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Composite rheology – I. Elastomer-filler interaction and its effect on viscosity

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Experimental results show that the viscosity of elastomer–filler systems cannot be explained as a simple equation depending only on filler loading, such as in the Einstein or the Guth–Simha–Gold models. The viscosity of elastomer–filler systems also depends on the temperature at which it is measured and the glass transition temperature, T_g, of the basic polymer. This finding seems to suggest two facts: (a) polymer melts are not simple Newtonian fluids but relaxational liquids in which the values of rheological data depend on the experimental observation time (or measured frequency) and temperature, (b) composite materials of elastomer–filler systems, will have the same T_g as the basic polymer if the fillers do not change the main-chain structure of the basic polymer. Therefore, one can conclude that the presence of filler broadens the relaxation spectrum but does not change T_g, and at T_g the basic polymer and the composite materials will have the same viscosity. A new model for the viscosity of elastomer–filler systems is developed from the concept of molecular structural relaxation and glass transition temperature of polymers.

1. Introduction

Recently, polymer scientists have become very interested in composite rheology because of the need to develop and process new composite materials with desired physical and mechanical properties. The rheological behaviour of composite materials not only governs the performance of end-products but also controls the fluid and heat transfer characteristics during polymer processing. Therefore, it is vitally important that the dynamic viscosity as a function of temperature shear rate, and filler loading during polymer processing, and also dynamic mechanical properties under various environments such as temperature, frequency, and strain, can be predicted.

Since polymer materials are relaxational liquids, that is, non-Newtonian fluids, the structural relaxation spectrum of polymers must be understood in order to predict their dynamic viscosity and mechanical properties. The present work is concerned with the viscosity of elastomer–filler systems at various temperatures, shear rates and filler loadings, and their importance in applications of elastomer mixing, mould design and moulding operations. A new model for predicting the viscosity of elastomer–filler combinations is proposed, based on the concept of the structural relaxation spectrum and the glass transition of polymers.

2. Consideration of methods

The research programme into polymer rheology can be divided into two different approaches, depending on convenience and the effectiveness of applications, respectively.

2.1. A scientific approach

Studying and modelling the structural relaxation spectrum of polymers is a prerequisite in understanding polymer rheology. Aspects of the thermodynamics and kinetics of the structural relaxation of polymers are indespensable in understanding the glass and rubber transition and, therefore, in predicting structure–property relationships of polymer systems. The model of a structural relaxation spectrum will give a physical insight for

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comprehension and prediction of dynamic mechanical properties, thermal stress, fracture mechanics, fatigue, yield stress, heat transfer between the metal–polymer melt interface [1, 2] and adhension of polymeric materials. Therefore, more effective tailoring of structures of polymers and design of composite materials with a desired property can be carried out.

2.2. An engineering approach

Although the model of a structural relaxation spectrum is an elegant way to understand polymer rheology, it might be more convenient, in applications of polymer processing, if the model could be simplified. One such approach is to use a simple equation, such as a power-law or some other viscosity model which will be a function of shear rate. Nevertheless, a good understanding of the structural relaxation and glass transition is also needed to simplify the model to be presented in this paper.

3. The structural relaxation spectrum and glass transition

A firm grasp of the concepts of structural relaxation and glass transition is essential to an understanding of polymer rheology, (as discussed recently by Hsich [3, 4]). Whether polymeric materials are used as elastomers or themoplastics depend on whether their glass transition temperatures, T_g, are lower or higher than room temperature. For the relationships between the relaxation spectrum dynamic mechanical properties and viscosity can be written as:

$$M'(\omega) = M_0 + (M - M_0)\int_0^{\infty} \frac{\omega^2 t^2}{1+\omega^2 t^2} g(t/t_R)\,dt \tag{1}$$

$$M''(\omega) = (M - M_0)\int_0^{\infty} \frac{\omega t}{1+\omega^2 t^2} g(t/t_R)\,dt \tag{2}$$

$$\begin{aligned}\eta'_s(\omega) &= \frac{G''(\omega)}{\omega}\\ &= (G - G_0)\int_0^{\infty} \frac{t}{1+\omega^2 t^2}\, g_s(t/t_R)\,dt\end{aligned} \tag{3}$$

$$\begin{aligned}\eta''_s(\omega) &= \frac{G'(\omega)}{\omega}\\ &= \frac{G_0}{\omega} + (G - G_0)\int_0^{\infty} \frac{\omega t^2}{1+\omega^2 t^2} g_s(t/t_R)\,dt\end{aligned} \tag{4}$$

$$\begin{aligned}\eta_0 &= \lim_{\omega \to 0} \eta'_s(\omega)\\ &= (G - G_0)\int_0^{\infty} t g_s(t/t_R)\,dt\end{aligned} \tag{5}$$

where M is a generalized modulus, (it can be either shear, bulk, longitudinal, or Young's modulus), $M'(\omega)$ and $M''(\omega)$ are the storage and loss modului, respectively. G is the shear modulus, $\eta'_s(\omega)$ and $\eta''_s(\omega)$ are the real and imaginary part of the shear viscosity, respectively. η_0 is the static or Newtonian viscosity, $g(t/t_R)$ is the structural relaxation function, t is the time, and t_R is the relaxation time which is a function of temperature. The subscripts ∞, 0, and s denote high frequency, low frequency, and shear, respectively. Therefore, once the relaxation function of a polymer is known it should be possible to predict the dynamic mechanical properties and viscosity of the polymer.

Since the structural relaxation spectrum is of primary importance in determining polymer rheology, the relaxation spectrum of polyisoprene is taken as an example before the elastomer–interaction is discussed. The mechanical spectrum of natural rubber gum is shown in Fig. 1. The values of the storage shear modulus, G', and mechanical loss, $\tan\delta$, are plotted for three different frequencies, i.e. $\omega = 0.1$, 1 and 100 rad $\sec^{-1}$ at a temperature ranging from −145 to 53° C. The data was taken by a Rheometrics Mechanical Spectrometer (RMS). A torsion-rectangular testing mode was used in the temperature range of −145 to −25° C, while a parallel-plate testing mode was used in the range of −15 to 53° C.

The glass transition temperature, T_g, and relaxation peak temperature are −63° C and −57° C at $\omega = 0.1$ rad $\sec^{-1}$; −59° C and −53° C at $\omega = 1$ rad $\sec^{-1}$; and −51° C and −45° C at $\omega = 100$ rad $\sec^{-1}$, respectively. It must be remembered that the temperature at which $\tan\delta$ peaks is very close to (usually a few degrees Celsius higher than) the peak of G'' because of the relationship between $\tan\delta$ and G'' (i.e., $\tan\delta = G''/G'$). Using a relaxation spectrum model of Equation 3, the relaxation peak of $G''(\omega)$ must occur when $\omega t_R = 1$, as has been mentioned by Bueche [5] and others, where the relaxation time, t_R, is a function of temperature. If the Arrhenius equation is used for relaxation time, i.e.

$$t_R = t_0 \exp(E/RT), \tag{6}$$

where t_0 is a constant and R is the gas constant, then, by combining the condition of $\omega t_R = 1$, the

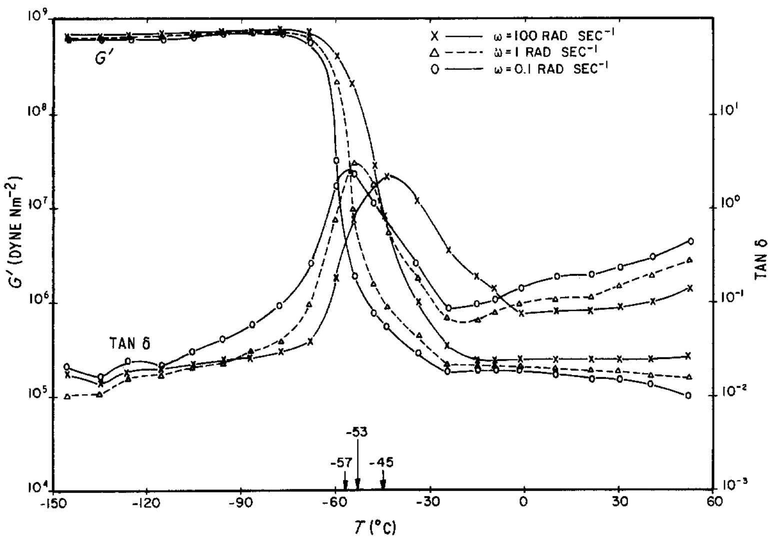

Figure 1 The mechanical spectrum of natural rubber gum.

activation energy, E, can be calculated as 234 kJ mol^{-1}. The activation energy of 234 kJ mol^{-1} is in the range of the energy of covalent bonds. This is a typical activation energy for the structural relaxation of glassy polyisoprene. (At higher temperatures, in the region of the polymer melt, the activation energy is about 41.84 kJ mol^{-1} or slightly less, which is ascribed to intermolecular forces.) A detailed discussion of structural relaxation will be given elsewhere [4]. In the following section, a discussion of how the phenomenon of structural relaxation and glass transition affects the composite rheology of elastomer–filler systems is given.

4. Elastomer–filler interaction and its effect on viscosity

Before the viscosity model of elastomer–filler systems is discussed, a brief discussion of the relationship of viscosity in the dynamic, steady shear, and static states is given. The relationship between dynamic and static viscosity has been shown in Equation 5. Although the relation between dynamic and steady shear viscosity seems quite complex, Bueche [5] has demonstrated that the dynamic viscosity $\eta(\omega)$ should be equal to the steady shear viscosity $\eta(\gamma)$ at a shear rate $\gamma = \omega$. Coleman and Markovitz [6] also have shown that

$$\lim_{\omega \to 0} \eta'(\omega) = \lim_{\gamma \to 0} \eta(\gamma) \qquad (7)$$

More recently, Kulicke and Porter [7] have found that the rheological behaviour of polystyrenes and polyacrylamides satisfies the relationship of Cox and Merz [8], i.e.

$$\eta^*(\omega) = [\eta'(\omega)^2 + \eta''(\omega)^2]^{1/2} = \eta(\dot{\gamma})|_{\dot{\gamma}=\omega} \qquad (8)$$

These equations show that there is a discrepancy between dynamic and steady shear viscosity for some polymer melts and solutions. However, it might be expected that introducing a shift factor would bring these two independently obtained values into reasonably good agreement.

5. Discussion of models of viscosity for an elastomer–filler system

5.1 The classical models

The effect of fillers on the viscosity of a fluid was studied by Einstein [9, 10] more than seven decades ago. In his study, Einstein developed a viscosity model based on the hydrodynamic theory of a Newtonian fluid. The Einstein model is expressed as

$$\eta = \eta_0(1 + 2.5\phi), \qquad (9)$$

where η and η_0 are the viscosities of the filled and unfilled fluid, and ϕ is the volume fraction of filler. By taking into account the hydrodynamic interactions between spheres, Guth, Simha and Gold [11, 12] modified Equation 9 to include a second order power of ϕ. The modified Einstein equation becomes

$$\eta = \eta_0(1 + 2.5\phi + 14.1\phi^2). \qquad (10)$$

Lee [13] extended hydrodynamic interactions to include three-body collisions of spheres. The result is that the viscosity model becomes a power series expansion up to a third order power of ϕ. The Lee model is written as

$$\eta = \eta_0(1 + 2.5\phi + K_2\phi^2 + K_3\phi^3), \quad (11)$$

where K_2 and K_3 are constants. Landel *et al.* [14] developed an empirical equation by studying the suspension of particles in Newtonian liquids. Their empirical equation is expressed as

$$\eta = \eta_0(1 - \phi/\phi_m)^{-2.5}, \quad (12)$$

where ϕ_m is the packing factor. Recently, Pliskin and Tokita [15] generalized the equation of Landel by considering the degree of orientation of the system. The new modified equation becomes

$$\eta = \eta_0(1 - \phi_e)^{-N}, \quad (13)$$

where ϕ_e is the volume fraction of rigid material and N is the parameter which describes the degree of orientation of the system. $N = 1.0$ for a completely laminated material, and $N = 2.5$ for the random suspension of discrete particles. Although the above equations work well for some liquids at a limited range of temperatures and shear rates, generally they do not apply to elastomer–filler systems at a wide range of temperatures and shear rates. This is because most of the above equations are developed for Newtonian fluids, while polymers are non-Newtonian. Polymers are relaxational liquids in which rheological behaviour is controlled by molecular structural relaxation. The data in Fig. 2 clearly demonstrates the shortcomings of the above models. As can be seen from the figure, the effect of fillers on the viscosity is more pronounced at high temperatures than at low temperature. Therefore, even if the above models can fit the data at one particular temperature, it might be expected that they cannot fit the data at other temperatures.

The viscosity data in Fig. 2 were taken from the uncured natural rubber compound having the composition outlined in Table I. The filler used in this study was an HAF type of carbon black. The data were taken by dynamic testing in the parallel-plate mode with the RMS operating at a frequency of ω = rad sec^{-1} and at temperatures of 52, 102, 127 and 152° C as shown in Fig. 2.

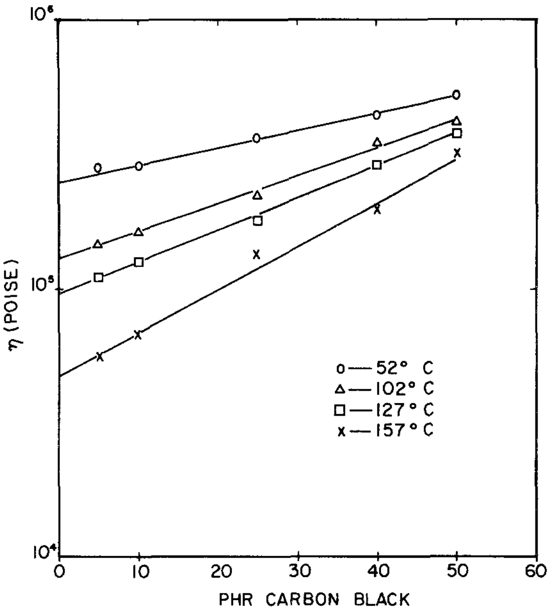

Figure 2 The relationship of viscosity against filler loading at various temperature.

5.2 The development of new models

As mentioned previously, the prediction of viscosity at various temperatures and shear rates is of vital importance in optimizing mould design and moulding operations. Therefore, it is necessary not only to be able to predict the viscosity at various filler loadings, but also at various temperatures and shear rates. Based on this need, a temperature-dependent viscosity model of elastomer-filler composites will be developed from the concept of structural relaxation and glass transition temperature.

As has been shown in Fig. 2, the dependence of viscosity on fillers is more pronounced at high temperature, but less pronounced at low temperature. This behaviour seems to suggest that the phenomenon of glass transition plays an important role in controlling the rheological behaviour of elastomer–filler composites. Therefore, the relaxation spectra of rubber compounds with and without filler were investigated. The results are shown in Fig. 3. The data were taken by a torsion-

TABLE I Composition of the natural rubber compound

Ingredient	phr*
Gum	100
Reogen	1
Stearic Acid	1
Zinc Oxide	5
Agerite HP-S	1
Agerite Resin D	1
Flexzone 3C	1.5
Wax	2

* Parts per hundred resin

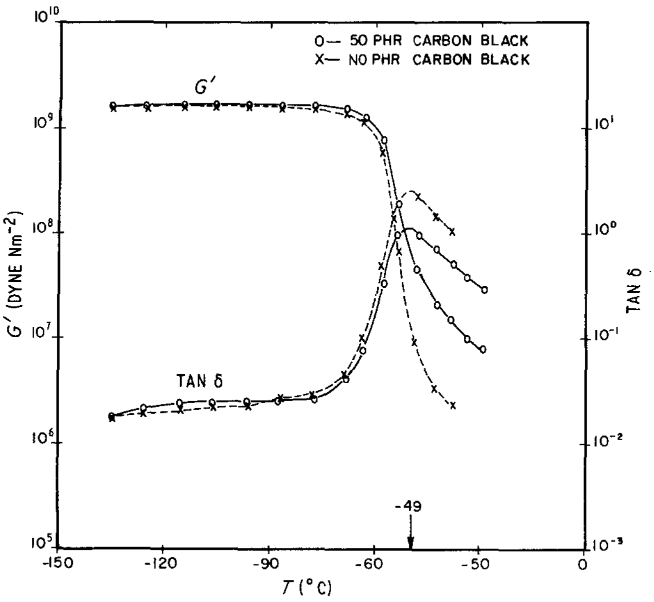

Figure 3 The mechanical spectra of rubber compound without filler and with 50 phr of filler.

rectangular testing mode of RMS at a frequency of $\omega = 10$ rad sec^{-1}. The glass transition temperature is the same for both filled and unfilled compounds. Figs. 4 and 5 are the relaxation spectra of the same two rubber compounds (i.e. the compound listed in Table I with 50 parts per hundred resin (phr) and 0 phr of carbon black) given in Fig. 3 at three other frequencies, i.e. $\omega = 0.1$, 1, and 100 rad sec^{-1}. As one can see from Fig. 1 and Figs. 3 to 5, the T_g which is the temperature intercepted by the two slopes of G' curve near the low temperature transition or relaxation region) and relaxation peak temperature T_{rp} are not changed for these three rubber coumpounds (gum, and the compound listed in Table I with 0 and 50 phr filler). The T_g and relaxation peak temperatures are given in Table II. These temperatures do not depend on filler loading or processing aids. Filler loading does however broaden the relaxation spectrum of the polymer system. Incidentally, the same conclusion, that filler loading broadens the relaxation spectrum, has also been observed in the study of cure kinetics of elastomers. The result will be presented elsewhere. The fact that the glass transition and relaxation peak temperatures do not depend on filler loading, but the relaxation spectrum does, is not difficult to explain. Since a filler such as carbon black does not change the main-chain structure of the polymer under consideration, the glass transition temperature of the

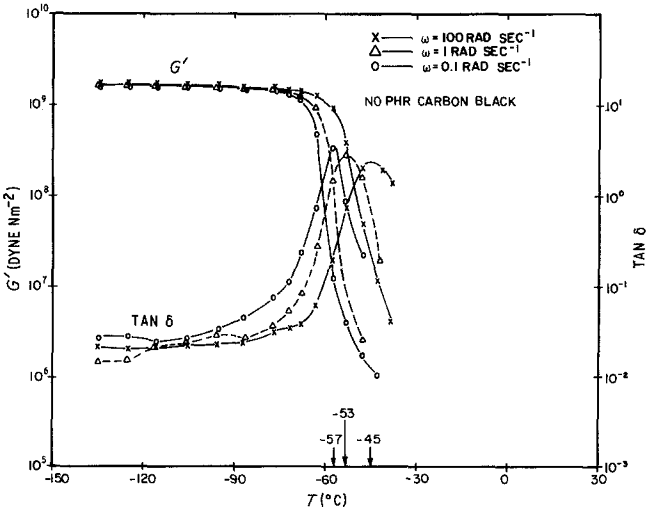

Figure 4 The mechanical spectra of rubber compound without filler at three different frequencies.

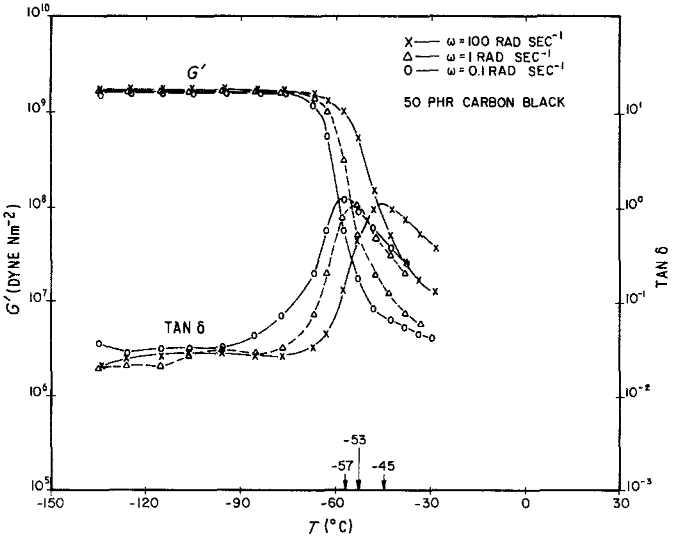

Figure 5 The mechanical spectra of rubber compound with 50 phr of filler at three different frequencies.

polymer is, therefore, unchanged. However, carbon black filler does affect the chain motion of the polymer system. This results in a broadening of the structural relaxation spectrum of the polymer as shown in Figs 4 and 5. The relaxation spectrum of the unprocessed natural rubber gum might be broader than that of the processed rubber compounds, as can be seen from a comparison of Figs 1, 4 and 5. This is due to the unprocessed gum, which tends to have a broader molecular weight distribution than the processed rubber. This is true because mixing processes tend to narrow the molecular weight distribution [16].

The phenomenom of glass transition is a relaxational process; therefore the physical and mechanical properties of glassy polymers depend on the thermal and mechanical history, and the method of experimental measurement. The details of glass transition and the definition of glass transition temperature have been discussed recently by Hsich [3] among others. It should be noted, as has been mentioned in [2], the temperature at which the static viscosity of polymer systems has a value of 10^{13} poise is defined as the glass transition temperature, T_g. An assumption is made that dynamic or steady shear viscosity also has the same value under an identical experimental condition at T_g for all polymer systems; then it can be concluded that rubber compounds, either with or without filler, will have the same viscosity at T_g because that study shows that the presence of fillers does not change T_g. Therefore, the glass transition temperature of polymer systems is not affected by filler loading. This explains why the dependence of viscosity on filler loading is less pronounced at low temperatures (which happen to be close to T_g).

TABLE II T_g and T_{rp} at various frequencies

ω (rad sec^{-1})	T_g (° C)	T_{rp} (° C)
0.1	−63	−57
1	−59	−53
19	−55	−49
100	−51	−45

From the above discussion, it can be concluded that the viscosity of elastomer-filler composites not only depends on the temperature at which the viscosity is measured, but also depends on the glass transition temperature of the polymer in question. As has been mentioned, to predict the viscosity as a function of filler loading, temperature, and shear rate, the structural relaxation spectrum of polymer systems must be studied. At a constant shear rate, or frequency, the viscosity of polymer–filler systems at various filler loadings depends on T_g and temperature, T. Also at $T = T_g$, the viscosity will have the same value at various filler loading. Therefore, the new viscosity model of elastomer–filler systems at a constant shear rate or frequency can be expressed as

$$\ln\left(\frac{\eta}{\eta_0}\right) = C\phi_\omega \frac{T}{T_g}(T - T_g), \qquad (14)$$

or

$$\ln\left(\frac{\eta}{\eta_r}\right) = C(\phi_\omega - \phi_r)\frac{T}{T_g}(T - T_g), \qquad (15)$$

where η_0 and η are the viscosities of unfilled and filled elastomer at a temperature, T, C is a constant

TABLE III The reference viscosity, η_r, at $\phi_r = 0.1+$

T(° C)	52	77	102	127	152	177
η_r(× 10^{-5} poise)	2.85	1.98	1.63	1.27	0.67	0.56

which depends on the surface of the fillers, ϕ_ω is the weight ratio of the filler to the basic polymer, ϕ_r is the weight ratio at a particular filler loading, (which can be used as a reference point for the viscosity calculation), and finally, η_r is the reference viscosity at a filler loading ϕ_r. Fig. 2 illustrates the variation of viscosity with filler loading at 10 rad sec^{-1}. The points represent experimental data obtained with the mechanical spectrometer in RMS, and the solid lines represent theoretical predictions using Equation 15. While other frequencies were investigated, $\omega = 10$ rad sec^{-1} gives the best fit for Equation 15. This is probably because the natural rubber compounds studied here have an average relaxation time of 0.1 sec ($t_r = 1/\omega$) in the temperature range of this study. The best fit of parameter C for HAF carbon black in Equation 15 is $C = 8.89 \times 10^{-3}$. The reference viscosity, η_r, at various temperatures, is listed in Table III. It can be seen from Fig. 2 that there is good agreement between the experimental values for viscosity and the theoretical predictions from Equation 15. Plots of viscosity against frequency at various temperatures and filler loadings are shown in Figs 6 to 9. The frequency in this study ranges from $\omega = 0.1$ to 100 rad sec^{-1}. It should be remembered, as has been shown in Equations 3, 4 and 5, that the dependence of viscosity on frequency is due to the structural relaxation of the polymer system. Therefore, when the frequency becomes infinitely small, the polymers behave as if they are Newtonian fluids in their flow characteristics.

Although a new model will be developed from the concept of structural relaxation and glass transition, a power-law, instead of the relaxation functions shown in Equations 1 to 5 will be used to simplify the shear rate dependent viscosity. Such a power-law model is more convenient for applications in mould design, injection moulding, and other moulding operations. However, the relaxation function can explain more elegantly variations in this dynamic viscosity over a wider range of shear rates and frequencies than the use of a power-law model, but a power-law model is

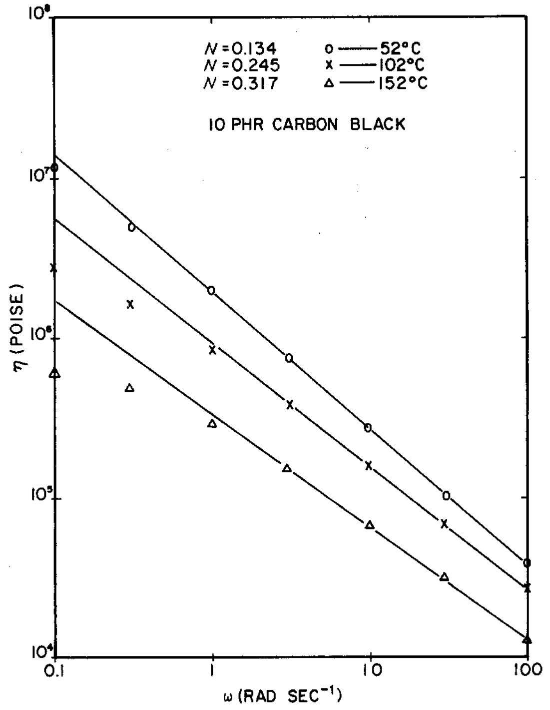

Figure 6 Viscosity against frequency at various temperatures for 10 phr of filler loading.

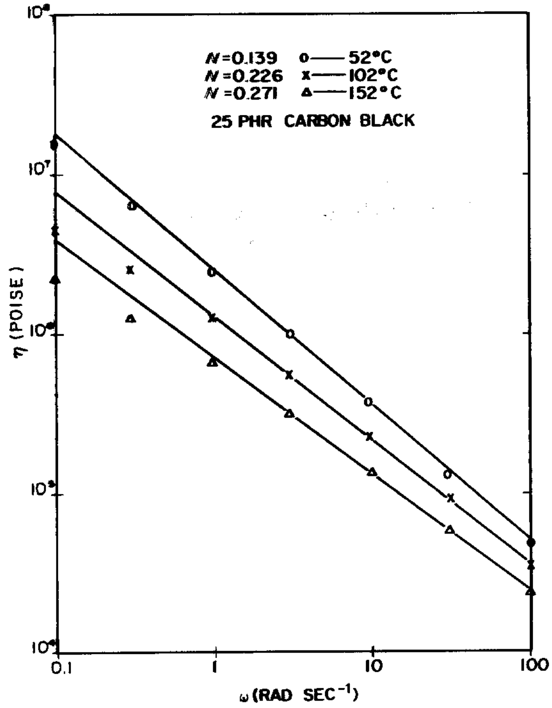

Figure 7 Viscosity against frequency at various temperatures for 25 phr of filler loading.

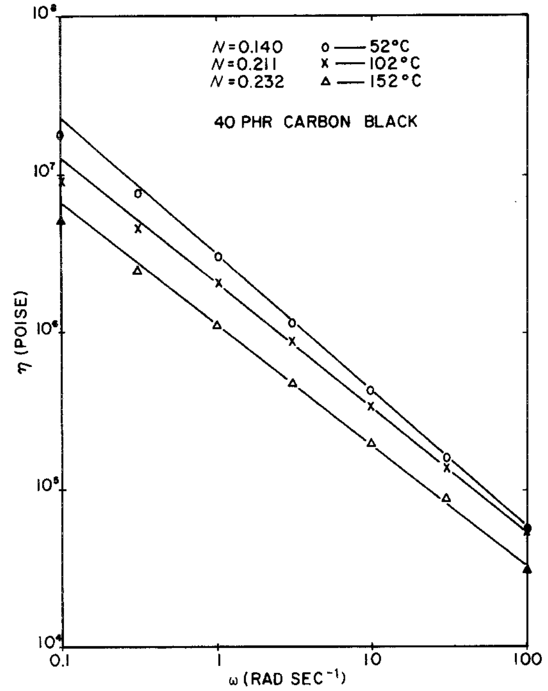

Figure 8 Viscosity against frequency at various temperatures for 40 phr of filler loading.

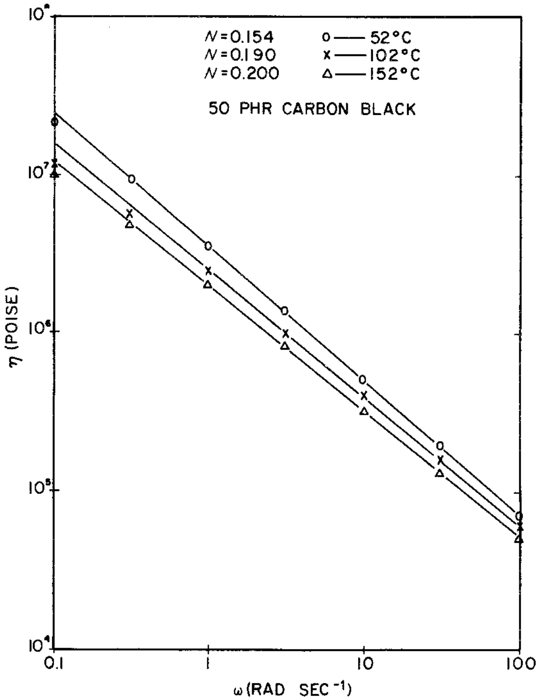

Figure 9 Viscosity against frequency at various temperatures for 50 phr of filler loading.

generally a good approach for a narrow range of shear rates or frequencies. Since in polymer processing we are more interested in the high shear rate range, only the high frequency range will be chosen for the fitting of a power-law if all the frequencies in Figs 6 to 9 can not be fitted. The viscosity at $\omega = 10\,\text{rad sec}^{-1}$ is again chosen as a reference point for the model. The power-law equation can then be written as

$$\eta = \left(\frac{\omega}{10}\right)^{n-1} \qquad (16)$$

where n is the index of power-law, (for a Newtonian fluid $n = 1$). The comparison between the experimental data and the theoretical calculations (solid-line plots) is shown in Figs 6 to 9. The result shows that the data at low frequency is lower than would be theoretically predicted by the power-law model. This finding is not surprising, because as frequency decreases the flow behaviour of polymers approaches that of a Newtonian fluid. The index of the power-law, n, for various temperature and filler loadings is listed in Table IV. The results of this study show that the flow behaviour of polymer systems approaches that of a Newtonian fluid as temperature increases, i.e., n increases with temperature. The increase of filler loading tends to decrease the value of n. This is probably due to the fact that filler loading broadens the relaxation spectrum of polymer systems as shown in Fig. 3. However, the value of n increases as filler loading increases at 52° C. It may be that the power-law is no longer applicable when the temperature is either close to the relaxation peak or in the rubbery plateau region. The lesser dependence of n on the temperature for high filler loading also indicates that high filler loading (up to a certain limit) will improve the control of moulding op-

TABLE IV The index, n, of the power-law model

ϕ_ω	n, at various temperatures (° C)					
	52	77	102	127	152	177
0.1	0.134	0.193	0.245	0.287	0.317	0.412
0.25	0.139	0.188	0.226	0.254	0.271	0.334
0.40	0.140	0.183	0.211	0.211	0.232	0.255
0.50	0.154	0.175	0.190	0.200	0.200	0.214

erations. The comparison of the viscosity data of the dynamic method and the high shear rate capillary rheometer will be discussed in a separate report.

6. Conclusions

A model of composite rheology for the viscosity of elastomer–filler is developed from the concept of the structural relaxation and glass transition of polymers. The model is based on the following phenomena:

(a) If the fillers do not change the main-chain structure of basic polymers, then the glass transition of polymer systems is independent of filler loading.

(b) At the glass transition temperature, T_g the viscosity of polymer systems at various filler loadings is the same.

(c) The effect of elastomer–filler interaction on viscosity depends on the surface and structure of fillers.

(d) The loading of fillers will broaden the relaxation spectrum of polymer systems.

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