

## Dynamic Mechanical Properties of Polymers

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### Synopsis

A technique, employing samples in the form of tuning forks, to measure the mechanical properties of polymers is presented. Results for low density polyethylene, polypropylene, and polycarbonates are shown. A large transition is observed for polypropylene at approximately  $+10^{\circ}\text{C}$  and a small transition at  $-100^{\circ}\text{C}$  for the polycarbonates. Polycarbonate data has also been obtained from 20 to  $150^{\circ}\text{C}$ , at approximately 70 cps. Effects of time, temperature, and history are presented.

### INTRODUCTION

The dynamic mechanical properties of polymers are of interest both from a technological and scientific point of view as illustrated by the voluminous amount of data to be found in the literature. In these investigations, relaxation processes occurring at both low and elevated temperature have been observed. The purpose of this paper is to present a new technique, employing samples in the form of tuning forks as well as the results of our investigation of both the low and high temperature relaxation behavior of bisphenol-A polycarbonate.

### Experimental Method

Polymer samples were prepared in the form of simple tuning forks by compression molding. The forks measured  $6\frac{1}{4}$  in. from base to tip, with 1 in. between the inner edges of the prongs which were 5 in. long. The cross section of the fork prong was  $\frac{1}{4}$  in. square. Thin strips of magnetic metals were attached (about 3 in. apart) to one arm of the fork to act as pickups for the audio signals.

The apparatus is shown in Figure 1. A block diagram (Fig. 2) shows the arrangement of electronic components used in conjunction with the transducer. In operation, the oscillator frequency was tuned to the natural resonant frequency,  $\nu_0$  of the tuning fork. The response of the fork was displayed as a maximum in the amplitude of the trace on the oscilloscope. Then the oscillator was detuned until the amplitude of response reached the rms value (0.707 of the maximum amplitude). The frequency at this point was noted as  $\nu_1$ . Similarly another frequency,  $\nu_2$ , was found corresponding to the rms value on the other side of the resonant frequency peak.

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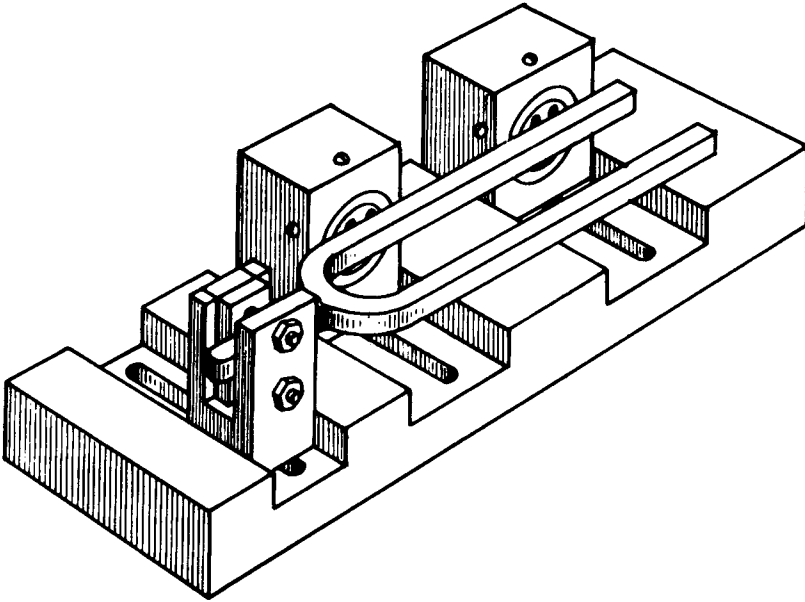


Fig. 1. Tuning for vibration apparatus.

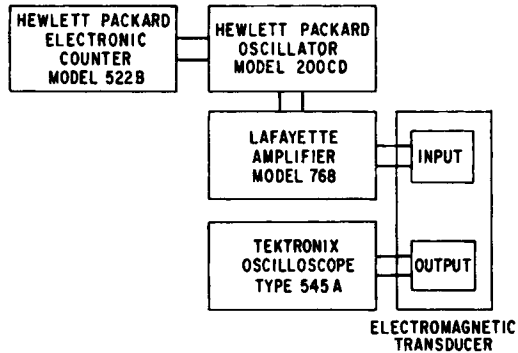


Fig. 2. Block diagram of electronic components.

From these three frequency measurements, the mechanical damping,  $\tan \delta$ , was calculated from:

$$\tan \delta = \frac{\nu_2 - \nu_1}{\nu_0} \quad (1)$$

The resonance frequency expressed as angular frequency,  $\omega_0$ , is related to the dynamic modulus,  $E(\omega)$ , by:

$$E(\omega) = K\omega_0^2 \quad (2)$$

where  $K$  is a constant of proportionality involving the sample shape and dimensions.

### Low Temperature Studies

For low temperature measurements the entire apparatus was placed into a cylindrical glass cell and capped with a piece of Styrofoam to form a covering  $3\frac{1}{2}$  in. thick. This cell was purged with cold, dry  $N_2$  to minimize the effects of moisture condensation. Next the cell was lowered into the cooling liquid, contained in a dewar flask, until the level of the cooling liquid was above the air space in the cell. Coolants used were liquid  $N_2$ , a slush mixture of alcohol and liquid  $N_2$ , and a dry ice-alcohol mixture, depending upon the temperature range of interest. A piece of Styrofoam was used to insulate the top of the cooling bath.

Frequency measurements were made as the system was allowed to warm up. With the alcohol baths the rate of warm-up was about  $2-3^\circ C$  per 15 min interval, and a somewhat slower rate than this was observed for liquid  $N_2$  alone (at least at lower temperatures). Frequency measurements were read from the oscillator dial. The temperature was measured by means of a thermocouple suspended in the cell at a point approximately 1 cm from the fork arm.

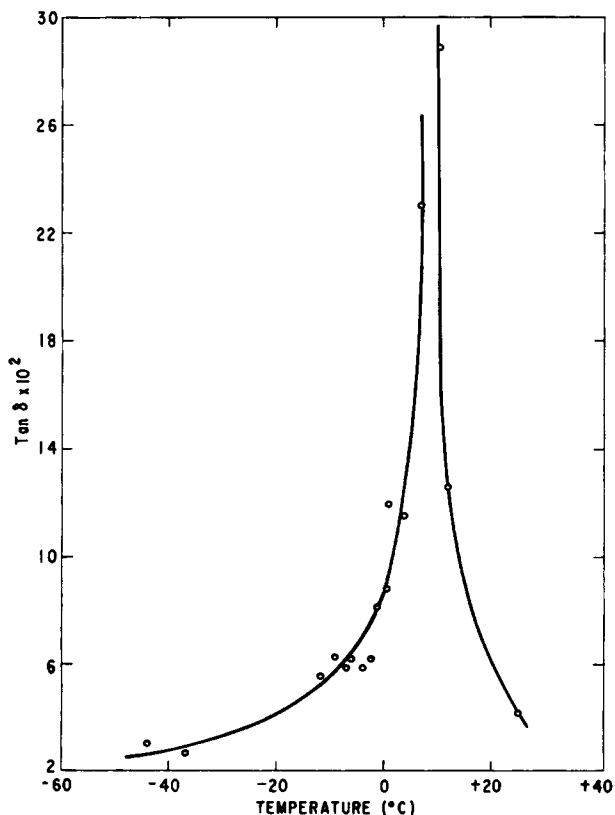


Fig. 3. Tan  $\delta$  as a function of temperature for polypropylene.

Preliminary runs were made using polypropylene and low density polyethylene. Figure 3 shows  $\tan \delta$  as a function of temperature for polypropylene. Figure 4 shows  $\tan \delta$  as a function of temperature for polyethylene together with a curve from the literature<sup>1</sup> for comparison.

In subsequent studies a Hewlett-Packard model 522B pulse counter was used to measure the frequencies. For those frequencies below 100 cps, the time constant,  $\tau$ , the reciprocal of the frequency, was measured. In terms of  $\tau$ ,  $\tan \delta$  is given by:

$$\tan \delta = \frac{\tau_0 (\tau_1 - \tau_2)}{\tau_1 \tau_2} \quad (3)$$

The precision of  $\delta$  is limited by the difference  $\tau_1 - \tau_2$ , or essentially the half-width of the resonance peak, the latter being found to be slightly nonsymmetrical.

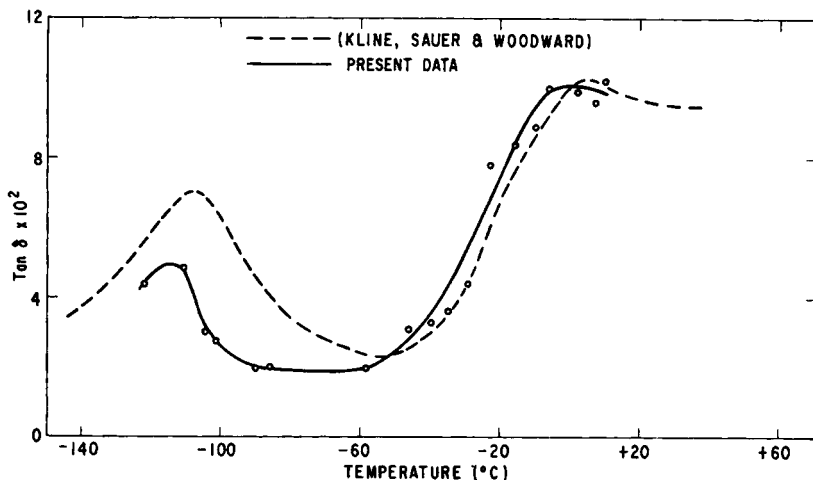


Fig. 4.  $\tan \delta$  as function of temperature for low density polyethylene.

For temperature measurements a second tuning fork was clamped into position just above the fork to be tested. This second fork, which remained static during the test, was imbedded with three thermocouples positioned at the tip of the prong, the center of the opposite prong, and the base of the fork. In general, 2 to 3 hr were required for the temperature of the static fork to attain a minimum value at the start of each run. A  $10^\circ\text{C}$  thermal gradient was found to exist between the ends of the fork.

Four Lexan<sup>®</sup> polycarbonate tuning forks from the same batch were obtained. Their resonant frequencies at room temperature were found to agree within 0.1 cps. The forms of  $E(\omega)$  and  $\tan \delta$  as a function of temperature for one of these forks (I), are shown in Figure 5, where a very broad  $\tan \delta$  peak is observed.

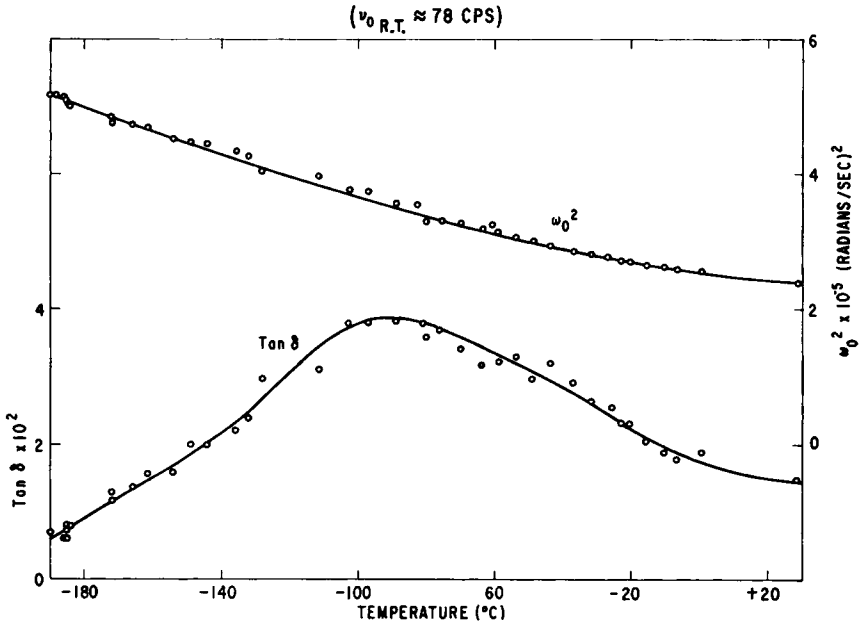


Fig. 5. Modulus and damping of Lexan polycarbonate as a function of temperature.

It can be shown that the change in  $E(\omega)$  cannot be accounted for on the basis of thermal expansion effects. If one considers eq. (2) in more detail, the effect of thermal expansion can be calculated:

$$E(\omega) = K\omega_0^2 = \frac{(\mu L^4)}{(I)} \omega_0^2 \tag{4}$$

where

- $\mu$  = mass per unit length
- $L$  = length of the specimen, exclusive of the base
- $I$  = moment of inertia =  $t^4/12$ , where  $t$  is the thickness of the test specimen.

Both  $L$  and  $t$  are functions of temperature through the thermal expansion effect. Each can be given by an equation of the form:

$$L = L_0 + \alpha_T T L_0 \tag{5}$$

where

- $L_0$  = length at a reference temperature
- $\alpha_T$  = linear coefficient of expansion ( $7 \times 10^{-5}/^\circ\text{C}$ ) for Lexan polycarbonate
- $T$  = the difference between the running temperature and the reference temperature (here chosen as room temperature).

Upon combining and simplifying, the  $K$  of eq. (2) can be expressed as:

$$K = \frac{12L_0^4\mu}{t_0^4(1 + \alpha_T T)} = K' \left( \frac{1}{1 + \alpha_T T} \right) \quad (6)$$

where  $K = K'$  at the reference temperature since  $T$  goes to zero.

Hence the dependence of  $E(\omega)$  on thermal expansion can be determined from the function  $(1/1 + \alpha_T T)$  which varies by about 1% from  $-190$  to  $+20^\circ\text{C}$ .

By determining the effect of changing the frequency, it is possible to calculate the activation energy giving rise to this peak. Attempts to measure higher frequency modes of the same fork were unsuccessful because the resonance curves became highly unsymmetrical as a result of coupling between the earphones.

To obtain lower frequencies one of the forks was shaved to a thickness of  $1/16$  in. The mechanical loss peak is shown in Figure 6, together with the loss peak from one of the  $1/4$  in. forks (II). For these last measurements the rate of warm-up of the bath was slowed down considerably.

From the temperature dependence of the frequency shift for Lexan polycarbonate (Fig. 6), the energy of activation,  $E_a$ , for the process can be calculated from

$$E_a = \frac{-R[\ln \omega_1 - \ln \omega_2]}{[(1/T_1) - (1/T_2)]} \quad (7)$$

$R$  = the gas constant.

$\omega_1$  and  $T_1$  = the angular frequency and absolute temperature at one peak

$\omega_2$  and  $T_2$  = the angular frequency and absolute temperature at the other peak

The value of  $E_a$  obtained was 10.3 Kcal/mole as compared to 7.7 Kcal/mole obtained by Krum and Müller,<sup>2</sup> who have observed a similar loss peak for polycarbonate at low temperatures from dielectric studies.

## DISCUSSION OF RESULTS

### Low Temperature Studies

The technique employed here to measure the mechanical properties has a distinct advantage in its ability to isolate the specimen properties from those of the measuring system. The excellent agreement between the results obtained by Sauer et al.<sup>1</sup> and our data, Figure 4, indicates the reliability of the technique.

With regard to polypropylene, Figure 3, it is obvious that at approximately  $+10^\circ\text{C}$ , we are going through a rather large transition, which corresponds to the glass transition temperature. Our results appear to be in good agreement with those recently reported by Van Schooten et al.<sup>4</sup> for polypropylene fractions.

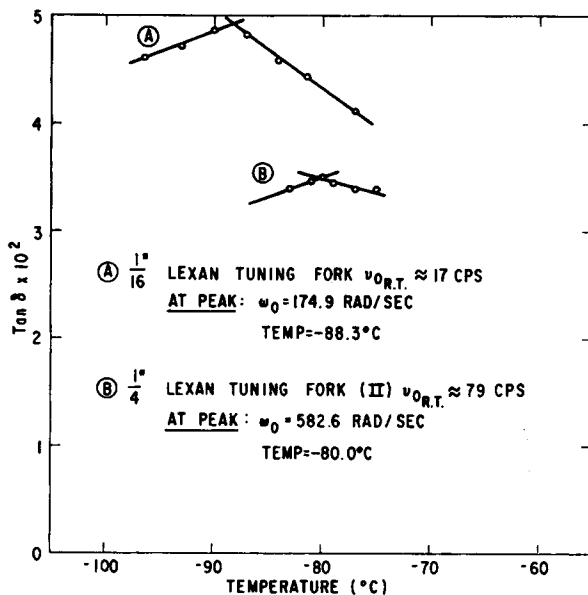


Fig. 6. Frequency dependence of peak in  $\tan \delta$ .

The polycarbonate data in Figure 6 shows a rather broad asymmetrical loss curve, as indicated previously, between  $-180$  to  $+20^\circ\text{C}$ . The shape of this loss curve suggests that there are three curves overlapped together. Similar data has been obtained by Illers and Breuer.<sup>5</sup>

Using nuclear magnetic resonance, it has been observed that there are two line width changes in the low temperature region, one at  $-150^\circ\text{C}$  and another at  $-50^\circ\text{C}$ . However, the frequencies of transition are of the order of 20 K.C.<sup>3,10</sup> The effect observed at  $-150^\circ\text{C}$  is probably related to  $-\text{CH}_3$  group mobility, while that at  $-50^\circ\text{C}$  is probably related to phenylene group motion. The dielectric loss data of Krum and Müller indicates also an asymmetrical loss curve.<sup>2</sup> It appears that this loss curve at low temperatures is composed of two loss peaks overlapped. Krum and Müller have been unable to separate this into two loss peaks by changing frequency, although a shift in combined peak is affected.<sup>2</sup>

Measurements at different frequencies, although shifting the peak of the loss curve, do not separate the loss curve into three curves as one might expect. This may be a result of the three loss curves having similar activation energies, which would cause the curves to shift the same amount as a result of change in frequency. Thus it might require a greater change in frequency than can be normally obtained by standard technique.

It appears that the two effects observed by NMR correspond to the two outside loss peaks observed by the mechanical technique, which then are associated with units possessing protons. The doublet observed by dielectric loss measurements correspond to the central and right-hand side of the mechanical loss curve, which should then be associated with parts of the

molecule possessing polarity; although it is possible that dielectric loss effects could be explained as a secondary effect, due to polar contaminants in the material, such as water. However, assuming that this is not the case, then the mechanical loss curve could be interpreted in the following way. The left side of the loss curve in Figure 5 is associated with methyl group mobility, which although normally observed to decrease at lower temperatures, may be reduced in mobility at higher temperatures, due to the steric hindrance of the phenylene group. The central part of the loss curve might be associated with the carbonate group, since it is observed with dielectric loss measurement, but not with NMR.

The right-hand side of the loss curve would thus, due to observation of dielectric loss and NMR, be associated with the phenylene carbonate group.

Although the evidence offered here is not conclusive, the proposed interpretation is not unreasonable.

It would be interesting to prepare specimens in which various parts of the polymer molecule are replaced by other groups. For example, if the hydrogens on the methyl groups are replaced by deuterium, the NMR curve would be expected to change. The lack of a change in NMR curve at  $-150^{\circ}\text{C}$  would then support the contention that it was due to methyl group mobility, and similarly, replacing the proton on the phenylene groups with deuterium, would prove useful.

However, until further work is done on substituted polycarbonates, it is difficult to be certain as to the primary causes of the relaxation effects.

### High Temperature Studies

In this part, we have focused our investigation on the behavior of Lexan<sup>®</sup> G.E. polycarbonate above room temperature. Of particular interest is the region between  $100$  and  $150^{\circ}\text{C}$ , where Peilstoecker has observed anomalies in the mechanical behavior of Makrolon, the German polycarbonate.<sup>6</sup>

The tuning forks used in this part of our investigation are similar to those described for low temperature studies. The following table serves to summarize identification of the forks whose properties were examined.

<i>Fork Designation</i>	<i>Thickness of Arm</i>	<i>Molding Conditions</i>
A	$1/4$ in.	Pressed at $200^{\circ}\text{C}$ , cooled in cycles by dropping $20^{\circ}\text{C}$ , raising $10^{\circ}\text{C}$
B	$1/4$ in.	Pressed at $180^{\circ}\text{C}$ , cooled in mold
C	$1/8$ in.	Pressed at $180^{\circ}\text{C}$ , cooled in mold
D and E	$1/4$ in.	Pressed at $180^{\circ}\text{C}$ , cooled in mold

The apparatus was fitted with Teflon coated leads which had been jacketed with copper ground cable, and finished by wrapping with vinyl electrical tape. The earphones were wound with Teflon coated wire and potted with RTV silicone rubber.



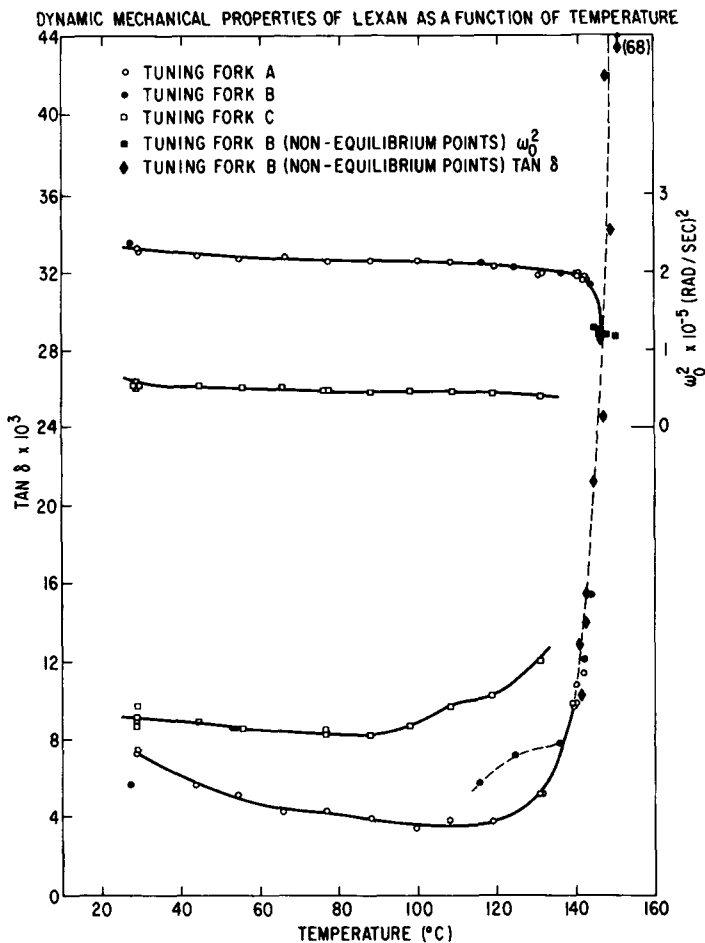


Fig. 7. High temperature behavior of  $\tan \delta$  and  $\omega_0^2$  of Lexan polycarbonate.

The temperature measurements were made using two thermocouples in a dummy Lexan polycarbonate fork, one being placed in the tip, the other in the base. A third thermocouple measures the ambient oven temperature.

The oven was modified by replacing the door with a  $\frac{1}{4}$  in. thick Pyrex glass plate insulated with fiber glass cloth. An opening was cut in the cloth to provide a means of viewing the inside of the oven. A small lamp suspended from the ceiling provided for illumination from within the oven.

A temperature gradient of  $11.5^\circ\text{C}$  was found to exist between the ceiling and floor of the oven at  $120^\circ\text{C}$ . A thermal gradient of  $4^\circ\text{C}$  was observed between the tip and base of the dummy fork, at an ambient oven temperature of  $160^\circ\text{C}$ .

Figure 7 shows  $\omega_0^2$  and  $\tan \delta$  for three Lexan polycarbonate tuning forks as a function of the dummy fork base temperature, after the establishment of thermal equilibrium as evidenced by the constancy of the thermocouple

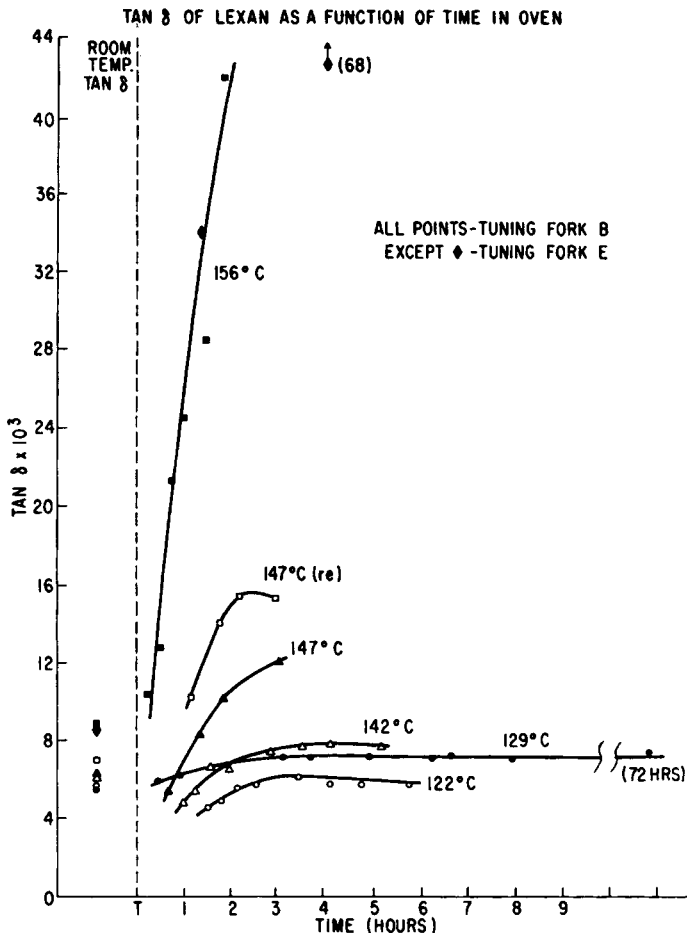


Fig. 8. Tan  $\delta$  as a function of time at various temperatures.

readings with time. For tuning forks *A* and *C*, the temperature changes were made without removal of the forks from the oven. In the case of fork *B*, the test piece was returned to room temperature between adjustments of the oven temperature.

It was found that a  $\sim 145^\circ\text{C}$  (for the  $\frac{1}{4}$  in. forks) and  $\sim 130^\circ\text{C}$  (for the  $\frac{1}{8}$  in. fork), the tuning forks became permanently distorted and unusable for further testing.

It was generally found that the fork arm not under test would deform first. This distortion may be due to inherent molding stresses, and failure to exactly balance the magnetic field of the earphone (although a compensating earphone was used for this purpose).

Figure 8 shows tan  $\delta$  as a function of time in the oven, with the ambient oven temperature as parameter. It is apparent that thermal equilibrium was not established for temperatures above  $145^\circ\text{C}$  since it has been noted

that distortion of the fork occurs above this temperature. During these runs the tuning fork was returned to room temperature between adjustments of the oven temperature. The upward drift in room temperature  $\tan \delta$  with increasing temperatures of heat treating is noticeable. Also of

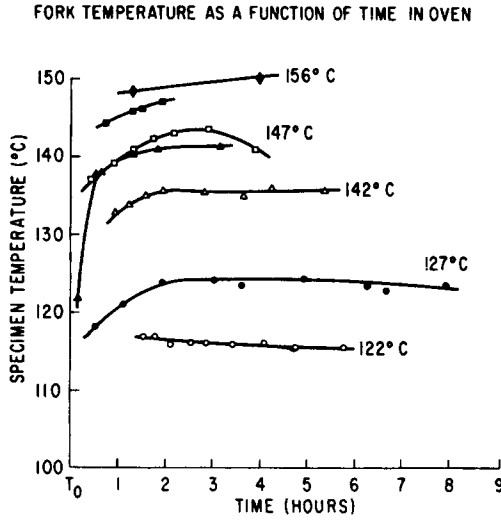


Fig. 9. Specimen temperature as a function of time in oven.

ROOM TEMPERATURE MECHANICAL PROPERTIES OF LEXAN TUNING FORKS AS A FUNCTION OF PREVIOUS HEATING

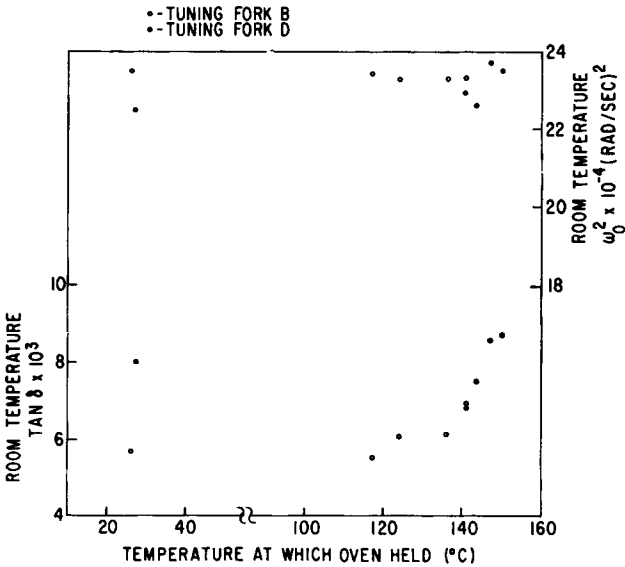


Fig. 10. Room temperature mechanical properties as a function of previous heating.

interest is the crossover of the 142 and 147°C curves with respect to the 129°C curve. The crossovers in  $\tan \delta$  curves of Figure 8 are not due entirely to the rate at which thermal equilibrium is being established. This can be seen from Figure 9 which shows no such crossover of the fork temperature with time. Virtually no change was observed in  $\tan \delta$  at 129°C, for 3 days, once thermal equilibrium was established.

Figure 10 shows the dynamic modulus and  $\tan \delta$  at room temperature plotted as a function of the temperature at which the sample was held prior to returning the sample back to room temperature.

## DISCUSSION OF RESULTS

### High Temperature Studies

As mentioned previously, the change in room temperature  $\tan \delta$  values of samples, which were conditioned at temperatures from 100–150°C, Figure 8, indicated that some type of change was occurring. Initially, it was felt that this might be due to removal of water and was probably associated with embrittlement, which leads to a change in the notched Izod impact strength of polycarbonate.<sup>8</sup> Subsequent studies on embrittled forks boiled in water indicated that water was not the primary cause. However, it was felt that this change in  $\tan \delta$  was related to the embrittlement phenomena. Dilatometric studies indicated that a change in density occurs between 100–130°C.<sup>8</sup> Thus the embrittlement phenomena may possibly be associated with change in molecular structure and in molecular volume. X-ray studies by Stein and Goldberg in this temperature region indicate a broadening and a rise in intensity of scattering for the main amorphous halo at a scattering angle of approximately 17°,<sup>9</sup> and studies of the birefringence as a function of temperature under constant strain have indicated a sudden change between 115 and 146°C in the heating up but not in cooling down. These data would also appear to support structural rearrangement.

It appears that much more work is necessary in order to clarify the phenomena of embrittlement.<sup>8</sup>

The small rise in  $\tan \delta$  values between 100 and 120°C for forks *B* and *C* appears to be similar to that found by Krum and Müller in their dielectric studies, and appears to be due to residual orientation, since examination under a polarizing microscope showed a large residual strain.<sup>7</sup> Fork *A* molded under more ideal conditions and carefully annealed does not show this effect. The rise in  $\tan \delta$  for forks *B* and *C* in the range 100–120°C is probably caused by the enhancement of the thermal free energy with the energy due to strained molecular segments, which increases the total free energy for these molecular segments. Such strained segments will thus move to a state of lower free energy by a relaxation process, which will cause a change in  $\tan \delta$ . For the unstrained fork *A*, there are none or a number of strained molecular segments and thus no apparent change in  $\tan \delta$ . Similar work has been carried out by other workers.<sup>10</sup>

In comparing our results on heat aging to those of Illers and Breuer, we find smaller changes in Young's modulus than they have found in the shear modulus. Since Young's modulus is dependent on both Poisson's ratio and the shear modulus, we can only conclude that Poisson's ratio must also be changing.

The data, in Figure 10, indicate that the mechanical properties of both samples at room temperature are dependent on thermal history. In particular, the  $\tan \delta$  values appear to be most dependent on thermal history.

### CONCLUSION

The results of this work have indicated the feasibility of using tuning forks for the measurement of the dynamic mechanical properties of polymers. We have suggested a systematic interpretation of the low temperature mechanical loss peak in polycarbonate by comparison with low temperature dielectric loss and NMR behavior. At temperatures just below  $T_g$ , changes occur in the mechanical properties of polycarbonate which may be related to an embrittlement of the material.

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