Extrusion Die Swell of Carbon Black-Filled Natural Rubber

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Synopsis

Extrusion die swell of natural rubber compounded with a wide variety of carbon blacks has been determined in a capillary rheometer using a long circular die. The range of variation of carbon black loading, surface area, and structure are, respectively, 10 to 60 phr, 44 to 124 m^2/g, and 78 to 120 cc/100 g. The effective carbon black volume fraction ϕ_e not participating in the strain recovery leading to die swell is assumed to be the sum of the actual filler volume fraction and the fraction of unextractable rubber determined experimentally for each compound. Bagley and Duffey's analysis of extrusion die swell of unfilled polymers as unconstrained elastic recovery was adopted for a filled elastomeric system whose relative shear modulus (G/G_0) is assumed to vary as $(1 - \phi_e)^{-N}$. The matrix shear modulus G_0, originally introduced by Nakazima and Shida on the basis of a linearized approximation, will depend on the shear stress level because of nonlinear deformation. The power N will vary with shear stress which changes the orientation of carbon black aggregates. Except for these features, die swell data for a wide range of carbon black compounds fall on a single curve when plotted in the manner of the predicted relation between the wall shear stress, die swell, and ϕ_e. Replacing ϕ_e by Medalia's ϕ' based on an equivalent sphere concept introduces a larger scatter around the mean curve.

INTRODUCTION

Controlling the elastic response of filled rubbers subjected to varying processing conditions and a variable composition is a major problem in rubber extrusion and calendering. This elastic response manifests itself as die swell in rubber extrusion and thickness swell in calendering. Measurements by Cotten[1] and White and Crowder[2] show that the extrusion die swell of carbon black-filled rubber compounds is influenced by the temperature, the strain history, and the composition of the polymeric system. For example, the extrusion die swell varies widely with reinforcing carbon black properties for black compounds having the same filler volume fraction and subjected to identical operating conditions. It would be quite useful, therefore, to have a relation for a particular rubber between the extrusion die swell, the filler volume fraction, and the filler properties when any filled compound of the same rubber is subjected to a given processing condition. Such a relation will be simpler than a comprehensive relation between extrusion die swell, filler volume fraction, properties of the filler as well as the polymer, and the strain history.

Cotten's[1] attempt to obtain a master curve of shear stress versus corrected die swell, $B/(1 - \phi)$, from his data of extrusion die swell B of various SBR compounds

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with filler volume fraction ϕ failed for high structure blacks. Medalia's[3] replacement of ϕ by an effective volume fraction of black aggregates ϕ' based on an equivalent sphere model of a black aggregate did not result in a master curve for a high-structure carbon black, N-220. White and Crowder[2] encountered an enormous amount of scatter while correlating the die swell with the variable [(ϕ × DBP*)/particle diameter] for carbon black compounds of SBR and BR-1 under constant extrusion conditions. More success is likely if the recent theories[4-7] for extrusion die swell of molten polymers are applied to filled rubbers with a better estimate of the effective volume fraction of black aggregates.

In this work, the extrusion die swell of carbon black-filled natural rubber compounds has been measured with a long capillary fitted in a capillary rheometer for a wide range of carbon black loading, surface area, and structure. The amount of rubber unextractable from any compound has been determined to provide an alternate estimate of the effective filler aggregate volume fraction. The theory of the solid-like response of the extrudate on emerging from a die as proposed by Nakazima and Shida[4] and developed further by Bagley and Duffey[5] has been used along with likely expressions for modulus reinforcement by fillers to obtain a master curve for the die swell data. Such a die swell master curve may also be quite useful for polymer–filler systems not used in this work.

THEORY

Whenever a rubber compound or a polymer melt is extruded through a capillary of diameter d_c, the extrudate diameter swells to a value d_e, larger than d_c. The ratio d_e/d_c, often denoted by B, is called the die swell. Metzner et al.[8] related the die swell to the normal stress differences by a macroscopic mass and momentum balance on the exiting fluid. Since the normal stress differences predicted thus from the die swell data on molten polystyrene were several orders of magnitude smaller than those from a cone-and-plate rheometer, Graessley et al.[6] considered the die swell to result from an unretarded solid-like recovery from elastic strain imparted to the highly viscous polymer in the capillary. This was suggested earlier by Nakazima and Shida,[4] who obtained the following relation between the die swell B and the recoverable shear strain $\bar{\sigma}$ averaged over the cross section:

$$\bar{\sigma} = B^2 - B^{-4} \qquad (1)$$

Following Nakazima and Shida's[4] analysis, Bagley and Duffey[5] treated the elastic melt as a Mooney material with a one-constant stored energy function W, so that

$$W = C_1 (I_1 - 3) + C_2 (I_2 - 3) \qquad (2)$$

with $C_2 = 0$, and obtained

$$(\bar{\sigma})^2 = B^4 - B^{-2} \qquad (3)$$

In terms of the principal extension ratios λ_1, λ_2, λ_3, the strain invariants I_1, I_2, and I_3 are as follows:

* DBP: Dibutyl phthalate absorption value.

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \tag{4}$$

$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2$$

Due to incompressible flow, I_3 is assumed to be unity and $\lambda_1 = B^2$, whereas $\lambda_2 = \lambda_3 = \lambda_1^{-1/2}$. The recoverable shear strain is usually defined on the basis of Hooke's law in shear, which seems to hold for most polymers:

$$\sigma = \tau J_0 \tag{5}$$

where τ is the shear stress and J_0 is the shear compliance. For an averaged recoverable shear strain $\bar{\sigma}$ and wall shear stress τ_w,

$$\bar{\sigma} = \tau_w \bar{J}_0 \tag{6}$$

where $\bar{J}_0$ is J_0 times a constant factor f arising out of the averaging process. Substitution of $\bar{\sigma}$ from eq. (6) into eq. (3) leads to

$$\frac{\tau_w}{(B^4 - B^{-2})^{1/2}} = \frac{1}{\bar{J}_0} \tag{7}$$

Bagley and Duffey[5] further simplified eq. (7) by relating the elastic shear modulus G to J_0 by

$$G = \frac{1}{J_0} \tag{8}$$

so that we obtain

$$\tau_w = \frac{G}{f} (B^4 - B^{-2})^{1/2} = \bar{G}(B^4 - B^{-2})^{1/2} \tag{9}$$

Since Nakazima and Shida's[4] approach should be regarded as a linearized approximation, the shear modulus G is a modulus of linear deformation which may depend on shear rates (and therefore for a given compound on τ_w). Further, the modulus G is time dependent. But for die swell in dies with large l/d_c ratio, the entrance strain may be assumed to have decayed so that the die swell should reflect the recovery from deformations due to steady shear flow.

For a given wall shear stress τ_w, reinforcement of the rubber by fillers will lead to a modulus G larger than that of the virgin polymer G_0. White and Crowder[2] have suggested that a mechanistic theory based on the continuum mechanical analysis of a suspension of particles in a viscoelastic medium provides a better explanation of filler reinforcement of polymer melts than the one based on the idea of a temporary entanglement network containing carbon black fillers. They have concluded that the relation between the modulus G of the reinforced melt and G_0 of the virgin polymer is likely to be as follows:

$$G(t, \pi_d) = G_0(t, n\pi_d)(1 + \alpha_1 f_1 \phi_e + \alpha_2 f_1^2 \phi_e^2 + \ldots) \tag{10}$$

where ϕ_e is an effective filler volume fraction containing the black as well as any occluded rubber; f_1 is an anisotropy factor; α_1 and α_2 are given constants; and n is a number greater than unity and is an increasing function of ϕ_e. This form was anticipated by Pliskin and Tokita,[9] who had suggested the use of theoretical expressions for viscosity variation with filler concentration to modulus variation

since theoretical derivations for composite moduli are somewhat simplistic. Pliskin and Tokita[9] have also shown that the viscosity η of filler-reinforced rubber varies with the effective filler volume fraction ϕ_e as

$$\eta/\eta_0 = (1 - \phi_e)^{-N} \tag{11}$$

where η_0 is pure gum viscosity and N is a parameter depending on the orientation of the fillers. An expanded form of eq. (11) will lead to an expression very similar to that for G/G_0 suggested by eq. (10). Landel et al.[10] had empirically suggested an equation similar to eq. (11) for the viscosity of a suspension of particles of arbitrary size and shape randomly distributed in a Newtonian liquid with $N = 2.5$ and $\phi_e = \phi/\phi_m$, where ϕ_m is the maximum volume fraction of particles. Brinkman[11] obtained the following relation for the composite shear modulus G for inert fillers at high values of ϕ:

$$G = G_0(1 - \phi)^{-5/2} \tag{12}$$

The shear modulus G of filler-reinforced elastomers may therefore be presumed to vary with an effective filler volume fraction ϕ_e as

$$G = G_0(1 - \phi_e)^{-N} \tag{13}$$

Combining eq. (13) with eq. (9) derived earlier, we get

$$\tau_w = \frac{G_0}{f} \frac{(B^4 - B^{-2})^{1/2}}{(1 - \phi_e)^N} \tag{14}$$

If a plot of τ_w versus $[(B^4 - B^{-2})^{1/2}/(1 - \phi_e)^N]$ from any set of die swell data yields a straight line, the relation given in eq. (14) may be considered suitable for describing the extrusion die swell of filled elastomers. However, N is unknown and N as well as G_0 are likely to depend on τ_w. Even if the value of N as well as its dependence on τ_w may be estimated by the procedure described below, G_0/f may depend on τ_w and the manner of plotting suggested above may not lead to a straight line. Nevertheless, an improvement over the results of Medalia's[3] efforts will be achieved if the die swell data of a large number of compounds having a wide range of filler volume fraction and filler properties collapse on a single curve obtained by plotting τ_w versus $[(B^4 - B^{-2})^{1/2}/(1 - \phi_e)^N]$.

For a given wall shear stress, the exponent N may be obtained from the slope of a log–log plot of $(B^4 - B^{-2})^{1/2}$ versus $(1 - \phi_e)$. The parameter N determined thus will depend, among others, on shear stress (or shear rate). From the results of viscosity of carbon black-filled elastomers, Pliskin and Tokita[9] have suggested that N depends on the filler orientation in the matrix and varies between 1.0 for a completely laminated material and 2.5 for a random suspension of discrete particles. For a given filler, a laminated arrangement will lead to a higher shear modulus than a random suspension. Thus, as orientation increases, N is likely to increase here, so that at higher shear stresses higher N is likely, unlike that for viscosity of filled rubbers. In carbon black-filled elastomeric systems, carbon black particles exist as anisotropic multiparticle aggregates.[3] Increase in the orientation of aggregates with increasing τ_w is thus quite likely.

A word about our choice of eq. (3) from Bagley and Duffey[5] is necessary. We could have chosen the expression

$$\tau_w = \sqrt{3}G(B^4 - 2B^{-2} - 3)^{1/2} \tag{15}$$

obtained by Vlachopoulos et al.[12] from the analysis of Graessley et al.,[6] who had

incorporated the possibility of variation of velocity as well as stored elastic energy with diametral position which Bagley and Duffey[5] did not. Additional expressions due to Mendelson et al.[13] and Tanner[7] are also available. However, Vlachopoulos et al.[12] have shown that the differences between eqs. (1), (3), and (15) are negligible for polystyrene. Further, they have shown that the differences between Tanner's[7] and Graessley et al.'s[6] expressions are not too great. Thus, the choice of eq. (14) based on eq. (3) is realistic. It is to be reemphasized here that only die swell from a long die is being considered to eliminate the effect of entrance strains.

The effective filler volume fraction ϕ_e in eq. (14) is the combined volume fraction of carbon black and the unextractable rubber as would be obtained in a bound rubber type of measurement.[9] The unextractable rubber consists of (1) bound rubber, the interparticular rubber and adsorbed rubber which is either physically or chemically bonded to the particle surface; (2) soluble rubber; inside the filler aggregates there is some polymer which cannot be extracted through network openings because of its molecular size.[9,14-16] For each rubber compound, the unextractable rubber content has to be measured to obtain ϕ_e:

$$\phi_e = \phi_{\text{carbon black}} + \phi_{\text{unextracted rubber}} \tag{16}$$

Such a definition is simple and clearly specifies the fraction of rubber which is taking part in supporting stresses in the system. Tokita and Pliskin[9] used it successfully for the viscosity of filled rubbers and further found that the tensile modulus variation at low strains fell on a single curve if such a ϕ_e is used. Of course, the gel portion of pure gum should not be considered in ϕ_e of eq. (16).

Other estimates of the effective filler volume fraction are those due to Medalia[3] and Kraus.[17,18] Medalia's[3] estimate of ϕ_e is

$$\phi' = \frac{1 + (0.02139)(\text{DBP}_{\text{abs}})}{1.46} \tag{17}$$

and is based on the postulate that a filler aggregate in rubber behaves as an equivalent sphere within which rubber is occluded, the amount of occluded rubber being equal to the amount of occluded DBP at a "soft ball" endpoint. Kraus's[17,18] estimate of ϕ_e is as follows:

$$\phi'' = a\phi \tag{18}$$

where

$$a = (24 + A)/(24 + A_0) \tag{19}$$

and A and A_0 are, respectively, the DBP values of any carbon black and a reference carbon black. Both ϕ' of Medalia[3] and ϕ'' of Kraus[17] emphasize the structure of the filler while neglecting polymer–filler bonds formally. The definition ϕ_e of eq. (16) does not neglect polymer–filler bonds. Further, the unextractable rubber increases significantly with filler structure (see Table III). Thus, ϕ_e of eq. (16) is likely to incorporate various features responsible for the three reinforcement modes[27] in filled rubber systems. None of the definitions ϕ_e, ϕ', and ϕ'' take into account the number of polymer–filler bonds which are broken during extrusion. However, measuring the unextractable rubber before and after extrusion may enable suitable alteration of ϕ_e as given by eq. (16).

TABLE I
Carbon Black Characteristics

Type	ASTM no.	Manufacturer	Surface area, m^2/g	DBP,[a] cc/g
ISAF-HM	N-220	Phillips	124	1.15
ISAF-LS	N-219	United	123	0.78
HAF-HS	N-339	Phillips	99	1.20
FEF	N-550	Phillips	44	1.19

[a] DBP: Dibutyl phthalate absorption value, ASTM D-2414-65T (1967).

EXPERIMENTAL

Preparation of Compounds

The natural rubber used was smoked sheet of grade RMA-1 from Plantation Corporation of India Ltd., Kottayam, Kerala, India. Only furnace-type carbon blacks with their properties listed in Table I were used in this study. The carbon black surface area was varied from 44 m^2/g to 124 m^2/g. The carbon black structure indicated by the DBP absorption value was varied from 78 cc/100 g to 120 cc/100 g. In an 8-in. laboratory mill, the carbon black was dry mixed with rubber at 100°C for 15 min without any oil or additives. Four carbon black loadings of 10, 25, 40, and 60 phr were used for each of the four blacks listed in Table I. The composition of each compound with a sample number is given in Table II.

Determination of Unextractable Rubber

The fraction of total rubber unextracted by solvent was found in the manner of Brennan,[16] Pliskin et al.,[9] Medalia,[19] and Cotten.[20] A sample weighing about 0.2 g was weighed on an analytical balance, cut into small strips, and placed inside

TABLE II
Sample Compositions of Natural Rubber Compounds

Sample no.	Carbon black	Filler load, phr
1	N-220	10
2	N-550	10
3	N-339	10
4	N-219	10
5	N-220	25
6	N-550	25
7	N-219	25
8	N-339	25
9	N-220	40
10	N-339	40
11	N-219	40
12	N-550	40
13	N-220	60
14	N-339	60
15	N-219	60
16	N-550	60

a preweighed cage of 200-mesh stainless steel wire cloth. The cage containing the sample was placed into a stoppered bottle containing 100 ml cyclohexane. The samples were stored at room temperature for 72 hr. The cage holding the unextracted rubber compound was then removed from the solvent, dried at 50°C to constant weight, and reweighed to obtain W_g, the weight of dried gel. The percentage unextracted rubber was calculated on the basis of the total amount of rubber available:

$$\text{unextracted rubber per cent} = [(W_g - F)/R] \times 100 \qquad (20)$$

where R is the weight of rubber in the original sample in which the weight of the filler is F. Equation (20) leads to the following value of the $\phi_{\text{unextracted rubber}}$ defined in eq. (16):

$$\phi_u = \phi_{\text{unextracted rubber}} = (1 - \phi) \, [(W_g - F)/R] \qquad (20a)$$

This estimate of ϕ_u contained any amount of gel preexisting in the natural rubber. The gel content of the unmilled natural rubber of this study was found to be 3%. This has not been subtracted from ϕ_u since all compounds will have the same contribution of this gel which will influence the die swell only marginally.

Measurement of Extrusion Die Swell

Since it is known from Bagchi[21] that most workers[22-24] in this field have used the gravimetric technique to obtain die swell of filled rubber samples, the gravimetric method was adopted in this work. When, at a given shear rate, the steady-state flow was established through the capillary fitted to the capillary rheometer, the extrudate was cut off as close as possible to the die and discarded. Then a strand about 2.0 cm long was allowed to be extruded and was cut off at the die. This strand was then allowed to relax for 2 hr, after which it was cut to a fixed 21-mm length and placed on a preweighed aluminum foil. After 24 hr, this foil with the strand was weighed. The die swell B ($= d_e/d_c$) was obtained from the following estimate of the diameter (mm) of the extrudate of length L (mm) and weight w (g):

$$d_e = (4w/\pi L\rho)^{1/2} \qquad (21)$$

where the density ρ (g/mm^3) of each of the 16 compounds was measured by the displacement method as per D-792, ASTM, part 27, 1965. The extrusion of the rubber compounds was carried out in a versatile capillary rheometer described in detail in Kumar.[25] The extrusion temperature was maintained at 107°C. For the die swell studies, a long capillary 1.08 mm in diameter and 29.9 mm long was used. Since the oil-free rubber compounds of this work exhibited melt fracture at low shear stress levels, the measurements were limited to low shear stresses to ensure smooth extrudates. To obtain extrudate surfaces unaffected by bubble bursts, each compound to be tested was cut in small strips and filled in the rheometer barrel such that there was no air gap.

Measurement of Wall Shear Stress

All die swell experiments simultaneously recorded the force on the piston as measured by a load cell and the downward speed of the piston as it pushed the polymeric compound out of the barrel and through the capillary. The capillary

rheometer used in this work was operated in the constant speed mode so that the piston speed was independent of its position in the barrel. The wall shear stress obtained from these measurements were affected by the pressure loss in the 90°-type capillary entrance section. So the true wall shear stresses were obtained by Bagley's[26] end correction formula

$$\tau_{wc} = \frac{R(\Delta P)}{2(l + Nd_c)} \qquad (22)$$

where l is the length of the capillary of diameter d_c and radius R and Nd_c is the fictitious tube length that has to be added to the actual capillary length l so that the correct pressure gradient in the capillary is known from the overall pressure drop ΔP. The entrance correction N was obtained graphically by plotting ΔP versus l/d_c at constant values of apparent shear rates for capillaries with different l/d_c values and determining the negative intercept on the l/d_c axis as shown in Figure 1. Three capillaries were used having l/d_c values of 27.8, 20, and 5, respectively, and the same capillary diameter. The value of the intercept N was found to be about 12 for the compound containing 10 phr N-220 carbon black. This compound has one of the lower values of viscosity among the various compounds used in this work. The value of the intercept for the compound containing N-220 carbon black at 60 phr loading was found to be 9. This compound had one of the highest values of viscosity among the various compounds of this
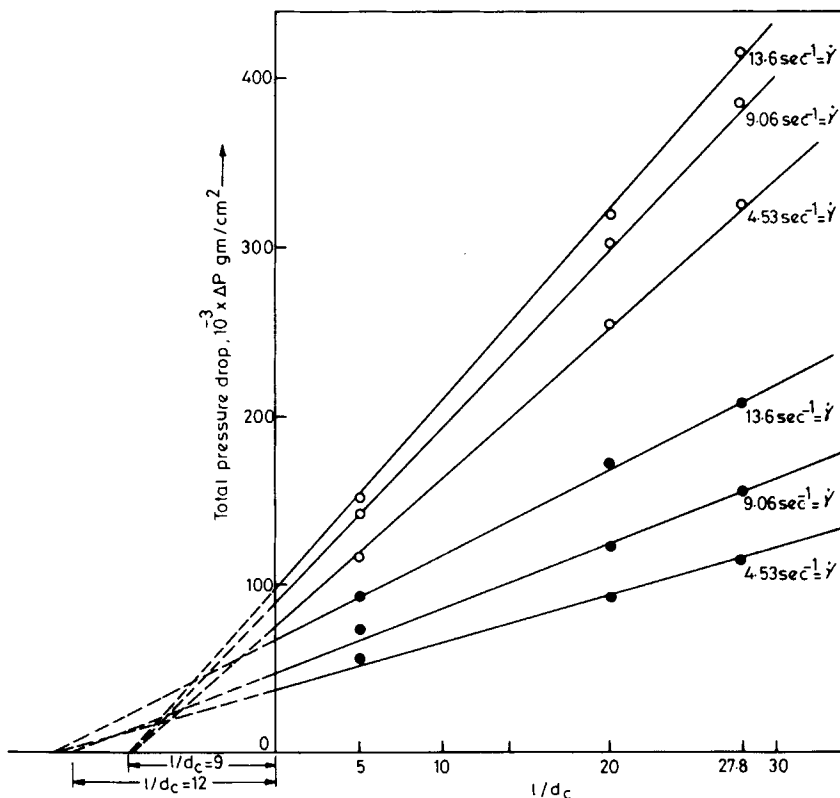

Fig. 1. Capillary end effect determination by Bagley's method; ΔP vs l/d_c for three values of apparent shear rates: (O) 60 phr N-220; (●) 10 phr N-220.

work. Further, the elasticity of this compound will be quite low compared to the compound with 10 phr loading. It was therefore expected that the intercept value at other loadings will be intermediate between these two values. Accordingly, instead of making measurements on every compound, the intercept values assumed are 11 for 25 phr loading and 10 for 40 phr loading, with no variation between carbon blacks.

No barrel pressure drop correction was made on the ΔP values used for end correction studies. Preliminary studies with representative black compounds revealed a negligible change in the force reading as the barrel length was traversed with the long die of l/d_c ratio 27.8 used for all die swell studies. For the second capillary of l/d_c ratio 20 used in end correction studies, preliminary studies also indicated negligible barrel pressure drop. This behavior is also encountered in the literature. For example, Penwell and Porter[28] as well as Boghetich and Kratz[29] had concluded that barrel frictional losses were negligible at high l/d_c values of the capillary. The conclusion of Einhorn and Turetzky[30] is similar. Only for the capillary of l/d_c ratio 5 used for end correction studies, the barrel pressure drop was found to be around 10% of the total pressure drop. The relatively minor effect of this on the end correction N suggested total neglect of correction for pressure drop in the barrel.

RESULTS AND DISCUSSION

The extrusion die swell B of each of the 16 carbon black-filled natural rubber compounds has been plotted separately against τ_{wc} in Figure 2. In this series of compounds with filler loading varying between 10 and 60 phr, the filler surface area was varied between 44 and 124 m^2/g while the DBP absorption value indicating the carbon black structure varied from 78 to 120 cc/100 g. Although quite
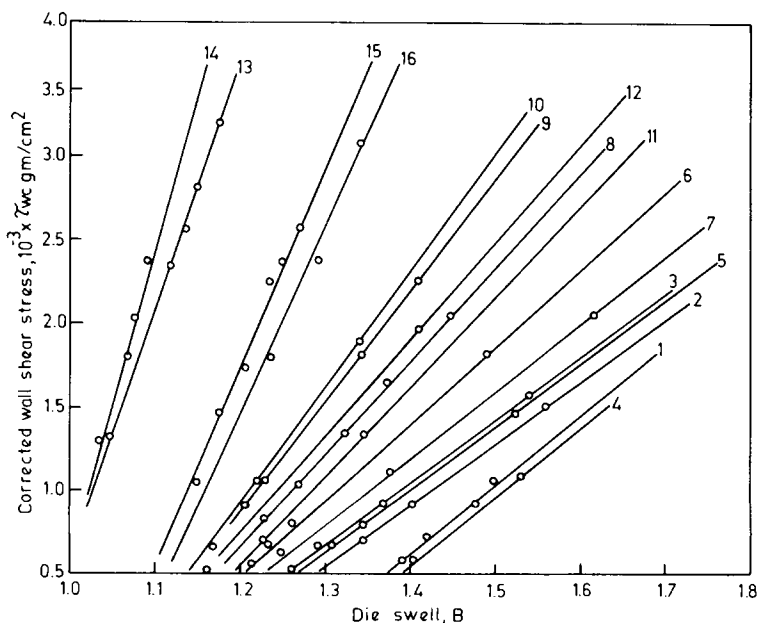

Fig. 2. Corrected wall shear stress vs die swell.

a few compounds have identical black loadings, Figure 2 shows that not a single pair of compounds has identical die swells at any shear stress level.   Figure 3 shows a plot of a free rubber volume fraction $1 - \phi_e$ based on definition (16) versus the die swell B for five values of τ_{wc}.   It indicates, however, that for a fixed τ_{wc} and a long die the die swell of natural rubber compounds with a wide variety of carbon blacks and a wide range of filler loadings correlate well with the free rubber volume fraction.   Thus, at constant τ_{wc}, the die swell increases as $1 - \phi_e$ increases.   The effective filler volume fraction ϕ_e used in Figure 3 has been determined for all the 16 compounds and reported in Table III.   If for a particular value of τ_{wc}, the curve of $1 - \phi_e$ versus B in Figure 3 contains less than 16 points, it is due to the fact that the die swell was not measured for some compounds either because of the onset of melt fracture or because of extremely low values of die swell.   In Figure 4, the free rubber volume fraction $1 - \phi'$ based on Medalia's definition (17) has been plotted against the die swell B for all the 16 compounds for the same values of τ_{wc} as in Figure 3.   A straight line has been drawn for each value of τ_{wc} to accommodate as many compounds as possible.   But it is obvious that there exists too wide a scatter to conclude that, for a fixed value of τ_{wc}, the die swell of natural rubber compounds with carbon black correlates well with the estimate of the free rubber volume fraction provided by $1 - \phi'$.

We would now like to find out whether increases in carbon black structure and decreases in particle size produce corresponding decreases in extrudate die swell B as was observed by White and Crowder[2] for SBR.   To this end, we select a pair of blacks whose surface areas are the same but the structures are quite different and another pair whose structures are the same but the surface areas are quite different.   This is shown in Table IV, where N-220 and N-219 have about the same surface area but N-220 has a much higher structure.   At the same loading, the die swell is always less with the black of higher structure, except at 25 phr.   Further, as the free rubber volume fraction increases, the die swell increases at
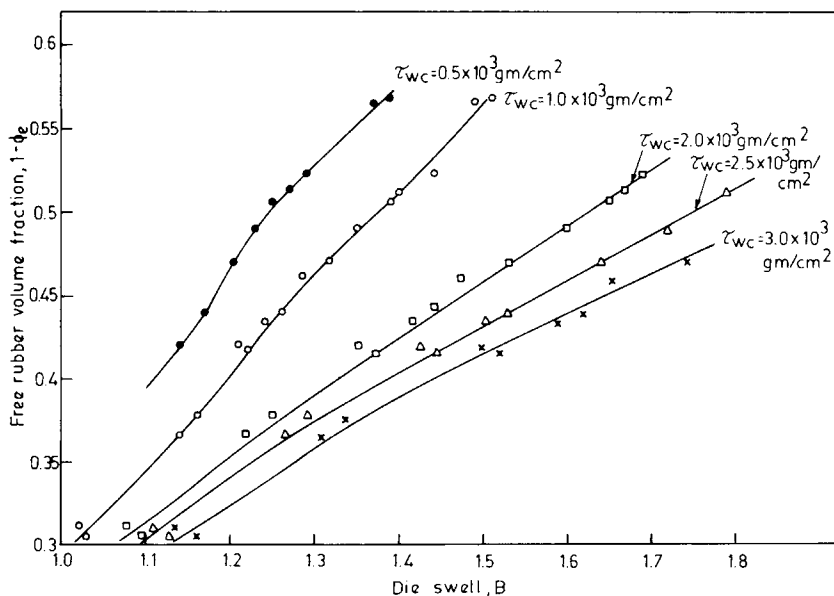

Fig. 3. Free rubber volume fraction vs die swell.

TABLE III
Effective Filler Volume Fraction ϕ_e of NR–Carbon Black Compounds

| Type of carbon black	Load, phr	Filler volume fraction ϕ	Unextracted rubber, eq. (20), %	Volume fraction of unextractable rubber ϕ_u	$\phi_e = \phi + \phi_u$	$1 - \phi_e$	Sample no.
N-220, S.A. 124 m²/g, DBP 1.15 cc/g	10	0.047	40.5	0.386	0.433	0.567	1
	25	0.110	42.5	0.378	0.488	0.512	5
	40	0.165	50.3	0.419	0.584	0.416	9
	60	0.228	60.7	0.468	0.696	0.304	13
N-550, S.A. 44 m²/g, DBP 1.19 cc/g	10	0.047	45.2	0.430	0.477	0.523	2
	25	0.110	47.2	0.420	0.530	0.470	6
	40	0.165	47.8	0.400	0.565	0.435	12
	60	0.228	51.2	0.394	0.622	0.378	16
N-339, S.A. 99 m²/g, DBP 1.20 cc/g	10	0.047	46.8	0.447	0.494	0.506	3
	25	0.110	49.8	0.450	0.560	0.440	8
	40	0.165	49.6	0.415	0.580	0.420	10
	60	0.228	59.6	0.460	0.688	0.312	14
N-219, S.A. 123 m²/g, DBP 0.78 cc/g	10	0.047	40.4	0.384	0.431	0.569	4
	25	0.110	44.8	0.400	0.510	0.490	7
	40	0.165	44.7	0.374	0.539	0.461	11
	60	0.228	52.6	0.406	0.634	0.366	15
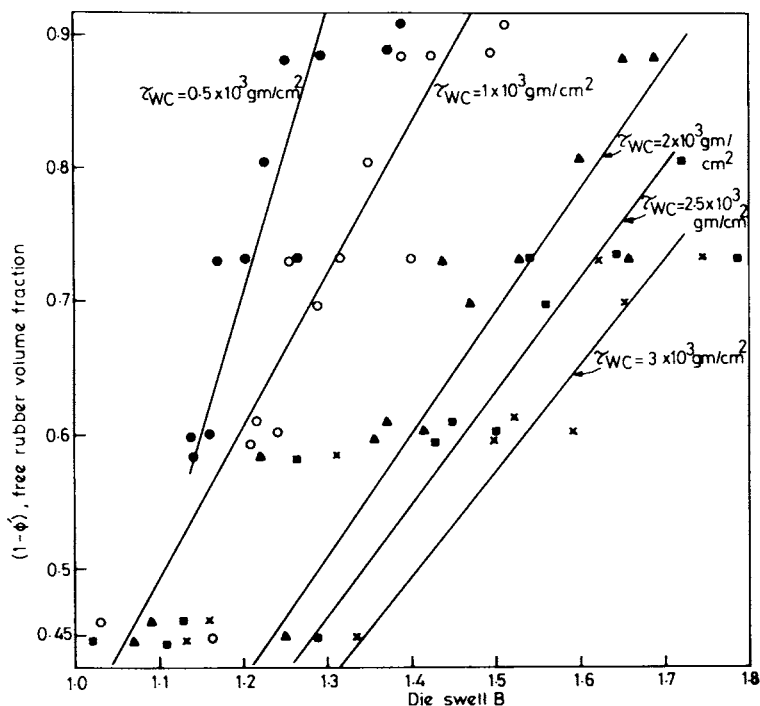
Fig. 4. Free rubber volume fraction according to Medalia[3] vs die swell. τ_{WC} (in g/cm²): (●) 0.5 × 10³; (O) 1.0 × 10³; (▲) 2 × 10³; (■) 2.5 × 10³; (×) 3.0 × 10³.

all loadings. For the pair N-339 and N-550 in the same table, the DBP values are almost identical but N-339 has a much larger surface area. One notices that N-339 compounds have lower die swell at all loadings. Further, at the same loading, an increase in free rubber volume fraction inevitably leads to higher die swell. Thus, the conclusions of White and Crowder[2] are valid for the NR com-

TABLE IV
Compound Die Swell Variation with Carbon Black Surface Area and Structure

Carbon black properties	Carbon black type			
	Structure variation		Surface area variation	
	N-220	N-219	N-339	N-550
Surface area, m²/g	124	123	99	44
DBP, cc/g	1.15	0.78	1.20	1.19
Black Loading				
10 phr				
B	less	more	less	more
$1 - \phi_e$	0.567	0.569	0.506	0.523
25 phr				
B	more	less	less	more
$1 - \phi_e$	0.512	0.490	0.440	0.470
40 phr				
B	less	more	less	more
$1 - \phi_e$	0.416	0.461	0.420	0.435
60 phr				
B	less	more	less	more
$1 - \phi_e$	0.304	0.366	0.312	0.378

pounds of this work. The anomalous behavior at 25 phr with N-220 and N-219 must have been due to accidental inadequate mastication and mixing of the compound during preparation.

We are not comparing any other combinations of blacks like N-220 and N-339 simply because while in this set there is an increase in surface area (less than that in the N-339, N-550 set), there is also a small increase in DBP. Therefore, there are possibilities of conflict between these two properties. Similar conclusions are valid for various other pairs of carbon blacks of this work. It is clear, however, that estimation of the free rubber volume fraction $1 - \phi_e$ is likely to be a still safer way of estimating an increase or decrease in die swell for a particular polymer–active filler system. If the filler surface properties affect the molecular weight distribution of the free rubber significantly, the above statement needs qualification, as is pointed out somewhat later.

The behavior of the die swell data of this work when plotted in the manner of Medalia,[3] i.e., τ_{wc} versus $B/(1 - \phi')$, where ϕ' is defined by eq. (17), will be investigated now. In Figure 5, for samples 1, 5, 9, and 13 of this work, τ_{wc} values were plotted versus $B/(1 - \phi')$, where B is the measured die swell and ϕ' is obtained from eq. (17). There is virtually no correlation, even though only the filler loading has been varied in these four samples, the carbon black in all four samples being N-220. Replacing ϕ' by ϕ_e or ϕ'' did not improve the correlation either. Therefore, the die swell data of all 16 compounds of this work were plotted in the manner of τ_{wc} versus $(B^4 - B^{-2})^{1/2}/(1 - \phi_e)^N$, as suggested by eq. (14). Before this was carried out, the value of the index N was determined at a particular value of τ_{wc} for all the compounds by plotting $(B^4 - B^{-2})^{1/2}$ versus $1 - \phi_e$ in a log–log plot shown in Figure 6. This was done for four values of τ_{wc}. In Figure 7, these values of N were used to plot all die swell data in the manner of eq. (14). It is clear from Figure 7 that almost all the data points cluster around a mean curve shown by the solid line. Considering that the data from all the 16
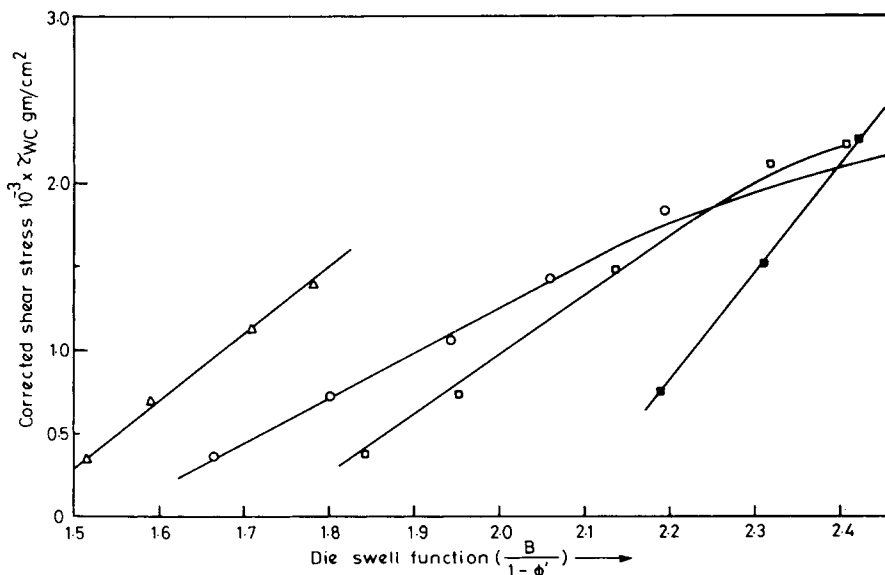

Fig. 5. Die swell plot according to Medalia[3]; τ_{WC} vs. $B/(1 - \phi')$ for N-220 carbon black at four loadings: (△) 10 phr; (O) 25 phr; (□) 40 phr; (■) 60 phr.
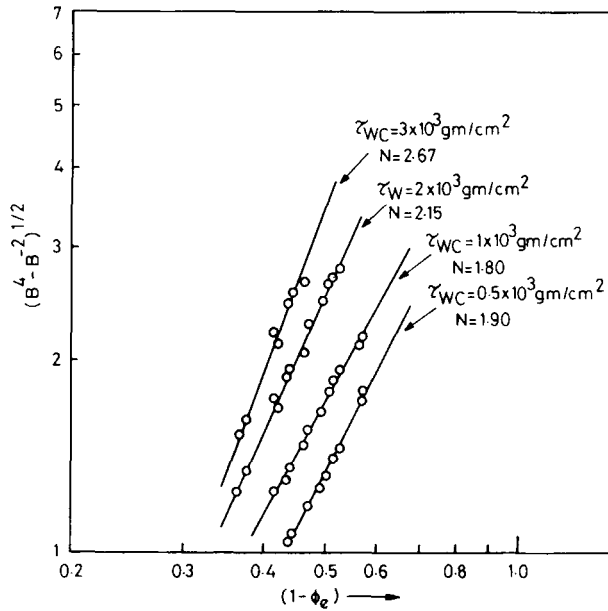
Fig. 6. Determination of N for particular shear stress. Die swell function $(B^4 - B^{-2})^{1/2}$ vs $1 - \phi_e$, the free rubber volume fraction, eq. (16).
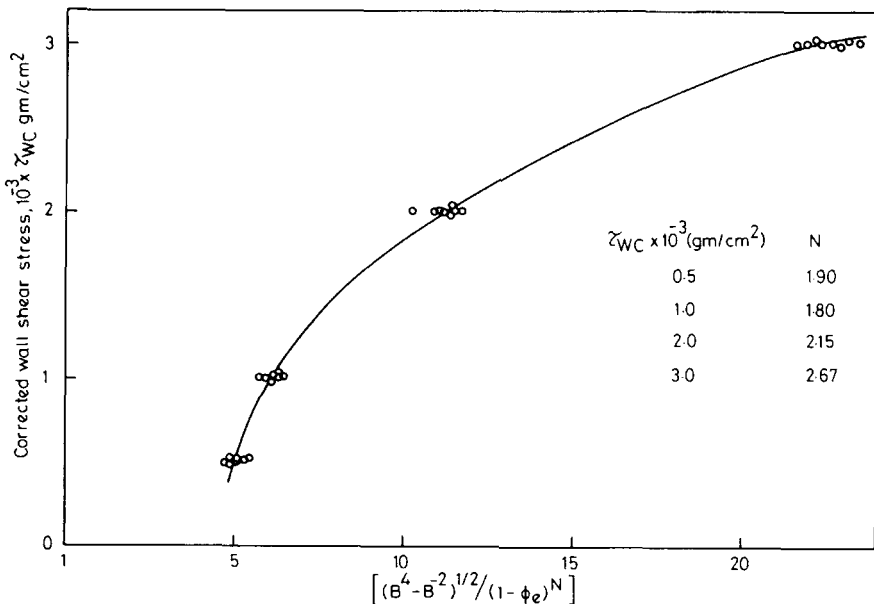

Fig. 7. Wall shear stress vs $(B^4 - B^{-2})^{1/2}/(1 - \phi_e)^N$ for all NR black compounds through a long die, $l/d_c = 27.8$, with ϕ_e determined from eq. (16) and N from Fig. 6. Plot of data according to eq. (14).

compounds over a range of shear stresses have been used in Figure 7, it may be concluded that the manner of plotting die swell data for filled rubbers suggested by eq. (14) may be much more useful than that suggested by Medalia.[3] Therefore, eq. (14) seems to represent a useful first step toward constructing a die swell master curve for all kinds of fillers dispersed in rubbers.

A look at the value of N obtained from Figure 6 indicates that N is increasing in general with increase in wall shear stress as was surmised earlier in the theory. However, this dependence of N on τ_{wc} is not enough to make the mean curve of Figure 7 a straight line, implying that the factor G_0/f of eq. (14) is a weak function of shear stress. In the framework of Nakazima and Shida's[4] theory, this is expected, since G_0 is a linearized approximation which will depend on the shear rate.

How well eq. (14) is able to correlate the present die swell data if the effective filler volume fraction estimate ϕ_c of eq. (16) is replaced by Medalia's[3] ϕ' of eq. (17) can be observed from Figure 8. The values of the slope N for four shear stress levels are also indicated in Figure 8. While the slope N increases in general with τ_{wc} (except for $\tau_{wc} = 1 \times 10^3$ g/cm^2) though somewhat more slowly than in Figure 6, the mean curve in Figure 8 fits the data with a much larger scatter at higher shear stress levels. This scatter would indicate that ϕ_e may be a better indicator of the effective filler volume fraction than ϕ'. In addition, the mean curve in Figure 8 has a much increased slope, indicating that a different and a higher estimate of G_0 is involved when ϕ_e is replaced by ϕ'. The behavior of a plot of all die swell data with ϕ'' of eq. (18) replacing ϕ' is exactly similar to that with ϕ' and is therefore not reproduced here.

It would be useful to consider the values of G_0 or G_0/f obtainable from Figures 7 and 8. While the estimate of G_0/f from Figure 8 is around 1×10^6 dynes/cm^2, that from the lower shear stress region of Figure 7 indicates a value of around 0.5×10^6 dynes/cm^2. Still smaller estimates of G_0/f are indicated from the slope at the higher shear stress region of Figure 7. These magnitudes of the shear
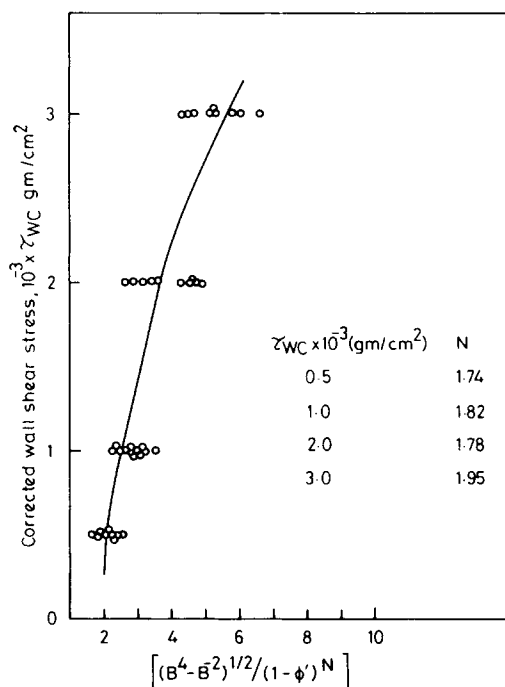

Fig. 8. Wall shear stress vs $(B^4 - B^{-2})^{1/2}/(1 - \phi')^N$ for all NR black compounds through a long die, $l/d_c = 27.8$, with ϕ' determined from eq. (17). Plot of data according to eq. (14).

modulus would appear to be characteristic of the transition between the rubbery plateau region and the flow region.

Estimating the amount of free rubber in a filled rubber sample may not be sufficient for predictive comparison of die swell between two compounds with the same volume fraction of two radically different carbon blacks. No estimate of the variation of the properties of the soluble rubber in the different compounds has, however, been made in this work, so that if there is any variation from compound to compound, their contribution to die swell is unknown. It is known from Cotten[1] that there is no appreciable die swell difference between SBR compounds containing the same loading of regular N-220 black and graphitized N-220 black. It is further known that regular N-220 black yields a much higher value of ϕ_e than does graphitized N-220 black. Even though these results apparently contradict the results of Figure 3 of this work, an explanation is possible in the framework of the theory presented earlier. It is shown in Table IV of Cotten[20] that the molecular weight of the soluble polymer increases considerably when a regular carbon black is replaced by the graphitized black of the same grade. This happens since high molecular weight fraction gets preferentially absorbed[20] on active carbon black surfaces. Estimating the shear modulus G_0 of the matrix from the theory of rubber elasticity as $G_0 = \rho RT/M_e$, where M_e is the average molecular weight between entanglements, it would appear that the number of entanglements in the soluble rubber will increase considerably as the soluble rubber molecular weight increases so that M_e will decrease and G_0 will increase. On the other hand, ϕ_e is decreased due to lower bound rubber formation since the graphitized blacks have relatively inactive surfaces. Since in eq. (14) the effect of an increase in G_0 will counterbalance the decrease of ϕ_e due to graphitization, it is quite possible that, at a constant shear stress, graphitization may not affect die swell. Further, since structure is relatively unaffected by graphitization, the N value reflecting aggregate morphology may not be changed by graphitization.

If there is any variation in the masticative breakdown from compound to compound, it may reflect on the properties of the soluble rubber and the quantity of adsorbed rubber and affect compound die swell. Cotten[20] has shown, however, that the variation in the molecular weight of the soluble rubber with different carbon blacks which is often attributed to the variation in masticative breakdown could be shown to be due to variation in preferential adsorption by filler surfaces of the high molecular weight fraction of the polymer. There are other aspects, incorporation of which along with soluble rubber studies would have lent greater rigor to this work. A wider range of filler volume fraction, filler surface activity, and types of fillers would have checked the utility of eq. (14) against a wider canvas. Testing over a wider range of shear stresses, if necessary by introducing oil in the compound, is also desirable. Some of the spread in the data may also be due to possible minor variation in the entrance correction values due to variation in carbon black type since variation due to loading only has been considered. The role of a small change in diameter even when nonelastic fluids emerge from the capillary need to be considered. No die swell studies with l/d_c variation was attempted since the present $l/d_c = 27.8$ was quite large. Further, no attempt was made to correlate die swell with the variable $[(\phi \times \text{DBP})/\text{particle diameter}]$ in the manner of White and Crowder[2] since they had encountered large scatter, and a correlation with τ_{wc} is more desirable for identical die geometries.

Many of these factors will be included in a more comprehensive future investigation.

CONCLUSIONS

An experimental investigation of the extrusion die swell of carbon black-filled natural rubber compounds was carried out. The die swell of the compounds increases as the effective filler volume fraction, defined as the filler volume fraction plus the fraction of unextractable rubber, decreases. With increasing structure and/or surface area of carbon black particles, die swell decreases. At constant shear stress, the die swells of all compounds are related only to the free rubber volume fraction obtained from unextractable rubber measurements. The die swell data of all compounds at all shear stresses for a wide range of carbon blacks fall on a single curve when plotted as τ_{wc} versus $(B^4 - B^{-2})^{1/2}/(1 - \phi_e)^N$. Bagley and Duffey's analysis of die swell of unfilled polymeric melts as unconstrained elastic recovery as originally proposed by Nakazima and Shida[4] seems to be applicable for a filled elastomeric system extruded through a long die when an appropriate expression for the composite shear modulus is used. The effect of variations in the soluble rubber properties on die swell due to preferential adsorption of high molecular weight fractions on the active filler surfaces needs closer scrutiny.

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