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DYNAMIC MECHANICAL PROPERTIES OF SOME POLYSTYRENE COMPOSITES

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LAWRENCE E. NIELSEN
AND
BIING-LIN LEE

OCTOBER 1971

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800 NORTH LINDBERGH BOULEVARD
ST. LOUIS, MISSOURI 63166

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. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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ABSTRACT

Dynamic shear modulus and damping ~~have been~~ were determined on polystyrene filled with glass beads which have been given surface treatments, ground glass, ground rock salt, and foams made by extracting the salt with water. Soaking the glass bead filled polystyrene in water and then redrying produces a permanent increase in damping. Data on ground glass and on rock salt composites illustrate the importance of maximum packing volume on the modulus. It is shown that moduli determined by torsional tests or by flexural tests are in error due to a polymer-rich skin. A simple method is given for correcting this error.

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DYNAMIC MECHANICAL PROPERTIES OF SOME POLYSTYRENE COMPOSITES

Lawrence E. Nielsen* and Biing-lin Lee**

Abstract

Dynamic shear modulus and damping have been determined on polystyrene filled with glass beads which have been given surface treatments, ground glass, ground rock salt, and foams made by extracting the salt with water. Soaking the glass bead filled polystyrene in water and then redrying produces a permanent increase in damping. Data on ground glass and on rock salt composites illustrate the importance of maximum packing volume on the modulus. It is shown that moduli determined by torsional tests or by flexural tests are in error due to a polymer-rich skin. A simple method is given for correcting this error.

(HPC 71-143 from the Monsanto/Washington University Association sponsored by the Office of Naval Research and the Advanced Research Projects Agency, Contract N00014-67-C-0218.)

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Introduction

Although there are now fairly extensive data on the elastic moduli and dynamic mechanical properties of filled polymers, most of these data give a very indefinite indication of how well the various theories are able to predict the properties. The data also do not clearly indicate what filler characteristics, such as the nature of the surface, are important in addition to concentration. A fairly powerful check on the theoretical equations is to compare two composites with identical filler concentration, filler shape, and filler packing except that the filler in one case is a rigid material and in the other case the filler is a gas (foam). We have been able to make such composites using soluble salts as fillers which could be extracted from the rigid polymer matrices by soaking the composites for long periods in water. These and other results indicate the importance of the type of packing of the filler particles. Yet in the past this important variable has usually been neglected. These same composites substantiate the conclusion of Nielsen and Lewis that the temperature dependence of the relative modulus is due to frozen-in stresses.

Another factor which makes comparison of experimental data with theory difficult is that all moduli of composites measured in torsion or flexure contain an inherent error. This error, which arises from a polymer-rich skin on the surface of the test specimens, can be as much as 5 to 10 percent in many cases. We have developed a simple approximate method of correcting this error.

Experimental

The shear moduli and damping were measured on a torsion pendulum described by Nielsen (1). The frequency was roughly one cycle per second for the rigid composites, and test speciments were 4" x 3/8" x 0.035". The ground and sieved rock salt had a maximum particle size of 53 microns. The glass beads (Cataphote Corporation Microbeads Div., Jackson, Miss. #4000 beads) had a distribution of sizes between 1 and 30 microns with nearly all the particles between 20 and 30 microns. Particles containing iron were removed by a magnet. The ground glass filler was made by grinding glass beads of about 500 microns diameter in a Spex Industries Mixer-Mill #8000-11. The ground glass was sieved to give particles between 20 and 30 microns in diameter. The polystyrene was Monsanto Company's Lustrex HH-101. The fillers were added to the polystyrene by mixing 20 minutes on a millroll at 170°C. Specimens were molded in sandwich spacer molds between aluminum sheets at 160°C. Salt was extracted from some of the test specimens by soaking them in water at room temperature for as long as six months. Both analyses for salt in the water and by scanning electron microscope photos indicate that essentially all of the salt could be extracted from the polystyrene composites to form a foam.

Some of the glass beads were treated with silanes to change their surface characteristics. The silanes were a dichlorodimethyl silane (General Electric Co., SC 3002) and γ-aminopropyltriethyloxy silane (Union Carbide, A-1100).

The filled materials were first tested dry. The specimens were then soaked in water for several months, redried, and tested again.

Results and Discussion

Typical data on shear modulus for glass in polystyrene are given in Figure 1 and Table I. These data are for unsoaked specimens The modulus increases with concentration of filler with ground glass being more effective than the glass beads at the same concentration. This is to be expected since the Einstein coefficient is 2.50 for spheres and slightly higher for the irregularly shaped ground glass particles. However, the main factor must be the differences in the maximum packing fraction of the two types of particles (2,3). The maximum packing fractions ϕ_m in air are 0.607 for the beads and 0.458 for the ground glass. Ritter (4) has found a similar behavior for beads compared to ground quartz.

Surface treatments have only a small effect on the shear modulus. Compared to the untreated beads, A-1100 silane slightly increases the modulus while the SC-3002 lowers the modulus. These results are anticipated since SC-3002 destroys adhesion between the polymer and the filler, and it tends to promote the formation of weak agglomerates.

It is believed that soaking composites in water weakens the interfacial bond between the phases in many cases. Soaking the glass bead specimens in water and then redrying them had very little effect on the modulus. However, the water soaking treatment had a large effect on the mechanical damping as measured by the logarithmic decrement Δ. Figure 2 shows that the reduced damping is greatly increased by the soaking treatment. It is expected that the reduced damping should be about 1.0 if all the damping comes from the polymer. Since all the values of $\Delta/\Delta_1\phi_1$ are greater than 1.0, it appears that additional damping is coming from friction between glass particles in agglomerates, friction between polymer and glass, or friction from polymer against polymer due to cracks formed as a result of stresses around the glass beads (2). (The subscript 1 refers to pure polymer, and ϕ is volume fraction.) At present the various damping mechanisms cannot be isolated. The damping is especially high for the SC-3002 treated beads. This material destroys the adhesion between polystyrene and glass and at the same time tends to promote the formation of agglomerates of glass beads. Either or both of these factors could be important in producing the high damping. Although the SC-3002 treated glass surfaces tend to repel water, the poor adhesion in this system probably allows water vapor to be rapidly transported along the interface. The effect of the water is to produce some kind of a permanent damage, since on redrying the specimens, the damping is permanently increased in all cases.

Data on polystyrene filled with ground rock salt are shown in Figures 3-5. Rock salt has a modulus about 10.1 times that of polystyrene (5). Salt increases the modulus of polystyrene, but when the salt is removed by extraction with water over a long period of time, a foam results which has air cells the same size and shape as the original salt particles. The foam has a lower modulus than pure polystyrene. The relative modulus of the salt-filled polymer increases with temperature, while that of the foam is independent of temperature. Extraction of the salt should relieve the frozen-in stresses in the polymer resulting from the mismatch in coefficients of expansion. This difference in behavior of the salt-filled and the void-filled materials gives additional support to the hypothesis of Nielsen and Lewis (6) that the temperature dependence of the relative modulus is due to these frozen-in stresses.

The modified Halpin-Tsai equations can be used to predict the moduli (7-10,2,3). The required equations are:

$$\frac{G}{G_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \qquad \text{(Rigid filler)} \qquad (1)$$

$$B = \frac{G_2/G_1 - 1}{G_2/G_1 + A} \qquad (2)$$

$$\psi = 1 + \frac{1 - \phi_m}{\phi_m^2}\,\phi_2 \qquad (3)$$

and

$$\frac{G}{G_1} = \frac{1 - B'\psi\phi_2}{1 + A'B'\phi_2} \qquad \text{(Foam)} \qquad (4)$$

$$A' = 1/A \qquad B' = \frac{G_1/G_2 - 1}{G_1/G_2 + A'} \quad . \qquad (5)$$

The modulus of the matrix (polystyrene) is G_1 while that of the material making up the filler phase is G_2, and the modulus of the composite is G. The constant A is related to the Einstein coefficient and is determined by the morphology of the system, including particle shape (10). The irregular shaped salt particles should have a value of A somewhat greater than that for a sphere (A = 1.5); a value of A = 2 fits the data well except for the highest concentration. Experimentally, the value of the maximum packing fraction ϕ_m of the ground salt was 0.60. The value of the shear modulus at the highest concentration of salt was surprisintly low, but a scanning electron microscope picture (Figure 6) gave an explanation. Many of the salt crystals had entrapped air cavities around them as a result of incomplete mixing and poor wetting of the salt by the polymer. These air cavities would drastically reduce the modulus.

Figure 7 shows the foam-like structure of the polystyrene after the salt had been extracted. The modulus of the foam was calculated using the same value of ϕ_m and the equivalent A' value as was used in the case of the salt-filled composite; the result is the lower solid curve in Figure 4. The experimental values are lower than the predicted values. By using an A' value of 1.8 instead of the predicted value of 0.5, the experimental data could be fitted by the dotted curve of Figure 4.

An A' value of 1.8 is characteristic of rod or crack-shaped particles rather than of irregular cubes. This suggests that the unexpected low modulus values for the foams might be the result of cracks formed in the polystyrene during the water extraction step. This seems reasonable as the osmatic pressure of the salt solution could exert large forces on the matrix material. However, no direct evidence of cracks was noted in the scanning electron microscope pictures.

Reduced damping data are shown in Figure 5. At 13 volume percent salt, the reduced damping has a value of 1.0 up to 70°C where the modulus of polystyrene starts to change rapidly, and the errors become large as the glass transition region is approached. At this low concentration of salt, essentially all of the energy dissipation occurs in the polymer. At higher concentrations of salt, the reduced damping becomes greater than 1.0, so new damping mechanisms, such as those discussed earlier, must become important.

Figure 4 shows the original experimental data, and also these data corrected for a "skin effect." The next section discusses how this effect arises and how to correct for it.

When composite specimens are made in molds, all the filler particles are restricted by the walls of the mold to the inside of the specimen - no part of a filler particle can extend out beyond the surface. Thus, the surface of a composite material is rich in polymer and lower than average in filler concentration as illustrated in Figure 8. This polymer-rich surface skin introduces an error in all moduli determined by flexural or torsional tests where the stress is not uniform throughout the cross section, but is a maximum at the surface. Thus, for composites containing rigid fillers, the measured apparent modulus is less than the true modulus, while for foams and rubber-filled composites, the measured modulus is greater than the true modulus (3).

From classical mechanics for specimens of rectangular cross section, the stiffness of any element of a specimen x distance from the center of the specimen is proportional to EX^3 where E is the Young's modulus for the material in the case of flexural tests or shear modulus in the case of torsional tests. Therefore, from Figure 8 the apparent modulus E_a of the composite is given by

$$E_a D^3 \doteq (E - E_1)(D - d)^3 + E_1 D^3 \qquad (6)$$

where E is the true modulus of the composite, E_1 is the modulus of the matrix material, D is the thickness of the specimen, and d is twice the thickness of the skin. The true thickness of the skin is generally unknown, but it should usually be about equal to the radius of the filler particles, so that d is approximately the diameter of the particles. Thus, the true modulus divided by the apparent modulus is

$$\frac{E}{E_a} \doteq \frac{E\,D^3}{(E - E_1)(D - d)^3 + E_1\,D^3} \qquad (7)$$

For rigid fillers, $E > E_1$ while for foams $E_1 > E$. Figures 9 and 10 give the magnitude of this correction factor as a function of E_a/E_1 for different ratios of specimen thickness to particle diameter. For many kinds of specimens the error can be from 5 to 20 percent unless the particle size is very small compared to specimen thickness or unless the modulus of the composite is only slightly greater (or less) than that of the matrix polymer.

In this paper the values of the shear modulus G are the uncorrected values. However, in the figures where experimental relative moduli G/G_1 are compared with theoretically predicted values, the moduli have been corrected for the skin effect as outlined above. In this work the corrections vary from about 2 to over 8 percent.

Lewis and Nielsen (3) studied the skin effect by using glass beads of different sizes in an epoxy resin. The true shear modulus G was determined by extrapolating to zero particle size. Their data may be used as a test of equation 7. Comparison of experiment and theory is given in Table II. It appears that the agreement is very good as shown by the last two columns of the table.

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The work described in this paper is part of the research conducted by the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research Contract N00014-67-C-0218, formerly N00014-66-C-0045.

Table I

Moduli of Glass-Filled Polystyrene

ϕ_2	T°C	Relative Shear Modulus G/G_1			
		Untreated Beads	A-1100 Treated	SC-3002 Treated	Untreated Ground Glass
.35	25	1.98	2.04	1.91	2.30
.35	80	2.08	2.09	1.91	2.41
.20	25	1.45			
.20	80	1.52			
.13	25	1.24			
.13	80	1.25			

ϕ_2 = Volume fraction of glass.

Table II

Effect of Polymer Skin on Shear Modulus

d	D/d	G_a/G_1 (Exp.)	G/G_a (Exp.)	G/G_a (Theory)
0	∞	2.44		
15	100	2.31	1.05	1.02
35	30	2.23	1.09	1.07
85	15	2.04	1.19	1.15
0	∞	1.96		
15	100	1.90	1.03	1.02
35	30	1.84	1.06	1.06
85	15	1.70	1.15	1.15

d = Average diameter of glass beads in microns

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List of Figures

1. Shear modulus of glass in polystyrene.

   ● Polystyrene, △ 13 volume % glass beads, ▽ 20 volume % beads, ⊡ 35 volume % beads, ⊙ 35 volume % ground glass.

2. Reduced damping of glass beads in polystyrene.
   A. A-1100 treated beads, B. Untreated beads, C. SC-3002 treated beads, D. Untreated beads after soaking and redrying, E. A-1100 treated beads after soaking and drying, F. SC-3002 treated beads after soaking and drying.

3. Relative modulus of polystyrene: Top - Filled with salt. Bottom - Foam resulting from extraction of salt.

4. Relative modulus of polystyrene filled with: Top - 33.5 v/o salt. Bottom - voids resulting from extraction of salt. Curves are theoretical predictions. ● Uncorrected experimental data. ⊙ Data corrected for skin effect.

5. Reduced damping of polystyrene filled with salt.
   A. 13 v/o salt, B. 20 v/o salt, C. 33.5 v/o salt.

6. Polystyrene filled with 33.5 v/o salt. Original magnification = 1800.

7. Polystyrene foam made by extracting 33.5 v/o salt with water. Original magnification = 460.

8. Schematic diagram of filled polymer showing the polymer-rich skin

9. Correction of modulus of specimens with rectangular cross section for skin effect. Filler is more rigid than matrix.

10. Correction of modulus of foams for skin effect when the specimens have rectangular cross sections.

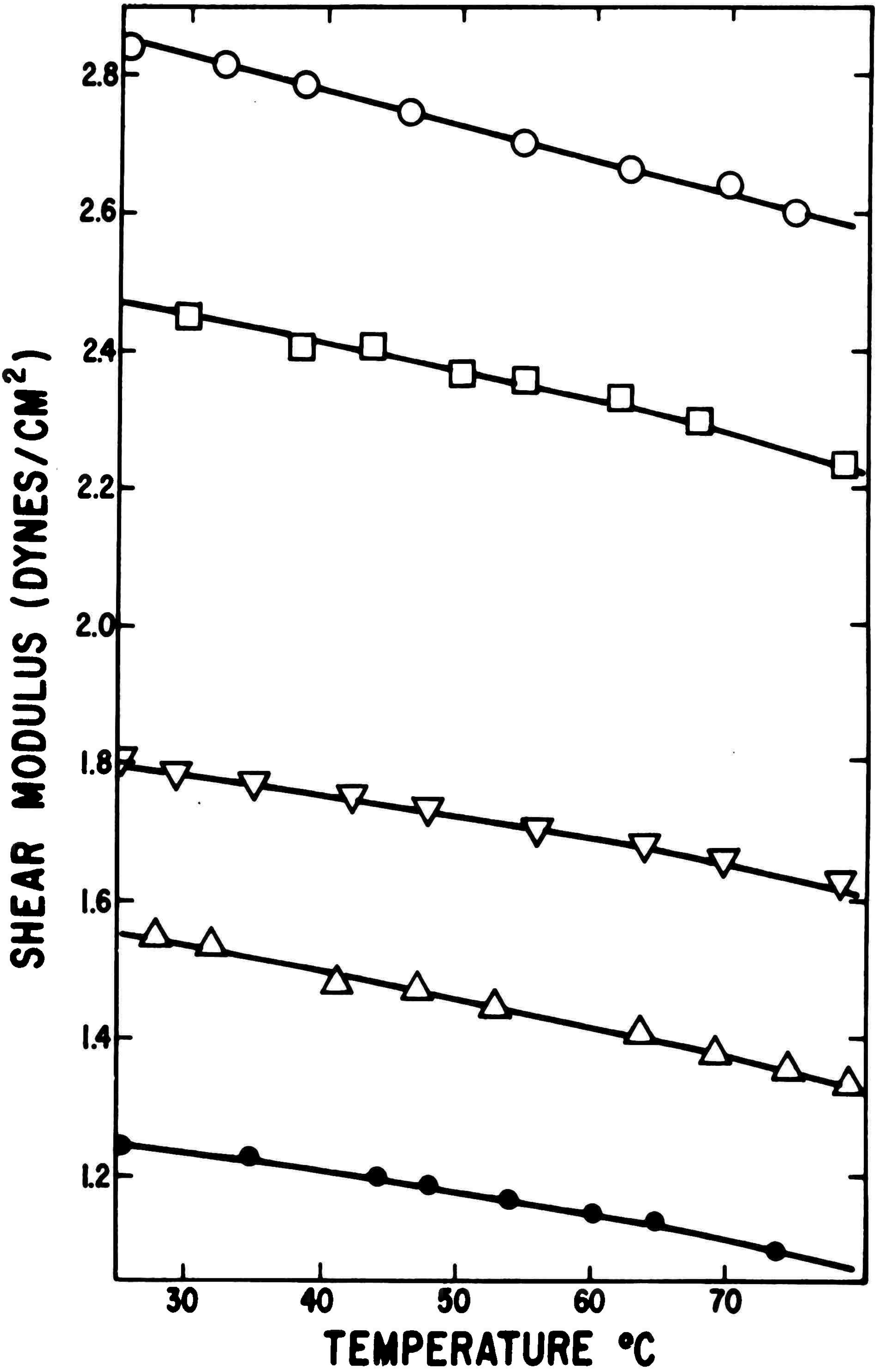

SHEAR MODULUS (DYNES/CM^2)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
30
40
50
60
70
TEMPERATURE °C

Figure 1

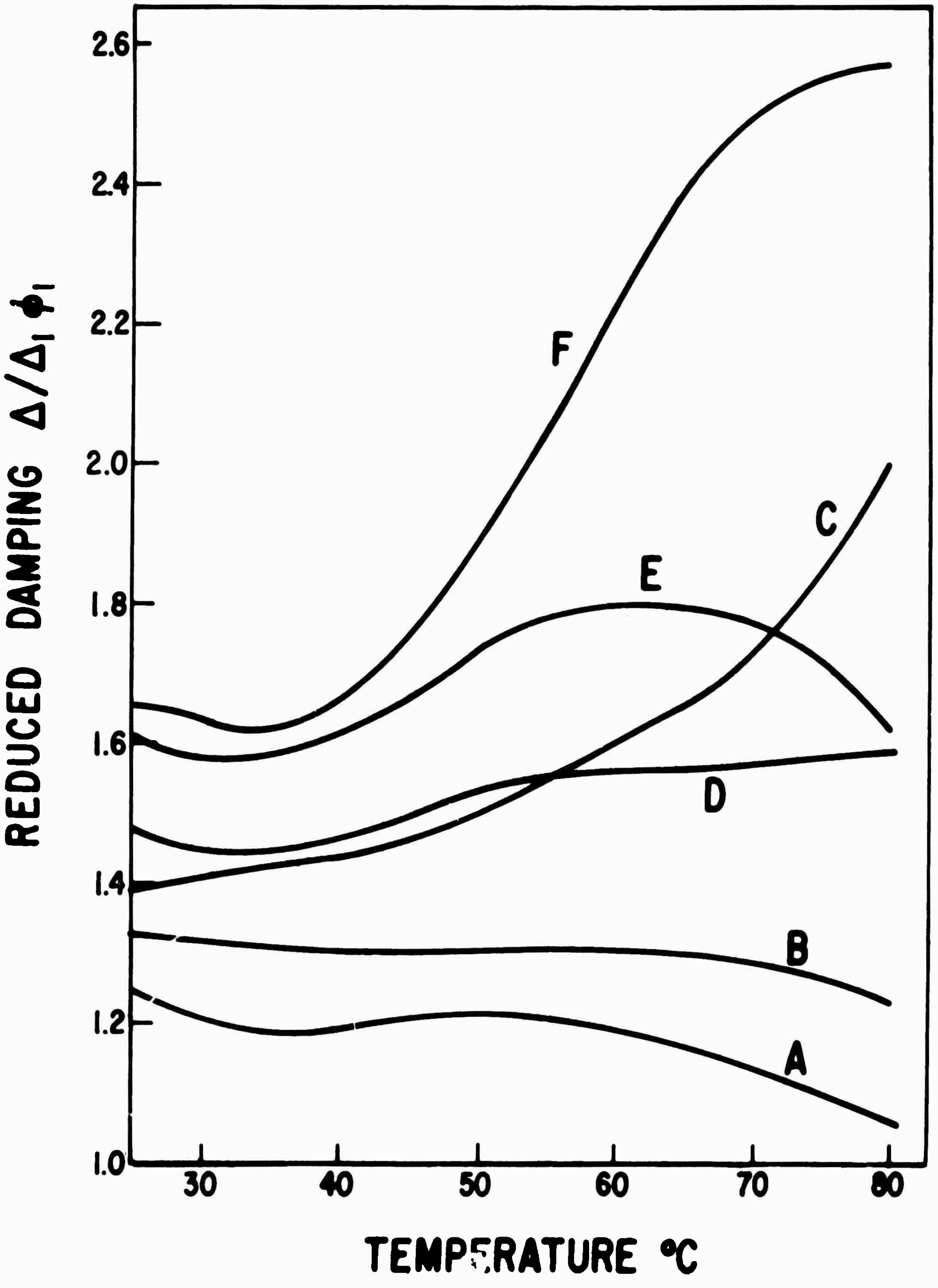

REDUCED DAMPING $\Delta/\Delta_1\phi_1$
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
30
40
50
60
70
80
TEMPERATURE °C
F
E
C
D
B
A

Figure 2

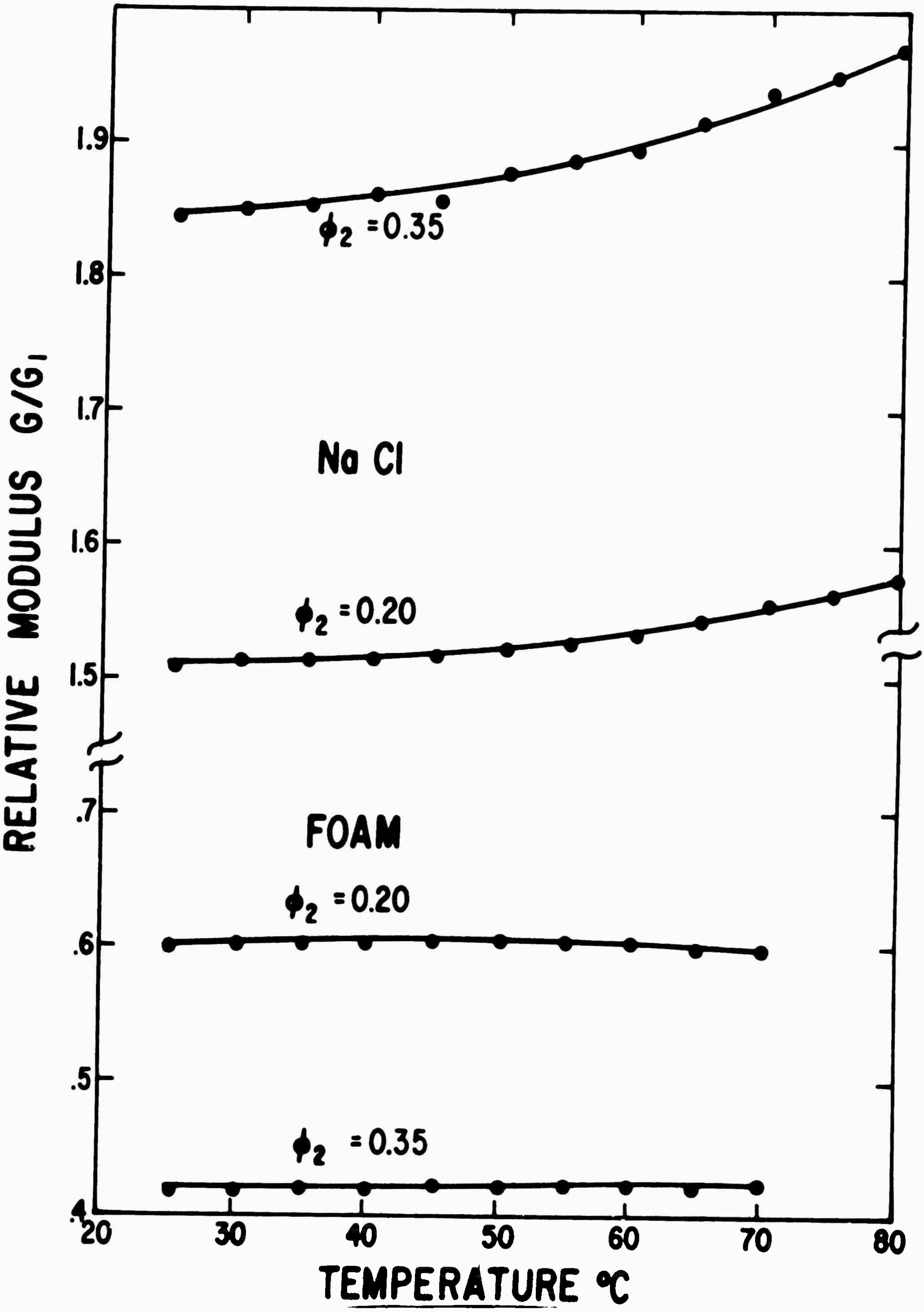

RELATIVE MODULUS G/G₁
TEMPERATURE °C
Na Cl
FOAM
ϕ₂ = 0.35
ϕ₂ = 0.20
ϕ₂ = 0.20
ϕ₂ = 0.35
1.9
1.8
1.7
1.6
1.5
.7
.6
.5
.4
20
30
40
50
60
70
80

Figure 3

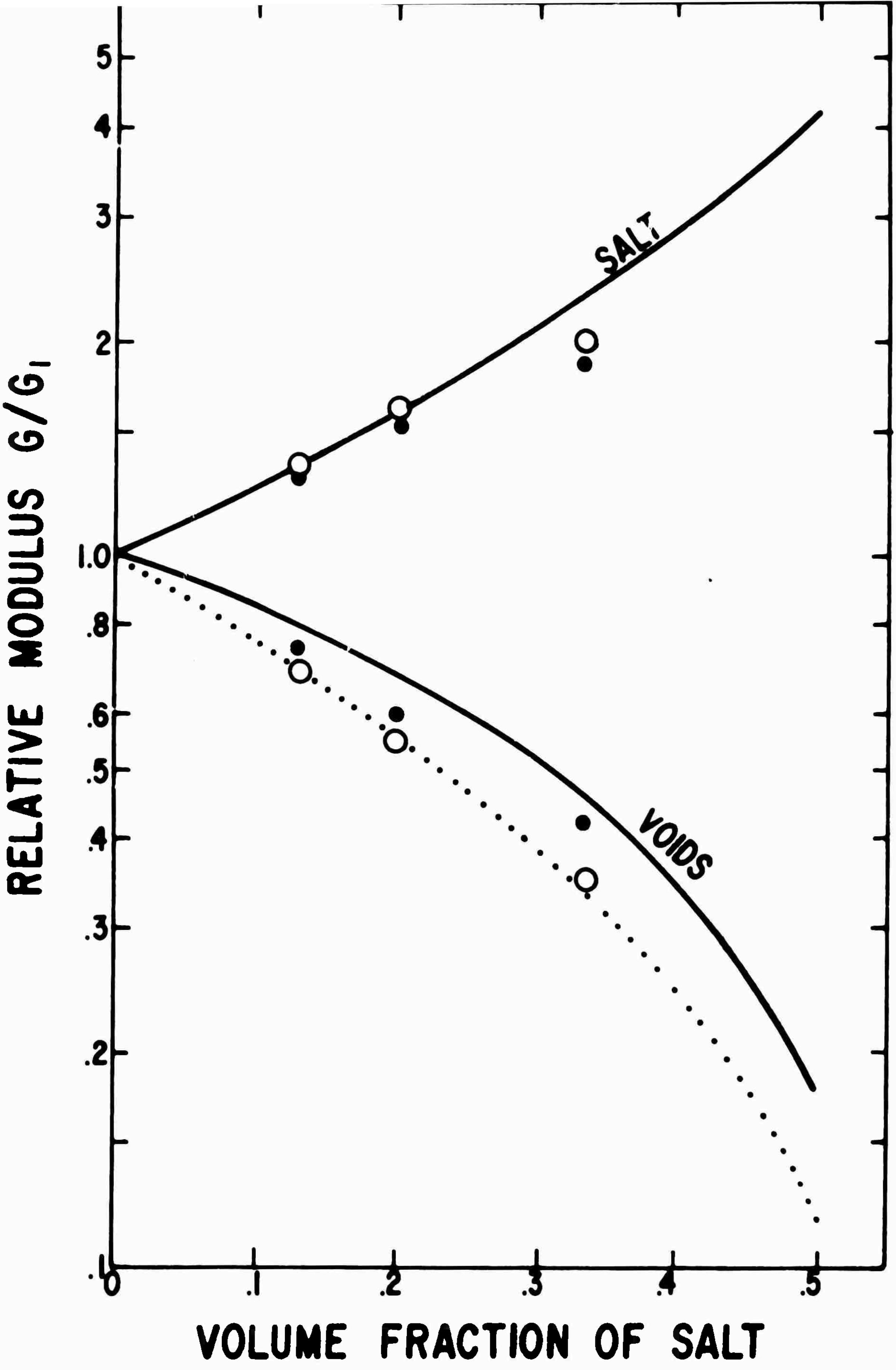

RELATIVE MODULUS G/G₁
5
4
3
2
1.0
.8
.6
.5
.4
.3
.2
.1
SALT
VOIDS
0
.1
.2
.3
.4
.5
VOLUME FRACTION OF SALT

Figure 4

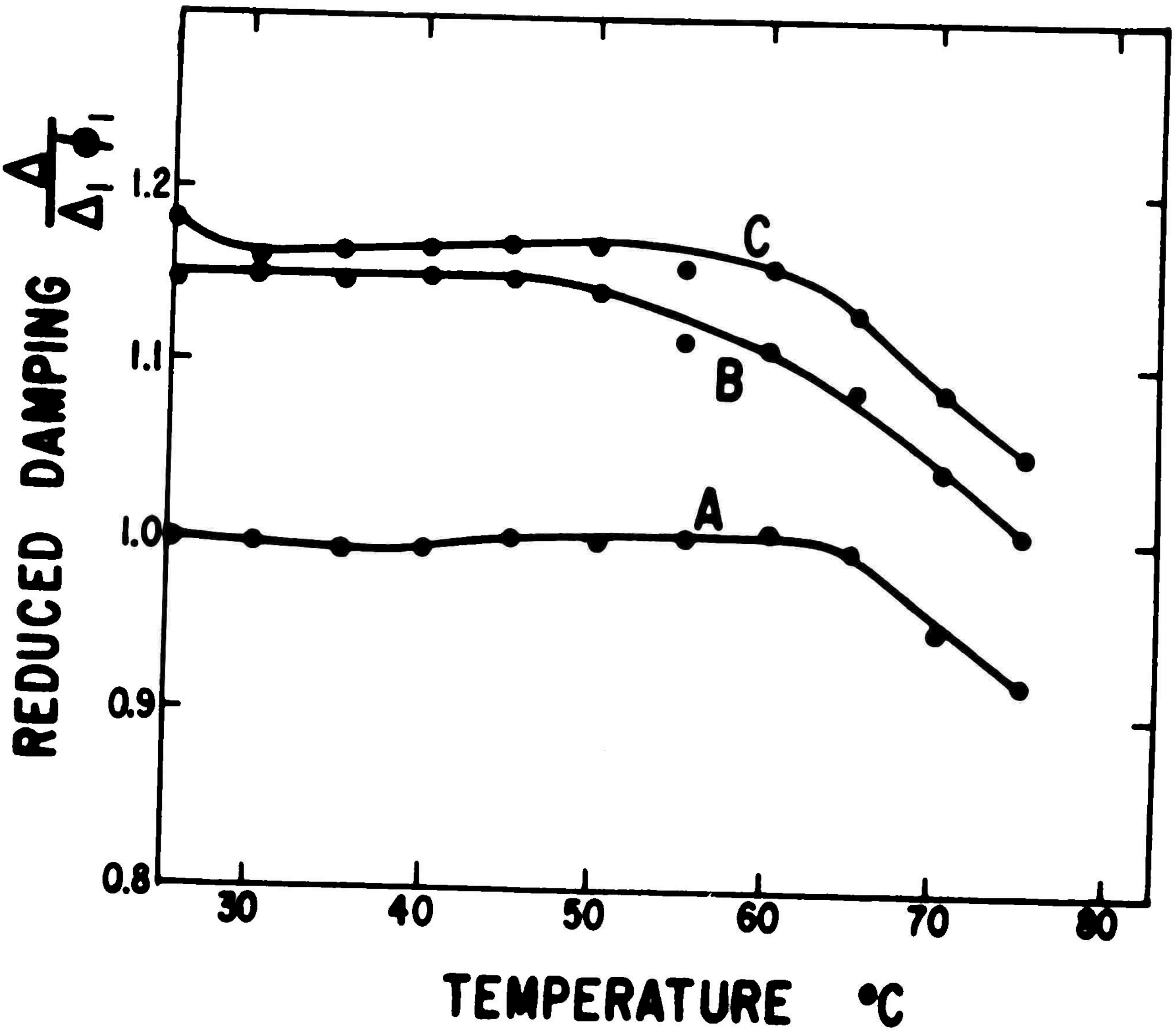

REDUCED DAMPING $\frac{\Delta}{\Delta_1}$ •
1.2
1.1
1.0
0.9
0.8
C
B
A
30
40
50
60
70
80
TEMPERATURE °C

Figure 5

NOT REPRODUCIBLE

Figure 6

NOT REPRODUCIBLE

Figure 7

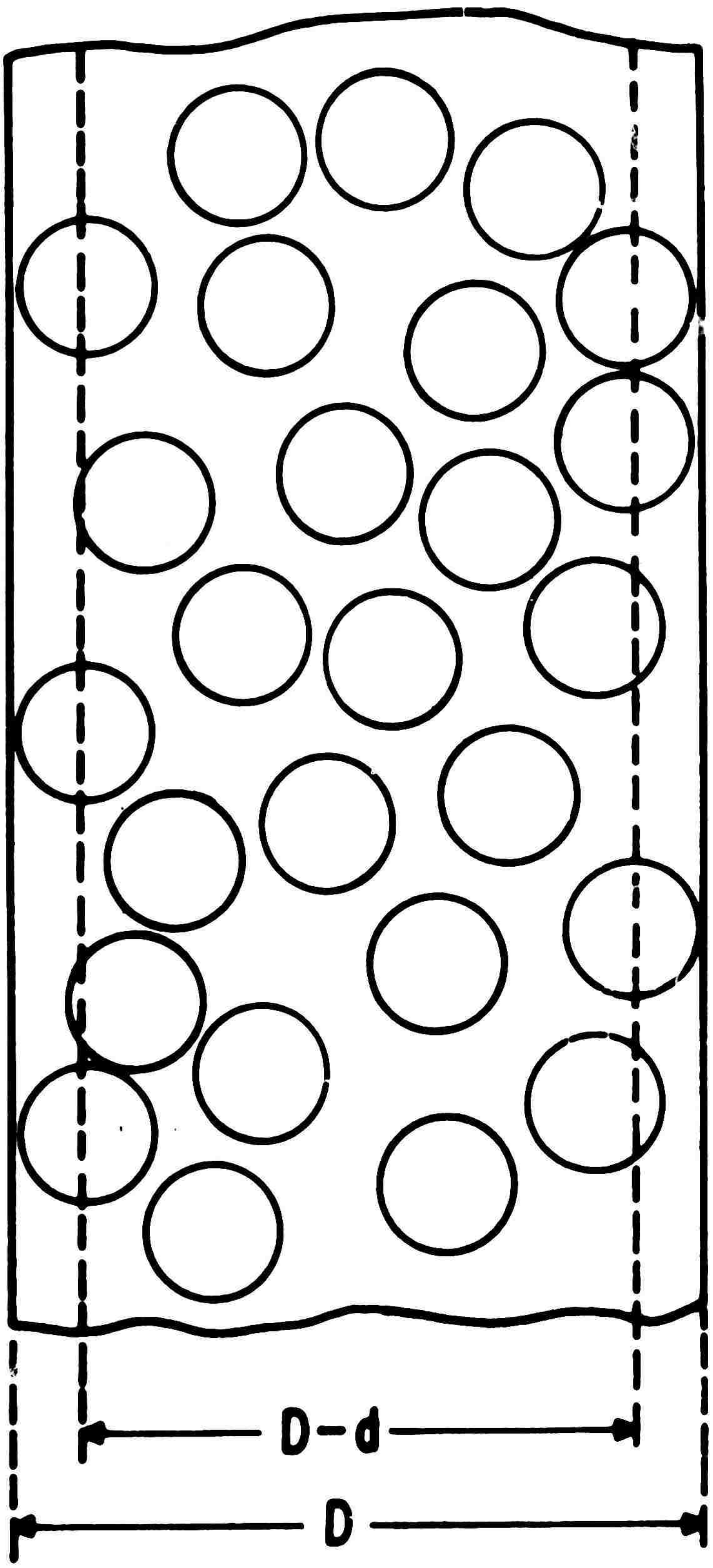


Figure 8

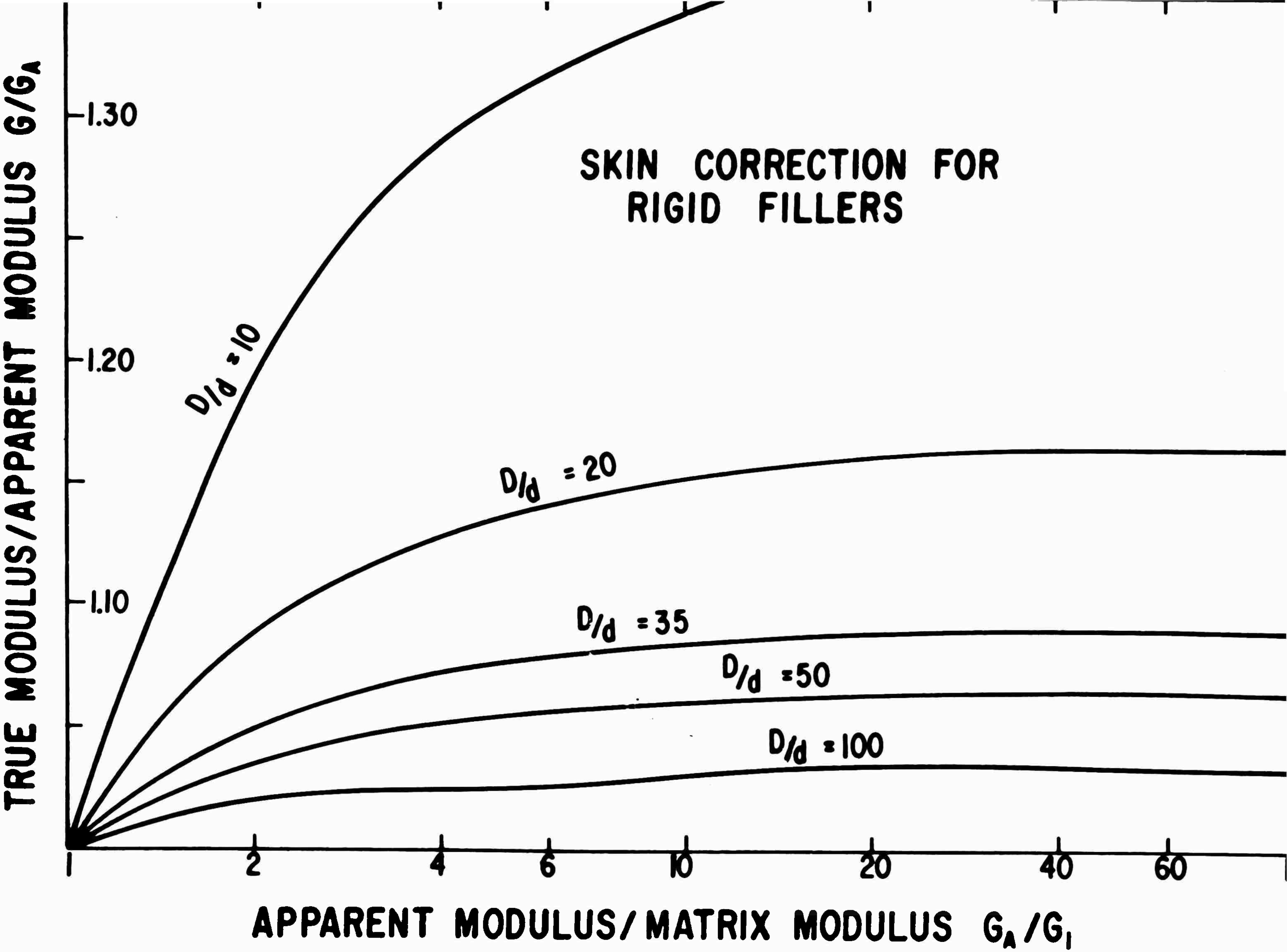
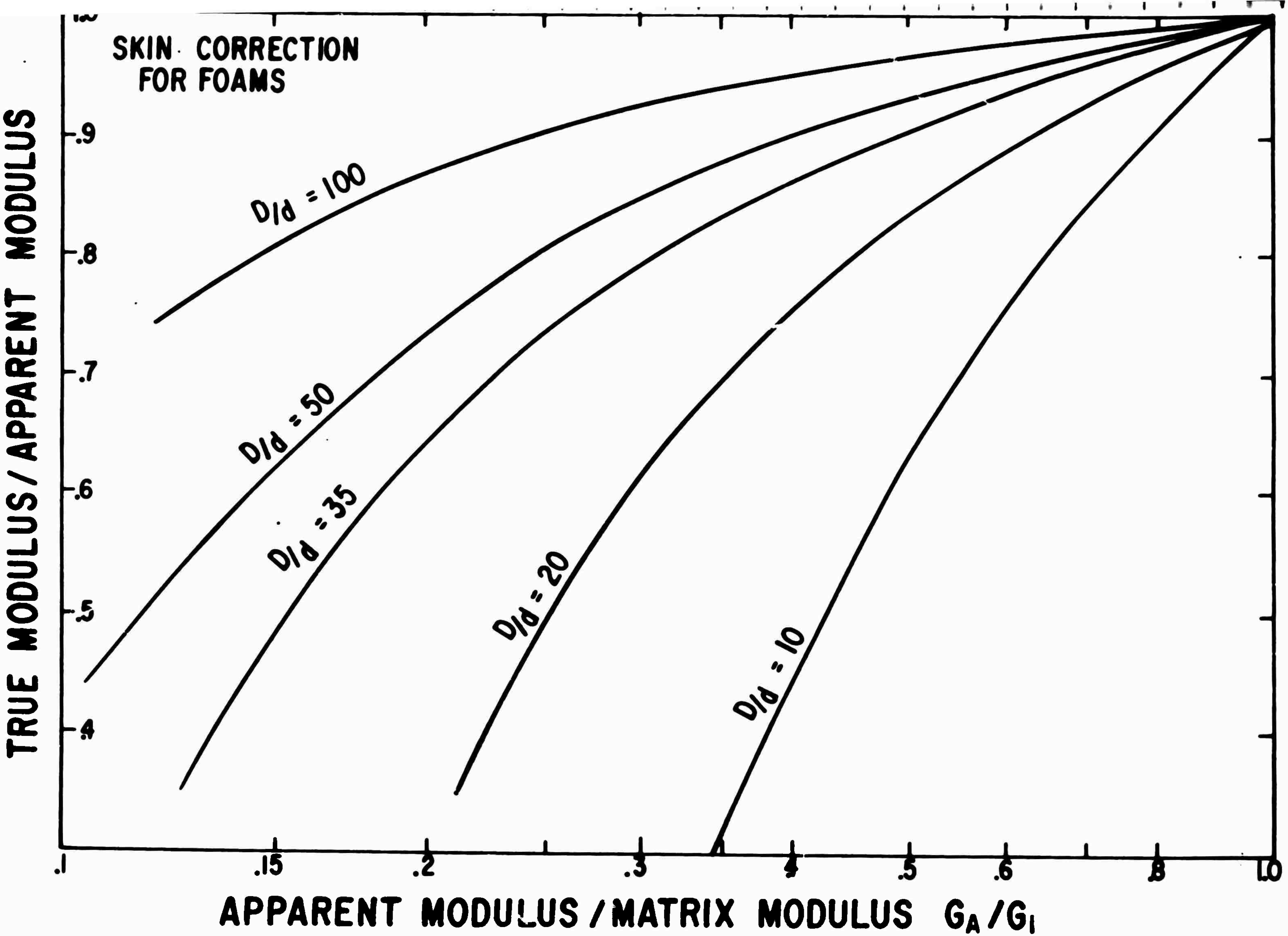

SKIN CORRECTION FOR
RIGID FILLERS
TRUE MODULUS/APPARENT MODULUS G/G$_A$
1.30
1.20
1.10
D/d = 10
D/d = 20
D/d = 35
D/d = 50
D/d = 100
1
2
4
6
10
20
40
60
APPARENT MODULUS/MATRIX MODULUS G$_A$/G$_1$

Figure 9


SKIN CORRECTION
FOR FOAMS
TRUE MODULUS/APPARENT MODULUS
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.8
.7
.6
.5
.4
D/d = 100
D/d = 50
D/d = 35
D/d = 20
D/d = 10
.1
.15
.2
.3
.4
.5
.6
.8
1.0
APPARENT MODULUS/MATRIX MODULUS G_A/G_I

Figure 10