

## Internal Friction in Polymer-Impregnated Hardened Cement Paste

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### Synopsis

Hardened cement paste (HCP) specimens were prepared with hydration times of 1, 3, 7, 28, and 180 days. Specimens were oven dried and subsequently impregnated with methyl methacrylate, *tert*-butylstyrene, polyethylene glycol, and an epoxy resin system via a vacuum-pressure technique. Internal friction ( $Q^{-1}$ ) of *in situ* polymerized specimens was measured over the temperature range from 100° to 500°K. Results indicate that the internal friction spectra of polymer-impregnated specimens closely parallels the internal friction spectra of the bulk polymers used for impregnation. Magnitudes of the internal friction peaks in the impregnated specimens were found to be less than that expected on the basis of volume fraction of polymer present. These results are attributed to hindered motion at the cement/polymer interface.

### INTRODUCTION

Internal friction measurements have proven to be a useful tool in the investigation of the structure/property relationships of a variety of polymeric and composite materials. In their comprehensive review article, Woodward and Sauer<sup>1</sup> summarized the results obtained by various workers on a large number of natural and synthetic polymers using a variety of measurement techniques. From these and other studies, it has become apparent that the mechanisms responsible for various mechanical relaxations, such as glass transitions, side group rotations, chain torsional motions and others, can be deduced from measurements of the internal friction as a function of temperature or frequency.

Internal friction measurements have also been applied with some success to the study of polymer-based composite materials. These materials are composites where the polymer serves as a matrix for a variety of inorganic fillers. Lewis and Nielsen,<sup>2</sup> Galperin,<sup>3</sup> and Jenness and Kline,<sup>4</sup> among others, have found the internal friction of polymer-based composites to be related not only to the internal friction of the matrix and filler phases but also to filler size and geometry, as well as possible filler/matrix interactions.

Although a number of studies have been carried out<sup>5-7</sup> with respect to the internal friction of hardened cement paste (HCP), no work has been reported concerning internal friction of polymer-impregnated hardened cement paste (PICP). Indeed, little is known concerning internal friction of systems where both polymer and matrix phase are continuous and interconnected systems. It

is the purpose of the present report to present results for the internal friction of HCP filled with a variety of polymers over a wide range of temperatures. By hydrating the cement for varying periods of time, the effect of cement maturity on the internal friction has also been studied.

## EXPERIMENTAL



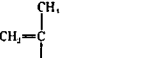

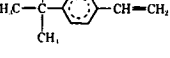
### Sample Preparation

All specimens were prepared using Type 1 portland cement. Pastes were prepared by adding the required amount of water to the cement and hand mixing for 2 min. Specimens with a water-to-cement ratio ( $w/c$ ) of 0.4:1 parts by weight were prepared by troweling the freshly mixed paste into rectangular PVC molds 0.635 cm  $\times$  0.762 cm  $\times$  12.7 cm in dimensions. Six specimens could be prepared at one time. The molds were precoated with a mixture of wax and oil to facilitate demolding procedures.

After casting, the specimens were placed in a fog room (100% R.H.) near 20°C for 20–24 hr. The castings were then carefully demolded and placed in a saturated limewater solution for the duration of the desired period of hydration. All hydration was carried out at ambient laboratory temperatures (18–25°C).

After the specimens had reached the desired maturity, they were removed from the limewater, trimmed to a length of 10.2 cm, and then placed in a vacuum oven at 75°C. Samples were continuously evacuated until loss of water equivalent to 1 mg/g of paste per day had been achieved. This process lasted approximately 72 hr. A cold trap contained in a Dewar flask filled with liquid nitrogen (bp = 81°K) was used to maintain a constant vapor pressure above the specimens. At

TABLE I  
Physical Characteristics of Monomers

Monomer	Structure	Molecular weight	Viscosity <sup>a</sup> , cps	Density, g/cm <sup>3</sup>	
				Monomer	Polymer
Epoxy Epon 828		370–384		1.09 <sup>c</sup>	1.16
styrene oxide		120	150–5400 <sup>b</sup>		
DEAPA		130			
Methyl methacrylate (MMA)		100.1	0.56	0.94	1.14
tert-Butylstyrene (TBS)		160.3	1.46	0.88	0.95
Polyethylene glycol (PEG)	HO-(CH <sub>2</sub> ) <sub>n</sub> -CH <sub>2</sub> -O- <sub>n</sub> -H	950–1050	50 <sup>d</sup>	1.08 <sup>d</sup>	1.21 <sup>e</sup>

<sup>a</sup> At 25°C.

<sup>b</sup> Viscosities measured on initial mix and after 6 hr (Cannon-Manning vacuum viscometer).

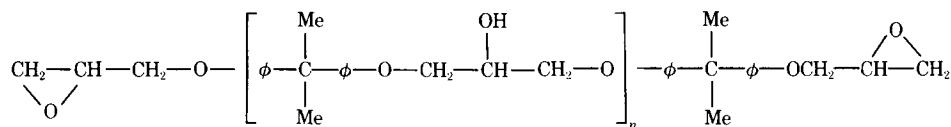
<sup>c</sup> Calculated from mix proportions.

<sup>d</sup> Melt at 75°C.

<sup>e</sup> Solid at 25°C.

the end of the drying period, the specimens were placed in sealed mason jars containing a small quantity of desiccant to prevent any adsorption of water.

Physical characteristics of monomers used are presented in Table I. The epoxy resin system was formulated using Epon 828, a diglycidal ether of bisphenol A with the following structure:



where  $\phi$  represents the phenyl group.

The average molecular weight of the resin is 370–384, yielding a weight per epoxide (WPE) of 185–192. An average WPE of 186 was chosen for calculational purposes. Properties and uses of this particular epoxy system have been discussed in previous publications.<sup>8,9</sup>

All monomers except *tert*-butylstyrene (TBS) were used as received. *tert*-butylstyrene (Dow Chemical Co.) was passed through a column of activated alumina at a rate of 20 ml/hr to remove inhibitor (*tert*-butylcatechol) added to the monomer before shipment. Monomers were catalyzed with the appropriate free-radical initiators before impregnation of the specimens. MMA (Rohm and Haas Co.) was catalyzed with 0.1% azobisisobutyronitrile (VAZO, Fisher Scientific Co.), and TBS was catalyzed with 0.5% *tert*-butyl peroxoate (Lucidol Inc.).

A detailed description of the impregnation apparatus is given by Whiting.<sup>10</sup> Samples are placed in the impregnation chamber and evacuated to 100 microns. Monomer is then introduced into the chamber and allowed to completely cover the specimens. The system is then brought up to 200 psig pressure with compressed nitrogen. Specimens were allowed to remain under pressure for 8 hr. At the end of this time, specimens were removed from the chamber, weighed, and subjected to the appropriate polymerization procedure.

Epoxy specimens were allowed to gel at ambient temperature for 24 hr. They were then placed in a laboratory oven at 75°C for an additional 24 hr and subsequently removed from the oven and allowed to cool slowly to room temperature. Specimens were stored in sealed test tubes prior to testing.

MMA-impregnated specimens were each placed in a test tube containing a saturated aqueous solution of MMA in hot (75–85°C) water. The tubes were sealed and placed in a water bath at 75°C for 24 hr. Specimens were then removed and placed in a vacuum oven at 75°C for an additional 24 hr to remove any water adsorbed by the specimens during polymerization. After drying, it was observed that some monomer had been depleted from the surface of the sample during the polymerization step. For this reason, the dried specimens were sanded to remove this depleted surface layer. Specimens were then placed in sealed test tubes prior to testing.

TBS-impregnated specimens were treated in a similar manner, with the exception that the polymerization was carried out at 85°C for 48 hr.

For impregnation with polyethylene glycol (PEG), a different procedure was employed. PEG is a waxy solid at ambient temperatures. Therefore, one must heat PEG to 75°C in order to obtain a fluid with a viscosity suitable for impregnation. Specimens were placed in molten PEG at 75°C and allowed to soak

until weight gain had reached equilibrium, approximately ten days. They were then removed from the oven, weighed, and allowed to cool back to room temperature.

Samples of bulk polymers for use as test controls were prepared in the form of rods and thin films. Cylindrical rods  $\frac{1}{4}$  in. in diameter were prepared by casting the catalyzed monomer into sealed glass tubes and curing under the conditions previously described. Films were prepared by curing the monomer between Teflon-coated aluminum foil held between smooth glass plates.

### Porosity Measurements

Porosity of the cement paste specimens was determined by the method of Copeland and Hayes.<sup>11</sup> Porosity data on a set of specimens prepared under the same conditions as the specimens used for impregnation are presented in Table II.

Volume loading of the specimens, in per cent, is expressed as

$$\text{volume loading (\%)} = \frac{\text{weight loaded (g)} \times 100}{\rho \times V_b} \quad (1)$$

where  $\rho$  is the density of monomer (or polymer) and  $V_b$  ( $\text{cm}^3$ ) is the bulk volume of the specimen.

### Dynamic Mechanical Testing

For dynamic mechanical testing of the bulk polymers (PMMA, PTBS, and epoxy resin) above  $300^\circ\text{K}$ , the Rheovibron direct-reading dynamic viscoelastometer (Model DDV-II, Toyo Baldwin Co.) was employed. The specimen, in the form of a thin (0.0025 cm) film, is rigidly held between two clamps which are wired into a strain gauge network. Excitation of one clamp by a sinusoidally oscillating voltage (110 Hz) sets the specimen into vibration the amplitude of which is transduced by the strain gauge on the opposing clamp. By electronically measuring the phase angle ( $\delta$ ) between applied strain and resultant stress, the internal friction ( $\tan \delta$ ) is directly determined.

All other specimens were tested in an apparatus developed by Kline.<sup>12</sup> The specimen is suspended by two cotton threads located just outside the nodes of the fundamental free-free flexural mode, approximately 1.25 cm from the ends

TABLE II  
Porosity of Hardened Cement Paste at Various Hydration Times

Specimen	Hydration time, days	Porosity, %
1-1	1	47.3
1-2	1	47.6
3-1	3	43.9
3-2	3	45.0
7-1	7	40.5
7-2	7	40.1
28-1	28	36.5
28-2	28	37.5
180-1	180	36.2
180-2	180	36.4

of the specimen. The specimen is excited in the audio frequency (600–3000 Hz) by a magnetostrictive transducer. The output signal is detected by a piezoelectric crystal pickup, amplified, filtered, and displayed both on an oscilloscope and a level recorder. The internal friction ( $Q^{-1}$ ) is expressed as

$$Q^{-1} = \frac{\Delta f}{f_1} \quad (2)$$

where  $\Delta f$  is the bandwidth at 3 db below the maximum rms amplitude and  $f_1$  is the resonant frequency.

For low-temperature measurements, specimens were cooled in a chamber surrounded by a Dewar flask containing liquid nitrogen. Testing was conducted at a heating rate of 1°K per minute. Data were taken at 5°K intervals. Tests were first conducted on unimpregnated (control) specimens, then these same specimens were impregnated and retested. In this way it is possible to make a better comparison between impregnated and unimpregnated specimens and to eliminate possible variances between specimens.

## RESULTS AND DISCUSSION

### Loading of Monomer and Polymer in HCP

Loading of monomer and polymer into the oven-dried HCP specimens is presented in Table III. All values are given on a volume per cent basis. The values given for epoxy "monomer" are based on the density of the unreacted formulation (1.09 g/cm<sup>3</sup>). Since the epoxy formulation begins to gel during the course of the impregnation, these values represent an upper limit on the monomer loading. From the data presented, it is evident that the loadings decrease as the maturity of the HCP increases. By using measured values of the total porosity (see Table II), it is possible to calculate the per cent of total porosity filled by monomer and polymer. These data are presented in Table IV. The per cent of total porosity filled also decreases with increasing maturity of the specimen.

These effects are most probably due to the changes occurring in the pore structure of HCP during the period of hydration. The permeability of HCP is greatly reduced between one and 180 days of hydration owing to both the de-

TABLE III  
Loading of HCP Specimens<sup>a</sup>

Maturity, days	Loading, vol-%							
	MMA		PEG		TBS		Epoxy	
	Mono- mer	Polymer	Melt	Solid	Mono- mer	Polymer	Mono- mer <sup>b</sup>	Polymer
1	41.5	34.2	42.4	37.9	39.4	36.6	41.5	39.4
3	34.8	28.8	37.5	33.5	33.4	31.0	35.2	33.4
7	28.6	23.6	32.8	29.2	28.9	26.9	24.2	22.9
28	22.3	18.4	26.1	23.3	24.2	22.5	16.2	15.3
180	21.3	17.5	23.5	21.0	20.4	18.9	15.3	14.4

<sup>a</sup> Water-to-cement ratio ( $w/c$ ) = 0.4.

<sup>b</sup> Based on density of epoxy system before onset of polymerization (1.09 g/cm<sup>3</sup>).

TABLE IV  
Per cent of Total Porosity Filled in HCP Specimens<sup>a</sup>

Maturity, days	vol-%							
	MMA		PEG		TBS		Epoxy	
	Mono- mer	Polymer	Melt	Solid	Mono- mer	Polymer	Mono- mer	Polymer
1	87.4	72.0	89.2	79.7	82.9	77.0	87.4	82.9
3	78.2	64.7	84.3	75.3	75.0	69.6	79.2	75.1
7	70.9	58.6	81.4	72.4	71.7	66.7	60.0	56.8
28	60.3	49.7	70.5	62.9	65.4	60.8	44.3	41.3
180	58.7	48.2	64.7	57.8	56.2	52.1	42.1	39.6

<sup>a</sup> Water-to-cement ratio ( $w/c$ ) = 0.4.

crease in total porosity and a shift in the pore size distribution toward smaller pore sizes.<sup>13</sup> One can see this more clearly by comparing the per cent of total porosity filled by MMA and epoxy between one and 28 days of hydration. At one day of hydration, the pore system is sufficiently coarse to allow easy ingress of both monomers, regardless of the large difference in viscosity between them (see Table I). At 28 days of hydration, however, the rate of penetration of the more viscous epoxy is decreased due to the smaller average diameter of pores available for flow. These conclusions are supported by more quantitative studies of the pore size distribution in PICP and will be discussed in detail in a separate publication.<sup>14</sup>

One might expect the molecular size to be an important factor in the per cent of available pore volume filled by any given monomer, since HCP has a large percentage of pores, especially at later ages, which are small enough to block the ingress of some of the monomers used. However, it is observed that the greatest loadings occur with PEG, which has the highest average molecular weight (MW) of all the monomers used and hence should be expected to show the least amount of penetration on size considerations alone. Two effects may help to explain or alter this hypothesis. One is that each PEG molecule is terminated by —OH groups, which should have a high affinity for the cement surface. Another is that PEG is water soluble and hence might exchange with the water on the surface of the gel during the period of soaking. However, PEG is solid at room temperature, and since the time (14 days) and temperature (75°C) were both longer and higher in the case of the PEG impregnations, one must be cautious in interpretation of these results.

Shrinkage of the monomer probably alters the amount of porosity eventually filled by polymer. It is evident from Table IV that, even though MMA monomer is able to fill a larger proportion of the pore spaces than TBS or epoxy, PMMA fills a smaller proportion of the porosity at all ages with respect to TBS and at early (one, three, seven days) ages with respect to epoxy. This is probably due to the larger shrinkage (18%) of MMA on polymerization as compared to TBS (7%) and the present epoxy system (6%).

#### Internal Friction of HCP and PICP

Internal friction of as-cured (undried) HCP as a function of temperature (100–273°K) is presented in Figure 1. A maximum is noted at about 195°K.

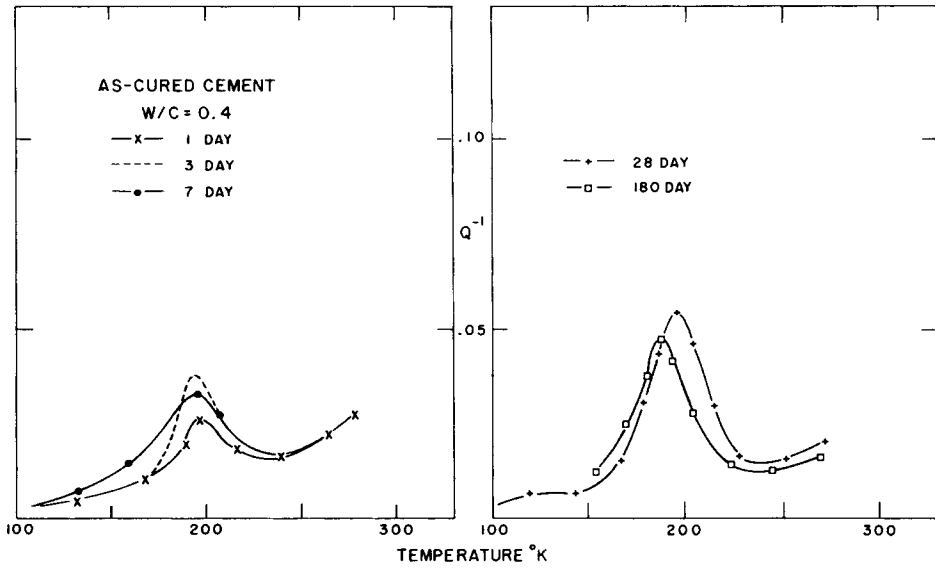


Fig. 1. Internal friction of as-cured HCP ( $w/c = 0.4$ ).

The magnitude of this peak appears to increase with time of hydration. This internal friction peak in the dynamic spectrum of HCP at 195°K has been previously studied by other workers.<sup>5,6</sup> Helmuth<sup>7</sup> has attributed this to a glass-like transition of water in an amorphous state adsorbed onto the surface of the cement

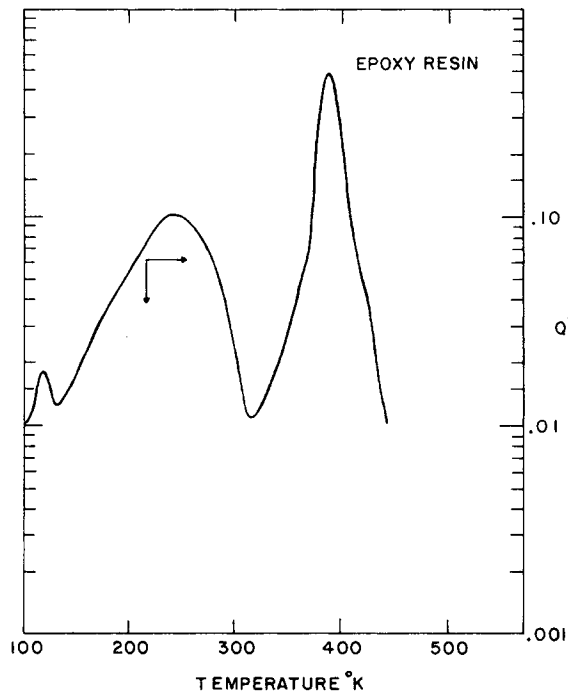


Fig. 2. Internal friction of epoxy resin.

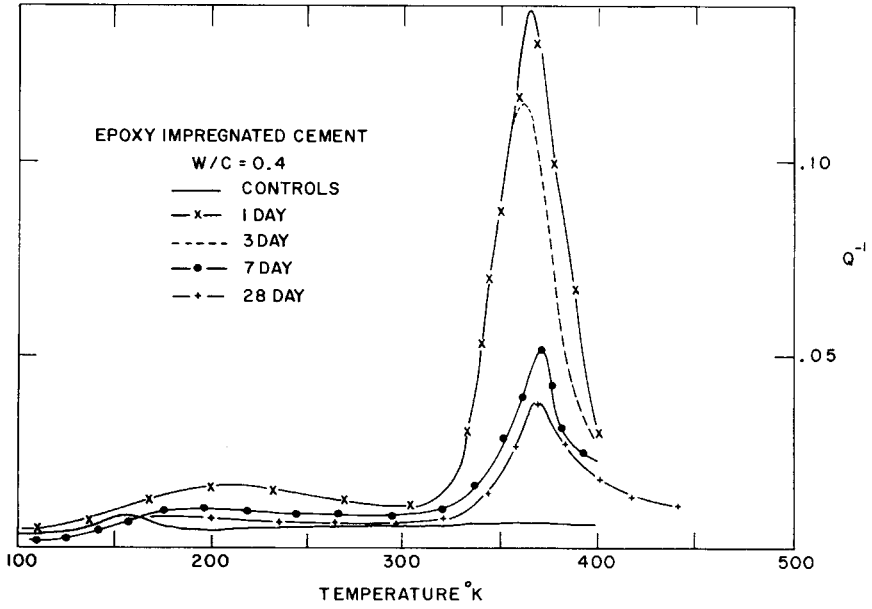


Fig. 3. Internal friction of epoxy PICP ( $w/c = 0.4$ ).

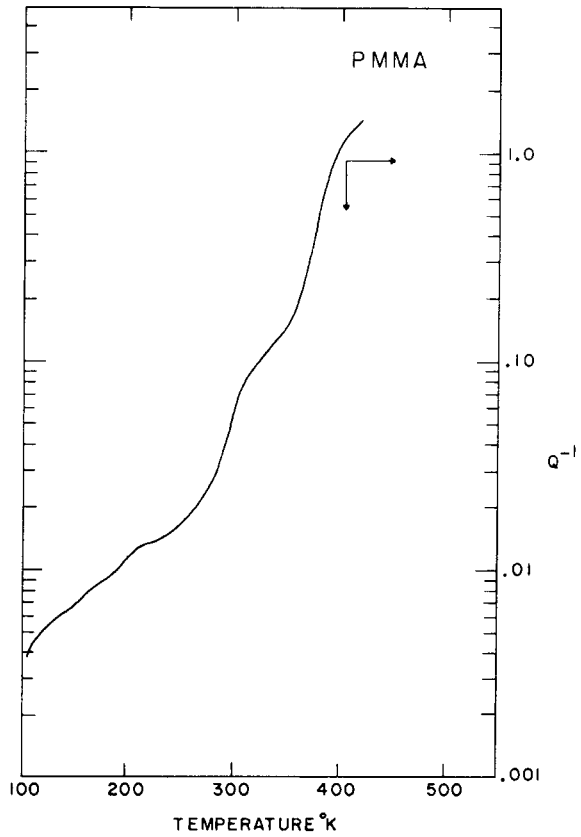


Fig. 4. Internal friction of PMMA.



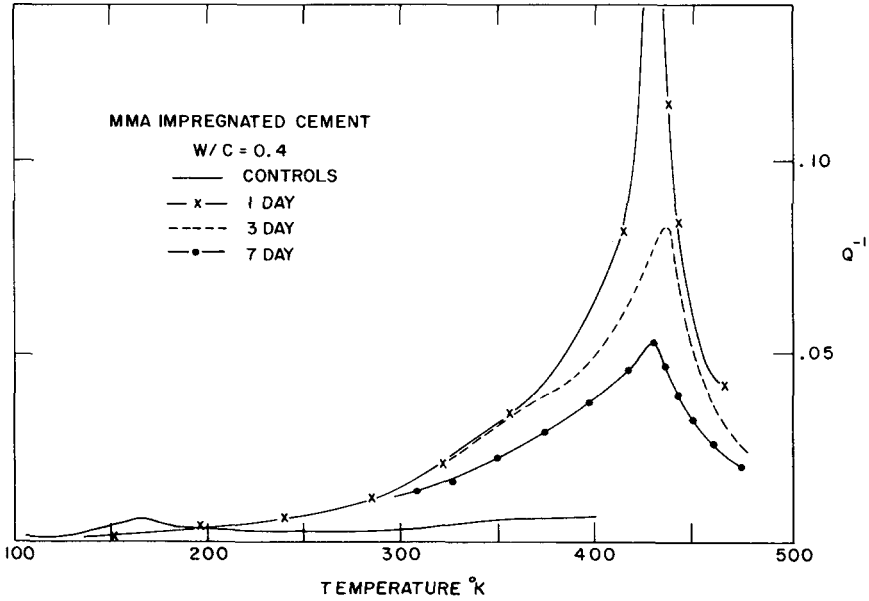


Fig. 5. Internal friction of PMMA. PICP ( $w/c = 0.4$ ) (1, 3, and 7 days of hydration).

gel. The magnitude of this peak has been shown<sup>6</sup> to be proportional to the internal surface of the HCP, as measured by water vapor desorption. In addition, the magnitude of this peak was found to be proportional to moisture content below a moisture content corresponding to approximately  $3V_m$ , where  $V_m$  is the volume of water necessary to completely fill a monolayer on the surface of the cement gel. In addition, Wittmann<sup>15</sup> has shown that the electrical conductance, capacitance, and absorption (as measured via Mossbauer spectroscopy) of HCP

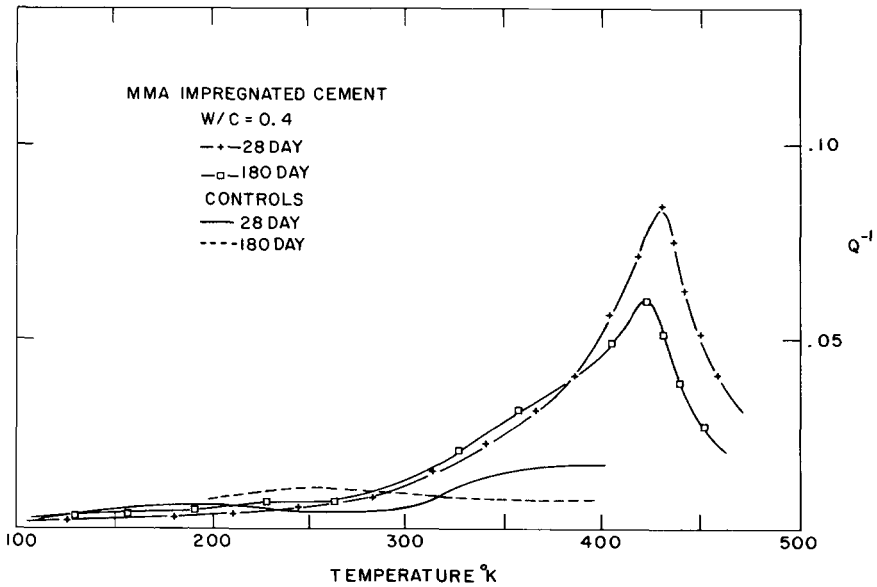


Fig. 6. Internal friction of PMMA. PICP ( $w/c = 0.4$ ) (28 and 180 days of hydration).

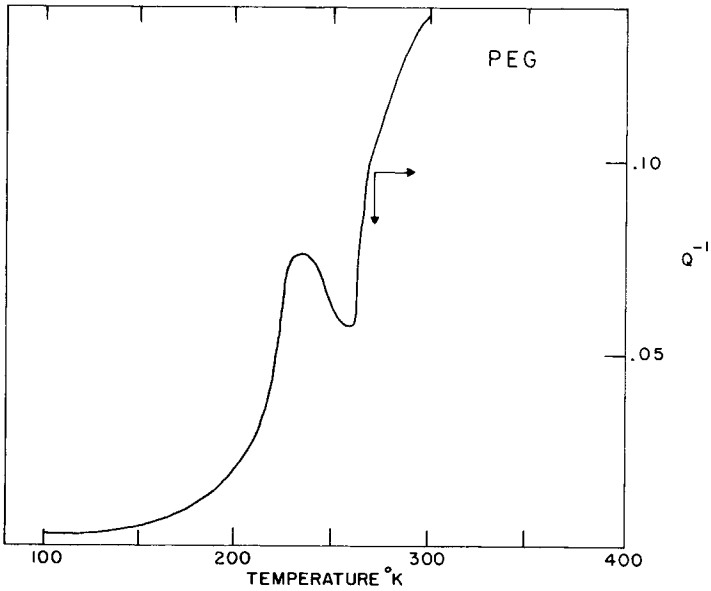
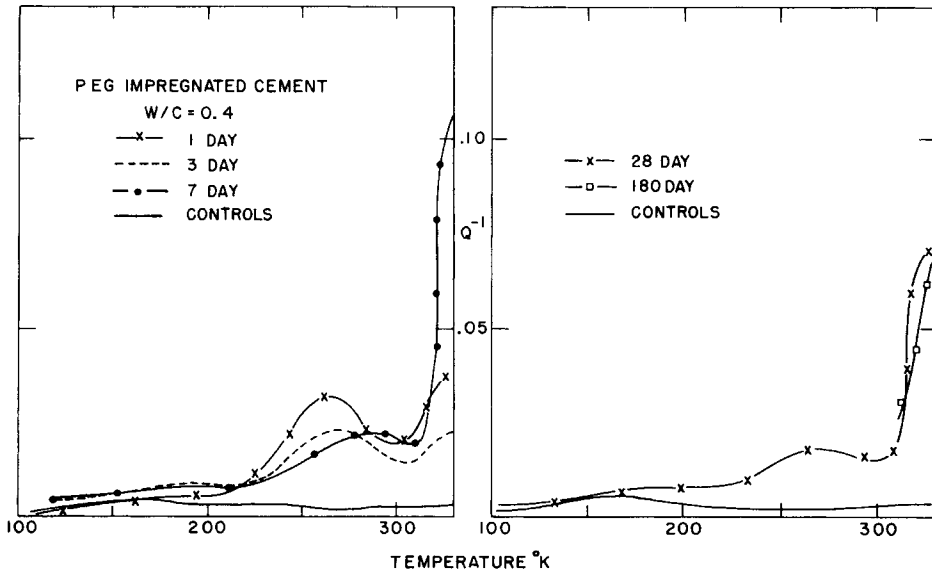


Fig. 7. Internal friction of PEG.

undergo significant changes in the same temperature region. Helmuth<sup>7</sup> has also shown that the thermal expansion of HCP undergoes a change in slope at about 160 $^{\circ}K$ . It has been previously shown<sup>16</sup> that the internal surface area of HCP increases with hydration time, and this study corroborates the suggestion that the internal friction peak near 195 $^{\circ}K$  is related to an interaction between the water in HCP and the internal surface of the gel phase.

Fig. 8. Internal friction of PEG. PICP ( $w/c = 0.4$ ).

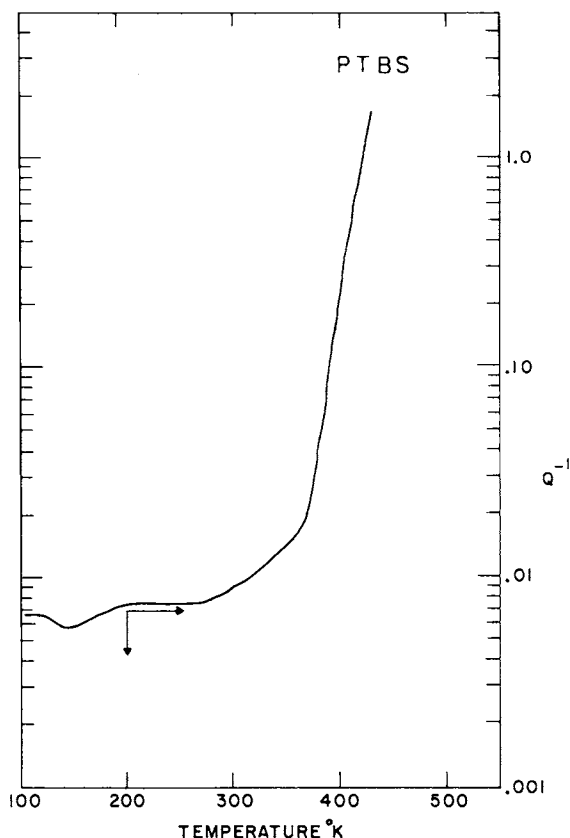


Fig. 9. Internal friction of PTBS.

Internal friction results for all oven-dried HCP control specimens (Figs. 3, 5, 6, 8, and 10) are relatively constant with temperature. The small peak evident at 155°K may be the residual adsorbate transition, which has been found<sup>6</sup> to shift to lower temperatures with decreasing moisture content. These low, relatively temperature-independent values of internal friction of HCP are fortunate for studies for PICP, since changes in internal friction in PICP can be relatively well delineated and associated with the polymer phase of any interfacial interactions.

Internal friction of both bulk epoxy resin and epoxy-impregnated cement paste is presented in Figures 2 and 3, respectively. As is known, the spectrum of the

TABLE V  
Comparison of  $Q_c^{-1}$  with  $v_f$  for  
Low-Temperature Damping Maxima in Epoxy PICP Specimens<sup>a</sup>

Maturity, days	$v_f$	$Q_c^{-1}$	$Q_c^{-1}$ (measured)
1	0.394	0.039	0.016
3	0.334	0.033	0.013
7	0.229	0.023	0.010
28	0.153	0.015	0.008

<sup>a</sup> Water-to-cement ratio ( $w/c$ ) = 0.4;  $Q_c^{-1}$  values are calculated from eq. (3),  $Q_c^{-1} = Q_f^{-1} \times v_f$ .

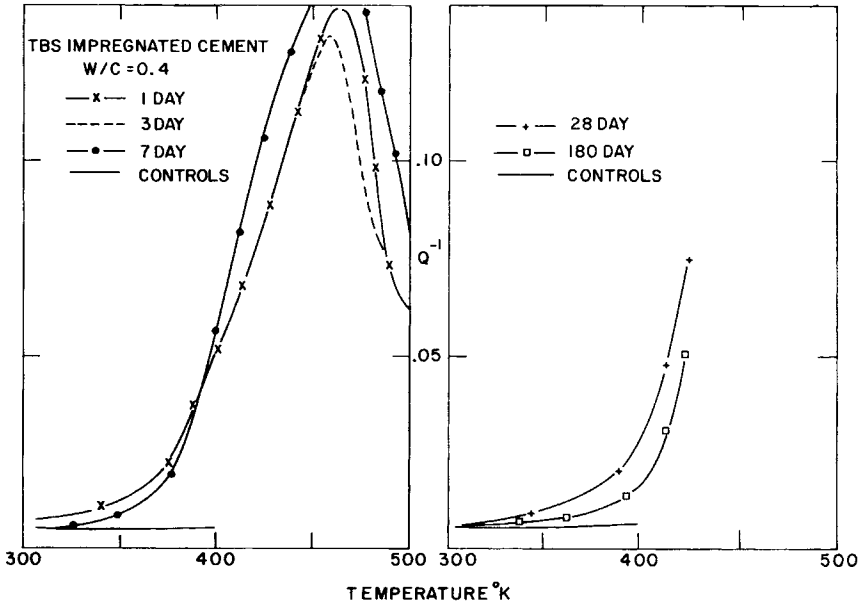


Fig. 10. Internal friction of PTBS. PICP ( $w/c = 0.4$ ).

bulk polymer exhibits two major peaks, one located at about 250°K and another at 385°K. Hirai and Kline<sup>17</sup> have attributed the peak at 250°K ( $\beta$ -peak) to either unreacted epoxide groups or —OH groups, while others<sup>18,19</sup> have attributed this peak to the crankshaft motion of ether groups. The peak at 385°K occurs near the glass transition temperature ( $T_g$ ) of the polymer. The spectrum of epoxy-impregnated HCP (Fig. 3) qualitatively follows the spectrum of the bulk epoxy system, although the peaks appear at slightly lower temperatures in this case. The very low values of  $Q^{-1}$  for the low-temperature peak make it difficult to determine the exact temperature at which it is maximized, especially in the case of the seven- and 28-day specimens.

The general reduction in magnitude of these peaks is assumed to be due to dilution of the epoxy by the cement phase and is much greater than would be expected on the basis of volume fraction of polymer present in the PICP. Nielsen<sup>20</sup> has proposed that the internal friction of filled polymers ( $Q_c^{-1}$ ) should follow the relationship

$$Q_c^{-1} = Q_m^{-1} \times v_m$$

where  $Q_m^{-1}$  is the internal friction of the unfilled polymer matrix at the same temperature and  $v_m$  is the volume fraction of polymer matrix. In systems such as PICP where the polymer can be considered as the filler, Nielsen's equation can be expressed as

$$Q_c^{-1} = Q_f^{-1} \times v_f \quad (3)$$

where  $Q_f^{-1}$  is the internal friction of the polymer filler and  $v_f$  is the volume fraction of polymer filler. A comparison of the calculated and experimental values of internal friction for this low-temperature peak (Table V), taking  $Q_f^{-1}$  at 250°K as 0.10 (Fig. 2) shows that the experimental values lie well below those

TABLE VI  
 Comparison of  $Q_{MR}^{-1}$  with  $\nu_f$  for Various PICP Specimens<sup>a</sup>

Maturity, days	$\nu_f$ polymer	% Decrease	$Q_{MR}^{-1b}$	% Decrease	$\nu_f \times Q_f^{-1}$
<b>Epoxy PICP<sup>c</sup></b>					
1	0.394	—	0.14	—	0.192
3	0.334	15.2	0.115	17.8	0.167
7	0.229	41.8	0.052	62.8	0.115
28	0.153	61.1	0.038	72.8	0.076
<b>PMMA PICP<sup>d</sup></b>					
1	0.342	—	0.15	—	0.444
3	0.288	15.7	0.084	44.0	0.374
7	0.236	30.9	0.052	65.3	0.306
28	0.184	46.2	0.085	43.3	0.239
180	0.175	48.8	0.060	60.0	0.227

<sup>a</sup> Water-to-cement ratio ( $w/c$ ) = 0.4.

<sup>b</sup>  $Q_{MR}^{-1}$  = Value of  $Q_c^{-1}$  at major relaxation temperature.

<sup>c</sup> For epoxy system,  $Q_f^{-1}$  = 0.50.

<sup>d</sup> For PMMA,  $Q_f^{-1}$  = 1.30.

predicted by Nielsen's equation. This may be the result of stress transfer to the lower damping matrix, which results in a smaller proportion of the available strain energy being available to the higher damping polymer. This assumes that strains in both polymer and matrix are approximately equal. Immobilization of the ether linkages or hydroxyl groups which have been postulated as being responsible for the low-temperature peak might also account for the decreased magnitude.

The peak centered about 385°K (Fig. 2) is attributed to the glass transition in the epoxy system. Reference to Figure 3 shows that the major transition in the PICP specimens occurs in roughly the same region. The peak appears to be broader in the PICP case, an effect which has been observed in the case of filled polymers.<sup>2-4</sup> Similar behavior seems to be evident when comparing the spectra of bulk PMMA (Fig. 4) with PMMA PICP (Figs. 5 and 6). The temperature of this peak will be denoted as the temperature of the major relaxation process ( $T_{MR}$ ), and the value of  $Q^{-1}$  at  $T_{MR}$  as  $Q_{MR}^{-1}$ .

It is instructive to compare the magnitude of this peak with the volume fraction of polymer loaded ( $\nu_f$ ). This is most easily done by calculating the relative decreases of  $\nu_f$  and  $Q_{MR}^{-1}$  with maturity of the HCP. This has been done for the epoxy and the PMMA PICP specimens in Table VI. The per cent decreases are relative to the first reported value of  $Q_{MR}^{-1}$ . One can see that the relative decrease in  $Q_{MR}^{-1}$  is somewhat greater than the relative decrease in  $\nu_f$ . In addition, the values of  $Q^{-1}$  calculated from Nielsen's equation are significantly higher than the experimental values. Thus, stress transfer effects and adsorption mechanisms may also be operative in determining the magnitude of  $Q_{MR}^{-1}$  as well as the low temperature damping maxima.

Internal friction results from PMMA and PMMA PICP are presented in Figures 4, 5, and 6. Bulk PMMA (Fig. 4) shows one major peak in the vicinity of 400–410°K ( $T_g$ ). No data were available above 410°K due to instrumental limitations. Results for PMMA PICP (Figs. 5 and 6) indicate the same general trend as for epoxy PICP, in that the internal friction spectrum of the impregnated

system qualitatively parallels that of the bulk polymer. In this case, however,  $T_{MR}$  appears at a slightly higher temperature than the corresponding peak ( $T_g$ ) in the bulk polymer. Lipatov<sup>21</sup> has noticed similar results in filled polymer systems.

Internal friction of PEG has been studied by a number of investigators.<sup>22-24</sup> PEG with a molecular weight of 1500 shows a relaxation of modulus and associated internal friction peak at about 245°K. In a study of the molecular weight dependence of this transition, Faucher et al.<sup>24</sup> found the  $T_g$  to approach the maximum temperature (256°K) at a molecular weight of 6000.

Changes resulting from PEG impregnation can be observed by comparing the plots of  $Q^{-1}$  versus  $T$  for the PEG PICP (Fig. 8) with the plot of  $Q^{-1}$  versus  $T$  for the bulk PEG (Fig. 7). The case of the PEG PICP, the  $T_g$ , as measured by the temperature at the maximum in the damping curve, has been shifted to approximately 265–270°K, as compared with 235–240°K for the bulk specimen. Since —OH groups have a high affinity for the cement gel, one might suggest that the chain ends are immobilized on the surface of the gel and hence limit the mobility of the polymer chains until a sufficiently high temperature is reached. In addition, the C—O—C groups in the chain might be affected by hydrogen bonding to the cement gel.

The final monomer used in this study, *tert*-butylstyrene (TBS), proved difficult to polymerize *in situ*. Internal friction results (Figs. 9 and 10) suggest this possible difficulty, as the magnitudes of  $Q_{MR}^{-1}$  (Fig. 10) are much higher than for the other PICP systems studied. Magnitudes in this case appear to increase, rather than decrease, with hydration time. For the 28- and 180-day specimens, no readings were obtainable above 430°K owing to excessive noise. Thus, it is possible that the hydrated cement in some way interferes with the polymerization of the monomer. These preliminary results seem to suggest that internal friction measurements might possibly be used to estimate the degree of monomer conversion during *in situ* polymerizations.

## CONCLUSIONS

1. Monomer loading into oven-dried hardened portland cement paste varies inversely with the hydration time of the paste phase. Differences in volume per cent loading between the four monomers studied (MMA, TBS, PEG, and epoxy resin) are greatest at longer hydration times.
2. Internal friction spectra of polymer-impregnated cement pastes qualitatively are related to the internal friction spectra of the bulk polymers used for impregnation.
3. So far as can be ascertained, magnitudes of internal friction peaks for epoxy- and MMA-impregnated specimens are less than what would be expected from the volume fraction of polymer present in the specimens and a simple rule of mixing.
4. Incomplete conversion of TBS monomer is probably reflected in large-magnitude internal friction peaks for the specimens impregnated with this monomer.

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