JOURNAL OF MATERIALS SCIENCE 19 (1984) 2997–3004

Composite rheology

Part 2 *Effect of filler on the mechanical properties of filled elastomers*

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A model has been developed for explaining the modulus behaviour of filled elastomers. This model is suitable over a broad temperature range extending from well below the glass transition temperature to well above the rubbery region (see Fig. 1 for region definition). Results show that the rheological behaviour of polymer systems is of critical importance in determining the effect of filler on modulus. In the rubbery region, the effect of filler on modulus is more pronounced than it is outside the rubbery region. Within the leathery region (glass transition region), the effect of filler on modulus is very sensitive to small changes in temperature, and, as the temperature approaches that of the glass transition temperature, the effect of filler on modulus becomes very small. Finally, in the glassy region, the effect of filler on modulus is small and insensitive to temperature changes.

1. Introduction

In a previous study [1], we examined the effects of filler loadings on polymer viscosity. We wish to expand this study to include the influence of filler on the mechanical properties of polymers such as modulus. Since we expect the effects of filler on mechanical properties will depend on temperature range, as well as on the rheological character of the polymer of interest, we studied the mechanical properties of filled polymers over a wide temperature range. Such a study is of practical interest since filled elastomers are commonly used as engineering materials over a wide service temperature range.

2. Composite mechanics and relaxation spectra of filled polymers

There are many models dealing with the mechanical properties of filled polymers. Recently, Chow [2] has given an extensive review of these models. These models generally give reasonable correlations between modulus and filler; however, these correlations rarely reflect temperature dependence or quantify polymer–filler interactions over a broad temperature range.

Conventionally, the hydrodynamic model which was developed by Einstein [3] is used to explain the viscosity of filled elastomer systems. The hydrodynamical model is written as:

$$\eta = \eta_0 (1 + 2.5\phi) \tag{1}$$

where η and η_0 are the viscosity of the filled and unfilled elastomer, respectively, and ϕ is the volume fraction of filler. Later, Guth and Gold [4] modified Einstein's model to include a second-order term. The modified model can be written as:

$$\eta = \eta_0 (1 + 2.5\phi + 14.1\phi^2) \tag{2}$$

By substituting modulus for viscosity in Equations 1 and 2, these hydrodynamic models have also been used in attempts to explain the modulus of filled elastomers [5, 6]. However, it has been found by Hsich [1] that the relationship between viscosity and filler loading is temperature dependent instead of having a simple rationship are shown in Equation 2. The effect of filler on viscosity is more pronounced at high temperatures, but less pronounced at low temperatures. In other words, the dependence of viscosity on filler can be expressed as a function of the tem-

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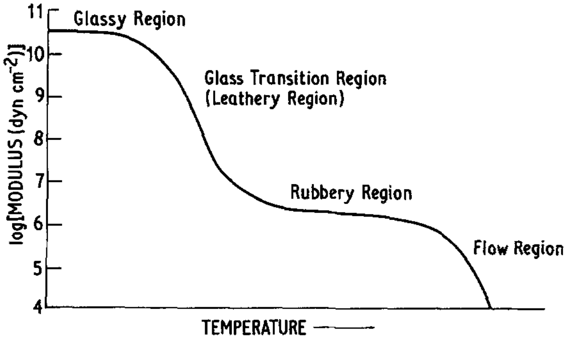

Figure 1 The mechanical spectrum of polymers.

perature difference $(T-T_g)$. When the temperature, T, is near the glass transition temperature, T_g, the difference in viscosity between filled and unfilled elastomers becomes small. It is expected that the modulus of filled elastomers will follow the same behaviour as viscosity.

Recently, the mechanical spectra of filled elastomer systems have been studied by Hsich *et al.* [7]. The shear storage modulus, G', and mechanical loss factor, tan δ, were obtained on natural rubber samples at various filler loadings. These data, measured at an angular frequency of $\omega = 10\,\mathrm{rad\,sec^{-1}}$ are replotted in Figs. 2 and 3. As has been mentioned earlier [1, 7], for these natural rubber samples, the glass transition temperature, T_g, and relaxation peak temperature, T_{rp}, are unaffected by filler loadings and/or degree of vulcanization.

Broadening the structural relaxation spectrum of polymers by increased filler loadings resulted in our extension of the leathery region into the rubbery region for high filler loadings as shown in Figs. 2, 3. As a consequence of this broadening effect, the statistical theory of Gaussian networks for the rubbery region [8] can no longer explain the mechanical properties of filled elastomers.

Flory [6] has stated that elastomeric materials can be considered to be in a non-relaxation state and to have a "perfect network" structure. The "perfect network" is defined as having no free chain ends; i.e. the primary molecular weight, M, is infinite. Then, from the statistical theory of Gaussian networks in an ideal rubbery state [8], the elastic modulus of a rubbery material can be expressed as:

$$E = \frac{3\rho R}{M_c}T \tag{3}$$

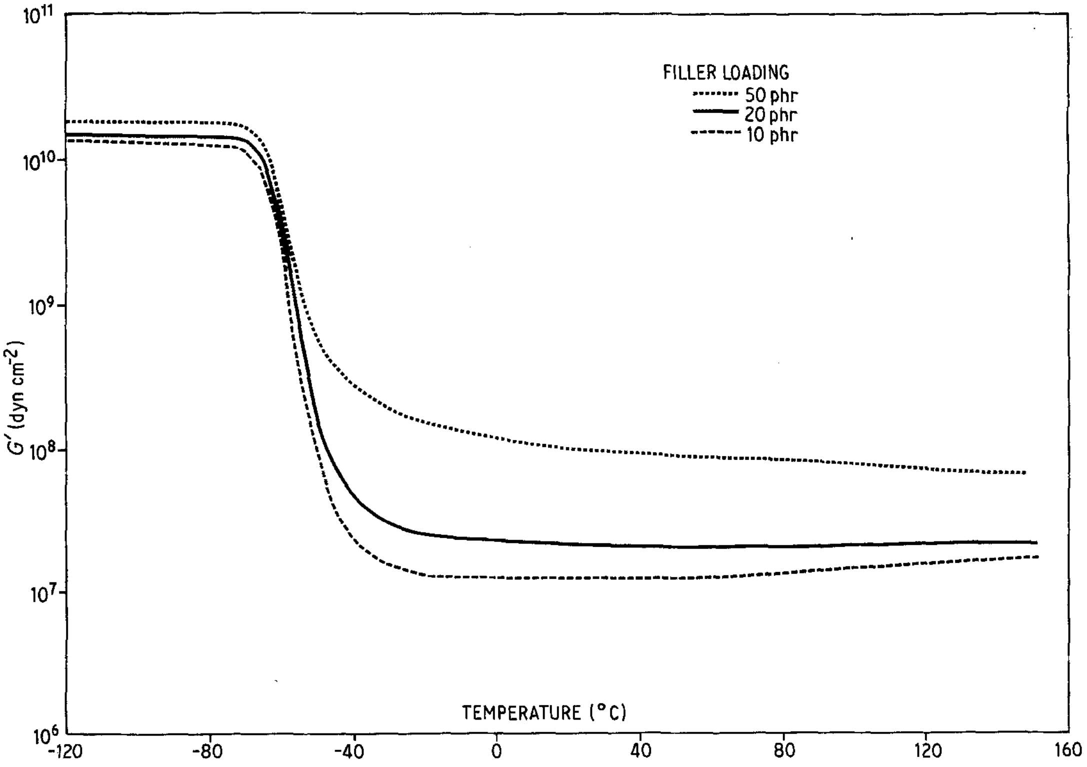

Figure 2 Relationship of the shear storage modulus, G', with temperature for three different filler loadings.

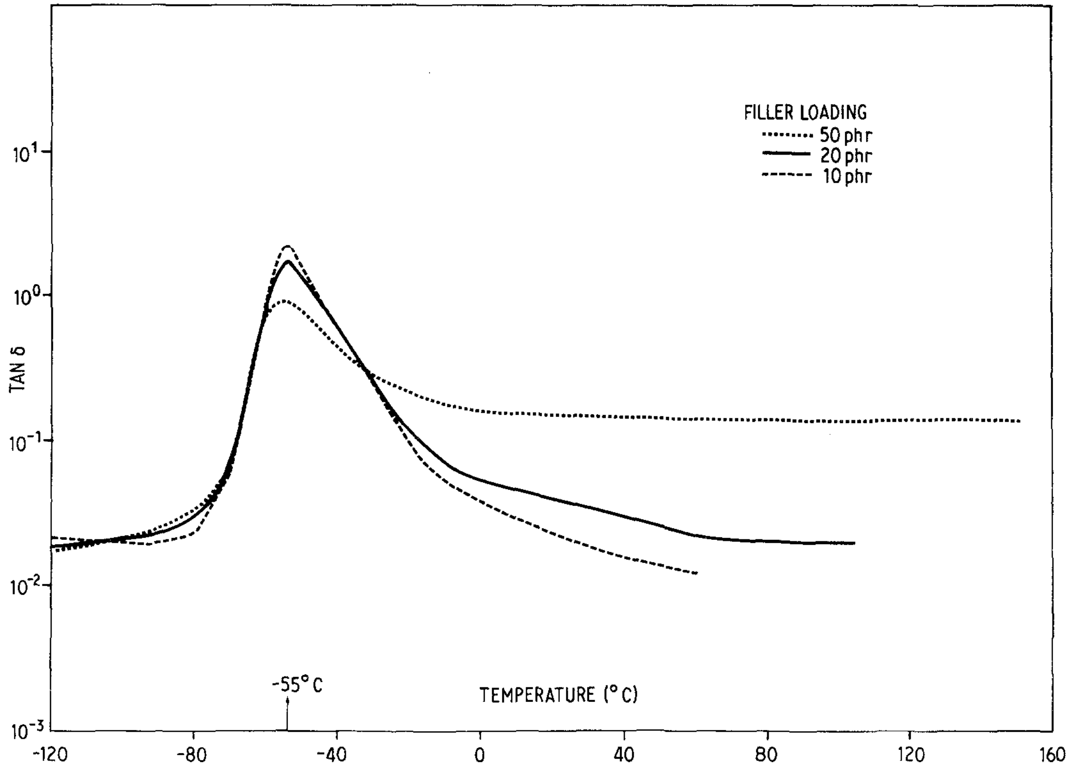

Figure 3 Relationship of the mechanical loss factor, tan δ, with temperature for three different filler loadings.

where ρ is the density, R is the gas constant, M_c is the molecular weight per cross-linked unit and M is the primary molecular weight of the polymer. For an ideal rubber, the elastic modulus, (or Young's modulus) E, is equal to three times the shear modulus, G. However, in practice, all networks have free chain ends which may be regarded as flaws in the structure. By considering these network defects, Flory [6] assumed that any real network must contain terminal chains bound at one end to a cross-linkage and terminated at the other by the end (free end) of a primary molecule. Then, the elastic modulus of a rubbery material can be modified from Equation 3:

$$E = \frac{3\rho R}{M_c} T \left(1 - \frac{2M_c}{M}\right) \qquad (4)$$

Recently, a hybrid equation which incorporates principles of the WLF equation [9] and the statistical theory of Gaussian networks for the rubbery state has been developed recently by Hsich *et al.* [7]. This equation explains and predicts the mechanical properties of filled and unfilled elastomers over a broad temperature range. The hybrid equation for the shear modulus of elastomers is written as:

$$G = G_0 \frac{T}{T_0} + \left(G_g - G_0 \frac{T}{T_0}\right) \exp \frac{-C_1 (T - T_g)}{C_2 + (T - T_g)} \qquad (5)$$

where G_g and G_0 are the shear moduli at the glass transition temperature, T_g, and the reference temperature, T_0, which is the lowest temperature at which ideal rubber behaviour begins. C_1 and C_2 are the same constants used in the WLF equation [9]. When C_1 is large, the exponential term in Equation 5 becomes negligibly small at temperatures considerably greater than T_g. In this case, Equation 5 can be simplified so that modulus is linearly proportional to temperature as in Equations 3 and 4.

On the other hand, if G_g/T is much larger than G_0/T_0, then Equation 5 resembles the WLF equation and can be written as:

$$G = G_g \exp \frac{-C_1 (T - T_g)}{C_2 + (T - T_g)} \qquad (6)$$

The hybrid equation (Equation 5) gives a satisfactory prediction of the mechanical properties of filled elastomers over a broad temperature

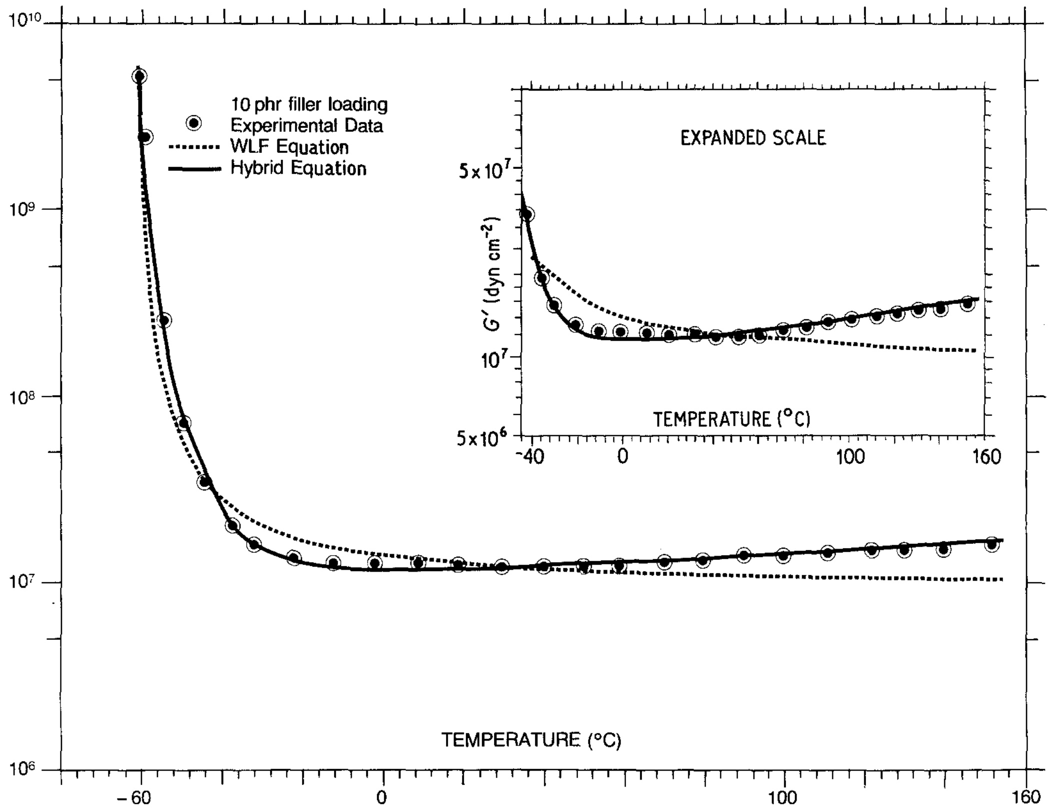

Figure 4 A plot of the shear storage modulus against temperature for natural rubber with 10 phr filler loading.

range. This can be seen from Figs. 4 to 6 which were replotted from [7]. Fig. 4 plots the shear storage modulus for natural rubber with 10 phr filler loading against temperature. It can be seen that at high temperatures (considerably above the glass transition temperature) modulus increases with increasing temperature. This is ideal rubbery behaviour as described by the statistical theory of Gaussian networks for the rubber state [12]. As filler loading increases to 20 phr, the trend of increasing modulus with increasing temperature is less pronounced as shown in Fig. 5. Here, the WLF equation also gives an improved prediction of the modulus. Finally, at a filler loading of 50 phr, the glass transition region or the structural relaxation spectrum becomes very broad. Consequently, both the WLF and hybrid equations give excellent predictions of the modulus over a broad temperature range as shown in Fig. 6. These data clearly show the broadening effects that increased filler loadings have on the polymer mechanical spectrum. Filler variations do not, however, have a marked effect on the glass transition temperature (Fig. 2).

The above discussion has demonstrated the effect of temperature on modulus at specific filler loadings. In the discussion to follow we will discuss the effect of filler on modulus at specific temperatures.

3. Experimental results and discussion

The shear storage modulus, G', of natural rubber at various filler loadings (carbon black N-330) was measured on a Rheometrics Mechanical Spectrometer operating in a torsion-rectangular testing mode at an angular frequency (ω) of 10 rad sec^{-1} at 0.2% strain.

Plots of the shear storage modulus against filler loading at various temperatures are shown in Figs. 7 to 9. Fig. 7 represents the rubbery region at temperatures from −40 to 100° C. Fig. 8, the glass transition region, has a temperature range from −60 to −45° C. Finally, Fig. 9 represents the glassy region at temperatures from −100 to −65° C. It can be seen from Figs. 7 to 9 that a linear relationship exists between modulus and filler loading at all temperatures when the data are plotted semi-logarithmically.

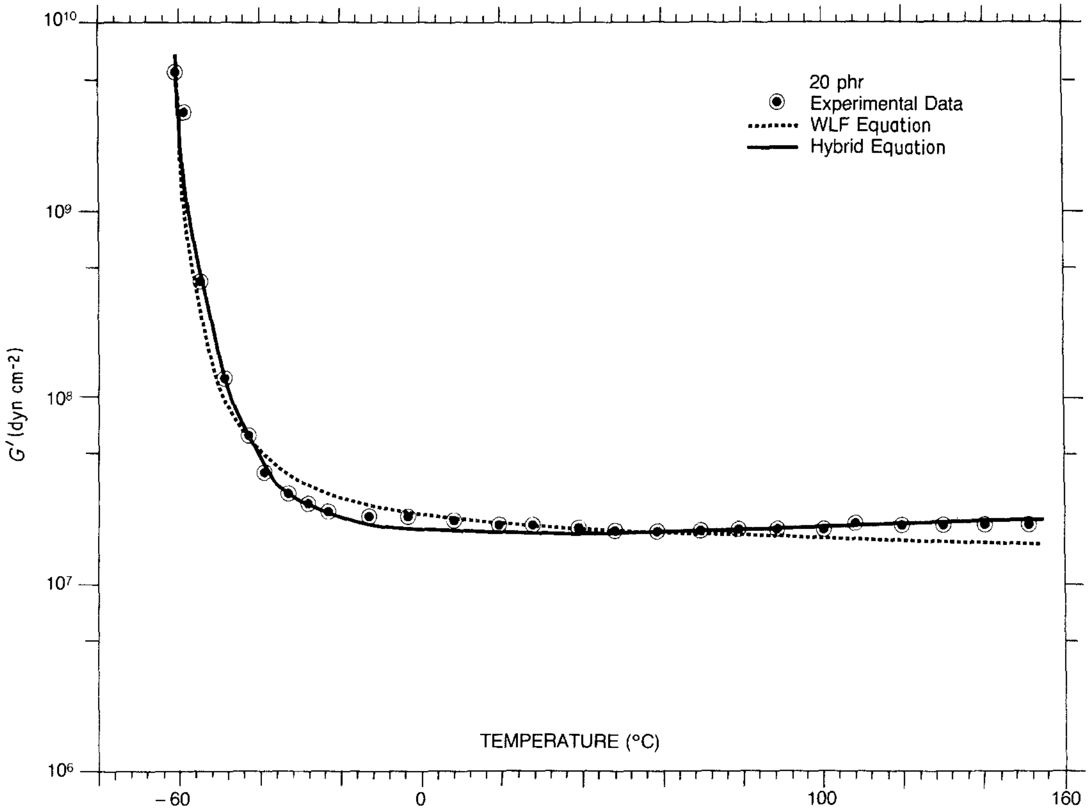

Figure 5 The shear storage modulus plotted against temperature for natural rubber with 20 phr filler loading.

Therefore, the shear storage modulus, G', can be expressed as a simple function of filler loading, ϕ, as follows:

$$\ln \frac{G'(\phi)}{G'(\phi_0)} = K(\phi - \phi_0) \qquad (7)$$

where $G'(\phi)$ and $G'(\phi_0)$ are the shear storage moduli at a filler loading, ϕ, and a reference filler loading, ϕ_0, respectively. K is the slope obtained from plots of ln G' against ϕ. K is a measure of the degree of polymer–filler interaction. In Fig. 10, there are plots of various values of the slope, K, against temperature. It can be seen from Fig. 10 that K is much more temperature sensitive in the glass transition region (−60 to −45° C) than in either the rubbery or glassy regions. We conclude that the degree of polymer–filler interaction in the glassy region is much less than the degree of polymer–filler interaction in the rubbery region. This large difference in polymer–filler interaction between these two regions is reflected by the high sensitivity of K in the glass transition region.

We can model K effectively by considering all three temperature regions separately. For example, from Fig. 10, we see that K decreases slightly with increasing temperature in the rubbery region (−40 to +120° C). A mathematical model describing this behaviour can be written as:

$$K = a - b\ln T \qquad (8)$$

where a and b are constants and T is temperature in degrees Kelvin. In the glass transition region, the model of K is more complicated because of its high temperature sensitivity. Modulus depends on temperature much the same as viscosity for filled elastomers at constant shear rate or frequency to be:

$$\ln \frac{\eta}{\eta_0} = C(\phi - \phi_0)\frac{T}{T_g}(T - T_g) \qquad (9)$$

where η and η_0 are viscosities at filler loading, ϕ, and a reference filler loading, ϕ_0, respectively, T is temperature, T_g is the glass transition temperature, and C is a constant. Similarly, a model for K in the glass transition region is given as:

$$K = c\frac{T}{T_g}(T - T_g) \qquad (10)$$

where c is a constant. Finally, in the glassy region,

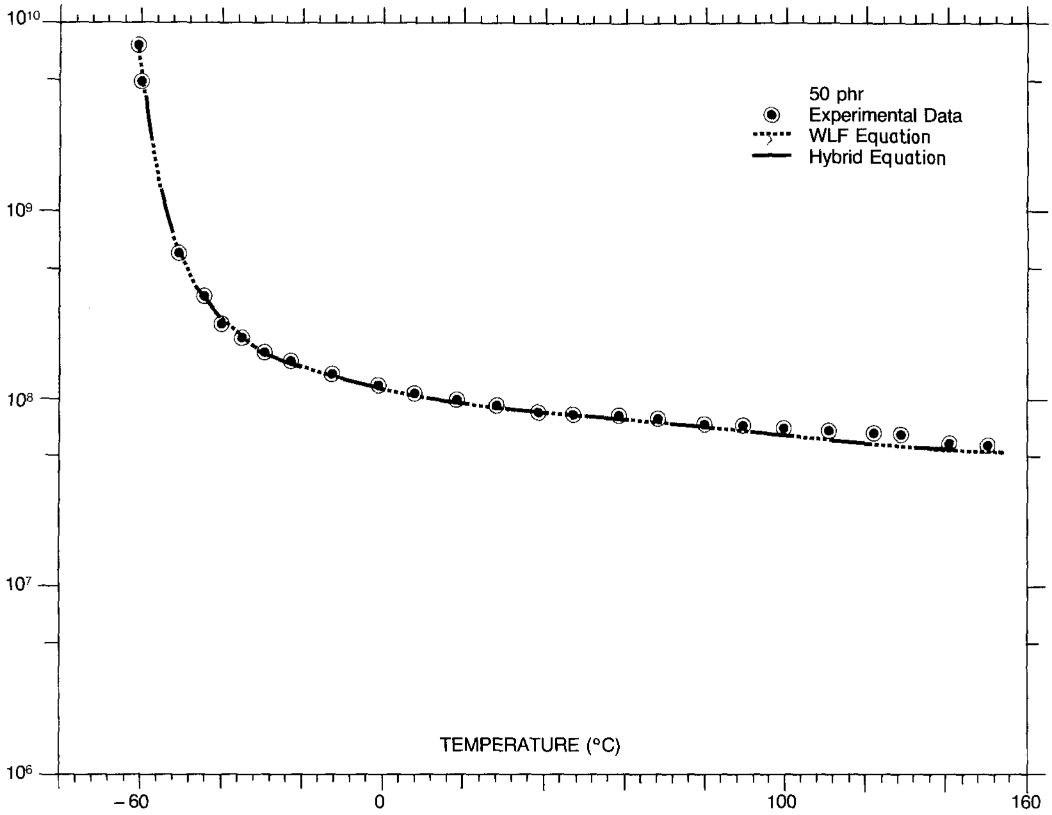

Figure 6 The shear storage modulus plotted against temperature for natural rubber with 50 phr filler loading.

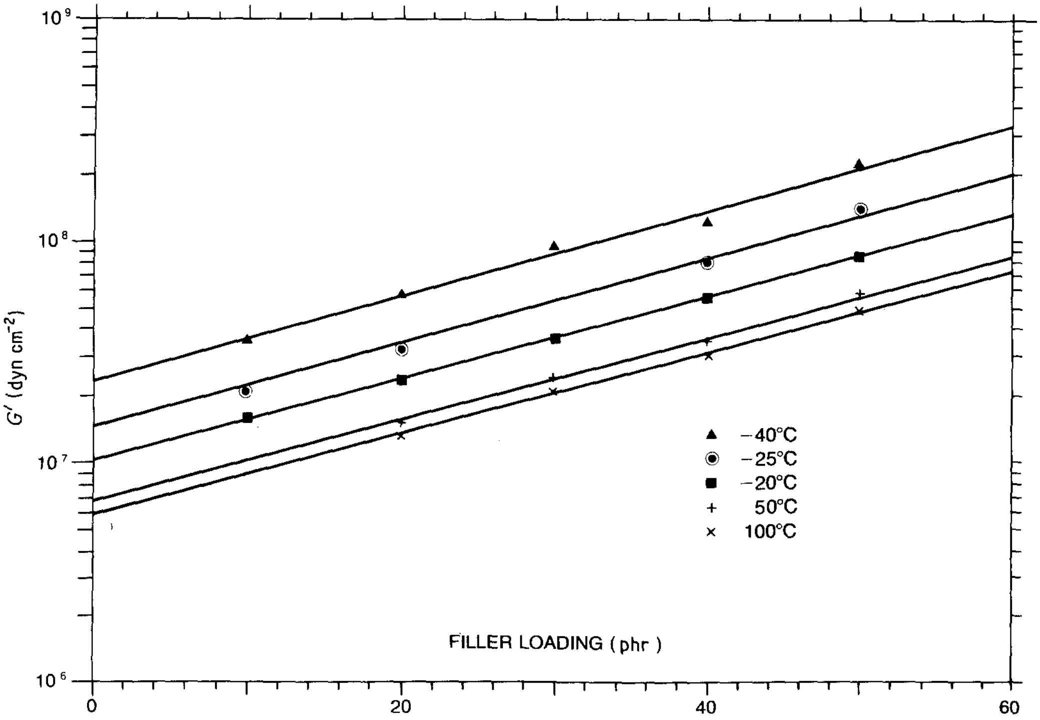

Figure 7 The shear storage modulus plotted against loading in the rubbery region.

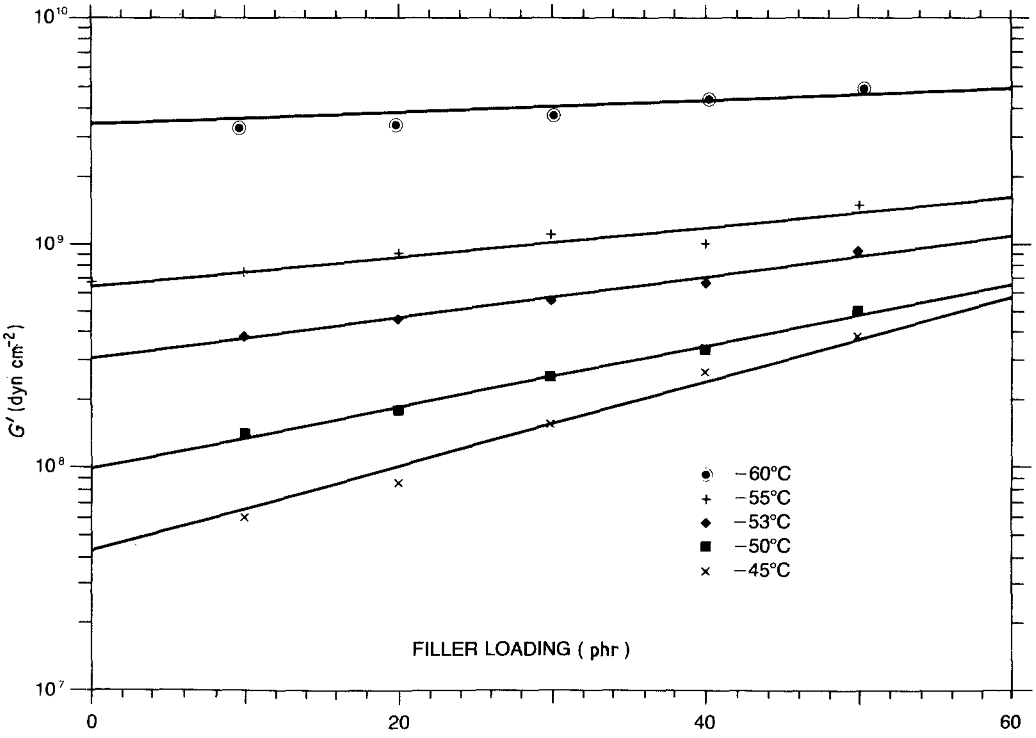

Figure 8 The shear storage modulus plotted against filler loading in the glass transition region.

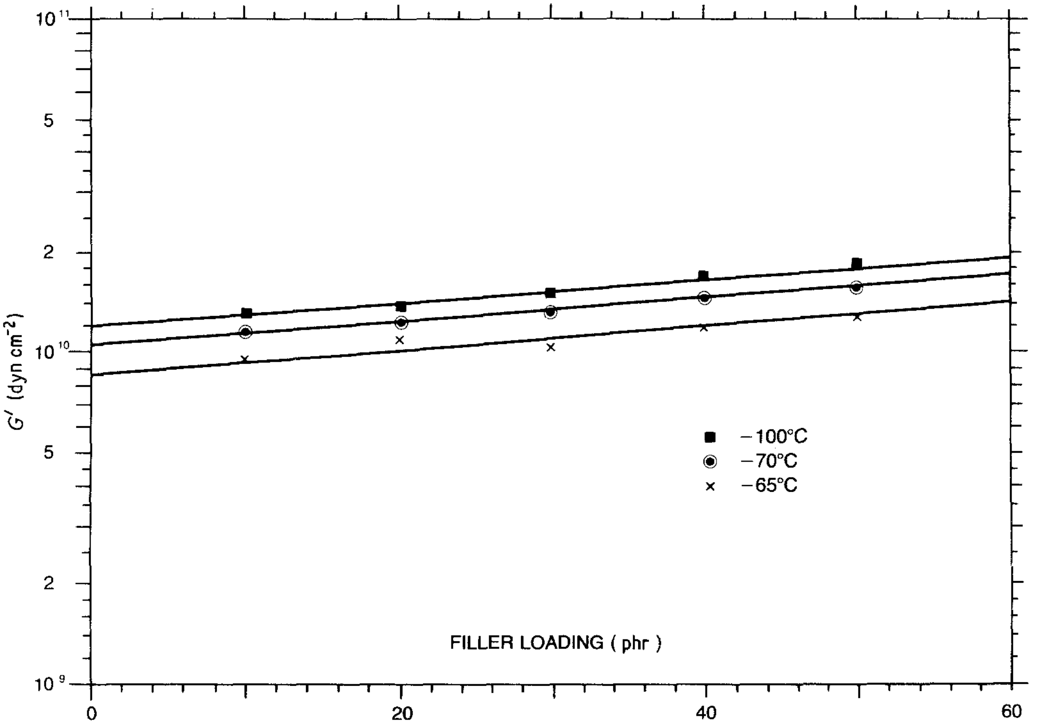

Figure 9 The shear storage modulus plotted against filler loading in the glassy state region.

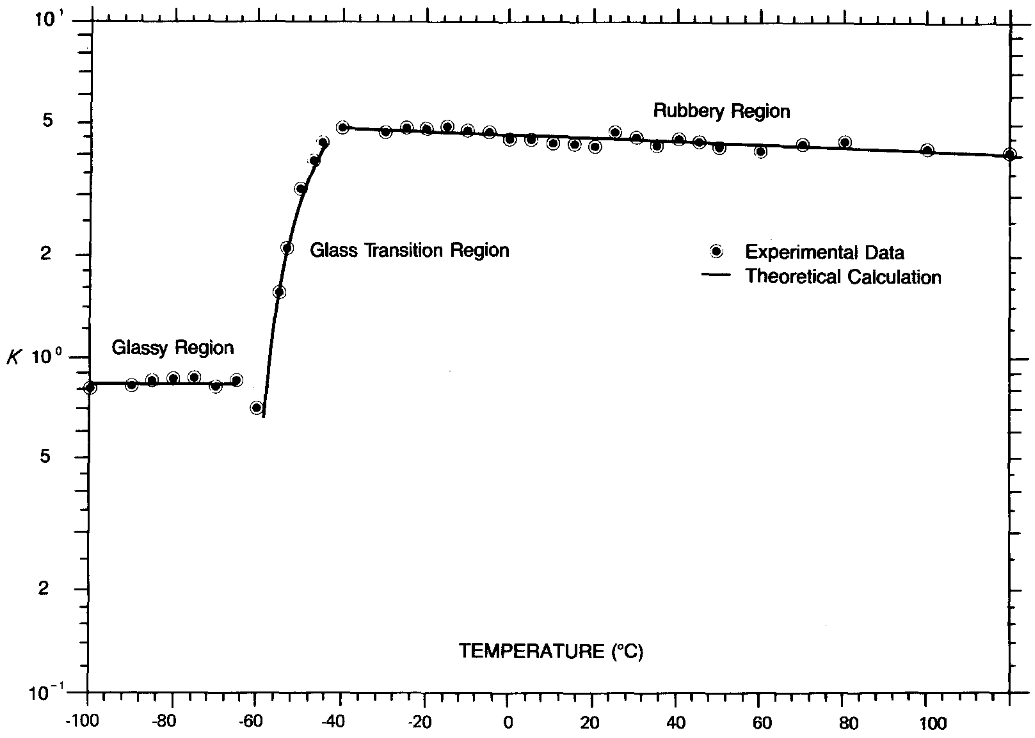

Figure 10 A plot of K against temperature.

the model for K is extremely simplified:

$$K = d \qquad (11)$$

where d is a constant.

Using Equations 8, 10 and 11 we calculated values of K from -100 to $+120^\circ$ C. These theoretical calculations are also plotted in Fig. 9. Values of the constants a, b, c and d used in these theoretical calculations were obtained by curve fitting the experimental data in Fig. 10 by a least squares technique. These values are listed in Table I. It can be seen in Fig. 10 that there is good agreement between the theoretical predictions and experimental values for K.

4. Conclusion

The effect of filler on the modulus of filled elastomers has been studied. The study indicates markedly different effects of filler on modulus depending on the temperature region in question. The effect of filler on modulus is much greater in the rubbery region than in the glassy region. This is exemplified by the high sensitivity of the degree of polymer–filler interaction in the glass transition region.

These filler effects have been successfully modelled according to the temperature range of interest, i.e. glassy region, glass transition region and rubbery region. There is excellent agreement between the filler effects measured experimentally and those predicted from these models.

TABLE I Polymer–filler interaction constants

Constant	Value
a	11.7
b	2.91
c (K^{-1})	0.248
d	0.830

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Received 8 July
and accepted 29 November 1983