature dependence is a function of the shear stress. This behavior is believed to be the result of particulate and crystalline structural changes which are sensitive to heat and mechanical history. Below the transition the structure is relatively stable within the time of observation. The increase of viscosity at the transition may well be explained by the melting of crystallites and subsequent recrystallization to more stable higher melting crystallites. Repetitive thermal analysis measurements provide supporting evidence for such a mechanism.

Reproducibility of the flow curves of PVC compounds is poor compared to polyethylene as shown in Fig. 7 for six separate runs. Even with a standardized operating procedure, a given PVC compound may have a somewhat different heat history because of the variations in the manner the sample is handled and preheated before the flow data are taken. This is illustrated in Fig. 8 which shows the results of three trials made at 190°C with a die having an L/D of 10. Reproducibility may be analyzed without making entrance or barrel corrections, since only one die was used and melt height at a given shear rate was arranged to be the same for each trial. All three trials were made starting from low shear rate. It is noted that

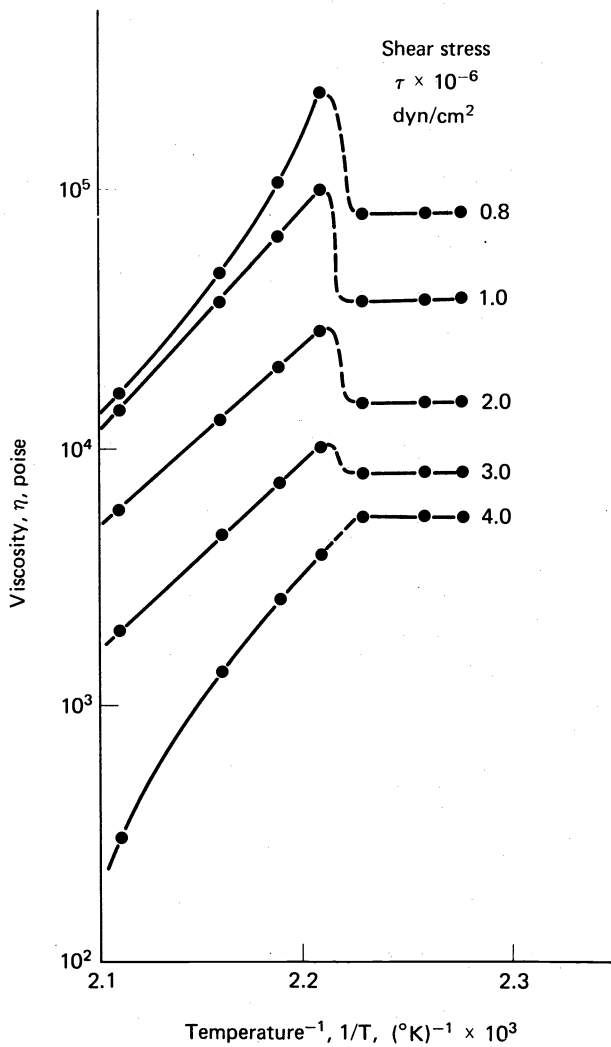


Fig. 6. Effect of Temperature on Viscosity at Constant Shear Stress.

the lower the starting shear rate, the higher the viscosity at a given shear rate. This may be interpreted that the longer the time of exposure at 190°C (under pressure) the higher the viscosity. Similar results have been reported for mechanical history (58,78).

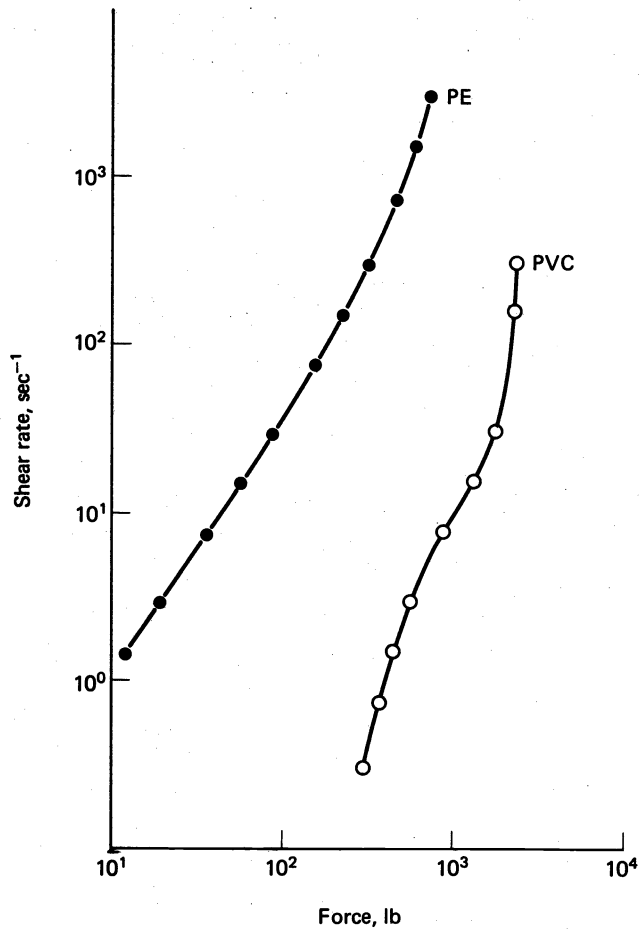


Fig. 7. Flow Curves for a PVC Compound and High Density Polyethylene at 180°C ($L/D = 39.4$) - Bars Represent Extreme Values.

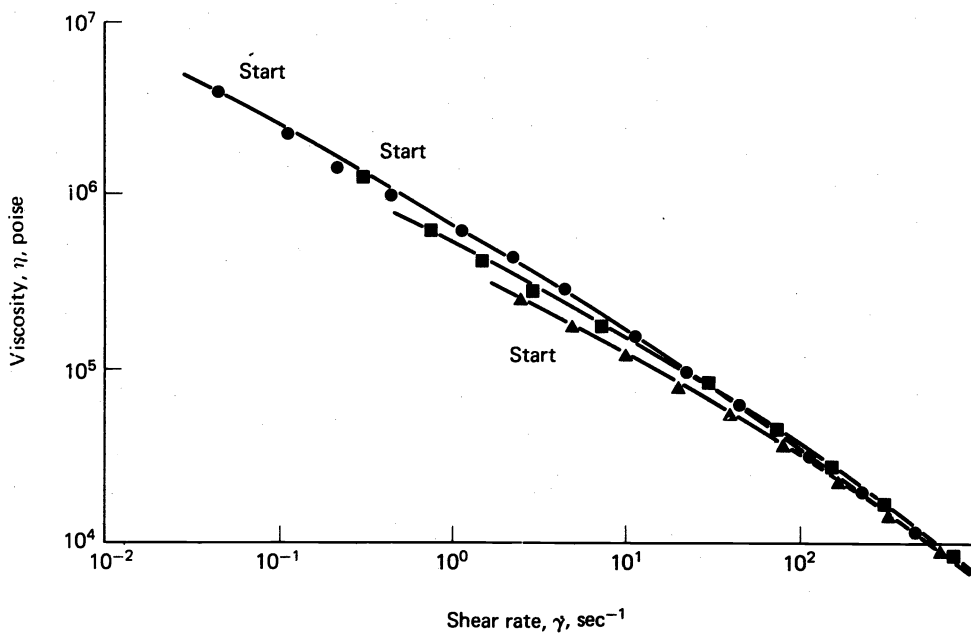


Fig. 8. Viscosity vs. Shear Rate for a PVC Compound Starting at Different Shear Rate Levels.

EFFECT OF PLASTICIZER ON FLOW

The flow behavior of plasticized PVC has been more thoroughly studied primarily because plasticizers reduce fusion time (76) and fusion temperature (86). This allows measurements to be made more easily (compared to rigid PVC). In many respects plasticizers function as lubricants especially at low concentrations and low temperatures. Many lubricants, in turn, also act as plasticizers.

Early rheological studies established the effect of plasticizers on the viscosity as a function of the shear rate, concentration and temperature (1,3,87,88). An equation for the limiting zero shear viscosity as a function of weight fraction of DOP plasticizer at 220°C was reported (1) showing the magnitude of the decrease in viscosity with increasing plasticizer concentration. In general, addition of plasticizer lowers the viscosity but does not change the shape of the viscosity-shear rate curve appreciably.

More recently (64) plasticizer was shown to have a pronounced effect on the melting rate and flow behavior with discontinuities reported for the shear rate-shear stress curve. Both mechanical and thermal history have also been observed to have a pronounced effect on the flow curves as well as on the physical appearance and properties quite analogous to rigid compounds (89)(90)(91)(92) but it has only been recently (34,40,93,94) that attempts have been made to relate morphology to the flow behavior. This is not surprising since techniques to handle liquid-like systems (plasticized surfaces) have only recently been developed.

In the useful range of plasticizer concentration some crystallinity is maintained to temperatures of the order of 180-190°C as demonstrated by the anomalous dependence of viscosity on molecular weight (92). Several authors (63,81,95) have demonstrated that viscosity shear rate curves, as a function of plasticizer concentration or temperature, could be superposed by suitable reduction procedures. In more recent studies (40), however, it was found that data was superposable at higher shear rates but that it was not possible to superpose the low shear rate data obtained at 170-200°C on a sample having a fixed plasticizer level (40 phr). (Fig. 9). It was suggested that superposition at high shear rates implied merging of

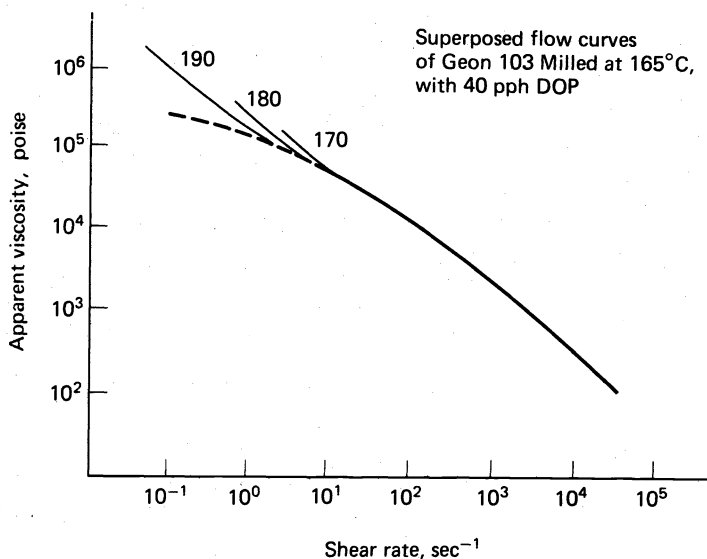


Fig. 9. Superposition of Melt Flow Data for Plasticized PVC Milled at 165°C with 40 phr DOP for 180°C, 190°C and 200°C Extrusion Temperature.

flow units leading to a more homogeneous sample. At low shear rates, however, particulate flow prevailed and depends on both the extrusion temperature and the plasticizer concentration. A plot of viscosity vs. reciprocal absolute temperature for this same sample (Fig. 10) milled at various temperatures showed a break in the curve around 175°C, the same temperature at which nodules appeared most distinct by SAXS and electron microscopy. Indeed this plot is quite analogous to those observed for rigid PVC (4,8).

A similar observation of the lack of superposition of flow data was found by Pezzin (96) who reported three transitions or "three sharp jumps of activation energy" for viscosity (at constant shear stress) plotted as a function of reciprocal absolute temperature for a sample of regular PVC and a sample of higher crystallinity (syndiotactic) PVC. The activation energies at constant shear stress were found to increase with increasing stress but did not vary monotonically with decreasing temperature. For regular PVC one break which varied with the stress level occurred around 175°C while the second break occurred around 195°C. For the more crystalline sample, corresponding breaks occurred around 180°C and between 205 and 215°C respectively, with both dependent on the magnitude of the stress. The similarity between the three transitions found in plasticized systems and unplasticized PVC is noteworthy and it is indeed difficult not to conclude that similar mechanisms are operative. While further experiments over wide temperature and process history are necessary to establish the relationship of morphology and rheology, the emerging model appears to be well defined.

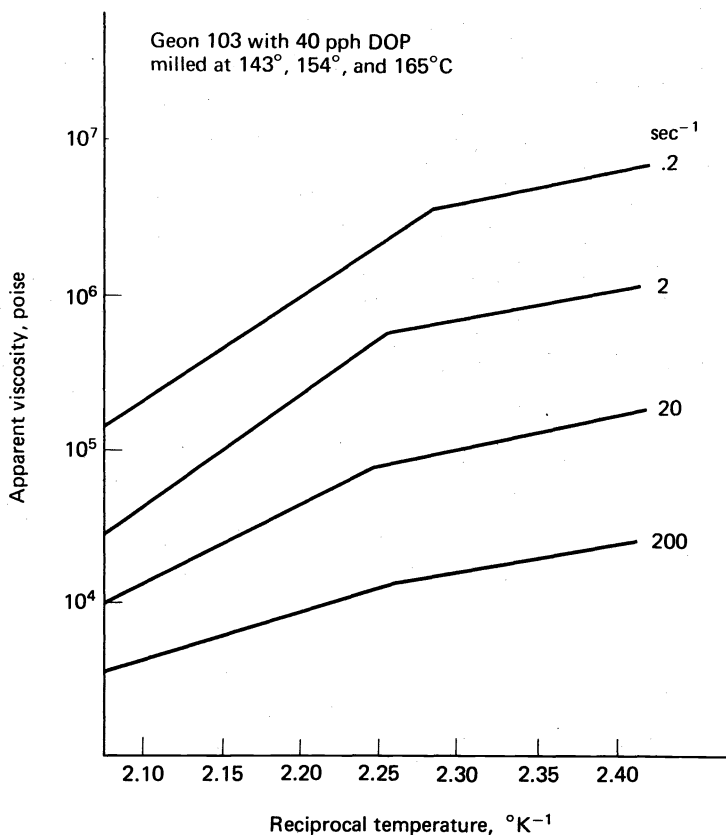


Fig. 10. Viscosity vs. Reciprocal of the Extrusion Temperature for PVC Milled at 165°C Containing 40 parts per Hundred DOP.

While the nature of the flow units and flow mechanisms have not been adequately defined, from the experimental data thus far available there can be little doubt that in rigid as well as plasticized PVC systems the particulate nature and crystallinity play a dominant role in the flow behavior. Furthermore, since thermal and mechanical history can alter both of these variables, sample preparation (process history) must be carefully controlled.

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