

Reservoir Effects in the Extrusion Rheometry of Compounded Rubbers

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Synopsis

Unvulcanized rubber compounds have been extruded from a constant rate extrusion rheometer having a low capillary L/d ratio. With a polychloroprene compound, the extrusion pressure decreased linearly as the piston height decreased and the results have been shown to be quantitatively in agreement with the suggestion that the reservoir and capillary behave as two extruders in series. With highly elastic rubber compounds, the extrusion pressure either increased continuously as the piston descended down the reservoir or increased to a maximum before falling to a final value. This suggests that as well as the reservoir height effect, there is an effect due to the viscoelasticity of the material. The height of the peak in the extrusion pressure versus piston height curve for natural rubber, was roughly proportional to the initial amount of charge in the reservoir and for both types of material, the final pressure was independent of the initial charge. These results would indicate that certain anomalous effects in extrusion rheometry are reflections of the behavior of the material in the reservoir as opposed to shear effects in the capillary. Even for rheometers with low capillary L/d ratios, consistent results can be obtained if the pressure drop across the capillary is calculated from observations taken when the reservoir is effectively empty.

Various workers have commented on anomalies which occur under certain conditions in the course of extrusion of polymers from extrusion viscometers.

With constant force viscometers the output rate of the material has been found to increase as the reservoir empties, and with constant rate of extrusion viscometers a gradual pressure drop has been found to occur as the piston descends through the reservoir.

Certain observers^{1,2} postulate that these effects are due to a definite polymer characteristic, i.e., a shift in the orientation of the polymer chains. Other workers suggest that the effects are due to the material having an appreciable resistance to flow in the reservoir of the rheometer.

Charley³ has carried out extensive work with the melt flow indexer using polypropylene and observed an increase in flow rate as the piston descended. The pressure in the reservoir just above the capillary was measured directly, and it was apparent that the pressure at this point was much lower than that calculated from the weight on the piston but increased almost linearly to the calculated pressure as the piston descended. Marshall and Riley⁴ have made measurements of the resistance caused by materials, viz., polyethylene and poly(vinyl chloride) in the cylinder of a commercial

TABLE I
Extrusion Pressure at Various Shear Rates and Piston Heights

Piston height L_b , in.	Total extrusion pressure at various apparent shear rates, P , lb./in. ²			
	298 sec. ⁻¹	460 sec. ⁻¹	698 sec. ⁻¹	1043 sec. ⁻¹
2.06	2480	2680	2960	3250
1.37	2360	2530	2790	3060
0.69	2240	2390	2640	2950
0	2080	2240	2450	2710

capillary rheometer and showed that the pressure, after passing a peak, assumed a linear change.

The purpose of this paper is to present experimental data which we have obtained with compounded unvulcanized rubbers (as opposed to thermoplastics, on which the aforementioned observations have been made) and to discuss the implications of the extrusion pressure versus piston height curves so derived. Experiments were performed with the use of an extrusion viscometer manufactured by A. Macklow-Smith.⁵ A description of this instrument together with the full experimental procedures for performing tests with rubbers has been previously reported by Devine and Ross.⁶ The dimensions of the extrusion system were as follows: length of reservoir L_b (max) = 2.75 in.; length of capillary L_c = 0.125 in.; radius of reservoir r_b = 0.3995 in.; radius of capillary r_c = 0.03125 in.

For a material which obeys a power law, eq. (1) should appertain if it is considered that the reservoir and capillary behave as two extruders in series.

$$(P - P_c)/P_c = (L_b/L_c) (r_c/r_b)^{(n+3)/n} \quad (1)$$

where P is the pressure at the piston, P_c is the pressure drop through the capillary, and n is the exponent in the power law which has the form

$$\text{shear rate} \propto (\text{shear stress})^n$$

Table I shows the experimentally observed values of P for various piston heights and at various apparent shear rates for a polychloroprene compound. The relation between piston height L_b and extrusion pressure P is a straight line (Fig. 1) as predicted by eq. (1). The values of n have been determined from the slopes of these lines and are recorded in Table II. When $L_b = 0$ the value of the extrusion pressure should be equivalent to the pressure drop through the capillary alone. The slope of the double logarithmic plot of wall shear stress based on this value, P_c , versus the apparent shear rate at the wall is also a measure of n and this value has been recorded in Table II, column 6.

End effects have not been taken into account. For both methods of calculating n the value of the capillary length has been obtained by direct measurement, but there is a remarkable coincidence between the two

TABLE II
Determination of n from Piston Height Curve and from Power Law Curve

Apparent shear rate, sec. ⁻¹	Extrusion pressure through capillary P_c , lb./in. ²	Wall shear stress in capillary, lb./in. ²	Slope of pressure drop vs. piston height curve $\frac{P_c}{L_c} \left(\frac{r_c}{r_b} \right)^{\frac{n+3}{n}}$	Flow-dependent parameter n	
				From piston height vs. pressure drop curve	From log shear rate vs. log shear stress curve
298	2080	260	192	3.98	4.18
460	2240	280	212	4.05	"
698	2450	307	244	4.15	"
1043	2710	339	252	3.99	"

differently derived values of n , and this appears to justify the suggestion (at least in this case and where capillaries of low L/d ratio are used) that the time-dependent effects are due to the decreasing resistance of the material in the reservoir and that the extrusion pressure through the capillary is only known when the reservoir is effectively empty.

Completely different characteristics were observed when a similar experiment was carried out with the use of a high polymer content, natural

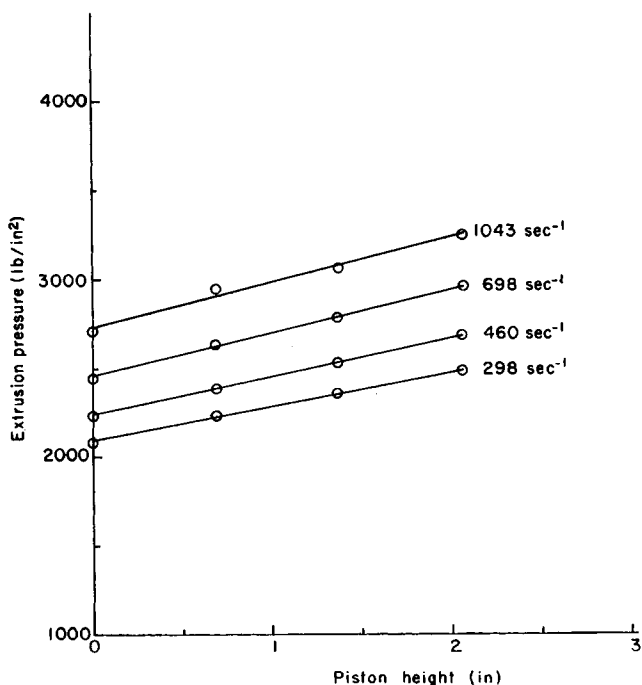


Fig. 1. Extrusion pressure vs. piston height for polychloroprene compound. Die diameter $1/16$ in.; length $1/8$ in.; temperature 90°C .

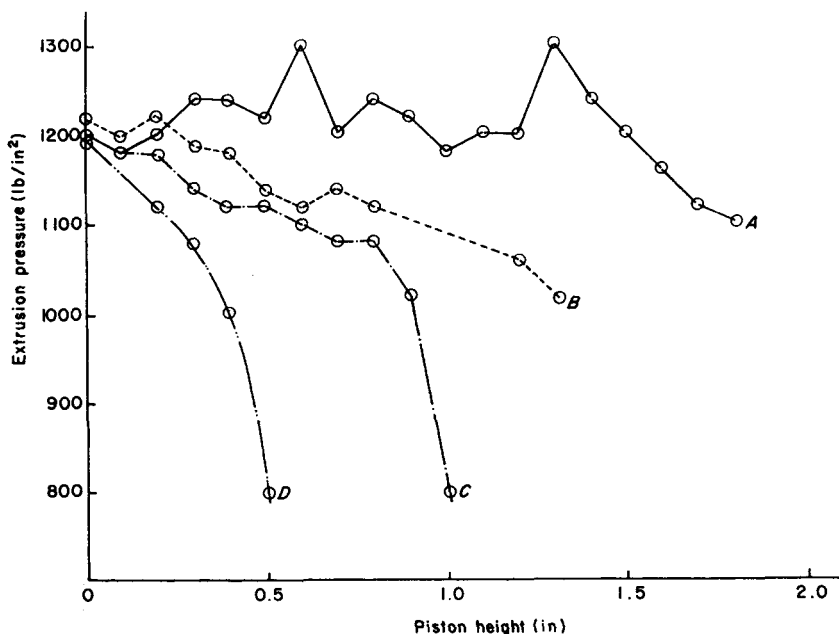


Fig. 2. Extrusion pressure vs. piston height for first natural rubber compound at various initial nominal heights of charge in barrel: (A) 2 in.; (B) 1.5 in.; (C) 1 in.; (D) 0.5 in. Shear rate 321 sec.^{-1} ; temperature 90°C .; die diameter $\frac{1}{16}$ in.; length $\frac{1}{8}$ in.

rubber compound. In this case, the extrusion pressure gradually increased to a final value, which was the same, irrespective of the initial amount of material in the reservoir (Fig. 2). This behavior appears to be a further demonstration of the effect, reported by Ballman,⁷ (who was able to measure the variables directly) that the force lags behind the plunger speed due to the time dependant viscoelastic nature of the polymer melt.

A further experiment with a batch of similar high polymer content natural rubber compound, showed the extrusion pressure to rise to a maximum before falling to the final value (Fig. 3). In deriving the above data each series of experiments was carried out within one batch of mixed compound.

It is suggested that in this case two effects are taking place simultaneously; there is the build up of pressure due to the bulk viscoelasticity of the material in the reservoir coupled with the drop in pressure due to the decreasing height of material in the reservoir.

The polychloroprene and the natural rubber compounds were quite different materials. The former would be described by a rubber technologist as "sluggish" or "dead," i.e., showing hardly any recovery after deformation, whereas the natural rubber compound was one commonly described as "nervy," i.e., being highly elastic as shown by its high resilience and quick recovery after deformation. The difference between the

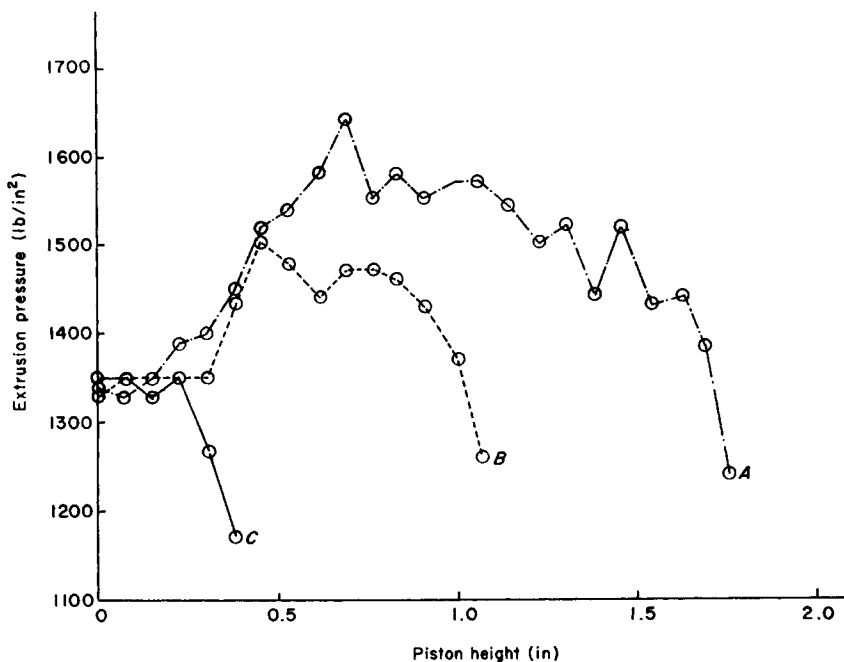


Fig. 3. Extrusion pressure vs. piston height for second natural rubber compound at various initial nominal heights of charge in barrel: (A) 2 in.; (B) 1 in.; (C) 0.5 in. Shear rate 321 sec.^{-1} ; temperature 90°C .; die diameter $\frac{1}{16}$ in.; length $\frac{1}{8}$ in.

materials is also illustrated by the die swell. Under the same conditions of extrusion the swell (expressed as the ratio, diameter of extrudate minus diameter of capillary/diameter of capillary) of the polychloroprene was in the region 11% as compared with 160% for the natural rubber material. During extrusion of this latter material the needle showed a continuous flickering which is reflected in the rough curve of Figures 2 and 3. This was associated with a rough extrudate in contrast to the very smooth extrudate and extrusion curve of the polychloroprene compound.

It is interesting to compare Figures 1 and 3 with the curves obtained by Rudin and Shreiber² for polyethylenes in a constant force rheometer. Figure 4 represents diagrammatically the output rate versus time curves obtained for low and high density polyethylenes when the output rate is plotted against time of extrusion. Polychloroprene (Fig. 1) and high density polyethylene (Fig. 4A) show curves, the gradients of which do not change sign as extrusion proceeds. On the other hand, the more elastic materials—natural rubber and low density polyethylene—show curves which exhibit a turning point. In the case of the constant rate rheometer the extrusion pressure passes through a maximum (Fig. 3) which would appear to have some correspondence with the minimum which occurs in the output rate curve of the constant force rheometer (Fig. 4B). It is suggested

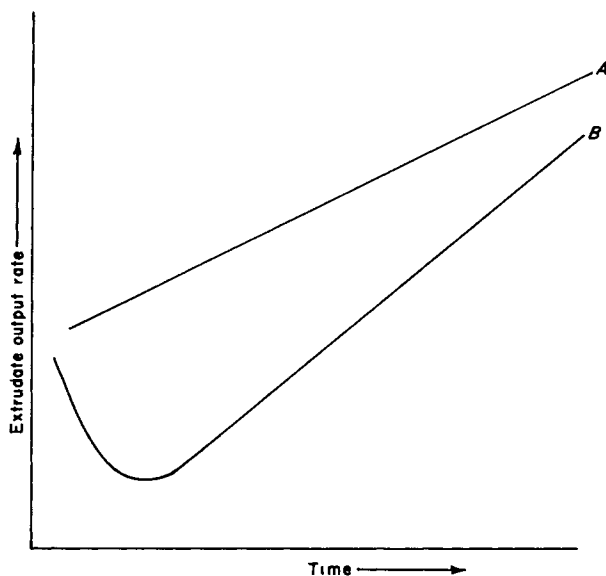


Fig. 4. Diagrammatic representation of output rate vs. extrusion time for polyethylene in constant force extrusion rheometer: (A) high density polyethylene; (B) low density polyethylene.

that the maximum and minimum respectively, of these curves are manifestations of the same, elastic effect.

Important results of this work with the natural rubber compound are that the height of the peak in the extrusion pressure curve was roughly in proportion to the amount of charge in the reservoir at the start of extrusion and in all cases the final extrusion pressure is independent of this initial amount. These results would indicate that the much discussed anomalous effect in extrusion rheometry are, to a large extent, reflections of the behavior of the material in the reservoir of the instrument as opposed to shear effects in the capillary.

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Résumé

Des composés du caoutchouc non vulcanisé ont été extrudés au moyen d'un rhéomètre d'extrusion à vitesse constante et possédant un rapport capillaire L/d faible. Avec un composé du polychloroprène, la pression d'extrusion diminue linéairement avec la diminution de la hauteur du piston et les résultats sont quantitativement en accord avec l'idée que le réservoir et le capillaire se comportent comme deux extrudeuses en série. Avec des composés de caoutchouc fortement élastiques, la pression d'extrusion ou bien augmente continuellement lors de la descente du piston dans le réservoir, ou bien augmente jusqu'à un maximum avant de tomber vers une valeur finale. Cela montre qu'en plus de l'effet dû à la hauteur du réservoir, il y a un effet dû à la viscoélasticité du matériau. La hauteur du pic dans le diagramme de la pression d'extrusion en fonction de la hauteur du piston, est rigoureusement proportionnelle à la quantité initiale de la charge dans le réservoir et pour les deux types de matériel, la pression finale est indépendante de la charge initiale. Ces résultats indiqueraient que certains effets anormaux dans la rhéométrie d'extrusion sont dus au comportement du matériau dans le réservoir et s'opposent aux effets de cisaillement dans le capillaire. Même pour des rhéomètres, possédant des rapports capillaires L/d faibles, on peut obtenir des résultats valables si la chute de pression dans le capillaire est calculée à partir des observations effectuées lorsque le réservoir est effectivement vide.

Zusammenfassung

Unvulkanisierte Kautschukmischungen wurden aus einem Extrusionsrheometer konstanter Geschwindigkeit mit einem niedrigen Kapillar- L/d -Verhältnis extrudiert. Bei einer Polychloroprenmischung nahm der Extrusionsdruck mit der Kolbenhöhe linear ab, und die Ergebnisse lassen sich quantitativ unter der Annahme verstehen, dass sich das Reservoir und die Kapillare wie zwei in Serie geschaltete Extruder verhalten. Bei hoch elastischen Kautschukmischungen nahm der Extrusionsdruck bei der Abwärtsbewegung des Kolbens im Reservoir entweder kontinuierlich zu oder stieg vor dem Afrall zum Endwert auf ein Maximum an. Das zeigt, dass neben dem Einfluss der Reservoirhöhe auch ein Einfluss der Viskoelastizität des Materials besteht. Die Höhe des Maximums in der Kurve Extrusionsdruck gegen Kolbenhöhe für Naturkautschuk war der Anfangsmenge der Füllung im Reservoir ungefähr proportional und bei beiden Materialtypen war der Enddruck unabhängig von der Anfangsfüllung. Diese Ergebnisse zeigen, dass gewisse anomale Effekte bei der Extrusionsrheometrie durch das zu den Scherungseffekten in der Kapillare entgegengesetzte Verhalten des Materials im Reservoir bedingt sind. Sogar für Rheometer mit niedrigem Kapillar- L/d -Verhältnis können konsistente Ergebnisse erhalten werden, wenn der Druckabfall längs der Kapillare aus Messungen mit praktisch leerem Reservoir berechnet wird.

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