A Hybrid Model for Mechanical Spectra of Filled and Unfilled Elastomers

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Synopsis

The dynamic mechanical properties of elastomers are of vital importance in determining the product design/performance relationship. Unfortunately, the statistical theory of Gaussian networks, commonly used for the ideal rubbery state, cannot adequately model the moduli of elastomers in engineering applications. The WLF equation, although not originally designed to predict moduli, has a functional form that predicts moduli for the range from T_g to $100°K$ plus T_g. A hybrid equation which incorporates elements of the WLF equation and the statistical theory of Gaussian networks in an ideal rubbery state has been developed for explaining the mechanical spectrum of elastomeric materials. The new equation satisfactorily models the mechanical properties for both filled and unfilled elastomers. This model shows that filler loading tends to broaden the relaxation spectrum. This finding agrees with a previous study on the viscosity of uncured elastomer-filler systems.

INTRODUCTION

Elastomers have been used as engineering materials in applications such as shock and vibration isolators for many years. In spite of this, we still lack a comprehensive understanding of the mechanical properties of elastomers at various filler loadings. Traditionally, elastomers are treated as materials in a classical "nonrelaxation" state. (For discussions of relaxation phenomena, see Refs. 1–3). As such, the theory of statistical mechanics of a network structure can be applied to describe the mechanical properties. Using this approach, Treloar[4] states that the elastic modulus of elastomers can be expressed as $E = 3\rho RT/M_c$, where R is the gas constant, T is the temperature, ρ is the density, and M_c is the molecular weight per crosslinked unit. From this theory of rubber elasticity, we can conclude that the modulus of "ideal rubbers" will increase with increasing temperature. An "ideal rubber" is defined as a rubber which is capable of storing all energy during deformation with no mechanisms for energy dissipation. Unfortunately, most elastomeric compounds do not behave as "ideal rubbers" over a broad service temperature range. Therefore, a study of the mechanical spectra of elastomers is needed to determine the temperature dependence of mechanical properties.

MECHANICAL SPECTRA OF POLYMERS

The mechanical spectra of polymers can be represented as in Figure 1. At very high temperatures in the "liquid flow" region uncrosslinked polymers behave as viscous liquids. In this region, a structural relaxation time τ of less than 0.1 s
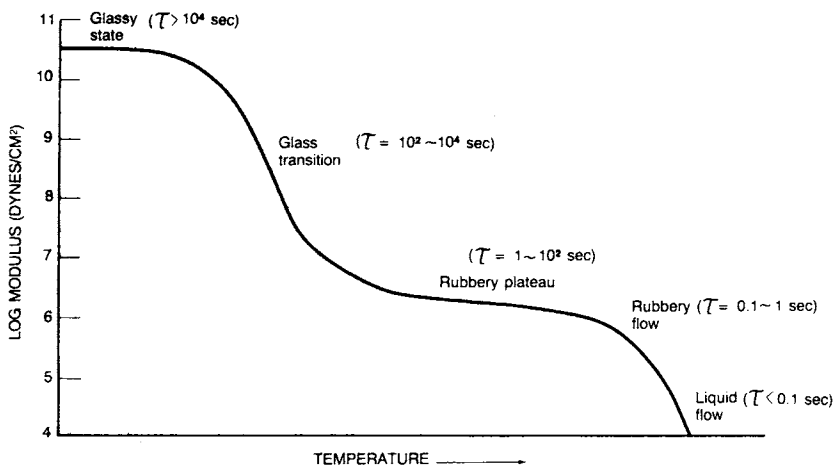
Fig. 1. The mechanical spectrum of polymers.

is common. The temperature in this region is commonly used in processing plastics. The temperature slightly below this region is the "rubbery flow" region. The structural relaxation time of molecules in this temperature region is on the order of 0.1–1 s. This is the processing temperature region of uncrosslinked elastomeric materials. With a further decrease in temperature, the "rubbery state" (or rubbery plateau) region will appear. Here, the structural relaxation time of nonvulcanized and vulcanized elastomers have been discussed recently by Hsich, Zurn, and Ambrose.[5,6]

As temperature further decreases from the "rubbery plateau" region, the mobility of the polymer chains decreases. In this "glass transition" region, the structural relaxation time increases to 10^2 to 10^4 s, and the mechanical loss factor, tan δ, of the polymers in this region is also high. At the low-temperature end of the glass transition region, there is a glass transition temperature T_g, in which the structural relaxation time is about 1800 s.[7] The glass transition temperature also can be defined as the intersection point between the slope of the modulus in the glassy state region and the slope in the glass transition region. Below the glass transition temperature, polymeric materials will be in the "glassy state," and their structural relaxation times are greater than 10^4 s. Generally, the use of materials as thermoplastics or elastomers will depend on the glass transition temperature, i.e., whether it is above or below room temperature.

The importance of understanding the structural relaxation spectra is seen in the following examples. In order to control the properties of polymers, one must know how to effectively use the structural relaxation time during material processing.

It is a common practice in polymer processing to increase the mechanical strength by inducing molecular orientation through stretching of the molecules. However, in order to tailor this supermolecular structure, one must be able to predetermine an optimum structural relaxation time which is equivalent to determining a particular operating temperature. In this case, the structural relaxation time at molecular stretching must be longer than the time required to freeze-in the desired structure during the cooling or quenching stage. If this condition is met, once the structure is formed, the molecules cannot reorient or

relax back to their original unstretched state during cooling. On the other hand, the structural relaxation time must be short enough (this is equivalent to a particular temperature or modulus as shown in Fig. 1), so that the molecules can be easily stretched without permanently fracturing the material. For typical thermoplastic materials, the optimum structural relaxation time during molecular stretching is on the order of 100 s. The actual value will depend on the operating speed of the process. As can be seen from Figure 1, the optimum structural relaxation time for molecular stretching is at the high temperature end of the glass transition region and at a temperature somewhat above the glass transition temperature.

In order to relieve thermal stress, one should anneal glassy polymers at long structural relaxation times or at low temperatures. Typically, a temperature just below the glass transition temperature is most satisfactory. In this way, the thermal stresses in glassy polymers can be easily released without fear of reforming those stresses during quenching to room temperature.

We have discussed the importance of understanding mechanical spectra (or structural relaxation spectra) in using polymeric materials. Snowdon[8] also has discussed the use of dynamic mechanical properties of elastomers in engineering material design. Kelley and Williams[9] have discussed the use of mechanical spectra in predicting the fatigue life of elastomers. As has been discussed by Hsich,[7,10] the physical and mechanical properties of glassy polymers will depend on the thermomechanical history of those polymers. In the rubbery state region, the mechanical properties can be tailored through the "interaction matrix," as has been discussed by Kelley and Williams.[9] More recently, a method of qualitative control on mechanical properties of elastomers by preprogramming cure conditions and/or filler loading has been developed.[5,6,11,12] In the discussion that follows, additional details about the effective use of elastomers as engineering materials via their mechanical spectra is presented.

MECHANICAL SPECTRA OF ELASTOMERS AND FILLER EFFECT

Classical Theory of Rubber Elasticity

Flory[13] has stated that elastomeric materials can be considered to be in a nonrelaxation 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,[4] the elastic modulus of a rubbery material can be expressed as

$$E = (3\rho R/M_c)T \tag{1}$$

where each of the symbols are as described earlier. 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[13,14] assumed that any real network must contain terminal chains bound at one end to a crosslinkage 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

eq. (1):

$$E = (3\rho R/M_c)T(1 - 2M_c/M) \tag{2}$$

As we can see from eqs. (1) and (2), the modulus of an ideal rubber is linearly proportional to the temperature. It should be noted that the ideal rubbery state considered by Flory[13] and others is a nonrelaxation state in which there is no mechanical energy dissipated during deformation. In such a case, the mechanical loss factor, tan δ, is negligibly small. This, of course, is not true for most engineering materials which, in many cases, have substantial amounts of energy dissipated during deformation. Also, in real elastomers ideal behavior is not exhibited until the temperature is much higher than T_g. In the following section, this is demonstrated experimentally.

Experimental Results on Mechanical Spectra of Elastomers

The elastomer chosen for the study of mechanical spectra is natural rubber. Because natural rubber has a large primary molecular weight and low tan δ (at room temperature and low filler loadings), it is considered to be an ideal rubber. The samples for study were prepared from the following recipe at various filler loadings:

Ingredient	phr
Natural rubber (SMR 5CV)	100
Reogen	1
Stearic acid	1
Zinc oxide	5
Agerite HP-S	1
Agerite resin D	1
Flexzone 3C	1.5
Wax	2
NOBS special	0.9
Monex	0.2
Sulfur	1.1
Dicup 40C	2

The filler used was carbon black N-330 from 0 to 50 phr (parts per hundred rubber). The samples were cured at 153°C for 10 min. The dynamic mechanical properties were recorded from a rheometrics mechanical spectrometer (RMS) operated in a torsion-rectangular testing mode with 1.5% strain at 10 rad/s angular frequency. The temperature for recording data ranged from −120°C to 160°C. The shear storage modulus G' and tan δ vs. temperature for three different filler loadings are shown in Figures 2 and 3, respectively. The mechanical spectra of cured natural rubber is very similar to that of uncured natural rubber reported previously.[15] However, the modulus of cured rubber is about one decade higher than that of the uncured rubber. The glass transition temperature T_g and relaxation peak temperature T_{rp} are at −61°C and −55°C, respectively. They are not affected by filler loading, as can be seen in Figures 2 and 3.

Since the temperature dependent behavior of mechanical properties is of primary interest in the use of elastomers as engineering materials, the shear storage moduli G' were plotted vs. temperature from −61°C to 160°C at filler loadings of 0, 10, 20, 30, 40, and 50 phr, as shown in Figures 4–9. Careful ex-
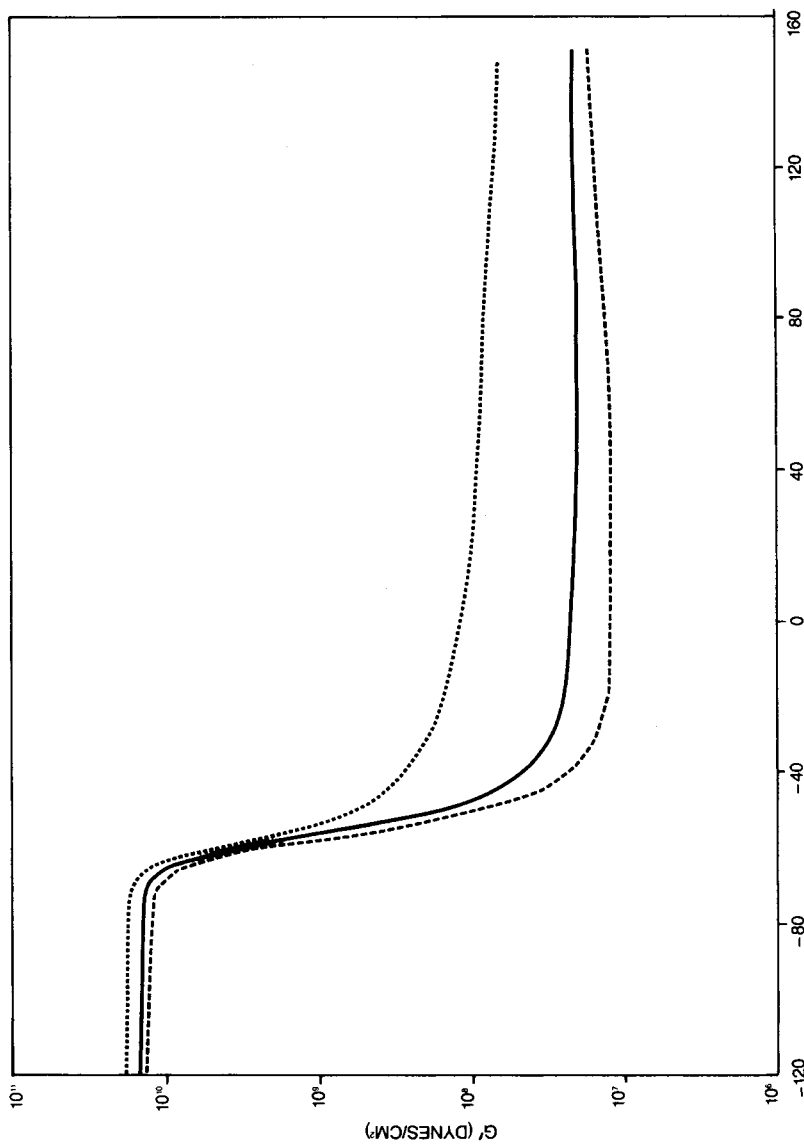
Fig. 2. Shear storage modulus G' vs. T for natural rubber at various filler loadings [phr: (·····) 50; (——) 20; (- - -) 10].
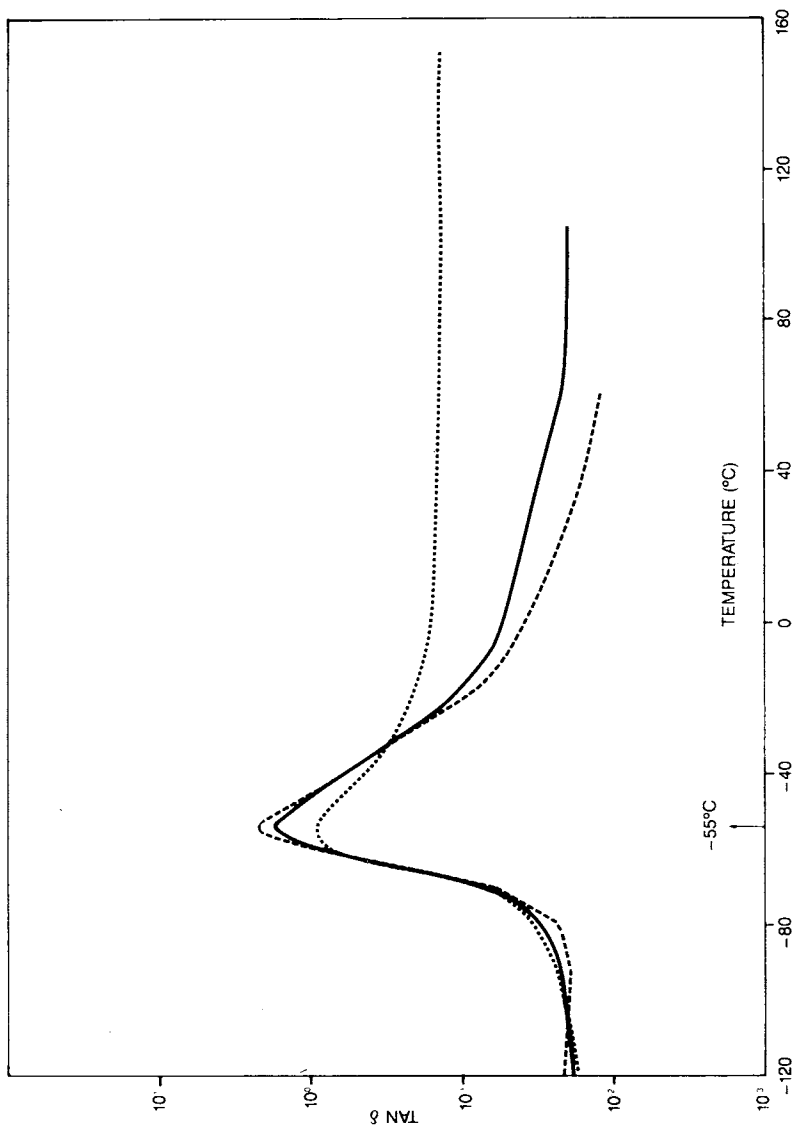
Fig. 3. Mechanical loss factor, tan δ, vs. T for natural rubber at various filler loadings [phr: (·····) 50; (——) 20; (- - -) 10].
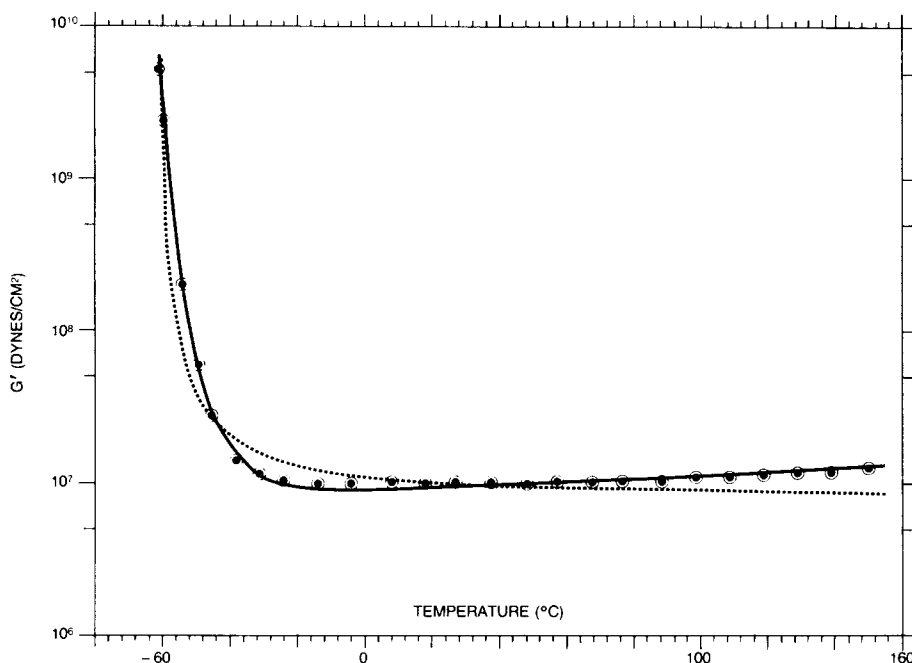
Fig. 4. G' vs. T for natural rubber at 0 phr filler loading [(⊙) experimental data; (·····) WLF equation; (——) hybrid equation].

amination of these data reveals some interesting trends. At high filler loadings, G' decreases with increasing temperature from T_g to 160°C (Figs. 8 and 9). At 20 or 30 phr filler loading, G' continues to decrease from T_g to room temperature, but then levels off to a constant value up to 160°C (Figs. 6 and 7). Finally, at low filler levels, G' decreases from T_g to room temperature, but actually increases from room temperature to 160°C. Such modulus increases with increasing temperature is behavior expected of an ideal rubber as discussed above. It is apparent that many elastomeric compounds, particularly in the service environment of most engineering materials, do not behave as ideal elastomers. For this reason, a model is needed for predicting mechanical properties of elastomers from T_g to high service temperatures.

A Hybrid Model of Mechanical Spectra of Elastomers

The mechanical properties of elastomers depend on the environmental temperature, the glass transition temperature, and the shape of the relaxation spectrum. For example, if T_g is close to room temperature and/or the structural relaxation spectrum is broad, then it is unlikely that the elastomeric material will behave as an ideal rubber over the entire usage temperature range. Therefore, the phenomenon of glass transition must be included in the interpretation of the mechanical spectra in the environmental temperature range of interest.

In the glass transition region, many thermodynamic, physical, mechanical, electrical, and chemical properties of polymers undergo striking changes. The
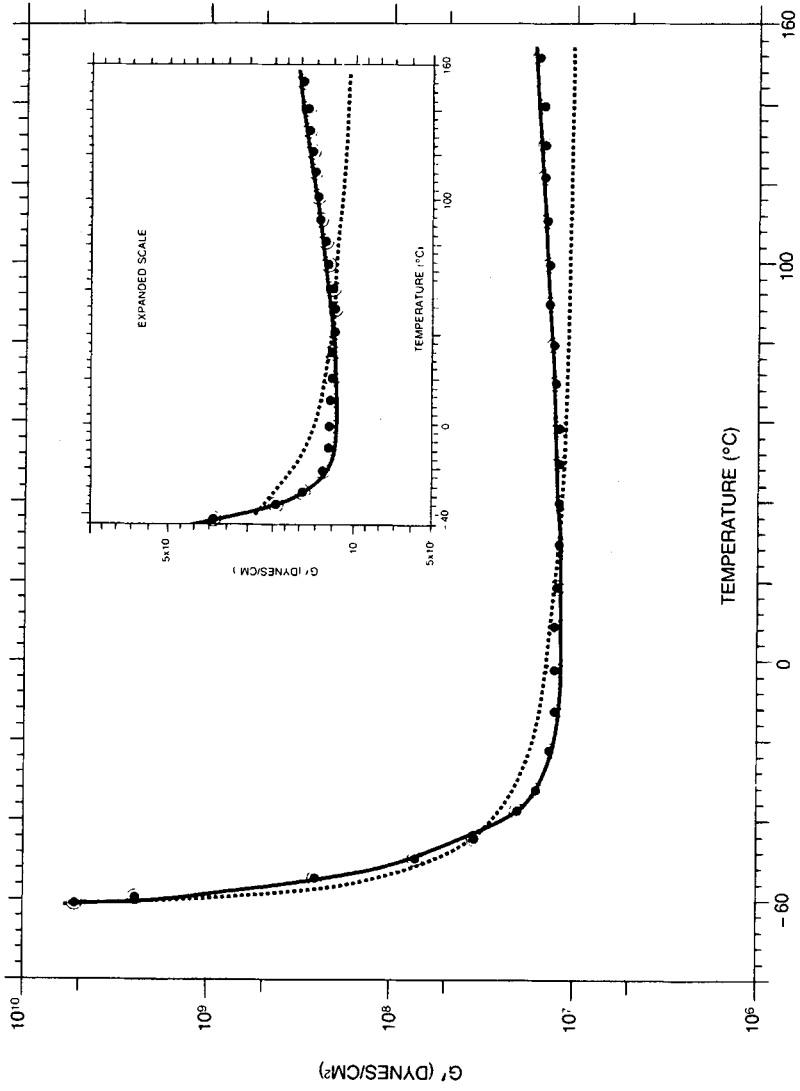
Fig. 5. *G'* vs. *T* for natural rubber at 10 phr filler loading (see Fig. 4 for symbols).
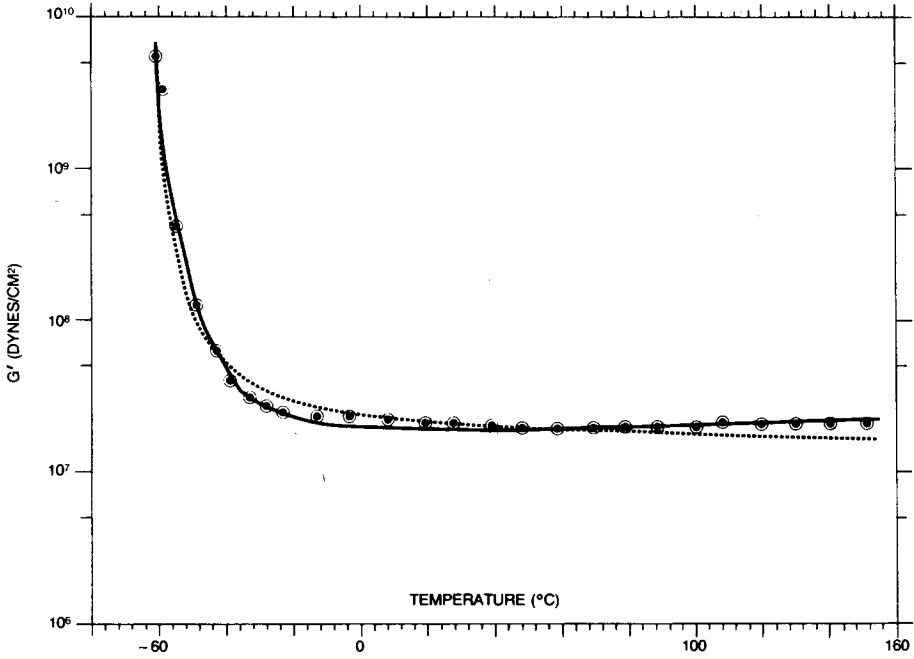
Fig. 6. G' vs. T for natural rubber at 20 phr filler loading (see Fig. 4 for symbols).
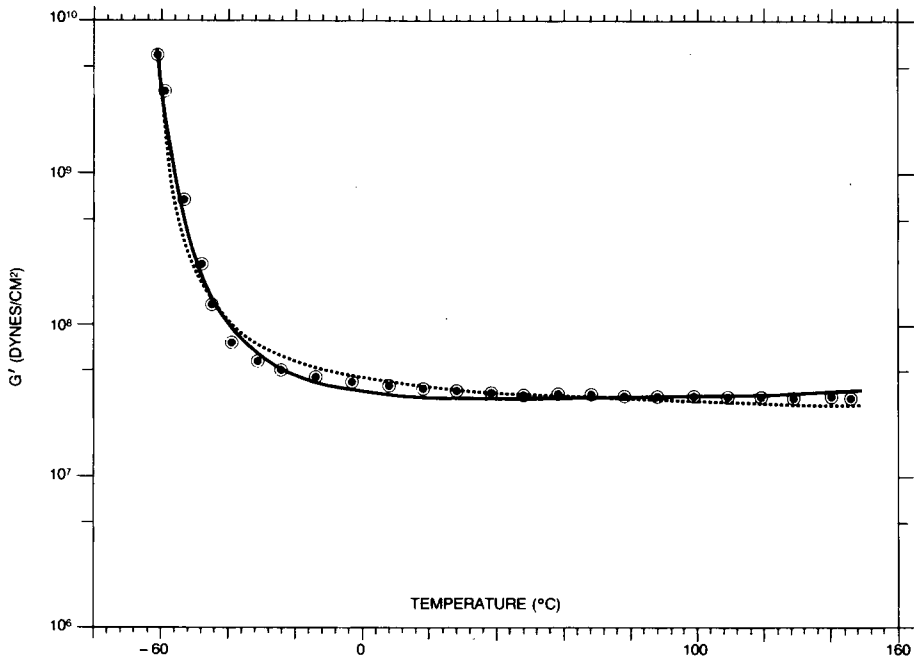

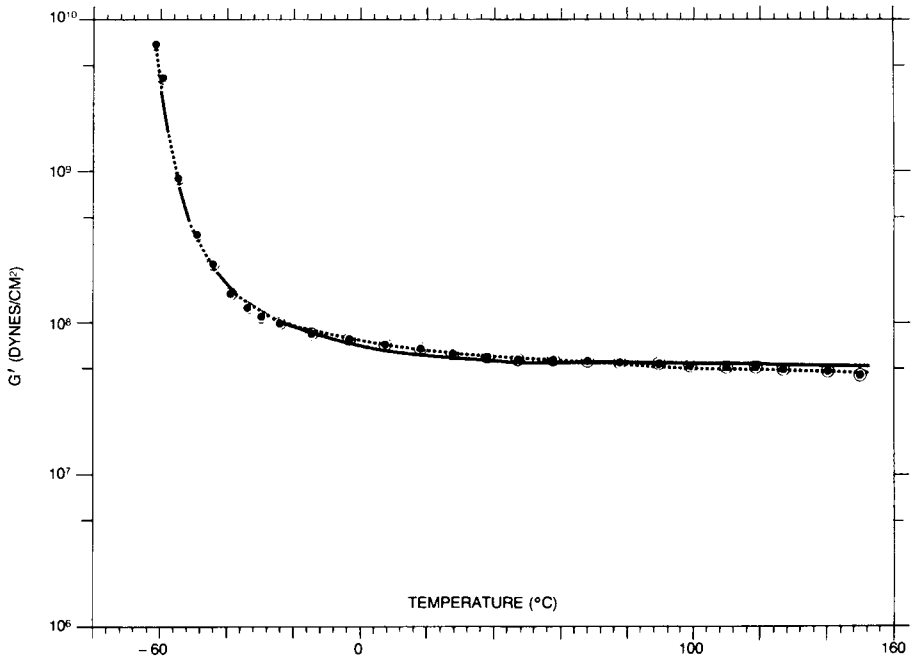Fig.7. G' vs. T for natural rubber at 30 phr filler loading (see Fig. 4 for symbols).

Fig. 8. G' vs. *T* for natural rubber at 40 phr filler loading (see Fig. **4** for symbols).
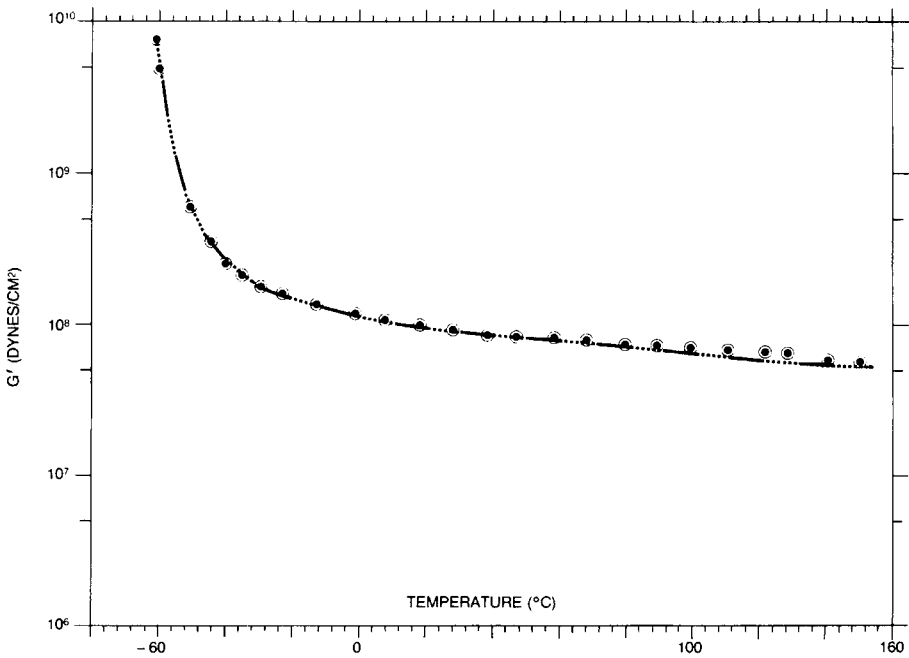

Fig. 9. G' vs. *T* for natural rubber at 50 phr filler loading (see Fig. **4** for symbols).

most obvious are those that occur in mechanical properties. For example, modulus and viscosity change by a factor of 10^3 over the glass transition region. There are many theories and hypotheses which are derived either from thermodynamic or relaxation aspects on the glass transition.[11,12,16] None of these explanations by themselves can be used to fully characterize glass transition. A complete explanation probably lies in a blend of these theories. Nevertheless, one of the most popular theories on the glass transition is the WLF equation.[17] In this equation, a_T is the shift factor defined as the ratio of the relaxation time at temperature T to the relaxation time at the glass transition temperature T_g, for a polymer in the temperature range from T_g to $T_g + 100°K$. The expression for a_T can be written as[17]

$$\ln a_T = -C_1(T - T_g)/C_2 + (T - T_g) \tag{3}$$

where C_1 and C_2 are constants which relate to the free volume and the difference of thermal expansion between the liquid and the glassy state of the polymer, respectively. In fact, the WLF equation can be correlated with Doolittle's free volume theory of viscosity in the glass transition region.[18] Then, the viscosity η at any given temperature T can be expressed as

$$\ln \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{4}$$

At temperatures above T_g and for nonideal rubbery behavior, G^* and G', the complex and storage dynamic moduli, are decreasing functions of temperature similar to the steady flow viscosity. Therefore, the WLF form was used as a preliminary prediction of G^* or G':

$$\ln \frac{G(T)}{G(T_g)} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{5}$$

where $G(T_g)$ is the modulus at T_g. From eq. (5), we can see that the modulus decreases with increasing temperature in the glass transition region. However, for elastomeric materials that behave as an ideal rubber, the modulus would increase with increasing temperature as shown in eqs. (1) and (2). Therefore, in order to predict the mechanical properties of elastomers over a broad temperature range, we need to develop a hybrid equation which includes aspects of both glass transition and rubber elasticity. Since a generalized autocorrelation function has served well to explain relaxation phenomenon,[5–7,9,11] an autocorrelation will be used again in modeling the mechanical properties of elastomers from the glassy to rubbery state. The hybrid equation for the shear modulus is expressed as

$$G(T) = G_0 \frac{T}{T_0} + \left(G(T_g) - G_0 \frac{T}{T_0}\right) \exp \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{6}$$

where G_0 is the shear modulus at a reference temperature T_0, the lowest temperature for an ideal rubbery state. If $G(T_g)$ is much larger than G_0 [or $G(T_g)/T \gg G_0/T_0$), then eq. (6) becomes the WLF form as shown in eq. (5). On the other hand, if the temperature in question is much higher than the glass transition temperature (i.e., $T \gg T_g$) and C_1 is large, then eq. (6) has the form of the elastic modulus expression shown in eqs. (1) and (2). This is true because the exponential term in eq. (6) becomes negligibly small. When the relationships

of $G(T_g)/T$ to G_0/T_0 and T to T_g are intermediate to those extremes discussed above, the WLF and/or elastic modulus equations are inappropriate by themselves for describing the polymer mechanical spectrum. It is in these instances when a combination of the two (the hybrid equation) is needed.

Equation (6) was used to fit the data of the shear storage modulus vs. temperature in Figures 4–9. The constants C_1 and C_2 and G_0/T_0 of the WLF equation and new model were determined by a least-squares minimization using Powell's method of conjugate directions.[19] Mathematically, Powell's algorithm minimizes the sum of the squared error between the normalized experimental points and the function to be fit by altering the constants of the function. Over several iterations, the total error can be reduced to a minimum, in this case, leading to the "best fit" values of the constants listed in Table I.

For filler loadings greater than 30 phr the values for G_0/T_0 at high filler loadings decrease. In fact, at 50 phr carbon black, the value of G_0/T_0 is negligibly small compared to values at low filler content. This is due to the fact that the lowest temperature for ideal rubbery behavior, T_0, if it exists at all, increases dramatically at high filler contents. Ideal behavior is not expected of a highly filled rubber because loading provides an energy dissipation mechanism.

The results of calculations from the new hybrid model were plotted in Figures 4–9 along with the experimental data. There is excellent agreement between the experimental results and those calculated from the hybrid model at all filler loadings. Results obtained from the WLF equation also are shown in Figures 4–9 for the purpose of comparison. The WLF equation, even though not intended to describe the mechanical spectra of elastomers, does very well at high filler loadings (Fig. 8 and 9). This is probably due to the broadening effect that high filler loadings have on the mechanical spectrum. In Figures 4 and 5, at temperatures considerably above the glass transition, the rubber at low filler loadings behaves as if in the ideal rubbery state. The hybrid equation (6) models such behavior and shows an increasing modulus in the rubbery region. An expanded temperature scale in Figure 5 illustrates this more clearly. As filler loading increases up to 20 or 30 phr, the upturn behavior of modulus with increasing temperature, starts to vanish as shown in Figures 6 and 7. When filler loading increases to 40 phr, the transition region from glassy to rubbery becomes broad. At this point, the rubbery plateau region is overshadowed due to the broadening phenomenon. Indeed, at high filler loadings, the constant G_0/T_0 is negligibly small compared with G_0/T in the hybrid equation (6). In this case, the hybrid equation (6) is essentially the same as the WLF equation. The data in Figures 8 and 9 and Table I substantiate this phenomenon. The broadening

TABLE I

Filler loading (phr)	Hybrid equation			WLF equation	
	C_1	C_2 (°K^{-1})	G_0/T_0 (dyn·cm^{-2}·°K^{-1})	C_1	C_2 (°K^{-1})
0	11.59	18.40	3.0×10^4	6.45	3.52
10	10.45	16.81	3.7×10^4	6.32	4.36
20	8.53	15.66	5.0×10^4	5.93	5.44
30	7.45	14.84	7.4×10^4	5.50	7.28
40	5.66	11.39	4.4×10^4	5.20	9.20
50	4.99	10.84	0	4.99	10.84

of the structural relaxation spectrum with increasing filler loadings for cured rubbers agrees with those results of a previous study on the viscosity of uncured rubbers.[15] A broadening of the chemical relaxation spectrum by increasing filler loadings also has been found in a study of the cure reaction.[5,6,11]

CONCLUSIONS

Both an understanding of the mechanical spectra of elastomers and the ability to model the mechanical properties of elastomers over a broad temperature range are important in improving material design and performance. For this reason, a hybrid equation which incorporates aspects of both glass transition and ideal rubbery behavior was derived. This new equation satisfactorily models the mechanical properties of elastomers over a broad temperature range and at a variety of filler loadings.

References

1. R. O. Davies and G. O. Jones, *Adv. Phys.*, **2**(7), 370 (1953).

2. R. O. Davies and Jones, *Proc. Roy. Soc. London*, **A217**, 426 (1953).

3. P. A. Egelstaff, *An Introduction to the Liquid State*, Academic, London and New York, 1967, pp. 118–198.

4. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Clarendon, Oxford, 1958, pp. 64–84.

5. H. S. Y. Hsich and R. J. Ambrose, *Organic Coat. Appl. Polym. Sci., Proc.*, **47**, 649 (1982).

6. H. S. Y. Hsich, R. M. Zurn, and R. J. Ambrose, *Am. Chem. Soc. Symp. Ser.*, to appear.

7. H. S. Y. Hsich, *J. Mater. Sci.*, **15**, 1194 (1980).

8. J. C. Snowdon, *Vibration and Shock in Damped Mechanical Systems*, Wiley, New York, 1968, Chap. 2.

9. F. N. Kelley and M. L. Williams, *Rubber Chem. Technol.*, **42**, 1175 (1969).

10. H. S. Y. Hsich, *J. Mater. Sci.*, **14**, 2581 (1979).

11. H. S. Y. Hsich, *J. Appl. Polym. Sci.*, **27**, 3265 (1982).

12. H. S. Y. Hsich, M. J Hronas, H. E. Hill, and R. J. Ambrose, *J. Mater. Sci.*, in press.

13. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca and London, 1971, Chap. 11.

14. P. J. Flory, *Chem. Rev.*, **35**, 51 (1944).

15. H. S. Y. Hsich, *J. Mater. Sci.*, **17**, 438 (1982).

16. G. E. Roberts and E. F. T. White, *The Physics of Glassy Polymers*, R. N. Haward, Ed., Wiley, New York, 1963, Chap. 3.

17. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).

18. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

19. M. J. D. Powell, *Comput. J.*, **7**, 155 (1964).