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Development of High Performance Composites

# THE GLASS TRANSITION TEMPERATURE OF FILLED POLYMERS AND ITS EFFECT ON THEIR PHYSICAL PROPERTIES

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# FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 873, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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# THE GLASS TRANSITION TEMPERATURE OF FILLED POLYMERS AND ITS EFFECT ON THEIR PHYSICAL PROPERTIES*

## Abstract

The glass transition temperature, dynamic shear moduli and bulk viscosities of Phenoxy PKHH 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 filler. The average transition temperature was described by a simplified two-phase mixture model of a layer of immobilized polymer surrounding each filler particle and the unaffected portion of the polymer matrix. The model predicts an increasing glass transition temperature to a limiting value at a certain filler concentration. From the measured moduli and the viscosities of the filled samples and the pure polymer, the relative reinforcement ratios in the glassy and viscous state were obtained as a function of the filler type and concentration. The modulus reinforcement ratios for the glass bead composite system follow the Kerner equation, while the clay-filled systems exhibit slightly higher reinforcement ratios. The viscosity reinforcements are strongly temperature dependent and do not follow conventional viscosity predictions for suspensions. It is suggested that the filler has a two-fold effect on the viscosity of the composite materials; one is due to its mechanical presence and the other 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

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isolate the purely mechanical contribution to the viscosity reinforcement. This mechanical part is approximately bounded by theoretical predictions for suspension viscosities due to Kerner, Mooney and Brodnyan.

It has been clearly shown that polymer matrix properties are modified by the presence of a filler. These modifications can be related to interactions between matrix and filler. The authors feel, however, that mechanical measurements are not direct enough to quantitatively assess the extent of the interaction and that more direct measurements of changes in the molecular structure should be more promising. Further work in the area of IR and NMR spectroscopy are in progress.

# THE GLASS TRANSITION TEMPERATURE OF FILLED POLYMERS AND ITS EFFECT ON THEIR PHYSICAL PROPERTIES

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## 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 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. 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. It has been found that some of the physical properties of composite materials depend on the nature of the phase boundaries between the reinforcing and matrix phases.

The earliest studies of composite properties were carried out on filled rubbers. Investigators found changes in thermodynamic properties [e.g., 1, 2, 3] and mechanical properties [e.g., 4, 5, 6] due to the presence of filler. Similar changes were detected in filled thermoplastic materials by Kargin [7, 8, 9], Lipatov [10, 11], Nielsen [12], Uskov [13] and others. These researchers found increases in mechanical properties with increasing filler concentration or increases in the glass transition temperature of the matrix. There is some contradictory data concerning the glass temperature. Van der Wal, et al [14], for example, observed no changes in the glass temperature of sodium chloride filled polyurethanes and Kumins [15] 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 [16, 17, 18] and shifts in viscoelastic relaxation times [19] similar to those found in filled polymers have been experimentally determined.

In spite of the extensive disagreement in the literature as to the actual mechanism of interaction between two or more specific materials, it is generally agreed upon that:

(1) Structures that contain non-adhering phases behave differently than those with adhering phases; (2) Couplers are used in order to promote a continuous adhesive structure through the phase boundaries; (3) The extent of interaction between phases is a highly specific phenomenon, determined by factors such as the degree of molecular contact at the interface and the interfacial area available.

Differences between adhering and non-adhering phases have been discussed in the literature. For example, recent studies of composite materials show that fracture toughness [20], ultimate tensile strength and ultimate elongation [21] are varied by changing the degree of adhesion between the constituents. Other physical properties such as the shear or tensile modulus are less affected by the state of adhesion, for reasons to be explained later.

It should be pointed out that the glass temperature of the composite is really the temperature at which the 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***. It will be shown that:

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*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 ± 1° C

**Ballotini Industrial GlasssBeads Size 3000, U. S. Screen No. 325 and finer, $d < 44\mu$, untreated surface.

Surface Area: 0.042 $m^2$/gm

***An attapulgite clay with a rod-like morphology and an average ultimate particle size of 200 A diameter and 1 micron length.

$L/d = 50$
Surface Area = 210 $m^2$/gm

(1) The glass transition temperature of the polymer is increased by the presence of filler.

(2) 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.

(4) The degree of interaction between the phases is related to the shift in the glass transition temperature.

## 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 at 120° C for over 100 hours.

After vacuum drying, the composite flakes were crushed in a mortar and the resulting powders were then compression molded into thin bars for modulus tests or cylindrical plugs for viscosity tests.

The other technique employed a heated roller mill for dispersing the filler material in the polymer matrix. Extensive cross-rolling was applied to insure 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 DuPont 900 Differential Thermal Analyzer (DTA). The basic principle of the DTA is to supply thermal energy to both a sample and an inert reference material [22]. The temperature difference between sample and reference is recorded. When a sudden change in specific heat or thermal conductivity occurs (such as that occurring at the glass transition temperature of the polymer), a change in the relative heating rate between sample and reference occurs. The change is picked up by a sensitive thermopile and is recorded automatically, thus marking the transition temperature of the material.

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 state to the solid one yielded the more reproducible results.

Dynamic shear moduli and damping capacities of the composites and the pure polymer were measured using a freely oscillating torsion pendulum [23]. The basic idea is to impose a sinusoidal torsional strain on the sample by means of an inertia member and to measure the frequency of oscillation and its decrease in amplitude with time. From this data, storage modulus, loss modulus and damping capacity can be calculated [24].

Viscosities of the materials above the glass transition temperature were measured using a parallel plate plastometer attached to an Instron testing machine. The only difference between this experimental technique and those used earlier by other investigators [25] is the application of a constant rate of deformation at increasing loads. A cylindrical sample is compressed between two parallel plates at a constant rate of deformation, maintaining the strain rate at less than $10^{-2}$ $sec^{-1}$. After an initial viscoelastic response, the measured force increased with the inverse fifth power of the distance between the plates. The Newtonian viscosity of the material is obtained by well-known methods [26] from the linear relationship between the logarithm of the compressive force and the logarithm of the sample height.

## 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 ($T_{go}$) is approximately 98° C, while that of a 40% filled composite is 4-5° C higher for glass beads as a filler, and 9-10° 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 cross linking on the glass temperature [29], may also be applicable to a reinforced polymer. The polymer matrix can be considered a mixture of polymer with reduced molecular mobility adjacent to the filler particles and of unaffected polymer with the same flexibility as in bulk. Reduced molecular mobility is equivalent to a decrease in the free volume fraction of the polymer or an increase in the glass temperature. It is assumed that there is a portion of the polymer matrix, with a characteristic transition temperature $T_{gA}$, which surrounds each filler particle. The volume of this layer is $V_A$ and can be expressed as:

$$V_A = V_T \phi_f \hat{S} \delta \qquad (1)$$

where $V_T$ is the total volume of the composite, $\phi_f$ is the volume fraction of filler, $\hat{S}$ is the specific surface area of filler ($cm^2/cm^3$) and $\delta$ is the "zone of influence" around each filler particle ($cm^3$ polymer/$cm^2$ filler). The volume of the unaffected part of the polymer $V_o$ is given by:

$$V_o = (1 - \phi_f) V_T - V_A \qquad (2)$$

This volume has a characteristic transition temperature $T_{go}$.

Assuming the free volume fractions are additive, one can express the "average" glass temperature of the composite as a volume fraction weighted average of the two zones:

$$T_{gc} = T_{gA} \phi_A + T_{go} \phi_o \qquad (3)$$

Since $\phi_A = V_A/(V_A + V_o)$ and $\phi_o = V_o/(V_A + V_o)$, substitution of (1) and (2) into (3) leads to:

$$(T_{gc} - T_{go}) = \hat{S} \delta (T_{gA} - T_{go}) \frac{\phi_f}{1 - \phi_f} \qquad (4)$$

By virtue of Equation (2), $\phi_f$ must have an upper bound of

$$V_A \leq (1 - \phi_f)\, V_T \tag{5}$$

or, from Equation (1):

$$\frac{\phi_f}{1 - \phi_f} \leq \frac{1}{\hat{S}\,\delta} \tag{6}$$

In dilute systems, the increase in glass temperature should be linearly proportional to $\phi_f/(1 - \phi_f)$. At higher filler loadings when aggregates are formed more easily, the unwetted clusters of filler particles would be equivalent to a decrease in the product $\hat{S}\,\delta$. Hence, the slope of Equation (4) should taper off at higher filler loadings. At a certain filler loading ($\phi_f = \frac{1}{1 + \hat{S}\,\delta}$) all the polymer will have been modified and no further increase in $T_{gc}$ should occur.

Obviously, the concept of a binary mixture in the matrix phase is a gross oversimplification. It is more likely that if there is a change in properties caused by the filler surface, the polymer matrix will change continuously as one moves from the surface to the bulk. This should result in a broadening of the measured transition region as well as an increase in the "average" glass temperature of the composite.

Although there is not sufficient data to quantitatively evaluate the various parameters, the experimental data shown in Figure 2 appear to correspond to the above mentioned concepts. Furthermore, Kwei [30] has used a similar approach to successfully explain sorption isotherms for filled systems.

Using Figure 2 to estimate a limiting value of $T_{gA}$, one can calculate $\delta$ from Equation (4) and subsequently approximate a zone of influence around an ideally dispersed particle. This simplified computation yields 200-1000 Å as the zone of modified matrix around each attapulgite inclusion depending on the amount of clustering. For the glass bead composite, one obtains 4-5 μ around each glass sphere.

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 damping capacity. Although the shifts in $T_g$ are here 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 near-infinite rise in the damping capacity of the material. The addition of 20% attapulgite suppresses this peak 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 damping peak is relatively low and a definite maximum is observed. Thus, the composite is beginning to exhibit noticeable strength and elasticity above the glass transition temperature. This is the kind of behavior one would expect from a crystalline or lightly cross-linked polymer.

Low temperature peaks at -67° C in the loss moduli and damping capacities are also observed, indicating a secondary glass 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 that Muus, McCrum and McGrew [31] found for increases in crystallinity in partially crystal polymers.

These data might be interpreted as follows: The low temperature transition involves specific short segments along the polymer chain. 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 polymer chains. The shift of the glass transition temperature and the decrease in viscous dissipation per unit volume of polymer leads 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 determined by Nagamatsu [19] 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 adsorption 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.

When the temperature is raised above the glass transition temperature, the polymer matrix softens to a highly viscous fluid. Experimental viscosity measurements for the two filled composite systems are shown in Figures 7 and 8. The curves depicting the viscosity of the glass bead system as a function of temperature resemble the WLF equation [32].

Figures 5 and 6 show that the storage moduli below $T_g$ are relatively insensitive to temperature; consequently, the modulus ratio $G_c/G_{mo}$ may be assumed as roughly constant. Figure 9 depicts the modulus reinforcement ratio as a function of filler content for both composite systems. The experimental values are compared with the theoretical predictions developed by Kerner* [33] and Hashin** [34] and good agreement is noticed for the glass bead system. This is not surprising since the Kerner equation was developed for systems with spherical particle symmetry and continuous stress

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*Kerner's equation (for spherical inclusions of 2 in a less rigid matrix of 1):

$$\frac{G_c}{G_1} = \frac{(G_2/G_1)\,X + \xi}{X + \xi} \tag{7}$$

where $$X = \frac{\emptyset_2}{(7 - \nu_1) + (8 - 10\nu_1)(G_2/G_1)}$$

$$\xi = \frac{1 - \emptyset_2}{15\,(1 - \nu_1)} \qquad \text{and } \nu_1 = \text{Poisson's ratio of matrix}$$

**Hashin's equation for the lower bound is identical with Kerner's equation (7). Hashin's equation for the upper bound can be obtained by writing Equation (7) for spherical inclusions of material 1 in a matrix of material 2.

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 cooling [35], thereby creating good stress transfer between phases at low deformation.

The clay particles are rod-like by nature and are also agglomerated in the composite. There is no direct analysis for the modulus reinforcement ratio of such a system. From Figure 9 it is apparent that the morphology and specific surface area have an effect.

Restricting the discussion to 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 reinforcement ratio $\eta_c/\eta_{mo}$ is dependent on the temperature, as shown in Figure 10. It can be seen that the experimentally determined viscosity reinforcement ratios do not follow any of the usual correlations, such as the Mooney [36] equation* or the Kerner [33] equation**, which have been used by several researchers [37] to successfully correlate viscosities of spheres in suspension.

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*Mooney equation:

$$\eta_R = \exp \frac{a\,\phi_f}{1 - S\,\phi_f} \qquad (8)$$

where $\phi_f$ = volumetric filler conc.

$S = \dfrac{1}{\phi\,\text{max}} \doteqdot 1.35$ for single spheres

$a = 2.50$ for single spheres

**Kerner equation [Equation (7) when $G_2/G_1 \rightarrow \infty$ and $v_1 = 0.5$]

$$\eta_R = 1 + \frac{2.5\,\phi_f}{1 - \phi_f} \qquad (9)$$

This equation is identical to the Mooney equation for low filler concentrations and with $S =$

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 viscosity reinforcement ratio should be based on this modified polymer matrix. Designating the viscosity of the polymer matrix exposed to the filler as $\eta_{mc}$ and that of the unaffected polymer as $\eta_{mo}$ one can write the relative viscosity as:

$$\eta_R = \frac{\eta_c}{\eta_{mo}} = \frac{\eta_c}{\eta_{mc}} \cdot \frac{\eta_{mc}}{\eta_{mo}} \tag{10}$$

where $\eta_c$ is the viscosity of the composite material.

The relative viscosity in Equation (10) can be thought of as representing two effects, namely,

$$\eta_R = \left\{\begin{matrix}\text{Mechanical} \\ \text{Reinforcement} \\ \text{due to Filler}\end{matrix}\right\} \qquad \left\{\begin{matrix}\text{Modification of the} \\ \text{Polymer Matrix} \\ \text{due to Filler}\end{matrix}\right\} \tag{11}$$

Assuming that the relative change in viscosity of the matrix, that is $(\eta_{mc}/\eta_{mo})$, 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:

$$\ln \frac{\eta_{T_g}}{\eta_T} = \frac{40\,(T - T_g)}{52 + T - T_g} \tag{12}$$

for $$T_g < T < T_g + 100$$

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 $T_{go}$ 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:

$$\ln \frac{\eta_{mc}}{\eta_{mo}} = \frac{2080\ (T_{gc} - T_{go})}{(52 + T - T_{gc})(52 + T - T_{go})} \tag{13}$$

Equation (13) assumes that the reference viscosity at the glass transition point is the same for filled and unfilled polymer.

Substituting Equation (13) into (10), the relative viscosity of a suspension with interaction between the constituent materials is given by:

$$\eta_R = \frac{\eta_c}{\eta_{mc}} \cdot \exp \frac{2080\ (T_{gc} - T_{go})}{(52 + T - T_{gc})(52 + T - T_{go})} \tag{14}$$

In Figure 11, the mechanical reinforcement $\eta_c/\eta_{mc}$ in Equation (14) is compared with the previously cited Mooney and Kerner equations. Except for the lowest filler concentration, the experimentally measured mechanical reinforcement part $\eta_c/\eta_{mc}$ 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 modulus reinforcement ratio of the glass bead composite system agrees well with the Kerner equation (Figure 9), one can see that the assumption [38, 39, 40]:

$$\frac{\eta_c}{\eta_{mc}} \approx \frac{G_c}{G_{mo}} \tag{15}$$

is approximately correct for this particular system.

The same type of analysis has been applied to the viscosity reinforcement of the clay-filled composites. Figure 12 depicts the experimentally measured viscosity reinforcements at five temperatures, which are compared with the Mooney equation for single spheres (9) and Brodnyan's [41] modification of the Mooney equation for elongated ellipsoids with $1 \leq L/D \leq 15$

$$\ell n\ \eta_R = \frac{[2.5 + 0.407\ (L/D - 1)^{1.508}]\ \varnothing_f}{1 - S\varnothing_f} \tag{16}$$

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

It will be noticed that the two bounds follow a function with increasing slope, whereas the experimental curves start out with a decreasing slope and have an inflection point. This type of deviation was already indicated by the data for the glass bead system (Figure 10). It is believed that the reinforcement effects due to changes in the matrix properties dominate the mechanical reinforcement at low filler concentrations. At higher filler loadings, especially with non-spherical filler geometries, the magnitude of the mechanical contribution to reinforcement outweighs that due to thermodynamic effects by far. Since the mechanical reinforcement increases roughly exponentially with increasing filler concentration and since the matrix properties change logarithmically, the differently weighted combination of the two can display an inflection point.

When the measured viscosity reinforcement ratios 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, $\eta_c/\eta_{mc}$, with the two limiting cases cited above. The corrected reinforcement ratios follow Equation (16) with L/D  7 which would imply average agglomerates of 19-25 filler particles, which agrees roughly with those observed on electron micrographs of fracture surfaces.

Comparing the viscosity reinforcement for the Attagel-Phenoxy system, Figure 13, with the respective modulus reinforcement, Figure 9, one can see that Equation (15) cannot be used as an approximation. This indicates that for non-spherical 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 modulus reinforcement ratio is about the same as the viscosity reinforcement ratio.

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. However, the experimental data imply that the interactions at the interface affect some of the bulk properties of the matrix over a considerable range of volume. Under certain conditions this can cause significant changes in the physical properties of the composite.

It is felt that this investigation has shown that tests measuring mechanical properties of the bulk composites are not sensitive enough to determine exactly what changes in the polymer morphology due to interactions do occur. Further refinements in the realm of bulk properties do not seem promising. However, more sophisticated measurements (such as NMR, IR spectra or viscoelastic properties) in the vicinity of the interface might lead to more insight into the type of interactions between phases. A separation of the interaction between phases into its various components might then be possible.

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Figure 1 - Droste and DiBenedetto

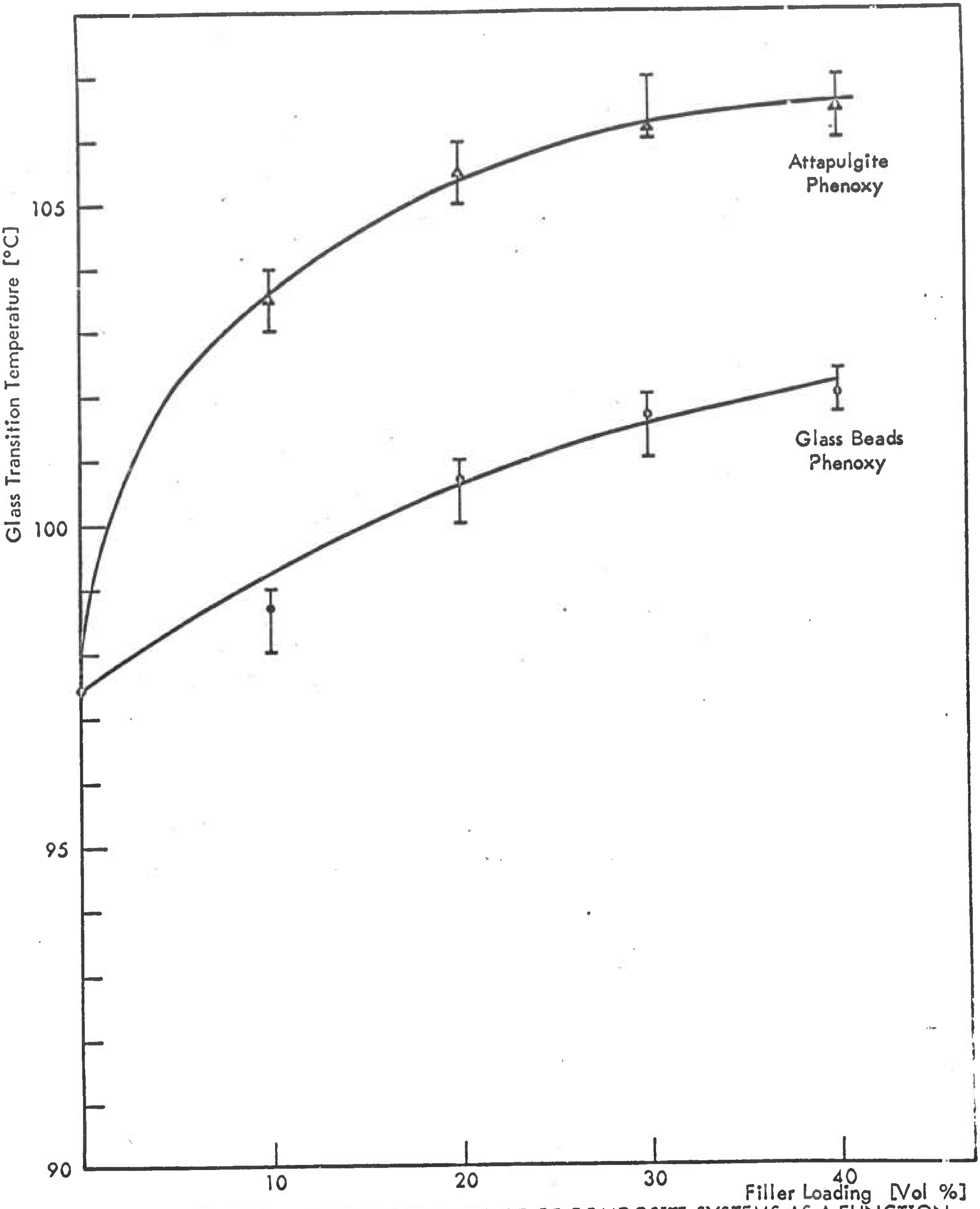

Figure 1. GLASS TRANSITION TEMPERATURE OF COMPOSITE SYSTEMS AS A FUNCTION OF FILLER CONCENTRATION

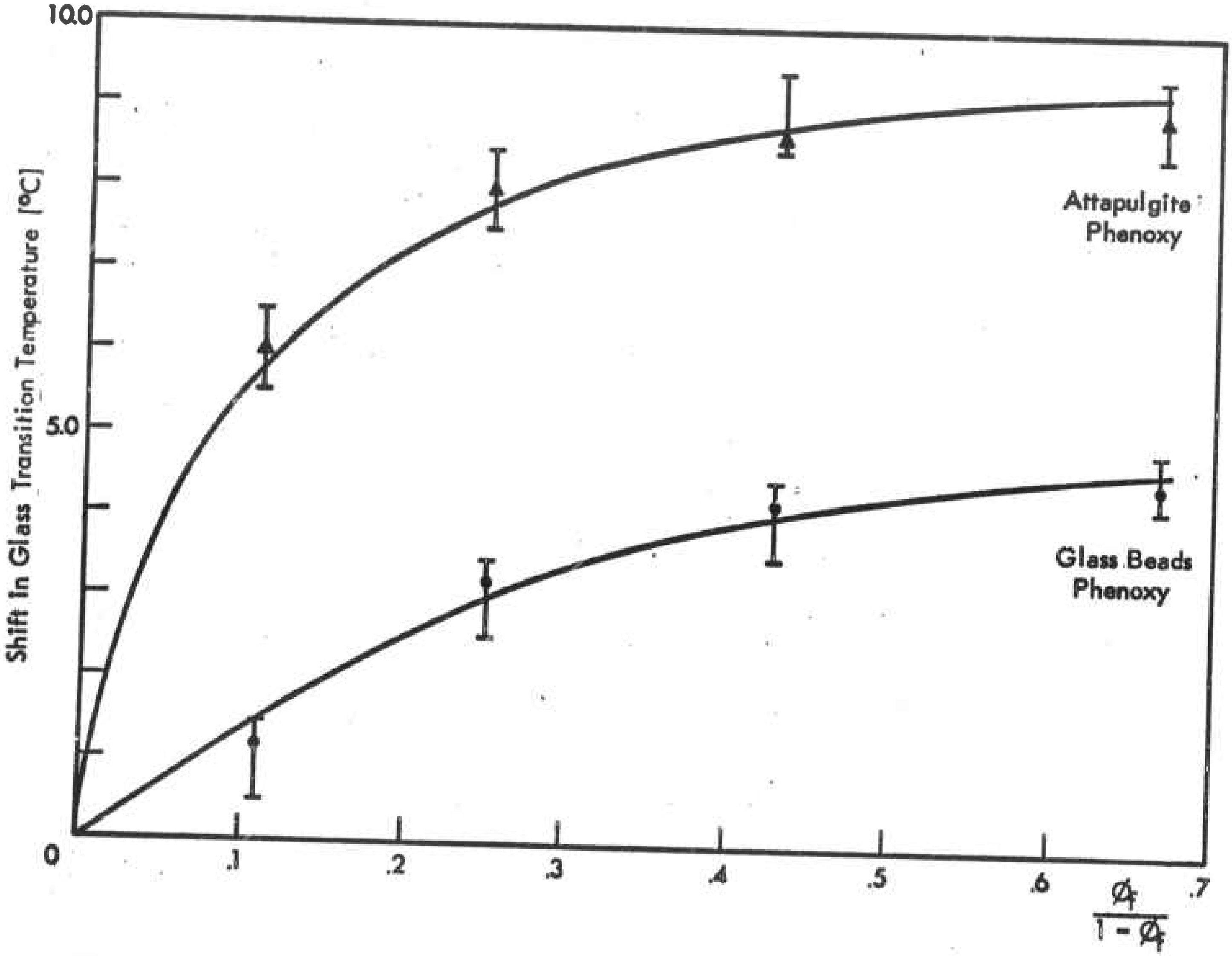

Figure 2. CHANGES IN GLASS TRANSITION TEMPERATURE AS A FUNCTION $\frac{\phi_f}{1-\phi_f}$ IN EQUATION (4)

Figure 3 - Droste and DiBenedet

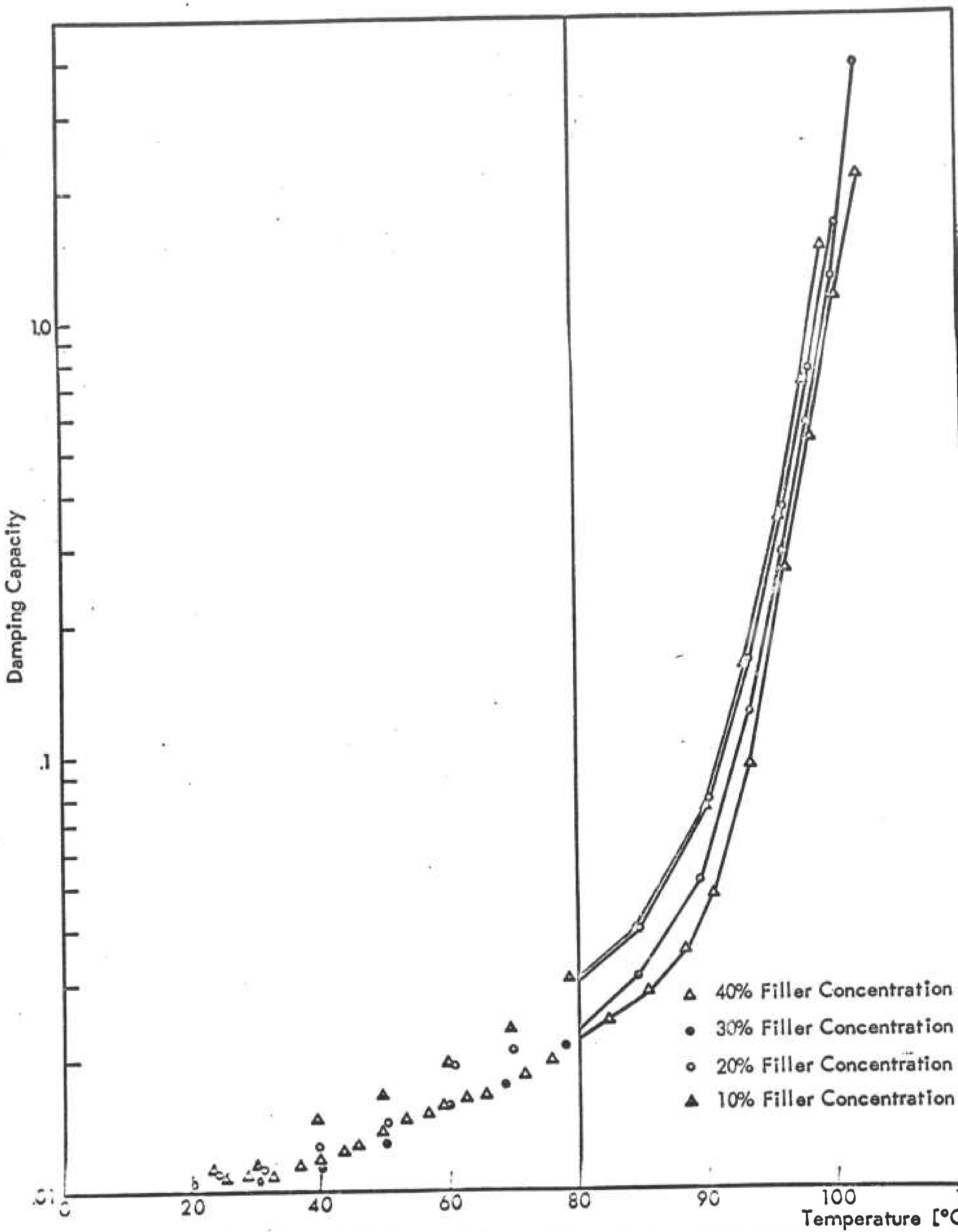

Figure 3. DAMPING CAPACITY OF THE GLASS BEAD-PHENOXY COMPOSITE AS A FUNCTION OF TEMPERATURE AND FILLER CONCENTRATION

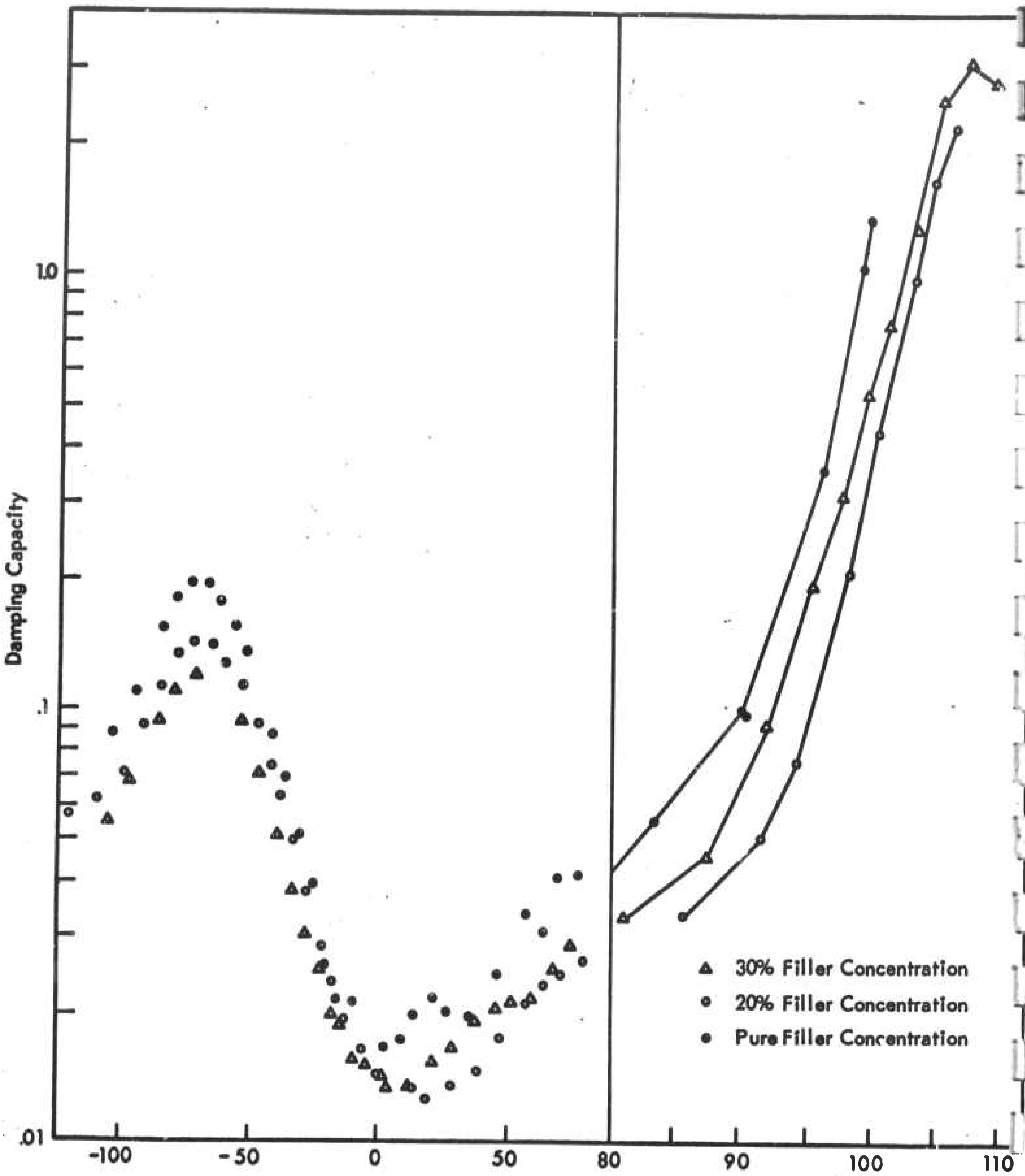

Figure 4. DAMPING CAPACITY OF THE ATTAPULGITE-PHENOXY COMPOSITE AS A FUNCTION OF TEMPERATURE AND FILLER CONCENTRATION

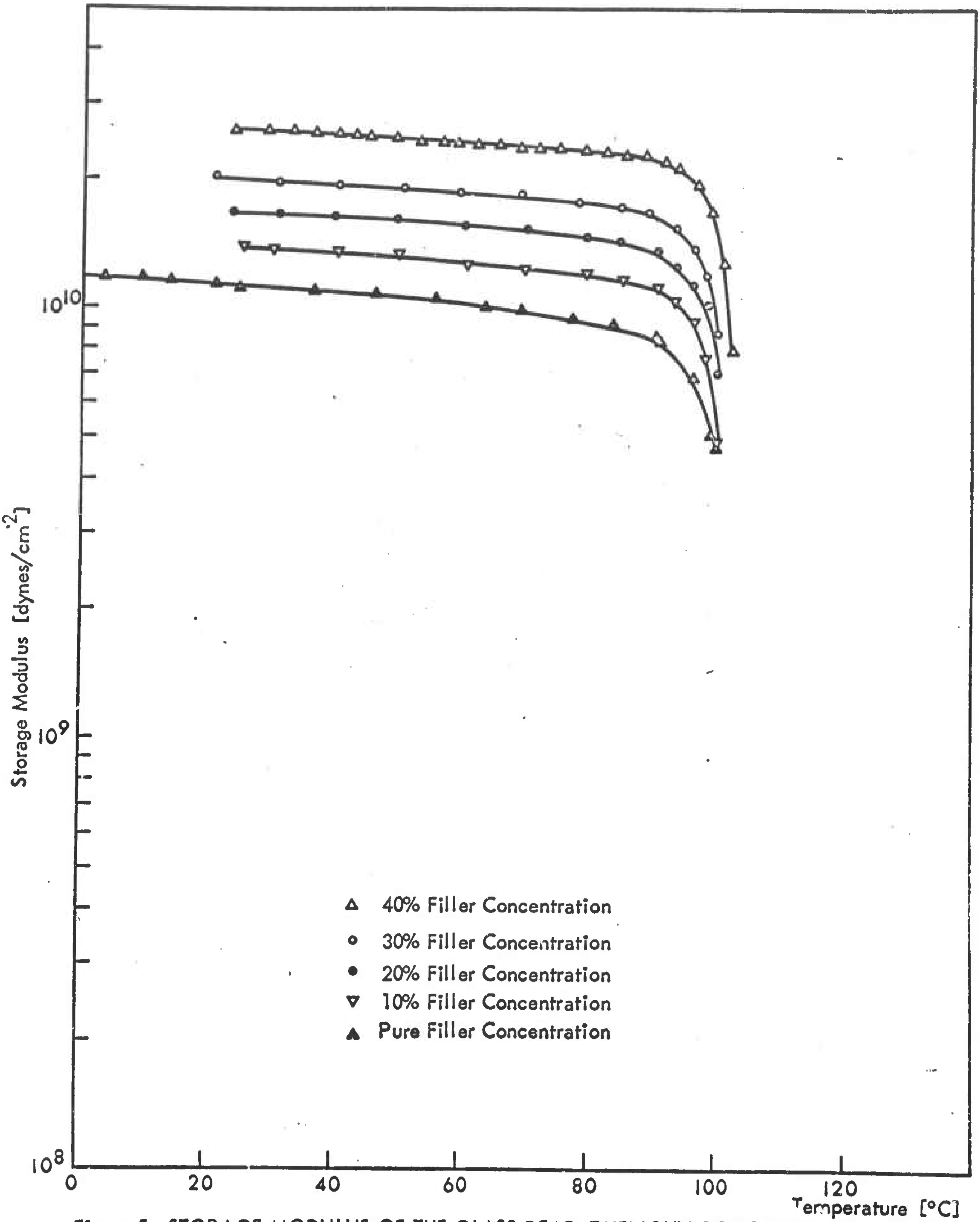

Figure 5. STORAGE MODULUS OF THE GLASS BEAD-PHENOXY COMPOSITE AS A FUNCTION OF TEMPERATURE AND FILLER CONCENTRATION

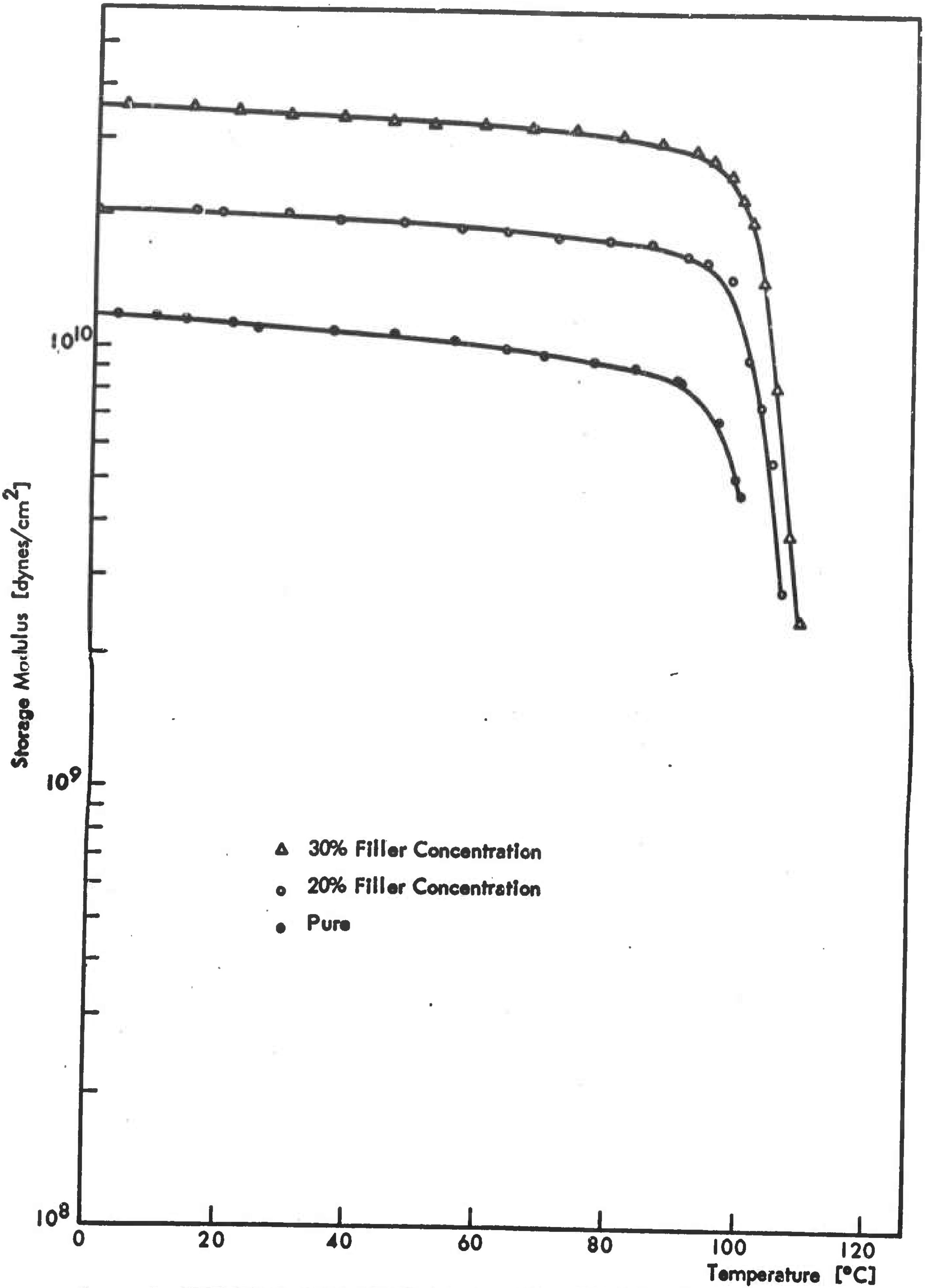

Figure 6. STORAGE MODULUS OF THE ATTAPULGITE-PHENOXY COMPOSITE AS A FUNCTION OF TEMPERATURE AND FILLER CONCENTRATION

Figure 7 - Droste and DiBene

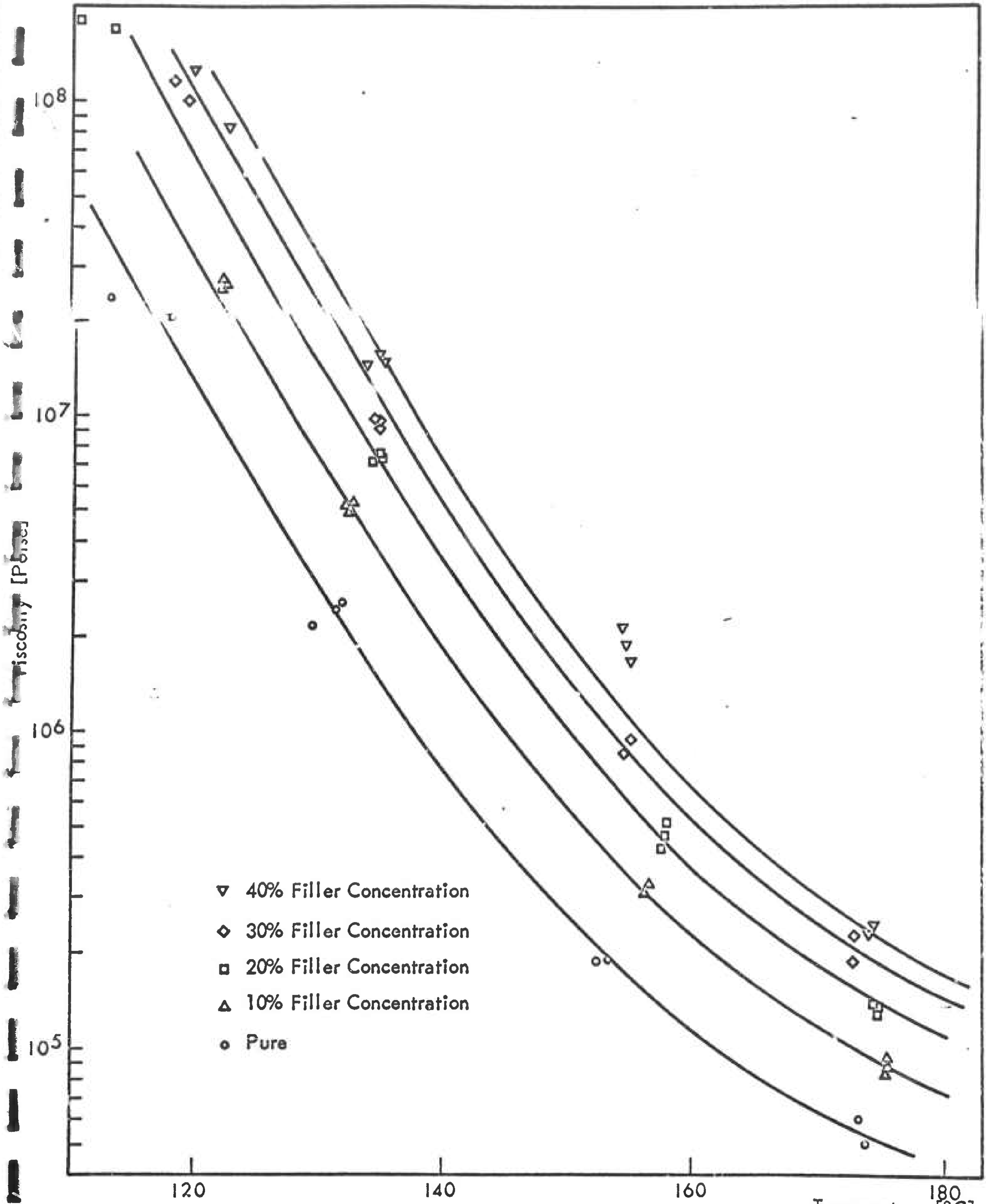

Figure 7. VISCOSITY OF THE GLASS BEAD-PHENOXY COMPOSITE AS A FUNCTION OF FILLER CONCENTRATION AND TEMPERATURE

Figure 8
Droste and DiBene

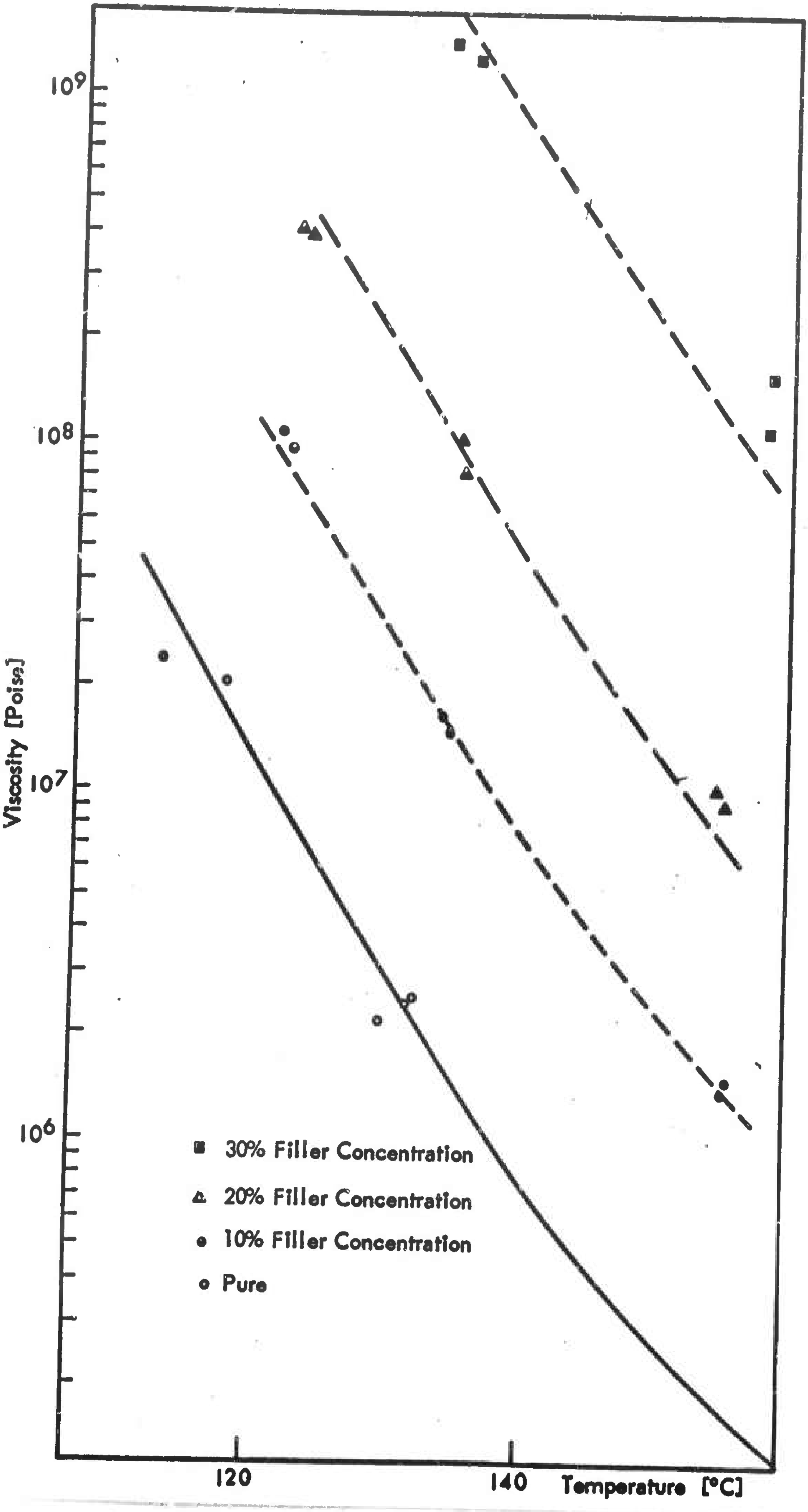

Figure 8. VISCOSITY OF THE GLASS BEAD-PHENOXY COMPOSITE AS A FUNCTION OF FILLER CONCENTRATION AND TEMPERATURE

Figure 9 - Droste and DiBenede

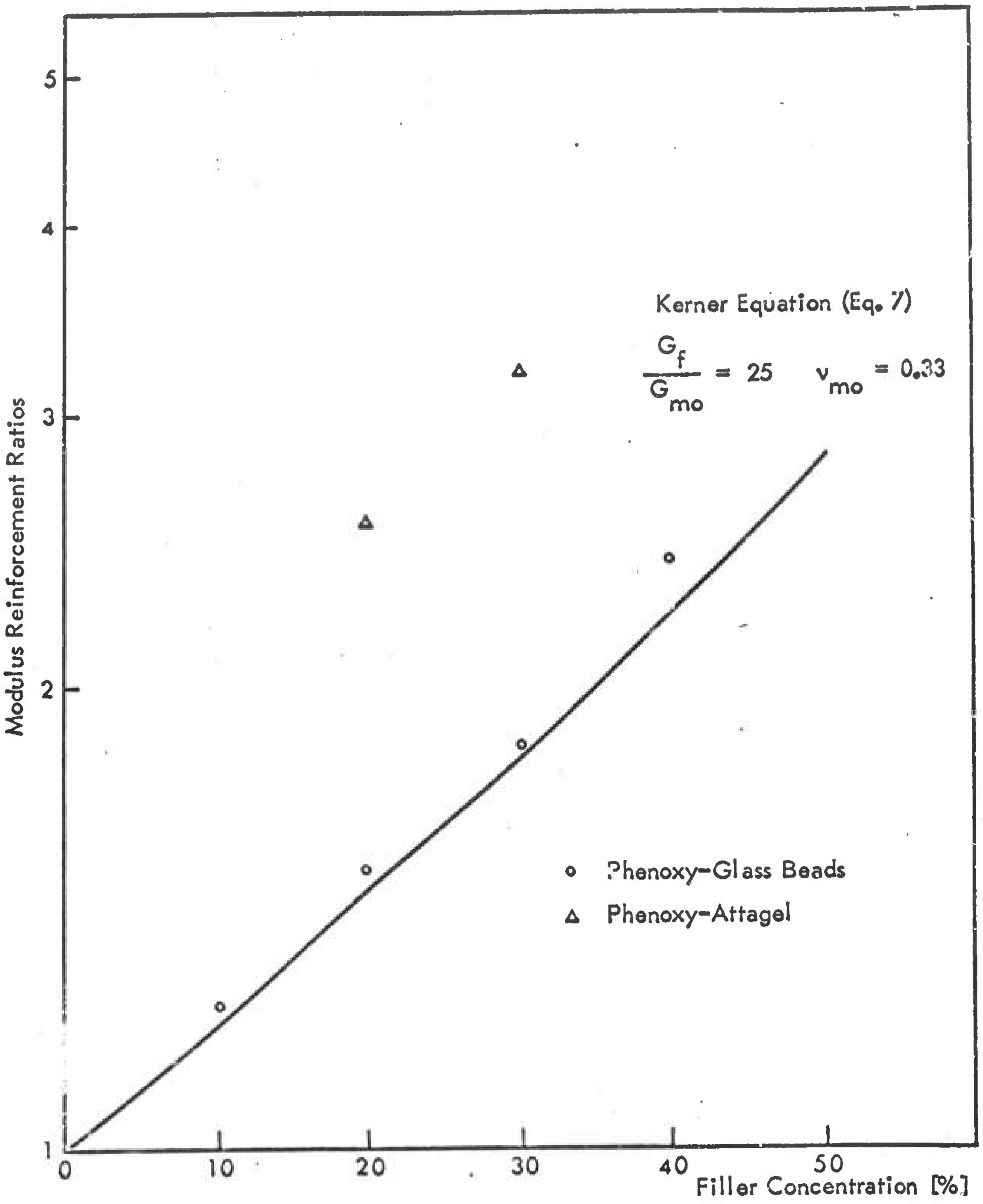

Figure 9. EXPERIMENTAL MODULUS REINFORCEMENT RATIOS AS A FUNCTION OF FILLER CONCENTRATION. THE DATA ARE COMPARED WITH THEORETICAL PREDICTIONS DUE TO KERNER.

Figure 10 - Droste and DiBenedetto

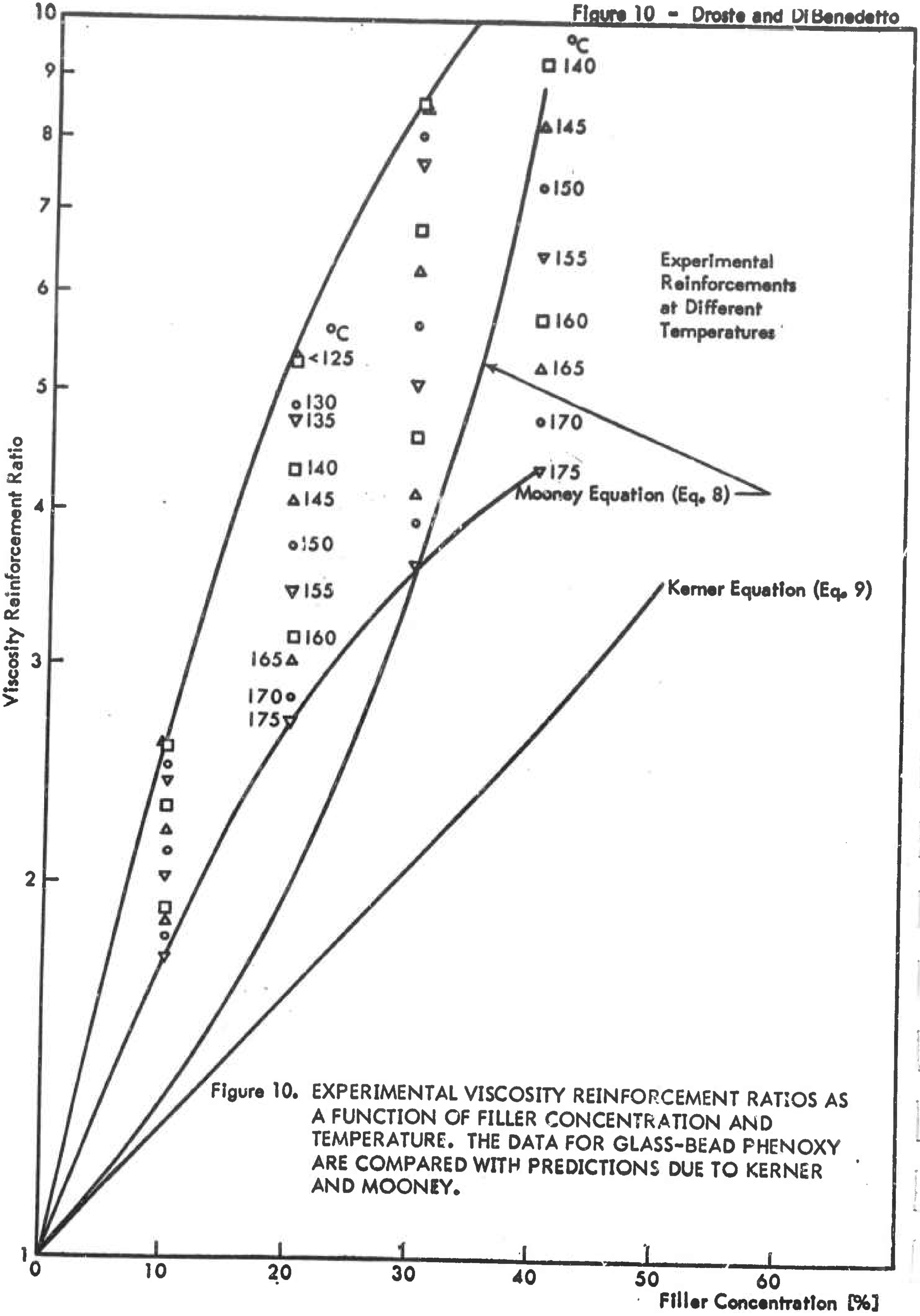

Figure 10. EXPERIMENTAL VISCOSITY REINFORCEMENT RATIOS AS A FUNCTION OF FILLER CONCENTRATION AND TEMPERATURE. THE DATA FOR GLASS-BEAD PHENOXY ARE COMPARED WITH PREDICTIONS DUE TO KERNER AND MOONEY.

Figure 11 - Droste and DiBenedetto

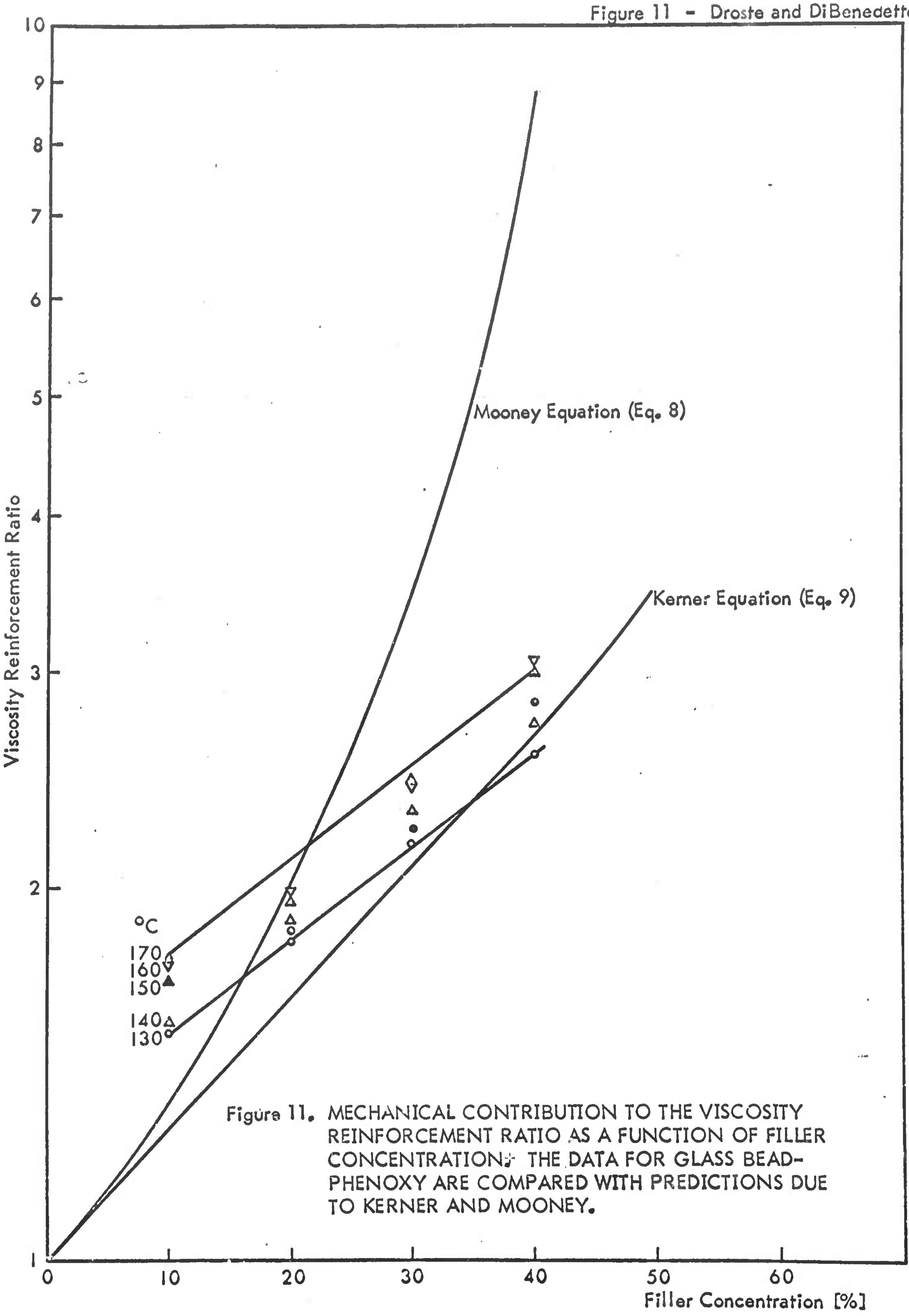

Figure 11. MECHANICAL CONTRIBUTION TO THE VISCOSITY REINFORCEMENT RATIO AS A FUNCTION OF FILLER CONCENTRATION; THE DATA FOR GLASS BEAD-PHENOXY ARE COMPARED WITH PREDICTIONS DUE TO KERNER AND MOONEY.

Figure 12 - Droste and DiBenedet

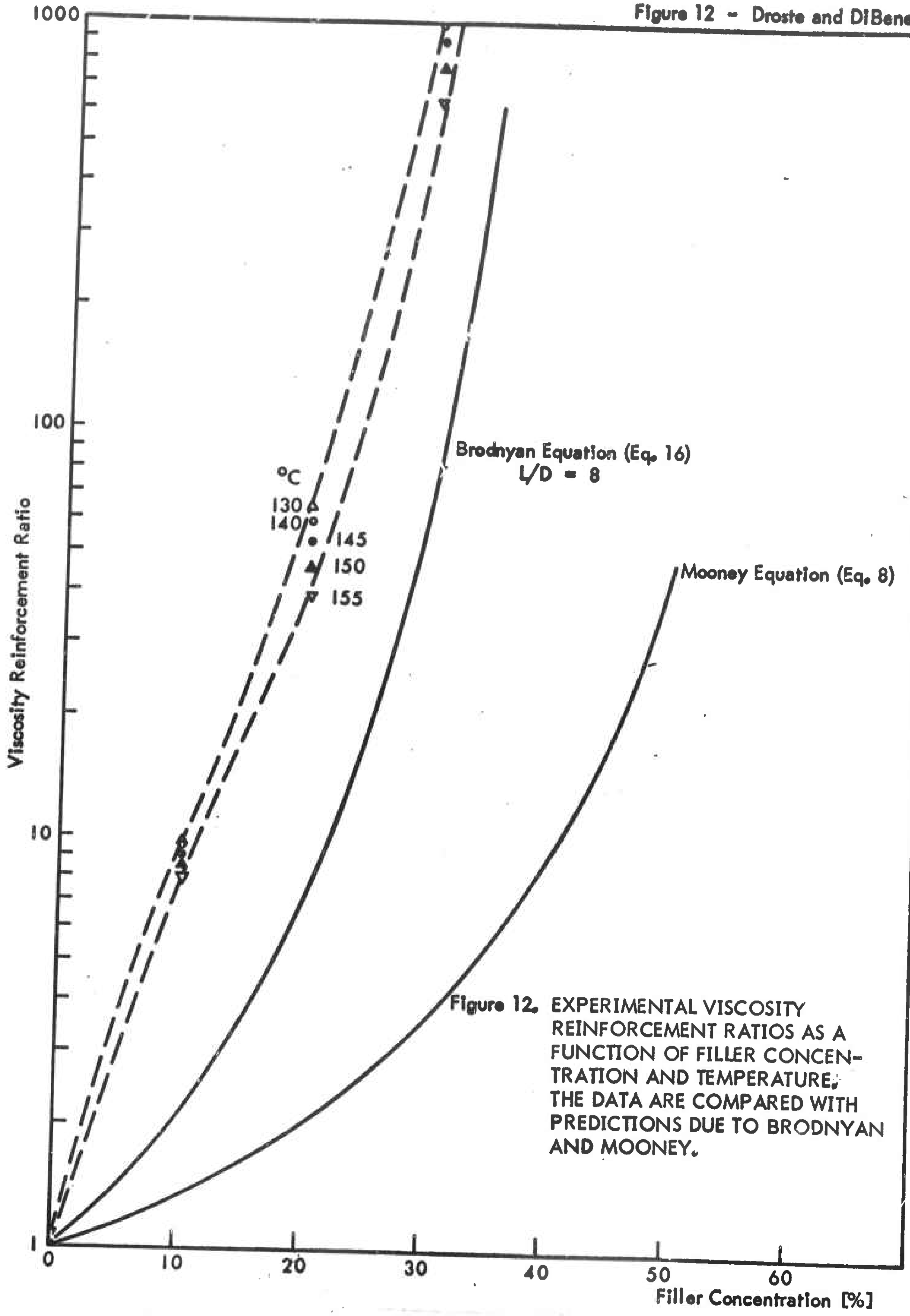

Figure 12. EXPERIMENTAL VISCOSITY REINFORCEMENT RATIOS AS A FUNCTION OF FILLER CONCENTRATION AND TEMPERATURE. THE DATA ARE COMPARED WITH PREDICTIONS DUE TO BRODNYAN AND MOONEY.

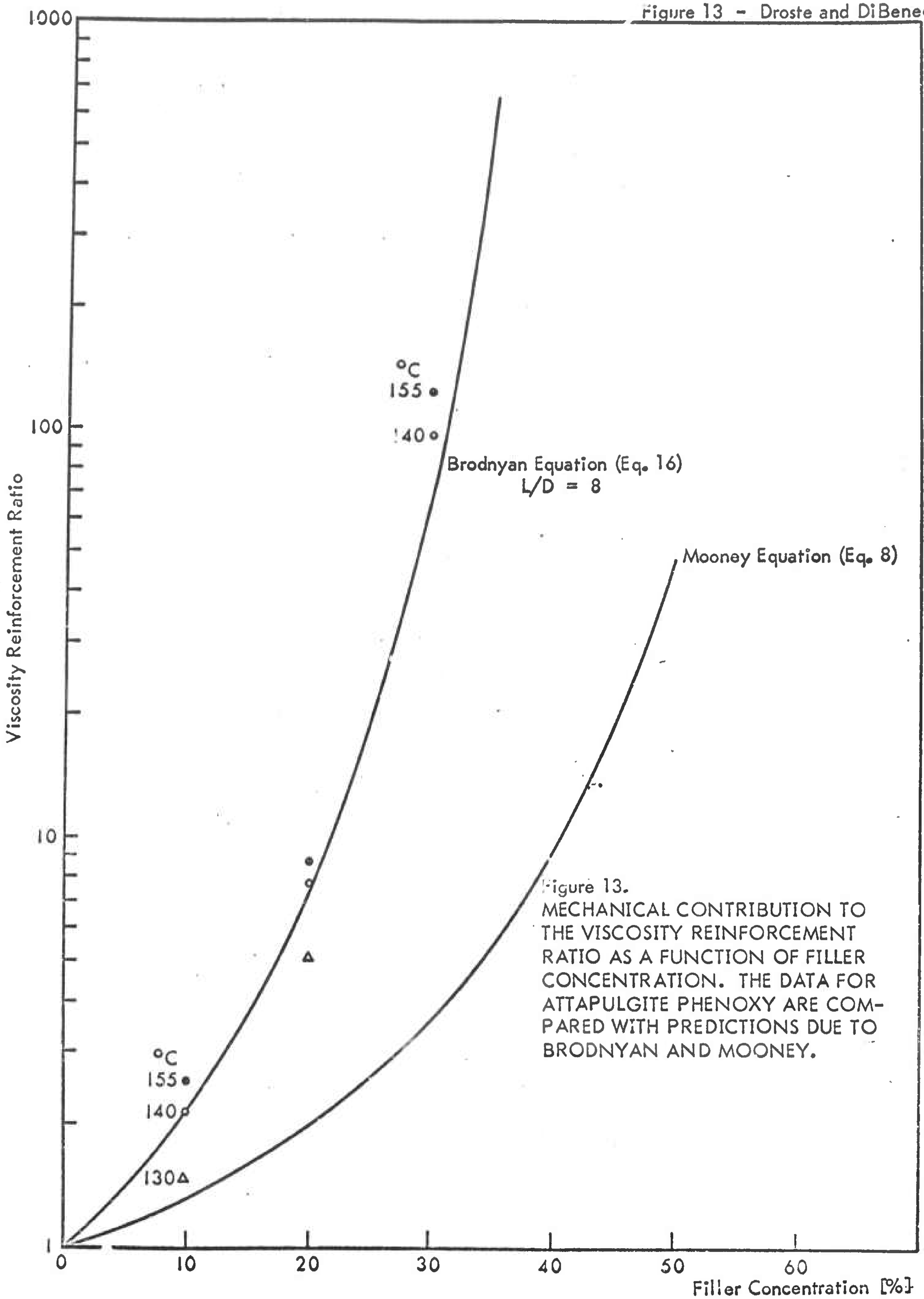

Figure 13.
MECHANICAL CONTRIBUTION TO THE VISCOSITY REINFORCEMENT RATIO AS A FUNCTION OF FILLER CONCENTRATION. THE DATA FOR ATTAPULGITE PHENOXY ARE COMPARED WITH PREDICTIONS DUE TO BRODNYAN AND MOONEY.

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13. ABSTRACT

The glass transition temperature, dynamic shear moduli and bulk viscosities of Phenoxy PKHH 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 filler. The average transition temperature was described by a simplified two-phase mixture model of a layer of immobilized polymer surrounding each filler particle and the unaffected portion of the polymer matrix. The model predicts an increasing glass transition temperature to a limiting value at a certain filler concentration. From the measured moduli and the viscosities of the filled samples and the pure polymer, the relative reinforcement ratios in the glassy and viscous state were obtained as a function of the filler type and concentration. The modulus reinforcement ratios for the glass bead composite system follow the Kerner equation, while the clay-filled systems exhibit slightly higher reinforcement ratios. The viscosity reinforcements are strongly temperature dependent and do not follow conventional viscosity predictions for suspensions. It is suggested that the filler has a two-fold effect on the viscosity of the composite materials; one is due to its

(continued)

Security Classification

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| polymer | | | | | | |
| phenoxy resin | | | | | | |
| glass beads | | | | | | |
| Attapulgite clay | | | | | | |
| composite | | | | | | |
| storage modulus | | | | | | |
| loss modulus | | | | | | |
| dynamic mechanical properties | | | | | | |
| damping capacity | | | | | | |
| reinforced plastic | | | | | | |
| viscosity | | | | | | |
| suspension viscosity | | | | | | |
| glass transition temperature | | | | | | |
| shift in glass transition temperature | | | | | | |
| mechanical reinforcement | | | | | | |
| relative viscosity | | | | | | |

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Abstract (continued)

mechanical presence and the other 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 the purely mechanical contribution to the viscosity reinforcement. This mechanical part is approximately bounded by theoretical predictions for suspension viscosities due to Kerner, Mooney and Brodnyan.

It has been clearly shown that polymer matrix properties are modified by the presence of a filler. These modifications can be related to interactions between matrix and filler. The authors feel, however, that mechanical measurements are not direct enough to quantitatively assess the extent of the interaction and that more direct measurements of changes in the molecular structure should be more promising. Further work in the area of IR and NMR spectroscopy are in progress.