The Glass Transition Temperature of Filled Polymers and Its Effect on Their Physical Properties*

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Synopsis

The glass transition temperature, dynamic shear moduli, and bulk viscosities of Phenoxy PKHH (a thermoplastic polymer made from bisphenol-A and epichlorohydrin) filled with glass beads and Attapulgite clay were investigated. The glass temperature of the polymer increased with increasing filler concentration and with increasing specific surface area of the filler. The data were interpreted by assuming that interactions between filler particles and the polymer matrix reduce molecular mobility and flexibility of the polymer chains in the vicinity of the interfaces. From the measured moduli and the viscosities of the filled and unfilled materials, the modulus reinforcement ratio in the glassy state and the relative viscosity in the viscous state were obtained as functions of the filler type and concentration. The relative modulus for the glass bead composite system follows the Kerner equation, while the clay-filled systems exhibit slightly greater reinforcement. The relative viscosities are strongly temperature dependent and do not follow conventional viscosity predictions for suspensions. It is suggested that the filler has a twofold effect on the viscosity of the composite materials; one is due to its mechanical presence and the other is due to modifications of part of the polymer matrix caused by interaction. Using the WLF equation to express all modifications of the matrix, one can isolate a purely mechanical contribution to the viscosity reinforcement. This mechanical part is approximately bounded by the theoretical predictions of Kerner,[32] Mooney,[36] and Brodnyan,[41] for suspension viscosities.

INTRODUCTION

The main objective of this work is to study the extent of interaction between a polymeric matrix and a rigidly elastic filler and its effect on certain macroscopic properties of the composite material. An attempt has been made to separate changes in physical properties of the composite into two contributions—one caused by the matrix undergoing modifications and one due to the mechanical reinforcement by the filler particles.

When an organic polymer is mixed with an inorganic reinforcing filler, the polymer must wet the surfaces of the filler in order to promote continuous phase boundaries. The strength across the phase boundaries, or adhesion, will naturally have effects on the stress-strain behavior. Recent studies of composite materials have shown that fracture toughness,[1] ultimate tensile strength, and ultimate elongation[2] are varied by changing the degree of

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adhesion between the constituents.   In addition, the presence of a second phase can modify the structure and morphology of the polymeric matrix in the vicinity of the phase boundaries.   Consequently, the average properties of a polymer in the presence of a second phase might be different from the bulk properties of the pure polymer.   These changes not only have an additional effect on the stress-strain behavior but could be a measure of the effectiveness of interaction between phases.

The past decade has brought forth a considerable amount of work on the effects of reinforcing fillers on the bulk properties of polymeric composites. The earliest studies of composite properties were carried out on filled rubbers.   Investigators found changes in thermodynamic properties[3-5] and mechanical properties[6-8] due to the presence of filler.   Similar changes were detected in filled thermoplastic materials by Kargin and co-workers,[9-11] Lipatov,[12,13] Nielsen,[14] Uskov,[15] and others.   In general, these researchers found increases in mechanical properties with increasing filler concentration or increases in the glass transition temperature of the matrix.   There are some contradictory data concerning the glass temperature.   Van der Wal et al.,[16] for example, observed no changes in the glass temperature of sodium chloride-filled polyurethanes, and Kumins and Roteman[17] indicated a decrease of glass temperature of TiO_2-filled polyvinylacetate at certain filler loadings.

Similar changes in mechanical and thermodynamic properties have been found in partially crystalline polymers.   It is probably not too remote to compare a filled polymer having good interactions at the internal phase boundaries with a partially crystalline polymer.   In the latter case, the dispersed crystalline regions are analogous to the filler particles.   Increases in glass transition temperature[18-20] and shifts in viscoelastic relaxation times[21] with increasing crystallinity have been experimentally determined.   The shifts are similar in magnitude to those found in filled polymers.

It should be pointed out that the glass temperature of the *composite* is really the temperature at which the amorphous *matrix* changes its thermodynamic properties, since an inorganic filler would not undergo such a change at this temperature.   If this glass temperature is measured accurately, it could be a measure of the change in matrix properties due to the addition of a second phase.   This phenomenon is independent of the mechanical reinforcement effect of the filler.

The following treatment is based on the assumption that if there is interaction between a filler and a polymer matrix, the molecular properties of the polymer matrix will be affected.   The nature of the molecular change will, of course, depend specifically on the type of interaction involved.   For example, a chemical reaction between the constituents can change the chemical constitution and average molecular weight of the polymer phase. On the other hand, a strong adsorption of polymer side groups on the filler surface may merely change the mobility and flexibility of part of the polymer chains.

These two types of interaction define the range of possible coupling effects

and although they differ energetically, they possess the common property that both restrict the mobility and flexibility of part of the molecule chains. In any specific composite system, it is likely that more than one phenomenon occurs that changes the properties of the polymer molecules.

The important point is that the average physical properties of the matrix material in the composite system are not necessarily the same as those of the pure unfilled material. It follows that a composite, in which a significant fraction of the polymer is in contact with a filler surface and which has interaction between filler and polymer, should exhibit the degree of interaction (regardless of mechanism) by changes in the thermodynamic and viscoelastic properties of the matrix.

Considered in this paper is the behavior of composites of Phenoxy PKHH filled with soda-lime glass beads and Phenoxy PKHH filled with Attagel 40. Phenoxy PKHH is a thermoplastic resin made by Union Carbide Corporation; repeating structure: $[O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(OH)-CH_2]$; molecular weight: about 31,000 g/g-mole; primary glass transition: $98 \pm 1°C$. The beads are Ballotini Industrial Glass Beads, size 3000, U.S. Screen No. 325 and finer, $d < 44$ μ, untreated surface; surface area: 0.078 m²/g. Attagel 40 is an Attapulgite clay with a rod-like morphology and an average ultimate particle size of 200 Å diameter and 1 μ length; L/D $\sim$ 50; surface area: 180–200 m²/g.

It will be shown that: (1) The glass transition temperature of the polymer is increased by the presence of filler. (2) Part of the increase in viscosity of the composite due to the presence of filler can be related to the shift in the glass transition temperature of the polymer phase. (3) The changes in physical properties of composite systems in the viscous state can be related to those in the glassy state at least for simple filler geometries.

EXPERIMENTAL PROGRAM

The composite specimens used in this work were prepared by two different techniques. In one, the polymer was dissolved in a solvent mixture of 40% acetone, 40% toluene, and 20% butanol, and the dried filler was mixed in the solution. The filler was ultrasonically dispersed, the solvent was slowly evaporated, and the composite paste was placed in a vacuum oven and predried at 120°C. Then the composite flakes were crushed in a mortar and the resulting powder was dried for another 100 hr. Thin bars for modulus tests or cylindrical plugs for viscosity tests were compression molded.

The other technique employed a heated roller mill for dispersing the filler material in the polymer matrix. Extensive crossrolling was applied to ensure good dispersion of the filler. The rolled material was also crushed to a powder and compression molded. A change in fabrication procedure had no effect on the experimental results.

Glass transition temperatures of the materials were measured using a du Pont 900 Differential Thermal Analyzer (DTA).[22] With increasing filler concentration, there is a diminishing response marking the glass transition

temperature because of dilution of the polymer phase. It can be difficult to measure the glass temperature of highly filled materials. It was found that measuring the transition point while cooling the sample from the viscous to the solid state yielded the more reproducible results. Dynamic shear moduli and damping capacities of the composites below their glass temperatures were measured with a freely oscillating torsion pendulum.[23,24] Viscosities of the materials above their glass temperatures were measured using a parallel plate plastometer,[25] attached to an Instron testing machine. The only difference between this latter experiment and those used earlier by other investigators[26] was the application of a constant rate of deformation (with $\dot{\gamma} < 10^{-2} \sec^{-1}$) at increasing loads.

RESULTS AND DISCUSSION

Figure 1 shows that the addition of filler to the phenoxy polymer causes an increase in the DTA-measured glass transition temperature of the composite (T_{gc}). This increase is larger for the Attapulgite-filled composite than for the glass–phenoxy system. The glass transition point of the pure polymer (T_{g0}) is approximately 98°C, while that of a 40%-filled composite is 4–5°C higher for glass beads as a filler and 8–9°C higher for Attapulgite. The functional dependence of the glass transition temperature on the filler concentration is similar to the dependence which Fox and Flory[27] and Ueberreiter and Kanig[28] determined for T_g as a function of molecular weight.

The concept of free volume, which has been employed successfully in explaining the effects of solvents, molecular weight, or degree of crosslinking on the glass temperature,[29] may also be applicable to a reinforced polymer. If it is assumed that the free volume is decreased when the polymer is adsorbed on the filler surfaces, the measured glass temperature should increase with increasing filler concentration. That portion of the polymer matrix V_A under the influence of the filler surfaces can be expressed by $V_A = V_T \phi_f \hat{s} \delta$, where V_T is the total volume of the composite, ϕ_f is the volume fraction of filler, $\hat{s}$ is the specific surface area of filler (cm²/cm³), and δ is a "zone of influence" around each filler particle (cm³ polymer/cm² filler). When $V_A = (1 - \phi)_f V_T$, (or $\phi_f = 1/(1 + \hat{s} \delta)$, all of the polymer phase is exposed to the influence of the filler. Qualitatively, one would expect the glass temperature to increase with ϕ_f, reaching a constant value as one approaches $\phi_f = 1/(1 + \hat{s} \delta)$.

This concept is somewhat of an oversimplification. It is more likely that if there is a change in properties caused by the filler surface, the polymer matrix will change continuously with increasing distance from the surface. This should result in a broadening of the measured transition region as well as an increase in the "average" glass temperature of the composite. Nevertheless, the shape of the curve in Figure 1 does seem to correspond to the above-mentioned concepts. Kwei[30] has used a similar approach suggesting that interactions between polymer and filler modify the polymer matrix at the interface. He was successful in explaining the changes in sorption isotherm for filled systems.
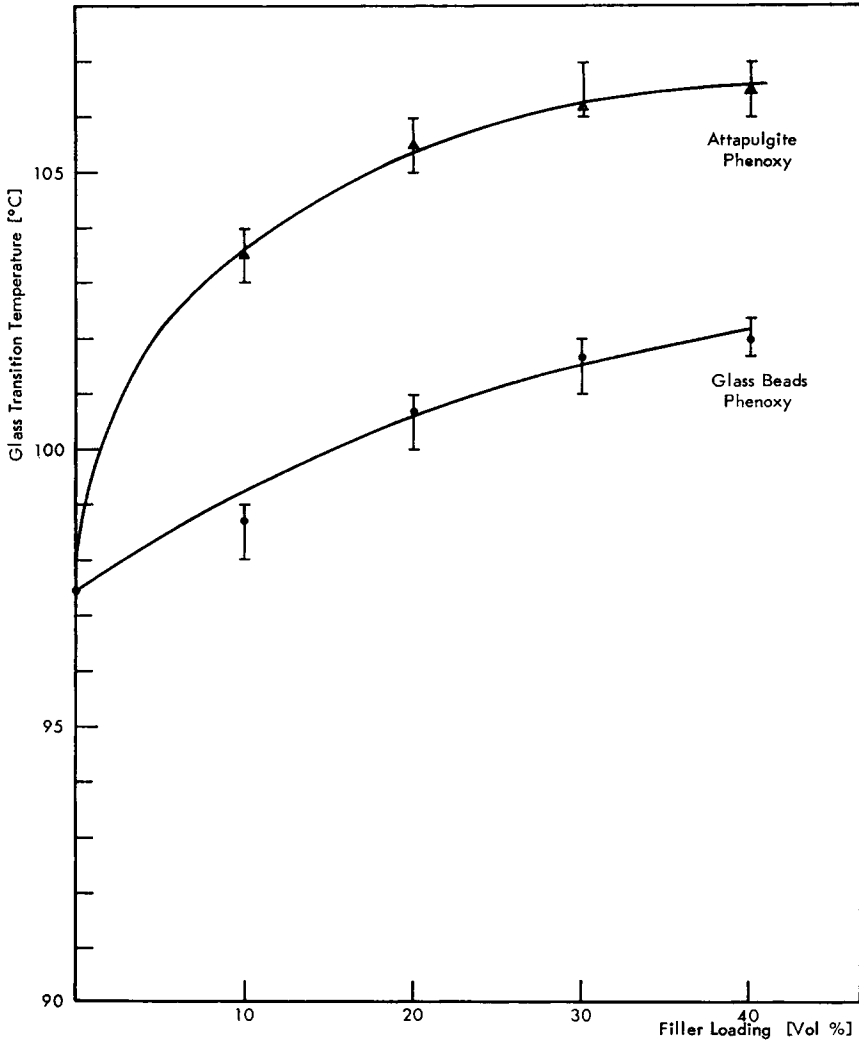
Fig. 1. Glass transition temperature of composite systems as a function of filler concentration.

As shown in Figure 2, an empirical relationship of the form

$$T_{gc} - T_{g0} = \Delta T_{g\infty} [1 - \exp(- B\phi_f)] \tag{1}$$

where T_{gc} and T_{g0} are the glass temperatures of the composite and of the unfilled polymer, respectively, $\Delta T_{g\infty}$ is a "maximum" glass temperature shift for the filled polymer and B is an empirical constant, describes the experimental data. When the glass temperature shifts are correlated in this way, the completely modified matrix approaches a maximum temperature shift of $\Delta T_{g\infty} = 9°C$. The constants B are 1.8 and 9.7 for the glass bead
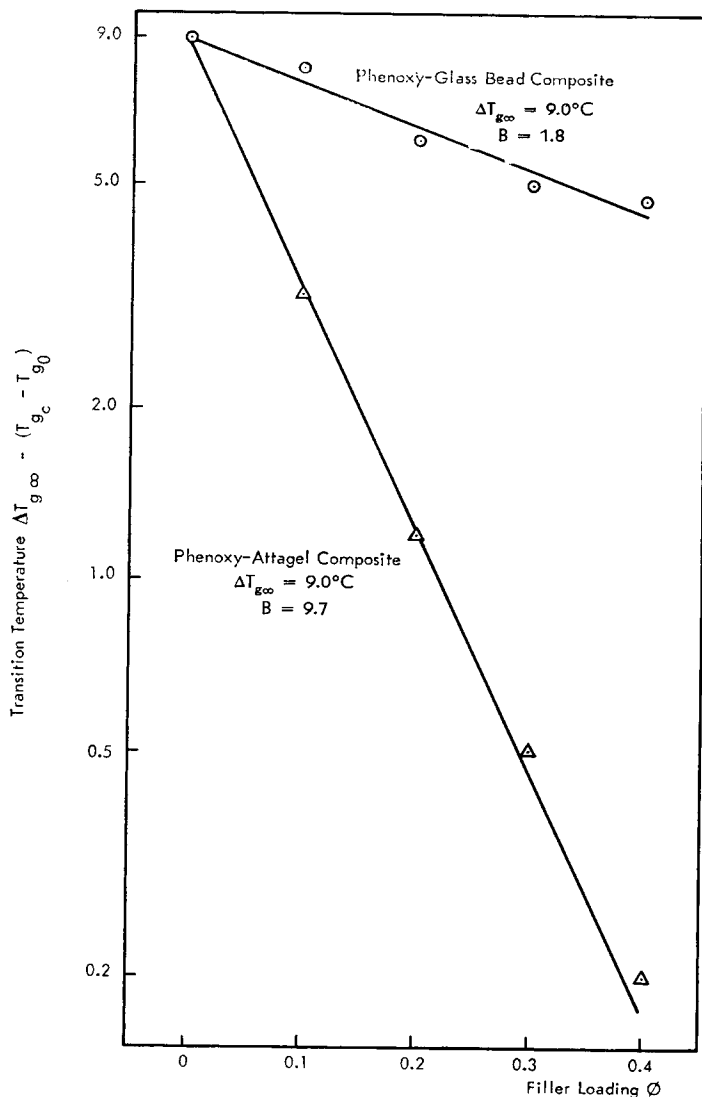
Fig. 2. Empirical correlation of the glass transition temperature in composite materials.

and Attapulgite filler, respectively. A simplified computation of the thickness of the "zone of influence" δ for the clay-filled composite, based on the known surface area of the Attapulgite and the approximate filler concentration at which the shift reaches a maximum, leads to a value of 35–100 Å, which means that the "zone of influence" is probably a monolayer of polymer molecules.

Similar shifts of the transition temperature were noticed in the dynamic mechanical response of the matrix. Figures 3 and 4 depict the effect of filler loading on the logarithmic decrement. Although the shifts in T_g are here
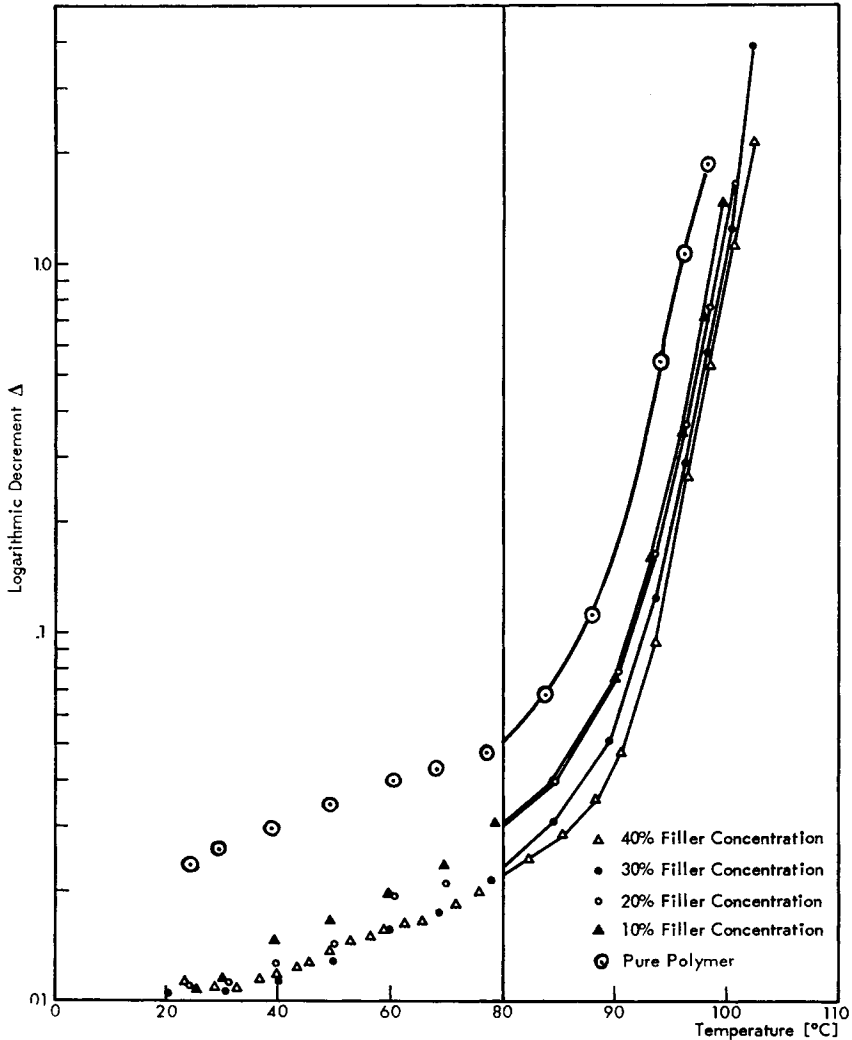
Fig. 3. Logarithmic decrement of the glass bead–phenoxy composite as a function of temperature and filler concentration.

more difficult to detect, they are at least of the same magnitude as measured on the DTA.

At the transition temperature of the pure polymer, the onset of rapid viscous flow causes a large rise in the logarithmic decrement of the material. The addition of 10% and 20% Attapulgite suppresses this increase somewhat, but viscous flow again predominates at a temperature that is a few degrees higher than for the pure polymer. At 30% filler concentration, the logarithmic decrement displays a definite maximum. Thus, the composite is beginning to exhibit noticeable strength and elasticity above the glass
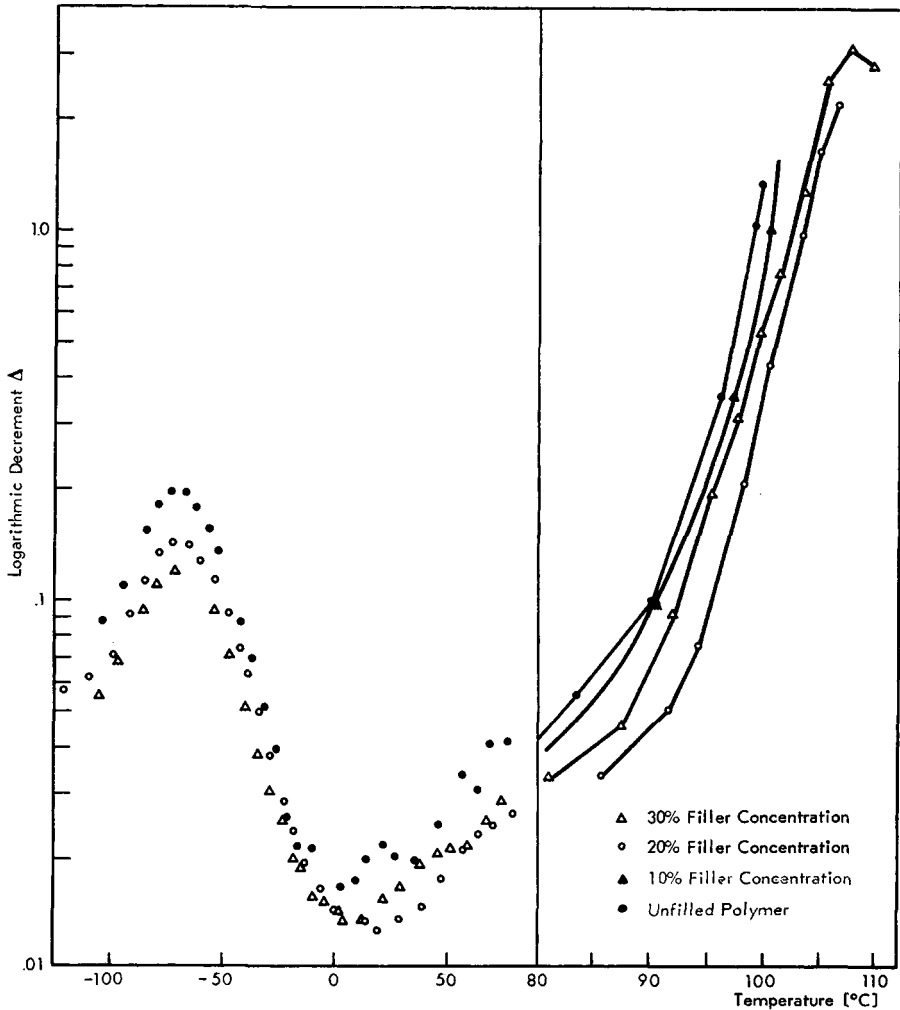
Fig. 4. Logarithmic decrement of the Attapulgite–phenoxy composite as a function of temperature and filler concentration.

transition temperature. This is the kind of behavior one would expect from a crystalline or lightly crosslinked polymer. In addition, the logarithmic decrement for this composite system has a higher absolute value than for the 20%-filled material at the same temperature. This indicates that higher loadings of submicron filler particles introduce a different damping mechanism, possibly caused by particle–particle interactions.

Low temperature peaks at $-67°C$ in the logarithmic decrement curve are observed, indicating a secondary transition for the polymer. Peak temperatures and the shape of the damping curves appear to be independent of filler concentration. Relative peak heights for the secondary transition decrease with increasing filler concentration, somewhat similar to results
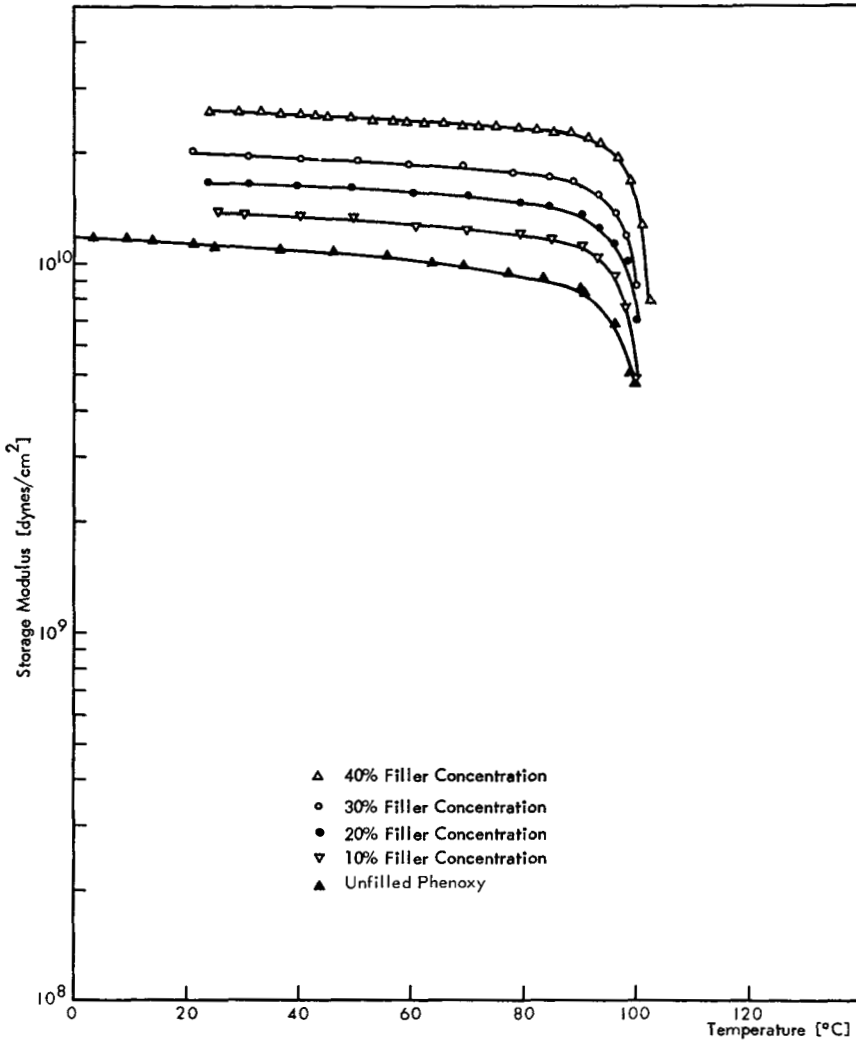
Fig. 5. Storage modulus of the glass bead–phenoxy composite as a function of temperature and filler concentration.

that Muus, McCrum, and McGrew[31] found for increases in crystallinity in partially crystalline polymers.

These data might be interpreted as follows: The low temperature transition involves specific short segments along the polymer chains.   Below the primary glass temperature, the flexibility and mobility of these short segments are not strongly affected by the presence of filler surface but rather are controlled by the free volume of the glassy matrix.   Thus, the portion of the relaxation spectrum associated with these motions is not significantly changed by the presence of filler.   The higher temperature transition, on the other hand, involves the flexibility and mobility of larger segments of the
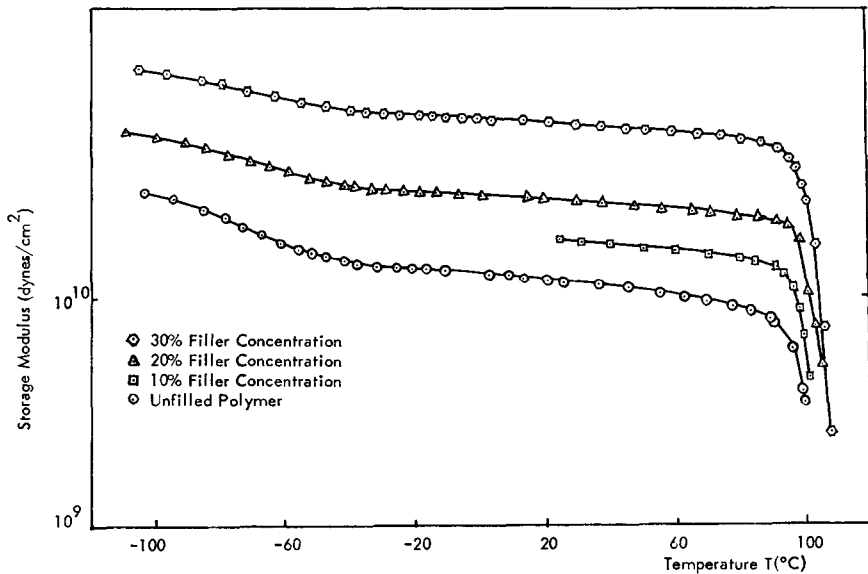
Fig. 6. Storage modulus of the Attapulgite–phenoxy composite as a function of temperature and filler concentration.

polymer chains. The shift of the glass transition temperature and the decrease in viscous dissipation per unit volume of polymer lead one to believe that the longer-range chain flexibility and mobility are inhibited. In other words, the relaxation spectrum in the longer relaxation time region is shifted to still longer times because of the presence of the filler. Similar results were obtained by Nagamatsu[21] investigating crystalline polymers.

A physical picture of a polymer chain being adsorbed at a few points along the chain and forming loops back into the bulk of the polymer is consistent with increases in glass transition temperatures or relaxation times. It should be pointed out, however, that this physical picture of the polymer morphology at the filler surface is purely hypothetical but is at least consistent with that which has previously been reported in the literature on the absorption of polymers on high energy surfaces.

Figures 5 and 6 show the effects of glass beads and Attapulgite clay as filler materials on the storage modulus of the composite. Because the experiments were carried out on an uncrosslinked, amorphous polymer of low molecular weight, the modulus tests were restricted to temperatures below the glass transition point. The storage moduli below T_g are relatively insensitive to temperature; consequently, the relative modulus G_c/G_{m0} (i.e., the ratio of the modulus of the composite to the modulus of the unfilled polymer) may be assumed as roughly constant. Figure 7 depicts the relative modulus as a function of filler content for both composite systems. The experimental values are compared with the theoretical predictions developed by Kerner[32] and Hashin[33] and good agreement is
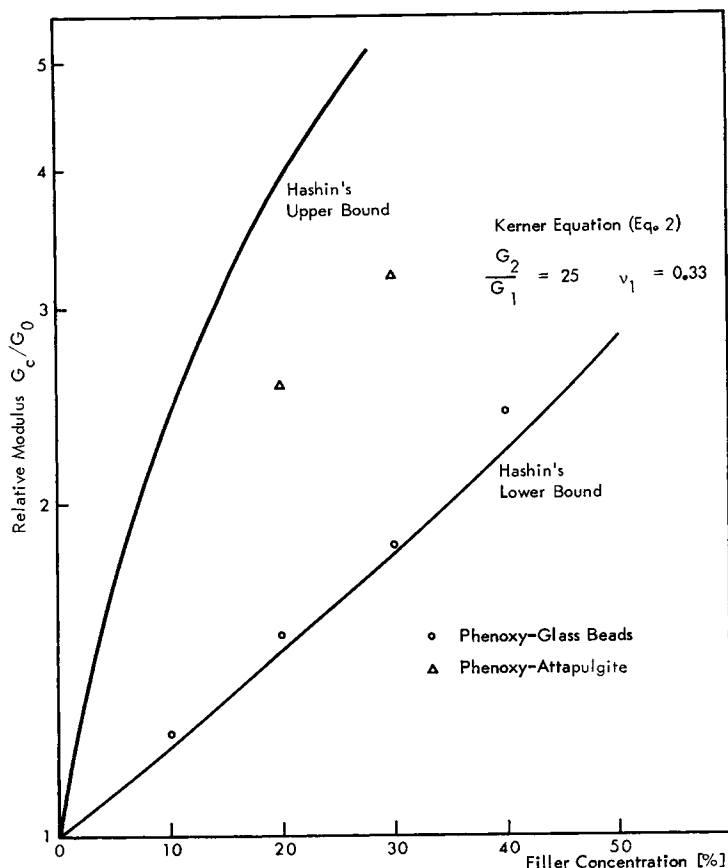
Fig. 7. Experimental relative moduli as a function of filler concentration. Data are compared with theoretical predictions of Kerner[32] and Hashin.[33]

noticed for the glass bead system. Kerner's equation (for spherical inclusions of 2 in a less rigid matrix of 1) is as follows:

$$\frac{G_c}{G_1} = \frac{(G_2/G_1)x + \xi}{x + \xi} \tag{2}$$

where $x = (\phi_2)/[(7 - \nu_1) + (8 - 10\nu_1)(G_2/G_1)]$, $\xi = (1 - \phi_2)/[15(1 - \nu_1)]$, and $\nu_1 =$ Poisson's ratio of matrix.

Hashin's equation for the lower bound is identical with Kerner's eq. (2). Hashin's equation for the upper bound can be obtained by writing eq. (2) for spherical inclusions of material 1 in a matrix of material 2.

The agreement is not surprising since the Kerner equation was developed for systems with spherical particle symmetry and continuous stress transfer at the phase boundaries. The polymer matrix is very nearly elastic below T_g and the difference in the volumetric expansion coefficients between the matrix and filler material puts the filler particles under compression upon
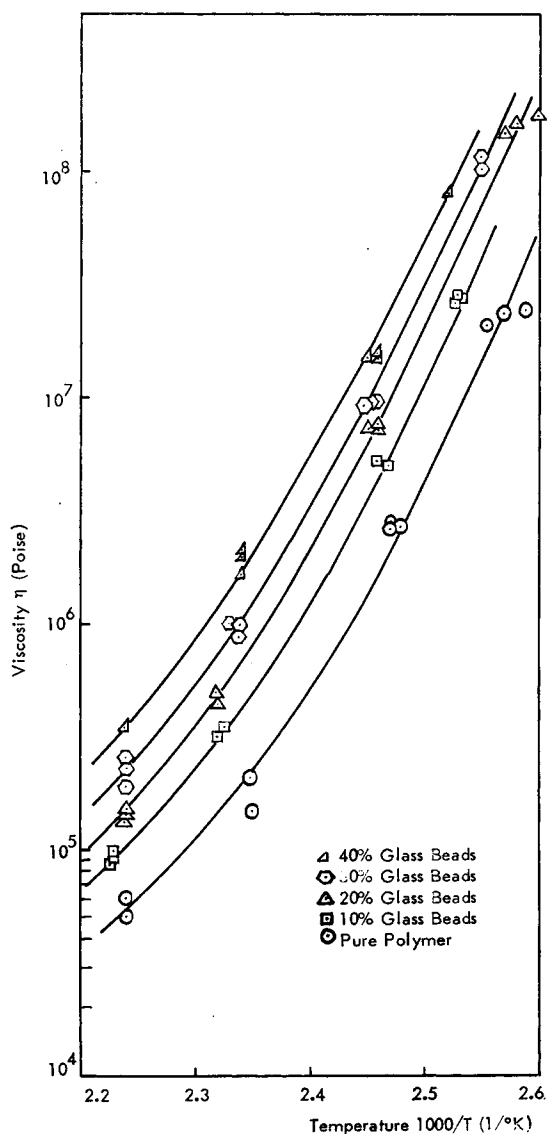
Fig. 8. Viscosity of various phenoxy–glass bead composites as a function of temperature.

cooling,[34] thereby creating good stress transfer between phases at low deformation. In contrast, the clay particles are rodlike by nature and are also agglomerated in the composite. There is no direct analysis for the relative modulus of such a system. From Figure 7 it is apparent that the morphology and specific surface area have an effect on the reinforcement ratio.

When the temperature is raised above the glass transition temperature, the polymer matrix softens to a highly viscous fluid. Experimental vis-
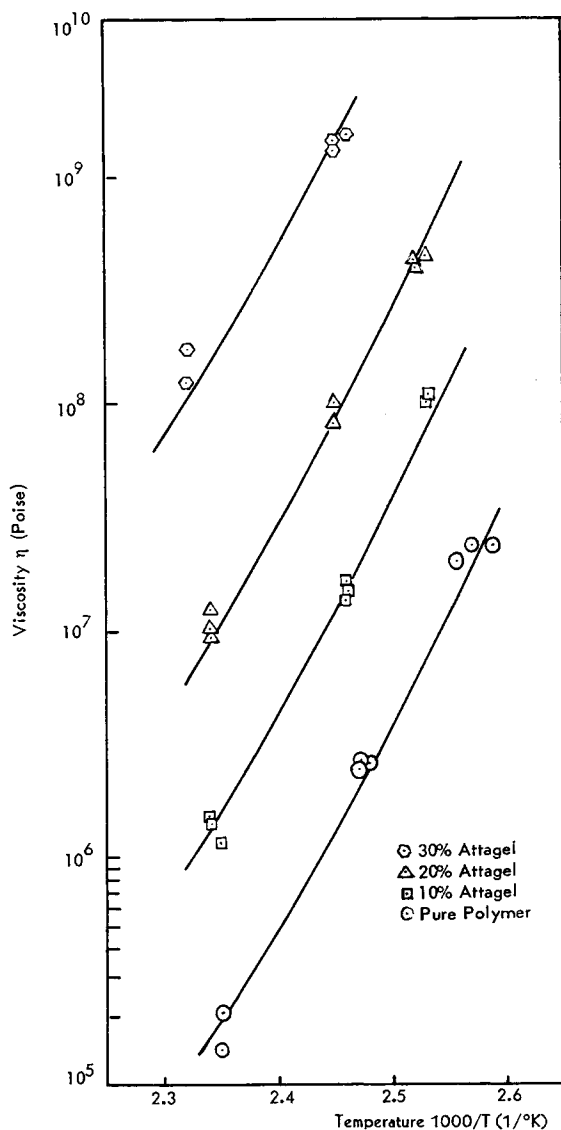
Fig. 9.–Viscosity of various phenoxy–Attapulgite composites as a function of temperature.

cosity measurements for the two filled composite systems are shown in Figures 8 and 9. The curves depicting the viscosity of the glass bead system as a function of inverse temperature resemble the WLF equation.[35]

For the glass bead composite system, one can express the reinforcement effect of the beads on the viscosity in a similar way as was done for the modulus. In the case of the viscosity, however, the relative viscosity η_c/η_{m0} is dependent on the temperature, as shown in Figure 10. It can be

seen that the experimentally determined relative viscosities do not follow any of the usual equations, such as the Mooney equation[36]

$$\eta_R = \exp\left(\frac{a\phi_f}{1 - s\phi_f}\right) \tag{3}$$
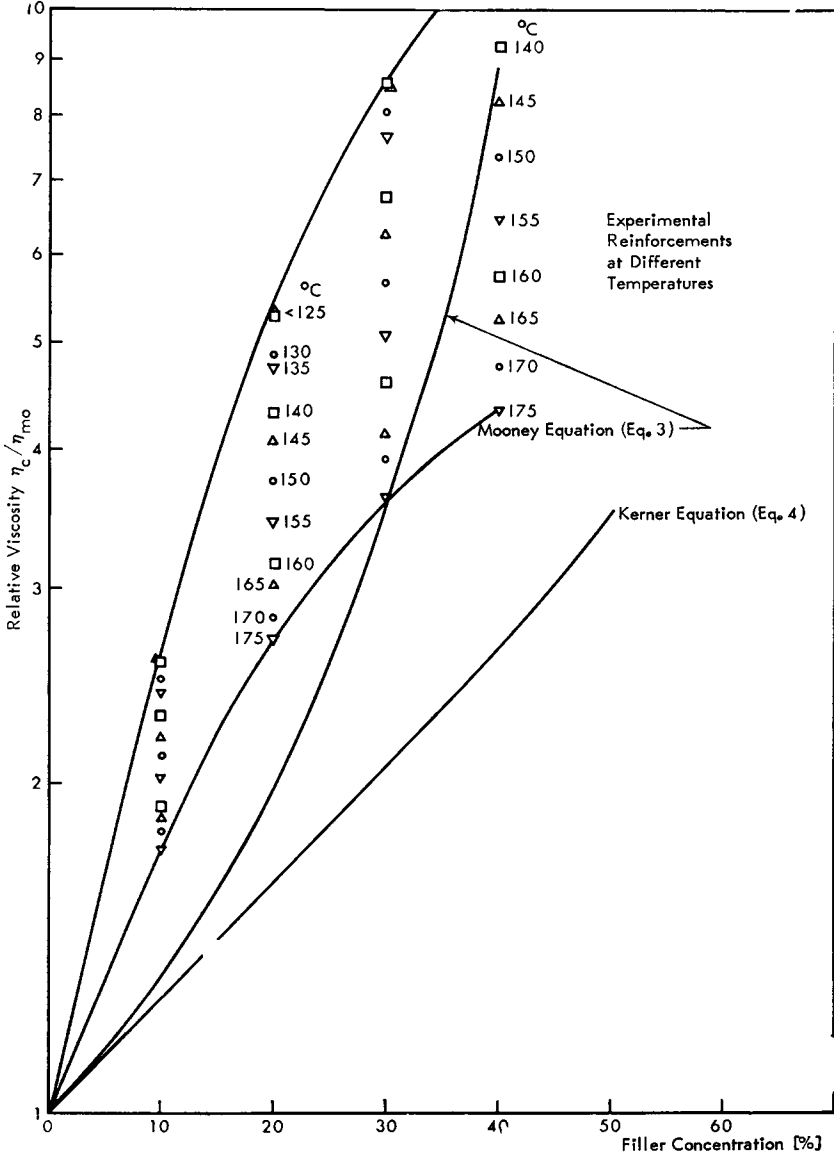

Fig. 10. Experimental relative viscosities as a function of filler concentration and temperature. Data for glass bead–phenoxy are compared with predictions of Kerner[32] and Mooney.[36]
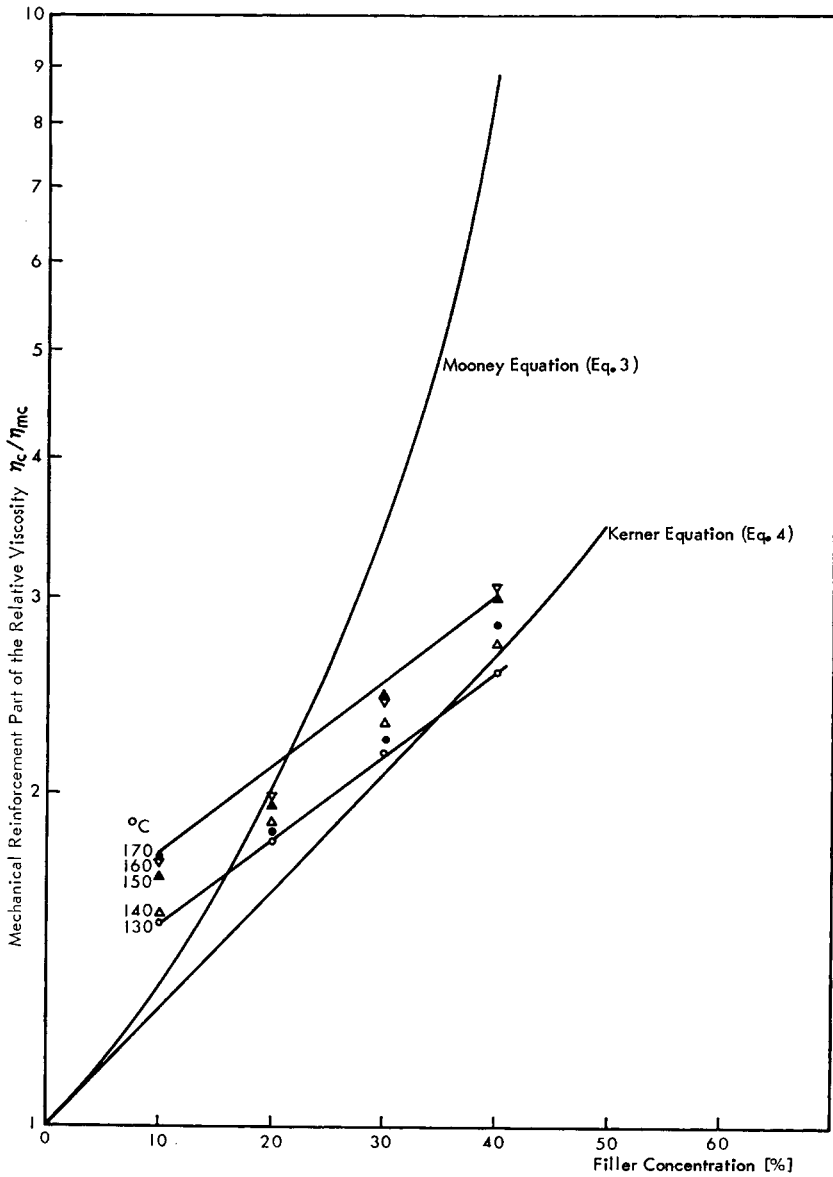
Fig. 11. Dependence of the mechanical reinforcement part of the relative viscosity on glass bead filler concentration.

where ϕ_f = volumetric filler concentration, $s = (1/\phi_{max}) \sim 1.35$ for single spheres, and $a = 2.50$ for single spheres, or the Kerner[32] equation [eq. (2) when $G_2/G_1 \rightarrow \infty$ and $\nu_1 = 0.5$]:
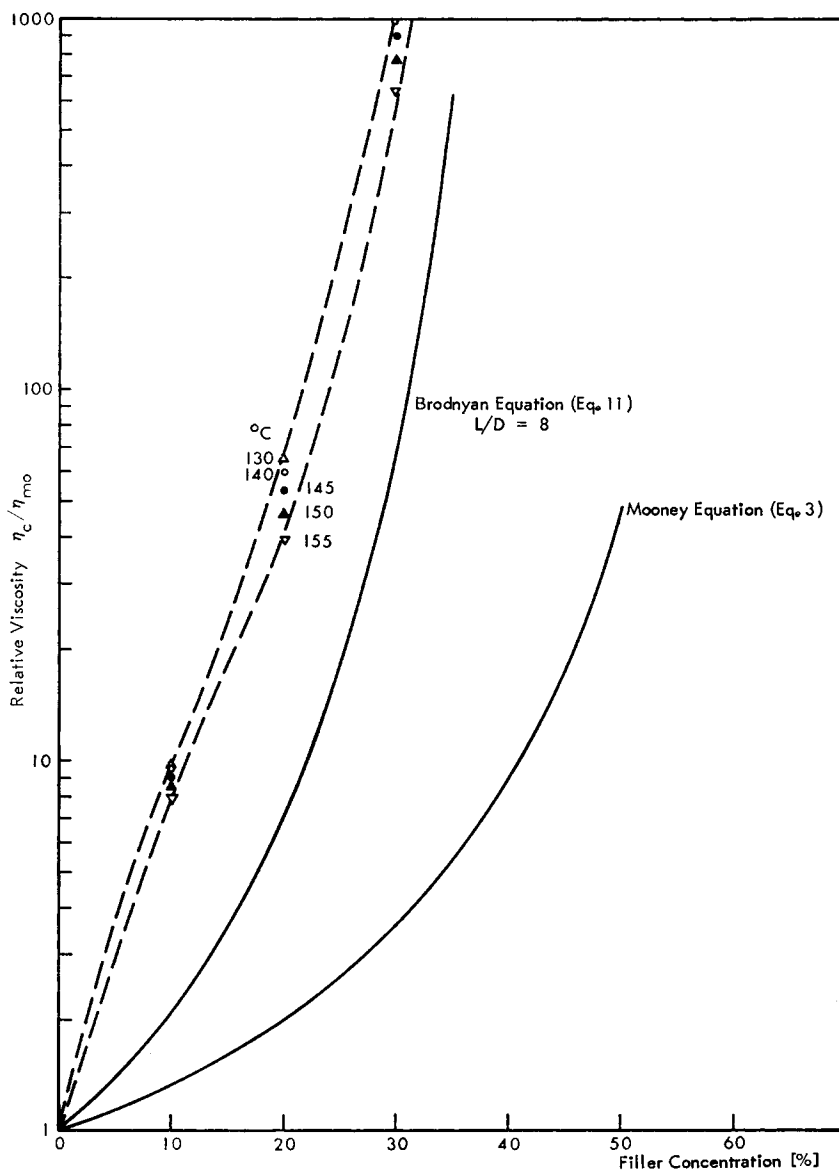
$$\eta_R = 1 + \frac{2.5 \ \phi_f}{1 - \phi_f}. \tag{4}$$

Fig. 12. Experimental relative viscosities as a function of filler concentration and temperature. Data are compared with predictions of Brodnyan[41] and Mooney.[36]

This equation is identical with the Mooney equation for low filler concentrations and with $s = 1.0$.

Equations (3) and (4) have been used by several researchers[37] to successfully correlate viscosities of spheres in suspension.

It was postulated earlier that the matrix in contact with the filler has properties different from those of the unfilled polymer because of restraints

in the molecular mobility. Hence, the relative viscosity should be based on this modified polymer matrix. Designating the viscosity of the polymer matrix exposed to the filler as η_{mc} and that of the unaffected polymer as η_{m0}, one can write the relative viscosity as

$$\eta_R = \frac{\eta_c}{\eta_{m0}} = \frac{\eta_c}{\eta_{mc}} \cdot \frac{\eta_{mc}}{\eta_{m0}} \tag{5}$$

where η_c is the viscosity of the composite material.

The relative viscosity in eq. (5) can be thought of as representing two effects, namely:

$$\eta_R = \begin{Bmatrix} \text{Mechanical} \\ \text{reinforcement} \\ \text{due to filler} \end{Bmatrix} \begin{Bmatrix} \text{Modification of the} \\ \text{polymer matrix} \\ \text{due to filler} \end{Bmatrix} \tag{6}$$

Assuming that the relative change in viscosity of the matrix, that is η_{mc}/η_{m0}, is due entirely to the shift in glass transition temperature and that the temperature dependence above T_g can be represented by the WLF equation, one can express the viscosity increase in terms of the shift in the glass transition temperature from the WLF equation as follows:

$$\ln \frac{\eta_{T_g}}{\eta_T} = \frac{40(T - T_g)}{52 + T - T_g} \tag{7}$$

for $T_g < T < T_g + 100$ and where T_g is the glass transition temperature of the polymer. If T_{gc} is the characteristic temperature of the polymer in the composite and T_{g0} is the characteristic temperature of the pure polymer, one can rewrite the WLF equation for the viscosity of a filled polymer relative to that of an unfilled polymer as

$$\ln \frac{\eta_{mc}}{\eta_{m0}} = \frac{2080(T_{gc} - T_{g0})}{(52 + T - T_{gc})(52 + T - T_{g0})}. \tag{8}$$

Equation (8) assumes that the reference viscosity at the glass transition point η_{T_g} is the same for filled and unfilled polymers.

Substituting eq. (8) into (5), one obtains the relative viscosity of a suspension with interaction between the constituent materials as

$$\eta_R = \frac{\eta_c}{\eta_{mc}} \exp \frac{2080(T_{gc} - T_{g0})}{(52 + T - T_{gc})(52 + T - T_{g0})}. \tag{9}$$

In Figure 11, the mechanical reinforcement η_c/η_{mc} in eq. (9) is compared with the previously cited Mooney and Kerner equations. Except for the lowest filler concentration, the experimentally measured mechanical reinforcement part η_c/η_{mc} is roughly bounded by the two theoretical predictions and is less dependent on the temperature. The experimental results follow the functional form of the Kerner equation more closely. Since the relative

modulus of the glass bead composite system agrees with the Kerner equation (Fig. 7), one can see that the relation

$$\frac{\eta_c}{\eta_{mc}} = \frac{G'_c}{G_{m0}}$$ (10)

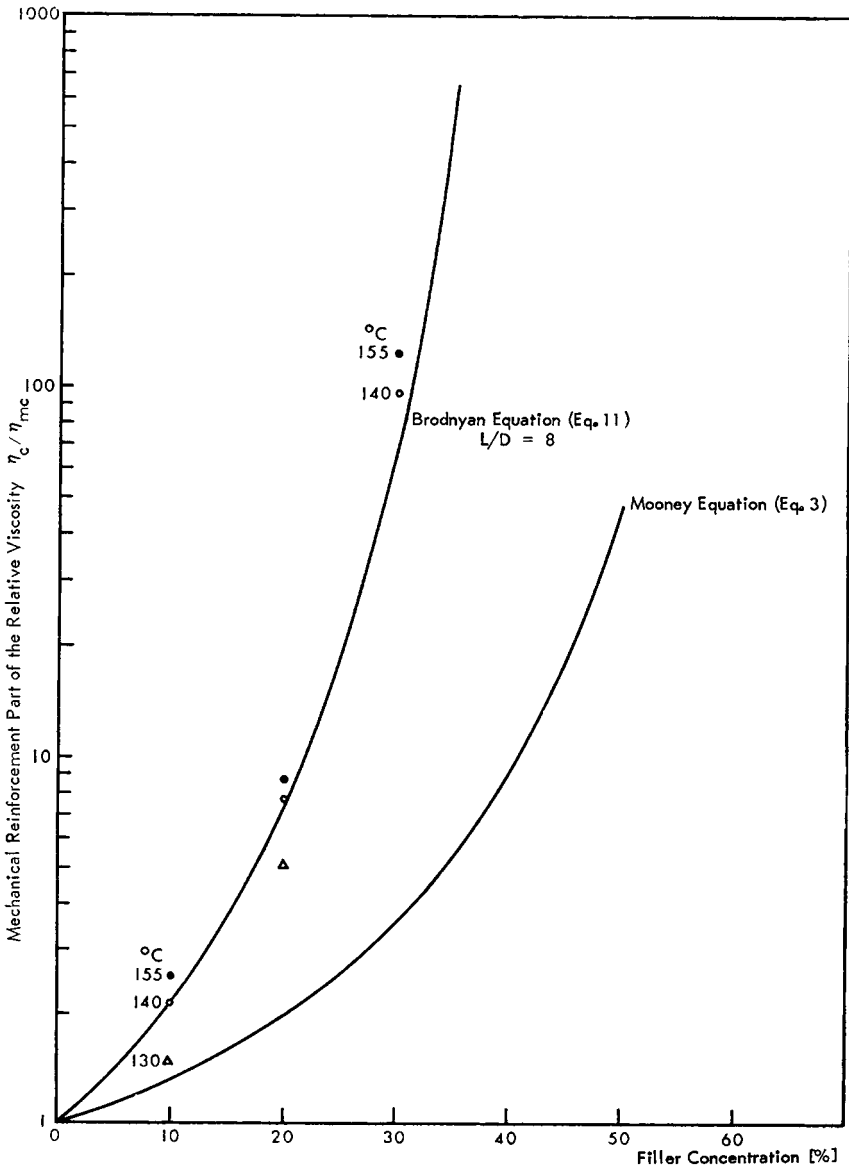is approximately correct for this particular system.[38-40]

Fig. 13. Dependence of the mechanical reinforcement part of the relative viscosity on Attapulgite filler concentration.

The same type of analysis has been applied to the relative viscosity of the clay-filled composites. This correlation is much more qualitative because the state of aggregation of the Attagel particles in the composite is not exactly known. Figure 12 depicts the experimentally measured relative viscosities at five temperatures, which are compared with the Mooney eq. (3) for single spheres and Brodnyan's modification[41] of the Mooney equation for elongated ellipsoids with $1 \leq L/D \leq 15$:

$$\ln \eta_R = \frac{[2.5 + 0.407(L/D - 1)^{1.058}] \phi_f}{1 - S\phi_f} \tag{11}$$

where ($1.35 \leq S \leq 1.91$) for spheres or rods.

When the measured relative viscosities are corrected for the shifts in the glass transition temperature, the contribution due to the mechanical reinforcement can be isolated. Figure 13 compares this contribution, η_c/η_{mc}, with the two limiting cases cited above. The corrected reinforcement ratios follow eq. (11) with $L/D = 8$, which would imply average agglomerates of 19–25 filler particles, which agrees roughly with those observed on electron micrographs of fracture surfaces.

Comparing the mechanical contribution to the relative viscosity for the Attagel–phenoxy system, Figure 13, with the respective relative modulus, Figure 7, one can see eq. (10) cannot be used as an approximation. This indicates that for nonspherical filler particles the flow of the composite melt depends very strongly on their shape and also on the extent of aggregation. For dispersed single spheres, however, it seems that the relative modulus is about the same as the relative viscosity.

In conclusion, it is felt that the upward shifts in glass transition temperature of polymeric composites indicate a decrease in the mobility of the polymer molecules in the vicinity of the interface. This decrease should be related to the degree of interaction between the filler material and the polymer and to the interfacial area available. Further quantitative separation of the restricted mobility into these two contributions has not been attempted. The experimental data show that the interactions at the interface have a significant effect on some of the bulk properties of the matrix. Under certain conditions this can cause significant changes in the physical properties of the composite.

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