

AD-751 017

VISCOELASTIC PROPERTIES OF 1,2 POLYBUTADIENE  
AND COMPARISON WITH OTHER RUBBERS

W. M. Madigosky, et al

Naval Ordnance Laboratory  
White Oak, Maryland

23 August 1972

DISTRIBUTED BY:

**NTIS**

National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE  
5285 Port Royal Road, Springfield Va. 22151

NOLTR 72-192

AD751017

VISCOELASTIC PROPERTIES OF 1, 2  
POLYBUTADIENE AND COMPARISON  
WITH OTHER RUBBERS

By  
W. M. Madigosky  
J. VonBretzel

23 AUGUST 1972

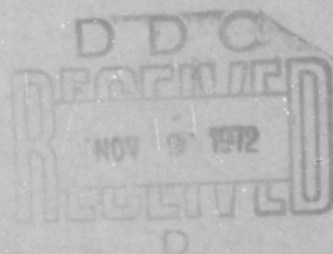
NOL

NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U.S. Department of Commerce  
Springfield VA 22151

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED

NOLTR 72-192



R  
24

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) NAVAL ORDNANCE LABORATORY WHITE OAK, SILVER SPRING, MARYLAND	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE  
VISCOELASTIC PROPERTIES OF 1,2 POLYBUTADIENE AND COMPARISON WITH OTHER RUBBERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)  
NOLTR 72-192 23 AUGUST 1972

5. AUTHOR(S) (First name, middle initial, last name)  
W.M. MADIGOSKY JIM VONBRETZEL

6. REPORT DATE 23 August 1972	7a. TOTAL NO. OF PAGES 23	7b. NO. OF REFS 8
----------------------------------	------------------------------	----------------------

8a. CONTRACT OR GRANT NO. b. PROJECT NO. MAT-03L-000/ZR00-001-010 Prob. No. 127 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NOLTR 72-192 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
---	--

10. DISTRIBUTION STATEMENT  
This document has been approved for public release distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Naval Ordnance Laboratory Silver Spring, Maryland 20910
-------------------------	--

13. ABSTRACT  
The dynamic viscoelastic properties of polybutadiene rubber consisting of principally 1,2 microstructure are of immediate interest to the Navy. These properties have been determined by measuring the velocity and attenuation coefficient of ultrasonic waves in the material from 300 kHz to 5 MHz and from -50°C to 100°C. The sound velocity was found to increase with decreasing temperature, leveling off both at high and low temperatures. This effect is attributed to the appearance of a crystalline shear elasticity at the lower temperatures. Peaks in the attenuation as a function of both temperature and frequency were observed, and relaxation times of the order 10<sup>-7</sup> to 10<sup>-8</sup> seconds are indicated. The loss curve in 1,2 polybutadiene is higher and broader than that for natural and GR-S (styrenebutadiene co-polymer), which are low-loss rubbers; but lower than for butyl, a high-loss rubber. It was also found that the data could be represented by reduced frequency or temperature plots by assuming that the dynamic properties undergo a transition which is exponentially proportional to the fractional free volume (Williams-Landel-Ferry formularization). The previously determined WLF constants (c<sub>1</sub>=12.7, c<sub>2</sub>= 35.5) reduce the temperature-frequency data satisfactorily. These results allow the data to be extrapolated to the low frequency region where measurements are limited by experimental difficulties and sample size.

IA

UNCLASSIFIED

Security Classification

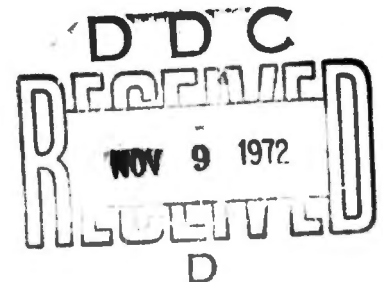
14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Viscoelastic properties 1,2 polybutadiene rubber ultrasonics						

VISCOELASTIC PROPERTIES OF 1,2 POLYBUTADIENE  
AND COMPARISON WITH OTHER RUBBERS

Prepared by:

W.M. Madigosky  
J. VonBretzel

ABSTRACT: The dynamic viscoelastic properties of polybutadiene rubber consisting of principally 1,2 microstructure are of immediate interest to the Navy. These properties have been determined by measuring the velocity and attenuation coefficient of ultrasonic waves in the material from 300 kHz to 5 MHz and from  $-50^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . The sound velocity was found to increase with decreasing temperature, leveling off both at high and low temperatures. This effect is attributed to the appearance of a crystalline shear elasticity at the lower temperatures. Peaks in the attenuation as a function of both temperature and frequency were observed and relaxation times of the order  $10^{-7}$  to  $10^{-8}$  seconds are indicated. The loss curve in 1,2 polybutadiene is higher and broader than that for natural and GR-S (styrene-butadiene co-polymer), which are low-loss rubbers; but lower than for butyl, a high-loss rubber. It was also found that the data could be represented by reduced frequency or temperature plots by assuming that the dynamic properties undergo a transition which is exponentially proportional to the fractional free volume (Williams-Landel-Ferry formalization). The previously determined WLF constants ( $c_1 = 12.7$ ,  $c_2 = 35.5$ ) reduce the temperature-frequency data satisfactorily. These results allow the data to be extrapolated to the low frequency region where measurements are limited by experimental difficulties and sample size.



Acoustics Division  
Physics Research Department  
NAVAL ORDNANCE LABORATORY  
White Oak, Silver Spring, Maryland 20910

NOLTR 72-192

23 August 1972

VISCOELASTIC PROPERTIES OF 1,2 POLYBUTADIENE  
AND COMPARISON WITH OTHER RUBBERS

The objective of the liquid state program at NOL is research on the physical and acoustical problems associated with liquids, glasses polymers and rubbers of interest to the Navy. The dynamic viscoelastic properties of principally 1,2 polybutadiene rubber are of immediate interest to the Navy for a possible wide range of acoustic applications. This work was supported under Task Number MAT-03L-000/ZR00-001-010 Problem 127.

ROBERT WILLIAMSON II  
Captain, USN  
Commander



Z.I. SLAWSKY  
By direction

TABLE OF CONTENTS

	PAGE
INTRODUCTION -----	1
EXPERIMENTAL METHOD -----	2
REDUCED VARIABLES -----	3
EXPERIMENTAL RESULTS -----	4
DISCUSSION AND CONCLUSIONS-----	6

ILLUSTRATIONS

FIGURE		PAGE
1	SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING BULK WAVE PROPAGATION CONSTANTS AT 5 MHz.	
2	SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING BULK WAVE PROPAGATION CONSTANTS FROM 300 TO 3000 kHz.	
3	ATTENUATION VS. TEMPERATURE OF 1,2 POLYBUTADIENE AT 5 MHz.	
4	VELOCITY VS. TEMPERATURE OF 1,2 POLYBUTADIENE AT 5 MHz.	
5	LONGITUDINAL MODULUS VS. TEMPERATURE AT 5 MHz.	
6	ATTENUATION PER WAVELENGTH VS. FREQUENCY OF 1,2 POLYBUTADIENE AT 24°C.	
7	TEST OF THE WLF REDUCTION FORMULA.	
8	ATTENUATION PER WAVELENGTH VS FREQUENCY OF 1,2 POLYBUTADIENE AT 24°C (COMPLETE CURVE) .	
9	VELOCITY VS. FREQUENCY OF 1,2 POLYBUTADIENE AT 24°C.	
10.	COMPARISON OF BULK WAVE ATTENUATION VS. TEMPERATURE AT 5 MHz OF 1,2 POLYBUTADIENE WITH THAT OF BUTAL, GR-S AND NATURAL RUBBERS .	

VISCOELASTIC PROPERTIES OF 1,2 POLYBUTADIENE  
AND COMPARISON WITH OTHER RUBBERS

## INTRODUCTION

1. Dynamic viscoelastic properties of a material can be obtained from a measurement of its sound velocity and attenuation coefficient. It has been established that in various hydrogen-bonded liquids and high polymers the longitudinal wave velocity increases with decreasing temperature and that the attenuation possesses a maximum with respect to temperature. This has also been verified for natural GR-S and butyl rubbers by Ivey et al. (1949) and for Buna-N by Nolle and Mifsud (1952). Both investigations employed ultrasonic frequencies. Similar effects were noted at low frequencies (1000 Hz) for natural rubber by McKinney et al. (1960), and for GR-S and butyl rubbers by Witte et al. (1949).
2. Decreasing frequency produces effects qualitatively similar to those produced by increasing temperature. Ivey et al. (1949) have obtained data covering a frequency range of seven decades by correlating low frequency data, in which the dynamic Young's modulus and loss factor are obtained, with high frequency or ultrasonic data. The data show that the dynamic moduli undergoes a transition and that the loss factor exhibits a maximum in the dispersion region. These effects are attributed to a crystalline shear elasticity that appears when the material is stressed at high frequencies.
3. The effect of temperature on the transition between the crystalline or glassy and rubbery states of a polymeric material has been explained in terms of a free volume model. The free volume is interpreted as the space available for a cooperative rearrangement to take place. If cooperative motions are prevented from occurring then the material shows the much higher modulus characteristic of a glass or a rigid solid. The assumption of the free volume theory is that there exists a critical value of the free volume which is just large enough to allow cooperative motions to take place. This critical volume determines a unique glass transition temperature for each material. From the work of Williams, Landel and Ferry, (1955) the free volume and its temperature dependence almost appear to be universal constants for a large number of polymeric materials. There is some variation, however, from one polymer to another and the "universal" constants should only be used as a last resort in the absence of other specific data.

4. There is an intimate connection between the kinetics of the glass transition temperature and viscous relaxation effects. Ultrasonic studies have demonstrated that the relaxation behavior of the moduli depend on the product of  $\omega\tau$  (where  $\omega = 2\pi f$ ,  $f$  = frequency,  $\tau$  = relaxation time) and one can change either  $\omega$  or  $\tau$  to study the dispersion properties. Changing the temperature changes the  $\tau$ . Thus one may measure the relaxation region of a material by either varying the temperature or the frequency. This is quite useful since the range of frequencies is often limited by experimental difficulties and sample size.
5. The free volume theory assumes that the marked increase in relaxation time (or viscosity) as the temperature is lowered, is related to the reduction of available free volume for molecular rearrangement. This concept is embodied in the WLF expression which relates  $\tau$  to the free volume and which holds with remarkable accuracy. Hence, one is free to cover the relaxation region of interest either as a function of frequency or of temperature and, by means of a simple shift factor (WLF equation), convert temperature data into frequency data or vice versa.
6. This report presents a detailed investigation of the viscoelastic properties of sodium polymerized 1,2 polybutadiene and compares the results with other elastomers. The studies are of particular interest with respect to the position and magnitude of the transition zone and the prediction of viscoelastic properties in the low kiloHertz region.
7. Polybutadiene rubber was obtained thru the alkali metal polymerization process providing a rubber of principally 1,2 microstructure (62±3% vinyl and approximately 32% trans and 6% cis 1,4), where the microstructure was determined from both infrared spectrometry and a determination of the glass transition temperature ( $T_g = -55^\circ\text{C}$ ). The density was 1.13 gm/cc and the compounding and vulcanization was similar to that reported by Barron (1943).
8. Two experimental techniques were used for measuring the ultrasonic properties. At 5 MHz the longitudinal velocity and absorption coefficient were measured as a function of temperature from  $+100^\circ\text{C}$  to  $-50^\circ\text{C}$  using standard ultrasonic pulse techniques (Madigosky and Litovitz, 1961). Additional absorption measurements were taken as a function of frequency from 300kHz to 3MHz using a Scientific-Atlanta Series 1000 Transmission Measurement System. Schematic diagrams of the two systems are shown in Figs. 1 and 2.
9. The sound velocity was obtained by measuring the transient time of a 5MHz pulse thru the sample. Sample thickness was measured with a dial micrometer. The change in sample thickness with temperature due to thermal expansion was calculated using  $\beta = .0007$  per  $^\circ\text{C}$ . The attenuation of the sample was obtained by comparing the amplitude of the first echo peak with and without the sample present. This value divided by the sample thickness gives the attenuation per unit length in db/cm. The accuracy of the sample insertion method was checked by

measuring the sound speed and absorption in different sample thickness and in several other elastomers for which values have been reported. We estimate the attenuation values are accurate to  $\pm 2\%$ .

10. In general the transmitting liquids used had negligible attenuation compared to that of the rubber so that the attenuation in the sample was obtained directly. This assumes that there is negligible reflection at the liquid sample interfaces, which is valid for the liquids used. Otherwise the sample loss,  $\alpha$ , is related to the insertion loss,  $L_1$ , and sample length,  $\ell$ , by

$$\alpha = (L_1 - L_r) / \ell \quad (1)$$

where the reflection loss,  $L_r$ , is the loss caused by reflection at the two surfaces of the specimen and is given by

$$L_r = 20 \log (z_1 + z_2)^2 / 4z_1 z_2 \quad (2)$$

where  $z = \rho v$  is the acoustic impedance,  $z_1$  refers to the coupling fluid and  $z_2$  to the specimen.

#### REDUCED VARIABLES

11. If relaxation theory is applicable, it is possible to construct reduced variables in which data taken at different frequencies and temperatures can be reduced to one curve. In order for a function of the parameters of a material to be reduced it is a necessary and sufficient condition for it to be a function of the temperature only through the product  $\omega\tau$ .

12. It is well established, both from a consideration of molecular mechanisms and by experimental observation for many systems, that a change in temperature shifts the relaxation time of both the shear and bulk moduli in direct proportion to the change in the shear viscosity. It is therefore logical to use the WLF formulation as a basis for deriving reduced variables. We define a reduced frequency,  $\omega_0$  as

$$\omega_0 = \omega\tau / \tau_0 = \omega\eta(T) / \eta(T_0) \quad (3)$$

where  $\omega$  is the frequency of measurement, and  $\eta(T)$  and  $\eta(T_0)$  are the shear viscosities at the temperature of measurement and the temperature,  $T_0$ , to which reduction is desired, respectively.

13. According to the WLF theory the viscosity dependence on temperature may be written

$$\log [\eta(T) / \eta(T_0)] = \frac{-C_1 C_2 (T - T_0)}{[C_2 + (T_0 - T_g)] [C_2 + (T - T_g)]} \quad (4)$$

where  $T_g$  is the glass transition temperature and  $C_1$  and  $C_2$  are constants of the material at  $T_g$ . For 1,2 polybutadiene these constants have been determined (Ferry, 1970) to be  $C_1 = 12.7$  and  $C_2 = 35.5$ .

14. The propagation of an longitudinal acoustic wave in a visco-elastic medium is usually determined by a linear combination of the compressional and shear moduli. It is convenient to define a complex longitudinal modulus

$$M^* = M' + iM'' = K^* + 4/3 G^* \quad (5)$$

whose real and imaginary parts are related to the experimental parameters by

$$M' = \rho v^2 \quad (6)$$

$$M'' = \frac{2\alpha\rho v^3}{\omega} \quad (7)$$

where  $v$  and  $\alpha$  are the measured sound speed and absorption coefficient, respectively. Typically, the real part of the modulus exhibits a limiting low frequency or static modulus  $M_0$ , and a limiting high frequency value  $M_\infty$ .

15. It is now possible to define a real reduced part of the total longitudinal modulus by the ratio

$$\frac{M' - M_0}{M_\infty - M_0} = m'(\omega\tau) \quad (8)$$

where  $M_\infty - M_0$  is the relaxational contribution to the total modulus and  $m'$  is a function of temperature only through the variable  $\omega\tau$  given by Eqs (3) and (4).

16. Similarly, a reduced imaginary part may be written

$$\frac{M''}{M_\infty - M_0} = m''(\omega\tau) \quad (9)$$

17. In what follows we will make use of the data reduction principle to obtain velocity and absorption data at frequencies that are inaccessible due to limitations in sample size and experimental apparatus.

#### EXPERIMENTAL RESULTS

18. Using the experimental apparatus shown in Fig. (1) the sound velocity and attenuation were measured at 5MHz. Figs. (3) and (4) show the measured attenuation coefficient and velocity as a function of temperature from  $-50^\circ\text{C}$  to  $100^\circ\text{C}$ .

19. The attenuation coefficient exhibits a bell shape typical of a relaxation process. As the temperature is changed, the attenuation

coefficient passes through a maximum. The magnitude and temperature of maximum attenuation depends on the frequency used. The lower frequencies have a correspondingly lower maximum value and the position of the absorption maximum is shifted towards lower temperatures.

20. Likewise, the velocity data show low and high frequency-independent limiting values typical of a relaxation process. In between these two limits the velocity depends on the product  $\omega\tau$  and hence is highly frequency and temperature dependent.

21. In the absence of other criteria the temperature dependence of  $V_\infty$  and  $V_0$  are usually obtained by extrapolations of the longitudinal moduli data. Fig. 5 shows the temperature dependence of the real part of the longitudinal modulus obtained from the data in Fig. 4, using  $M = \rho V^2$ . The temperature dependence of the density was estimated by

$$\rho = 1.13 / (1 + 0.0007 (T - 25)). \quad (10)$$

22. The temperature dependence of the low frequencies or static modulus  $M_0$  was obtained by extrapolating the high temperature data and is given by

$$M_0 = 2.52 - 0.0113T (^\circ\text{C}) \quad (11)$$

23. Experimental difficulties at low temperatures limit our ability to determine  $M_\infty$  accurately. The temperature dependence of  $M_0$ , however, was observed to agree with the value for natural rubber as determined by McKinney et al. (1960). It was therefore assumed that the fractional slopes  $(\frac{1}{M_\infty} \frac{\partial M_\infty}{\partial T})$ , of the two rubbers were equal. Hence we

$$\text{estimate} \quad M_\infty = 6.23 - 0.0213T (^\circ\text{C}) \quad (12)$$

which in Fig. (4) appears to be a reasonable fit to the low temperature data.

24. The attenuation versus temperature data may now be transformed to frequency data using Eqs. (3) (4) and (9). The result at  $24^\circ\text{C}$  is shown in Fig. (6) in terms of the loss per wavelength versus frequency. The data covers the frequency range of  $10^5$  to  $10^9$  Hz.

25. In addition to the attenuation data at 5 MHz, data were taken as a function of frequency from 300 kHz to 5 MHz. These results are shown in Fig. 7 where the data are given by the individual points and the solid curve is the WLF reduction of the 5 MHz data repeated from Fig. 6. The agreement between the two is excellent and thus verified the use of the WLF reduction technique.

26. Since the above data do not provide information, except by extrapolation, in the  $10^4$  to  $10^5$  Hz frequency region, data were taken at 300 kHz from  $25^\circ\text{C}$  to  $90^\circ\text{C}$ . These data were again transformed using the WLF equation and the results are shown in Fig. 8. The completed attenuation curve now covers the frequency range for  $10^4$  to  $10^9$  Hz.

27. A similar WLF transformation was performed on the velocity data and the results are shown in Fig. 9.

#### DISCUSSION AND CONCLUSIONS

28. The curves for the attenuation and velocity versus temperature, Figs. 3 and 4, and versus frequency, Figs. 8 and 9, show a behavior typical of that found in other rubbers. The attenuation exhibits a peak, which occurs approximately in the region of maximum rate of change of velocity. The curves are very broad, extending over four to five decades in frequency, or 120 degrees in temperature.

29. Figure 10 compares the bulk wave attenuation (db/cm) versus temperature at 5 MHz in 1,2 polybutadiene with that reported for natural (Heava), GR-S (butadiene-styrene co-polymer), and butyl rubbers. The loss in 1,2 polybutadiene is higher and broader than that for natural and GR-S, which are low loss rubbers; but lower than that for butyl, a high loss rubber. These curves would have relatively the same form at all frequencies, but as the frequency is decreased the curves decrease in amplitude and shift to lower temperatures. The attenuation per unit length of sample decreases very rapidly with decreasing frequency. For example from Fig. 8 the attenuation at 24°C and 20 kHz would be only 2.7 db per meter. The velocity-frequency curve for 1,2 polybutadiene indicates, that for frequencies below 1 MHz the velocity is normally 1400 meters/sec and independent of frequency.

30. The attenuation and velocity vs frequency curves, Figs. 8 and 9, indicate that the relaxation mechanisms responsible for loss and dispersion in 1,2 polybutadiene have relaxation times of the order  $10^{-7}$  seconds. The relaxation spectrum is too broad to be explained by a single relaxation time, and it is not clear whether a series of individual times or a continuous distribution of times are operative.

REFERENCES

1. Modern Synthetic Rubbers, H. Barron, D. Van Nostrand Co., Inc., N.Y., 2nd edit., p. 174 (1943).
2. Viscoelastic Properties of Polymers, J.D. Ferry, John Wiley & Sons, Inc., N.Y., 2nd edit., p. 316 (1970).
3. D.G. Ivey, B.A. Mrowca, and E. Guth, App. Phys. 20, 486 (1949).
4. W.M. Madigosky, and T.A. Litovitz, J. Chem. Phys. 34, 489 (1961).
5. J.E. McKinney, H.V. Belcher, and R.S. Marvin, Trans. Soc. Rheol., 4, 347 (1960).
6. A.W. Nolle, and J.F. Mifsud, J. Appl. Phys. 24, 5 (1953).
7. M.L. Williams, R.F. Landel, and J.D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).
8. Witte, Mrowca, and Guth, J. Appl. Phys. 20, 48 (1949).

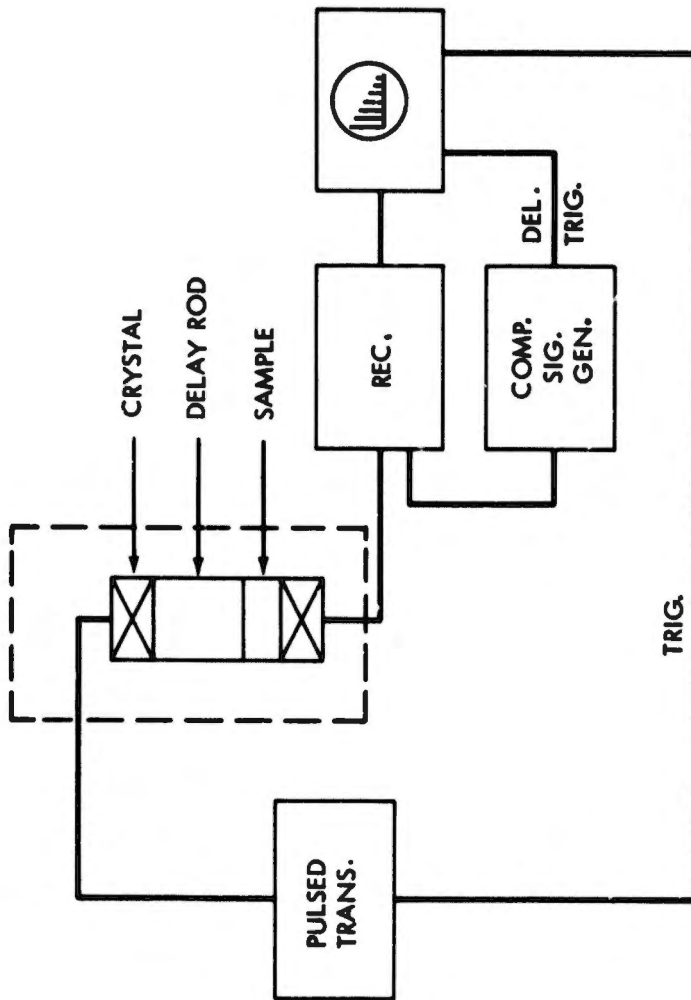


FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING BULK WAVE PROPAGATION CONSTANTS AT 5 MHz.

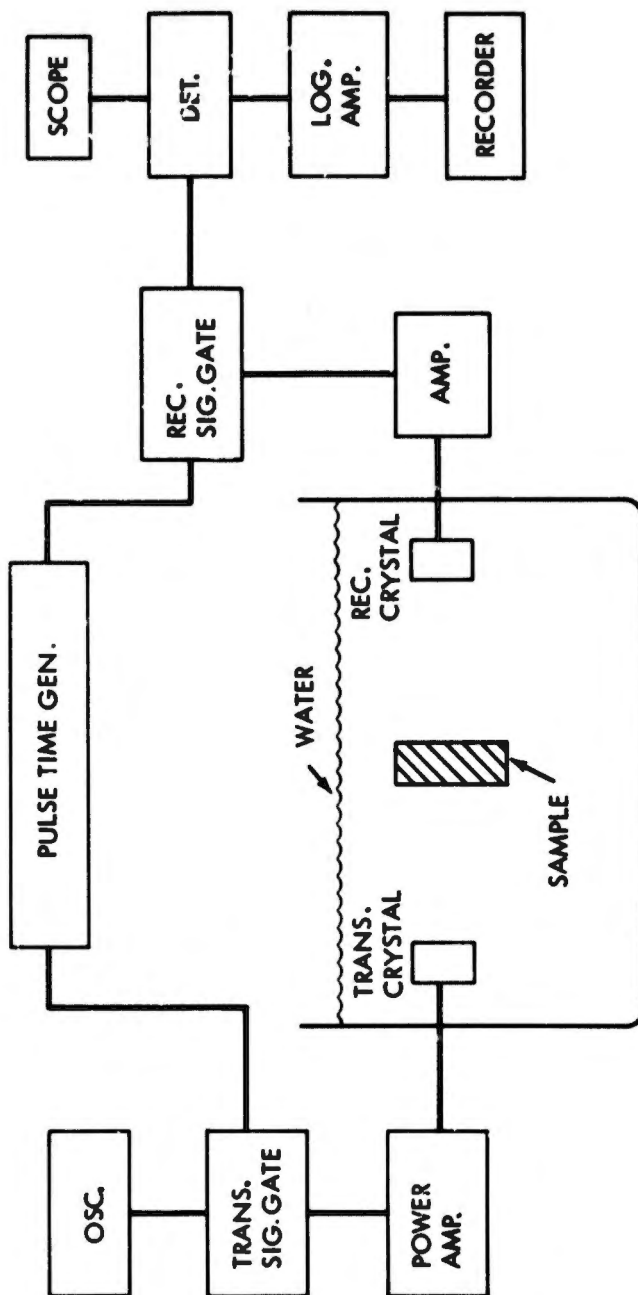


FIG. 2 SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING BULK WAVE PROPAGATION CONSTANTS FROM 300 TO 3000 kHz.

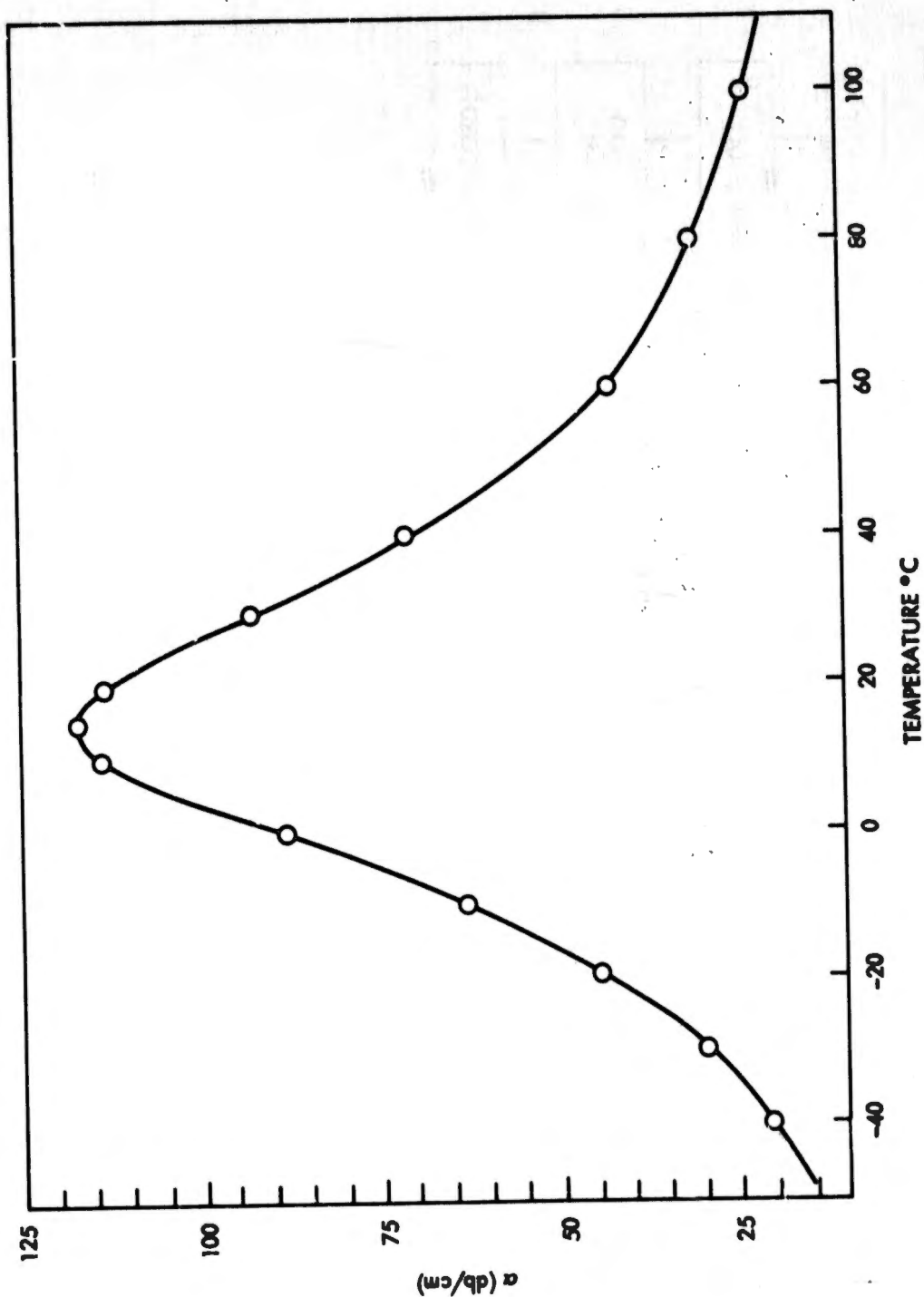


FIG. 3 ATTENUATION IN db PER cm VS TEMPERATURE OF 1, 2 POLYBUTADIENE AT 5 MHz.

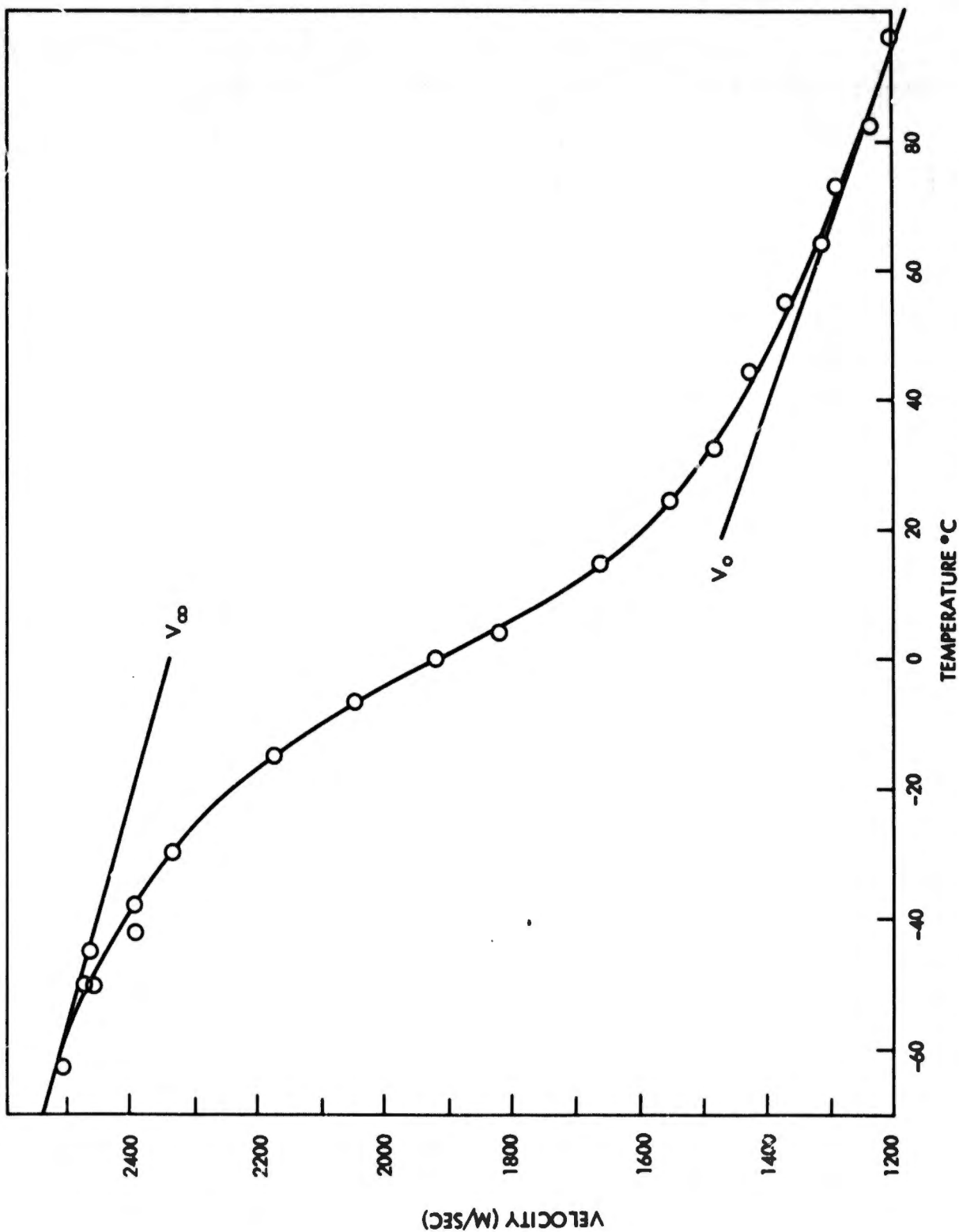


FIG. 4 VELOCITY VS TEMPERATURE OF 1, 2 POLYBUTADIENE AT 5 MHz.  $V_{\infty}$  AND  $V_0$  ARE THE HIGH AND LOW FREQUENCY VALUES OF THE VELOCITY, RESPECTIVELY.

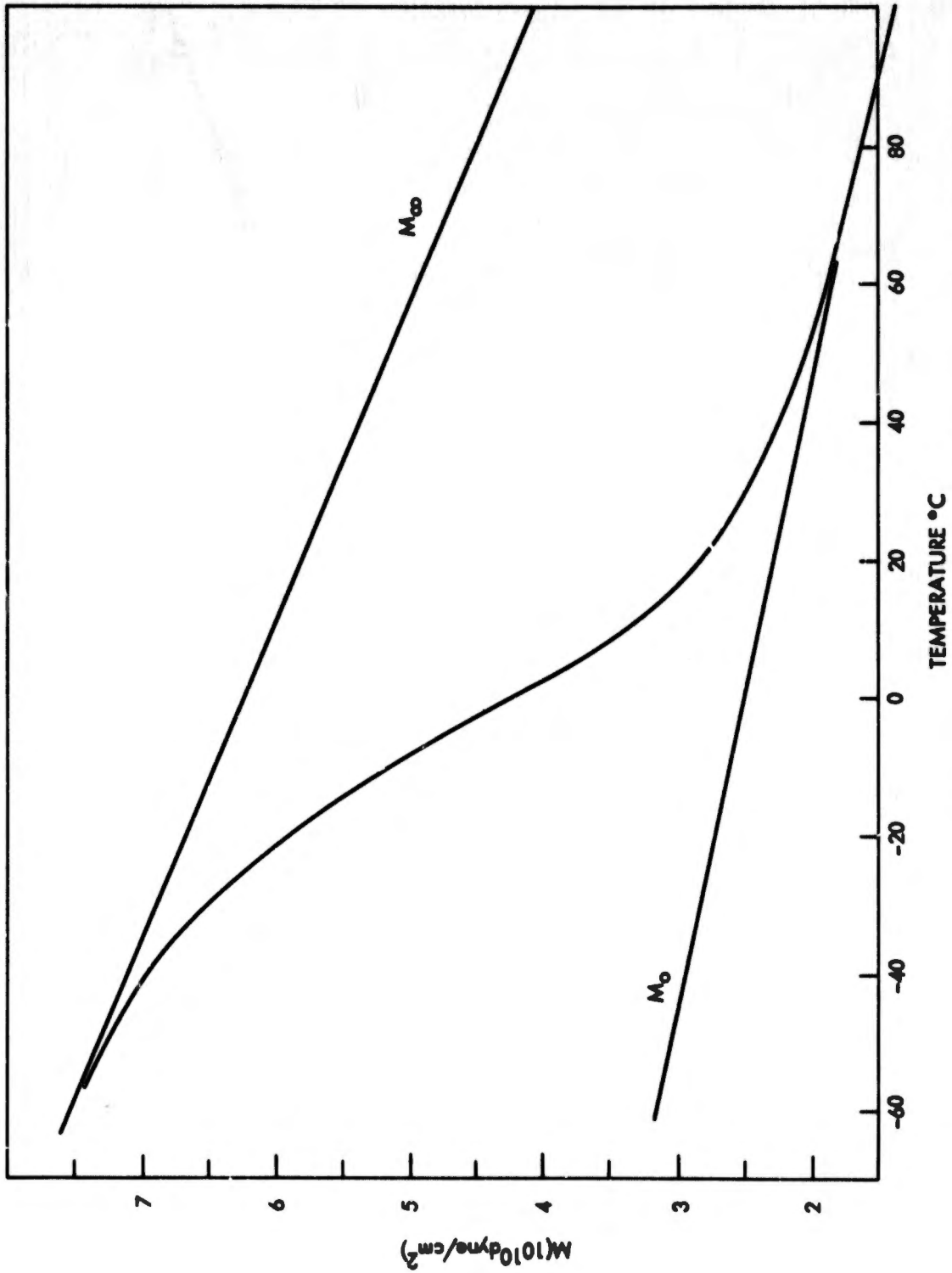


FIG. 5 LONGITUDINAL MODULUS VS TEMPERATURE AT 5 MHz CALCULATED FROM THE DATA IN FIG. 4.  $M_0$  AND  $M_\infty$  ARE THE LOW AND HIGH FREQUENCY VALUES OF THE MODULUS, RESPECTIVELY.

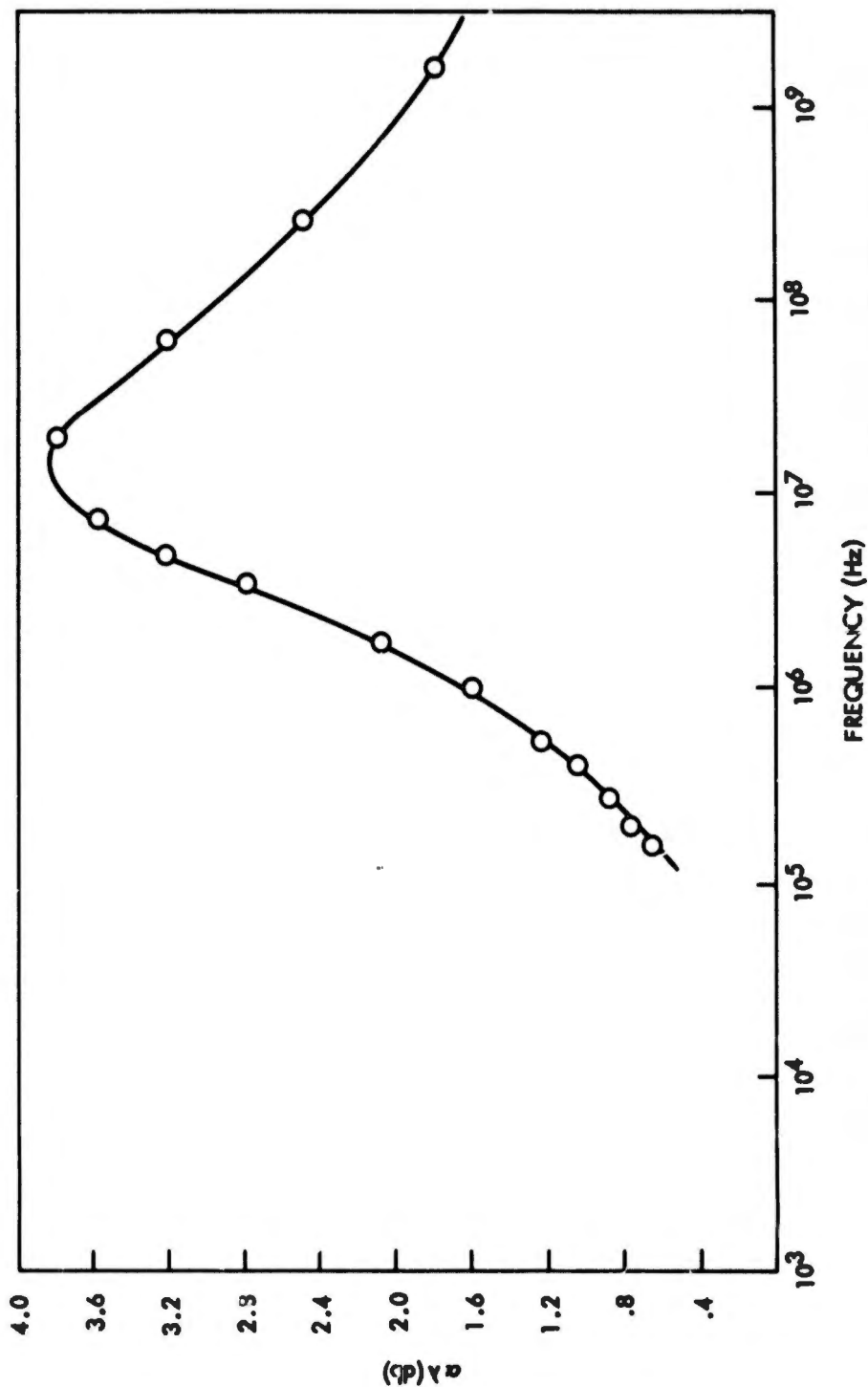


FIG. 6 ATTENUATION PER WAVELENGTH VS FREQUENCY OF 1,2 POLYBUTADIENE AT 24°C. THE RESULT WAS OBTAINED BY A WLF CONVERSION OF THE TEMPERATURE DATA SHOWN IN FIG. 3.

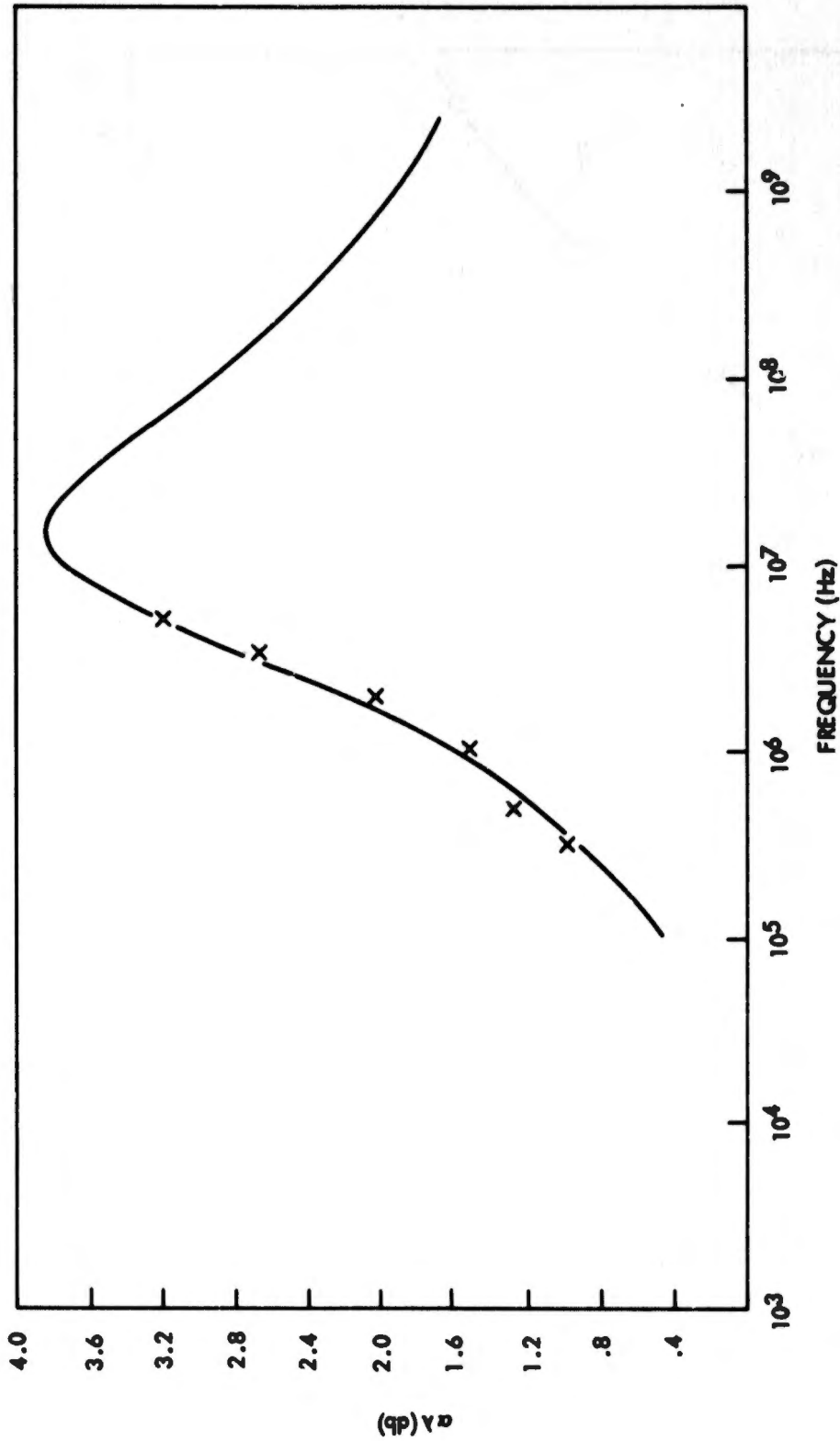


FIG. 7 TEST OF THE WLF REDUCTION FORMULA. THE CURVE IS THE WLF REDUCTION OF THE 5 MHz TEMPERATURE DATA TO 24°C. THE CROSSES ARE DATA TAKEN AS A FUNCTION OF FREQUENCY FROM 300 kHz TO 5 MHz AT 24°C.

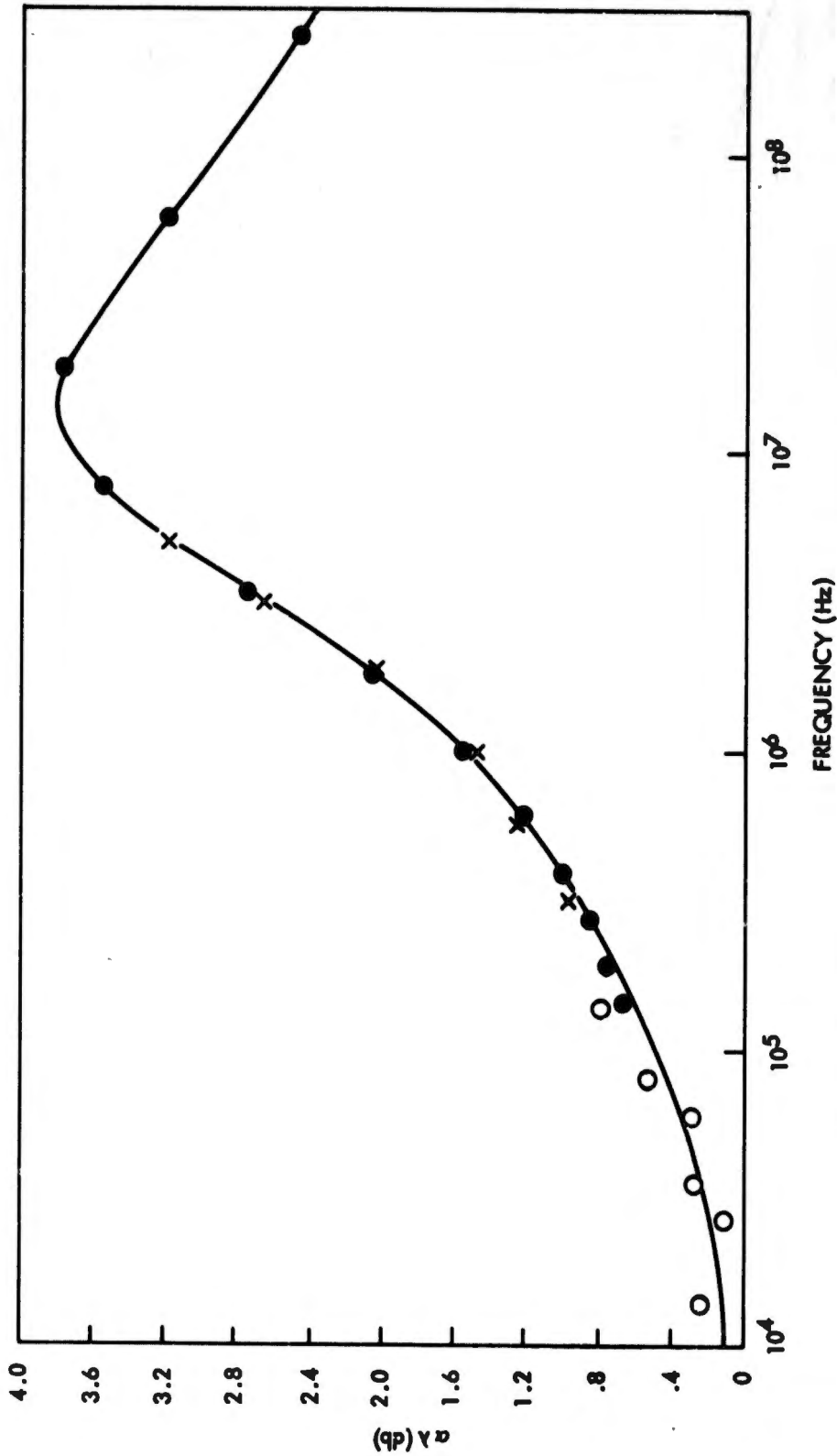


FIG. 8 ATTENUATION PER WAVELENGTH VS FREQUENCY OF 1.2 POLYBUTADIENE AT 24°C. (●) WLF REDUCTION OF 5 MHz TEMPERATURE DATA. (X) FREQUENCY DATA AT 24°C. (O) WLF REDUCTION OF 300 kHz TEMPERATURE DATA.

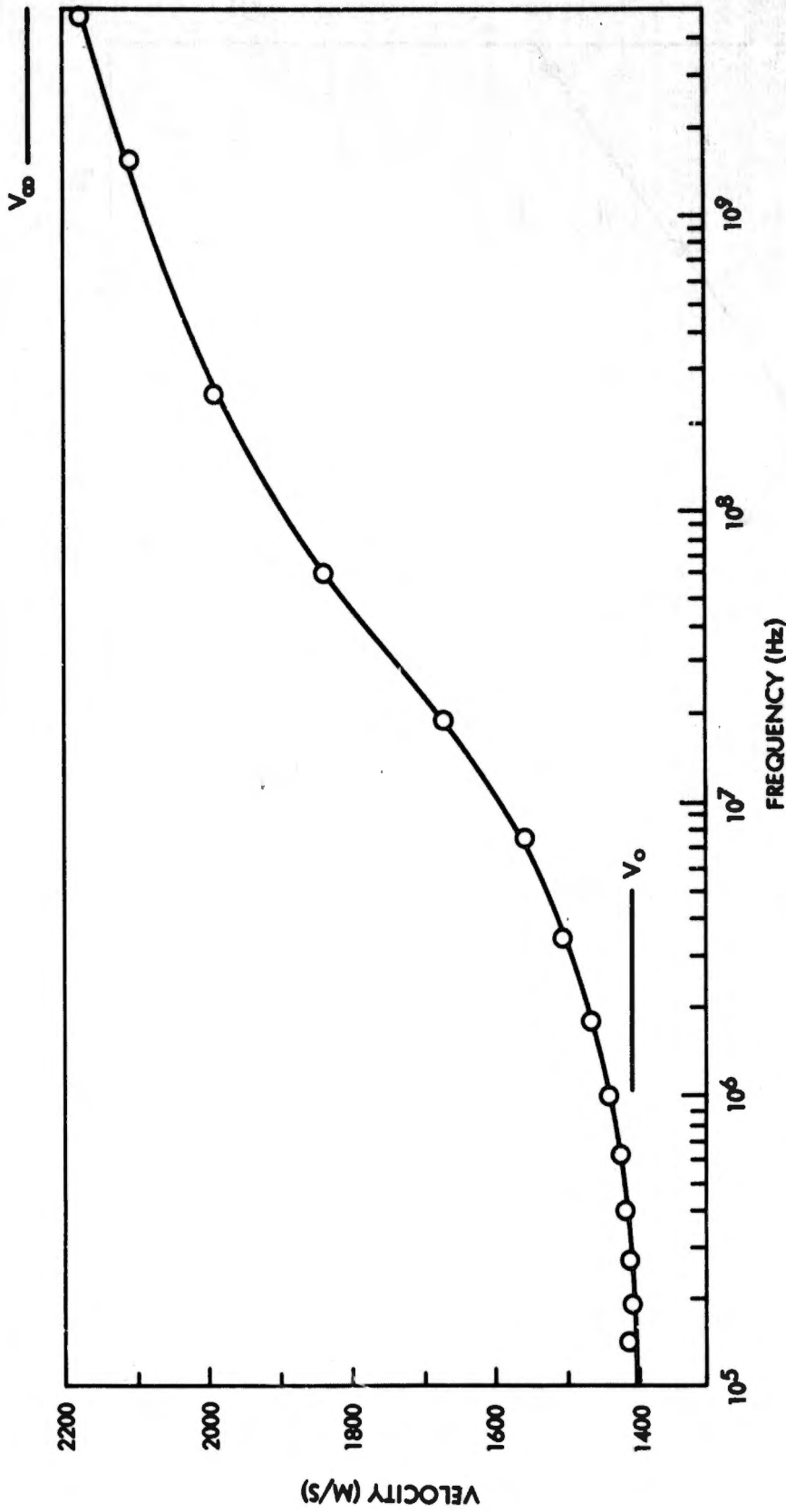


FIG. 9 VELOCITY VS FREQUENCY OF 1, 2 POLYBUTADIENE AT 24°C  
THE DATA WAS OBTAINED BY MEANS OF THE WLF REDUCTION FORMULA.

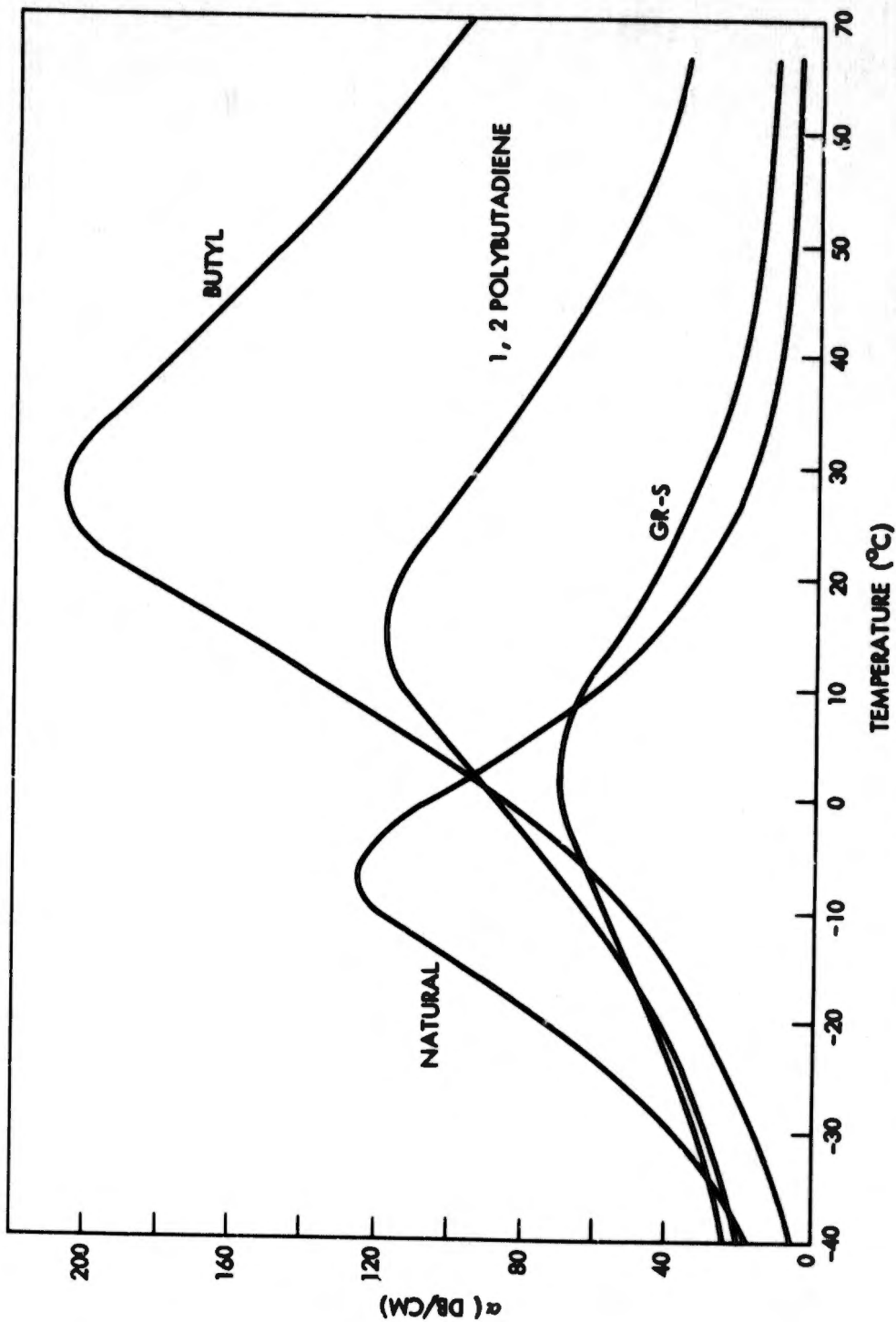


FIG. 10 COMPARISON OF BULK WAVE ATTENUATION VS TEMPERATURE AT 5 MHz FOR 1, 2 POLYBUTADIENE WITH THAT OF BUTYL, GR-S AND NATURAL RUBBERS.