

# Acoustic Properties of Transparent Polysiloxanes

D. BOSC and P. MAUGUEN, *Centre National d'Etudes des Télécommunications à Lannion B, Division OCM, Département FCO, Route de Trégastel, 22301 Lannion, France*

## Synopsis

It is well known that the glass transition temperature of polydimethylsiloxane elastomers lies close to  $-120^{\circ}\text{C}$ . According to the time temperature superposition principle, we may state that these materials keep their caoutchoutic state when they are excited by a 10 MHz mechanical wave. This is an important point particularly for acoustooptic applications. Thus, in the range of 1–10 MHz, materials with good efficiency are missed; low acoustic wave velocity is needed to give the best conditions, which means to be in a caoutchoutic state for polymeric materials. With this work, we show that three polysiloxanes, polymerized under different conditions, do not fulfill this condition. Thus the shift of  $T_g$  with frequency is very large and these polymers reach their glassy state at relatively low frequency. The acoustic wave velocity is in good agreement with mechanical predictions provided by master curves of the Young modulus.

## INTRODUCTION

The acoustic properties of polymers are usually studied as a means to follow the relaxation of macromolecular chains. In this case acoustic wave velocity and attenuation in polymers are measured at some given frequencies from a few megahertz to 1 GHz.<sup>1</sup>

These data yield the elastic characteristics and short time relaxations. Thermoplastics and most elastomers are in a glassy state at these frequencies, and the acoustic wave velocity in these materials reaches usually  $2000\text{ m s}^{-1}$ ,<sup>2,3</sup> the sample has to be heated above the glass transition temperature. In order to do that and because of the high level of acoustic attenuation at high frequency, polymers are never used in acoustic device as deflectors or modulators; their figures of merit are much lower than crystals such as  $\text{PbMoO}_4$ ,  $\text{TeO}_2$ , or  $\text{HgS}$ . These materials take advantage of a high refractive index but their use is limited to frequencies up to 1 MHz, because the critical width ( $W$ ) for acoustooptic effect is too large. In fact, we know it is given by

$$W = 2N_0V_s^2/l/f^2$$

Thus  $W$  of the useful acoustooptic materials as  $\text{TeO}_2$  and  $\text{PbMoO}_4$  for 10 MHz will reach 30 and 1030 mm, respectively.

For acoustooptic modulation, where  $V_s$  is the acoustic wave velocity,  $l$  the wavelength of the optical beam,  $f$  the acoustooptic frequency, and  $N_0$  the refractive index. Below  $W$  the acoustooptic yield decrease quickly (Raman-Nath

case). On the other hand, the figure of merit  $M_2$  for an acoustooptic material in relation with the diffraction efficiency is defined by

$$M_2 = N_0^6 P^2 / P_0 / V^3$$

with  $P$  the photoelastic coefficient and  $P_0$  the density.<sup>4</sup> Therefore, materials with very low velocity at frequency above 1 MHz acquire great importance. Such performances are usually found in a single crystal of  $\text{TeO}_2$ , or in some liquids such as fluoroalcanes,<sup>5</sup> the velocity of which at 2 MHz can be as low as 500 m s<sup>-1</sup>.

Yet, around 10 MHz, experimental values of 200–1000 m s<sup>-1</sup> have been obtained in solid amorphous materials such as transparent silicones elastomers.<sup>6</sup> These results have stimulated further studies on acoustic properties. These were investigated in the light of mechanical properties.

### GOAL OF THIS STUDY

It is well known, in polymers, according to the time–temperature superposition principle, that the  $T_g$  increases with the deformation rate. This shift depends on the polymer but it is often of ten degrees by decade of frequency.

We assume that polymers with a low Young modulus and very low  $T_g$  retain their elastic properties under these conditions. Transparents elastomers were chosen because their  $T_g$  is located below  $-100^\circ\text{C}$ .

The longitudinal  $V_l$  and transversal  $V_t$  ultrasonic wave velocities are related to the elastic modulus by the following expressions:

$$V_l = [(K + 4G/3)/P_0]^{1/2} \text{ and } V_t = (G/P_0)^{1/2}$$

where  $K$  and  $G$  are respectively the bulk and shear modulus and  $P_0$  the volumic mass. Therefore, the velocity vs. Young modulus  $E$  and the Poisson coefficient may be expressed by

$$V_l = (E/P_0)^{1/2} \{ (1 - m) / [(1 - 2m)(1 + m)] \}^{1/2}$$

If  $m$  is high (0.45 for example) and the volumic mass close to 1 g cm<sup>-3</sup>, simplifications lead to

$$V_l = 19.7(10^{-3})E^{1/2}$$

with MKSA units for  $E$  and  $V_l$ .

According to the time–temperature superposition principle, we can estimate where glass transition is located at 10 MHz. The classical WLF's rule give the shift of the glass temperature induced by the frequency; for example, this shift can be expressed by

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$

were  $\log a_T \approx \log(\nu_{T_g}/\nu_T)$ .

For 1 decade of frequency,  $\log a_T = -1$  and  $T - T_g \approx 3$  K, that is to say, 3 K/decade; this means the  $T_g$  (measured at very low frequency) is shifted by 21 K above when frequency becomes 10 MHz. Polydimethylsiloxane elastomers have  $T_g$ 's close to  $-120^\circ\text{C}$  (measurement by DSC method). As the  $T_g$  is shifted by a few decades, therefore, we state that these materials are in their caoutchoutic state. Thus a low acoustic wave velocity at this frequency may be expected.

To reach the acoustic wave velocity in transparent polysiloxanes, we measured the Young's modulus at a few low frequencies for different temperatures, and built the master curves giving the evolution of modulus or acoustic wave velocity vs. frequency at  $20^\circ\text{C}$ . These would provide the particular frequency where  $T_g$  is close to ambient temperature. These data will be supported by direct measurement of ultrasonic (10 MHz) and sonic (4 KHz) wave velocity. This work enables to know whether these polymers keep or not their caoutchoutic state (i.e., low modulus) and low acoustic wave velocity at the useful frequencies ( $\sim 1$  MHz) for acoustooptic modulation<sup>6</sup> (Fig. 1). The goal of this work is the localization of  $\nu_g^{20^\circ\text{C}}$ , with regard to the glassy or the caoutchoutic states.

### EXPERIMENTAL

#### Samples

One or two parts room temperature or UV cured silicone elastomers: RTV 141 from Rhone Poulenc, Sylgard 182 and 184, and Optigard X3-6662 from Dow Corning were chosen. Their glass transition temperature lies in low fre-

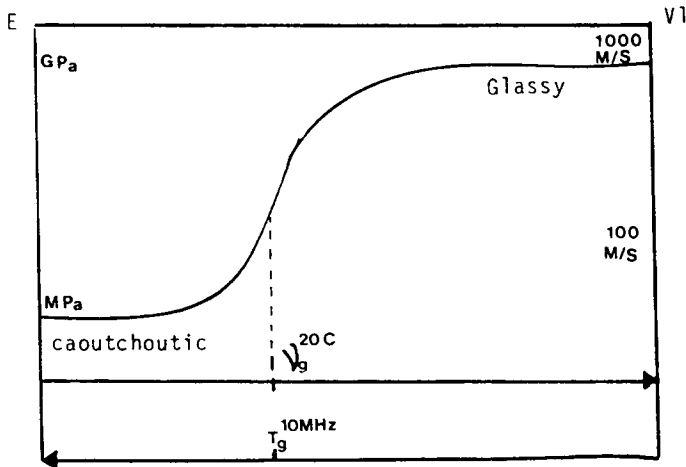


Fig. 1. Schematic glass transition for elastic modulus or acoustic wave velocity vs. frequency at  $20^\circ\text{C}$  or temperature at 10 MHz.

quency conditions at  $-120^{\circ}\text{C}$ , and their Young modulus is a few megapascal under the same conditions at room temperature.<sup>7,8</sup>

### Method

The viscoelastic properties were determined by using a viscoelasticimeter Metravib with excitation frequencies: 7.80–15.6–31.2–62.5–125 Hz in the temperature range from  $-100$  to  $20^{\circ}\text{C}$ .

The acoustic wave velocity is calculated from the diffraction of a laser beam (HeNe at  $6328 \text{ \AA}$ ) by the acoustic grating generated by a HF probe (10 MHz) (Fig. 2) or by the delay time between two diffracted beams, when the acoustic wave is modulated around 10 MHz, and crossing the sample at different distances from the electrode.

At low frequencies we use an acoustic wave generator working between 1 and 4 kHz. The measurement of the diffracted optical signal depletion when the laser beam is being removed from the acoustic source provides the acoustic wave attenuation; it will be given in decibel per centimeter (dB/cm).

## RESULTS

### $T_g$ Change with Frequency

The Complex Young modulus was measured at low frequencies, below room temperature, for RTV 141 (with 20% catalyst concentration by weight) and for SYLGARD 182 (with 10% catalyst concentration). From these data the master curves (Fig. 3) were built, they show that the transition frequencies are very low (10 and 50 KHz) comparatively to what would be expected. The behavior of these materials is like that of polybutadiene though it has a  $T_g$  close to  $-5^{\circ}\text{C}$ .<sup>9</sup> Additional thermal analysis was performed on several samples; some of them exhibited an additional DSC peak at  $-45^{\circ}\text{C}$  according to other observations.<sup>7</sup> However, all of the samples had a  $T_g$  peak close to  $-120^{\circ}\text{C}$ . The mechanical analysis was only performed on two samples because different con-

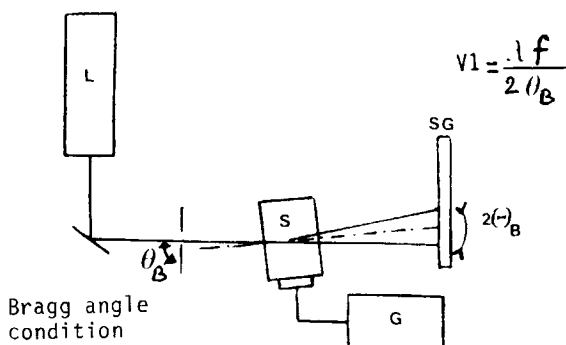


Fig. 2. Angle diffraction measurement between order 0 and 1 to reach acoustic velocity  $V_l$  of a sample  $S$  (under Bragg conditions) in an acoustooptic cell actuated by a function generator;  $L$  is a HeNe laser and  $SG$  a screen position gauge.

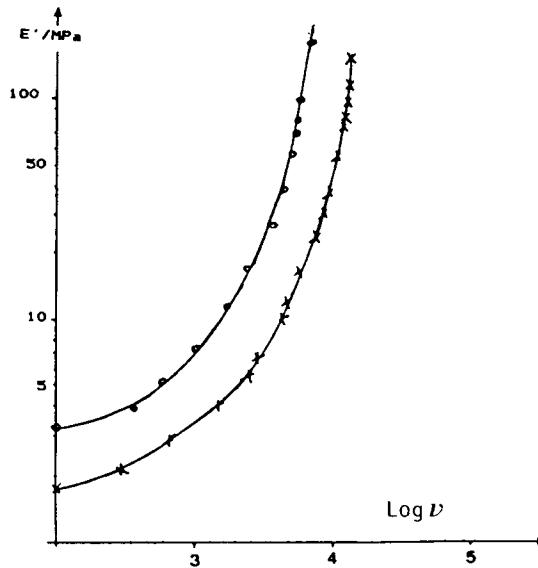


Fig. 3. Master curves for RTV 141 (x) and Sylgard 182 (o).

centrations of catalyst part in all samples did yield an unvarying acoustic wave velocity ( $1000 \text{ m s}^{-1}$ ).

From these data, the shift WLF law coefficient was calculated:

$$\log a_T = \frac{C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}} \text{ with } T_{\text{ref}} = 293 \text{ K}$$

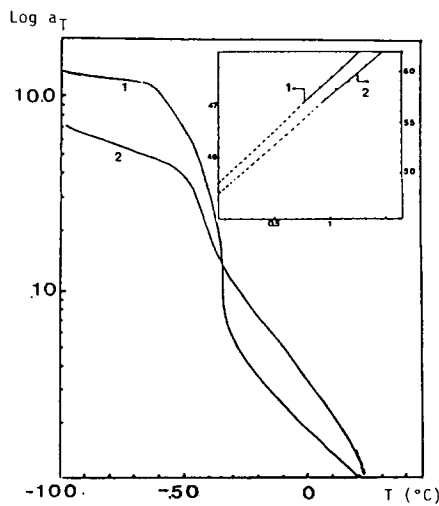


Fig. 4.  $\log a_T$  vs. temperature and  $100/\log a_T$  vs.  $100/(T - T_{\text{ref}})$  (inset) for the determination of  $C_1$  and  $C_2$  for RTV 141 (1) and Sylgard 182 (2).

TABLE I  
Shift Coefficients  $S_1$  and  $S_2$  (for RTV 141 and Sylgard 182, Respectively)  
over a Large Range of Frequency and  $T_g$  Valuation at 10 MHz

| $\nu$ | 100 | 700 | 4000 | 7000 | 10,000 | 15,000 | 10 MHz      |
|-------|-----|-----|------|------|--------|--------|-------------|
| $S_1$ | 50  |     | 20   |      | 20     | 1000   | $T_g$ 170°C |
| $S_2$ |     | 50  |      |      | 200    |        | $T_g$ 80°C  |

In Figure 4, is represented,  $\log a_T$  vs. temperature; it shows the important shift of temperature (inset) with frequency above  $-100^\circ\text{C}$  until  $-50^\circ\text{C}$  ( $C_1 = -2.2$ ,  $C_2 = -4.58$  K for RTV 141 and  $C_1 = -2.09$  and  $C_2 = -20.35$  K for Sylgard 182 between  $-100$  and  $-60^\circ\text{C}$ ).

To have an idea of the shift of  $T_g$  with frequency, we introduce the shift coefficient  $S$ , which is the slip of the  $T_g$  produced by the frequency change. These data can be easily yielded by the curves  $\log a_T$  vs. temperature;  $S$  given in degree by decade is listed in Table I. For every sample,  $T_g$  is clearly rejected above room temperature when frequency of the acoustic wave is around 1 MHz. Then these samples are in a glassy state at 1 MHz and the acoustic wave velocity would be high ( $\sim 1000$  m s $^{-1}$ ).

### Acoustic Measurement

To know whether mechanical measurement approximately enables us to predict the acoustic wave velocity, we directly measured it in the range provided by the available devices (a few kHz and a few MHz) (Fig. 5). Figure 6 shows the good agreement between mechanical and acoustic properties; the samples are in a caoutchoutic state at low frequency and in a glassy state, at high frequency. The acoustic wave attenuation measured at 7.5–8.5–10 and 12 MHz is not excessive as Table II shows. This is an indication to locate the  $T_g$  for these frequencies at a temperature much higher than room temperature. Also

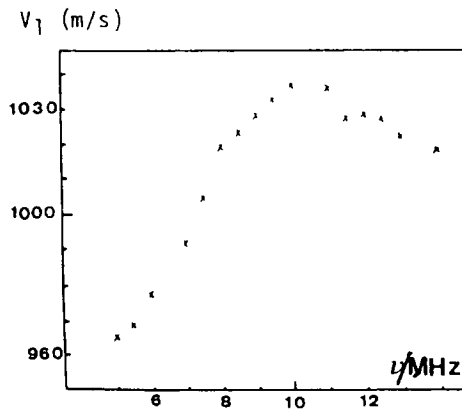


Fig. 5. Acoustic wave velocity close to 10 MHz for RTV 141 with 20% by weight of catalyst part.

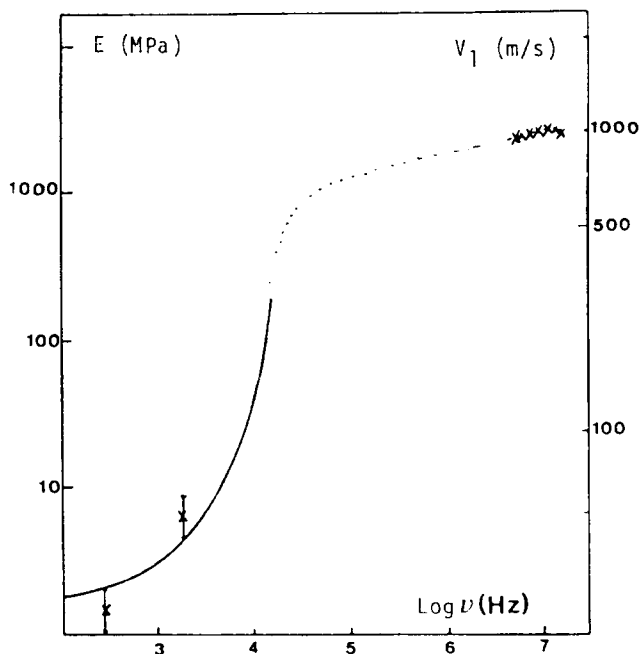


Fig. 6. Mechanical (—) and acoustic measurement (×) vs. frequency for RTV 141.

we can observe that frequency dependence of the acoustic wave attenuation do not follow a quadratic law in this frequency range.

### CONCLUSION

This work has shown that the  $T_g$  of polydimethylsiloxane elastomers is located above room temperature when they are excited by a 10 MHz acoustic wave, or, according to the time-temperature superposition principle, the glass transition frequency at 20°C is below 1 MHz (10 kHz at 50 kHz). We have verified that  $T_g$  at low frequencies is located at  $-120^\circ\text{C}$ , but a very large shift coefficient leads to a higher  $T_g$  than that would be expected comparatively with other elastomers. Acoustic velocity measurements were in good agreement with mechanical measurements. The level of the acoustic velocity and the weak acoustic attenuation at 10 MHz would indicate that the transition is rejected at very high temperature.

These results show that these materials under a 10 MHz acoustic excitation are clearly in a glassy state; this explains the relatively high acoustic wave velocity ( $\sim 1000 \text{ m s}^{-1}$ ). However, as different as the two part ratio of room

TABLE II  
Acoustic Wave Attenuation  $\alpha$  with Frequency Close to 10 MHz for RTV 141

| $\nu$ (MHz)      | 7.5 | 8.5  | 10  | 12  |
|------------------|-----|------|-----|-----|
| $\alpha$ (dB/cm) | 7.4 | 10.3 | 5.8 | 9.4 |

temperature elastomers may be, their behavior is the same.<sup>10</sup> Yet these transparent polymers yield an acoustic velocity lower than transparent thermoplastic materials, which provides a good efficiency close to 1 MHz for acoustooptic applications.

The authors are indebted to G. Froyer for helpful discussions to P. Grosso for acoustooptic experimental assistance and F. Perrin for some sample preparations.

### References

1. K. Adachi et al., *Polymer*, **22**, 1032 (1981).
2. R. S. Witte and B. A. Mrowca, *J. Appl. Phys.*, **20**(6), 481 (1949).
3. J. Arman, *Acustica*, **43**, 212 (1979).
4. I. C. Chang, *Opt. Eng.*, **24**(1), 132 (1985).
5. F. H. M. Jongsma, *Ultrasonic*, **9**, 233 (1979).
6. D. Bosc and Ph. Grosso, *2nd Int. Conf. Pass. Compon.*, Paris, Nov. 1987.
7. G. W. Fugate and J. A. Wilson, *18th Int. SAMPE Tech. Conf.*, Seattle, WA, Oct. 1986.
8. Ph. M. James, E. M. Barral, et al., in *Polymer Character, by Thermal Methods Analysis*, Dekker, New York, 1974, p. 135.
9. G. Lechermeier, thesis, Lyon Univ., France, April 1976.
10. F. Perrin, P. Grosso, and D. Bosc, unpublished.

Received April 13, 1989

Accepted July 18, 1989