

## An Empirical Model for Viscosity of Filled and Plasticized Elastomer Compounds

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### Synopsis

An empirical model is proposed for viscosity of elastomers containing one or more fillers and/or one or more plasticizers. Only one coefficient for each filler and plasticizer is required, and the coefficients themselves are viewed as basic filler and plasticizer characteristics. The model has found wide applicability to many elastomer systems.

### INTRODUCTION

Most commercial elastomer formulations contain various amounts and types of fillers and/or plasticizers, all of which exert major effects on the viscosity of the system. A means of predicting the viscosity of a proposed formulation is obviously highly desirable since viscosity control is crucial to processing operations. To date, considerable work has been done on the viscosity of elastomer-filler systems, considerably less on elastomer-plasticizer systems, and virtually none on the complete elastomer-filler-plasticizer systems. The purpose of this work was the development of a viscosity model for the elastomer-filler-plasticizer system which could be used for prediction.

Any discussion of viscosity of filled elastomer systems must begin with the Einstein equation<sup>1</sup>:

$$\eta = \eta_0(1 + 2.5c) \quad (1)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the filled and unfilled medium, respectively, and  $c$  is the volume fraction of filler. This equation applies to non-Newtonian liquids containing suspended, noninteracting, spherical particles. To account for larger particle concentrations and thus significant interactions among particles, eq. (1) was modified by Vand,<sup>2</sup> Simha,<sup>3</sup> and Guth, Simha, and Gold<sup>4</sup> by including higher powers of  $c$  in the Einstein equation. The latter is as follows:

$$\eta = \eta_0(1 + 2.5c + 14.1c^2). \quad (2)$$

While these expressions appear adequate for low concentrations of glass beads and large-particle thermal blacks, they are very much inadequate for fine-particle fillers and high concentrations of even coarse fillers.

One reason for their inadequacy is that filler particles dispersed in elastomers are generally surrounded by an adsorbed layer of insoluble elastomer, which effectively increases the volume fraction of dispersed particles. Brennan, Jermyn, and Boonstra<sup>5</sup> attempted to deal with this problem by adding the so-called bound-rubber contribution to the filler volume fraction in the Guth equation. This improved it but still left major deficiencies.

More recently, Pliskin and Tokita<sup>6</sup> actually estimated the thickness of the adsorbed elastomer layer and calculated a more precise effective volume fraction of filler,  $c_e$ . They then derived the following equation:

$$\eta/\eta_0 = (1 - c_e)^{-N} \quad (3)$$

where  $N$  is a measure of the degree of orientation of the system which is dependent, among other things, upon shear rate. This equation provided a very good fit for several carbon black-elastomer systems.

In contrast to filled elastomer systems, viscosity of plasticized elastomers has received very little theoretical treatment in the literature. The work of Kraus and Gruver<sup>7</sup> is an exception. They proposed the following equation:

$$\eta(c) \cong \eta(1)c_p^{3.4} \quad (4)$$

where  $c_p$  is the volume fraction of polymer,  $\eta(c)$  is the viscosity of the mixture, and  $\eta(1)$  is the viscosity of the elastomer. In the non-Newtonian region, they added a term for shear rate dependence.

The viscosity models discussed thus far have been, for the most part, mechanistic in nature. That is, they were based, at least partially, upon an understanding of the physical realities of the systems involved. Such models are indispensable for ultimate understanding, but are often too cumbersome for use as predictive tools, even when they are accurate. In this work, an empirical approach was employed to find a model which adequately described the viscosity of elastomers containing both filler(s) and plasticizer(s).

### DEVELOPMENT OF EMPIRICAL MODEL

A model relating filler and plasticizer concentrations to viscosity is not hard to find. The simple two variable quadratic polynomial

$$\eta = b_0 + b_1F + b_2P + b_{11}F^2 + b_{22}P^2 + b_{12}PF \quad (5)$$

where  $\eta$  is the Mooney viscosity,  $ML_4$  or  $MS_4$ ;  $F$  is the filler level;  $P$  is the plasticizer level; and  $b_0$ ,  $b_{ij}$ , and  $b_{ij}$  are fitted coefficients is almost always adequate. The major problem with this model is the interaction term  $b_{12}PF$ . The presence of this term means that the filler behavior is characterized only in the presence of the specific plasticizer used in the evaluation, and the results cannot be applied when another plasticizer is used. The same argument applies to the plasticizer behavior in the presence of

the filler employed. Even if the interaction term could be omitted, we would still require two coefficients each to characterize the filler behavior and the plasticizer behavior.

What we would ideally like to have is a simple linear equation of the following form:

$$f(\eta) = b_0 + b_1P + b_2F. \quad (6)$$

In this case, the plasticizer and filler behavior are each characterized by only one coefficient, and furthermore, filler and pigment act independently. To find such a function, the family of transformations proposed by Box and Cox<sup>8</sup> are employed as follows:

$$\begin{aligned} f(\eta) &= \frac{\eta^\lambda - 1}{\lambda} & \lambda \neq 0 \\ &= \ln \eta & \lambda = 0 \end{aligned} \quad (7)$$

where  $\eta$  is the Mooney viscosity,  $f(\eta)$  is a transformed version of  $\eta$ , and  $\lambda$  is a variable parameter.

In practice, several values of  $\lambda$  are chosen, usually in the interval  $\pm 2$ . For each  $\lambda$ , a regression analysis is run for both the linear model, eq. (6), and the quadratic model, eq. (5), on the transformed dependent variable  $f(\eta)$ . From the resultant regression statistics for the fitted equations, the mean squares due to both linear and quadratic effects are calculated as discussed by Draper and Smith.<sup>9</sup> These will be denoted by  $MS_L$  and  $MS_q$ , respectively. Since we desire a linear model, we want to find a  $\lambda$  value for which the quantity

$$F' = MS_q/MS_L \quad (8)$$

is minimized. We therefore construct a plot of  $F'$  versus  $\lambda$  and select  $\lambda$  resulting in the smallest  $F'$ . The transformation family of eq. (7) is equivalent to the simple power transformation as follows:

$$g(\eta) = (\eta)^\lambda. \quad (9)$$

The only difference is that eq. (7) is continuous at  $\lambda = 0$ , whereas eq. (9) is not. It is therefore clear that  $\lambda = -1$  is equivalent to  $1/\eta$ ,  $\lambda = 0.5$  is equivalent to  $\sqrt{\eta}$ ,  $\lambda = 1$  is equivalent to  $\eta$ , etc.

### Example

To illustrate the procedure, three fillers and one type of oil were studied in SBR-1500 in a  $6 \times 4$  factorial design as shown in Table I. Mooney viscosity was measured at 100°C after 4 min with the small rotor. For each filler, regression analyses were run at several values of  $\lambda$ , and an  $F'$  value was calculated for each  $\lambda$ . A plot was then constructed of  $F'$  versus  $\lambda$ , as shown in Figure 1. Clearly, for all three fillers the model became considerably more linear as  $\lambda$  was decreased from its initial value of 1.0. For Silica A,  $F'$  reached a minimum between  $\lambda = 0$  and  $\lambda = -1$ .

TABLE I  
Mooney Viscosity  $MS_1$  at 100°C as Function of Filler and Oil Levels in SBR-1500<sup>e</sup>

Naphthenic Oil, <sup>d</sup> phr		Filler, phr					
		0	12	24	36	48	60
0	a	26	28	30	32	34	37
	b	26	38	50	76	108	157
	c	25	30	35	40	50	60
10		18	19	20	21	24	24
		17	26	37	53	83	124
		18	21	24	28	33	41
20		12	14	14	16	17	17
		13	20	27	37	57	87
		13	15	17	20	24	29
30		—	12	12	13	14	14
		—	15	22	27	41	63
		11	14	15	17	18	25

<sup>a</sup> N990, Cabot Corporation. <sup>b</sup> Silica A, Hi-Sil 233, PPG Industries. <sup>c</sup> Silica B, Hi-Sil EP, PPG Industries. <sup>d</sup> Circolite Process Oil, Sun Oil Co. <sup>e</sup> SBR 1500, Phillips Petroleum Co.

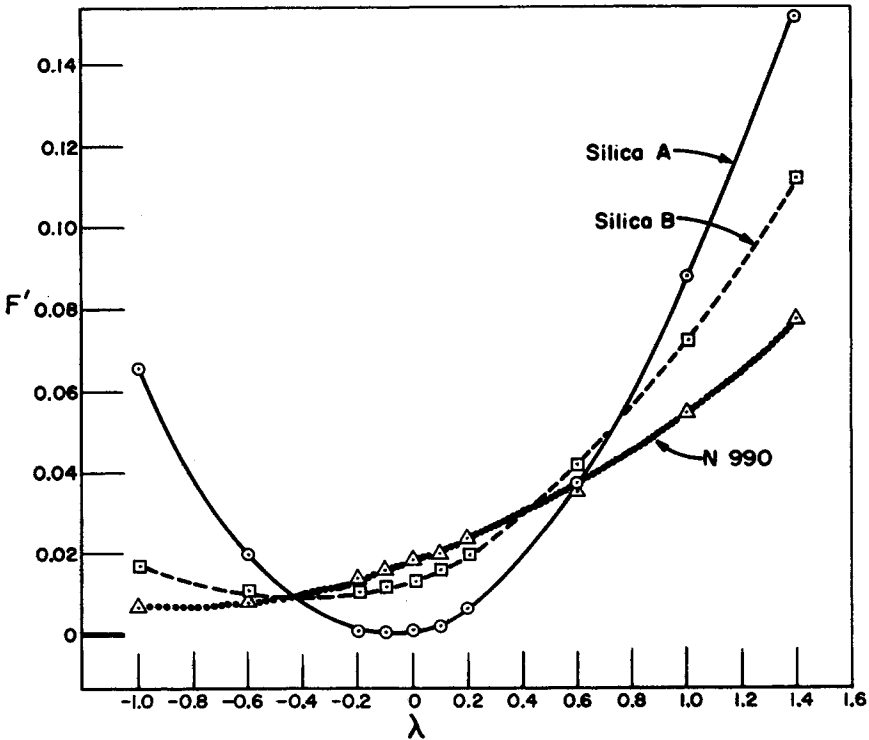


Fig. 1. Fractional contribution of quadratic terms as a function of  $\lambda$ .

For Silica B, the minimum was in the vicinity of  $-0.6$ ; and for N990, the minimum was somewhere at  $\lambda < -1.0$ . Even though the three pigments showed different optimal  $\lambda$ , the  $F$  values at  $\lambda = 0$  appeared to be a good compromise, as they were all near their respective minimum values. Since  $\lambda = 0$  corresponds to the logarithmic transformation, these results indicate that the following equation should provide a good approximation to viscosity behavior as a function of pigment and plasticizer levels:

$$\ln \eta = b_0 + b_1 F + b_2 P \quad (10)$$

where  $b_0$ ,  $b_1$ , and  $b_2$  are parameters fitted via regression analysis;  $F$  is filler (pigment) level in phr;  $P$  is plasticizer level in phr; and  $\eta$  is Mooney viscosity ( $MS_4$  or  $ML_4$ ).

To simplify the equation, we note that when  $F = P = 0$ ,  $b_0$  becomes the log of the viscosity of the unfilled elastomer, which we will denote  $\ln \eta_0$ . For simplicity, let us also set  $b_1 = \gamma$ ; and since  $b_2$  will always be negative, we set  $b_2 = -\phi$ , resulting in

$$\ln \eta = \ln \eta_0 + \gamma F - \phi P. \quad (11)$$

Other equivalent forms of this equation are

$$\ln \left( \frac{\eta}{\eta_0} \right) = \gamma F - \phi P \quad (12)$$

and

$$\frac{\eta}{\eta_0} = \exp(\gamma F - \phi P) = \exp(\gamma F) \exp(-\phi P). \quad (13)$$

The regression analysis results for the fitting of the Table I data to eq. (11) are given in Table II. The ranges for the parameters  $\gamma$  and  $\phi$  indicate 95% confidence intervals. The regression  $F$  ratio and standard error both reflect the adequacy of fit of the equation. Since the viscosity was fitted in logarithmic units, the following approximation holds:

$$\Delta(\ln \eta) \cong \frac{\Delta \eta}{\eta}. \quad (14)$$

Since the standard error is an interval in logarithmic units, it then is an approximation to the fractional error in Mooney units. Thus, the errors for the three equations range from approximately 5.1% to 7.2%. The

TABLE II  
Regression Results for Data of Table I Fitted to Eq. (11)

	$\ln \eta_0$	$\gamma_s$	$\phi_s$	Regression $F$ ratio	Standard error
N990	3.218	$0.006 \pm 0.001$	$0.031 \pm 0.003$	297	$6.8 \times 10^{-2}$
Silica A	3.2122	$0.031 \pm 0.001$	$0.032 \pm 0.002$	2041	$5.1 \times 10^{-2}$
Silica B	3.1975	$0.014 \pm 0.002$	$0.030 \pm 0.003$	356	$7.2 \times 10^{-2}$

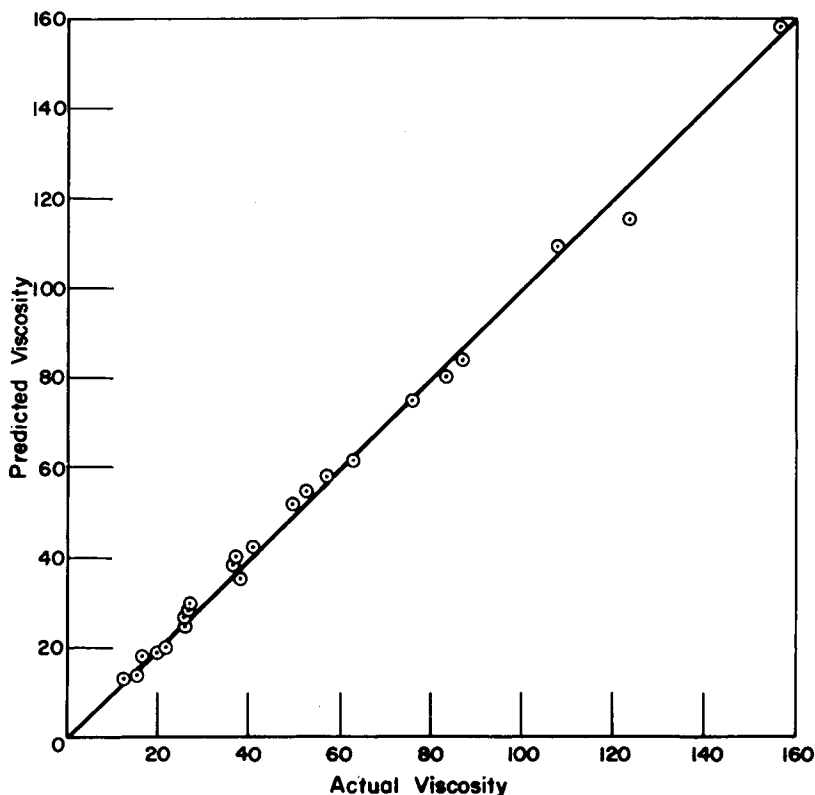


Fig. 2. Actual vs. predicted viscosity ( $MS_4$  at  $100^\circ\text{C}$ ) for Silica A.

adequacy of the fitted equations for the three different pigments is shown in Figures 2-4, where actual viscosity is plotted against viscosity predicted by the fitted equation. It is clear that these equations are excellent predictive models. The overlapping confidence intervals for  $\phi$  for the three different fillers in Table II is further evidence that filler and plasticizer are noninteracting.

The transformation family given in eq. (7) has been evaluated on many different elastomer-filler-plasticizer systems, both from our laboratory and from other suppliers' literature, and these encompassed many different elastomer, plasticizer, and filler types. The results indicated that the logarithmic model, eq. (11), is of quite general validity as a good predictive model.

#### $\phi$ and $\gamma$ as Plasticizer and Pigment Characteristics

Since eq. (11) appears to be a good predictive model for most elastomer, filler, and plasticizer types, we can view  $\phi$  and  $\gamma$  as basic characteristics of a plasticizer and filler, respectively. They will arbitrarily be defined as the plasticizer viscosity coefficient and filler viscosity coefficient, respectively.

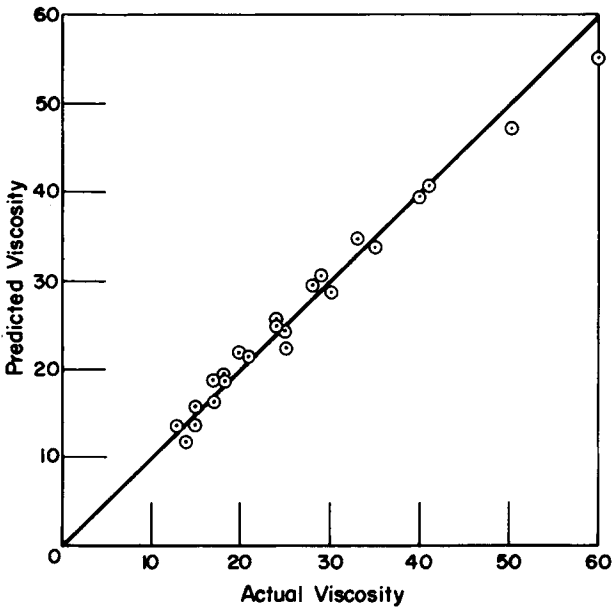


Fig. 3. Actual vs. predicted viscosity ( $MS_4$  at  $100^\circ C$ ) for Silica B.

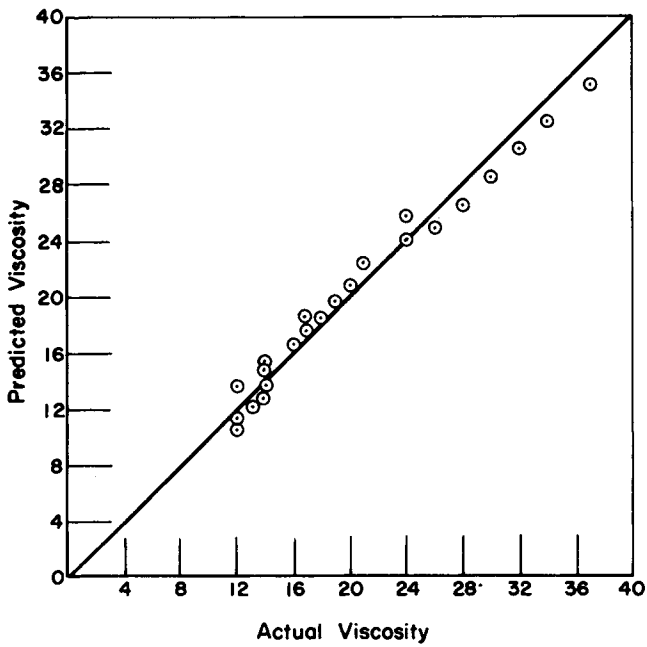


Fig. 4. Actual vs. predicted viscosity ( $MS_4$  at  $100^\circ C$ ) for N990.

The availability of these indices can be quite useful to the compounder. For example, if  $\phi$  and  $\gamma$  are available for a particular elastomer, all the compounder requires is a measure of the viscosity of the raw elastomer,  $\eta_0$ , to be able to predict the viscosity of filled and plasticized compounds. Furthermore, if we select an arbitrary elastomer as a reference, we can calculate  $\phi$  and  $\gamma$  for various fillers and plasticizers and thus have a means of comparing viscosity performance. Since eq. (11) is valid for viscosity measured with either the small or large rotor, we will subscript  $\phi$  and  $\gamma$  to indicate which viscosity we are referring to. For example, for small rotor viscosities, we will have  $\phi_S$  and  $\gamma_S$ ; and for large rotor viscosities,  $\phi_L$  and  $\gamma_L$ . In a later section, we will see that  $\phi_L \cong \phi_S$  and  $\gamma_L \cong \gamma_S$  in many instances.

### Additional Example

As a further example, consider the pigment-plasticizer study shown in Table III for NBR. With the exception of the first compound (raw polymer), the compounds comprise a rotatable central composite design with five replicated center points.<sup>10</sup> The replicated center points permit an  $F$  ratio for lack of fit to be calculated for any equation fitted to the data. This  $F$  ratio gives us a means for testing whether the fitted equation is representationally adequate. Figure 5 shows the  $F$  ratio for lack of fit and the regression  $F$  ratio as a function of the transformation parameter  $\lambda$  for the fit of eq. (6) to the NBR data.

Here again, the regression statistics were optimal near  $\lambda = 0$ , indicating the adequacy of eq. (11). The excellent fit of this equation is shown in

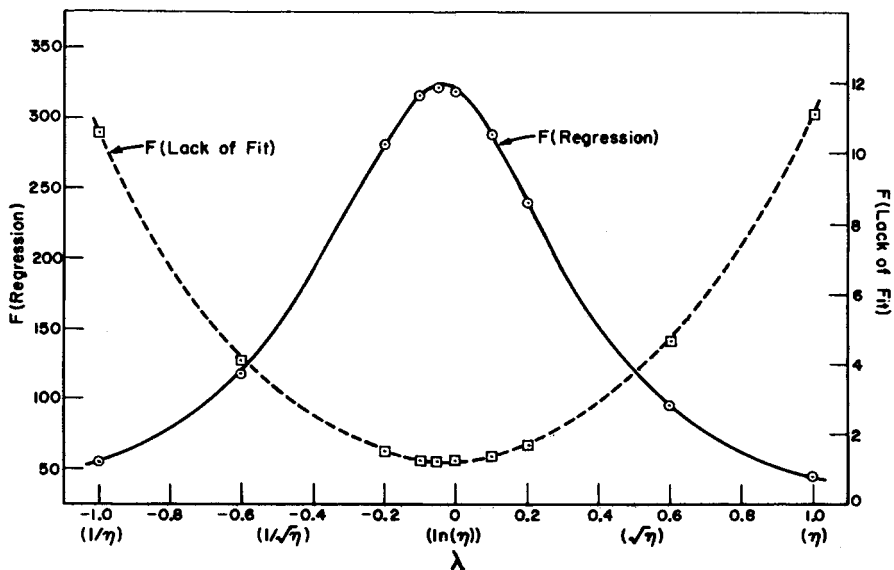


Fig. 5. Regression statistics vs.  $\lambda$  for filled and plasticized NBR.



TABLE III  
Data and Regression Results for NBR Example

A. Formulations													
NBR <sup>a</sup>	100												
Silica A	—	20	20	60	60	40	40	11.72	68.28	40	40	40	40
Aromatic oil <sup>b</sup>	—	10	30	10	30	5.86	34.14	20	20	20	20	20	20
Mooney viscosity													
ML <sub>4</sub> at 100°C	45	58	41	—	106	104	56	38	—	97	74	78	83
MS <sub>4</sub> at 100°C	22	28	18	93	54	57	30	20	100	41	40	42	45
B. Viscosity													
C. Regression Results													
F Regression	319.5												
F Lack of fit	1.27												
R <sup>2</sup> × 100	98.5												
Standard error	0.069												
Std. dev. of center points	0.074												
	$\phi_s = 0.024 \pm 0.003$												
	$\gamma_s = 0.029 \pm 0.005$												
	$\ln \eta_0 = 3.068$												
	$\eta_0 = 21.5$												

<sup>a</sup> Hycar 1052, B. F. Goodrich Chemical Co.

<sup>b</sup> Sundex 790, Sun Oil Co.

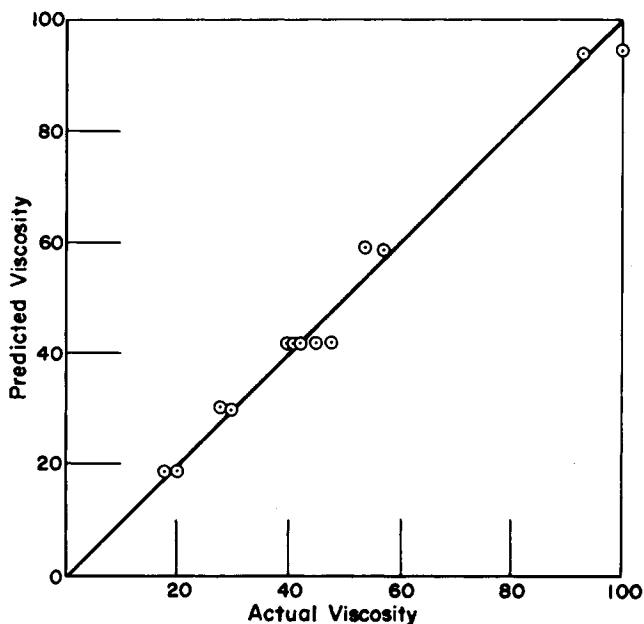


Fig. 6. Actual vs. predicted viscosity ( $MS_1$  at  $100^\circ\text{C}$ ) for NBR system.

Figure 6, where actual viscosity is plotted against predicted viscosity. Other regression statistics and the resulting viscosity coefficients are also shown in Table III. Note that the viscosity coefficients for Silica A in NBR ( $0.029 \pm 0.005$ ) and that for Silica A in SBR ( $0.031 \pm 0.001$ ) have overlapping confidence intervals, so that it cannot be concluded that Silica A exhibits different viscosity behavior in NBR than in SBR.

In this example, we worked with  $F$  (lack of fit) and  $F$  (regression), whereas in the first example we minimized the  $F$  ratio for quadratic versus linear effects. Either method will result in the same optimal  $\lambda$  value, because by minimizing the quadratic tendency in the model, we are in essence improving the fit (removing the bias) of a linear model. The options available in the regression analysis computer program being used will determine which method will be easiest to accomplish.

In analyzing the results of Table III, the point for the raw-polymer viscosity was not employed, although it could have been. Since this particular point lies outside of the design limits, it can be used to give an idea of the accuracy of extrapolations. It has been pointed out that regression equations generated from response surface designs should not be used for extrapolation.<sup>11</sup> There is one exception to this rule, however, and that is when the equation is known to be mechanistic. In this case, extrapolations should give reasonable results. We might consider, then, that if the logarithmic model produces reasonably accurate extrapolations, it may possibly be a partially mechanistic model, i.e., it may have some theoretical justification. From the fitted equation, the predicted value for

$\eta_0$  turned out to be 21.5 compared to the actual value of 22. This degree of accuracy for extrapolations to zero filler and plasticizer has been found for most of the systems evaluated. This indicates that the linear logarithmic model may indeed have some theoretical justification. At any rate, it is an excellent predictive model.

**Filler and Plasticizer Mixtures**

It has been shown that fillers and plasticizers affect viscosity (on the logarithmic scale) independently of each other and that the effects are linear. It may also be reasonable to assume that two or more pigments in an elastomer system also exert independent and linear effects on logarithmic viscosity. If this is true, it should be possible to predict the viscosity of such a system from the following equation:

$$\ln \eta = \ln \eta_0 + \sum_{i=1}^k \gamma_i F_i \tag{15}$$

where  $\eta$  is the viscosity of the filled elastomer,  $\eta_0$  is the viscosity of the elastomer gum, and  $\gamma_i$  is the viscosity coefficient for filler  $F_i$ .

To test this hypothesis, three fillers, Silica A, Silica B, and N774 black, were evaluated simultaneously in SBR as shown in Table IV. Regression results and estimated viscosity coefficients are also shown here. The resultant equation was as follows:

$$\ln \eta = 3.91 + 0.038 (\text{phr Silica A}) + 0.014 (\text{phr Silica B}) + 0.006 (\text{phr N774}). \tag{16}$$

TABLE IV  
Data and Results for Filler Mixtures in SBR

<i>A. Formulations</i>											
SBR-1500	100										
Silica A	5	5	15	15	17.5	2.5	10	10	10	10	10
Silica B	5	15	5	15	10	10	17.5	2.5	10	10	10
N774 <sup>a</sup>	15	5	5	15	10	10	10	10	17.5	2.5	10
<i>B. Mooney Viscosity</i>											
ML <sub>4</sub> at 100°C	73	78	95	121	114	66	96	80	84	79	89
<i>C. Regression Results</i>											
<i>F</i> Regression						54.7				$\ln \eta_0 = 3.91$	
Standard error						0.044				$\eta_0 = 49.9$ (ML <sub>4</sub> )	
$R^2 \times 100$						95.4					
Std. dev. of duplicated point						0.034					
<i>D. Viscosity Coefficients</i>											
<i>Filler</i>										$\gamma_L$	
Silica A										0.036 ± 0.007	
Silica B										0.014 ± 0.007	
N774 <sup>a</sup>										0.006 ± 0.007	

<sup>a</sup> Cabot Corporation.

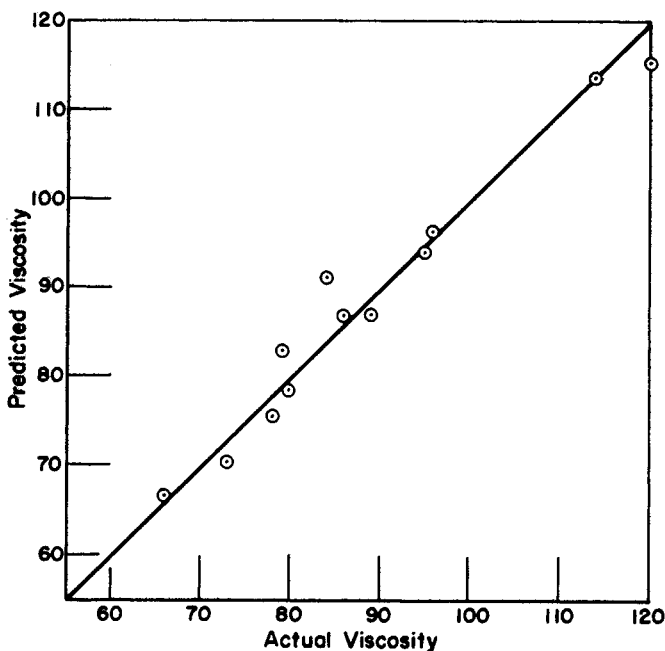


Fig. 7. Actual vs. predicted viscosity ( $ML_4$  at  $100^\circ C$ ) for pigment mixtures in SBR.

The degree of fit of this equation is shown in Figure 7, where actual viscosity is plotted against predicted viscosity. As can be seen, the fit is relatively good. Furthermore, in Table IV, lack of fit can be tested by dividing the standard error by the standard deviation for the duplicated point and squaring. This results in an approximate  $F$  ratio for lack of fit equal to 1.67, a value which is not significant. From this test and the appearance of Figure 7, we then have no reason to reject the hypothesis of additivity of different fillers. Furthermore, the fact that the confidence intervals for Silica A and Silica B overlap those found in Table II lends further support to this hypothesis.

Continuing along these lines, it is expected that for a mixture of plasticizers in an elastomer, the following equation would hold:

$$\ln \eta = \ln \eta_0 - \sum_{i=1}^k \phi_i P_i \quad (17)$$

where  $\eta$  is the viscosity of the plasticized elastomer,  $\eta_0$  is the viscosity of the gum elastomer, and  $\phi_i$  is the viscosity coefficient of plasticizer  $P_i$ . Furthermore, for elastomers containing more than one type of filler and more than one type of plasticizer, we would ultimately expect the following equation to be a good predictor:

$$\ln \eta = \ln \eta_0 + \sum_{i=1}^k \gamma_i F_i - \sum_{j=1}^m \phi_j P_j \quad (18)$$

where the terms are defined as above.

TABLE V  
Data and Results for Filler and Plasticizer Mixtures in SBR

A. Formulations										
SBR 1500	100	100								
Silica A	—	15	—	—	15	15	15	30	30	30
N330 <sup>a</sup>	—	15	15	30	—	15	30	—	15	30
Naphthenic Oil	—	10	10	20	10	20	—	20	—	10
Cumarone indene resin <sup>b</sup>	—	10	20	10	10	—	20	20	10	—
B. Mooney Viscosity										
ML <sub>1</sub> at 100°C	51	61	36	39	55	54	88	50	124	133
MS <sub>1</sub> at 100°C	29	34	20	21	30	30	49	27	68	74
C. Regression Results										
<i>F</i> Regression	405						ln η <sub>0</sub> = 3.95			
Standard error	0.003									
R <sup>2</sup> × 100	99.6									
D. Viscosity Coefficients										
γ <sub>L</sub> (Silica A)	= 0.027 ± 0.002									
γ <sub>L</sub> (N330)	= 0.013 ± 0.002									
φ <sub>L</sub> (oil)	= 0.028 ± 0.003									
φ <sub>L</sub> (resin)	= 0.014 ± 0.003									

<sup>a</sup> Cabot Corp.

<sup>b</sup> Cumar MH 2<sup>1</sup>/<sub>2</sub>, Allied Chemical Corp.

To evaluate eq. (18), a series of SBR formulations was mixed containing various combinations of two fillers: Silica A and N330 black and two plasticizers; naphthenic oil and a coumarone-indene resin. Formulations and viscosities are shown in Table V. The resultant viscosity coefficients and relevant statistics from the regression analysis are also shown. Note that the viscosity coefficients for Silica A and naphthenic oil agree well with those found in Table II. The excellent fit of this equation to the data is illustrated in Figure 8. It would, of course, be unrealistic to expect such good agreement with all or even most studies containing this many ingredients, but our findings here lend considerable support to the utility of the model.

### Incremental Changes in Viscosity

One of the problems frequently confronting a compounder is the estimation of the change in viscosity resulting from the addition or reduction of filler or plasticizer in an existing compound. We can get a good approximation for this purpose by differentiating eq. (12) as follows:

$$\frac{\partial \eta}{\partial F} = \gamma \eta_0 \exp(\gamma F) \exp(-\phi P) = \gamma \eta \tag{19}$$

and

$$\frac{\partial \eta}{\partial P} = -\phi \eta_0 \exp(\gamma F) \exp(-\phi P) = -\phi \eta. \tag{20}$$

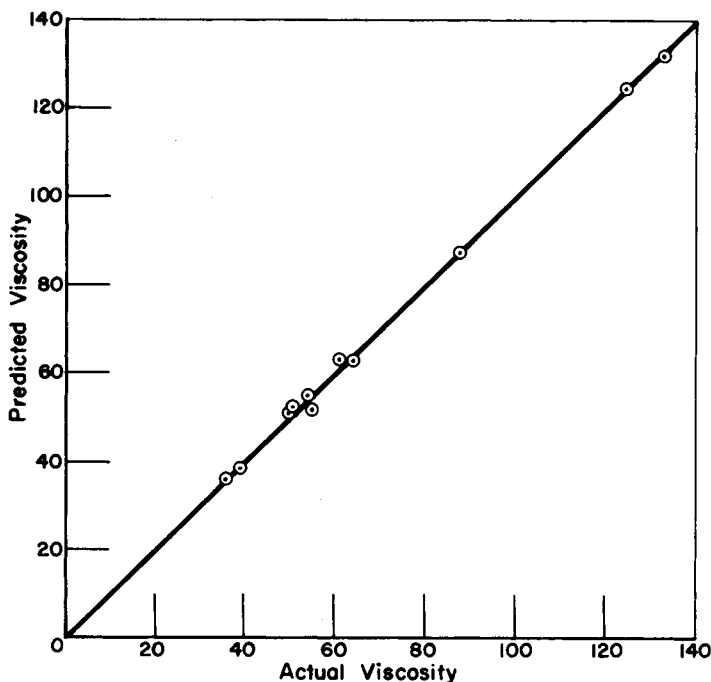


Fig. 8. Actual vs. predicted viscosity ( $ML_4$  at  $100^\circ C$ ) for pigment and plasticizer mixtures in SBR.

These equations tell us that the approximate change in viscosity per part of filler or plasticizer is obtained by multiplying the viscosity coefficient by the viscosity of the compound. For example, suppose we have an N990-filled SBR with a viscosity coefficient for the black of 0.006 at a viscosity level for the compound of 70. Then, the approximate increase in viscosity per part of N990 would be  $0.006 \times 70 = 0.4$  units. If the compound in question contains several fillers and plasticizers, and we want the incremental effect of only one filler or plasticizer, the result is the same. For example, the effect of filler  $i$  and plasticizer  $j$  would be as follows:

$$\frac{\partial \eta}{\partial F_i} = \gamma_i \eta \quad (21)$$

and

$$\frac{\partial \eta}{\partial P_j} = -\phi_j \eta. \quad (22)$$

Equations (19)–(22) represent the instantaneous rates of change of viscosity with filler or plasticizer. These estimates will give good approximations for changes in pigment or plasticizer levels up to about 10–15 phr. For larger changes, however, eq. (18) should be employed, rewritten as follows:

$$\eta = \eta_0 \exp\left(\sum_{i=1}^n \gamma_i F_i\right) \exp\left(\sum_{j=1}^m -\phi_j P_j\right). \quad (23)$$

The change in viscosity resulting from a change in filler loading from  $F_1$  to  $F_1'$  will then be

$$\Delta\eta = \eta_0 \exp\left(\sum_{i=2}^n \gamma_i F_i\right) \exp\left(\sum_{j=1}^m -\phi_j P_j\right) [\exp(\gamma_1 F_1') - \exp(\gamma_1 F_1)]. \tag{24}$$

An analogous result will hold for changes in plasticizer levels.

### Methods for Calculating Viscosity Coefficients

The viscosity coefficients  $\phi$  and  $\gamma$  can be estimated quite easily. To estimate both of them, as little as three compounds are required. For example, Figure 9 shows the viscosity of one level each of Silica A and oil in SBR-1500, as well as the viscosity of the raw rubber given the same amount of processing. The viscosity coefficients are then the natural

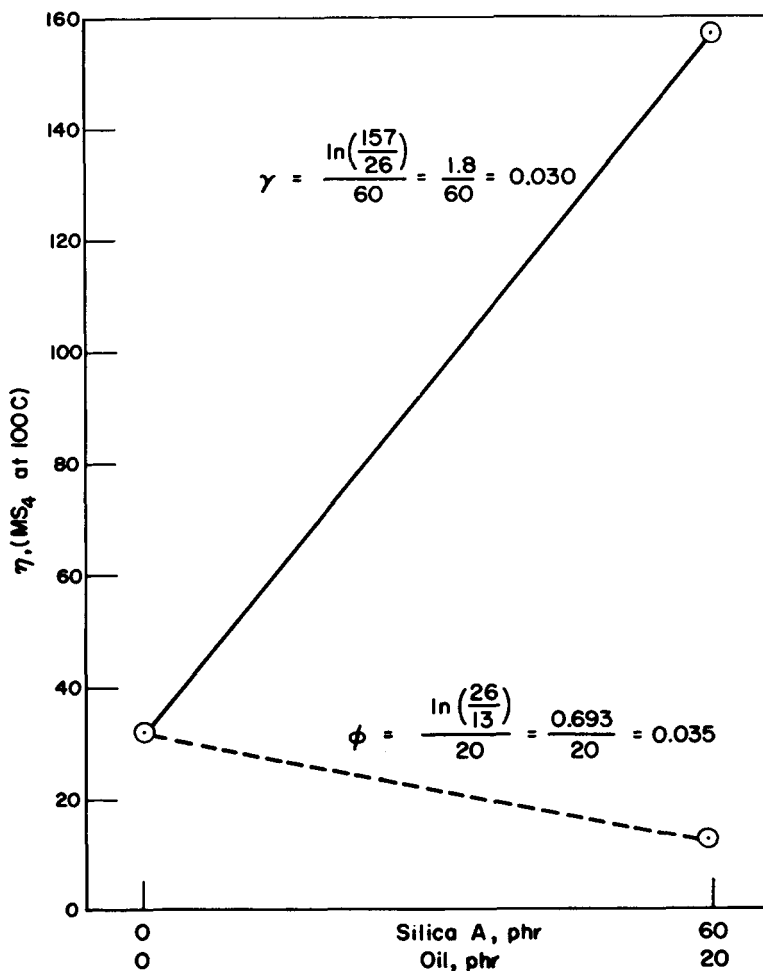


Fig. 9. Calculation of  $\phi$  and  $\gamma$ .

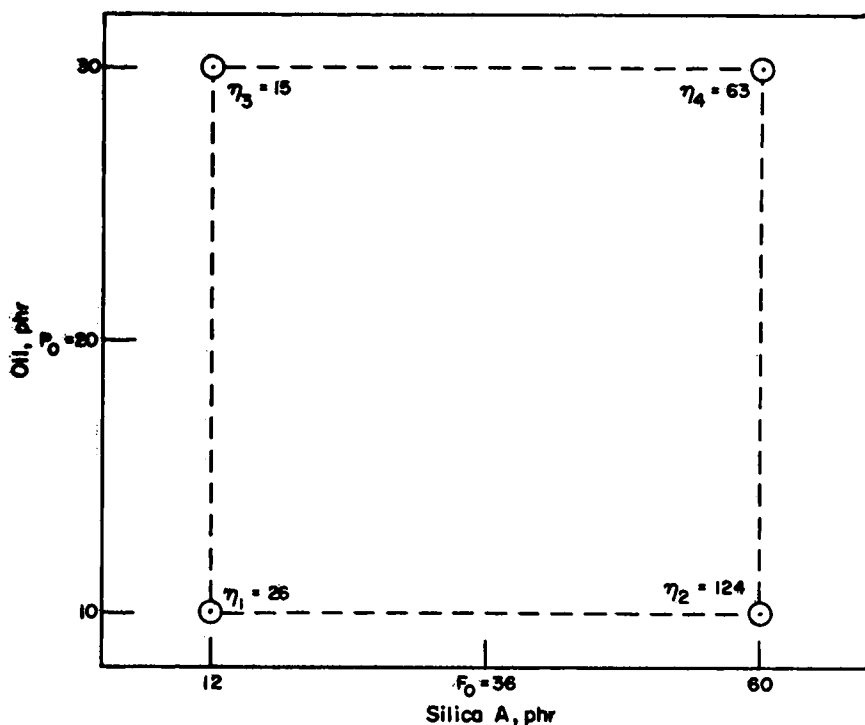


Fig. 10. Simultaneous estimation of  $\phi$  and  $\gamma$  using a  $2^2$  factorial design.

logarithm of the ratio of the largest to the smallest viscosity divided by the change in phr for the variable in question, as follows:

$$\gamma, \phi = \frac{\ln\left(\frac{\eta_{\text{largest}}}{\eta_{\text{smallest}}}\right)}{\Delta\text{phr}} \quad (25)$$

The points in Figure 8 were taken from Table I, and it is interesting that  $\phi$  and  $\gamma$  estimated from only three compounds are remarkably close to the coefficients obtained using all of the data. Of course, the more data we use, the more accurate the coefficients will be.

A more efficient method for calculating  $\phi$  and  $\gamma$  simultaneously is to employ a  $2^2$  factorial design, as shown in Figure 10. A  $2^2$  factorial design simply consists of two variables at two levels each. In Figure 10, the viscosities are shown corresponding to points denoted  $\eta_1$  through  $\eta_4$ . From these four viscosities, the viscosity coefficients are calculated as follows:

$$\gamma = \frac{1}{2(\Delta\text{phr})} \left[ \ln \frac{\eta_2 \eta_4}{\eta_1 \eta_3} \right] = \frac{1}{96} \left[ \ln \frac{(124)(63)}{(26)(15)} \right] = 0.031 \quad (26)$$

$$\phi = \frac{1}{2(\Delta\text{phr})} \left[ \ln \frac{\eta_1 \eta_2}{\eta_3 \eta_4} \right] = \frac{1}{40} \left[ \ln \frac{(26)(124)}{(15)(63)} \right] = 0.031 \quad (27)$$



where  $\Delta\text{phr}$  is the difference between the highest and lowest filler or oil levels. Furthermore, if we let  $F_0$  be the center of the filler range (i.e., 36 phr) and  $P_0$  be the center of the plasticizer range (i.e., 20 phr), we can calculate  $\ln \eta_0$  as follows:

$$\begin{aligned}\ln \eta_0 &= 1/4 \ln (\eta_1 \eta_2 \eta_3 \eta_4) - \gamma F_0 + \phi P_0 \\ &= 1/4 \ln [(26)(124)(15)(63)] - 0.031 (36) + 0.031 (20) \\ &= 3.222.\end{aligned}\quad (28)$$

Thus, our equation is as follows:

$$\ln \eta = 3.22 + 0.031F - 0.031P. \quad (29)$$

Notice that these results compare favorably with those of Table II.

We can obtain one additional bit of information from this design, the  $P \times F$  interaction effect  $I_{PF}$ , as follows:

$$I_{PF} = \frac{1}{2} \left[ \ln \left( \frac{\eta_{1\eta_4}}{\eta_2 \eta_3} \right) \right] = \frac{1}{2} \left[ \ln \frac{(26)(63)}{(124)(15)} \right] = -0.063. \quad (30)$$

The significance of this interaction effect is as follows. If eq. (29) adequately represents the data,  $I_{PF}$  should be merely an estimate of experimental error since there is no real interaction. Since  $I_{PF}$  represents a logarithmic interval as discussed previously, it represents fractional error (disregarding the sign). Therefore, if 6.3% is a reasonable error estimate, we conclude that our equation is adequate. Comparing this result with the standard error in Table II, we can see that our equation is adequate.

The  $2^2$  factorial design is only one of many types of designs suitable for estimation of viscosity coefficients, and the interested reader is referred to texts on statistical experimental design and response surface methodology for other designs.<sup>12,13,14</sup> In choosing a design, one must keep in mind that the more precision required for estimation of  $\phi$  and  $\gamma$ , the more points a design must contain. Also, if the experimenter is prepared to accept the log linearity of viscosity, he can use two level designs such as  $2^k$  and  $2^{k-p}$  factorials. If, however, he wants to test this linearity, second-order response surface designs must be employed.

### Large Versus Small Rotor Viscosities

Suppose we take eq. (12) and let  $\eta_S$  = small rotor viscosity and  $\eta_L$  = large rotor viscosity. Further assume that the relationship between  $\eta_S$  and  $\eta_L$  is as follows:

$$\eta_L = a\eta_S \quad (31)$$

where  $a$  is a constant. Then it is clear that the same parameters would be obtained in eq. (12) regardless of the rotor used, since  $a$  will cancel out in the ratio of two viscosities as follows:

$$\frac{\eta_L}{\eta_{0L}} = \frac{a\eta_S}{a\eta_{0S}} = \frac{\eta_S}{\eta_{0S}} \quad (32)$$

Unfortunately, eq. (31) does not always hold and a more realistic relationship is

$$\eta_L = b + a\eta_S \quad (33)$$

where  $b$  is a constant generally in the vicinity of  $\pm 5$  and  $a$  is approximately 1.8. Because of the constant term  $b$ , the ratio of two viscosities for a given rotor will be a function of the rotor used, and thus  $\phi$  and  $\gamma$  must always be subscripted to indicate which rotor was used. Naturally, if  $b$  is near zero,  $\gamma_L \cong \gamma_S$  and  $\phi_L \cong \phi_S$ .

## CONCLUSIONS AND RECOMMENDATIONS

It has been illustrated that the viscosity of an elastomer compound can be approximately predicted by a linear logarithmic model which employs only one parameter for each filler and/or plasticizer in the formulation. It has been suggested that these parameters be thought of as basic characteristics of pigments and plasticizers. They could then be quoted in suppliers' literature as a possible alternative to tabular data or contour plots for viscosity prediction. It may also be useful to select some standard elastomer, such as the National Bureau of Standards' SBR 1503 as a medium for comparing the coefficients since they will generally vary among elastomer types.

A natural extension of this work would be to relate viscosity coefficients of fillers to particle size, structure, and shear rate. Analogously, for plasticizers, it would be interesting to find what relationships exist between, say, polarity, molecular weight, and viscosity, and viscosity coefficients in various elastomers.

It is recognized that the viscosity model proposed in this paper will be inadequate for some systems. On the other hand, it has been found adequate for such a wide variety of systems that it should find wide applications.

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