

Influence of Carbon Black on Processability of Rubber Stocks. V. Extrusion*

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Synopsis

A study of postextrusion relaxation (shrinkage) rates identified two separate processes, only one of which is influenced by carbon black structure and surface area. One of these processes is thought to be a solidlike fast elastic recovery and was found to be influenced by carbon black and polymer characteristics. The other process reflected slow randomization of oriented molecular chains: it was mainly influenced by polymer nature and carbon black had almost no effect. In the previous paper of this series, work with various carbon blacks in SBR-1500 indicated that both types of polymer deformation originate within the converging flow region at the die entrance, where extensional flow takes place. In the present work the extensional flow behavior of five polymers (filled with various carbon blacks) was examined at elevated temperatures. The magnitude of shrinkage caused by molecular alignment was related to extensional viscosity of the rubbers. This confirms the hypothesis stated above. Extensional viscosity was measured using the previously described instrument, which is inexpensive to construct, easy to operate, and can be attached to any standard stress-strain tester. The characteristics of extensional flow are defined and it is shown that for polymeric materials it differs substantially from shear flow, since a rapid orientation of the molecular chains takes place during the extensional flow. The effect of carbon black on the extensional viscosity at elevated temperatures is illustrated.

INTRODUCTION

The dimensional stability and extrudate appearance are the two most important problems encountered during extrusion of rubber goods. The dimensional stability is related to the phenomenon of extrusion shrinkage, i.e., shrinkage of extrudate in the axial direction accompanied by swelling in the radial direction. In the plastics industry it is more common to measure the swelling of the extrudate. However, since there is no net change in volume, there is a direct mathematical relationship between die swell and extrusion shrinkage. The extrudate appearance describes the smoothness of the surface and tearing at the edge of the extrudate. Poor extrudate appearance is due to fracture of the rubber compound; this phenomenon is known in the plastics industry as melt fracture.

Although both phenomena are widely known, their origins are not well understood. In an earlier publication Cotten and Thiele¹ stressed the significance of extensional flow and presented some initial data on SBR containing various carbon blacks. In the present work these studies were extended to examine the correlation between the extensional flow characteristics, extrusion shrinkage, and extrudate appearance.

The behavior of polymer melt at the die entrance is particularly important in most commercial processes where the rubber is extruded through short dies (i.e., length-to-diameter ratio L/D less than 5). However, the great majority of

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rheological studies have been concerned with shear flow through long capillaries, and much less attention was given to polymer flow at the die entrance. From flow visualization studies, a number of investigators noted that at the die entrance the polymer flow converges in the center, leaving a "dead space" surrounding the central region. The polymer in the dead space is being circulated by vortices and does not participate in the flow through the die at low stresses. Above some critical shearing stress, Bagley and Birks² observed that a number of flow lines extending into the capillary have fractured, snapped back from the die entry region. The upward snap-back of the central material was compensated for by a rush of material from the dead space. This effect was also found by other investigators.^{3,4} Cogswell⁵ pointed out that extensional flow occurs whenever there is a convergence of flow lines, such as in the die entrance region, while the more familiar shear flow takes place within the die. Thus, the snap-back fracture of flow lines in the central region may be interpreted as a failure of the material to sustain large extension imposed in that region. The concept of extensional flow in the convergent region at the die entrance is further supported by the work of Han,⁶ who observed the behavior of tracer particles (copper powder) suspended in molten polystyrene flowing through a converging channel. He found that particles on the centerline travel faster than others, and there was no evidence of circulatory motion.

While there is still a lack of fully satisfactory mathematical treatment of convergent flows at die entrance, many authors agree to the presence of significant extensional flow at the die entrance. This subject was reviewed recently by Cogswell,⁹ who summarized various mathematical approaches taken by the different investigators.

The extensional flow may be best visualized as a deformation caused by forces acting in a direction perpendicular to the opposite faces of a cube, while simple shear flow may be similarly described as a result of forces acting tangentially to the opposite faces of a cube. Polymers differ substantially in their response to shear and extensional flow. In shear flow there is a velocity gradient within the material causing some rotation of larger entities; the distance between particles on the same slip surface does not change, while the separation of other particles increases linearly with time. In extensional flow the velocity remains constant throughout the material, and the separation of particles changes exponentially with time. Large polymer molecules become oriented much more rapidly in the extensional flow field.

Since extensional flow creates much greater molecular orientation than the shear flow, several authors attempted to relate the die swell (or extrusion shrinkage) to the events occurring at the die entrance. Locati¹⁰ attempted to equate the extrusion shrinkage with entrance pressure loss assuming that perfectly elastic deformation occurs at the die entrance in the region of extensional flow. Cotten¹¹ identified two relaxation processes causing extrusion shrinkage and suggested that these are caused by the deformation occurring in the extensional flow region at the die entrance and that the polymer is actually relaxing during the flow through the die as well as afterward.

This approach is at variance with the more common view relating die swell to the normal forces generated by shear flow within the capillary. For instance, Tanner¹² considers an elastic recovery at the die exit to balance the stresses developed during the shear flow through the die, while White¹³ reproduced the same

result using a single Maxwell model in a homogeneous shear. Han⁶ suggested that "die swell occurs as a result of disorientation of macromolecules which have been oriented *within* the capillary by the high shear field" (*italics added*).

The effect of carbon black on shear viscosity has been examined thoroughly in a multitude of studies. White and Crowder⁷ have shown that shear viscosity of SBR and BR containing carbon black increases with increasing surface area, structure, and loading of carbon black. However, the effect of carbon black diminishes with increasing rate of shear. The extensional flow characteristics at room temperature of SBR containing various carbon blacks were studied by Cotten and Thiele,¹ who have shown that the stress continues to increase with increasing extension of the material, and even at the very slow extensional rate the material ruptures before reaching a steady value of stress. The authors analyzed the observed extensional flow curves in terms of the Denn–Marrucci⁸ equation. They showed excellent log–log correlation of extensional rate with values of viscosity coefficient and relaxation time obtained by application of the Denn–Marrucci equation over a time scale from 0.001 to 0.2 sec⁻¹. These findings suggest that comparisons of various rubbers at a low extensional rate will reflect accurately comparative ratings of the same materials at a much higher rate of extension. It was also shown that carbon black surface area influences the curvature of the flow curve and elongation at break, while the black structure affected only the relative level of flow curves.

In contrast to the earlier experiments,¹ which were carried out at room temperature, the present measurements of extensional viscosity were run at the same temperature (100°C) as the extrusion, making the comparisons more meaningful.

EXPERIMENTAL

Extensional Flow Measurements

The extensional rate $\dot{\epsilon}$ is usually defined as

$$\dot{\epsilon} = (1/l)(dl/dt) \quad (1)$$

If $\dot{\epsilon}$ is constant then eq. (1) becomes

$$\dot{\epsilon} = [\ln (l_t/l_0)]/t \quad (2)$$

where l_t is the length of a given element at time t and l_0 is its initial length while the total Hencke strain ϵ is equal to

$$\epsilon = \ln (l_t/l_0) \quad (3)$$

From eq. (3) it follows that

$$l_t = l_0 \exp (\dot{\epsilon}t) \quad (4)$$

i.e., in order to maintain a constant extensional rate, the separation of any two particles within the material must grow at an exponential rate.

In the earlier publication¹ the instrument satisfying these requirements was described and a schematic diagram of such a rheometer is shown in Figure 1. In the present work the rheometer was placed inside an air oven in order to permit measurements at elevated temperatures. In previous experiments¹ it was ob-

TABLE I
Analytical Characteristics of Carbon Blacks

| Carbon black type | (N ₂)SA, m ² /g | DBPA, cc/100 g |
|-------------------|--|----------------|
| N231 | 117 | 92 |
| N330 | 80 | 103 |
| N550 | 44 | 119 |
| N539 | 42 | 109 |

served that the actual extensional rate $\dot{\epsilon}_A$ was appreciably smaller than the rate calculated, $\dot{\epsilon}_c$, from the circumferential speed of the rollers. The ratio $\dot{\epsilon}_c/\dot{\epsilon}_A$ varied from 1.7 to 2.1 depending on the composition of the sample. This correction factor was significantly reduced by a small modification of the instrument. The two rollers are now held together by a spring having a spring constant of 90 N/cm. Furthermore, the spring is so adjusted that there is no force exerted until roller separation exceeds 0.4 mm. This latter adjustment depends on the sample diameter; in this work all samples were obtained by extrusion through a 2 × 2-mm die. The value of the correction factor, $f = \dot{\epsilon}_c/\dot{\epsilon}_A$, was found to decrease as the temperature was increased, at 100°C the factor varied from 1.05 to 1.25.

The detailed description of the equipment and summary of the necessary calculations can be found in the previous publication.¹ It should be sufficient to add that all force measurements were corrected for the weight of the sample and stress was calculated per actual cross-sectional area at the particular instant of time.

Sample Preparation and Testing

All rubber stocks were prepared in a model B Banbury, operating at 77 rpm and cooled with running water. The standard mixing cycle consisted of mixing rubber alone for 2 min prior to addition of carbon black, followed by a further 5.5 min of mixing with carbon black. All stocks had good carbon black dispersions with ratings of B3 to C3 (ASTM D-2663, method B).

For extensional flow measurements, the fully compounded materials were allowed to rest overnight, were then remilled for 1 min on a two-roll mill, extruded using a Brabender extruder, model 100 (C. W. Brabender, South Hackensack, NJ) equipped with a 2 × 2-mm cylindrical die, and run at 100°C, using a screw speed of 50 rpm. The extruded strand was cut into 200-cm lengths, dusted with talc, placed loosely on waxed paper, and allowed to relax overnight prior to testing. The actual cross-sectional area of the extrudate was determined by weighing a known length of extrudate on the day of the extensional viscosity test and utilizing the density value calculated from individual densities of components (1.86 g/cc for carbon black, 0.935 g/cc for SBR).

Mooney viscosities of rubbers were measured using a standard ASTM D-1646 technique. Rebound resilience was measured using the Goodyear Healey rebound pendulum (ASTM D-1054). The structure of carbon blacks was characterized by their DBPA value (ASTM D-2114), and their nitrogen surface area, (N₂)SA, measured using ASTM D-3037 method C. Analytical characteristics of carbon blacks used in this study are given in Table I.

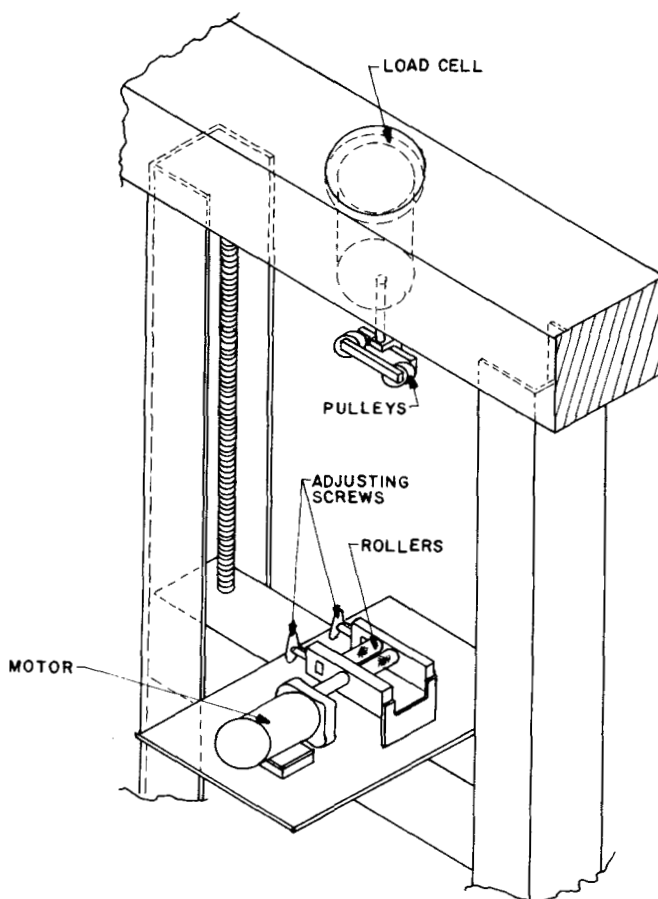


Fig. 1. Schematic diagram of apparatus.

Elongation at break of uncured compounds was measured on samples extruded through the Brabender extruder (see above). The extrudates were allowed to relax overnight, and their elongation at break was obtained by operating the Instron tensile tester at a constant speed of 10 cm/min, with the initial sample length of 14 cm, giving an elongation rate of 70%/min. The test temperature was 100°C. The mean value of 30–40 breaks was reported.

Extrusion shrinkage measurements were performed by utilizing a Goettfert viscometer (model HKR-2000; Goettfert, Buchen-Odenwald, Germany) with an attached Monsanto die swell detector (Monsanto Co., Akron, OH), which is based on a scanning laser beam principle. Both instruments and experimental procedure have been described in an earlier publication.¹⁴ In the present work, the polymer was extruded at 100°C through a 2 × 2-mm die at the desired rate. When equilibrium conditions were reached, the extrudate was cut just below the laser beam, the extrusion stopped, and the extrudate allowed to relax for 5 min prior to taking the measurements of the diameter.

Die swell B is commonly defined as the ratio of cross-sectional areas of the extrudate and the die, i.e.,

$$B = (d_j/d_c)^2 \quad (5)$$

where d_j and d_c are the diameters of extrudate and die, respectively. Extrusion shrinkage L is another parameter widely used in rubber industry and it is defined as the percent decrease in extrudate length. If there is no change in volume, these two parameters are related by

$$L = (1 - 1/B) \times 100 \quad (6)$$

All measurements of shear viscosity were performed using the Goettfert viscometer equipped with 1×30 -mm die and operating at 100°C . Shear stress τ and shear rate γ are defined by the following equations:

$$\tau = \frac{P}{4[(L/D) + \epsilon]} \quad (7)$$

$$\gamma = \frac{32Q}{\pi D^3} \quad (8)$$

where P is total pressure drop across the capillary die having a diameter D and length L , Q is volumetric flow rate, and ϵ is the Couette correction. The apparent viscosity η is given by the ratio of shear stress to shear rate at the particular value of shear rate.

RESULTS AND DISCUSSION

Extrusion Shrinkage

The extrusion shrinkage phenomenon has been described in terms of either development and dissipation and normal forces⁶ or as a function of molecular orientation.¹⁵ While the two approaches are not mutually exclusive, the present study is interpreted in terms of the molecular picture.

Typical plots of extrusion shrinkage versus the time lapsed since exit from the die are shown in Figure 2 for N330 black in five polymers. The data clearly indicate two recovery regions: the fast (solidlike) recovery region takes place in less than 0.02 sec and is followed by a much slower recovery due to molecular disorientation. In the subsequent discussion, L_0 denotes a reading taken at 0.02 sec and represents the magnitude of the fast recovery region. Extrusion shrinkage after 4 min of relaxation, $L_{4.0}$, is equal to approximately 95% of the ultimate shrinkage observed after 18 hr of relaxation.¹⁴ The difference, $\Delta L = L_{4.0} - L_0$, represents to the first approximation the magnitude of extrusion shrinkage that occurred during the slow recovery period.

In the earlier study¹¹ it was shown that at constant carbon black loading in SBR-1500, carbon black surface area and structure influence the L_0 value but have almost no effect on ΔL . This study has been extended now to other polymers, and it was found that the effect of carbon black is similar in all rubbers tested (Fig. 2). In particular, the value of ΔL remained independent of carbon black properties; however, ΔL was found to be affected by the polymer. As Table II shows, ΔL is equal to approximately 14–16% for natural and butyl rubbers, while SBR and BR gave ΔL values typically in the 26–29% range. On the other hand, the values of L_0 were influenced by both the nature of the polymer phase and the carbon black characteristics.

Since ΔL originates from disorientation of molecular chains that became oriented in the extensional flow region at the die entrance,¹¹ it may be expected

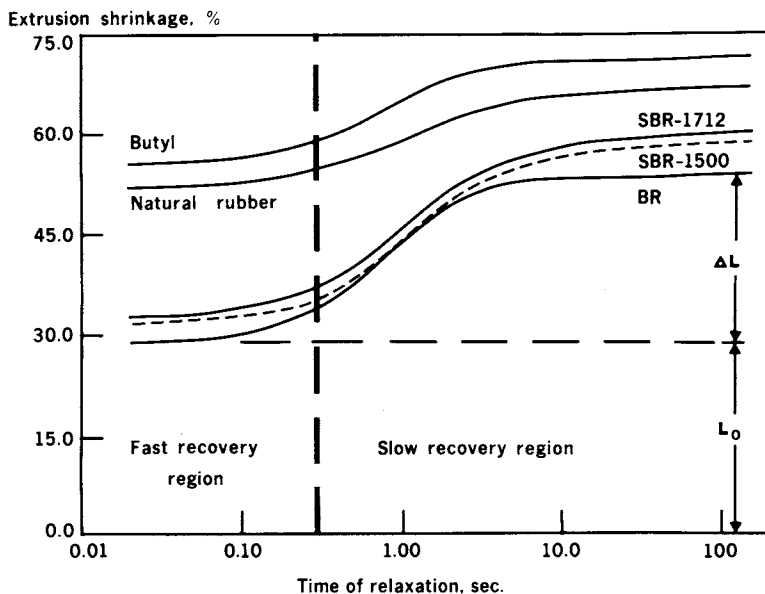


Fig. 2. Postextrusion relaxation of various rubbers containing 50 phr N330 black.

that the degree of orientation should be a function of the stress required at a given rate of deformation. Thus, ΔL should be related to extensional viscosity, assuming that the differences in internal friction are not significant. In filled materials, the extensional viscosity depends also on loading and morphology (size and shape) of filler aggregates.¹ Thus, it is not surprising that for any given carbon black there is a correlation between the ΔL values and extensional viscosity measured at different strains (elongations): the two polymers giving the lowest ΔL values have also the lowest extensional viscosity (Table II). Note that extensional viscosity at a given extensional rate depends on the actual strain¹ for all carbon-black-filled rubbers.

The same two polymers (i.e., natural and butyl rubbers) have also the highest L_0 values, suggesting that some dependence may exist between the two types of deformation. The polymers exhibiting low extensional viscosity give low ΔL values and high L_0 values, indicating a strong molecular network that can store more energy during deformation.

No correlation was found between extrusion shrinkage and Mooney viscosity (shear flow) or resilience of uncured compounds (Table II).

Extrudate Appearance

The melt fracture phenomenon in polymers has been studied extensively in the plastics industry, and a number of mechanisms have been proposed¹⁶ to account for the observed behavior. However, Everage and Ballman¹⁷ have pointed out the fallacy of relating melt fracture phenomenon to shear flow measurements since numerous direct visualization studies of velocity profiles²⁻⁴ and streaming birefringence patterns of melts⁶ indicate that melt fracture is often initiated at die entrance in the region of extensional flow. Tokita and Pliskin¹⁸ studied the processability of elastomers (SBR, BR) and in particular their yield

TABLE II
Extrusion Characteristics in Various Rubbers^a

| Carbon black type | Polymer | Mooney viscosity ML-4 | Resilience R.E. | Extension viscosity ^b MPa-sec at | | Extrusion Shrinkage ^c $\frac{\Delta L}{L_0}$, % |
|-------------------|----------|-----------------------|-----------------|---|------------------|---|
| | | | | $\epsilon = 0.5$ | $\epsilon = 1.5$ | |
| N231 | NR | 75 | 57.4 | 6.11 | 23.8 | 54.0 |
| | Butyl | 92 | 25.4 | 8.68 | 22.4 | $\frac{15.1}{d}$ |
| | BR | 87 | 30.9 | 20.0 | 38.4 | 29.7 |
| | SBR-1712 | 74 | 42.6 | 14.5 | 49.3 | 37.5 |
| | SBR-1500 | 89 | 51.2 | 17.0 | 64.0 | 37.5 |
| N330 | NR | 76 | 59.7 | 4.42 | 13.7 | 52.4 |
| | Butyl | 90 | 25.7 | 6.97 | 13.8 | 55.6 |
| | BR | 74 | 30.6 | 15.9 | 36.7 | 28.8 |
| | SBR-1712 | 70 | 43.6 | 13.2 | 43.4 | 32.8 |
| | SBR-1500 | 90 | 53.6 | 14.4 | 37.4 | 29.1 |
| N550 | NR | 67 | 62.8 | 2.92 | 9.59 | 51.8 |
| | Butyl | 92 | 28.1 | 5.28 | 8.40 | 47.5 |
| | BR | 58 | 32.3 | 8.91 | 21.2 | 30.0 |
| | SBR-1712 | 68 | 51.8 | 9.79 | 19.2 | 23.1 |
| | SBR-1500 | 86 | 57.4 | 11.5 | 22.6 | 25.4 |
| N539 | NR | 67 | 64.1 | 2.92 | 9.07 | 52.0 |
| | Butyl | 91 | 27.6 | 4.96 | 8.07 | 49.7 |
| | BR | 58 | 32.2 | 8.87 | 21.5 | 29.1 |
| | SBR-1712 | 65 | 50.0 | 8.78 | 18.6 | 25.4 |
| | SBR-1500 | 83 | 58.0 | 10.8 | 20.2 | 26.9 |

^a Measurements done at 100°C, using 2 X 2-mm die.

^b Extensional viscosity at extensional rate of 0.006 sec⁻¹.

^c Rubber extruded at a shear rate of 360 sec⁻¹.

^d Smooth extrudate could not be obtained.

TABLE III
Elongation at Break as a Function of Mixing Time in a Model B Banbury

| Time of mixing, min | Elongation at break, % | |
|---------------------|------------------------|------------|
| | N326 black | N330 black |
| 1.0 | — | 31 |
| 1.5 | — | 23 |
| 2.0 | 44 | 46 |
| 4.0 | 87 | 160 |
| 6.0 | 150 | >220 |

and rupture characteristics. They identified “cheesy” and crumbling compounds as those exhibiting a low elongation at break. These observations are particularly significant when considered in relation to the discussion of extensional flow. Cogswell¹⁹ has recently pointed out that extensional flow occurs not only at the die entrance but also at the die exit, where a thin layer at the extrudate surface is subjected to extension when it accelerates from zero velocity at the die wall to the average velocity of the extrudate. Thus, the polymer having low elongation to break may cause flow discontinuities at the die entrance, such as those observed by Bagley and Birks,² leading to non-uniform cross section of extrudate (“bamboo” effect). Such a polymer may also exhibit crazing of the surface, or even tearing of the extrudate, due to extensional flow region at the die exit. The latter effect would be further enhanced with dies of non-uniform cross section such as the Garvey die (ASTM method D-2230), which is 6 mm thick in its thickest section and 1.0 mm at the thinnest edge. In present experiments a “mini-tread” die specially designed by Laube²⁰ was employed in order to avoid curling of the extrudate that was observed with the Garvey die. The “mini-tread” die is a modified slit die, 16 mm wide, 1 mm long (i.e., “land”), 4 mm thick in the center, and tapering off to 1 mm at each end.

In order to test the relationship between extrusion appearance and extension to break, a number of compounds was prepared by mixing 50 phr carbon black with butadiene rubber (BR) in a model B Banbury mixer for various time periods. These compounds were then extruded through the Brabender extruder at 100°C using the “mini-tread” die. The appearance of extrudates is shown in Figure 3. As the time of mixing increased, both the surface roughness and the number

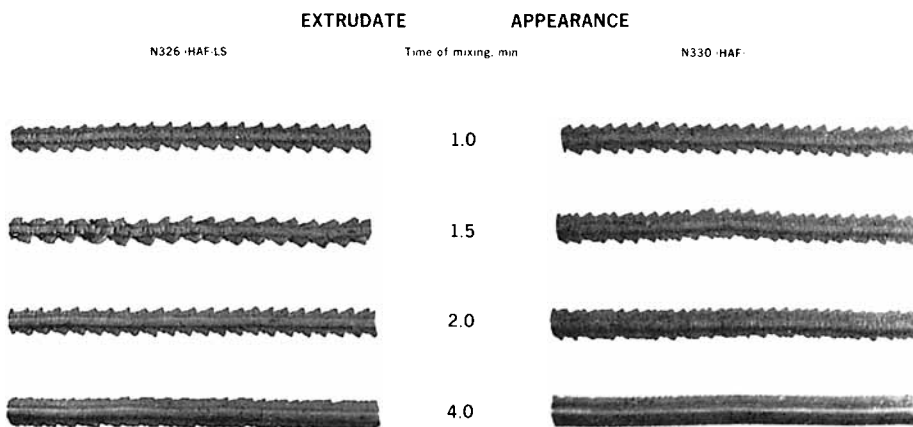


Fig. 3. Extrudate appearance.

of cuts at the edges decreased. At each mixing time, the N326 black gave poorer extrudate than N330 black.

The measurements of elongation at break (Table III) are in agreement with the visual observations of extrusion appearance. At mixing times of 1.0 to 2.0 min, the elongation at break remained very short, less than 50%. At the mixing time of 4.0 min, elongation at break of the N330 compound improved dramatically to 160% while N326 black still remained at less than 100%. A further improvement was noted at 6.0 min mixing time. From these observations it would appear that satisfactory processability can be obtained with compounds having an elongation at break greater than 100–150%.

The extrudate from the 2×2 -mm cylindrical die also had some fine surface discontinuities, but these were less pronounced than those observed with extrudates from the "mini-tread" die. This difference was caused by additional tearing of rubber during the passage through the irregularly shaped die. For a power law fluid (such as rubber), where $\tau = (\eta_0/\gamma_0)\gamma^n$, it can be shown that the average linear velocity of fluid flowing at constant pressure P through a cylindrical die of radius R is

$$V = \frac{\eta\gamma_0 R}{3n + 1} \left(\frac{RP}{2\eta_0 \cdot \gamma_0 L} \right)^{1/n} \quad (9)$$

where η_0, γ_0 are constants, n is equal to approximately 0.28 for rubbers, and the other symbols have been defined already. Therefore, the linear velocity V is proportional to $R^{(1+1/n)}$; i.e., for rubbers it is approximately proportional to the fourth power of the radius. Thus, the ratio of velocities in the thick section ($R = 2.0$ mm) and thin section ($R = 0.5$ mm) of the "mini-tread" die would be approximately equal to 256 if the two sections were not connected. With the actual open geometry of this die, the ratio of the velocities is not as great, but it still introduces a very large strain between the thin edge and the center of the die.

CONCLUSIONS AND SUMMARY

Evidence has been presented correlating both extrusion shrinkage and extrudate appearance with the behavior of rubbers during the extensional flow. Since the extensional flow occurs at the die entrance and some relaxation takes place within the die, the significance of extensional flow is particularly important with the short dies, such as the ones commonly used in the rubber industry.

At the die entrance and the die exit the polymer is being subjected to extensional flow which causes significant orientation of macromolecules and deformation of molecular network. If the imposed strain is greater than the elongation at break of the compound, fracture of the rubber occurs and results in poor extrusion appearance: torn edges and rough surface.

A good correlation was found between visual rating of extrudate appearance and the elongation at break of butadiene rubber stocks mixed for different times with N330 and N326 blacks.

The process of extrusion shrinkage can be separated into two distinct regions. At very short times of less than 0.02 sec after exit from the die, the observed extrusion shrinkage is attributed to elastic (solidlike) recoil of polymer network. This is followed by a much slower process believed to represent disorientation of macromolecular chains. This behavior was established for five elastomers with four grades of carbon black.

The magnitude ΔL of extrusion shrinkage occurring during the slow relaxation region was shown to increase with increasing extensional viscosity of the rubber containing a given carbon black. There is also an inverse relationship between the ΔL value and the extent of extrusion shrinkage L_0 that was completed during the initial fast recovery region.

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