Dynamic mechanical and ultrasonic properties of polyurea

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Dynamic mechanical analysis (DMA) and ultrasonic measurements were carried out to study the temperature and frequency dependences of viscoelastic properties of polyurea. Master curves of Young’s storage and loss moduli were developed from the DMA data. Relaxation spectra were subsequently calculated by means of two approximate models, and the apparent activation energy of molecular rearrangements was also determined based on the temperature dependence of the time–temperature shift factor. Velocity and attenuation of longitudinal and shear ultrasonic waves in polyurea were measured in the 0.5–2 MHz frequency range between \( \frac{1}{C_0} \) \( \sim \) 60 and 30 \( \degree C \) temperatures. The complex longitudinal and shear moduli were computed from these measurements. Combining these results provided an estimate of the complex bulk and Young’s moduli at high frequencies. The results of the DMA and temperature and frequency shifted ultrasonic measurements are compared and similarities and deviations are discussed.

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\section*{1. Introduction}

Polyureas are a class of segmented block copolymer derived from the chemical reaction between an isocyanate and an amine. Similar to the segmented polyurethanes, polyurea generally microphase separates into high-\( T_g \) “hard” domains and relatively low-\( T_g \) “soft” domains (Fragiadakis et al., 2010; Das et al., 2007; Yi et al., 2006; Pathak et al., 2008). The hard segment domains, which form thread-like, crystalline structures, are typically dispersed in the continuous soft segment matrix (Das et al., 2007). The hard segments are extensively hydrogen-bonded and function as both reversible physical cross-links and reinforcing fillers, thus providing good mechanical properties (Pathak et al., 2008). By tailoring the underlying hard and soft domain structure through chemistry, polyurea offers a wide range of mechanical properties, from soft rubber to hard plastic. Together with its rapid polymerization and fire, abrasion, and corrosion resistance, polyurea has a myriad of applications in the coating industry, e.g. on transportation vehicles, pipelines, steel buildings and marine constructions (Shime and Mohr, 2009). More recently, it has been used either as a protective coating on metallic structures and buildings or an inserted layer in a blast-tolerant sandwich structure to impart improved blast resistance (Tekalur et al., 2008; Mock and Balizer, 2005; Amini et al., 2006; Bahei-El-Din and Dvorak, 2006; Amini et al., 2010a,b).

As an elastomer, polyurea exhibits viscoelastic behavior, which depends strongly on the strain rate (or frequency) and temperature, as well as pressure. A number of studies have been carried out to determine and interpret the viscoelastic behavior of polyurea, in order to understand its performance. Das et al. (2007) researched the dynamic mechanical properties of polyurea at low frequencies. Yi et al. (2006) and Sarva et al. (2007) studied the stress–strain behavior of polyurea in uniaxial compression over a range of strain rates from \( 10^{-3} \) s\(^{-1} \) to \( 10^4 \) s\(^{-1} \) in quasi-static tests and split Hopkinson pressure bar (SHPB) tests, and found that the flow stress magnitude of polyurea increases as the strain rate increases. Roland et al. (2007) reported the stress–strain measurements in uniaxial...
tension at intermediate strain rates (0.06–573 s⁻¹) using a drop weight test instrument, and subsequently they extended the strain rate to 830 s⁻¹ (Pathak et al., 2008). More recently, Shime and Mohr (2009) further evaluated the rate sensitive response of polyurea in a strain rate range of 10¹ to 10⁶ s⁻¹, using a modified SHPB system.

Because of its application as an impact-resistant coating, the response of polyurea to very high strain rates (high frequencies) is of some importance. However, the highest strain rate provided by the SHPB system is limited to frequencies higher than 10⁶ Hz. Characterizing rubbery polymers in such high frequency regions is difficult, even at small amplitudes. Typical dynamic mechanical analyzers are limited to frequencies below 100 Hz (Roland et al., 2007). When the frequency is higher than 1 MHz, we are not aware of any published literature on measuring the modulus by applying known values of the stress and measuring the strain (Sinha and Buckley, 2006). Under such conditions, an ultrasonic technique appears to be a valuable method to measure response in high frequency regions. In addition, the previous researchers have not reported the relaxation spectrum of polyurea. The relaxation spectrum is an inherent material property and dependent on molecular relaxation times. Therefore it should be theoretically independent of the experimental technique (Alvarez et al., 2007). Bulk behavior of polyurea, which is fundamentally different from the shear properties and considerably difficult to measure directly at high frequencies, is also rarely addressed.

In the present investigation, we report the results of a series of tests performed to study the temperature and frequency dependence of the viscoelastic behavior of polyurea, including results obtained using dynamic mechanical analysis (DMA) and ultrasonic wave measurements. Master curves are developed from the DMA data and relaxation spectra are then obtained. Ultrasonic wave measurement is carried out over the frequency range from 0.5 to 2 MHz at temperatures from −60 to 30 °C. Both longitudinal and shear waves are studied. From the calculated complex longitudinal and shear moduli, complex bulk and Young’s moduli at high frequencies are estimated. Finally, the results of the DMA and temperature and frequency shifted ultrasonic measurements are compared. The similarities of the two sets of measurements are analyzed, and the applicability of the theory is discussed.

2. Experimental details

2.1. Material

The polyurea was prepared by the reaction of a polycarboamide-modified diphenylmethane disocyanate (Isionate 2143L, Dow Chemical) and poly(tetramethyleneoxide-di-p-aminobenzoate) (Versalink P-1000, Air Products). In order to ensure that the reaction is completed and has produced some cross-linking, a stoichiometric ratio of 1.05:1 isocyanate to amine was used herein. First, the two components were degassed separately under 1 torr vacuum until most of the entrapped air bubbles were removed. Then, they were mixed for a few minutes while still under vacuum. Finally, the mixture was cast into a Teflon mold to obtain the test samples. Prior to measurements, the samples were cured at room temperature (25 °C) in an environmental chamber maintained at 10% relative humidity for two weeks.

2.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was conducted using a TA Instruments Dynamic Mechanical Analyzer 2980, using the corresponding software to collect and analyze the experimental data. The samples measured approximately 3 mm thick by 10 mm wide and were clamped at a free length of 17.5 mm. Both ends were cantilevered, i.e., they were constrained from rotation and sliding at both ends by clamping plates and excited into a sinusoidal transverse displacement at one end with a strain amplitude of 15 μm. The experiments were performed over the temperature range from −80 to 70 °C, stepping upwards in increments of 3 °C. At each temperature step, five frequencies of 1, 2, 5, 10 and 20 Hz were tested sequentially. Thermal soaking times of 3 min at the beginning of each step minimized the effects of thermal gradients. Liquid nitrogen was used to cool the system to sub-ambient temperature.

2.3. Ultrasonic measurement

The ultrasonic system used in the present work was built upon a personal computer (PC) system. As illustrated in Fig. 1(a), it consists of a Matec® TB-1000 tone-burst signal generating and receiving card, Panametrics® contact transducers, a 100:1 attenuator, and a Tektronix DPO 3014 digital phosphor oscilloscope. The dashed rectangle in Fig. 1(a) represents the temperature control chamber. Toneburst signals of given frequencies are sent from the card to the transmitting transducer, propagate through the sample to the receiving transducer, and eventually sent directly to the oscilloscope. The received signals differ in arrival time and amplitude because of both the different thicknesses of samples sandwiched between the two transducers and the wave speed in the material. In essence, the small thickness experiment is the calibration needed to
remove the effect of interface impedance between the transducer and the sample, as well as the time-delay in the electronics and the transducers. Therefore comparison between the large and small thickness tests represents only the effect of extra material on the time-delay (wave speed) and transmission amplitude (material loss).

2.3.1. Longitudinal wave measurement

A pair of V133-RM Panametrics® contact transducers was used to generate and receive longitudinal ultrasonic signals. The nominal element size of the transducer is $\phi 8.9 \times 10.7$ mm and the nominal center frequency is 2.25 MHz. Braider oil was used to achieve better surface coupling between the transducers and the sample. Samples used in longitudinal wave tests have the dimensions $13 \times 13 \times 6$ mm. The temperature of the sample was varied stepwise by 10 °C decrements from 30 to −60 °C and at each step was stabilized 10 min to minimize the effects of thermal gradients. Measurements were made in the frequency range from 0.5 to 2 MHz.

A detailed procedure is provided here. As illustrated in Fig. 1(b), first, one sample was inserted between the two transducers. The received signal was recorded at each temperature step. In the second test, two samples (including the first one) were inserted between the two transducers. The received signal was also recorded at each temperature step. By comparison of the signals from these two tests, the time shift and amplitude change of the received signal were obtained. For example, Fig. 2 shows the two received signals at 0 °C and 1.6 MHz. “Signal 1” represents the received signal when just one sample was used; “Signal 2” represents the received signal when two samples were used. Consequently, the velocity in the sample can be calculated according to the relation:

$$v_L = \frac{d}{t};$$  \hspace{2cm} (1)

where $d$ is the thickness of the second sample (measured at room temperature), $t$ represents the time shift observed between the two tests, as indicated in Fig. 2.

The attenuation coefficient per unit thickness, $\alpha$ (Neper/cm), is given by

$$\alpha = \frac{1}{d} \ln \frac{A_0}{A};$$  \hspace{2cm} (2)

where $A_0$ and $A$ are the amplitudes of the received signals from the first and second test respectively, as indicated in Fig. 2. Average values from at least six pairs of peaks were used in the following calculation.

2.3.2. Shear wave measurement

A pair of V153-RM normal incidence shear wave transducers was used to generate and receive shear ultrasonic signals. The nominal element size of the transducer is $\phi 17.8 \times 16$ mm and the nominal frequency is 1 MHz. The transducers were in contact via a thin film of a shear wave couplant on the sample surface. As illustrated in Fig. 1(b), a block diagram of ultrasonic experiment setup is shown. The dashed rectangle in (a) represents the temperature control chamber, which contains the sample and transducers, as shown in (b) where three sample configurations are shown. The first two configurations are used (with one and two sample pieces, respectively, to measure the time of travel for two thicknesses) for longitudinal waves. The bottom configuration is used for shear wave measurements. The aluminum rod delays the shear wave compared to the longitudinal component. In this configuration, two thin samples of different thicknesses were used.
Fig. 1(b), an aluminum rod was inserted in the wave path between the generating transducer and the sample to delay the shear waves compared to the longitudinal waves which inevitably accompany the generation of the shear wave by the piezoelectric transducers. This method has been used by some researchers (Cunningham and Ivey, 1956; Bezot and Hesse-Bezot, 2002). The dimension of the aluminum rod is quite critical (Cunningham and Ivey, 1956). Since longitudinal waves travel faster than shear waves in metal rod, the length of the aluminum rod should be long enough to ensure that the effect of the longitudinal waves on the receiving transducer is over before the shear waves arrive. However, if it is too long, the shear signals will be seriously attenuated, and reflected longitudinal waves may interfere with the shear waves. The diameter must be such that there are no interference effects due to longitudinal waves coming from the sides of the rod. The rod used herein is 76.2 mm in diameter and 50.8 mm long. Since shear waves are highly attenuated in elastomers, it is necessary to use very thin samples. In order to avoid introducing interfaces which are comparable in thickness to that of the sample, two samples of 0.77 and 1.22 mm thicknesses were used. Unlike the longitudinal wave measurement, only one sample was employed in each test. The shear wave velocity and attenuation were also calculated according to Eqs. (1) and (2).

Because of the substantial attenuation in polyurea at higher temperatures, shear wave transmission in the frequency region from 0.5 to 2 MHz was not reliably measured at temperatures exceeding 0 °C. Consequently, samples were studied from 0 to −50 °C, stepping downwards in decrements of 10 °C. The hold time at each temperature was increased to 20 min due to the utilization of the aluminum rod.

3. Theory

Problems involving wave propagation in linear viscoelastic media are generally solved using Laplace or Fourier transforms; see, for example, Liu and Subhash (2006) or Zhao and Gary (1995), respectively. Here we consider the simple case of the propagation of a single frequency harmonic plane wave through an isotropic homogeneous linear viscoelastic medium. In the frequency domain after Fourier transform the wave equation is

\[ M'' \ddot{u} + i \omega \dot{u} = \rho \omega^2 u, \]

where \( u \) is the phasor form of particle displacement from its equilibrium position (in the x direction for longitudinal waves, and in a transverse direction for shear waves); \( \rho \) is the density; \( M'' \) represents the effective complex modulus for the considered wave polarization (longitudinal or shear); \( \omega \) is the angular frequency. The wave velocity is given by the usual relation:

\[ c' = c'' = \frac{M'}{\rho} \times \omega^{1/2}. \]

The direct solution of Eq. (4) gives:

\[ M' = \rho \left[ (c')^2 - (c'')^2 \right], \quad (5a) \]

\[ M'' = 2 \rho c' c''. \quad (5b) \]

where \( M' \) and \( M'' \) are the real and imaginary components of \( M' \), i.e., storage and loss moduli respectively.

The harmonic solution of Eq. (3) is:

\[ u = u_0 \exp \left\{ i \omega \left( \frac{1}{c'} - \frac{x}{c''} \right) \right\} \]

\[ = u_0 \exp \left\{ i \omega t \left\{ \exp \left( -\frac{iox}{c'} \right) \right\} \right\} \]

\[ = u_0 \exp \left\{ i \omega t \exp \left\{ -\frac{\omega c' x}{(c')^2 + (c'')^2} \right\} \exp \left\{ -\frac{\omega c' x}{(c')^2 + (c'')^2} \right\} \right\}. \]

Comparing Eq. (6) with the attenuated harmonic wave with phase velocity \( c' \), and amplitude attenuation constant \( c' \):

\[ u = u_0 \exp \left\{ i \omega t - i \left( \frac{\omega}{c'} \right) x \right\}, \]

the real and imaginary parts of the complex velocity are given by the relations:

\[ c' = \frac{c}{1 + r^2}, \quad (8a) \]

\[ c'' = \frac{cr}{1 + r^2}, \quad (8b) \]

where the dimensionless parameter \( r \) is defined by

\[ r = \frac{2c}{\omega}. \]

From Eqs. (5) and (8) we find:

\[ M' = \frac{\rho c^2 (1 - r^2)}{(1 + r^2)^2}, \quad (10a) \]

\[ M'' = \frac{2 \rho c^2 r}{(1 + r^2)^2}. \quad (10b) \]

For longitudinal wave transmission, the quantity \( M' \) represents complex longitudinal modulus \( L'' \):

\[ M' = L'' = K' + \frac{4}{3} G', \quad (11) \]

where \( K' \) is the bulk modulus. In shear tests, the modulus is simply the shear modulus of the material:

\[ M'' = G'. \quad (12) \]

From the two complex moduli \( K' \) and \( G' \), the complex Young’s modulus can be calculated from the relation:

\[ E' = \frac{9K'G'}{3K' + G'}. \quad (13) \]

Separating the real and imaginary parts of Eq. (13) will lead to quite complicated expressions for the storage and loss components. The calculations in this work were made using the complex form of Eq. (13).

4. Results and discussion

4.1. DMA results

Fig. 3 shows the temperature dependence of the storage and loss components of the complex Young’s modulus at five frequencies obtained from DMA low frequency measurements. It can be seen that only one relaxation peak oc-
The mechanical behavior of polyurea is dictated by proper combination of time (frequency) and temperature. The results in Figs. 4 and 5 represent the proper way of combining these two variables based on the method of reduced variables (Ferry, 1980).
The relaxation spectrum $\Phi(\tau)$, represents the contribution of moduli by relaxation mechanisms whose time constants are around $\tau$ (Ferry, 1980):

$$E'(\omega) = E_0 + \int_{-\infty}^{\infty} \left[ \Phi(\omega^2\tau^2) \right] d\ln \tau,$$

$$E''(\omega) = \int_{-\infty}^{\infty} \left[ \Phi(\omega^2\tau^2) \right] d\ln \tau,$$  \hspace{1cm} (15a)

The relaxation spectrum $\Phi$ can be calculated from the frequency dependence of $E'$ and $E''$, by the first approximation formula suggested by Ferry (1980):

$$\Phi(\tau) = E'(d \log E'/d \log \omega) \bigg|_{1/\omega=\tau},$$

$$\Phi(\tau) = E''(1 - d \log E''/d \log \omega) \bigg|_{1/\omega=\tau},$$  \hspace{1cm} (16a)

where $\tau$ is the relaxation time and $d$ represents differentiation.

A modified second approximation, given by Williams and Ferry (1953), provides the following formulas for determining $\Phi$:

$$\Phi(\tau) = A E(1 - \left| \frac{d \log E'}{d \log \omega} - 1 \right|) \bigg|_{1/\omega=\tau},$$

$$\Phi(\tau) = B E(1 - \left| \frac{d \log E''}{d \log \omega} \right|) \bigg|_{1/\omega=\tau},$$  \hspace{1cm} (17a)

where $m$ is the slope of a plot of $\log \Phi$ (from the first approximation calculation) against $\log \tau$. Calculations of $\Phi$ derived from the data of Fig. 4 based on the first approximation and the modified second approximation formulas are depicted in Fig. 6. There is good agreement between the values from the storage ($E'$) and loss moduli ($E''$). This agreement is a confirmation of the internal consistency of the experimental data (Williams and Ferry, 1954), since the storage and loss moduli are based on two independent physical measurements; nevertheless they result in the same relaxation spectrum.

An apparent activation energy for the $\alpha$-relaxation processes, $E_a$, can be determined from the temperature dependence of $E'$ and $E''$ through the shift function $\alpha_T$ (Wang and Ploehn, 1996):

$$E_a = R \frac{d[\ln(\alpha_T)]}{d(1/T)} = 2.303R \frac{d[\log(\alpha_T)]}{d(1/T)},$$  \hspace{1cm} (19)

where $R = 8.314$ J mol$^{-1}$ K$^{-1}$ is the gas constant. $E_a$ for polyurea was obtained by calculating the numerical derivative of $\log(\alpha_T)$ and was plotted as a function of temperature in Fig. 7. The value of $\log(\alpha_T)$ described by WLF equation, Eq. (19) is converted into the form:

$$E_a = 2.303R \frac{C_1C_2T^2}{(C_2 + T - T_0)^2},$$  \hspace{1cm} (20)

where $C_1 = 18.86$, $C_2 = 161.1$ and $T_0 = 1$ °C. The calculated $E_a$ from Eq. (20) is also shown in Fig. 7. The two sets of data are in good agreement, except at temperatures close to the two ends of the temperature region. This is due to the lower accuracy of the shifting procedure as stated previously. It can be seen the calculated $E_a$ increases with decreasing temperature as the glass transition is approached. This behavior primarily reflects changes in a segmental or monomeric friction coefficient, which involves volume.

![Fig. 7. Temperature dependence of the apparent activation energy for the $\alpha$-relaxation processes in polyurea.](image-url)
and energy requirements for local co-operative motions (Bueche, 1953; Fox and Flory, 1950).

4.2. Ultrasonic measurement

The longitudinal wave velocity and attenuation coefficient per unit thickness as a function of temperature at 1.6 MHz are depicted in Fig. 8. It can be seen that the longitudinal wave velocity increases monotonically with decreasing temperature, while the attenuation coefficient per unit thickness peaks around the glassy transition at a value of about 1.8 Neper/cm. Similar behavior has been observed by Nolle and Mowry (1948) and Ivey et al. (1949) for some rubbers. These curves have relatively the same form at all measured frequencies.

Fig. 9 shows the longitudinal wave velocity as a function of frequency at all temperatures. It can be seen that the longitudinal wave velocity is relatively insensitive to frequency in the region studied. The frequency dependence of attenuation per wavelength and attenuation coefficient per unit thickness is illustrated in Fig. 10. Only data points for which the sample thickness is more than twice the wavelength are shown. The measured attenuation coefficient per unit thickness is a nearly linear function of frequency with the slope proportional to the wave speed (Fig. 10(b)). Therefore, attenuation per unit wavelength is almost constant as a function of frequency; see Fig. 10(a). Figs. 9 and 10(b) suggest that material properties are frequency-insensitive under these conditions.

From the primary data on longitudinal wave velocity and attenuation coefficient per unit thickness, the longitudinal storage modulus $L'$ and longitudinal loss modulus $L''$ are calculated from Eq. (10), as shown in Fig. 11.

The shear wave measurement was conducted at 5 temperatures ($-50$, $-40$, $-20$, $-10$, $0$ °C) using 8 separate voltage pulses with apparent excitation frequencies of 0.6–2.0 MHz (0.2 MHz step size). However, the transmitted shear stress wave frequency content was not substantially different from one excitation to others. The apparent frequency of the transmitted stress waves seems to be close to 1 MHz, the design frequency of the transducers. We believe that this effect is due to the significant impedance mismatch between the transducers and samples, which makes transmission more difficult at other frequency values. At each temperature, we calculated the average values of velocities and attenuations per wavelength at all apparent excitation frequencies and found the apparent frequency of the stress wave. We averaged the measured attenuation and wave velocity for those cases that were close to 1 MHz. The rest of the data is not reported and used here. Figs. 12 and 13 show the velocity and attenuation per wavelength of shear wave as a function of temperature respectively. Similar to the longitudinal wave velocity, shear wave velocity increases rapidly with decreasing temperature. However, the attenuation per wavelength of shear wave decreases as temperature decreases.

Fig. 8. Longitudinal wave velocity and attenuation coefficient per unit thickness in polyurea as a function of temperature at 1.6 MHz.

Fig. 9. Longitudinal wave velocity as a function of frequency.

Fig. 10. Attenuation per wavelength (a) and attenuation coefficient per unit thickness (b) of longitudinal wave as a function of frequency.
The shear storage and loss moduli were also calculated from the velocity and attenuation using Eq. (10) and their temperature dependence is shown in Fig. 14. The points at $-30\degree C$ and temperatures higher than $0\degree C$ are based on the interpolated and extrapolated portions of the velocity and attenuation curves in Figs. 12 and 13. The shear storage modulus increases sharply as the temperature decreases. The calculated shear loss modulus at $-30\degree C$ is much higher than that at $40\degree C$, which might be due to experimental error.

The storage and loss components of the complex bulk modulus at 1.0 MHz are calculated from Eq. (12) and are plotted as a function of temperature, as shown in Fig. 15. Similar to the longitudinal and shear storage moduli, the bulk storage modulus is demonstrated to increase with decreasing temperature. The magnitudes of shear storage moduli are approximately 3% of the bulk storage modulus at higher temperatures, as expected for a nearly incompressible material. Near the glass transition, this percentage increases as the temperature decreases. The bulk viscous loss is non-zero at all temperatures.

From the complex bulk and shear moduli, the Young’s storage and loss moduli are evaluated and master curves at a reference temperature $T_{ref} = 1\degree C$ are constructed by reducing these calculated data based on the TTS principle. The shift factor obtained from the DMA data is used here. Correction to the moduli was made by multiplying the data at temperature $T$ by a factor $(T_{ref}/T)$. Comparison between master curves of the complex Young’s modulus from DMA data and ultrasonic measurement data is shown in Fig. 16. The two master curves of Young’s storage modulus are in agreement with each other. In contrast, the agreement of the two master curves is poor in the case of
5. Summary and conclusions

In this work, the viscoelastic properties of polyurea were examined by dynamic mechanical analysis and ultrasonic measurements. The former was carried out over the temperature range from −80 to 70 °C at five frequencies. Master curves were constructed for the complex Young’s modulus. Relaxation spectra were subsequently calculated by means of two successive approximation methods. Temperature dependence of the apparent activation energy was also determined, which shows an increase approaching the glass transition. The apparent activation energy represents the relaxation mechanism controlled by the availability of free volume. The profile agrees with earlier WLF expectations and is distinguished from a constant value as postulated in a rate kinetic model (Williams et al., 1955). Velocity and attenuation of both longitudinal and shear ultrasonic waves were measured in polyurea in a frequency range 0.5–2 MHz and the temperature range −60–30 °C. The complex longitudinal, shear, bulk and Young’s moduli were computed from the ultrasonic measurement data with the aid of relationships between mechanical properties. Master curves of Young’s storage and loss moduli were deduced from these values by using the shift factors determined from the DMA measurements and compared with those derived from the DMA data. It is noteworthy that by applying the time–temperature superposition principle, one can predict the shear stiffness at ultrasonic frequencies using only DMA data. However, the predicted loss clearly is below the experimental measurements at high frequencies. We believe that at higher frequencies, the hard domains of polyurea become resonators and therefore contribute to higher loss throughout the material. It is expected that by control of size, properties, and distribution of hard domains in block copolymer and introduction of other nano-scale or micro-scale inclusions, the loss spectrum can be enhanced and tailored towards specific applications.

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References


Fig. 15. Bulk storage and loss moduli as functions of temperature at 1.0 MHz. The hollow points are based on the curve-fitting done in Figs. 11 and 12.

Fig. 16. Master curves of Young’s storage and loss moduli at a reference temperature $T_{ref}=1^{\circ}C$. The hollow points are from the interpolated and extrapolated portions of the ultrasonic measurements.


