Dynamic Mechanical Analysis

03/28/2026

The characterization of the viscoelastic behavior of polymers and other amorphous materials is essential for predicting their time- and temperature-dependent mechanical response. Dynamic Mechanical Analysis (DMA) provides a robust experimental framework for probing this behavior across a range of temperatures and frequencies. The resulting data are commonly represented using a *Prony* series expansion of the relaxation modulus, which forms the basis for linear viscoelastic constitutive models in finite element analysis and structural simulations.

The relaxation modulus $E(t)$ for an isotropic linear viscoelastic material is expressed in the time domain as a *Prony* series:

$$E(t) = E_\infty + \sum_{i=1}^{N} E_i \exp\left(-\frac{t}{\tau_i}\right)$$

where E_∞ is the long-term equilibrium modulus, E_i are the relaxation strengths, and τ_i are the relaxation times. The instantaneous or glassy modulus is then given by

$$E_0 = E_\infty + \sum_{i=1}^{N} E_i$$

In the frequency domain, the storage modulus $E'(\omega)$ and loss modulus $E''(\omega)$ derived from the Fourier transform of the relaxation modulus become:

$$E'(\omega) = E_\infty + \sum_{i=1}^{N} E_i \frac{\omega^2\tau_i^2}{1+\omega^2\tau_i^2}$$

$$E''(\omega) = \sum_{i=1}^{N} E_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2}$$

The objective of the fitting procedure is to determine the discrete set of parameters $\{E_i, \tau_i\}$ for $i = 1 \ldots N$ along with E_∞ (or equivalently E_0) such that the model predictions optimally match the experimental DMA data across the measured temperature and frequency ranges.

DMA Sample Requirements

The fidelity of the *Prony* series parameters is fundamentally constrained by the quality of the DMA test specimens and the experimental protocol. Specimen preparation must adhere to rigorous standards to ensure that the measured response reflects the intrinsic material behavior rather than artifacts of sample geometry or fixture interaction.

Specimen geometry is dictated by the material's stiffness and the intended testing mode. For polymers in the glassy to rubbery transition, rectangular specimens tested in single or dual cantilever bending are common, with typical dimensions of $50 \times 12 \times 3$ mm, though thickness should be adjusted to maintain a measured stiffness within the transducer's optimal range. Alternatively, for softer materials in the rubbery regime, tension or shear sandwich configurations are preferred to achieve adequate force signals. The aspect ratio must be chosen such that the specimen's natural frequency does not interfere with the forced oscillation measurements; a length-to-thickness ratio exceeding 10 is generally advisable for flexural modes.

Surface finish and dimensional accuracy are critical. Specimens should be machined or molded with parallel faces, and any surface imperfections or residual stresses introduced during fabrication must be eliminated through appropriate annealing or conditioning protocols. Moisture content significantly influences viscoelastic response, particularly for hygroscopic polymers; therefore, specimens should be stored in a desiccated environment and tested under controlled humidity conditions, or the equilibrium moisture content should be reported as part of the material state.

The specimen's linear viscoelastic range must be established prior to the main test series. A strain amplitude sweep at a representative frequency (*e.g.*, 1 Hz) and temperature (*e.g.*, the midpoint of the intended range) identifies the strain below which the storage modulus remains constant—typically below 0.1% for glassy polymers and up to 1% for elastomers. All subsequent frequency sweeps must be conducted within this linear regime to satisfy the superposition principles underlying the time-temperature superposition (TTS) procedure.

DMA Test Procedure

The experimental procedure is designed to capture the material's viscoelastic response over a broad frequency range by leveraging the time-temperature superposition principle. A series of isothermal frequency sweeps is performed across a temperature range spanning the glass transition region and extending into the rubbery plateau.

Temperature selection should cover the full transition zone of interest. For a typical amorphous polymer, this may range from $T_g - 50^\circ\mathrm{C}$ to $T_g + 80^\circ\mathrm{C}$. Temperature increments should be sufficiently fine—typically 3 to 5°C—to resolve the rapid changes in modulus through the glass transition. Each isothermal step requires adequate stabilization time, generally 3 to 5 minutes after the temperature setpoint is reached, to ensure thermal equilibrium throughout the specimen. Premature data acquisition leads to thermal gradients that distort the measured viscoelastic functions.

At each isothermal temperature T_k, a frequency sweep is conducted over a logarithmic range, typically from 0.1 Hz to 100 Hz or the maximum frequency supported by the instrument's dynamics. A minimum of 6 to 8 frequency points per decade is recommended to capture the curvature of the relaxation spectra. The oscillation amplitude is held constant within the previously determined linear viscoelastic range.

Data recorded for each frequency ω and temperature T include the storage modulus $E'(\omega, T)$, loss modulus $E''(\omega, T)$, and the loss tangent $\tan\delta = E''/E'$. Additionally, the phase angle δ should be monitored for consistency, as abrupt changes may indicate specimen slippage, fixture resonance, or the onset of nonlinearity.

Time-Temperature Superposition

The raw DMA data consist of isothermal modulus curves as functions of angular frequency. To construct a master curve spanning an extended frequency range, the time-temperature superposition principle is invoked. This principle asserts that the viscoelastic response at a reference temperature

T_{ref} can be related to that at another temperature T through a horizontal shift factor a_T and, for modulus, a vertical shift factor b_T. The reduced frequency is defined as $\omega_r = a_T\omega$.

The master curve construction proceeds by selecting a reference temperature, typically chosen near the midpoint of the glass transition or at the intended service temperature. For each isothermal curve, horizontal shift factors a_T are determined by shifting the modulus curves along the frequency axis to achieve optimal superposition with the reference curve. The vertical shift factor b_T is often omitted for amorphous polymers above T_g if the modulus is normalized, but in rigorous treatments it is included to account for temperature-induced density changes and is defined as:

$$b_T = \frac{\rho(T)T}{\rho(T_{\text{ref}})T_{\text{ref}}}$$

where $\rho(T)$ is the density at temperature T. For many engineering polymers, the vertical shift is small and often neglected without significant loss of accuracy, though for precise constitutive modeling it should be retained.

The shifting procedure is performed using an optimization algorithm that minimizes the discrepancy between adjacent curves, typically using the storage modulus and loss modulus simultaneously or by minimizing the deviation of $\tan\delta$ across temperatures. The resulting shift factors a_T as a function of temperature are then fitted to the *Williams-Landel-Ferry* (WLF) equation:

$$\log_{10}(a_T) = \frac{-C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})}$$

where C_1 and C_2 are material constants. This functional form is valid for temperatures ranging from T_g to $T_g + 100^\circ\text{C}$. Below T_g, an Arrhenius-type equation is often more appropriate:

$$\ln(a_T) = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)$$

where E_a represents the activation energy and R the universal gas constant. The choice of reference temperature must be consistent with the selected shift function.

Once the shift factors are determined, the reduced frequency master curve is assembled by horizontally shifting each isothermal dataset to the reference temperature. The combined dataset now represents the material’s viscoelastic response over an extended reduced frequency range, often spanning 10 to 15 decades.

Numerical Methods for Prony Series Fitting

With the master curve data available in the frequency domain—comprising reduced frequency ω_r and corresponding storage modulus $E'(\omega_r)$ and loss modulus $E''(\omega_r)$—the *Prony* series parameters are obtained through nonlinear regression. The fitting problem is ill-posed in the sense that many combinations of relaxation times and strengths can produce nearly identical modulus curves. Consequently, regularization and careful selection of the number of terms N are essential.

Selection of Relaxation Times

A common approach is to preselect the relaxation times τ_i logarithmically spaced over the range of reduced frequencies covered by the master curve. Let

$$\tau_i = \tau_{\min} \cdot 10^{(i-1)\Delta} \text{ for } i = 1, \ldots, N$$

where $\tau_{\min}$ is chosen slightly smaller than the inverse of the maximum reduced frequency and $\tau_{\max}$ slightly larger than the inverse of the minimum reduced frequency. The number of terms N is typically between 5 and 15; too few terms yield poor representation of the transition, while too many lead to overfitting and numerical instability.

Linearized Formulation for Storage Modulus

If the relaxation times are fixed, the storage modulus expression becomes linear in the unknown coefficients E_i and E_∞. For each data point j at reduced frequency ω_j, we have:

$$E'_j = E_\infty + \sum_{i=1}^{N} E_i \frac{\omega_j^2 \tau_i^2}{1 + \omega_j^2 \tau_i^2}$$

This can be cast in matrix form as $\mathbf{A}\mathbf{x} = \mathbf{E}'$, where $\mathbf{x} = [E_\infty, E_1, \ldots, E_N]^T$ and the design matrix $\mathbf{A}$ has elements $A_{j,1} = 1$ for the equilibrium modulus column and $A_{j,i+1} = \omega_j^2 \tau_i^2 / (1 + \omega_j^2 \tau_i^2)$. A non-negative least squares (NNLS) solution is enforced because relaxation strengths must satisfy $E_i \geq 0$ to ensure thermodynamic consistency. The NNLS algorithm yields a physically admissible solution while simultaneously permitting some coefficients to become zero, effectively reducing the model order.

Nonlinear Optimization with Both Moduli

For greater accuracy, both storage and loss moduli can be fitted simultaneously using a weighted nonlinear least squares approach. The objective function is:

$$\chi^2(\{E_i, \tau_i\}, E_\infty) = \sum_{j=1}^{M} w'_j \left(E'_{\text{model}}(\omega_j) - E'_{\text{exp}}(\omega_j)\right)^2 + \sum_{j=1}^{M} w''_j \left(E''_{\text{model}}(\omega_j) - E''_{\text{exp}}(\omega_j)\right)^2$$

where w'_j and w''_j are weights that can be chosen inversely proportional to the experimental variance or set to unity if the uncertainty is uniform. This optimization is typically performed using the *Levenberg–Marquardt* algorithm, which combines the robustness of gradient descent with the efficiency of Gauss–Newton near the minimum. Initial guesses for τ_i are obtained from the peak positions of $E''(\omega)$ in the master curve, as each relaxation time corresponds approximately to the inverse of the frequency at which the loss modulus exhibits a peak for a given mode. The initial E_i can be estimated from the drop in storage modulus across each frequency decade.

Regularization and Model Selection

To mitigate overfitting, *Tikhonov* regularization is often incorporated, penalizing large variations in successive relaxation strengths. The regularized objective becomes:

$$\chi^2_{\text{reg}} = \chi^2 + \lambda \sum_{i=1}^{N-1} (E_{i+1} - E_i)^2$$

---

where λ is a regularization parameter selected via the L-curve criterion or cross-validation. Alternatively, the *Akaike Information Criterion* (AIC) can guide the selection of the number of *Prony* terms by balancing goodness-of-fit against model complexity:

$$\mathrm{AIC} = M \ln\left(\frac{\chi^2}{M}\right) + 2N$$

The model with the lowest AIC value is preferred.

Shift Factors and Temperature Dependence

The shift factors derived from the master curve construction are integral to the final constitutive model, as they enable the prediction of viscoelastic behavior at any temperature within the range of the WLF or *Arrhenius* fit. The *Prony* series parameters are determined at the reference temperature T_{ref}. To obtain the relaxation modulus at an arbitrary temperature T, the reduced time concept is employed:

$$E(t,T) = E_\infty + \sum_{i=1}^{N} E_i \exp\left(-\frac{t}{a_T \tau_i}\right)$$

Thus, the shift factors scale the relaxation times, effectively shifting the entire *Prony* series along the logarithmic time axis. It is critical that the WLF parameters C_1 and C_2 are reported alongside the *Prony* coefficients, as they constitute the complete temperature-dependent model.

The determination of the WLF constants from the experimentally derived a_T values is performed via linear regression on the transformed equation:

$$\frac{1}{\log_{10}(a_T)} = -\frac{C_2}{C_1}\frac{1}{T - T_{\mathrm{ref}}} - \frac{1}{C_1}$$

Plotting $1/\log_{10}(a_T)$ against $1/(T - T_{\mathrm{ref}})$ yields a straight line from which C_1 and C_2 are extracted. For materials exhibiting a narrow transition, the WLF parameters often approximate universal values of $C_1 \approx 17.44$ and $C_2 \approx 51.6$ when $T_{\mathrm{ref}} = T_g$, though significant deviations are common and must be determined empirically.

Parameter Validation

Validation of the fitted *Prony* series parameters is indispensable to ensure the model's predictive capability and physical consistency. Validation should be performed through multiple independent checks, both within the frequency domain and through time-domain experiments.

Frequency Domain Validation

The fitted model must be compared against the original master curve data that were not used in the fitting process if a training-validation split was employed. In the absence of such a split, a cross-validation approach can be implemented by omitting a subset of the data points during fitting and subsequently comparing the model predictions to the omitted points.

The relative error in storage modulus and loss modulus should be evaluated across the entire reduced frequency range. Special attention should be paid to the glassy region (high reduced frequency) and the rubbery plateau (low reduced frequency), where the modulus should asymptotically approach E_0 and E_∞, respectively. The loss modulus should exhibit a single broad peak for most amorphous polymers; the presence of multiple spurious peaks may indicate an overfitted *Prony* series.

Time Domain Validation
The ultimate test of the *Prony* series parameters lies in their ability to predict time-domain responses such as creep compliance or stress relaxation. A stress relaxation test conducted at a constant strain within the linear viscoelastic range provides a direct measurement of $E(t)$. The predicted relaxation modulus from the *Prony* series using the shift factors at the test temperature should be superimposed onto the experimental relaxation data. Discrepancies often reveal inadequacies in the master curve construction, particularly if the horizontal shifting was performed suboptimally.

Alternatively, creep compliance $J(t)$ can be predicted from the relaxation modulus via the convolution integral. The relationship in the Laplace domain, $\bar{J}(s)\bar{E}(s) = 1/s^2$, can be inverted numerically to obtain $J(t)$. A close match between the predicted and measured creep compliance confirms the consistency of the *Prony* parameters across transformation domains.

Thermodynamic Consistency Checks
Several thermodynamic constraints must be satisfied by the fitted parameters. All relaxation strengths must be nonnegative: $E_i \geq 0$. The equilibrium modulus E_∞ must be nonnegative and should approach the rubbery plateau modulus measured independently at low frequencies and high temperatures. The instantaneous modulus $E_0 = E_\infty + \sum E_i$ should be consistent with the glassy modulus measured at high frequencies or low temperatures.

Furthermore, the loss modulus must satisfy the *Kramers–Kronig* relations, which connect the real and imaginary parts of the complex modulus. While numerical approximations of these relations can be applied, a simpler check is to ensure that the loss tangent peak is captured accurately and that the model does not exhibit negative dissipation at any frequency.

Sensitivity Analysis
A sensitivity analysis should be conducted to assess the influence of the fitted parameters on the model response. This involves perturbing each E_i and τ_i by a small fraction and observing the resulting change in the modulus prediction. Parameters to which the response is highly sensitive must be determined with greater precision, whereas insensitive parameters may be consolidated or eliminated to simplify the model without sacrificing accuracy.

Concluding Remarks

The fitting of *Prony* series parameters from DMA test data is a methodical process that integrates rigorous experimental practice, careful data reduction via time-temperature superposition, and numerically stable optimization techniques. The resulting viscoelastic model captures the material's time- and temperature-dependent mechanical behavior, enabling accurate simulations of polymer components under diverse loading conditions. Adherence to the protocols outlined herein—from specimen preparation through validation—ensures that the fitted parameters are both physically meaningful and predictive, forming a reliable foundation for advanced engineering analysis.