

Extrusion Characteristics of Poly(vinyl Chloride)

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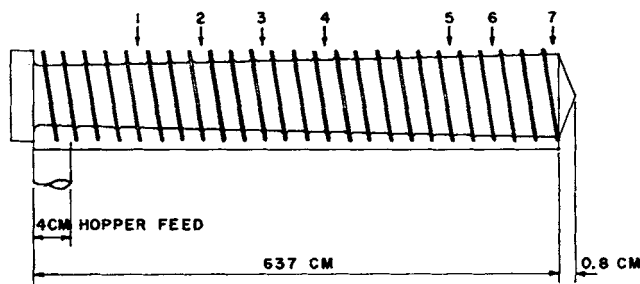
Synopsis

The general flow properties of poly(vinyl chloride) in a capillary rheometer have been compared to the flow behavior in a screw extruder. It was found that the flow behavior can be characterized by either method to within the experimental accuracy of the instruments. The viscosity of the melt in the extruder barrel was calculated from its pressure profile.

The general flow properties of poly(vinyl chloride) (PVC) in a capillary rheometer have previously been investigated.¹ To further our understanding of the processing characteristics of PVC, parallel investigations have been conducted by using flow through rheometers and extruders.

EXPERIMENTAL

The rheometer mainly used in this study was the Sieglaff-McKelvey rheometer as previously described.¹ An Instron rheometer was also used, employing 60° entrance angle circular dies, extruding at constant rate under steady-state conditions. The extruder used in the extrusion experiments is a conventional 1-in. extruder, the screw being a standard, gradual compression, single-stage screw of compression ratio 4/1, helix angle 17.7°, length/diameter ratio 24/1. The extruder barrel was drilled to accept melt thermocouples and flat-faced pressure transducers (0-5000 psi \pm 0.05%, 0-10,000 psi \pm 0.05%, Fig. 1). These were inserted in the barrel such that their probes made close contact with the polymer melt surface. Pressure and temperature measurements were recorded simultaneously by use of a rapid-response multichannel recorder. A set temperature could be maintained throughout the extruder, the pressure drop at the die being obtained by the transducer located at the die entrance. Volumetric flow rates were determined by weighing timed samples of extrudate. Under these conditions, it was possible to calculate the rheological shear parameters. At each particular screw speed, extrusion was continued until steady mean pressures were indicated. This is required, as even under steady-state conditions, the die pressure exhibits slight random variations. These irregular fluctuations are caused by the movement of the polymer melt zone, which is in a thermodynamically unstable state, surging back and forward along the extruder barrel, as the



1" SCREW EXTRUDER
Fig. 1. Extruder screw design.

position of instantaneous equilibrium changes. Standard circular dies of varying length and diameter were used.

The PVC resins studied were Diamond Alkali Company's PVC-30, 40, 450, and 500. These resins were characterized by osmometry, light scattering, gel permeation column (GPC) fractionation, and viscosity determinations as shown in Table I. The polymer molecular weights increase in the order of their numerical designation exhibiting almost normal Gaussian distribution with a relatively narrow spread of molecular weights. As PVC is not thermally stable at processing temperatures, all samples contained 3 phr of a stabilizer (Thermolite T-31) incorporated in the resin. For the rheometer samples, this was accomplished by milling and then compression molding of the samples, the resultant slabs being cut into rods suitable for insertion in the rheometer barrel. For the extruder, the stabilizer was blended directly with the PVC resin in powder form. The corrected forms of the equations relating to the flow of polymer melts in cylindrical tubes, derived as previously described,¹ are as follows:

$$\tau_w' = [R\Delta P/2(L + NR)] \quad (1)$$

$$\dot{\gamma}_w' = [(3n + 1)/n](Q/\pi R^3) \quad (2)$$

where τ_w' is the corrected shear stress at the wall, R the tube radius, ΔP the pressure drop across the capillary length L , NR the Bagley length correction factor expressed as a function of the radius, $\dot{\gamma}_w'$ the corrected

TABLE I
Characterization of Resins

	GPC fractionation		Light scattering, $M_w \times 10^{-3}$	Viscosity	
	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$		$M_v \times 10^{-3a}$	$M_v \times 10^{-3b}$
PVC-30	—	—	—	26	19
PVC-40	43	96	—	54	45
PVC-450	40	108	117	74	93
PVC-500	47	136	132	83	114

^a $[\eta] = 4.41 \times 10^{-5} M_v^{0.91}$.

^b $[\eta] = 2.4 \times 10^{-4} M_v^{0.77}$.

shear rate at the wall, Q the volumetric flow rate, and n the slope of the $\log \tau_w$ versus $\log \dot{\gamma}_w$ plots, where τ_w and $\dot{\gamma}_w$ represent the uncorrected shear stress and rate, respectively. In addition to capillary corrections, losses in the barrel were also subtracted.² The corrected values of τ_w and $\dot{\gamma}_w$ were calculated by a regression analysis fit of the flow data obtained using at least three capillaries of L/D from 10 to 30. This more careful analysis yielded results which were at variance with the previously reported¹ data for these PVC samples.

The Power Law, eq. (3),

$$\eta = \eta_0(\dot{\gamma}'/\dot{\gamma}_0')^{n-1} \quad (3)$$

is then used to represent η , the viscosity at shear rate $\dot{\gamma}'$, and η_0 , the standard state viscosity at a standard shear rate ($\dot{\gamma}_0'$) of 1 sec.⁻¹.

Continuous polymer melt pressure traces monitored by pressure transducers mounted in the extruder barrel exhibit regular and irregular sinusoidal variations. In normal steady-state extrusion, a minimum pressure is recorded when the leading edge of the extruder screw passes under the transducer. The pressure increases until the trailing edge reaches the transducer when the pressure drops rapidly. This cycle is continuously repeated under steady-state extrusion conditions to give a sawtooth pressure curve. A common variant on this pattern is when the inverse occurs, that is a maximum pressure at the leading edge and a minimum at the trailing edge. Under these conditions an inverted sawtooth appears. Other more irregular and distorted pressure cycles can be obtained due to nonisothermal flow and nonsteady-state flow conditions. McKelvey and Wheeler³ have shown that assuming isothermal Newtonian flow and neglecting leakage flow, the eqs. (4) and (5) may be derived to calculate melt viscosities based on the simplified flat-plate Newtonian flow model:

$$S = \delta P/\delta t = (6\mu V^2/H^2)(\phi \cos^2 \theta + \sin^2 \theta) \quad (4)$$

$$\phi = 1 - (Q/Q_D) \quad (5)$$

where S is the slope of the pressure-time cycle, μ the melt viscosity, H the channel depth, ϕ the flow function, θ the screw helix angle, Q the volumetric flow rate, Q_D the drag flow rate, and V the radial screw velocity. For each screw, that is for each value of θ , there will be a critical value of the flow function for which the term $(\phi \cos^2 \theta + \sin^2 \theta)$ becomes zero, resulting in the slope of the pressure traces being zero. Values of ϕ exceeding this value will yield positive slopes and normal sawtooth pressure profiles. For the particular screw used, theoretical value of the flow function was -0.099 .

RESULTS AND DISCUSSION

Molecular Weight

Flow data corresponding to the extrusion of PVC-30, 40, 450, and 500 over a temperature range of 170–210°C. are listed in Table II. Generally,

TABLE II
Flow Properties of Resins

Sample	Temp. T , °C.	n (slope)	η_0 , poise $\times 10^6$	E_γ , kcal./ °K.
PVC-30	170	0.38	0.64	28.4
	180	0.42	0.33	"
	190	0.47	0.14	"
PVC-40	180	0.40	1.26	25.7
	190	0.49	0.70	"
	200	0.50	0.37	"
PVC-450	180	0.25	2.90	28.4
	190	0.33	1.45	"
	200	0.43	0.63	"
PVC-500	190	0.40	1.47	24.7
	200	0.47	0.70	"
	210	0.55	0.39	"

as the molecular weight is increased, the values of η_0 increase and n decrease. Also with increasing temperature, η_0 decreases and n increases. Many experimentally derived equations describe the viscosity as a function of the molecular weight for polymer melts. The well-known Bueche relation⁴

$$\log \eta_0 = 3.5 \log M_w + K_1 \quad (6)$$

may be combined with a relation based on light-scattering data⁵

$$[\eta] = 4.41 \times 10^5 M_w^{0.91} \quad (7)$$

to give the relation

$$\log \eta_0 = 3.8 \log [\eta] + K_2$$

where M_w is the molecular weight and $[\eta]$ is the intrinsic viscosity.

In Figure 2 are plotted values of $\log \eta_0$ versus $\log [\eta]$ for each of the temperatures studied. Linear plots result, parallel to each other and each with a slope of 3.8, in agreement with the derived relation.

Effect of Temperature

The commonly accepted functional relationship between polymer melt viscosity and temperature is the Andrade equation

$$\eta = \text{constant} \exp \{E_\gamma/RT\} \quad (8)$$

where E_γ is the apparent energy of activation for viscous flow at constant shear rate, R the gas constant, and T the absolute temperature. The relation is valid only over a limited temperature range. Plots of $\log \eta_0$ against $1/T$ (Fig. 3) are linear, not unexpected as the temperature range covered is only 20°C. for each sample. The plots are parallel to each other, the measured activation energies being recorded in Table II. The variation in these values is within experimental accuracy. The activation energy

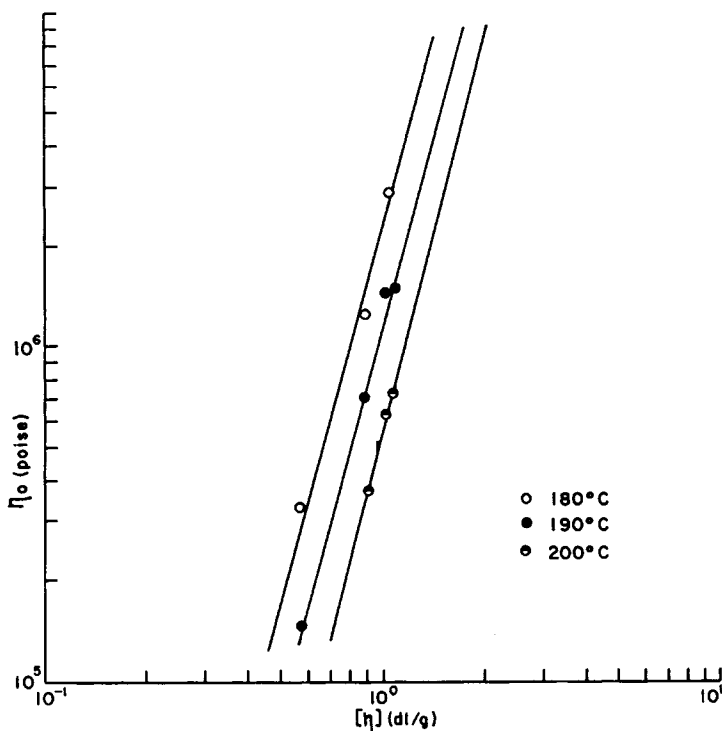


Fig. 2. Melt viscosity vs. intrinsic viscosity for PVC resins.

for viscous flow is then essentially independent of polymer molecular weight over the range of molecular weights studied in this report. The previously reported¹ data indicated a variation of activation energy with molecular weight. This effect was an artifact due to various losses in the rheometer barrel. A wider range of molecular weights might be expected to reveal some divergence if the critical molecular weight for chain entanglement present in other polymers is also present in PVC.

Effect of Diluent

Samples of PVC-450 resin containing 9, 16, 23, and 33 phr di-2-ethyl-hexyl phthalate (DOP) were prepared. Flow data concerning these samples are listed in Table III. As expected, the viscosity decreases with increase in plasticizer content while the slope n of the flow curves increases. In Figure 4, the standard-state viscosity is plotted against the log of the polymer concentration. The plots are essentially parallel and could be fitted by the expression:

$$\log \eta_0 = A \log W + B \quad (9)$$

where W is the polymer concentration in per cent by weight.

As with the unplasticized polymers, plots of log viscosity against inverse temperature (Fig. 5) are both linear and parallel over a 20°C. tem-

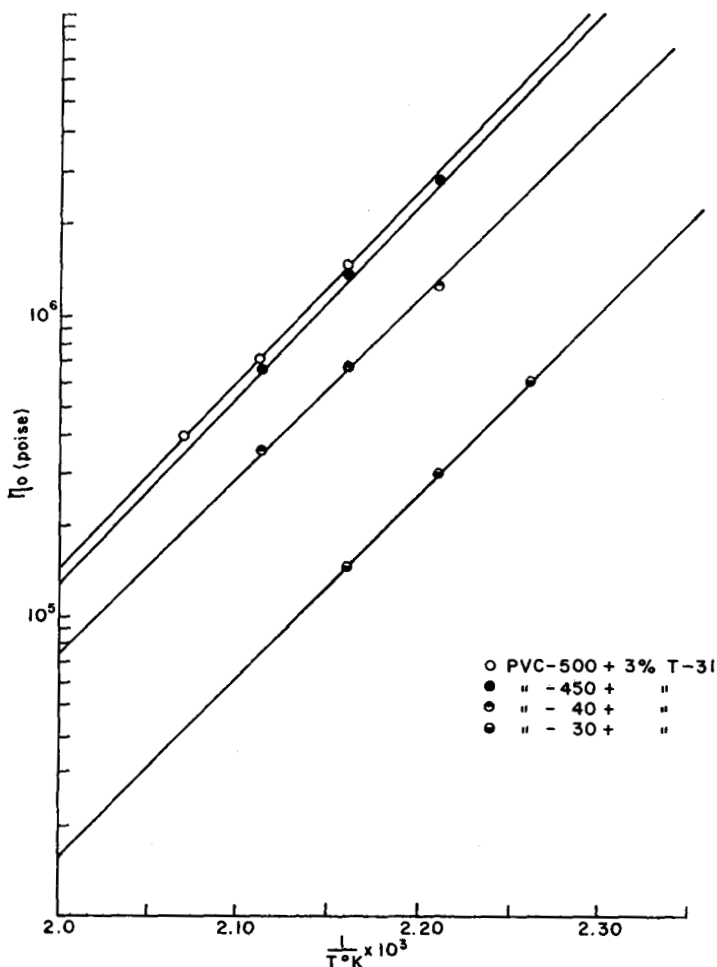


Fig. 3. Andrade plots of melt viscosity vs. reciprocal temperature for PVC resins.

perature interval with the sole exception of the most highly plasticized sample. The apparent activation energies are listed in Table III and with the exception of the value for 33 phr plasticizer content, are equal to the value for the unplasticized sample (28.4 kcal./°K.).

Within the known accuracy of these measurements, the addition of plasticizer has not changed the energetics of the flow for the system. This is at variance with previously reported findings⁵ on the behavior of plasticized PVC. The change in free volume of the system generated by the addition of plasticizer should be expected to exert an effect on the energetics of flow based on the additivity of free volumes of polymer and diluent. It is surmised that the known pseudo-crosslinked nature of PVC enables a considerable addition of plasticizer to occur without affecting the free volume available to the polymer and thus not changing the energetics of

TABLE III
PVC-450 Containing DOP

DOP content, phr	Temp. T , °C.	n (slope)	η_0 , poise $\times 10^6$	E_η , kcal./°K.
9	170	0.37	2.30	29.1
9	180	0.36	1.27	"
9	190	0.34	0.73	"
16	170	0.26	1.20	30.3
16	180	0.40	0.48	"
16	190	0.41	0.265	"
23	170	0.27	0.55	30.1
23	180	0.405	0.27	"
23	190	0.48	0.137	"
33	170	0.40	0.177	23.8
33	180	0.48	0.085	"
33	190	0.52	0.045	"

the system. In this sense, the additivity-based theories of viscosity for polymer-solvent systems appear to be untenable for this system. The change in activation energy for the most heavily plasticized sample may indicate that a limit has been exceeded, beyond which the additivity of free volumes is once more applicable.

Comparison of Flow through Rheometer and Extruder Dies

Blends of PVC-30 and PVC-500 were prepared and extruded through the dies of an Instron rheometer and the 1-in. extruder. The rheological data relating to flow through the dies are listed in Table IV. The close correspondence between the derived values and prior results of extrusion of the same compounds via the Sieglaff-McKelvey rheometer¹ shows that the same flow processes are operative in both rheometers and the extruder, thereby justifying the application of rheometer derived data to commercial extrusion apparatus.

The capillary end corrections were by no means as accurately determined as those for the rheometer, nor were the actual capillary dimensions as

TABLE IV
Flow Data from Rheometer and Extruder

No.	Sample composition		$[\eta]$	Temp. T , °C.	Rheometer data		Extruder data	
	PVC-30, %	PVC-500, %			n (slope)	$\eta_0 \times 10^6$, poise	n (slope)	$\eta_0 \times 10^6$, poise
2	90	10	0.56	193	0.52	0.37	0.50	0.64
4	60	40	0.75	"	0.49	1.64	0.45	2.52
5	40	60	0.92	"	0.47	2.91	0.41	4.20
6	20	80	0.95	"	0.44	5.57	0.40	6.60

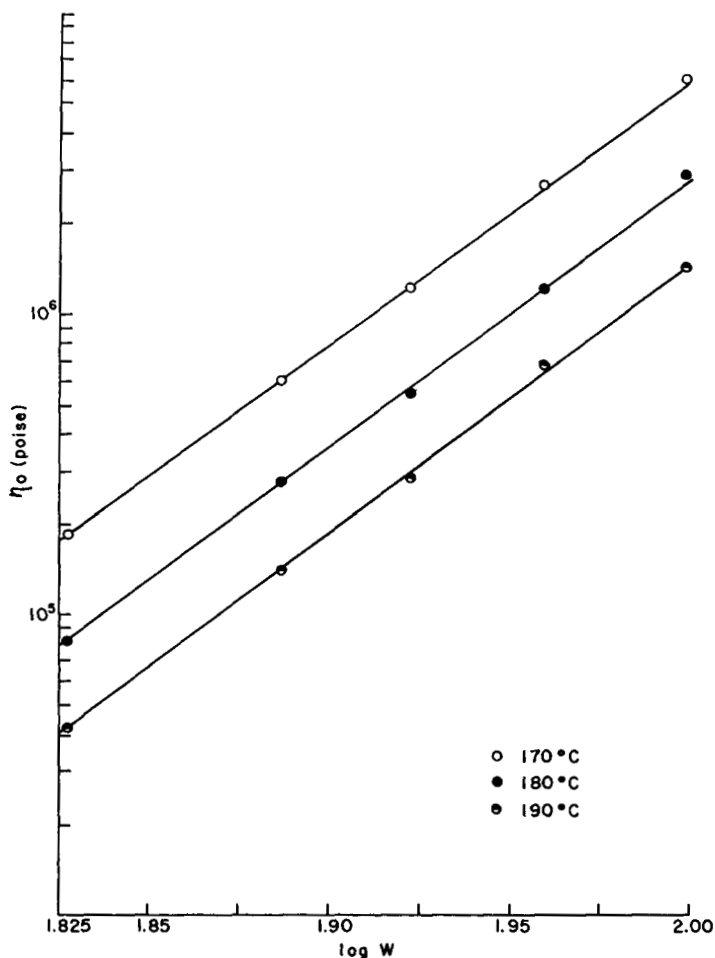


Fig. 4. Melt viscosity vs. polymer weight concentration in DOP diluent.

precisely known due to the small surface defects found with any commercial scale instrument in constant use. The small "hang up" in the die, negligible for commercial purposes, nevertheless alters die dimensions by measurable amounts. Also, the die temperature is subject to more fluctuation about the set point than that in the rheometer. Therefore, the extruder-derived results are less accurate and exact correspondence cannot be expected. Schreiber⁶ showed for polyethylene that the flow data obtained from a high-speed viscometer and a Hartig 2¹/₂-in. extruder concur within experimental limits, provided the extruder is operating without any cooling. Carley⁷ found that rheological data are directly applicable to commercial extruders as long as the extruder is operating under steady-state conditions. Identical surface characteristics of the extrudate are obtained from both rheometer and extruder under similar conditions. The same occurrence

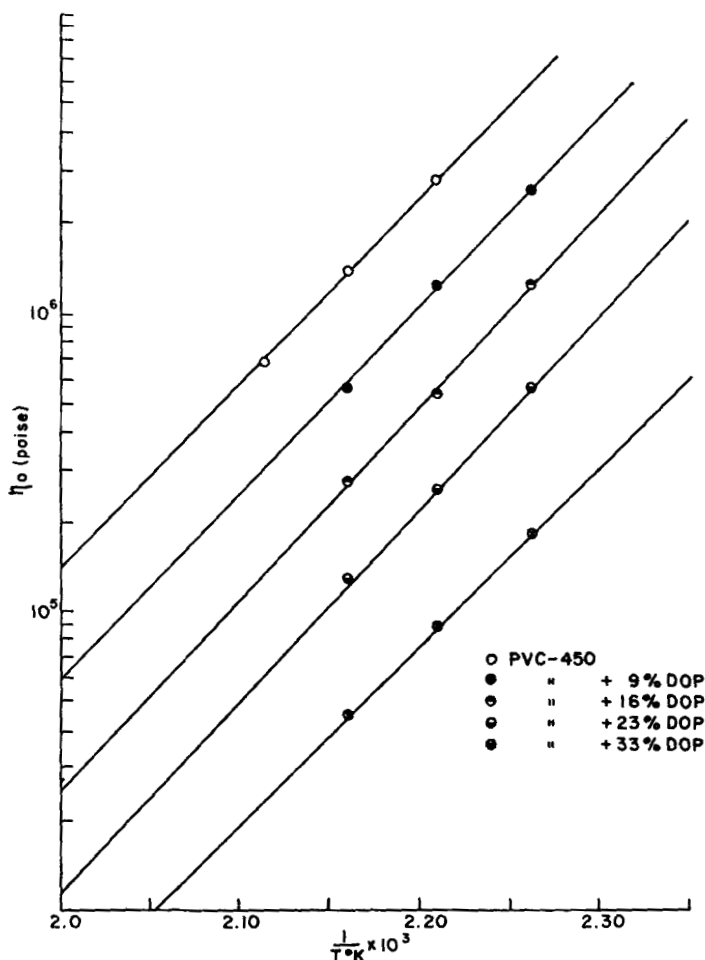


Fig. 5. Andrade plots of melt viscosity vs. reciprocal temperature for plasticized PVC.

of smooth extrusion, land, and inlet fracture may be observed. It is inferred that for the operative experimental conditions, previous shear history exerts little influence on the flow behavior of the polymeric melt. As long as the pressure variations in the melt delivered to the die are slight, as is the operative condition in most steady-state extrusions, the extruder may be treated as a pressure feed to a capillary, when the extruder functions simply as a rheometer.

Flow in Extruder Barrel

PVC-52701, a commercial formulated, rigid PVC blend based on PVC-450, was extruded at 193°C. over a range of extruder screw speeds and pressure traces obtained for all six transducers located at positions 2 to 7

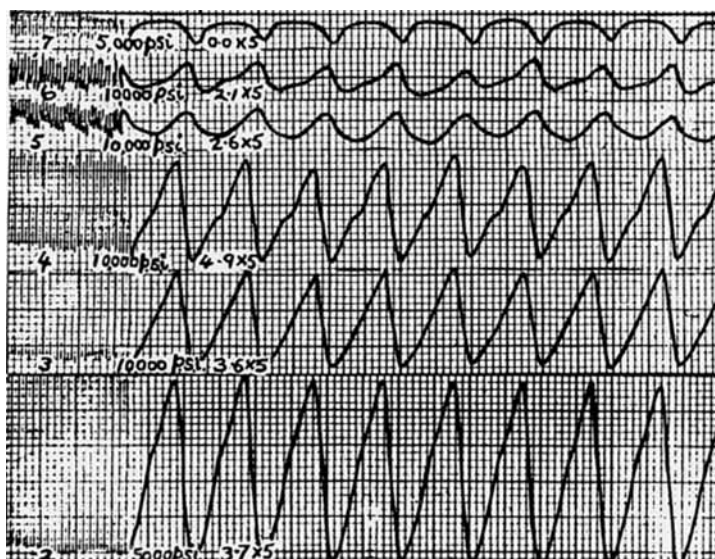


Fig. 6. Extruder pressure traces for PVC compound.

(Fig. 1). Typical pressure traces are shown in Figure 6. These show the normal sawtooth profile at positions 2 to 6 changing to the inverted form at position 7. In Table V, the calculated values for the flow function and melt viscosities are listed. The flow function values are in agreement with the experimental profiles, as values for ϕ exceed -0.1 for positions 2-6 and are less than -0.1 at position 7 as predicted. The calculated melt viscosities are of the right order for PVC melt extrusion, a gratifying result in view of the invalid assumption of isothermal Newtonian flow. No viscosity calculation is made corresponding to position 6 in view of the magnitude of the error in the $(\phi \cos^2 \theta + \sin^2 \theta)$ term as ϕ approaches -0.1 . With increase in screw speed corresponding to increasing shear rate at the barrel surface, the viscosity decreases, as previously demonstrated for flow through the die.

TABLE V
Flow of PVC-52701 in Extruder Barrel

Transducer position	15 rpm		20 rpm		25 rpm		30 rpm		35 rpm	
	ϕ	μ	ϕ	μ	ϕ	μ	ϕ	μ	ϕ	μ
7	-0.36	1.2	-0.34	1.0	-0.31	1.0	-0.29	0.7	-0.28	0.7
6	-0.11	—	-0.06	—	-0.06	—	-0.04	—	-0.04	—
5	0.02	8.0	0.06	5.5	0.06	4.8	0.07	3.8	0.08	2.9
4	0.32	6.3	0.35	4.9	0.35	3.9	0.36	3.6	0.36	3.5
3	0.46	7.2	0.47	5.9	0.47	5.0	0.48	4.8	0.49	4.0
2	0.56	6.2	0.58	4.8	0.58	3.8	0.58	3.7	0.59	3.3

CONCLUSIONS

In the preceding discussion, we have examined the generalized flow behavior of PVC in rheometers and in extruders over the normal processing range. As can be seen, rheometer-derived data are directly applicable to steady-state extrusion conditions. The McKelvey-Wheeler method of calculating *in situ* polymer melt viscosities yields approximately correct values and as such should find wide use.

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Résumé

Les propriétés générales d'écoulement du chlorure de polyvinyle dans un rhéomètre capillaire ont été comparées au comportement de l'écoulement dans un extrudeur à vis. On a trouvé que le comportement d'écoulement peut être caractérisé par les deux méthodes dans les limites de la précision expérimentale de ces instruments. La viscosité du polymère fondu dans l'extrudeur a été calculée au départ de la dépendance en fonction de la pression.

Zusammenfassung

Die allgemeinen Fließseigenschaften von Polyvinylchlorid in einem Kapillarrheometer wurden mit dem Fließverhalten in einem Schraubextruder verglichen. Es wurde gefunden, dass das Fließverhalten mit jeder der beiden Methoden innerhalb der Versuchsgenauigkeit des Instruments charakterisiert werden kann. Die Viskosität der Schmelze in der Extrudertrommel wurde aus ihrem Druckprofil berechnet.

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