

TABLE I  
Effect of Pressure Fluctuations on Time Dependence of  
Output Rate for Polyethylene Sample 3  
(Extrusion at 175°C.)

Experiment A		
Time after first pressure imposition, min.	Output rate, g./min.,	
	At 300 psi	At 150 psi
1	1.092	
3		0.336
4	1.120	
6		0.344
7	1.127	
9		0.343
10	1.150	
12		0.349
13	1.162	
15		0.356
16	1.180	
18		0.355
19	1.196	
21		0.356
22	1.209	
24		0.353
25	1.211	
27		0.356

Experiment B		
Time after first pressure imposition, min.	Output rate, g./min.,	
	At 400 psi	At 200 psi
0.5	1.867	
1.5		0.539
2.0	1.925	
3.0		0.553
3.5	1.957	
4.5		0.559
5.0	2.004	
6.0		0.554
6.5	2.030	
7.5		0.560
8.0	2.073	
9.0		0.557
9.5	2.087	
10.5		0.557

melts in a biconical rheometer. The data in Figure 1 again indicate the distinctive polymer characteristic of the time-dependent increase in output rate. However, the results cannot be attributed to the effects described by Skinner.<sup>4</sup> Both in intermittent and continuous shear experiments, the viscometer reservoir is being exhausted and, consequently, if the time dependence were the result of increasing pressure drops across the capillary die it would have to be observed during both methods of operation.

In a second sequence of experiments, continuous extrusion was studied under applied pressures which cycled sys-

tematically between two finite levels. Typical data are given in Table I. In experiment A, pressure was alternated between 300 psi (for 1 min.) and 150 psi (2 min.), while in B the cycle was 400 psi (1/2 min.) and 200 psi (1 min.). The time drift at each of the higher applied pressures is unmistakable, while at the respective lower pressures a minor rise is initially noted but after a few cycles the output rate remains constant. Once again the results are consistent with the hypothesis of slow changes in melt configuration under applied stress.<sup>1</sup> In terms of extrusion at the respective higher stresses, the short residence times at lower but finite stress are not sufficient to counteract tendencies to disentanglement and chain orientation, which are suggested as necessary for the establishment of steady states. The output rates therefore rise, and the periods necessary to the attainment of steady states appear to be longer than when higher stresses are continuously applied. On the other hand, in terms of extrusion at the lower stresses the residence times at higher stress promote the establishment of steady states with a consequent reduction in the duration of the time-dependent increase in output rates.

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### A Reply to Skinner's "Polymer Rheology"

Mr. Skinner is to be commended for his letter<sup>1</sup> pointing out a little appreciated source of error in the melt flow index test, namely, the resistance to flow in the reservoir. His analysis of the magnitude of the correction is right, but we disagree with his remark that his example represents an extreme. Further, we prefer to differ with him on his conclusion regarding the error connected with the friction between plunger and barrel. We suggest here practical answers to both of these problems.

We have made actual measurements of the resistance caused by the plastic in the cylinder for materials having much higher  $n$  values than the example given by Skinner. We define  $n$ :

$$n = \frac{d}{d} \frac{[\log (4Q/\pi r_c^3)]}{[\log (P_{sc}/2L_c)]} \quad (1)$$

TABLE I  
Characteristics of Materials Used

Polymer	Type	Melt index, g./10 min., 190°C.	Cylinder temp., °C.	$n$
Polyethylene	Ziegler process	0.03	190	3.3 <sup>a</sup>
Polyvinyl chloride				
A Plasticized		0.135	150	6.4 <sup>b</sup>
Polyvinyl chloride				
B Plasticized, filled		0.46	150	5.8 <sup>b</sup>

<sup>a</sup> Determined in long capillary with end correction.

<sup>b</sup> Determined in short capillary with no end correction.

The materials included a Ziegler-type linear polyethylene and two different commercial polyvinyl chloride compounds. Table I describes these materials and their high  $n$  values. These had very large cylinder resistances, as expected from Skinner's relationship.

The experiments were run in a commercial capillary rheometer similar to the Merz and Colwell<sup>2</sup> design, having a  $\frac{3}{8}$ -in. diam. cylinder approximately 12 in. long. Two capillaries were used including the standard melt flow index size (ASTM D1238-57T) and one with  $L_c/r_c = 33.3$ . Figure 1 shows a recording of force versus length of plastic remaining in the cylinder as the material is discharged at constant rate. After passing through a peak, expected from rate minima reported by Schreiber,<sup>3</sup> the pressure assumed a linear change, as predicted by Skinner's relation. In the extreme, as much as 58% of the total pressure was lost in the reservoir in our experiments. In the case of PVC materials, this corresponds to 99% loss in flow rate if the pressure is held constant. Clearly, flow rate measurements on these materials are not useful if they are carried out under conditions of varying pressure loss in the reservoir.

Skinner reported the relation:

$$P_b/P_c = (L_b/L_c)[r_c/r_b]^{(n+3)/n} \quad (2)$$

TABLE II  
Determination of  $n$  from Resistance in Reservoir

Resin	Die, in.	Shear rate,		Corrected,			$n$
		$(n+3)Q$	$L_b$ , in.	$L_c$ , in.	$P_c$ , lb.	$P_b/P_c$	
Polyethylene	0.0825 × .315	1020	5.8	0.645	117	0.49	3.24
	0.0825 × .315	1020	10	0.645	117	0.90	3.40
	0.0825 × .315	102	5.8	0.562	51	0.55	3.19
	0.0825 × .315	102	10	0.562	51	0.96	3.22
	0.060 × 1.00	276	10	1.210	200	0.275	3.51
Polyvinyl chloride A	0.0825 × .315	1540	8	0.645	156	1.39	6.7
Polyvinyl chloride B	0.0825 × .315	1430	4.22	0.645	61.5	0.75	7.0

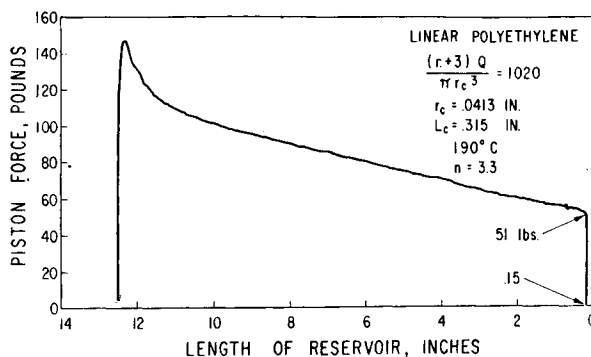


Fig. 1. Force vs. length with linear polyethylene.

where  $P$ ,  $L$ , and  $r$  refer to pressure, length, and radius, respectively, and subscripts  $b$  and  $c$  refer to the barrel (reservoir) and capillary, respectively. To test eq. (2) quantitatively, one should correct  $L_b$  and  $L_c$  for end effects. We have not measured the end effects, but have approximated capillary end corrections from those reported by Bagley<sup>4</sup> for branched polyethylenes. Table II lists results of the calculation of  $n$  based on eq. (2) with an end correction to  $L_c$ . The results of the calculation agree with values of  $n$  listed in Table I, confirming that eq. (2) applies.

The fact that PVC compound B did not show as good agreement as the other materials may be because a filler was present. Further, end effects are not known for the PVC compounds and the values for  $n$  in Table I are certain to be low because this correction was not made. Better agreement with theory is to be expected for both PVC materials when end corrections are made.

Skinner reports that the resistance to piston motion caused by the film of plastic around the piston should increase in relative importance with shorter capillaries and with larger barrel diameters. He is correct about the effect of capillary length, but not about the effect of barrel diameter. At constant pressure and piston speed, the friction force increases in proportion to the circumference of the piston, whereas the pressure force increases with the area of the piston. Therefore, the friction force must decrease in importance, not only because of the ratio of circumference to area but also because required piston speeds are lowered

Skinner apparently misinterpreted the equations of Marker, Early, and Aggarwal<sup>5</sup> on this matter.

Small barrels are used for various reasons, one being to shorten heat-up time. Small barrels may cause significant piston friction, but the magnitude is difficult to measure or calculate. The use of a piston ring is suggested to reduce this source of error.

A pressure transducer at the bottom of the barrel overcomes both sources of error, but this is not practical with the melt flow index apparatus. We suggest the use of a Teflon O ring on the piston and an indicator for piston displacement. The indicator provides information needed to interpret readings at any length of reservoir, and offers the extra benefit of a volume measurement, thus eliminating the need of weighing the extrudate.

We recommend that users of the melt flow index test consider their need for these modifications to their equipment.

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## ERRATUM

### Characterizing Impact Behavior of Thermoplastics

(*J. Appl. Polymer Sci.*, **6**, 332-337 1962)

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On page 335 reference 3 should read U. S. Patent 2,362,589 (1944).

## CORRIGENDUM

We regret that an editorial error in processing the paper by A. N. Gent (*J. Appl. Polymer Sci.*, **6**, 433-441, 1962) resulted in a misstatement of the title of the article. The correct title is: "Relaxation Processes in Vulcanized Rubber. I. Relation between Stress, Relaxation, Creep, Recovery, and Hysteresis."