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Internal Friction Study of Diluent Effect on Polymers at Cryogenic Temperatures

Mitchel Shen[a][b]; Jack D. Strong[a]; Helmar Schlein[a]
[a] Science Center, North American Rockwell Corporation, Thousand Oaks, California [b] Department of Chemical Engineering, University of California, Berkeley, California

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Internal Friction Study of Diluent Effect on Polymers at Cryogenic Temperatures

MITCHEL SHEN,* JACK D. STRONG, and HELMAR SCHLEIN
Science Center
North American Rockwell Corporation
Thousand Oaks, California

SUMMARY

The dynamic mechanical properties of polystyrene/ethyl benzene, polymethyl methacrylate/water, polyethyl methacrylate/ethyl hexyl adipate, and poly-2-hydroxyethyl methacrylate/water were studied between 10 and 100°K. A free-decay resonance acoustic spectrometer was designed for this purpose. It was found that the presence of diluents causes the low-temperature loss peaks of the polymers in question to shift to higher temperatures. This observation is compatible with the hypothesis that at very low temperatures, the diluent molecules are immobilized to occupy free space between adjacent polymer chains. The hindering action of these molecules on the kinetic motions of the side groups of the polymer thus renders greater thermal energy necessary to initiate the relaxation processes.

INTRODUCTION

It is well known that incorporation of diluents in amorphous polymers almost invariably produces a depression of primary glass transition temperatures [1]. Its effect on the low-temperature sub-T_g relaxations, however, is not always easy to predict. Dynamic mechanical data in the literature have

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*Present address: Department of Chemical Engineering, University of California, Berkeley, California.

shown that the position of the loss peaks can be shifted to lower [2-5] or higher [6, 7] temperatures by the presence of diluents in the polymer. In some instances, no shift of the existing loss peaks was observed [2, 4, 8, 9]. In other polymer-diluent systems, appearance of new peaks was reported [10, 11]. Obviously, here the nature of the polymer and the diluent, and their interaction, plays a major role.

In a recent publication [7], we proposed a "dual mechanism" to interpret the effect of diluent on the internal friction data of some polymethacrylates. It was suggested that at moderately low temperatures, the diluents are still sufficiently mobile to exert a "normal" plasticizing effect in lowering the beta relaxations. At lower temperatures, the diluents themselves are "frozen in." They now act to hinder the molecular motions responsible for the relaxation, thus causing the gamma loss peaks to shift to higher temperatures. At some concentration of the diluent, these two peaks merge to form a single loss peak. On the basis of this hypothesis, loss peaks at very low temperatures would invariably be shifted to higher temperatures by the presence of diluents. In this paper we have therefore conducted further internal friction measurements down to liquid helium temperatures. An automatic free-decay instrument was constructed for use with a forced fluxural resonance transducer. Several polymer-diluent systems were studied, including both polar and nonpolar substances.

EXPERIMENTAL

Monomers were mixed with their respective diluents and the solutions were polymerized by ultraviolet radiation [12]. The following monomer-diluent pairs were prepared: styrene/ethyl benzene, ethyl methacrylate/ethyl hexyl adipate, and 2-hydroxypropyl methacrylate/distilled water. Polymethyl methacrylate was similarly prepared, and distilled water was later incorporated by swelling. Samples were machined to the approximate dimensions of 0.3 X 0.3 X 10cm^3. Two small iron tabs were glued to the ends of the samples to provide magnetic coupling with the transducer. The block diagram for the free-decay acoustic spectrometer is shown in Fig. 1. The sample was clamped at its nodal points. An Exact Electronic Type 305 function generator was used to supply sine waves at audio-frequencies, which were transmitted to one end of the sample by an Electro Model 3055A magnetic coil. An identical detector coil was used on the other end of the sample to receive the output response. (A Hewlett-Packard Model 467A power amplifier was used at very low temperatures to overcome

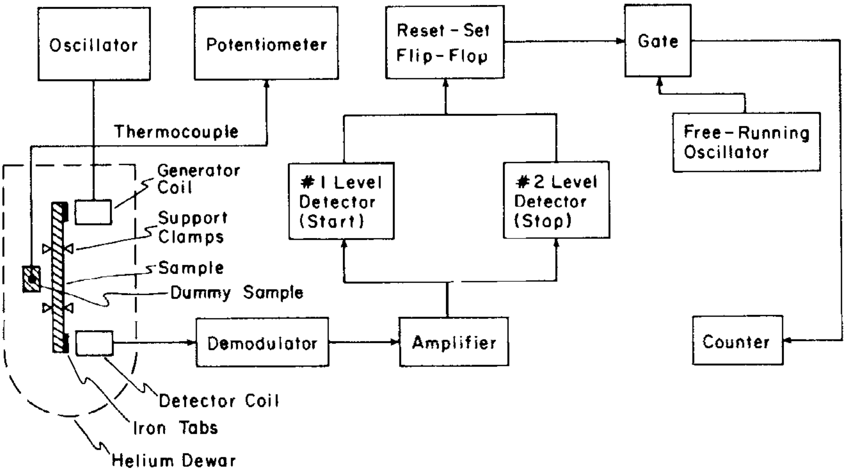

Fig. 1. Block diagram for the free-decay acoustic resonance spectrometer.

difficulty generated by the impedance mismatch of the transducers.) The generator and detector signals were applied to the horizontal and vertical plates of a Heathkit Model 10-10 cathode ray oscilloscope. The frequency at which the characteristic Lissajous pattern on the oscilloscope became a maximum was the resonant fequency f_0. Thus one can readily calculate the dynamic storage modulus by the following equation [13]:

$$E' = 0.9464(\ell^2 f_0^2/t)^2 \rho \qquad (1)$$

where ℓ is the length, t the thickness, and ρ the density of the sample, all in cgs units.

To determine the internal friction, the driving signal was suddenly removed from the sample at resonance. The vibrational amplitude of the sample was then a decaying sinusoidal curve, whose envelope approximated exponential form. The sinusoidal portion was removed by the demodulator. The rectified exponential envelope can then be utilized to calculate internal friction [14-16]:

$$Q^{-1} = (\Delta t/\pi)\ell n(A_0/A) \qquad (2)$$

where A_0 and A are the two arbitrarily chosen amplitudes on the envelope, and Δt is the time required for the decay from A_0 to A.

The central feature of our instrument is its ability to accurately measure the time interval between amplitudes A_0 and A. The most expedient procedure is to fix the two amplitudes at definite known voltage levels. In all of the experiments the resonant amplitude of the sample is always adjusted so that it is higher than A_0 by a fixed amount. When the decay is initiated, the amplitude (in volts) starts to drop exponentially. When it reaches the first fixed amplitude level A_0, the number of oscillations of a free-running high-frequency oscillator begins to be counted. Counting is continued until the amplitude reaches level A. The reciprocal of the number of oscillations registered during this interval is the time required in the calculation of Q^{-1}. The actual method to accomplish this is described in the following paragraph.

The decaying sinusoidal signal, which is now rectified to dc, is suitably amplified and brought to the input of two level detectors. Two operational amplifiers without feedback are used as level detectors, and they are adjusted for such levels of the available signal as one wishes to detect. It is imperative that the level detectors operate in the prescribed order. The output of detector No. 1, which is set to the higher amplitude A_0, will upon triggering set one input of a set-reset flip-flop. The output of detector No. 2, which triggers at a value less than that of No. 1, resets the abovementioned flip-flop. Thus, the flip-flop is in the "set" state during the interval A_0 to A which is equal to Δt. To determine this time interval, the "set" condition opens one input of an AND gate. The signal on another input of the same gate is a free-running 200-kc pulser, the exact frequency of which has been accurately calibrated. The output of the gate during this time interval consists of pulses, the number of which is displayed on a Hewlett-Packard 5512A electronic counter.

Cryogenic temperature was achieved in a Janis Model RD helium Dewar. A chromel-constantan thermocouple embedded in a dummy sample was used to monitor the temperature. All data were taken during warm-up (warm-up rate, about 1°K/min or less). An approximately constant rate was maintained by means of a small heater at relatively high temperatures (above 20°K).

After each run, the data were transferred onto IBM cards. They were then calculated by a Control Data 6600 computer. Numerical results from the computer were directly fed to a CalComp digital incremental plotter, which then yielded plots of E', E'', and Q^{-1} vs. temperature. The dynamic loss modulus was calculated by

$$E'' = E'Q^{-1} \qquad (3)$$

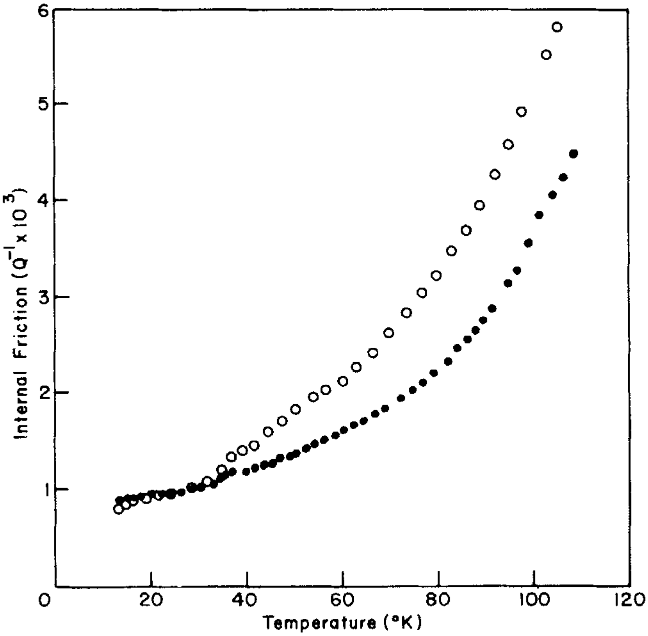

Fig. 2. Internal friction-temperature plot for poly-2-hydroxypropyl methacrylate (○) and poly-2-hydroxypropyl methacrylate swollen with 5.9% water by volume (●).

RESULTS AND DISCUSSION

In our previous paper [7], we reported that poly-2-hydroxypropyl methacrylate (PHPMA) between 77°K and its glass transition temperature exhibits a loss peak near 173°K. Upon incorporation of 0.5% water, this loss peak becomes a broad shoulder around 200°K while a new peak near 230°K appears. At 1% water in PHPMA, only one peak around 213°K remains. Our interpretation was that the 173°K peak in undiluted PHPMA can be attributed to the conformational change of the $-CH_2CHOHCH_3$ portion of the ester side group (gamma mechanism). The gamma peak is shifted to 200°K with the addition of 0.5% water. The new peak near 230°K is the beta peak of PHPMA due to the motion of the entire ester group, which is not observed in the undiluted sample due to its proximity to the primary glass transition. Thus, water has acted as a plasticizer in creating greater free volume, allowing the beta relaxation to occur at a

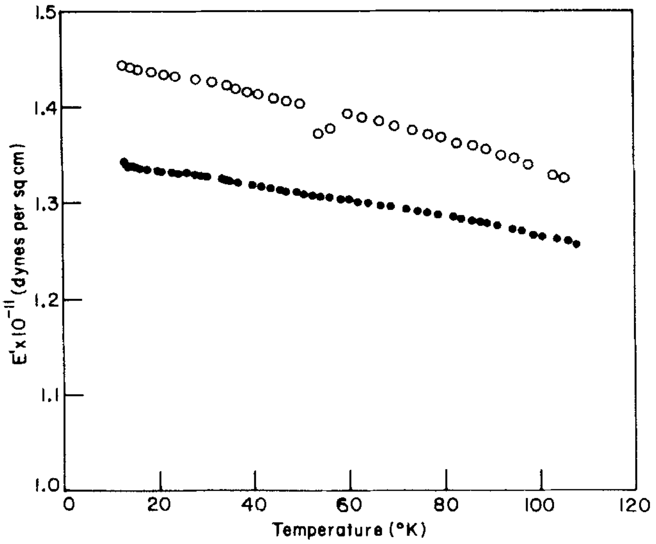

Fig. 3. Dynamic storage modulus-temperature plot for poly-2-hydroxypropyl methacrylate (○) and poly-2-hydroxypropyl methacrylate swollen with 5.9% water by volume (●).

lower temperature with increased strength. However, at lower temperatures, water molecules may have themselves been immobilized to occupy free space between adjacent chains. They now act to hinder the kinetic motions of the side groups and cause the gamma peak to shift to a higher temperature. At 1% water in PHPMA, the elevated gamma peak and the lowered beta peak merge to form one peak at 213°K.

Figure 2 shows the internal friction-temperature plot for PHPMA and PHPMA with 5.9% (by volume) water. No relaxation peaks are evident in this very-low-temperature region. However, the increased internal friction at the higher temperature end must represent the onset of the gamma peak in PHPMA. Clearly, this peak is displaced to a higher temperature by the inclusion of 5.9% water, in agreement with our earlier results [7] above 77°K.

Figures 3 and 4 illustrate the behavior of dynamic storage and loss moduli, respectively, of PHPMA and PHPMA with 5.9% water as a function of temperature. The presence of water apparently depresses the storage modulus somewhat, which is just the reverse of what we observed previously [7]. The cause of this discrepancy is not known at present.

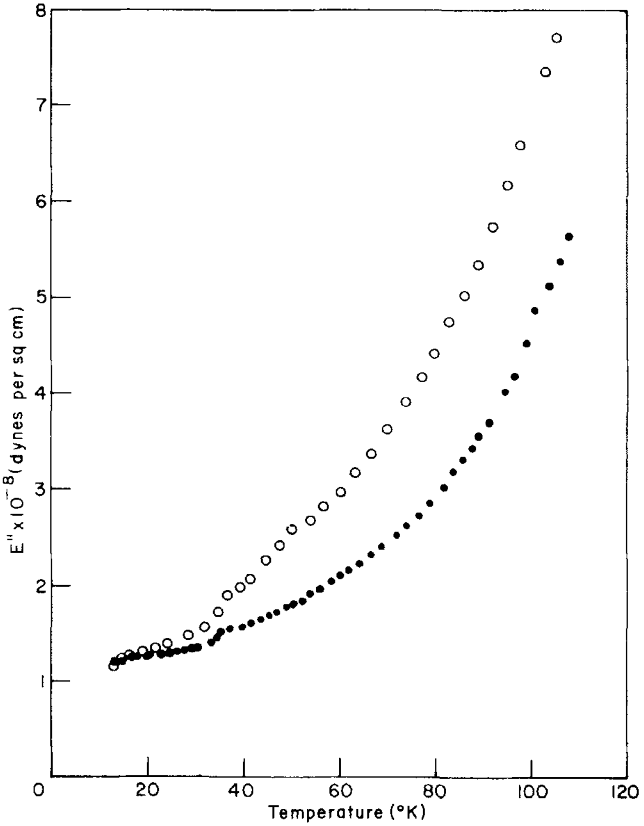

Fig. 4. Dynamic loss modulus-temperature plot for poly-2-hydroxypropyl methacrylate (○) and poly-2-hydroxypropyl methacrylate swollen with 5.9% water by volume (●).

The Q^{-1}-T plot for polystyrene (PS) and PS diluted by 1% and 5% ethyl benzene is given in Fig. 5. The undiluted PS exhibits a loss peak around 30°K. With increasing dilution, this peak, designated as delta peak, is seen to move to higher temperatures. At 1% ethyl benzene, the delta peak is near 35°K; at 5%, it is near 45°K. At the same time, the strength of Q^{-1} increased from 3.7 X 10^{-3} for undiluted PS to 4.2 X 10^{-3} with 1% diluent to 7.2 X 10^{-3} with 5% diluent at their respective peak temperatures. This increase in the delta relaxation temperature can plausibly be interpreted as due to the hindering action of the immobilized ethyl benzen molecules between the phenyl side groups of polystyrene.

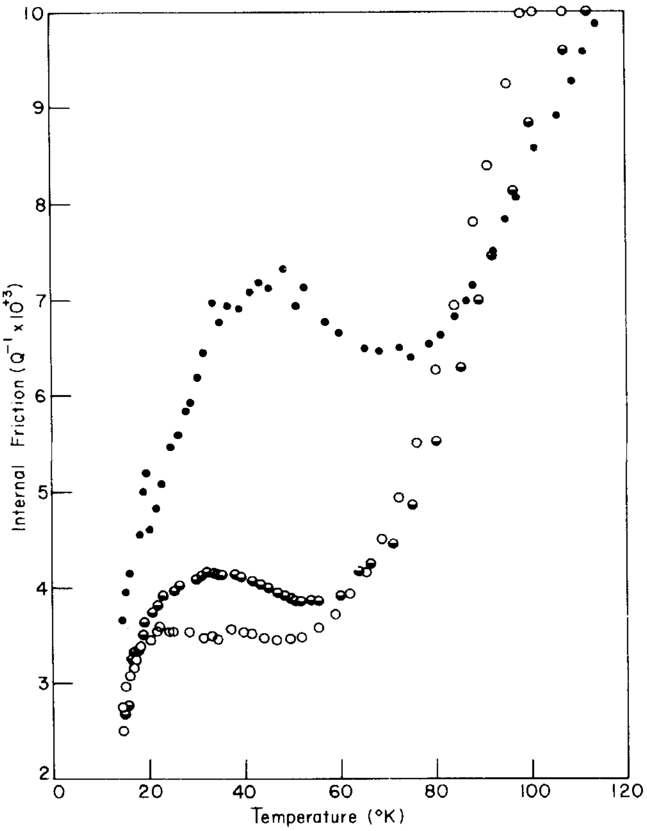

Fig. 5. Internal friction-temperature plot for polystyrene (○) and polystyrene swollen with 1% (◒) and 5% (●) ethyl benzene.

Sinnott [17] reported a loss maximum at 38°K for PS at a frequency of 5.6 cps, and Crissman and McCammon [16] found a similar peak at 48°K (6290 cps). The mechanism for this delta relaxation process was attributed to the wagging or oscillation of the pendant phenyl groups [17]. It is not clear why our results show the delta peak (determined at 883 cps) to be at a lower temperature than that found by Sinnott at 5.6 cps.

Figure 5 also shows the onset of an internal friction peak at the higher-temperature side. This observation is compatible with the maximum in mechanical loss at ~130°K (10 cps) reported earlier [18, 19]. This peak, designated as gamma peak [19] was attributed to the irregularities in the

Table 1. Dynamic Mechanical Data of Polystyrene and Polyethyl Methacrylate

Polymer	f_0, cps	Q^{-1}	T_1, °K[a]	E′ dyn/cm^2	E″ dyn/cm^2	Ref.
Polystyrene	6290		48			[24]
″	5.6		38			[17]
″	883	3.5×10^{-3}	30	6.02×10^{10}	2.13×10^{8}	This work
″ (2% EB)[b]	1015	4.1×10^{-3}	35	6.14×10^{10}	2.54×10^{8}	″
″ (5% EB)	883	7.2×10^{-3}	45	4.83×10^{10}	3.45×10^{8}	″
Polyethyl methacrylate	470		62			[25]
″	9836		52			[24]
″	9		41			[17]
″	808	1.2×10^{-2}	60	6.48×10^{10}	7.76×10^{8}	This work
″ (1% EHA)[c]	753	1.55×10^{-2}	65	1.25×10^{10}	1.92×10^{8}	″

[a] T_1 refers to the temperature at which the internal friction is a maximum. For polystyrene it is the delta peak; for polyethyl methacrylate it is the gamma peak.

[b] Swollen with ethyl benzene.

[c] Swollen with ethyl hexyl adipate.

polymer structure. During polymerization, it is possible for head-to-head additions to occur, thus producing sequences containing two methylene groups. These "weak joints," due to their relatively small steric hindrance, undergo motions that are similar to those occurring in polyethylene. Illers and Jenckel [19] found that gamma peaks in polystyrene may not occur under certain polymerization conditions in which such irregular structures do not form, which explains the fact that these relaxation processes were not found by several other workers [20, 21]. Takayanagi [22], on the other hand, suggested that the gamma relaxation was associated with the restricted rotation of the phenyl groups. Illers and Jenckel [23] also found that incorporation of diethyl phthalate shifted the gamma peak in PS to higher temperatures. There is some indication in Fig. 5 that ethyl benzene produces a similar effect. Again this effect could be attributed to the hindrance of the immobilized ethyl benzene molecules. These data are summarized in Table 1.

It is of interest to note that in their study of the effect of water on the relaxation behavior of poly-2-hydroxyethyl methacrylate, Janacek and Kolarik [9] suggested the possibility that water molecules bind with the polymer side chains through hydrogen bonding, thus causing the gamma relaxation to require higher activation energy. It would be difficult to conceive of a similar mechanism for our polystyrene/ethyl benzen system, since they are both hydrocarbons.

Polyethyl methacrylate has been reported (Table 1) to undergo a relaxation process at 41°K (9 cps) [17], 52°K (9836 cps) [24], or 62°K (470 cps) [25]. Our data (Fig. 6) show such a loss peak at 60°K (808 cps). Again, the literature data do not appear to agree on the frequency-temperature correlation. Crissman et al. [24] suggested the differences in sample composition and purity as a possible cause for this discrepancy. Figure 6 also shows that introduction of 1% ethyl hexyl adipate into PEMA shifts the loss peak to around 65°K. The peak is now considerably broadened, rendering the location of the maximum point difficult.

The internal friction-temperature curves for polymethyl methacrylate and PMMA with 0.6% water are given in Fig. 7. At very low termperatures there is an upswing which could be part of a loss peak. Several authors [26, 27] found in their nuclear magnetic resonance studies (30 Mc/sec) a relaxation process near 80°K. Sinnott [28] estimated that such a process, designated epsilon relaxation, would occur below 4°K in dynamic mechanical investigations. He attributed epsilon relaxation in PMMA to the rotation of the methyl group on the ester side chain. Recently, Hara [29], in his dielectric study at 60 kc/sec, also found the onset of such a peak. He

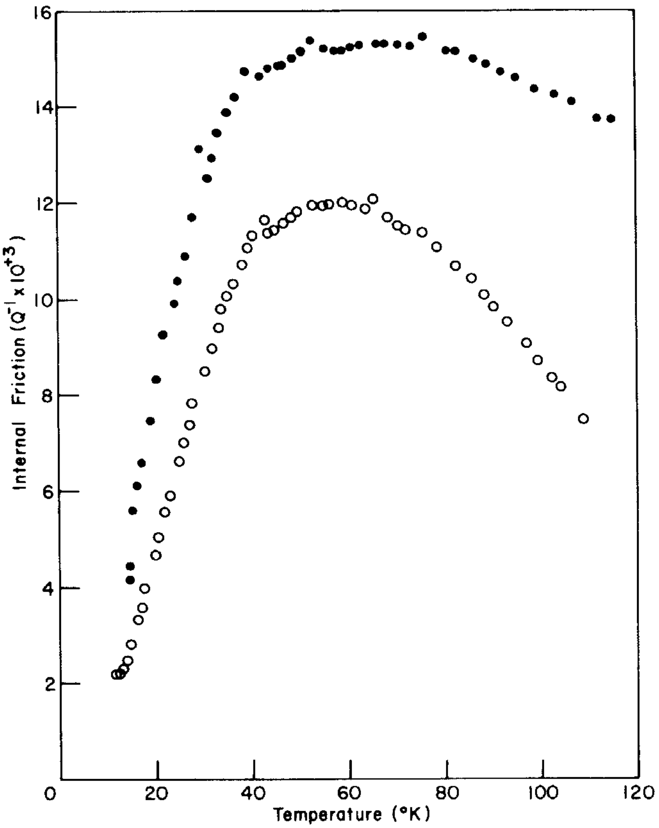

Fig. 6. Internal friction-temperature plot for polyethyl methacrylate (○) and polyethyl methacrylate swollen with 1% ethyl hexyl methacrylate (●).

noted, however, that dipole reorientation of methyl groups is not normally detectable in dielectric measurements, thus casting some doubt on the validity of the aforementioned mechanism.

Figure 7 also shows a very small maximum near 40°K. Owing to its very small magnitude, its presence cannot be definitely established at the present time. The onset of a loss peak near 100°K must be the gamma peak previously found by several workers [26-28], which was assigned to the rotation of the α-methyl groups on the main PMMA chain. There is a slight hint in Fig. 7 that the gamma peak of PMMA is shifted to a higher temperature by the inclusion of 0.6% water.

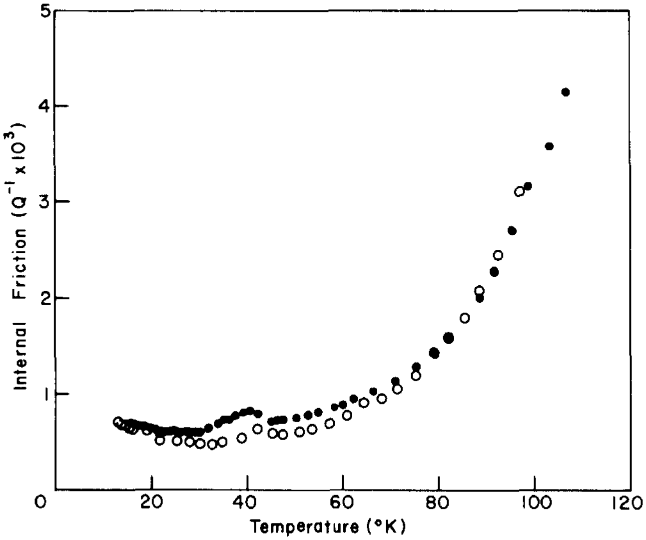

Fig. 7. Internal friction-temperature plot for polymethyl methacrylate (○) and polymethyl methacrylate swollen with 0.6% water (●).

CONCLUSIONS

The data presented in this work can all be plausibly interpreted in terms of the hindering effect of the immobilized diluent molecules at very low temperatures. Our tentative conclusion, based on the limited evidence available thus far, is that "high-temperature" relaxations such as beta relaxations are often shifted to lower temperatures by the incorporation of diluents. The rationale is that here the low-molecular-weight liquids are still sufficiently mobile to act as plasticizers. At very low temperatures, however, the liquids are themselves immobilized to give an "antiplasticization" effect. The temperature at which such "transition" occurs must be determined by the nature of the polymer and the diluent in question.

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Discussion of Paper by Mitchel Shen, Jack D. Strong, and Helmar Schlein

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R. F. Landel: 1. In the PEMA plasticized with ethyl hexyl adipate, the internal friction curve appeared to be increased bodily, without much change in shape, while in the PS plasticized with ethyl benzene there is a change in shape of the Q^{-1}-T plot. Are these differences to be associated with differences in the relative effects on the loss and storage properties in the two cases?
2. Have you had a chance to, or do you plan to, investigate the pure ethyl hexyl adipate?

M. Shen: 1. The Q^{-1}-T curve for polyethyl methacrylate is very broad and thus appears to have increased bodily. Actually, its internal friction increases just as for polystyrene. The apparent change in shape for polystyrene is due to the onset of gamma transition around 150°K. The delta peak is shifted to a higher temperature by the presence of diluents and thus is partially merged with the gamma peak at high diluent concentration.
2. No. Our instrument at present cannot be used to measure the internal friction of liquids.

A. M. Hermann: What is the H_2O content of poly-2-hydroxypropyl methacrylate after drying and is the polymer cross-linked?

M. Shen: Poly-2-hydroxypropyl methacrylate was dried in a vacuum oven at 60°C for several weeks. We did not analyze its water content after drying. The infrared spectrum of this polymer in the frequency region of interest was too broad to permit analysis. The polymer was cross-linked by a dimethacrylate. However, the degree of cross-linking is low and does not affect the internal friction of the host polymer.

R. F. Robbins: 1. Did the addition of diluents change the resonant frequency?
2. Why did the 30°K relaxation of polystyrene show as a shoulder rather than a peak?

M. Shen: 1. Yes. It is reflected in the storage modulus changes [see Eq. (1) in text]. However, as shown in Table 1, the change in frequency is relatively small, so that the loss peak temperature is not appreciably affected.
2. The 30°K relaxation of polystyrene should be a peak. The shoulder-like appearance is due to experimental scatter.

J. A. Sauer: Dr. Shen mentioned that he found the low-temperature peak in PS at a somewhat lower temperature than that reported by Sinnott despite the fact that his measurements were made at higher values of measuring frequency. Actually, the loss peak in PS is fairly flat and it is difficult to designate a specific temperature for its maximum. In view of this, and in view of the fact that Dr. Shen's data show some scatter and irregularities in the test points near the peak maximum, it is perhaps not surprising that there is some small disagreement between reported values.