The Rheological Properties of Vinyl Chloride–Vinyl Acetate Copolymers

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Synopsis

Copolymers of vinyl chloride–vinyl acetate have been prepared with different vinyl acetate contents and molecular weights and under different polymerization conditions. A rheological study of these copolymers indicates that they behave in some ways like externally plasticized PVC. For instance, as the vinyl acetate content increases, the melt viscosity decreases, the flow activation energy decreases, and the copolymer becomes more Newtonian. However, the critical shear rate for melt fracture increases, resembling the addition of elastic polymers to PVC. An increase in copolymer molecular weight has a similar effect on the rheological behavior as in PVC, except that the flow activation energy is observed to increase rather than decrease. Decreasing the polymerization temperature affects the flow properties of the copolymer, probably due to changes in degree of branching and crystallinity. A copolymer made by the delayed addition of vinyl chloride, having a more random structure than one made by the conventional batch method, exhibited quite different flow behavior. It had a lower melt viscosity, higher critical shear rate, and lower flow activation energy.

INTRODUCTION

Vinyl chloride–vinyl acetate copolymers with vinyl acetate contents ranging from 5% to 15% are particularly useful copolymers in plastics processing. They are used in the compression molding of phonograph records and for calendered vinyl sheet and floor tiles. While the rheological properties of polymer melts of poly(vinyl chloride) and polyolefins have received extensive study over the past decade, no detailed study has been reported for vinyl chloride–vinyl acetate copolymers. Rangnes[1] produced melt viscosity curves for a series of copolymers containing 12% to 17% vinyl acetate, and Thomas and Hinds[2] reported a decrease in melt viscosity as the vinyl acetate content increased.

The data presented in this paper cover the effect of copolymer composition, molecular weight, and structure on the rheological behavior.

EXPERIMENTAL

Preparation of Copolymers

Copolymers were prepared by conventional suspension polymerization. Water, vinyl chloride, vinyl acetate, a polymeric suspending agent, and

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dilauryl peroxide initiator were charged into a 100-gallon stainless steel autoclave and polymerized at temperatures ranging from 60° to 70°C for about 10 hr. Copolymers with vinyl acetate contents ranging from 6% to 17% were prepared and washed, centrifuged, and then dried in a fluidized bed drier. The vinyl acetate contents of the copolymers were determined by infrared analysis, and an assessment of the molecular weight was obtained by measuring the intrinsic viscosity in nitrobenzene at 25°C.

Polymerizations were carried out under controlled conditions in such a way that a series of copolymers was produced, varying only one of the parameters (e.g., vinyl acetate content), while other variables, such as molecular weight, polymerization temperature, etc., were kept constant.

TABLE I

Copolymers Used in this Study

Co-polymer no.	Vinyl acetate, wt-%	$[\eta]$	Polymerization temperature, °C	Dumping pressure, psig	Remarks
1	6.5	0.241	65	22	
2	12.5	0.241	65	22	
3	17.2	0.241	65	22	
4	6.2	0.272	65	22	
5	12.2	0.272	65	22	
6	17.2	0.273	65	22	
7	14.0	0.257	65	22	normal batch technique
8	14.0	0.257	65	22	delayed addition
9	12.7	0.273	60	22	technique
10	12.4	0.272	65	22	
11	12.5	0.273	70	22	
12	16.3	0.257	65	22	
13	16.0	0.259	65	60	

One copolymer (copolymer 8) was copolymerized using the delayed addition technique. The vinyl chloride was added in a delayed fashion throughout the reaction in order to produce a more random copolymer. This copolymer was prepared with the same intrinsic viscosity and vinyl acetate content as copolymer 7, which was polymerized by charging all the monomers initially to the autoclave (normal batch technique).

Before commencing the rheological measurements, a small constant amount of barium–cadmium stabilizer was compounded with the copolymer in an internal high-speed mixer, keeping the stock temperature below 40°C.

The copolymers used in the study are shown in Table I.

Melt Viscosity

Melt viscosities were measured using the Instron capillary rheometer over two decades of shear rate and between 140° and 160°C. The temperature range chosen is the range in which most vinyl copolymer processing is carried out, including compression molding and calendering.

After charging the powder compound into the barrel of the rheometer, it was given a preheat period, and the flow curve was obtained by varying the cross-head speed, while the extrusion pressure was recorded by the load cell. The capillary die had a diameter of 0.05 in. and a length-to-diameter ratio of 20. A flat entry die was the type used. The well-known Bagley and Rabinowitsch corrections were not applied. It has been reported[3] that such corrections are small for poly(vinyl chloride).

Critical Shear Rate (γ_{crit})

The onset of flow instability, or turbulent flow, resulting in melt fracture[4,5] is manifest by a discontinuity in the curves of log shear stress versus log shear rate. The shear rate at which the melt fracture occurs is the "critical shear rate," and these were recorded in the case of all the copolymers studied.

Activation Energy of Viscous Flow ($\Delta E\gamma$)

Applying the Arrhenius equation

$$\eta = Ae\Delta E/RT$$

to the melt viscosity data, at various temperatures, enables one to obtain the activation energy of viscous flow. The $\Delta E\gamma$ values so obtained were at a constant shear rate of 1 sec^{-1} over a temperature range of 140°–160°C.

Non-Newtonian Index (n)

As in previous rheological studies of poly(vinyl chloride),[5] the curves of log shear stress (τ) versus log shear rate (γ) are straight lines with a point of inflexion where the onset of melt fracture occurs. If the viscosity relationships for the copolymers are represented by the power law

$$\eta = \eta_0 \left(\frac{\gamma}{\gamma_0}\right)^{n-1}$$

where η_0 is the standard state viscosity at a standard shear rate, γ_0, of 1 sec^{-1}. The non-Newtonian index, n, may be obtained from the slope of the curves in the region up to the critical shear rate; n values were obtained for all the copolymers.

RESULTS AND DISCUSSION

Effect of Vinyl Acetate Content and Molecular Weight

In Figures 1–3, it is observed that an increase in the vinyl acetate content decreases the melt viscosity, as expected, since the vinyl acetate acts as an

internal plasticizer.   The curves in Figure 3 are displaced upward as the molecular weights of these copolymers are higher compared to those in Figure 2.   Figures 4 and 5 also show the effect of vinyl acetate content and molecular weight on the apparent melt viscosity at two extrusion tempera-
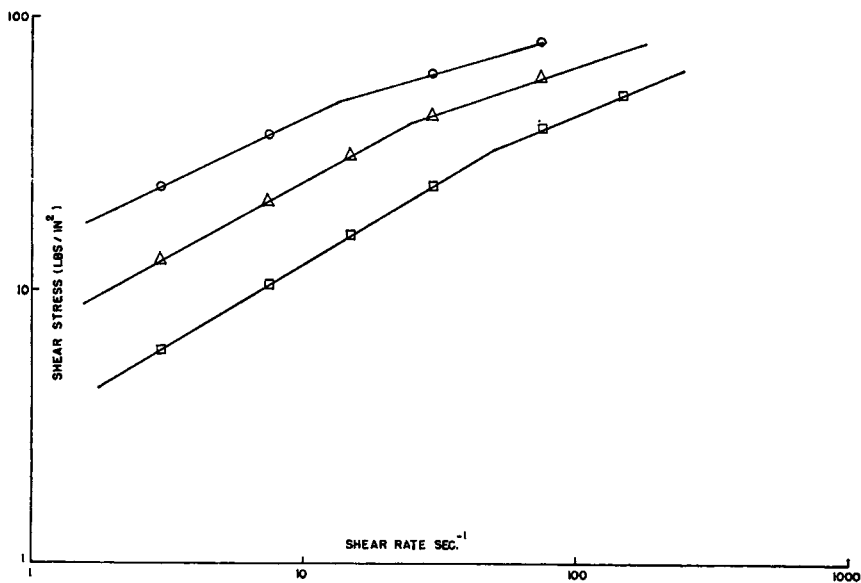

Fig. 1. Shear stress vs. shear rate at 141°C for copolymers 1, 2, and 3; [η] 0.241.   Vinyl acetate content: (⊙) 6.5; (△) 12.5%; (□) 17.2%.
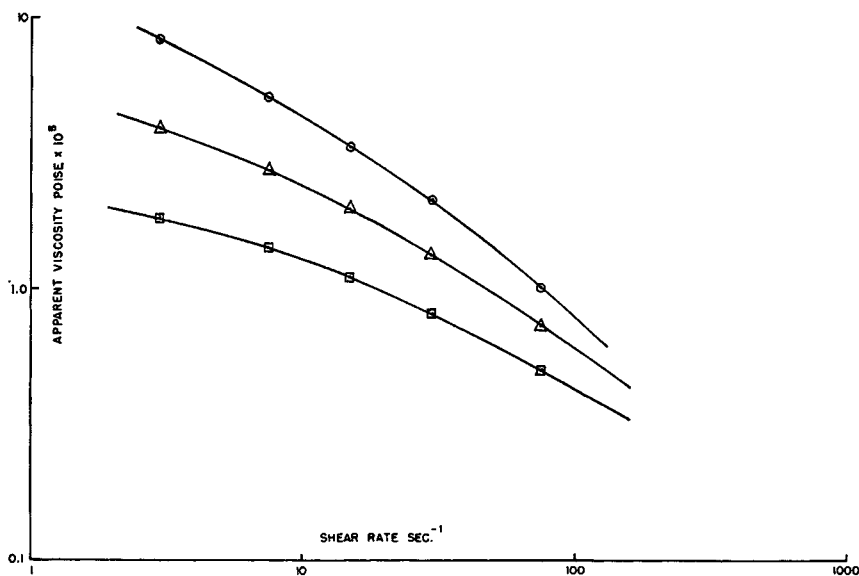

Fig. 2. Apparent viscosity vs. shear rate at 141°C for copolymers 1, 2, and 3; [η] 0.241. Vinyl acetate content: (⊙) 6.5%; (△) 12.5%; (□) 17.2%.

TABLE II
Effect of Molecular Weight and Vinyl Acetate Content on Rheological Parameters

Co-poly-mer	Non-Newtonian index n			Critical shear rate			App. viscosity,[a] poise, $\times 10^5$			$\Delta E\gamma$, kcal/mole
	141°	151°	160°	141°	151°	160°	141°	151°	160°	
1	0.47	0.60	0.65	13.5	30.0	42.0	14.5	4.7	2.15	50.0
2	0.54	0.65	0.71	26.0	40.0	50.0	5.6	2.3	1.20	28.6
3	0.58	0.73	0.75	50.0	66.0	70.0	2.3	0.93	0.50	10.7
4	0.52	0.53	0.57	6.0	12.0	20.0	20.0	11.4	6.0	53.0
5	0.57	0.59	0.64	15.0	17.0	30.0	8.6	4.8	2.10	37.5
6	0.59	0.61	0.70	21.0	25.0	40.0	5.4	2.35	1.20	28.6

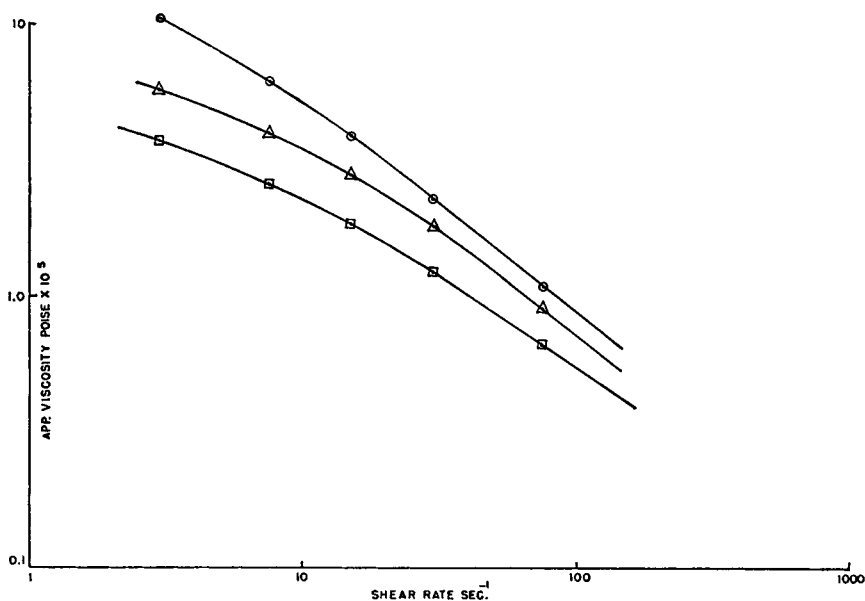[a] At a constant shear rate of 1 sec.$^{-1}$.

Fig. 3. Apparent viscosity vs. shear rate at 141°C for copolymers 4, 5, and 6; [η] 0.272. Vinyl acetate content: (○) 6.2%; (△) 12.2%; (□) 17.2%.

tures. It can be seen that up to about 8% vinyl acetate, the effect of the vinyl acetate content on melt viscosity is linear, above this there is a decrease in slope. Low molecular weight copolymers exhibit a linear relationship between apparent melt viscosity and vinyl acetate content at the highest extrusion (temperature 160°C). The marked difference in melt viscosity at low acetate levels for copolymers of different molecular weights becomes much less as the vinyl acetate level increases to 12–16%.

Summarizing, it can be stated that (a) as the molecular weight increases, the melt viscosity increases; (b) as the vinyl acetate increases, the melt viscosity decreases; (c) as the extrusion temperature increases, the melt viscosity decreases. The non-Newtonian index, n, is observed to increase (Table II) with extrusion temperature and vinyl acetate content of the co-

polymers, i.e., the copolymer approaches closer to Newtonian behavior. This increase in n with increased plasticizer concentration has also been reported by Mayrick and Sieglaff,[6] using an external plasticizer, dioctyl phthalate, with poly(vinyl chloride).
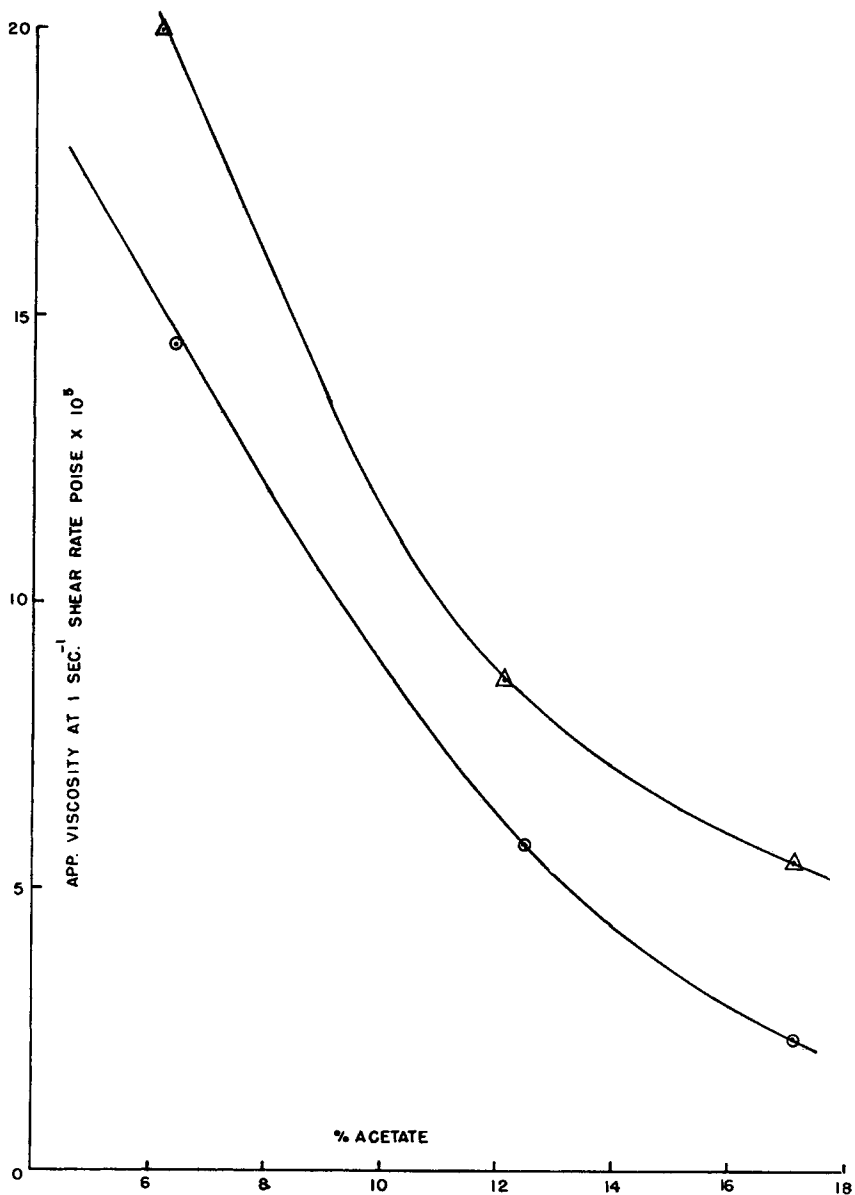

Fig. 4. Apparent viscosity vs. per cent vinyl acetate at 141°C for copolymers of different molecular weight: (⊙) [η] 0.241;   (△) [η] 0.272.
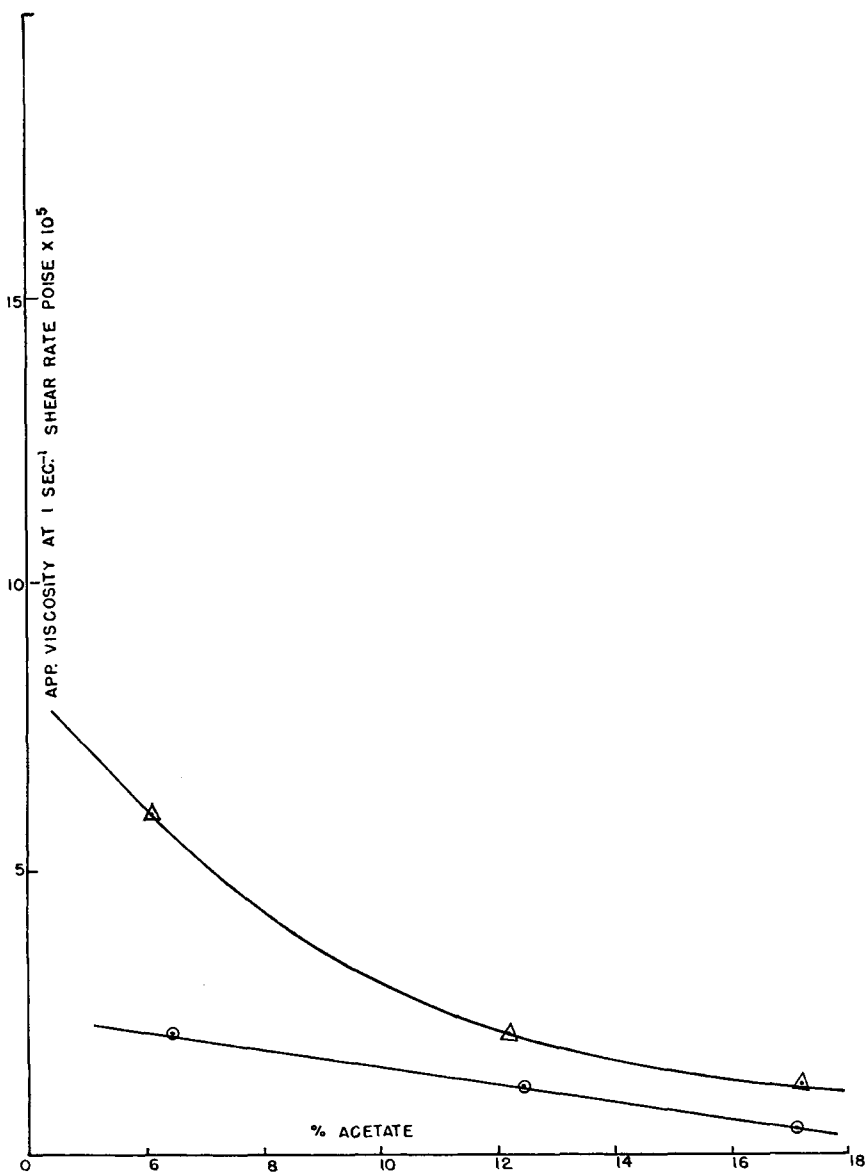
Fig. 5. Apparent viscosity vs. per cent vinyl acetate at 160°C for copolymers of different molecular weight: (⊙) [η] 0.241; (△) [η] 0.272.

The effect of increasing molecular weight is to reduce the value of n. Thus, the higher molecular weight copolymers are more non-Newtonian, a result in keeping with reported data[3,6] for homopolymer PVC.   Arrhenius-type plots of log apparent viscosity versus reciprocal absolute temperature (Fig. 6) are linear, but not parallel, for copolymers with different vinyl acetate contents and different molecular weights, over a 20°C temperature

range.   The results given in Table II show that (a) the activation energy
for viscous flow at constant shear rate ($\Delta E\gamma$) decreases with an increase in
vinyl acetate level in the copolymers and (b) $\Delta E\gamma$ increases with molecular
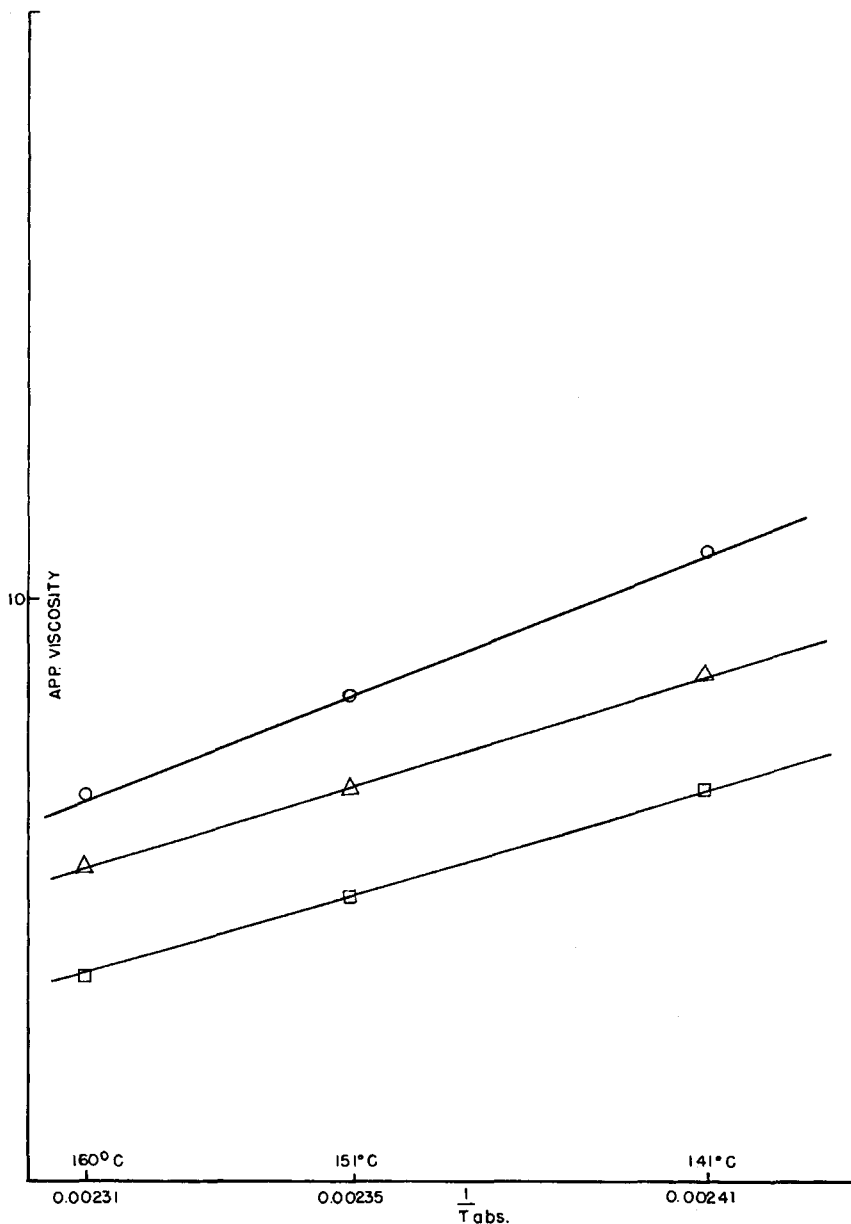weight.   The increase is more marked for higher vinyl acetate copolymers.

Fig. 6. Log apparent viscosity vs. $(T° \text{ abs})^{-1}$ for copolymers 1, 2, and 3; $[\eta]$ 0.241.
Vinyl acetate content: ($\odot$) 6.5%; ($\triangle$) 12.5%; ($\square$) 17.2%.

Fukasawa[7] has found that plasticization of PVC affects the melt flow activation energy in this direction due to changes in free volume resulting from plasticizer addition. Mayrick and Sieglaff[6] have also reported that above a critical concentration of added plasticizer, $\Delta E\gamma$ decreased. The observed increase in $\Delta E\gamma$ with copolymer molecular weight is opposite to the effect reported for homopolymer PVC, although the influence of molecular weight on the flow activation energy of PVC is not clear-cut. Some workers have reported that $\Delta E\gamma$ is either constant[6] or decreases[5] with increasing molecular weight. Collins and Metzger[3] have found that $\Delta E\gamma$ decreases with molecular weight and that PVC exhibits two activation energies, one in the low-temperature range and one at higher temperatures. The copolymers containing vinyl acetate are expected to be more branched than homopolymer PVC, since vinyl acetate is notoriously susceptible to branching. The increase in $\Delta E\gamma$ with molecular weight for these copolymers may well be due to their greater degree of branching, and it is interesting to note that molecular weight appears to have little effect on $\Delta E\gamma$ for low-acetate copolymers, whose degree of branching would be less, but is more marked as the vinyl acetate content increases.

As far as the critical shear rate is concerned, from Table II it can be seen that γ_{crit} increases with increasing vinyl acetate content and with extrusion temperature. On the other hand, it decreases as the molecular weight of the copolymer is increased. It has been shown[8] that the addition of an elastic polymer or an internal lubricant increases elasticity and decreases melt fracture, whereas addition of low molecular weight nonelastic materials to PVC does not have the same effect. The effect of molecular weight on the critical shear rate is in agreement with the results found for homopolymer PVC.[5]

The Effect of Copolymer Structure

The monomer reactivity ratios for vinyl chloride–vinyl acetate copolymerization are 1.68 and 0.23, respectively.[9] This results in a progressive change of average composition of the copolymer during polymerization with the initially formed copolymer being richer in vinyl chloride. The final copolymer produced at 100% conversion is a heterogeneous mixture of chains with compositions varying over wide limits. The distribution of vinyl acetate units in the chains would tend more toward a block copolymer structure than a random copolymer, particularly for copolymer molecules produced when most of the vinyl chloride is depleted. On the other hand, when the addition of a portion of the vinyl chloride monomer is added in the "delayed" fashion throughout the reaction (as in copolymer 8), the copolymer composition of chains produced throughout the reaction is more homogeneous and the sequence distribution of monomer units tends more toward a random arrangement.

A comparison of the rheological properties of copolymer 7 produced by the batch technique with those of copolymer 8, produced by delayed addition, is in essence a comparison of an approximate block structure with one
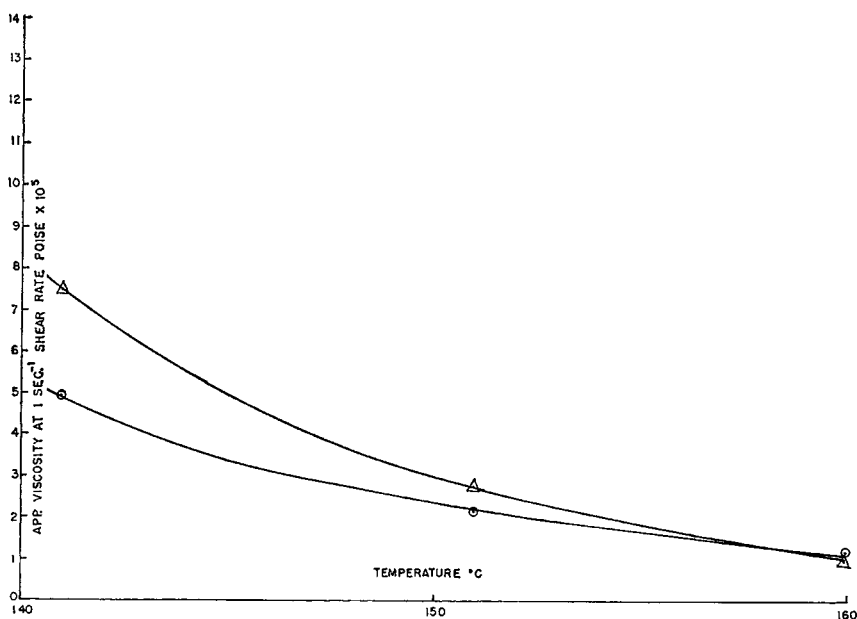
Fig. 7. Apparent viscosity vs. temperature for copolymers 7 and 8 showing the difference between delayed monomer addition (⊙) and normal batch-polymerized copolymer (△).

having a more random arrangement of monomer units, the molecular weight and total vinyl acetate content being held constant,

The data of Figure 7 indicates that the more random copolymer (copolymer 8) has the lower melt viscosity, at least up to 160°C and has a higher critical shear rate (Table III). The random copolymer is more Newtonian at low shear rates and has a lower $\Delta E\gamma$ for melt flow, 29 kcal, compared to 34 kcal for copolymer 7. These results agree well with those of Kraus and Gruver,[10] who first reported the effect of random arrangement of monomer units on rheological properties. They showed that for butadiene–styrene copolymers, a tendency to a longer block sequence resulted in (a) a greater non-Newtonian behavior, particularly at low shear; (b) a higher temperature coefficient of viscosity; and (c) an increase in melt viscosity.

The lower melt viscosity of the copolymer made by delayed addition may be explained in terms of a higher degree of branching. It seems plausible that vinyl acetate sites introduced into the chain early in the reaction (due to delayed feeding of vinyl chloride) should have a greater probability of branching than the block-type vinyl acetate units incorporated late in the the reaction, as in the batch technique. It is known that branched poly-(vinyl acetate) has a lower melt viscosity than linear poly(vinyl acetate) of the same weight-average molecular weight.[11]

A further observation, which reinforces the suggestion that the delayed copolymer may be more branched, is the higher die swelling (indicating a higher melt elasticity) for copolymer 8 compared to copolymer 7 (Fig. 8).

TABLE III
The Effect of Polymerization Variables on Rheological Parameters

Co-polymer	Non-Newtonian index n			Critical shear rate			App. viscosity,[a] poises $\times 10^5$			$\Delta E\gamma$, kcal/ mole
	141°	151°	160°	141°	151°	160°	141°	151°	160°	
7	0.51	0.55	0.70	26	34	38	7.5	2.7	1.0	34.0
8	0.54	0.61	0.82	31	41	48	4.9	2.1	1.15	29.0
12	0.58	0.64	0.67	48	84	95	3.0	1.12	0.64	17.0
13	0.70	0.79	0.85	24	32	38	2.2	0.75	0.55	10.5

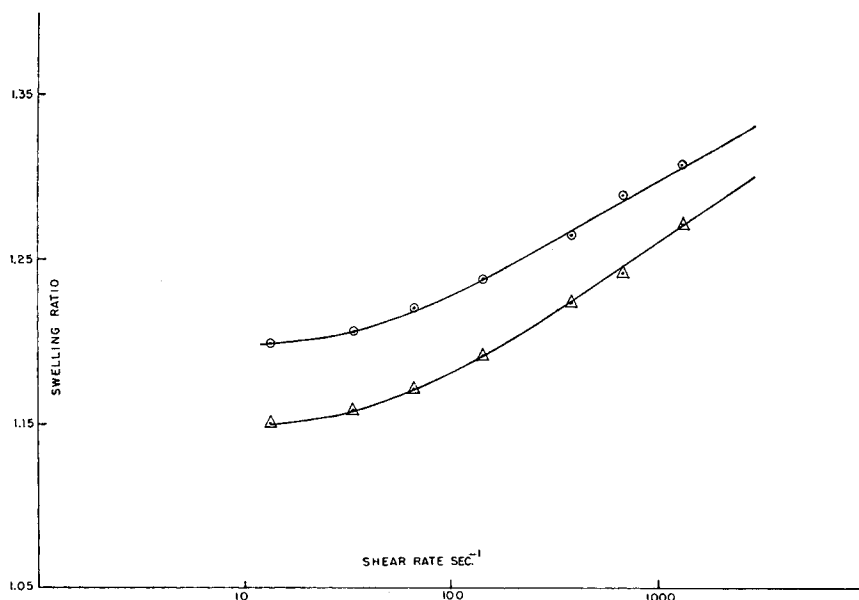[a] At a constant shear rate of 1 sec^{-1}.

Fig. 8. Swelling ratio vs. shear rate for copolymer 7 (△) and copolymer 8 (⊙), at 150°C.

Branched polymers, particularly polyolefins, have been reported[12] to exhibit greater melt elasticity than linear polymers. The effect of a longer block sequence of vinyl acetate units on the flow properties, in agreement with the above observations, is seen for copolymer 12 (Fig. 9 and Table III). Copolymers 12 and 13 were prepared in a similar manner, but the copolymerization in the former case was allowed to continue to a higher conversion (terminated at 22 psig pressure) compared to copolymer 13 (terminated when the pressure had dropped only to 60 psig). Copolymer 12 should therefore contain longer blocks of vinyl acetate. The average vinyl acetate content of this copolymer is marginally higher than the lower conversion copolymer (16.3% compared to 16.0%), as expected. However, the melt viscosity of copolymer 12 is greater than copolymer 13; it has a higher n value (more Newtonian) and a lower $\Delta E\gamma$.
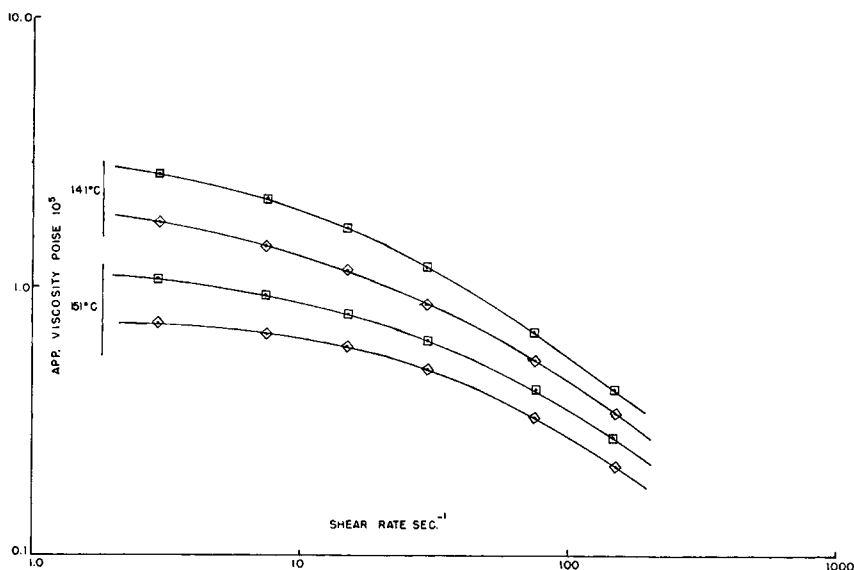
Fig. 9. Apparent viscosity vs. shear rate for copolymer 12 (□) and copolymer 13 (◇), at 141° and 151°C showing effect of dumping pressure.

Effect of Polymerization Temperature

It is well known that the branching index increases with polymerization temperature for poly(vinyl chloride),[13−16] and it is likely that this applies also to the copolymerization of vinyl chloride with vinyl acetate. The three copolymers prepared at three different polymerization temperatures differ in their flow parameters (Table IV, Fig. 10). It can be seen that a decrease in polymerization temperature produces an increase in melt viscosity, an increase in non-Newtonian behavior (n decreases), an increase in $\Delta E\gamma$, and a decrease in critical shear rate.

Little is known regarding the effect of branching on the rheological behavior of poly(vinyl chloride). However, these data are consistent with the changes reported[12] for melt viscosity, non-Newtonian behavior, and flow activation energy as a result of a decrease in the length of short-chain

TABLE IV
Effect of Polymerization Temperature on Rheological Parameters

Co-poly-mer	Non-Newtonian index n			Critical shear rate			App. viscosity,[a] poises $\times 10^5$			E, kcal/ mole
	140°	151°	160°	141°	151°	160°	141°	151°	160°	
9	0.54	0.56	0.59	10	14	19	10.0	5.2	2.40	39.8
10	0.57	0.59	0.64	15	17	30	8.6	4.8	2.10	37.5
11	0.58	0.69	0.77	18	21	40	7.5	3.3	1.40	34.0

[a] At a constant shear rate of a sec^{-1}.

branching in polyethylene. The observed increase in melt viscosity as the polymerization temperature is lowered may be interpreted in terms of a lower degree of branching, analogous to the results of Hogan et al.[17] for polyethylene.

The degree of crystallinity of conventionally polymerized poly(vinyl chloride) is between 3% and 10%,[18,19] and its syndiotacticity increases with decreasing temperature of polymerization.[20] Although the difference between the lowest and highest polymerization temperatures used to prepare copolymers 9, 10, and 11 was only 10° (60° to 70°C) and the presence of comonomer units in the chain would be likely to reduce the degree of crystal-
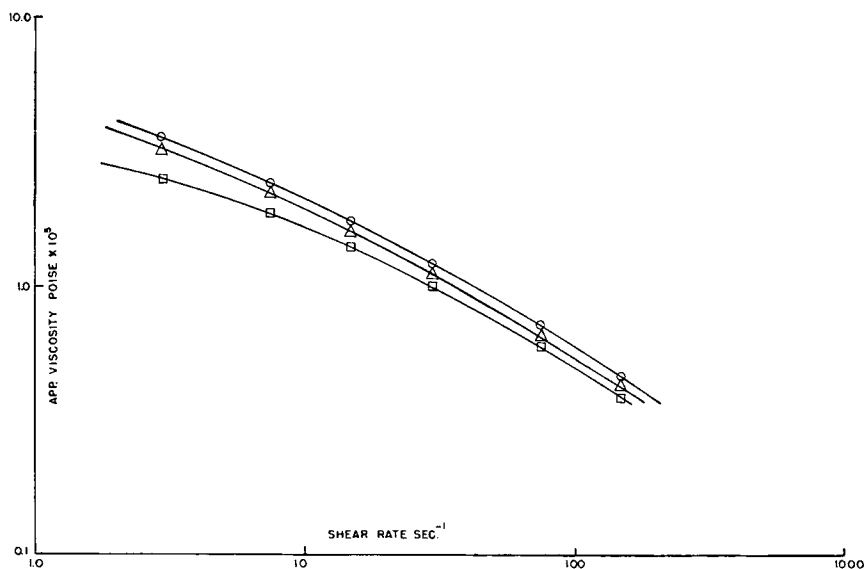

Fig. 10. Apparent viscosity vs. shear rate at 151°C for copolymers 9, 10, and 11 polymerized at different temperatures: (⊙) 60°C; (△) 65°C; (□) 70°C.

linity below that of the homopolymer, the effect on the rheological properties of polymerization temperature may be attributable to small crystallinity changes. Pezzin et al.[21] have pointed out that the rheological properties of plasticized PVC are governed to a large extent by the crystallinity of the polymer and that even small changes in the degree of crystallinity can affect the rheological behavior to a marked degree.

If the increase in $\Delta E\gamma$ observed with a decrease in polymerization temperature is a result of small changes in crystallinity, this would be in accord with the suggestion made by Collins and Krier[22] to explain the two activation energies found for PVC at low and high temperatures. They observed that the flow activation energy was greater at temperatures where crystallites are present compared to temperatures where the crystalline structure disappears.

CONCLUSIONS

The vinyl acetate content, the molecular weight, as well as the polymerization conditions all have an effect on the rheological behavior of vinyl chloride–vinyl acetate copolymers.   The effect of vinyl acetate content on the flow properties is similar to the effect of external plasticizer addition to PVC.

As the vinyl acetate content increases, (1) the melt viscosity decreases, (2) the copolymer becomes more Newtonian, (3) the critical shear rate increases, and (4) the flow activation energy decreases.

As the molecular weight increases, (1) the melt viscosity increases, (2) the copolymer becomes less Newtonian, (3) the critical shear rate decreases, and (4) the flow activation energy increases.

Varying polymerization conditions at constant vinyl acetate level and constant molecular weight produces copolymers which are structurally different, as there are considerable differences in their flow behavior.

Copolymers that are more random and structurally more homogeneous have (1) a lower melt viscosity, (2) a higher critical shear rate, (3) a lower flow activation energy, (4) a high melt elasticity, and (5) are more Newtonian in behavior.

The conversion (or pressure) at which the copolymerization is terminated affects the rheological properties of the copolymer, and this may be due to a change in the length of vinyl acetate blocks.

Lowering the polymerization temperature produces (1) an increase in melt viscosity, (2) a decrease in critical shear rate, (3) an increase in non-Newtonian behavior, and (4) an increase in the flow activation energy.

The influence of polymerization temperature has been interpreted in terms of branching and/or crystallinity changes by analogy with polyolefins in the absence of reliable PVC data.

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