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Thermochimica Acta 392–393 (2002) 1–12

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Method for analysis of dynamic mechanical thermal analysis data using the Havriliak–Negami model[☆]

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Received 15 November 2000; accepted 17 April 2001

Abstract

A new method is presented for analysis of single frequency dynamic mechanical thermal analysis (DMTA) data in the complex plane. The applicability of the method is restricted to cases where the polymer is thermorheologically simple and whose dynamic mechanical properties are well described by the Havriliak–Negami (HN) model. The method involved two steps: (1) the HN model was used to describe the shape of the complex plane representations of the DMTA data; and (2) the HN relaxation time (τ) was solved for at each temperature over which experimental measurements were made. This procedure resulted in the determination of four temperature independent HN parameters (α, β, E_0, and E_∞) and one temperature dependent parameter, $\tau(T)$. These model parameters were then used to calculate the dynamic mechanical properties over a range of temperatures and frequencies. The calculated moduli and loss factors were generally in good agreement with the experimental values for two elastomeric materials, neoprene and plasticized polyvinylchloride, that were subjected to the analysis procedure, over an 80° temperature range and three decades of frequency. It was also demonstrated that complex plane analysis of frequency multiplexed DMTA data could be used to calculate shift factors for time–temperature superposition. The corresponding master curves for storage modulus and loss factor created by horizontal shifts along the log(frequency) axis were smooth, providing additional support to the validity of the analysis procedure.

Keywords: Havriliak–Negami; Viscoelasticity; Time–temperature superposition

1. Introduction

Time–temperature superposition is commonly used with dynamic mechanical thermal analysis (DMTA) of polymeric materials to extend the frequency range of the measurement. This is typically accomplished by an empirical approach in which constant temperature data segments are shifted along the log(frequency) axis, such that adjacent segments overlap and a smooth master curve is obtained [1]. An alternative to the conventional approach for generation of master curves from DMTA data is to use viscoelastic models that include frequency and temperature as variables. Once model parameters are fit to experimental data, the models may be used to predict the polymer dynamic mechanical properties over a wide range of temperature and frequency.

The dynamic mechanical and dielectric relaxation behavior of polymers in the frequency or time domains has been described by a number of models, including the single relaxation time Cole and Cole [2], Davidson and

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[☆] Presented at the 28th NATAS Conference, Orlando, FL, USA, 4–6 October 2000.

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PII: S0040-6031(02)00064-3

Cole [3], Havriliak and Negami [4], and Kohlrausch–Williams–Watts (KWW) equations [5]. The Havriliak–Negami (HN) model relates the complex modulus (E^*) to the rubbery plateau modulus at low frequencies (E_0) and the glassy plateau modulus at high frequencies (E_∞) through the following equation [4,6]:

$$E^*(\omega) = \frac{E_0 - E_\infty}{[1 + (\mathrm{i}\omega\tau)^\alpha]^\beta} + E_\infty \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency, $\mathrm{i} = \sqrt{-1}$ is the unit imaginary number, α is related to the width of the loss peak, β controls the asymmetry of the loss peak, and τ is the relaxation time. The parameters α and β can take on values between 0 and 1. Hartmann et al. have shown that the five parameter HN model can accurately describe the dynamic mechanical behavior of polymers in the frequency domain, including the height, width, position, and shape of the loss peak [6].

In order to use the HN model for analysis of DMTA data, it is necessary to somehow incorporate the temperature dependence of the complex modulus, $E^*(T)$. This may be accomplished by making some or all of the HN parameters temperature dependent. Alig et al. used this approach in [7] by introducing a linear dependence of the plateau moduli on temperature, and giving the relaxation time a temperature dependence that could be described by a Vogel–Fulcher equation [8,9]. The method of Alig et al. required a total of nine adjustable parameters be fit to the experimental data.

A new approach is described in this paper for the analysis of DMTA data in the context of the HN model. The method involves the fit of four temperature independent HN parameters in the complex plane of E^*, followed by a direct calculation of the temperature dependent relaxation time $\tau(T)$ from the HN equation. There is no specific functional dependence for τ on temperature assumed, and there are no additional parameters introduced. The method described yields not only the HN model parameters from single frequency DMTA data, but allows one to predict the complex modulus over a wide range of temperatures and frequencies.

2. Materials

Isodamp C-1002, a plasticized polyvinylchloride, was obtained from EAR Division of Cabot Corp. A neoprene elastomer, an underwater transducer material, was nominally manufactured to specifications of 5109S [10], except that it contained approximately 60 ph carbon black.

3. Experimental

All experimental data were collected on a TA Instruments DMA 2980 machine, using the tension-film clamping arrangement. Specimens were excited using a 20 μm dynamic displacement, and a small preload (0.2 N) to ensure that the specimens were always in tension. For the Isodamp C-1002, measurements of the complex Young's modulus were made over a temperature range from −60 to 40 °C, in 5 °C intervals, at the following frequencies: 0.2, 0.3, 0.6, 1, 2, 3, 6, 10, 20, 30, 60, 125, 150, and 175 Hz. For the neoprene elastomer, measurements were made over a temperature range from −80 to 50 °C in 5 °C intervals, except in the region of the glass transition (−45 to −12 °C), where the measurements were made in 2 °C intervals. The frequencies used for the neoprene elastomer were 0.2, 0.3, 0.6, 1, 2, 3, 6, 10, 20, 30, 60, 125, and 150 Hz. The temperature was allowed to come to equilibrium and held constant while measurements were made at each frequency. The temperature was then incremented in a stepwise fashion throughout the temperature range, with measurements being made under isothermal conditions.

4. Complex plane analysis

For thermorheologically simple materials [11] (i.e. those for which time-temperature superposition is a valid procedure), analysis of dynamic mechanical data in the complex plane offers some useful insights and advantages. The complex Young's modulus is defined in terms of its real (storage modulus, E') and imaginary (loss modulus, E'') components:

$$E^* = E' + iE'' \tag{2}$$

$$\tan\delta = \frac{E''}{E'} \tag{3}$$

where tan δ is also known as the loss factor. Jones [12,13] has shown that for thermorheologically simple polymers, the log(tan δ) versus log(storage modulus) plot, also known as Wicket plot, forms an inverted U-shaped curve. Furthermore, if the complex modulus of a polymer is determined for various temperatures and frequencies, then all loss factor-modulus points associated with these temperatures and frequencies will lie on a unique curve. Jones has demonstrated this for several polymers, including polystyrene, an acrylic adhesive, a polyvinylchloride copolymer, and a plasticized polyvinylchloride [12,13]. Our experience in this laboratory has confirmed similar results for a number of other polymers. Another complex plane representation often used for dynamic mechanical data is the Cole–Cole plot, in which the loss modulus (E'') is plotted against the storage modulus (E'). As in the case of the Wicket plot, the Cole–Cole data for a given polymer lie on a unique curve that is independent of temperature and frequency.

If one has data for the complex modulus over a narrow range of frequencies, or for that matter at a single frequency over a wide range of temperatures (i.e. DMTA data), it is not immediately obvious from Eq. (1) how one might extract the five HN parameters from this data. However, it is possible to do this in two steps: (1) plot the modulus in the complex plane, and solve for α, β, E_0, and E_∞; and (2) solve for τ at each temperature over which measurements were made. This approach is based on the following assumptions.

(a) The complex plane representation of the modulus is independent of τ. An analysis of Eq. (1) demonstrates that either the Wicket plot or Cole–Cole representation of the complex modulus computed from Eq. (1) depends on four of the five HN parameters: α, β, E_0, and E_∞. However, the Wicket plot is essentially invariant of the HN relaxation time τ, as demonstrated in Fig. 1.

(b) The only temperature dependent HN parameter is τ. While there is no a priori reason for this to be true, it will be shown that temperature independent values for α, β, E_0, and E_∞ may be successfully employed to describe the temperature and frequency dependent complex modulus.

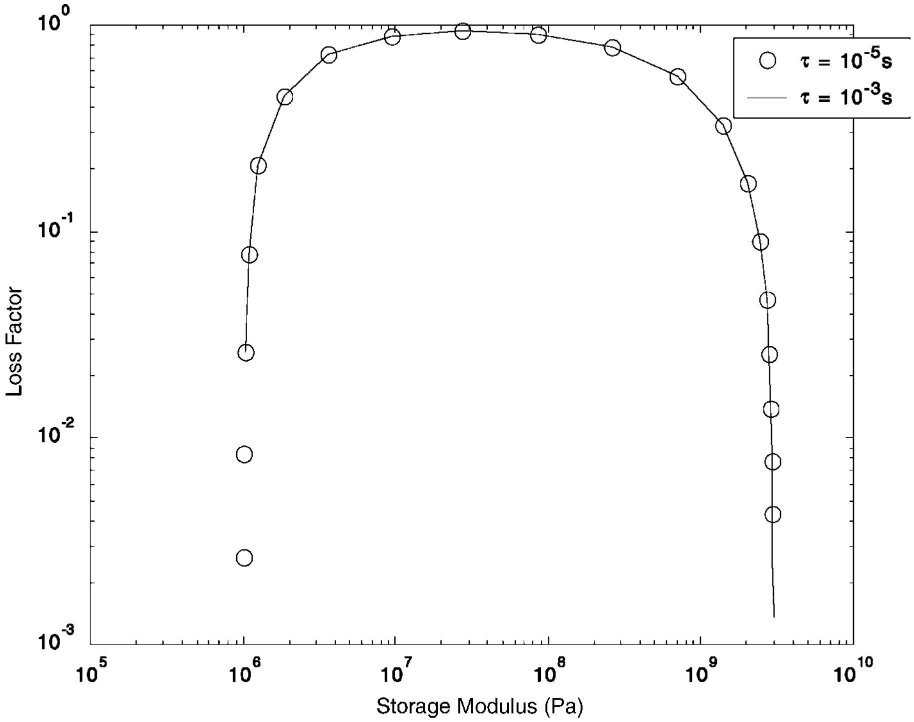

Fig. 1. Wicket plot for two hypothetical polymers with HN parameters $\alpha = 0.5$, $\beta = 0.5$, $E_0 = 1$ MPa, $E_\infty = 3$ GPa, and either $\tau = 10^{-5}$ or 10^{-3} s. The frequency range for the calculations was 10^{-7}–10^{12} Hz.

The detailed procedure for step (1) is discussed below. The procedure for step (2) is discussed in the next section.

Trial values for α, β, E_0, and E_∞ were used to compute $E^*(\omega)$ according to Eq. (1), setting $\tau = 1$ and over the frequency range 10^{-20}–10^{15} Hz. The degree of fit of the calculated complex modulus to the experimental modulus for each set of trial parameters was examined in the complex plane, using either the Cole–Cole (E'' versus E') or Wicket plot (log(tan δ) versus $\log E'$) analysis. For the Cole–Cole plot, the error function used was related to the sum of the squares of the differences between the experimental and calculated loss moduli, E'', over a given range of storage moduli, E'.

Cole–Cole error function

$$f_1 = \frac{\sum_{E'} |E''_{\text{exp}} - E''_{\text{calc}}|^2}{\sum_{E'} |E''_{\text{exp}}|^2} \tag{4}$$

where E''_{exp} is the experimentally determined loss modulus and E''_{calc} is the calculated loss modulus. For each set of trial parameters, the error function was computed over the range of E' for which there was an overlap of experimental and calculated data. The corresponding error function used for the Wicket plot was as follows.

Wicket error function

$$f_2 = \frac{\sum_{E'} |\log(\tan\delta_{\text{exp}}) - \log(\tan\delta_{\text{calc}})|^2}{\sum_{E'} |\log(\tan\delta_{\text{exp}})|^2} \tag{5}$$

where tan δ_{exp} is the experimentally determined loss factor, and tan δ_{calc} is the calculated loss factor.

A multi-parameter optimization was carried out using the Matlab software's optimization toolbox to find values for the parameters α, β, E_0, and E_∞ that minimized the error functions f_1 and f_2. The most consistent results and the fastest convergences were reached by first optimizing with respect to the Cole–Cole function f_1, then with respect to the Wicket function f_2.

Fig. 2 shows the storage and loss modulus of Isodamp C-1002 over a range of temperatures and at a frequency of 1 Hz. The results of the fitting procedure described above are shown in Fig. 3 and tabulated in Table 1. It can be seen from Fig. 3 that the four temperature independent HN parameters (α, β, E_0, and E_∞) describe the complex plane behavior of Isodamp C-1002 quite well. The same procedure was

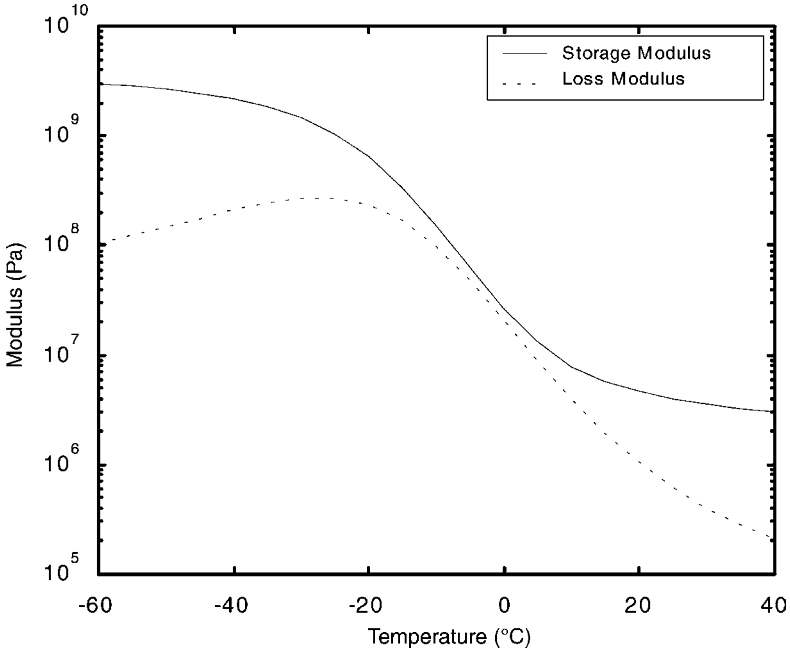

Fig. 2. DMTA data for Isodamp C-1002 at 1 Hz. Sample was excited in tension.

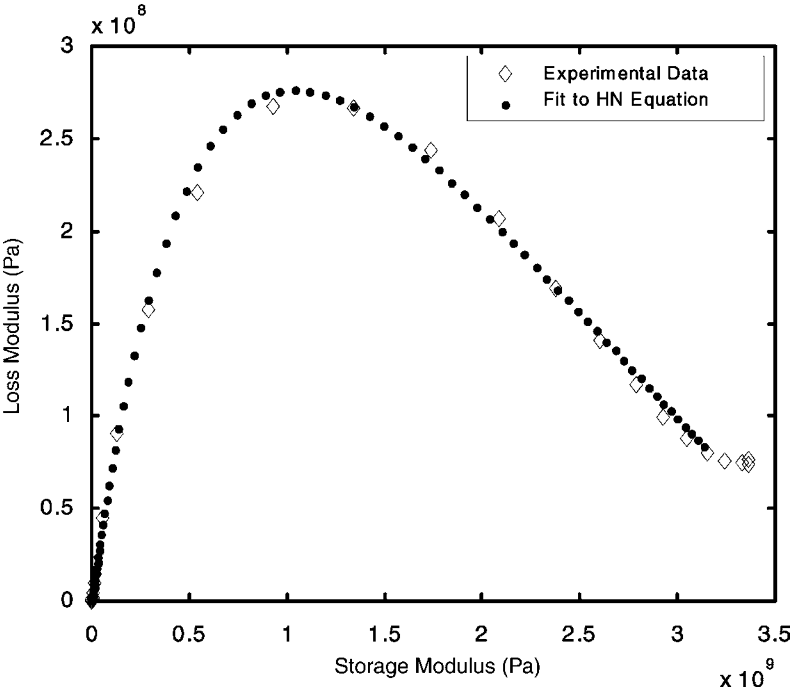

Fig. 3. Cole–Cole plot for Isodamp C-1002 at 1 Hz (data taken from Fig. 2). The best fit HN parameters (excluding τ) were $\alpha = 0.440$, $\beta = 0.165$, $E_0 = 3.03$ MPa, and $E_\infty = 3.86$ GPa.

applied to the neoprene elastomer, and the results tabulated in Table 1. The HN model (Eq. (1)) describes the dynamic mechanical behavior of the neoprene elastomer specimen quite well, except at the lowest and highest moduli. This is especially true for moduli less than 2×10^7 Pa, where the HN model data is markedly different from the experimental data. The DMTA experiments and the complex plane fitting procedure was repeated a number of times for replicate specimens of each elastomer (Table 2). The

Table 1
Temperature independent HN parameters determined from complex plane analysis of DMTA data for two different elastomeric specimens

HN parameter	Isodamp C-1002	Neoprene elastomer
α	0.440	0.605
β	0.165	0.452
E_0 (Pa)	3.03×10^6	2.28×10^7
E_∞ (Pa)	3.86×10^9	4.41×10^9

Table 2
Averages and standard deviations (S.D.) for the temperature independent HN parameters determined for three replicate samples of Isodamp C-1002, and five replicate samples of the neoprene elastomer

		α	β	$\log(E_0)$ (Pa)	$\log(E_\infty)$ (Pa)
Isodamp C-1002 (three replicates)	Average	0.454	0.322	6.537	9.541
	S.D.	0.030	0.172	0.059	0.048
Neoprene elastomer (five replicates)	Average	0.582	0.493	7.255	9.621
	S.D.	0.038	0.167	0.044	0.044

statistical variability of results in Table 2 is due mainly to factors such as the precision of the instrument, reproducibility of the clamping conditions and isotropy of the sample, rather than robustness of the analysis technique. The experimental results for two specific elastomer specimens and their associated HN parameters in Table 1 are the subject of further analysis described below.

5. Havriliak–Negami relaxation time

Using the α, β, E_0, and E_∞ values from Table 1, and the associated experimental complex moduli, $E^*(\omega, T)$, it should be possible to calculate the relaxation times $\tau(T)$ from Eq. (1). This may be accomplished analytically if τ can be isolated from other variables in that expression. Using the Matlab symbolic toolbox to solve this problem yielded the following expression for τ:

$$\tau = -i^* \exp\frac{\{\log(\exp(\log((E_0 - E_\infty)/(E^* - E_\infty))/\beta) - 1)/\alpha\}}{\omega} \tag{6}$$

Applying Eq. (6) to the data for Isodamp C-1002 resulted in the relaxation times shown in Fig. 4. Note that the results of this calculation were complex, and only the real part is considered here. The temperature dependence of the relaxation time follows an Arrhenius relationship:

$$\tau = A \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

where T is absolute temperature, R the gas constant, E_a the Arrhenius activation energy, and A is a constant. The activation energy determined by least squares analysis of a plot of $\log(\tau)$ versus $1/T$ was $E_a = 2.25 \times 10^5$ J mol^{-1}. This value is higher than the value of $E_a = 1.53 \times 10^5$ J mol^{-1}, which has been reported elsewhere [12] for Isodamp C-1002.

The relaxation time was also derived from Eq. (1) and the α, β, E_0, and E_∞ values from Table 1 using numerical methods. For Isodamp C-1002, this yielded

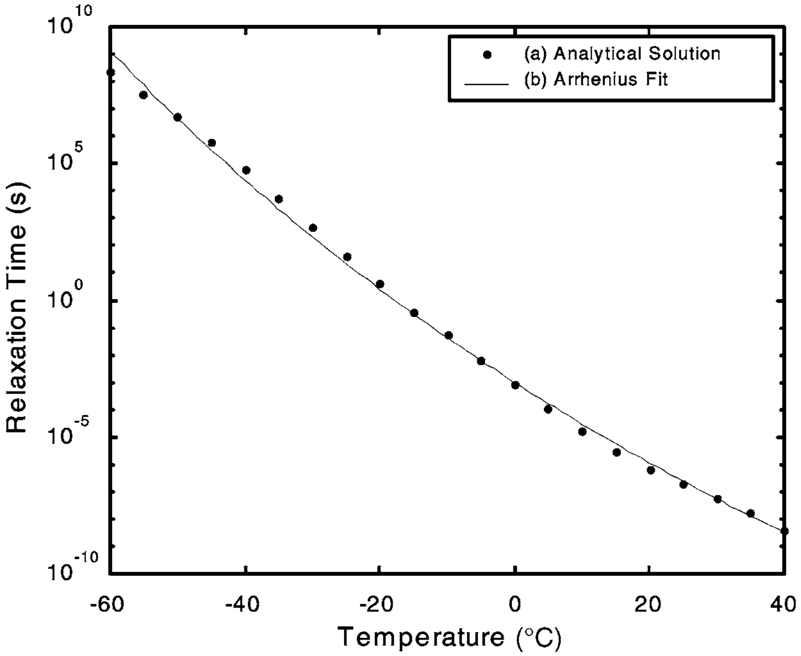

Fig. 4. HN relaxation time τ for Isodamp C-1002 calculated from α, β, E_0, E_∞ (Table 1), and the complex modulus (E^*) at 1 Hz according to Eq. (6). The temperature dependence of the relaxation time follows an Arrhenius relationship, with an activation energy of $E_a = 2.25 \times 10^5$ J mol^{-1}.

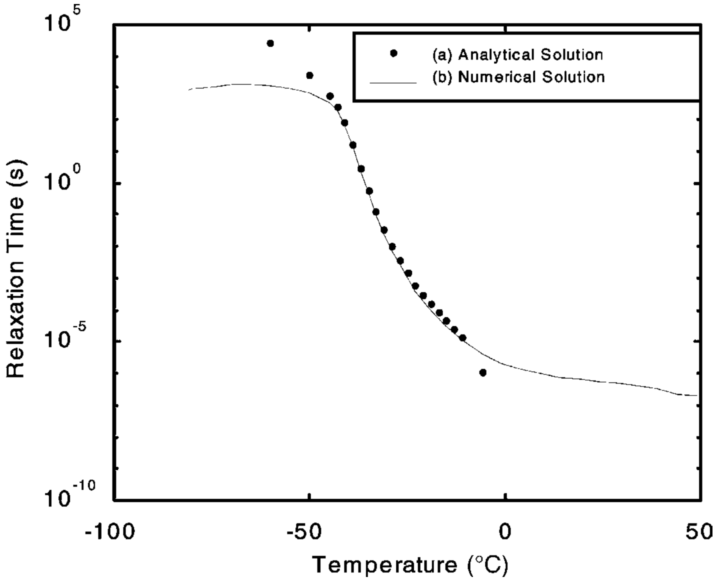

Fig. 5. HN relaxation time τ for the neoprene elastomer calculated from α, β, E_0, E_∞ (Table 1), and the complex modulus (E^*) at 1 Hz: (a) τ calculated directly from Eq. (6) (analytical method); and (b) τ solved from Eq. (1) using numerical methods.

nearly identical results to the analytical method. The analytical solution given by Eq. (6) is compared to a numerical solution for τ using Eq. (1) for the case of the neoprene elastomer in Fig. 5. It can be seen that the analytical solution is in agreement with the numerical solution from −43 to −10 °C, but outside this temperature range the analytical solution gives negative results for τ (not shown on semi-log plot). This can be attributed to a poor fit of the HN equation outside the transition region for the neoprene elastomer (for the numerical solution, the value of τ was constrained to be positive).

6. Prediction of dynamic mechanical properties

So far, it has been shown that analysis of DMTA data in the complex plane may be used to derive four temperature independent HN parameters, and the temperature dependent relaxation time. In this section, the applicability of the analysis method to the prediction of dynamic mechanical properties at various frequencies and temperatures will be explored. Specifically, it will be shown that it is possible to use single frequency DMTA data to predict the complex modulus over a range of frequencies and temperatures. The temperature range for prediction will be limited to the range over which the HN relaxation time has been determined.

Calculation of the complex modulus at a given temperature (T) and frequency (ω) using Eq. (1) is straightforward once α, β, E_0, E_∞, and $t(T)$ have been determined from the procedure described above. Fig. 6 shows the real part of the complex moduli for Isodamp C-1002 that were determined experimentally by DMTA over three decades of frequency (0.2–175 Hz), and at several different temperatures. The complex moduli that were predicted from the complex plane analysis of 1 Hz DMTA data compares favorably with the experimental data over the range of frequencies studied, especially at 0 °C, which is in the glass transition region for this polymer. The relaxation time for each temperature was found by interpolation of the data in Fig. 4. For Isodamp C-1002, the relaxation times at −30, 0, and 20 °C were found to be 1.65×10^{2}, 1.02×10^{-3}, and 1.34×10^{-6} s, respectively. The corresponding experimental data and calculations for neoprene elastomer are shown in Fig. 7 for the storage modulus and Fig. 8 for the loss factor. Again, the agreement between experimental data and calculations based on complex plane analysis is very good. Note that the calculations accurately predict the

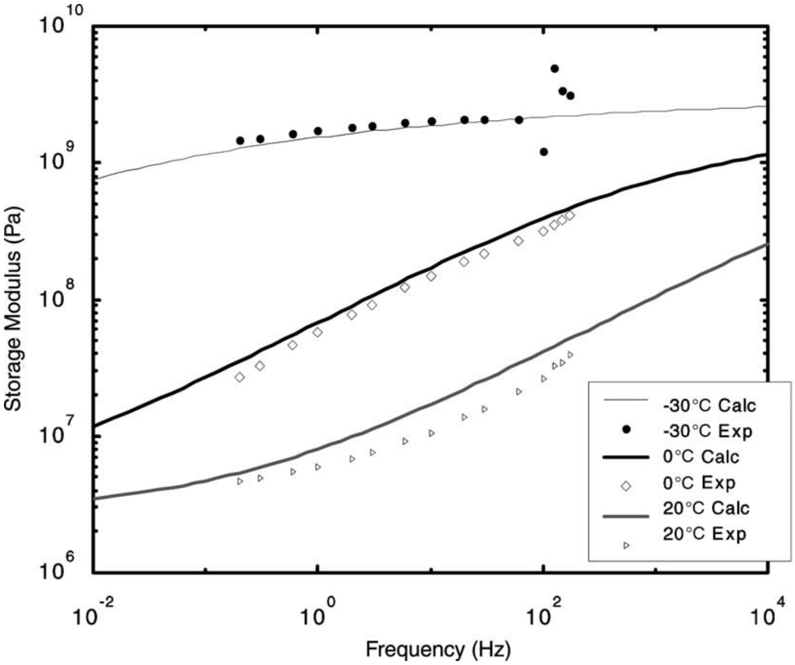

Fig. 6. Experimental and calculated storage moduli for Isodamp C-1002 over a range of frequencies and at three different temperatures. The moduli were calculated from Eq. (3) using the HN parameters in Table 1 for Isodamp C-1002, and the relaxation times from Fig. 4.

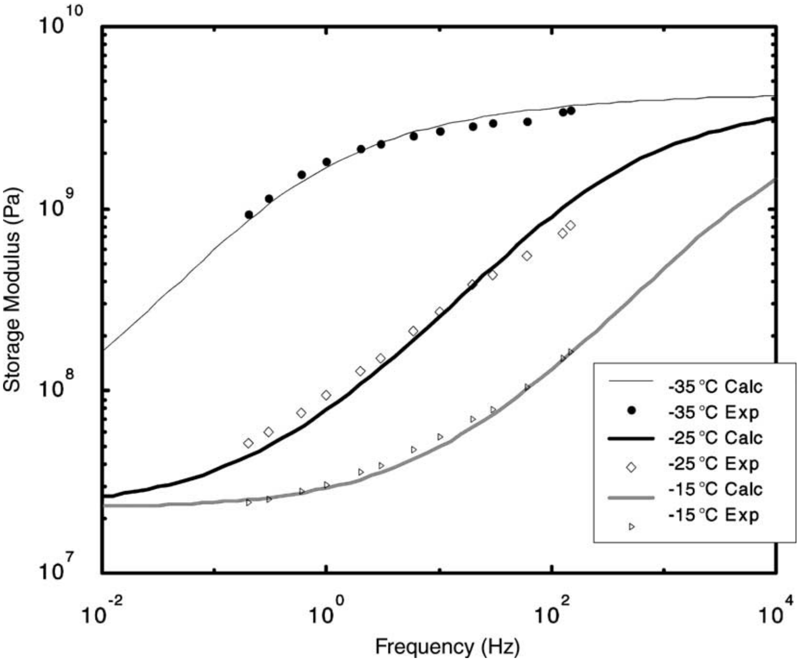

Fig. 7. Experimental and calculated storage moduli for the neoprene elastomer over a range of frequencies and at three different temperatures. The moduli were calculated from Eq. (1) using the HN parameters in Table 1 for neoprene elastomer, and the relaxation times from Fig. 5b.

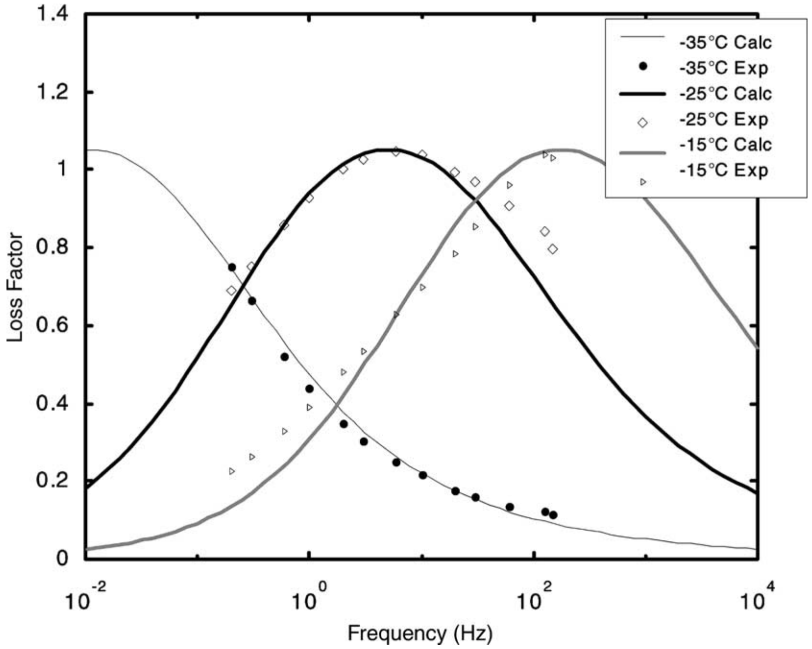

Fig. 8. Experimental and calculated loss factors for the neoprene elastomer over a range of frequencies and at three different temperatures. The loss factors were calculated from Eqs. (1)–(3) using the HN parameters in Table 1 for neoprene elastomer, and the relaxation times from Fig. 5b.

location and shape of the peak in the loss factor curve for a temperature of −25 °C.

It is also possible to calculate the modulus-temperature dependence at frequencies other than 1 Hz, by utilizing the full temperature range of relaxation times derived in the complex plane analysis. Fig. 9 shows the experimental and calculated storage modulus data for Isodamp C-1002 over the temperature range −60 to 40 °C, and at 0.2, 1, 30, and 150 Hz. The temperature dependence of the calculated storage moduli agree quite well with the experimental data, with the exception perhaps of the 150 Hz data at low temperature. The calculations were based entirely on the analysis of 1 Hz DMTA data, using the HN parameters derived from complex plane analysis. Calculated DMTA curves for neoprene elastomer also agree quite well with experimental data (Fig. 10), except in the low modulus, high temperature region, where the degree of fit to the HN model in the complex plane was poor. The shape and location of the loss factor peaks for neoprene elastomer were well captured by the analysis, including the broadening of the peak with increasing frequency (Fig. 10).

7. Master curves

An additional means of investigating the robustness of the analysis method presented here is to examine its success in producing smooth master curves from frequency multiplexed DMTA data. Fig. 11a shows experimental unshifted storage modulus data for Isodamp C-1002 over the frequency range 0.2–175 Hz, and at 5 °C temperature increments between −60 and 40 °C. The discrete temperature segments can readily be distinguished from one another in the glass transition region, and are labeled accordingly. A master curve at 0 °C was created by shifting the temperature segments along the frequency axis by a shift factor a_T given by

$$a_T = \frac{\tau}{\tau_0} \tag{8}$$

where τ is the relaxation time at temperature T (taken from Fig. 4), and τ_0 is the relaxation time at the reference temperature of 0 °C (1.59×10^{-3} s). As shown in Fig. 11b, the resultant master curve is a smooth function of frequency. This master curve also

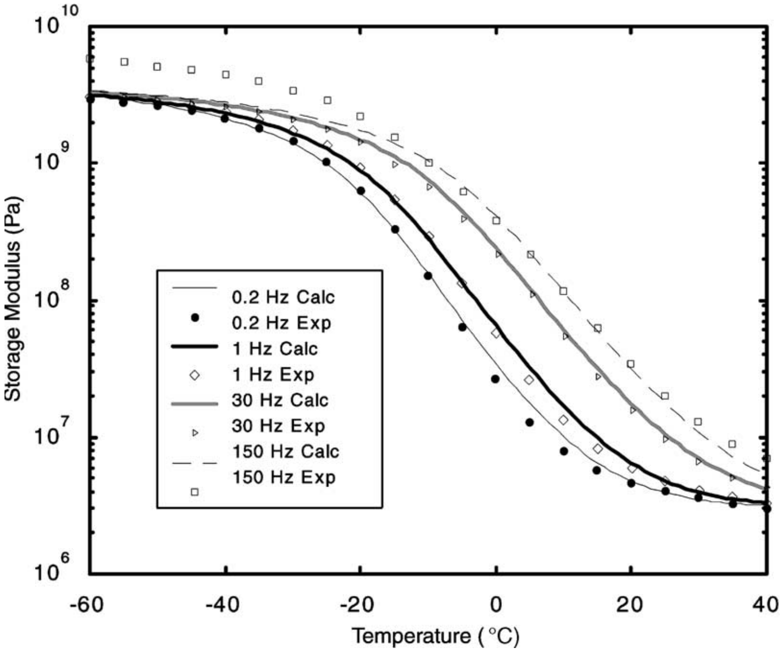

Fig. 9. Experimental and calculated storage moduli for Isodamp C-1002 over a range of temperatures and at four different frequencies. The moduli were calculated from Eq. (1) using the HN parameters in Table 1 for Isodamp C-1002, and the relaxation times from Fig. 4.

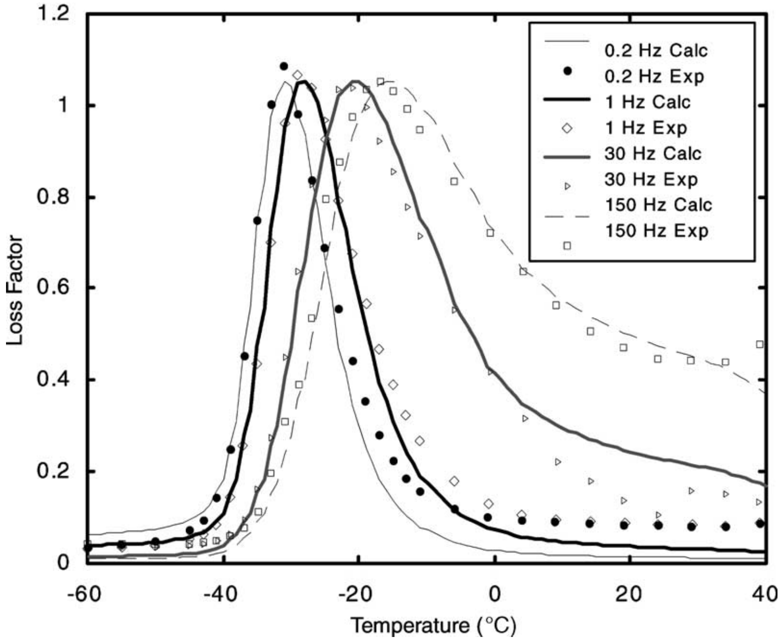

Fig. 10. Experimental and calculated loss factors for the neoprene elastomer over a range of temperatures and at four different frequencies. The loss factors were calculated from Eqs. (1)–(3) using the HN parameters in Table 1 for the neoprene elastomer, and the relaxation times from Fig. 5a.

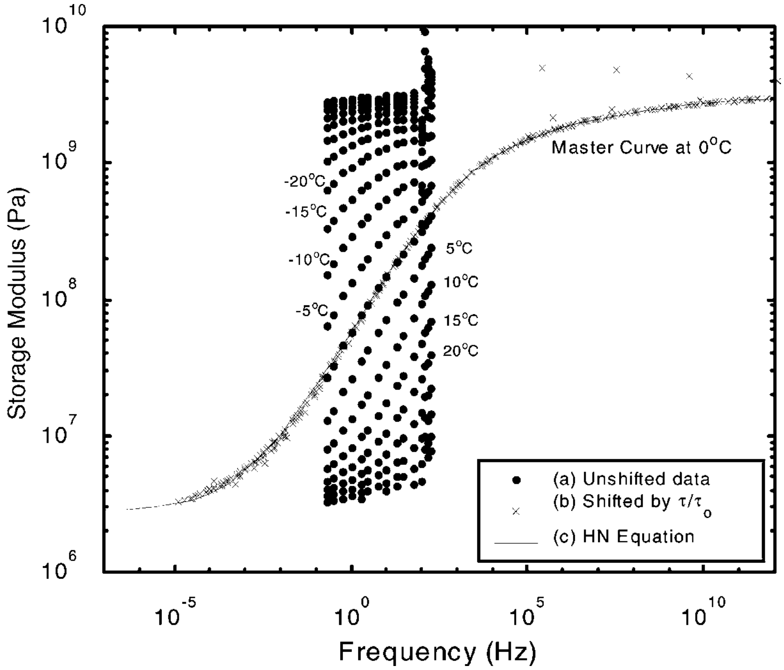

Fig. 11. (a) Multiple fixed frequency DMTA data for Isodamp C-1002 over the temperature range −60 to 40 °C, and at frequencies ranging from 0.2 to 175 Hz. (b) Master curve at 0 °C constructed by shifting data along the frequency axis by the ratio τ/τ_0, where $\tau_0 = 1.02 \times 10^{-3}$ s is the relaxation time at 0 °C (Fig. 4). (c) Calculated according to Eq. (1) using $\tau_0 = 1.59 \times 10^{-3}$ s and the HN parameters in Table 1 for Isodamp C-1002.

agrees quite well with the predictions based on Eq. (1), the HN parameters in Table 1 for Isodamp C-1002, and the relaxation time $\tau_0 = 1.59 \times 10^{-3}$ s (Fig. 11c). Note that the HN parameters, relaxation times, and shift factors were all derived from 1 Hz DMTA data, but were successfully applied to frequency multiplexed DMTA data.

8. Conclusions

It has been shown that complex plane analysis of DMTA data may be used to predict the complex modulus of thermorheologically simple polymers as a function of temperature and frequency. The method described involved deriving four temperature independent HN parameters (α, β, E_o, and E_∞) and the temperature dependent relaxation time τ from single frequency DMTA data. These five HN parameters were then used to calculate the complex modulus as a function of temperature and frequency. Agreement with experimental data was generally good for two elastomeric materials investigated, Isodamp C-1002 and a neoprene elastomer.

The method described is restricted to thermorheologically simple polymers, whose dynamic mechanical properties may be described by the HN model. The accuracy of the predicted properties is limited by the degree to which the experimental data may be fit to the HN model in the complex plane. In the case of the neoprene elastomer, there was generally a good fit of the experimental data to the HN model in the complex plane, with the exception of the low modulus region. As a result, the high temperature predictions for the neoprene elastomer were less accurate than the lower temperature predictions.

Shift factors were derived from the temperature dependent relaxation times, and applied to frequency multiplexed data to create master curves. The resultant curves had overlapping temperature segments and were smooth functions of frequency.

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